

**EGE UNIVERSITY GRADUATE SCHOOL OF NATURAL AND
APPLIED SCIENCES**

(PhD THESIS)

**PREPARATION AND CHARACTERIZATION OF
METAL NANO PARTICLES MODIFIED COMPOSITE
FILM ELECTRODES; AND THEIR APPLICATIONS**

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ÖZET**METAL NANO PARÇACIK MODİFİYE KOMPOZİT FİLM
ELEKTROTLARIN HAZIRLANMASI, KARAKTERİZASYONU VE
UYGULAMALARI**

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Bu tez çalışmasının iki ana hedefinden ilki, yakıt pillerinde anot ve katot materyali olarak kullanılmak üzere katalitik etkinliği yüksek kompozit modifiye yüzeyler hazırlamak, yüzey karakterizasyonlarını yapmak ve çeşitli yakıtlara yönelik elektrokimyasal uygulamalarını gerçekleştirmektir. Bu amaçla, farklı metal nanoparçacıklar ile modifiye edilmiş polimer film (poli p-aminofenol) ve ftalosiyanın-karbon nanotüp modifiye kompozit elektrotlar hazırlanarak alkali ortamda hem metanol ve dimetilamino boranın (DMAB) yükseltgenmesi hem de oksijenin elektrokatalitik indirgenmesi incelenmiştir. Dimetilamino boran yükseltgenmesi için en iyi katalitik etkinlik, Ag ve Au nano parçacıkların elektrokimyasal olarak ardışık modifiye edildiği poli(p-aminofenol) (PAP) camımsı karbon elektrot (GCE) yüzeyinde elde edilmiştir. Nanoparçacık modifiye edilmiş ftalosiyanın-karbon nanotüp (Pc-CNT) kompozit elektrotlar ile alkali ortamda yapılan metanol ve DMAB yükseltgenme çalışmalarında en iyi katalitik etkinlik sırası ile elektrokimyasal biriktirme ile oluşturulmuş Au-Pt nano parçacık modifiye bakırftalosiyanın-karbon nanotüp (CuPc-CNT) GC ve altın nanoparçacık modifiye CuPc-CNT/GC elektrotta gerçekleşmiştir. Oksijenin, alkali ortamda elektrokimyasal indirgenme tepkimesi incelendiğinde ise, en iyi katalitik yüzeyin platin nanoparçacık modifiye CuPc-CNT/GC elektrot yüzeyi olduğu saptanmıştır.

Tezin ikinci hedefi ise teofilin (TP) ve kafeinin (CAF) tayini için seçimli ve duyarlı bir modifiye elektrot geliştirmektir. Bu amaçla yeni sentezlenmiş organik gruplar ile fonksiyonelize edilmiş mangan ftalosiyanınler (2eOHMnPc) karbon nanotüpler ile biraraya getirilerek kompozit modifiye yüzeyler hazırlanmış ve

sülfirik asit ortamında teofilin ve kafeinin elektrokimyasal davranışı incelenmiştir. Hazırlanan 2eOHMnPc-CNT/GC elektrotlar ile gerçek örnek analizindeki TP ve CAF içeriği yeşil çay, kola ve ilaçta tayin edilmiştir. TP ve CAF tek başına bulunduğu koşullarda belirtme alt sınırları sırasıyla 6.6×10^{-9} M ve 5.0×10^{-8} M olarak saptanmıştır. Bu analitlerin bir tanesinin derişimi sabit tutulup diğerinin derişimi incelendiğinde belirtme alt sınırları TP ve CAF için sırasıyla 8.1×10^{-9} M ve 3.0×10^{-7} M olarak saptanmıştır.

Hazırlanan metal nano parçacık modifiye polimer film ve ftalosiyanın-karbon nanotüp elektrot yüzey karakterizasyonları, X-ışını foto elektron spektroskopisi, taramalı elektron mikroskobu, enerji dağılım X-ray spektroskopisi, geçirimli elektron mikroskobu, X-ışını kırınımı ve elektrokimyasal impedans tekniği ile gerçekleştirilmiştir.

Anahtar Kelimeler: yakıt pili, oksijen, dimetilamino boran, metanol, kafein, teofilin, metal nanoparçacık, modifiye elektrotlar.

ABSTRACT**PREPARATION AND CHARACTERIZATION OF METAL NANO PARTICLES MODIFIED COMPOSITE FILM ELECTRODES; AND THEIR APPLICATIONS**

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The first of the two main objectives of this thesis is that to prepare composite modified electrode surfaces with high catalytic activity which used as an anode and cathode material in fuel cells, characterize their surface morphology and perform electrochemical applications. For this purpose, various metal nanoparticles modified polymer film (poly p-aminophenol) and phthalocyanine-carbon nanotube modified composite electrodes were prepared in order to investigate the both methanol and dimethylamine borane (DMAB) oxidation and electrocatalytic oxygen reduction. The best catalytic activity for DMAB oxidation was obtained on sequentially electrochemical deposited Ag and Au nanoparticles modified poly(p-aminophenol) (PAP) film glassy carbon electrode (GCE). In methanol and DMAB oxidation studies on nanoparticles modified phthalocyanine-carbon nanotube composite electrodes in alkaline medium, the best catalytic activity for methanol and DMAB oxidation performed at electrochemically deposited Au-Pt modified copper phthalocyanine-carbon nanotube (CuPc-CNT)GC and gold nanoparticles modified CuPc-CNT/GC electrodes, respectively. In case of investigation of electrochemical oxygen reduction reaction in alkaline medium, the best catalytic surface was established as platinum nanoparticles modified CuPc-CNT/GC electrode surface.

Second objective of the thesis is that to develop modified electrodes for the selective and sensitive determination of theophylline (TP) and caffeine (CAF). For this purpose, new synthesized organic groups functionalized manganese phthalocyanines (2eOHMnPc) combined with carbon nanotubes in order to obtain composite modified surfaces and electrochemical behaviour of TP and CAF was investigated in sulphuric acid medium. The TP and CAF content in real sample analysis of green tea, cola and medicine was determined with the prepared 2eOHMnPc-CNT/GC electrodes. The detection limits of individual TP and CAF were established as 6.6×10^{-9} M ve 5.0×10^{-8} M, respectively. In case of the constant concentration of one analyte with increasing concentration of other, the limit of detection values were calculated as 8.1×10^{-9} M ve 3.0×10^{-7} M for TP and CAF, respectively.

The surface characterizations of prepared metal nanoparticles modified polymer film and phthalocyanine-carbon nanotube electrode were performed by X-ray photoelectron spectroscopy, scanning electron microscopy, energy dispersive X-ray spectroscopy, transmission electron microscopy, X-ray diffraction and electrochemical impedance spectroscopy.

Keywords: Fuel cell, oxygen, dimethylamino borane, methanol, caffeine, theophylline, metal nanoparticles, modified electrodes.

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ABBREVIATIONS

<u>Symbol</u>	<u>Explanation</u>
AFM	Atomic force microscopy
CAF	Caffeine
CMEs	Chemically modified electrodes
CNT	Multiwall carbon nanotube
CV	Cyclic voltammetry
DMAB	Dimethylamine borane
EIS	Electrochemical impedance spectroscopy
FC	Fuel cell
GCE	Glassy carbon electrode
MNPs	Metal nanoparticles
ORR	Oxygen reduction reaction
PAP	Poly(p-aminophenol)
Pc	Phthalocyanine
RDE	Rotating disk electrode
SDS	Sodium dodecil sulphate
TP	Theophylline

1. INTRODUCTION

Nanoscience and nanotechnology is a developing field, which incorporate every science discipline and engineering. In accordance with the development of “nanotechnology and advanced materials technology”, design, fabrication and characterization of nanometer-sized functional materials need to be improved. The advances in scientific and technological area basically depend on the fabrication methods of this improved nano materials, which also help scientists to understand the physical and chemical background of nano-sized systems. “Bottom-up” and “top-down” methods are used for the fabrication of materials. The “top-down” method called lithography that like carving the marble. Small desired structure obtained by removing the unwanted part of the large-scale material. In controversy of this method, “Bottom-up” technique incorporates the small components such as few atoms or molecules to form larger structures. The electrochemical electrode reaction process mainly depends on the characteristics of surface material and electrode/electrolyte interface. Activity, selectivity and sensitivity of the electrode reaction can be improved with the controlling of surface properties (Ventura et al., 2004; Ariga et al., 2013).

The study of the modified electrode surfaces was a focal point of the most researches that improve the poor characteristics of conventional solid based unmodified electrodes. Chemically modified electrodes (CMEs), provide the special electrical, optical, chemical, electrochemical and other desirable properties to solid conventional electrodes. Choosing the suitable modifier is the key step for developing the desired electrode surface in order to facilitate the electrode reaction, reduce the over potential, meliorate the electrocatalytic activity and prevent the electrode deterioration. CMEs can be prepared by sorption, covalent modification, polymer film coatings, coating of inorganic materials and Langmuir-Blodgett methods. The CMEs with desired characteristics can be successfully used for the various application fields such as electroanalysis of compounds and fuel cells (Fagan-Murphy et al., 2015; Kissinger and Heineman, 1996).

Energy demand increases by the increment of world population. Unfortunately, our mainly energy source was depend on fossil fuels which were limited in earthcrust and cause an environmentally harmful greenhouse emissions which effect the global warming (Atilgan and Azapagic, 2015; Sastre et al., 2015). Therefore, renewable energy sources especially fuel cells are important alternative for energy production.

Researchers all over the world were studied to find efficient anode material and appropriate fuel for fuel cell applications. For this purpose, various kinds of fuels (e.g. methanol and dimethylamine borane) were studied on different modified surfaces.

A promising alternative to the hydrogen-based problem, such as deposition and transportation drawbacks, is to use methanol as a fuel in liquid form. methanol attracting great interest as a fuel due to the simple and cheaply synthesis, easy storage, relatively reduced system weight, high energy density, and low emission profile (Jeon et al., 2015; Mehmood et al., 2015). Another alternative fuel is dimethylamine borane which is a borane derivative. It has amine groups which was used recently by the researchers as a fuel (Martins and Nunes, 2008). In fuel cell technology, oxygen is a critical component that cathodic reaction all based on it. Air or pure oxygen feed to the cell and chemical reaction between anode and cathode generate the power of the cell. Oxygen reduction reaction studied in different acidic and alkaline mediums, which affect the reaction rate (Karabiberoğlu, 2014).

The chemical and electrochemical properties of chemically modified composite electrodes are also important for electroanalysis. When chemically modified electrodes compared with common solid electrodes, the surface modification can be supplied a major control of electrode characteristics and reactivity. In addition, chemically modified composite electrodes are also used in electroanalysis. They have the key role to achieve sensitive and selective determination of organic and inorganic compounds with high stability and accuracy. In this thesis, new types of phthalocyanine chemically modified composite electrodes were used for simultaneous determination of theophylline and caffeine.

Theophylline (TP) is commonly used as bronchodilator medicine and cures the chronic /acute obstructive pulmonary disease, neonatal apnea and asthma that approximately 90% of it metabolized in human liver. Theophylline founding a place in the top three drugs which mostly watching clinically due to its narrow therapeutic range. The use of theophylline for bronchodilation activity is therapeutic only within the narrow range of $10\text{-}20\text{ mgL}^{-1}$, while higher levels than that resulted in toxicity, tachycardia, seizures even death and lower levels are non-therapeutic.

This makes the determination of theophylline concentration is critical (Shipovskov and Ferapontova, 2008; Hegde et al., 2009; Amare and Admassie, 2012a). Caffeine (CAF) is a xanthine derivative that its intake was advised which stimulate the central nervous system. However, excessive intake of CAF causes restlessness, insomnia, jitters, anxiety, increasing or irregular heart rate (Srdjenovic et al., 2008, Sultan, 2014). TP and CF are naturally found in especially green tea, cacao beans, coffee, cola, etc. (Gao et al., 2013). The similar structure and simultaneous existence of TP and CAF in natural medium let the researchers to investigate these compounds together.

1.1 The Aim of the Thesis

There were two main objectives of this thesis; the first aim was to design various composite electrodes, which prepared by composition of metal nanoparticles with polymer film or phthalocyanines with carbon nanotubes on glassy carbon electrodes (GCE) for electrocatalytic oxidation of methanol and dimethylamine borane and electrocatalytic reduction of oxygen. A series of optimization studies were performed such as changing the type of metal nanoparticles, phthalocyanine, polymer cycle number, phthalocyanine-carbon nanotube ratio, supporting electrolyte and concentration of electrolyte using cyclic voltammetry, chronoamperometry and rotating disk electrodes to obtain the best catalytic active electrode surfaces.

The second goal of this thesis was to prepare modified electrodes for sensitive and selective determination of theophylline and caffeine. Based on this purpose, newly synthesized type of organic functional groups attached manganese phthalocyanine was composed with multiwalled carbon nanotubes to form a unique surface with high surface area. Synthesized manganese phthalocyanine carbon nanotube modified glassy carbon electrode was used for determination of theophylline and caffeine in tea sample, medicine and baverages. The modified electrode surfaces were characterized by cyclic voltammetry, scanning electron microscopy (SEM), energy dispersive X-Ray spectroscopy (EDX), transmission electron microscopy (TEM), X-Ray photoelectron spectroscopy (XPS), X-Ray diffraction (XRD) and electrochemical impedance spectroscopy (EIS).

1.2 Modified Electrodes

Notwithstanding, solid based electrode materials have satisfactory properties such as mechanically stable and a larger anodic potential range. In addition, the easy and simple to use of solid bare electrodes is much easier especially in flow systems due to their mechanical stability and hardness. However, conventional solid electrodes have some drawbacks, which must be overcome in order to supply the demand that mentioned above. For instance, many compounds need high overpotentials in analytical applications that cannot be determined by solid electrodes which have narrow potential window. In addition, unmodified solid electrodes have memory effect due to the adsorption of reaction products on their surface which deteriorate the electrode, passivate it and resulted in the unstable behavior in further applications (Ciucu, 2014).

There is an increasing demand in analytical applications to use new materials with meliorated chemical and physical properties in order to obtain selective and sensitive signals for analytes. Therefore, the common electrode surfaces need modification with particular chemicals, which can impart higher sensitivity, selectivity, reproducibility and stability to electrochemical devices.

The study of the modified electrode surfaces was a focal point of the most researchs that improve the poor characteristics of conventional solid based unmodified electrodes. The hystorical background of modified electrodes based on the studies of Lane and Hubbard investigated the tendency of irreversibly chemisorbed olefins on platinum electrodes that were electroactive (Lane and Hubbard, 1973). This study followed by Moses and coworkers who investigated the covalent bonding of amine, pyridine, and ethylenediamine ligands to the tin oxide electrode surfaces. In addition, this group was the first to use X-ray photoelectron spectroscopy (XPS or ESCA) to illuminate the modified surface that they confirmed the formation of a Si-O-Sn bond and surface modification (Moses et al., 1975). Finally, Murray mentioned the deliberately immobilized foreign molecules on electrode surfaces that first introduced with the term of “chemically modified electrodes” by him (Murray, 1980).

Chemically modified electrodes (CMEs), provide the special electrical, optical, chemical, electrochemical and other desirable properties to solid conventional electrodes.

Choosing the suitable modifier is the key step for developing the desired electrode surface in order to facilitate the electrode reaction, reduce the over potential, meliorate the electrocatalytic activity and prevent the electrode deterioration. CMEs successfully used for the preconcentration and detection of trace organic and inorganic compounds with high selectivity and sensitivity (Fagan-Murphy et al., 2015).

1.2.1 Preparation of chemically modified electrodes

Chemically modified electrodes classified by their preparation routes. The five categories of chemically modified electrodes described in following paragraphs based on the classification of Martin and Foss. These groups are; sorption, covalent modification, polymer film coatings, coating of inorganic materials and langmuir-Blodgett methods (Kissinger and Heineman, 1996)

Physisorption or physical adsorption is an easily reversible adsorption type due to the weak Van der Waal's interactions between adsorbed molecules and bare electrode surface. Physisorption can be occur in any pressure and temperature and resulted in the multilayer formation on the electrode surface. In addition, the type of adsorbed compound was determining the strength of the adsorption (Webb, 2003). Modification of organic and organometallic complexes by physical adsorption on electrode surface can be achived by several ways such as drop-dry technique and dip coating (Zen et al., 2003). For instance, phenothiazine derivatives psysically adsorbed on graphite electrode surface by dropping the phenothiazine containing dimethylformamide on graphite and allowing for the solvent evaporation at room temperature. This modified electrode was used for the investigation of NADH (Dicu et al., 2000).

Chemisorption is an irreversible adsorption technique due to the formation of strong bond between adsorbed molecule and electrode surface which caused by the electron sharing. Adsorbed compound and surface can be compatible for interaction that chemisorption is selective process, which only formed in monolayer form (Webb, 2003). Ions and many organic cyclic compounds strongly adsorbed on carbon and metal surfaces. For instance, thiol-containing groups are predisposition to bond on the gold surfaces, which formed monolayers called “self assembled monolayers (SAM)”. Flink and coworkers studied the characterizations and applications of SAM on GCE and gold surfaces and inlighten the interactions between analytes and surfaces (Flink et al., 2000).

Covalent bond formation is another way to prepare modified electrode surfaces which occurred between the functional groups of electrode and attached molecule (Kissinger and Heineman, 1996). It can be obtained by the controlling the oxidation and reduction potentials or synthetic way. For instance, electrode surface (e.g. GCE, gold, Pt) treated with oxidative procedure to form active functional groups which followed by the linkage of material and component (such as; amino groups, aryl groups, ferrocene, py-Ru(NH₃)₅, viologen). The modified electrodes prepared by covalent bonding that can be used in many sensing applications (Bard and Faulkner, 2001).

For example, Tammeveski and coworkers bonded anthraquinone group on glassy carbon electrode surface. Repetitive potential cycle between 0.65 and -0.45 V applied to GCE in diazonium salt and tetrabutylammonium tetrafluoroborate containing acetonitrile which then deposited 10 minutes under constant potential. Anthraquinone modified GCE used for investigation of oxygen reduction (Tammeveski et al., 2001).

Coating electrodes with polymer films is another and most common method of surface modification. Polymer films can be formed on electrode surface with several ways such as; electrodeposition, dip or spin coating, thermal and photochemical polymerization. Various polymer types were used for various analytes determination. “Redox polymers” are one of the types of polymer that have oxidizable or reducible groups. “Ion exchange polymers” such as nafion and polystyrene sulfonate etc. have charged parts which allowed ionic species interaction with their porous-like structure.” “Biological polymers” which generally used in sensing applications are made up of enzymes or proteins. “Coordinating polymers” have ability to interact with metal ions in order to incorporate them in polymer structure. In addition, “electronically conductive polymers”, such as polypyrrole, polythiophene, polyaniline etc. were common type of polymer, which used in wide range of application fields (Bard and Faulkner, 2001; Kissinger and Heineman, 1996).

Coatings with inorganic materials means various inorganic matrices such as metal oxides, clays, zeolites transition-metal hexacyanides have been used for conventional electrode modifiers due to their ion-exchange behavior and stable characteristics in case of high temperature and oxidizing agents. Inorganic materials that have electrochromic behavior can be simply modified on electrode surface as a thin film (Bard and Faulkner, 2001).

Langmuir-Blodgett (LB) methods

Thin films can be prepared from three techniques called Langmuir-Blodgett (LB) techniques, the self-assembled monolayer and layer-by-layer (LbL) assembly. Irving Langmuir and Katharina Blodgett were developed a technique to form layered films in the beginning of 1930s. The method based on the amphiphilic monomolecular layer (Langmuir film) formation on water surface which then transformed on to solid material. LB technique provides the control of film thickness while it needs some extra machine such as film balance apparatus. Many materials that formed by LB technique used in photoelectronic devices and sensor applications (Ariga et al., 2013; Kissinger and Heineman, 1996).

1.2.2 Types of chemically modified electrodes and their applications

There has been a great expansion in research of designing composite modified materials especially for electrode modification, which have spesific characteristics based on the synergistic contribution of two or more functional materials. These conductive modifiers such as; metal nanoparticles (Lin et al., 2015; Segura et al., 2015), carbon nanotubes (Ayan et al., 2013; Bakır et al., 2011), polymers (Koçak and Dursun, 2013; Ulubay and Dursun, 2010), metal oxides (Özdokur et al., 2014; Çakar et al., 2013), phthalocyanines (Li et al., 2015; Nascimento et al., 2013) and graphenes (Ikhsan et al., 2015; Rajabzadeh et al., 2014) were commonly used for modified electrode preparation. The detailed information about modifiers, which were used in this thesis, can be found in the following paragraphs.

1.2.2.1 Metal nano particles

Metal nanoparticles (MNPs) or nanometer-sized metal particles have attracted great technological and scientific interests because of their unique properties, such as strong optical, electrical and electromagnetic enhancement which significantly differ from their bulk counterparts. Therefore, MNPs, improved the catalytic activity of the surfaces where they modified (Karabiberoğlu, 2014). The combination of metal nanoparticles with some supporting materials such as polymer films and carbon nanotubes, composite nanomaterials, showed higher electrocatalytic activity and remains stable for long period of time as compared single existence of MNP on conventional electrodes (Bakır et al., 2011; Taei and Ramazani, 2014; Hui et al., 2015).

MNPs can be synthesized on different materials by various techniques such as, hydrothermal synthesis by precipitation (Cote et al., 2003), radio-frequency co-sputtering technique (Serano and Pal, 2003), sol–gel process (Lee et al., 2001), chemical reduction technique (Esparza et al., 2007), cyclic voltammetry (Ulubay and Dursun, 2010) and electrochemical deposition combined with nanoimprint lithography (Yang et al., 2009) etc.

Considering the all MNP preparation techniques, electrochemical methods provide to control the size and density of high purity metal nanoparticles with low cost and short time. Short-term electrodeposition prompted to form narrow diametered MNPs while relatively higher size and amount of MNPs were acquired with increasing electrodeposition time. The smaller the size of the MNP, higher the surface area and improve the catalytic efficiency (Mohanty, 2011; Guo and Wang, 2007).

Among various kinds of MNP, gold nanoparticles are one of the most frequently studied metals in electrochemical applications (Guo and Wang, 2007). In addition, platinum is probably the most-preferred catalytic surface for enormous range of applications. Due to the high cost of noble metal, platinum, many researchers study to reduce the platinum content of electrode material. For this purpose, Pt nanoparticles, Pt thin-film electrodes and Pt alloys were prepared which contain few amount of metal as compared to the bulk forms of electrodes (Wee et al., 2007; Paulus et al., 2002). In order to extinguish the higher costs of nobel metals, non nobel metal nanoparticles were used as an alternative which also show excellent catalytic behavior in analytical applications (Hui et al., 2015; Ulubay and Dursun, 2010).

MNPs were found various application fields as medicine, optics, photochemistry, electrochemistry, catalysis etc. One of the most important areas of MNPs is their usage as catalysts in fuel cells. The metal nano particles modified electrodes have been also used in electroanalysis application for organic and inorganic compounds. Some recent studies about fuel cell and electroanalysis application are given following paragraphs (Karabiberoğlu, 2014; Muraviev, 2005).

Electrochemically synthesized platinum nanoparticles decorated on the Nitrogen-doped graphene sheets (Pt/N-Gr) to prepare the modified electrode surface. Characterization techniques such as FTIR, TEM, SEM and XPS were proving the existence of compounds on the electrode surface. The modified electrodes not only used for the cathodic oxygen reduction reaction in fuel cells but also used for the anodic fuel (hydrazine, methanol and ethanol) oxidation successfully. The modified electrode exhibited long-term stability and poisoning tolerance as compared to the commercial electrodes (Navaee et al., 2015)

Shang et al. studied the trimetallic nickel-palladium-gold hollow nanoparticles for methanol oxidation in alkaline media. First of all, chemical reduction of nickel nanoparticles by sodium borohydride carry out in an aqueous solution. NiNPs used as a template for galvanic displacement reaction, which used for the preparation of NiPdAu NPs. Chronoamperometric and CV studies exhibited the higher catalytic activity and stability of NiPdAu/C catalysts towards methanol oxidation as compared to the commercial Pd/C and Pt/C. The trimetallic nanoparticles dispersed carbon catalyst was a great candidate as an anode material for DMFCs. (Shang et al., 2015).

The chemically synthesized antimony nanoparticles (SbNPs) and multiwalled carbon nanotubes (MWCNT) combined to construct a composite electrode using carbon paste as substrate (SbNP-MWCNT). The square-wave adsorptive stripping voltammetric analysis of trace heavy metals, Pb^{2+} and Cd^{2+} , achieved successfully by the developed electrode (Ashrafia et al., 2014).

In conclusion, the existence of MNPs on catalyst surfaces provided the increasing activity by large surface area and unique properties, which was desired for both fuel cell applications and analytical determinations.

1.2.2.2 Carbon nanotubes

As is known, considerable attention focused on nanometer-sized structures, which show great catalytic activity due to their high surface area to volume ratio and their interface effective properties. Carbon nanotubes are one of the most attracted material in this field. The historical roots of carbon nanotubes (CNTs) started with 60s that Roger Bacon produced graphene sheets rolled into scrolls, which supported with the microscopic and diffraction results.

CNTs actually discovered by Sumio Iijima in 1991, which published as “helical microtubules of graphitic carbon”, these soon, known as multiwalled carbon nanotubes. Two years later Iijima published another type of 1.37 nm diametered single graphene cylinder which today known as single wall carbon nanotube. While multiwalled carbon nanotubes consisted of more than one rolled graphenes that telescoped, single walled carbon nanotubes only formed from a single graphene sheet. The wrapping of the graphene sheet to form cylindrical nanotubes can be occurred with different angels. CNTs sorted by this angle values as zigzag, chiral and armchair which affect their property that resulted in the metallic (armchair) or semiconducting (zigzag) CNTs. Figure 1.1 represents the rolled forms of graphene sheet and types types of carbon nanotubes (Ventra et al., 2004).

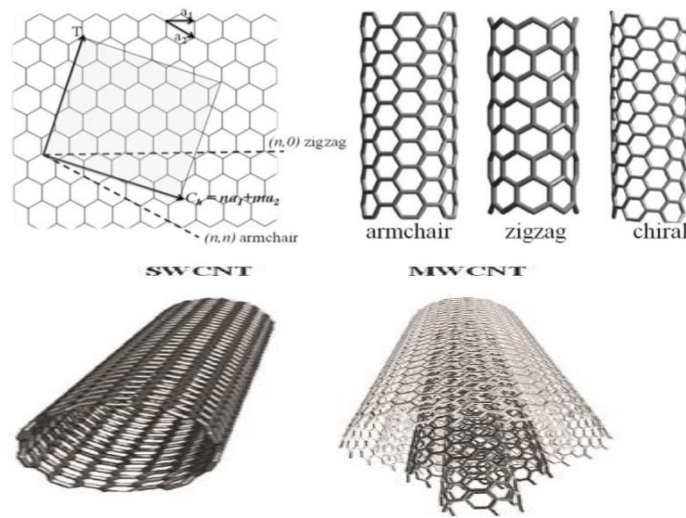


Figure 1.1 Rolled types of graphene sheet and types of carbon nanotubes (Single walled and multiwalled), (Adapted from Kanoun et al., 2014; Choudhary and Gupta, 2011).

CNTs have excellent thermal and electrical conductivity, large surface area as compared to the other carbon-based materials. Moreover, CNTs formed with sp^2 bonded carbons that are stronger than sp and sp^3 bonds that provide the improved properties such as flexibility and tensile strength (Yang et al., 2015; Martins-Júnior et al., 2013). The special properties of CNTs like high surface area, excellent conductivity and good biocompatibility resulted in a wide range of application fields such as; environmental remediation, sensor applications, electronic devices and medicine applications (Martins-Júnior et al., 2013; Gendron et al., 2015; Dursun and Gelmez, 2010; Cerovac et al., 2015; Jeong et al., 2015).

The large surface to volume ratios and active sites of CNTs provide golden opportunity to functionalization and effective analytical applications especially sensitive determination of trace organic and inorganic molecules (Dursun and Gelmez, 2010; Cerovac et al., 2015; Swamy and Venton, 2007; Zare and Nasirizadeh, 2010; Salimi et al., 2015). In addition, CNTs are insoluble in water due to their non polar nature, while they can be covalently or noncovalently functionalized which make them preferable material as electrode material (Vashist et al., 2011).

Narayana and coworkers studied multiwalled carbon nanotube with serin polymer in order to investigate the epinephrine oxidation in the presence of serotonin and folic acid. In the first step, the electrode was covered with multiwalled carbon nanotube by dropcasting and in the second step the MWCNT covered electrode immersed in the serin monomere containing solution to prepare serin polymer on the MWCNT surface by five repetitive potential cycles. The modified electrode characterized with electrochemical impedance technique and it was used for electrochemical determination of epinephrine with 0.6 μM LOD (Narayana et al., 2015).

In other study, gold nanoparticles were prepared by immersing the multiwalled carbon nanotube modified carbon paste electrode in 6 mM HAuCl_4 containing KNO_3 solution and applying the constant potential. Nitrite was successfully determined at GNPs /MWCPE by monitoring the oxidation peak with higher peak current values as compared to the unmodified CPE and MWCNTs-modified electrode. The linear range was found as 0.05–250.0 mM with a detection limit of 0.01 μM . The real sample analysis of nitrite in sausage, tap water, mineral water, salami and cheese were carrying out successfully by modified electrode (Afkhami et al., 2014).

Single walled carbon nanotubes composed with cobaltphthalocyanines and used as an efficient gas sensor for dimethyl methylphosphonat (DMMP). SEM, TEM images and IR spectrums prove the existence of components on the electrode surface and TGA results exhibited the stability of material. The synergetic effect of the SWNT and CoPc shows a higher catalytic activity to DMMP as compared to the bare SWNT (Wang et al., 2011).

CNTs were also studied by our research group that acid treated multiwalled carbon nanotubes prepared for determination of 2,6-diaminopurine (2,6-DAP) in pH 7.4 phosphate buffer solution. Two-electron two-proton involved oxidation process and also physicochemical studies carry out at this electrode surface successfully. In addition, oxygen reduction reaction was investigated with the Cu-Au bimetallic nanoparticles decorated carbon nanotubes modified GCE. Oxygen reduction monitored with four electrons one-step pathway on this modified electrode that can be used as efficient cathode material for fuel cell applications. In other study, multiwalled carbon nanotubes modified glassy carbon electrode was decorated with electrochemically formed platinum nanoparticles, which showed excellent catalytic behavior towards ascorbic acid, dopamine and uric acid oxidation (Ayan et al., 2013; Bakır et al., 2011; Dursun and Gelmez, 2010).

1.2.2.2 Phthalocyanines

Phthalocyanines (Pc) are macrocyclic organometallic compounds, which incidentally discovered by Braun and Tcherniac in 1907. Pcs first studied in 1933 by one of the professors of Imperial College of Science and Technology (Nas et al., 2013). Their unique 18- π electron conjugated system structure, which have similarity with porphyrins, consisting of four isoindole units with nitrogen linkage. Phthalocyanines were denominated by their central part, which have ability to accommodate more than 60 elements. The physical features change based on the kind of incorporated element. If hydrogens take place in the system, phthalocyanines abbreviated as H₂Pc means “metal free phthalocyanine”. In addition, if one or two metals included in the phthalocyanine structure, it was called “metal phthalocyanine” which abbreviated as MPc (Sakamoto and Ohno-Okumura, 2009).

MPcs are green to bright blue coloured materials that they one of the most studied organometallic macrocyclic materials. The metastable α and stable β forms are the most popular polymorphic phases of MPcs. The chemical versatility of Pc compounds provide the easy substitution of wide range of compounds on the ring. In addition, electronic delocalization provides high chemical thermal stability to Pc molecules as compared to the other molecular materials make them important material in scientific researches and technological area (Claessens et al., 2008; Afify et al., 2015; Nkosi and Ozoemena, 2008; Wang et al., 2011).

MPcs have special physico-chemical properties such as; thermal and chemical stability, ability to contain various kinds of metal that change the electron transfer rate, easily substitution of the ring to form various Pc derivatives that they used in many application fields in technological area. MPcs attracted great interest not only for their applicability in dyes but also as important backbone for new molecular materials for electronic devices. Figure 1.2 represents the some application areas of phthalocyanines in the structure figure of Pc (Wang et al., 2011; Sakamoto and Ohno-Okumura, 2009).

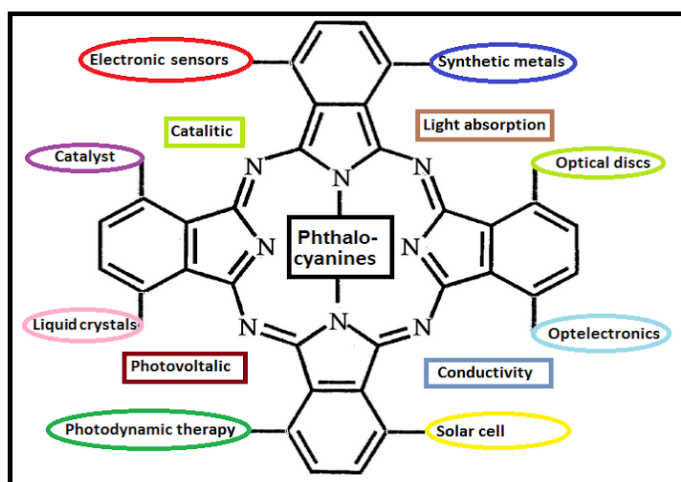


Figure 1.2 Application fields of phthalocyanines. (Adapted from Sakamoto and Ohno-Okumura, 2009).

Pcs needed to used with another conductive and stable supporting materials due to some limitations of themselves while using as an electrode material. These limitations are; the low electronic transfer rate due to their low electrical conductivity and the other one, weak adsorption behavior on the conventional electrode materials (GCE, gold etc.) which resulted in the peeling off the Pcs from electrode surface that cause poor stability. In order to overcome these problems stable and more conductive supporting materials such as graphenes, polymer films and carbon naotubes were used with Pcs (Devasenathipathy et al., 2015; Li et al., 2015; Pillay et al., 2009).

Combination of two or more components to form multicomponent modified surfaces or hybrids were attracting great interest in many areas of new technologies. Among various kinds of components, CNTs and MPc were promising materials to combine to form hybrids that have improved more efficient and special characteristic as compared to their individual forms. MPc complexes can be combined covalently or non-covalently with CNTs. Without any

substituted parts, MPcs were adsorbed non-covalently by π - π interactions on to CNTs. However, covalent linkage with amide bond formation observed in case of amino-substituted MPcs combined with CNTs (Wang et al., 2011; Moraes et al., 2010).

Mugadza and Nyokong combined single walled carbon nanotubes (SWCNT) with iron tetraaminophthalocyanine (FeTAPc) in order to improve the activity of bare GCE towards amitrole and diuron. First, SWCNTs were treated with thionyl chloride to form SWCNT-COCl. Then it refluxed with FeTAPc in DMF, centrifuged and dried. GCE immersed in FeTAPc-SWCNT containing DMAF suspension for 5 minutes and dried which denoted as FeTAPc-SWCNT (dendrimer)-GCE. The electrochemical behaviour of amitrole and diuron were studied and they found linearly increased concentration range as 5.0×10^{-5} to 1.0×10^{-4} M for amitrole and diuron with 2.15×10^{-7} and 2.6×10^{-7} M LODs, respectively on FeTAPc-SWCNT (dendrimer)-GCE (Mugadza and Nyokong, 2010).

Moraes et al described a paraffin/MWCNT/CoPc composite electrode for epinephrine determination in pH 6 phosphate buffer solution by DPV. In order to prepare the composite electrode, paraffin, MWCNT and CoPc were mixed in a mortar and heated until it was melted. Then filled into a syringe and attached with a copper wire for conductivity. The electrode abbreviated as paraffin/MWCNT/CoPc composite electrode. It was successfully used for the determination of epinephrine in synthetic solution as well as human urine sample. The linear range was found from 1.33 to 5.50 μ M, with a detection limit of 15.6 nM on the proposed electrode that has also long lifetime (Moraes et al., 2010).

In other study, pencil graphite electrode (PGE) was first covered with overoxidized polypyrrole nanofiber, which then modified with cobalt (II) phthalocyanine tetrasulfonate (CoPcTS) to improve electrocatalytic activity of electrode towards glucose oxidation in alkaline media. Disposable PGE immersed in the pyrrole containing 0.1M LiClO₄ + 0.1M Na₂CO₃ solution and potential scans between 0.00 and 0.80 V. Polymer modified electrode over-oxidized in NaOH which followed immersion of electrode in 5×10^{-4} M CoPcTS containing aqueous solution for 150 min for CoPcTS adsorption. The resulted PG/OPPyNF/CoPcTS used for glucose determination which were successfully achieved with an LOD value of 0.1mM and linear concentration range between 0.25 to 20 mM (Özcan et al., 2008).

Jeevagan and John published that polymer film of nonperipheral amine substituted nickel (II) phthalocyanine (p-4 α -Ni^{II}TAPc) modified glassy carbon electrode enhanced the electrocatalytic oxidation of guanosine 5-monophosphate (GMP). p-4 α -Ni^{II}TAPc/GC electrode prepared by applying 15 repetitive cyclic potential scans between -0.15 and 0.90 V to GCE in N,N-dimethylformamide solution containing 1 mM of p-4 α -Ni^{II}TAPc monomer and 0.1 M tetrabutylammonium perchlorate. The selectively and sensitive determination of GMP studied in the presence of high guanine concentration by differential pulse voltammetry. The 0.005–1 mM linear range obtained for GMP with a detection limit of 5×10^{-6} M on p-4 α -Ni^{II}TAPc/GCE (Jeevagan and John, 2013).

1.2.2.2 Conducting polymer films

Conducting polymers (CPs) are special materials, which discovered in mid-1970s and their real value was recognized in 2000 with the Nobel Prize for Chemistry. Alan Heeger, Alan MacDiarmid and Hideki Shirakawa are collaborating scientists who discovered the first inherently conducting polymer, polyacetylene, They called as intelligent materials due to their unique properties. The conductive character of CPs provides to use them in electronic tools like computers. In addition, CPs easily combined with stimuli-recognition sites which gained them various information-evolution capability (Wallace et al., 2009).

The electrochemically active polymers divided into two categories are; ion conducting polymers and electron conducting polymers. Electron conductive polymers are also categorized by their electron transport mode, which are “redox polymers” and “electronically conducting polymers”. Redox polymers consisted of localized redox sites, which have oxidation and reduction ability as well as provide transferring of electrons between their neighbours. Polymers, which prepared by oxidative or reductive polymerization of benzoid, nonbenzoid and heterocyclic compounds that their bonds were reorganized by electrochemical transformation called as electronically conducting polymers. The most widely used polymers; Polyaminophenol (PAP), polypolypyrrole (PPy), polyaniline (PANI) and poly-(3,4-ethylenedioxythiophene) (PEDOT) are known as electronically conducting polymers (Inzelt, 2008). The delocalization of π -bonded electrons over the polymeric structure provides electron affinity, decreased ionization potentials and conductivity to the polymers. CPs are good electrical conductors due to their high conductivity to weight ratio and also have special optical properties. The electrical, optical and magnetic characteristics of CPs were

close to the metals that they also called as “synthetic metals” (Ates, 2013; AL-Oqla et al., 2015).

There is an increasing interest on the preparation of polymerized surfaces which can be obtained by chemical or electrochemical methods. If the polymeric structure was used as electrode material, the electrochemical polymerization recommended which was easy way for preparation of thin films. Chemical route were preferred if the polymer needed in large scales which also provide post covalent modification possible (Inzelt, 2008).

Conductive polymers found wide range of application field due to their special characteristics. For instance, conductive polymers used as polymer electrolytes in form of a liquid, gel or solid, which have an important role for ionic conduction in the electrochromic devices. In case of combination of conducting polymers with inorganic materials such as zirconium dioxide nanocrystals to form composite polymer electrolytes, they behave highly meliorated ionic conductivity (Puguan et al., 2015). CPs very often used in energy technologies especially in proton exchange membrane fuel cells. Polymers with high mechanical, thermal, and chemical stability, low gas permeability and high conductivity are required in energy technologies that are crucial parameters for PEM materials (Miyake et al., 2015). Conducting polymer coatings were used in order to improve the corrosion resistance of metals. Therefore polymers coated on the bipolar plates of fuel cells (Deyab, 2014). Moreover, CPs used membrane in electro-separation methods especially for wastewater treatment. Electrical field was applied to the both sides of conductive electroactive membranes that resulted in the transportation of organic molecules electroactive ions etc. (Karimi et al., 2014). The most interesting application field of CPs is their usage as biomaterial for tissue engineering due to their biocompatible and biodegradable behavior and suitable nature that allows cells or tissue cultured upon them (Balint et al., 2014). In addition, CPs were frequently used in sensor application as an electrode material. Various organic and inorganic compounds were detected with conductive polymer modified surfaces (Joseph et al., 2014; Zhang et al., 2013).

PAP, PPy, PANI and PEDOT are the most widely studied conductive polymers in wide range of research areas (Dallas and Georgakilas, 2015). Aminophenols (APs) are compounds that have $-OH$ and $-NH_2$ groups in the phenyl ring, which have ability to oxidize at those parts. The hydroxyl group oxidized to quinone and quinone reduced again during oxidation process. APs

show different electrochemical properties based on the position of -OH and -NH_2 groups, which named as “ortho, meta and para”. Figure 1.3 shows the structure of p-aminophenol (4-aminophenol) (Thenmozhi et al., 2011a; 2011b).

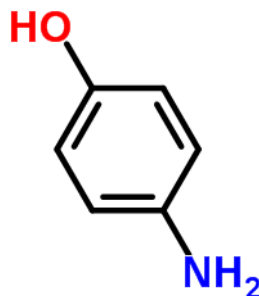


Figure 1.3 Structure of 4-aminophenol.

Polymer film modified electrodes were studied by many researchers, which described in the following paragraphs.

Liu and coworkers described electrochemical polymerization of ortho aminophenol on GCE in 5 mM SDS containing HClO_4 solution. Stable polymer film (POAP/GCE) was obtained by 60 repetitive cycles between -0.1 and $+0.75$ V. Then POAP/GCE was immersed in the platinum containing acidic solution to form platinum nanoparticles on electrode surface. The resulted modified electrode was used successfully for L-cysteine determination by amperometry. (Liu et al., 2010)

In other biosensor study, graphite electrode was modified with 4-aminophenol which followed by immobilization of acetylcholinesterase. AFM and EIS techniques prove the surface modification. Diclorvos, organophosphate pesticide, was investigated and determined with the modified electrode. The detection limit was calculated as $0.8 \mu\text{M}$ that modified electrode not only a good backbone for enzyme immobilization but also a good sensor for sensitive determination of diclorvos (Melo et al., 2011).

Ghanbari and Hajheidari studied biologically important molecules with pyrrole based modified electrodes. First, pyrrole was modified on the glassy carbon surface from the solution containing 0.15 M pyrrole, 0.10 M LiClO_4 , and 0.10 M carbonate by applying constant potential. The electrode kept in 0.10 M HClO_4 solution to remove the carbonate ions. Then, PPy film was over-oxidized in the presence of NaOH. The Cu_xO nanowires formed on the PPy/GCE by

applying constant potential which followed by applying constant potential to $\text{Cu}_x\text{O-PPy/GCE}$ in $\text{Zn(NO}_3)_2$ containing 0.1 M KNO_3 to form ZnO nanosheets. The resulted modified electrode denoted as $\text{ZnO-Cu}_x\text{O-PPy/GCE}$ that used for the selective and sensitive simultaneous determination of the ascorbic acid, dopamine and uric acid. The LOD values were found as 25, 0.04, and 0.2 μM for AA, DA, and UA, respectively (Ghanbari and Hajheidari, 2015).

Our research group also studied conducting polymer modified electrodes for sensitive determination of biologically important compounds. In our first study, glassy carbon electrode immersed in pyrrole containing sodium dodecyl sulfate (SDS) solution and polymerized with three potential cycles between -0.35 and 0.85 V. Electrode rinsed with water and then over oxidized in NaOH to form hydroxylated structure more porous structure. The PPy/GCE was decorated with copper nanoparticles with CV. Ultra sensitive determination of dopamine (LOD: 0.85 nM) and uric acid (LOD: 0.8 nM) successfully carry out at nano-Cu/PPy/GCE electrode in phosphate buffer solution. Our last study with polymerized surfaces was describing the polymerization of p-aminophenol monomer in SDS containing HClO_4 solution. In order to obtain better conductivity and larger surface area, PAP/GCE was over-oxidized in NaOH, which denoted as Ox-PAP/GCE. This modified electrode shows excellent catalytic activity for simultaneous determination of ascorbic acid, epinephrine and uric acid with high reproducibility and long-term stability as compared to the PAP/GCE and Bare GCE in pH 7.4 PBS. The detection limits were calculated as 1 μM , 6.5 nM and 0.18 μM for ascorbic acid, epinephrine, and uric acid, respectively (Ulubay and Dursun, 2010; Koçak and Dursun, 2013).

1.3 Fuel Cell Application

Energy is a curicial issue for the worldwide countries due to the increasing population and proportional growing demand. The world's energy mainly obtained from fossil energy sources such as oil while the reserves are diminishing which make their price higher and higher day by day (Edwards et al., 2008). In addition, another subject for increasing demand in clean energy technologies all over the world is, aming to decrease the greenhouse gases emissions (e.g., NO_x , CO_2 , and SO_x) which resulted in change in global climate (Antunes et al., 2010). There is urgent need to find more sustainable energy sources. The renewable energy sources such as wind turbines, solar photovoltaic systems and fuel cells are good candidates for the generation of electricity.

Fuel cells that invented firstly in 1839 by Sir William Robert Grove are electronic devices, which convert chemical energy in to the electrical energy (Subsingha and Sarakarn, 2012). They consist of anode, cathode and electrolyte which schematically shown in Figure 1.4. The electrode plates, gas pressure, operation temperature such parameters that affect the fuel cell efficiency. Fuel feed to the cell system, for instance hydrogen, then it reaches the catalyst plate, it separates into protons and electrons. The free electrons at the anode, flow through the external circuit. Oxygen from the air or direct oxygen feed to the other part of the system. At the cathode, electrons from the external circuit, oxygen and protons combine to form water and heat.

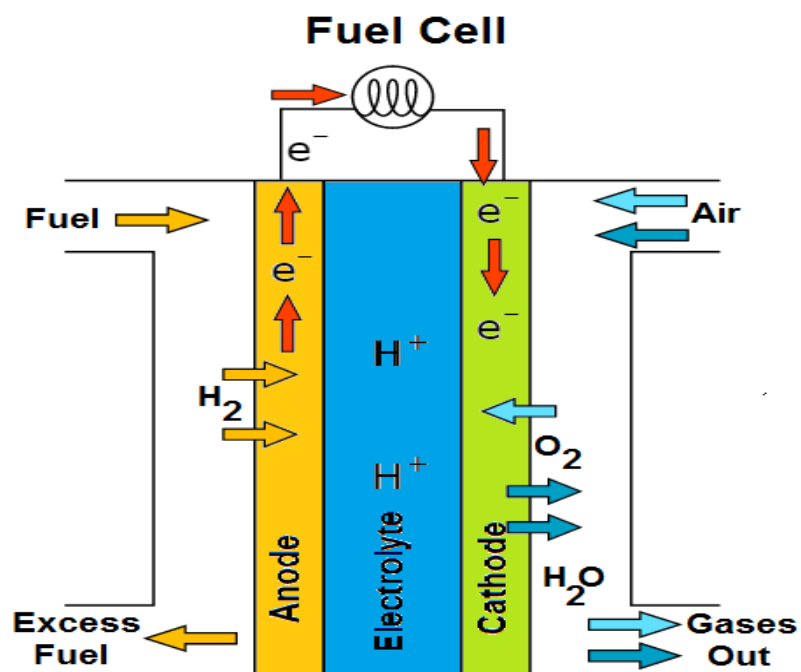


Figure 1.4 Schem of fuel cell.

Fuel cell classified with their fuel types, operating temperatures and electrolyte types that simple comparison of fuel cell types were shown in Table 1.1. Each system has advantages and disadvantages but all have aimed to faster the reaction rate, which results in the increment of current values and power of the system.

PEM fuel cells consist of bipolar plates and a membrane electrode assembly, which involve catalyst, gas diffusion layer and proton exchange membrane. The electrolyte membrane blocking electrons and allows only protons to pass (Liu et al., 2015). Hydrogen is a gas that should stored under high pressure (up to 70

MPa) due to its low density (0.089 g/L) which results in tremendous volumes for application as a fuel. (e.g., 6 kg of hydrogen will occupy a 5 m diametered spherical volume). Nevertheless, hydrogen still needs to be improved as compared to the gasoline, which contains approximately six times as much energy as a liter of hydrogen (Yang et al., 2010). In light of this fact, hydrogen supply problem solved by extracting the hydrogen from fuels or use directly another type of fuels such as ethanol, methanol etc. for energy conversion.

A promising alternative to the hydrogen-based problem is to use methanol as a fuel in liquid form (i.e. not extracting the hydrogen from the methanol) which called direct methanol fuel cell. They have attracting great interest due to the simple and cheaply synthesis of methanol, easy storage of fuel, relatively reduced system weight, high energy density, and low emission profile. They have found many application fields; forklifts, scooters, military equipments and especially in portable electronics devices such as mobile telephones, laptops etc. The performance of DMFC system strongly depends on the catalyst structure. Catalyst efficiency significantly change by the preparation technique that catalytically active electrode material preparation is a critical issue to improve the durability and energy power of the fuel cell systems (Jeon et al., 2015; Mehmood et al., 2015; Vielstich, 2003).

Alkaline fuel cell (AFC) is another type of fuel cell, which operates below 200⁰C, was used on the Apollo and Shuttle Orbiter craft. However its fame, some problems such as slow reaction rate, need to be overcome. Noble metal containing porous electrodes and high operating pressures applied for this purpose. In addition, AFCs need to the CO₂ free fuel and air supplies. The KOH solution is react with CO₂ and form K₂CO₃ that decrease the power of cell by blocking the diffusion and decreasing the hydroxyl concentration (Merle et al., 2011; Brushett et al., 2012; Larminie and Dicks, 2003).

Molten carbonate and solid oxide fuel cells are high temperature cells as compared to the others. In solid oxide fuel cell (SOFC), high reaction rates can be obtained due to the high operation temperatures (600 to 1000⁰C). In addition, they provide direct gas use without any separation unit. However, manufacturing of ceramic cells are too expensive and need complex cooling systems. Molten carbonate fuel cells need CO₂ to work and not need any expensive catalyst due to the high operating temperatures result in the increment of reaction rate (Larminie and Dicks, 2003).

Table 1.1 Comparison of different types of fuel cell (Larminie and Dicks, 2003).

Fuel cell type	Temperature	Mobile Ion	Comments
Proton exchange membrane fuel cell (PEMFC)	30-100 ⁰ C	H ⁺	Vehicles and mobile applications.
Alkaline (AFC)	50–200 ⁰ C	OH [−]	Used in space vehicles, e.g. Apollo, Shuttle.
Direct methanol (DMFC)	20–90 ⁰ C	H ⁺	Suitable for portable electronic systems of low power, running for long times
Solid oxide (SOFC)	500–1000 ⁰ C	O ^{2−}	Suitable for all sizes of CHP* systems, 2kW to multi-MW.
Molten carbonate (MCFC)	~650 ⁰ C	CO ₃ ^{2−}	Suitable for medium- to large-scale CHP* systems, up to MW capacity
Phosphoric acid (PAFC)	~220 ⁰ C	H ⁺	Large numbers of 200-kW CHP* systems in use.

* CHP: Combined heat and power.

The common vehicle companies such as Ford, Honda, General Motors, Toyota and Peugeot are committed to developing fuel cell cars, however systems need some improvement for totally supply all requirements (Antunes et al., 2010). The main application areas of fuel cells are; mobile power systems, combined heat and power systems, portable electronic devices such as mobile phones and computers (Budde et al., 2015; Erdinc and Uzunoglu, 2010).

In conclusion, fuel cells are long lasting, reliable and simple systems. Their small system structure provides the portable usage. Fuel cells are silent systems as compared to the other energy converters but most importantly, they have low emission profile, which is desired by all countries to avoid global warming. Despite all advantages, fuel cells still need to be improved in terms of costs (Larminie and Dicks, 2003).

1.3.1 Oxygen electroreduction

The oxygen reduction reaction (ORR) has great importance for human life for not only its important role in respiration but also its use in fuel cells. Oxygen reduction has also crucial importance in batteries, electrosynthesis of hydrogen peroxide, gas sensors, chlorine/alkali manufacturing and metal corrosion (Duan et al., 2015; Tiburcio-Silver and Sánchez-Juárez, 2004; Dafydd et al., 2005).

In fuel cell technology, oxygen is a critical component that cathodic reaction all based on it. Air or pure oxygen feed to the cell and chemical reaction between anode and cathode generate the power of the cell. Oxygen reduction reaction studied in different acidic and alkaline mediums, which affect the reaction rate (Karabiberoğlu, 2014).

The oxygen reduction reaction occurs follows two main pathways in acidic or alkaline aqueous solutions. First way is two-steps and 2-electron reduction pathway from O_2 to hydrogen peroxide (H_2O_2) and from hydrogen peroxide to H_2O (Vaik et al., 2004; Ohma et al., 2010) and second one is direct 4-electron reduction pathway from O_2 to H_2O (Prakash and Joachin, 2000; Huang et al., 2005). Scarsely, it follows the 1-electron reduction pathway from O_2 to superoxide in non-aqueous and/or in alkaline solutions (Ghanema et al., 2015).

Table 1.2 Oxygen reduction reactions and related thermodynamic electrode potentials (Zhang, 2008).

	Oxygen reduction reactions	Thermodynamic electrode potential V	Electrolyte
One step & 4 electron pathway	$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$	0.401	Alkaline solution
Two steps & 2 electron pathway	$O_2 + H_2O + 2e^- \rightarrow HO_2^- + OH^-$	-0.065	
	$HO_2^- + H_2O + 2e^- \rightarrow 3OH^-$	0.867	
One step & 2 electron pathway	$O_2 + 4H^+ + 4e^- \rightarrow H_2O$	1.229	Asidic solution
Two steps & 2 electron pathway	$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$	0.70	
	$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$	1.76	
Superoxide pathway	$O_2 + e^- \rightarrow O_2^-$	Depend on the solvent type	Non aques solvent
	$O_2^- + e^- \rightarrow O_2^{2-}$		

Researchers all over the world were studied oxygen reduction reaction on different modified surfaces in different mediums. Some examples of these researches were mentioned in the following paragraphs:

Although the U.S. Department of Energy limited the platinum loading at the long-term goals for PEMFC performance, the platinum need in the cathode material still remains due to the limitation problems of oxygen reduction reaction. Such as oxygen diffusion at low potentials and high overpotential (Wee et al., 2007).

Cheaply manufactured, simply prepared platinum nanoparticles doped Nitrogen-doped graphene sheets (Pt/N-Gr) prepared by the repetitive potential is cycles from 3V to +3V in acetonitrile solution which have long-term stability. The electrocatalytic activity of the prepared composite toward the reduction of O_2 was investigated by cyclic voltammetry and compared with commercial platinum/carbon which was more active in terms of peak potentials and the current densities (Navaee et al., 2015).

Another work was studied by the helping of Pt nanoparticle-titanium dioxide/multi-walled carbon nanotube (Pt-TiO₂/MWCNT). Chemical vapour deposition, atomic layer deposition and magnetron sputtering techniques were used for synthesizing the composite material and then it was employed to oxygen reduction reaction both acid and alkaline media. The surface composition of Pt-TiO₂/MWCNT catalysts was characterised using XPS, SEM. Pt-TiO₂/MWCNT was compared with that of commercial Pt/C catalyst, and bulk Pt. TiO₂ incorporation into the catalyst was develop the electrocatalytic activity of modified surface towards the ORR. The same mechanism observed towards oxygen reduction on Pt-TiO₂/MWCNT and Pt/C catalysts (Jukk et al., 2014).

Polymer modified surfaces were scarcely active towards oxygen reduction without metal content that many researchers combine the polyers with other materials especially metals. The low amount of platinum loaded on the electrode surface after the electrochemical polymerization of p-(4-amino-3-hydroxynaphtalene sulfonic acid) on glassy carbon electrode. The electrocatalytic activity of the platinum modified p-(AHNSA)/GCE towards oxygen reduction reaction is investigated by rotating disk, cyclic voltammetry and chronoamperometry. While polymer modified glassy carbon electrode shows a poor reduction behavior, two electron reduction of oxygen to hydrogen peroxide,

platinum containing p-(AHNSA)/GCE shows a direct four electron reduction of oxygen to water (Zewde and Admassie, 2012).

In addition, different groups studied alternative non-platinum catalysts. Alexeyeva et al., studied oxygen reduction reaction with chemically deposited gold nanoparticles modified carbon nanotubes in 0.5 M H_2SO_4 using the rotating disk electrode. They compared the prepared modified electrode with that of a bulk gold electrode and exhibited the improved effect of AuNP/MWCNT catalyst on which oxygen reduction occurred more positive potentials than Au electrode. (Alexeyeva, et al., 2010).

Nanohybrid materials were also studied for investigation of ORR, which prepared by combination of reduced graphene oxide (rGO) and Fe_3O_4 nanoparticles. Graphene-based structures are attracting new interest for energy applications as electrode material. Nitrogen-rich carbon nanosheets were used as crosslinker for chemically coupling metal oxide nanoparticles to reduced graphene oxide that yield to the homogenous growth of Fe_3O_4 nanoparticles on rGO. Nanohybrids exhibited more catalytic activity towards oxygen reduction reaction than Pt/C catalyst (i.e. high current density, electron transfer number and stability) (Liu et al., 2015).

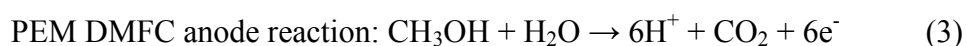
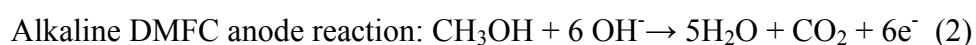
Investigation of oxygen reduction reaction was also in the scope of our research group that metal ad layered single crystal electrodes were used as cathode catalysts. Pd, Cd and Zn ad layers were prepared by under potential deposition technique. All electrodes were studied oxygen saturated in 0.1 M NaOH solution and compared with Pd disk electrode. Potential shift in positive direction and current increment were observed at 1/5 ML Pd ad-layer modified Au(111) electrode (Dursun et al., 2009). In other study, Pt modified on single crystal surface with two different techniques, electrochemical deposition and deposition by replacement of Cu on Au (111). These electrodes and Pt disk electrode were investigated in O_2 saturated alkaline medium. Electrochemically deposited Pt ad-layer modified Au(111) electrode served as a good cathode surface for oxygen reduction via 4-electron transfer as compared to the all other electrodes (Dursun et al., 2011). We also studied oxygen reduction on Cu-Au bimetallic nanoparticles modified carbon nanotube glassy carbon electrode. Noteworthy current improvement and potential shift obtained that modified electrode as compared to the glassy carbon electrode, multiwalled carbon nanotube modified, monometallic Cu and Au modified multiwalled carbon

nanotube GCE in alkaline medium that oxygen reduction reaction follows one-step and 4-electron pathway (Bakır et al., 2011).

1.3.2 Methanol electrooxidation

Methyl alcohol, methanol, is a colorless organic compound which was found in the human body in small quantities while high concentrations are harmful for humans in case of taking by digestion. Methanol was an important compound especially in fuel cells due to its usage as a fuel which also significant compound for manufacturing of industrial goods and chemical feedstocks. Direct methanol fuel cells are one of the most popular fuel cells due to their portable characteristic, relatively high energy density and simple design which use the methanol as a fuel for energy conversion (Zhen and Wang, 2015; Wu et al., 2014).

Methanol is refueling quickly, easily handle and store with an advantage of its low costs. Methanol can be produced from natural gas, coal, hydrogen, and biomass. Stainless steel should be used as can glass for storage of methanol. Plastics are not suitable due to its well ability of solving (Larminie and Dicks, 2003; Zhen and Wang, 2015). Direct methanol fuel cells are varies based on the electrolyte type. They denoted as “alkaline DMFC” in case of using alkaline electrolyte, while they denoted as “PEM DMFC” if proton exchange membranes used. The anode reactions changed depend on the electrolyte type. The overall DMFC reaction and anodic reactions was stated below in equations 1,2,3 (Larminie and Dicks, 2003).



Methanol concentration effect the crossover of CO_2 to the cathode that related to the decrease of energy density in system. Methanol should be feed to the cell sytem about 1 M that to prevent the crossovers in high concentration values (Dohle et al., 2002). Moreover, water addition was crucial for the formation of CO_2 that is the final product of methanol oxidation. Water dissociates and acts as an oxygen donor for the reaction. The total oxidation of methanol releases six electrons that passes through the outer circuit and then consumed at the cathode.

The electrolyte concentration remains almost stable by the protons diffusion from the anode to the cathode (Vielstich, 2003).

Methanol oxidation occurs by choosing one of the pathways from top to bottom that shown in Figure 1.5 which mostly depends on the electrode material and structure. The lower right edge compounds are more stable than others that reaction follows possible that route. In detail explanation, three basic steps can be followed with the arrows. Each time one down and one right step occur the 3 step-2 electron process which totally release six electrons. First, methanol is oxidized to formaldehyde. Then formaldehyde turns to formic acid. Finally, formic acid reacts to form carbon dioxide.

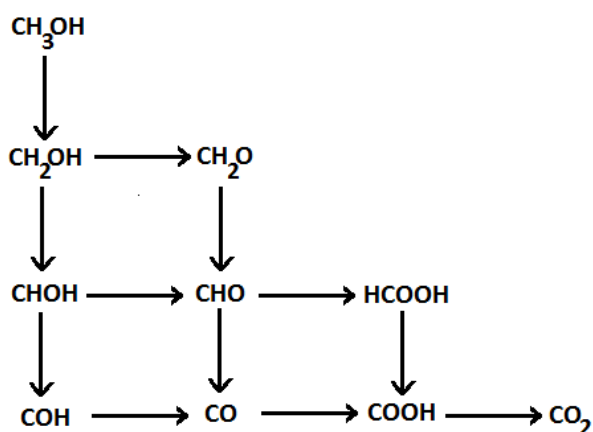


Figure 1.5 Methanol oxidation stages on DMFC anode (Adapted from Larminie and Dicks, 2003).

Definition of the adsorbed species and intermediates that formed during methanol oxidation was studied by several techniques. Supporting electrolyte also effect the amount of the products. Infrared spectroscopy gives an opinion about the formed intermediates such as; CO , COH , COC etc., during the methanol oxidation for instance on $\text{Pt}(100)$, $\text{Pt}(110)$ and $\text{Pt}(111)$ electrode surfaces (Iwasita, 2002). Differential electrochemical mass spectroscopy (DEMS) is a technique, which is the combination of electrochemical technique with mass spectroscopy. This technique, allows determining the reaction intermediates that formed on the electrode surface in a short period. DEMS has a membrane, which let the permation of volatiles while it splits the electrolyte from the vacuum (Baltruschat, 2004). Another method to obtain the yields of HCHO and HCOOH is to analysis of the anodic solution by HPLC after the electrolysis. After that, charge balance of the reaction let to the calculation of CO_2 yield (Batista et al., 2003).

Researchers all over the world were studied methanol electrooxidation reaction on different modified surfaces in different mediums in order to obtain the higher catalytic activity and energy density. Some recent researches were mentioned in the following paragraphs.

Lou and coworkers suggested an alternative effective electrode material to methanol oxidation in acidic conditions as 0.5 M H_2SO_4 solution. Well-distributed small diametered Pt/CeO₂/CNTs nanohybrids were prepared by layer-by-layer multistep procedure. Pt/CeO₂/CNTs were good candidates for electrode modifiers, which facilitate the methanol oxidation by inhibiting the catalyst poisoning. This behavior attributed to the oxygen carrying capacity of CeO₂. Pt/CeO₂/CNTs show good activity towards methanol oxidation as compared to the Pt/CNTs nanohybrids and commercial Pt/C electrocatalyst (Lou et al., 2015).

Recently, Yang and coworkers studied the methanol and ethanol oxidation in alkaline solution. The uniformly distributed Pd-Pt alloy nanoparticles synthesized by the ultrasonic assisted strategy and formed composite electrode with carbon nanotubes. The comparison of monometallic and bimetallic surfaces exhibits the success of the designed bimetallic surfaces towards alcohol oxidation. This behavior can be attributed to the synergistic effect of metals and carbon nanotubes. Bimetallic nanoparticles modified composite electrode not only has higher if/ib (forward peak current of methanol/backward peak current of methanol) ratio but also more stable than other monometallic surfaces which proved by the chronoamperometric study. In addition, the Pt content effect the current and potential value of methanol oxidation peak that it was also optimized which bring about the design of efficient anode material for fuel cells (Yang et al., 2016).

In recent decades, graphene based composite materials was employed in many applications. Copper phthalocyanine-3,4',4'',4'''-tetrasulfonic acid tetrasodium salt (TSCuPc) and graphene composed via ultrasonication which followed by the chemical reduction of platinum on composite electrode with the help of ultrasonication. Pt nanoparticles modified on non-covalently functionalized graphene SCuPc-graphene. The offered electrode show good stability and more catalytic activity in terms of peak current as compared to the Pt/graphene and commercial Pt/C in acidic medium (Zhong et al., 2013a).

Polymer film electrodes without metal content shows poor kinetic towards the methanol oxidation. In another study, cyclic voltammetry was used for the methanol electrooxidation on a PPy film modified with platinum microparticles decorated electrodes in acidic media. Platinum microparticules and PPy film was formed on the electrode surface by the application of constant potential. Perchlorate ion was doped on the electrodes which facilitate the activity as compared to the Pt/PPy/Ni and Pt electrodes. The performance of the electrode was also changed depending on the amount of platinum. The chemical properties of the suggested electrode surface was proved by the XPS characterization technique (Becerik et al., 2001).

In recent years our group has been also studied the electrocatalytic oxidation of methanol with different types of modified electrodes. The obtained results have been compared with published data and common bare electrodes results for same conditions. Our study describes the modification of single crystal Au(111) electrodes with Pd and Pt ad layers by UPD technique. A higher catalytic activity was obtained for methanol oxidation with Pd or Pt ad-metal modified single crystal Au(111) compare with bare single crystal Au(111) and Pd, Au, Pt polycrystalline surfaces. The best catalytic activity towards methanol oxidation was considered in terms of both the increase in peak current and the positive shift in peak potential as compared to the polycrystalline surfaces and Au(111) single crystal electrode (Koçak et al., 2011).

1.3.3 Dimethylamine Borane electrooxidation

Energy demand increases by the increment of world population. Unfortunately, our mainly energy source was depend on fossil fuels which were limited in earthcrust and cause an environmentally harmful greenhouse emissions which effect the global warming (Atilgan and Azapagic, 2015; Sastre et al., 2015). Therefore, renewable energy sources especially fuel cells are important alternative for energy production. Researchers all over the world were studied to find efficient anode material and appropriate fuel for fuel cell applications. For this purpose, various kinds of fuels (e.g. ethanol, formic acid, hydrazine etc.) were studied on different modified surfaces, while only a few studies based on dimethylamine borane (DMAB) oxidation was found in the literature. Some recent researches were mentioned in the following paragraphs.

DMAB ($C_2H_{10}BN$) is a water-soluble, white crystalline solid defined with a CAS number of 74-94-2. The molecule structure of DMAB was shown in Figure 1.6. DMAB used in various areas such as electroless metal deposition, polymerization catalyst, reduction of organic compounds and fuel cell applications. (National Toxicology Program, 2008; Martins and Nunes, 2008; Liao et al., 2012; Muench et al., 2014). DMAB consumes hydroxide that generally studied at higher pH values when they used as a reducing agent (Plana and Dryfe, 2011).

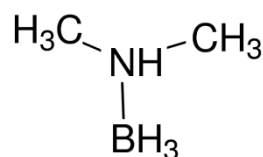
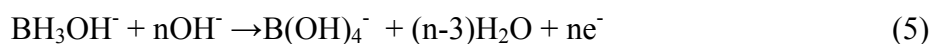


Figure 1.6 Chemical structure of DMAB.

The electrooxidation of DMAB at Au surfaces proposed as to follow the pathways expressed with equations 4 and 5. According to the possible CE mechanism, DMAB was first reacts with OH^- and dissociate to form free amine (dimethylamine) and $-\text{BH}_3$ containing species such as BH_3OH^- (Plana et al., 2011).



In DMAB catalytic oxidation, different possible oxidation products such as; boric acid, borate, boron oxide or other kind of borate anions can be formed depending on the reaction conditions (Sadik et al., 2005; Sverdlov and Shacham-Diamand, 2003). In addition, the BH_3OH^- oxidation occurred at potentials more negative than BH_4^- that make DMAB efficient alternative for fuel cells (Finkelstein et al., 2009).

Sporadic studies were published for DMAB oxidation by researchers over decades. Plana and Dryfe studied DMAB on polycrystalline substrates such as gold and platinum disk and glassy carbon electrodes over the wide range potentials. Pt and Au electrodes have characteristic oxide formation and reduction peaks in the anodic and cathodic scans, respectively in alkaline solution without DMAB.

Au and Pt electrodes show different behavior towards DMAB oxidation. While hydrogen adsorption/desorption peak observed at negative potentials on Pt electrode, the main oxidation peak was occurred at more positive potential as compared to the Au electrode. The sharp peak observed on the cathodic scan named as reactivation peak was smaller than that of Au electrode. The reactivation peak attributed to the re-appearance of the DMAB oxidation process, by the removal of the metal oxide via chemical reduction by DMAB. The DMAB or derivative has strong and rapid transition with gold surface, which occurs with a sharp peak, while the small peak observed for Pt electrode suggested the weak interaction (Plana and Dryfe, 2011).

The electrocatalytic oxidation of DMAB and comparison with borohydride was employed on platinum electrodes in 3 M NaOH with cyclic voltammetry and polarization curves. Borohydride and DMAB exhibit different behavior, while both have multiple peak characteristic on Pt electrodes. Four to six electron involved in the borohydride oxidation, while four to five electrons transferred in the presence of DMAB. Sharp peak at negative potentials attributed to hydrogen evolution on Pt based surfaces. The main oxidation peak of both compounds was occurred at more positive potentials than Au surfaces. Borohydride and DMAB oxidation occurred at -70 mV and -30 mV, respectively. According to the experimental results, borohydride was more preferable compound for fuel cell application as compared to the DMAB due to its 16% higher power density (Martins and Nunes, 2008).

Plana and coworkers also studied DMAB oxidation on single crystal gold electrode. They proposed more clear information about intermediates and mechanism of DMAB with the help of in situ Fourier transform IR reflection absorption spectroscopy (FTIRRAS). They investigate the DMAB oxidation on three basal planes of gold electrode (Au(111), Au(110), Au(100)) which exhibits different behaviour in terms of oxidation peak current and potential. The sharp peak observed during the cathodic scan that called as reactivation peak observed for all types of single crystal electrodes. While there is a debate about the responsible species for this peak, they suggested that it attributed to the oxidation of DMAB or intermediate on the cleaned surface by the removing of gold oxides from the surface. According to the FTIR spectras, adsorbed intermediates such as $\text{BH}_2(\text{OH})_2^-$, $\text{BH}(\text{OH})_3^-$ and more oxidised product at very high potentials, such as BO_2^- or B_4O_7^- are proposed. Finally, they express that DMAB has two oxidation waves. The first oxidation wave on the voltammogram corresponds to the three-

electron transfer and the second step involves a further three-electron transfer, which gave the full six-electron transfer. (Plana et al., 2011).

1.4 Electroanalysis Application

Quantitative determination of inorganic or organic compounds at trace levels are always attracted great interest. The studies extent, aimed the selectively and sensitive determination of these compounds with simple, fast and cheap techniques. Electroanalytical techniques supply these demands as compared to the other chromatographic and spectrometric analysis. Chemically modified electrodes were easily prepared, cheaply synthesized and gave an opportunity to fast, selective and sensitive determination with its easily functionalized nature which was crucial in electroanalytical applications.

One of the scopes of this thesis is that determination of caffeine and theophylline. The aim of this part is to develop selective and sensitive chemical sensor for simultaneous determination of caffeine and theophylline using newly synthesized functionalized MnPc and CNT composed modified glassy carbon electrode.

1.4.1 Theophylline

1.4.1.1 Chemical properties of Theophylline

Theophylline (TP) with a molecule formula of $C_7H_8N_4O_2$ is named as 1,3-dimethyl-3,7-dihydro-1H-purine-2,6-dione by IUPAC. TP is an odorless organic solid that molecule structure was shown in Figure 1.7. TP is a member of xanthines which also named as 3-methylxanthine or dimethylxhyanthine that has similar structure and pharmacological effect with caffeine and theobromine. TP is naturally found in tea and cocoa beans. (National Toxicology Program, 1998; Xia et al., 2013; Chae et al., 2012a).

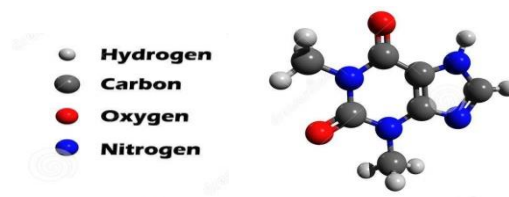


Figure 1.7 Chemical structure of theophylline.

Theophylline is commonly used as bronchodilator medicine and cures the chronic /acute obstructive pulmonary disease, neonatal apnea and asthma that approximately 90% of it is metabolized in human liver. Theophylline occupies a place in the top three drugs which are mostly watched clinically due to its narrow therapeutic range. The use of theophylline for bronchodilation activity is therapeutic only within the narrow range of $10\text{--}20\text{ mgL}^{-1}$, while higher levels than that resulted in toxicity, tachycardia, seizures even death and lower levels are non-therapeutic. This makes the determination of theophylline concentration critical (Shipovskov and Ferapontova, 2008; Hegde et al., 2009; Amare and Admassie, 2012a).

Magdum and coworkers proposed an oxidation mechanism for theophylline which involves totally two electrons and two protons that is shown in Figure 1.8. In addition, TP oxidation resulted in the destruction of the π bond conjugate system (Malode et al., 2012; Magdum et al., 2015).

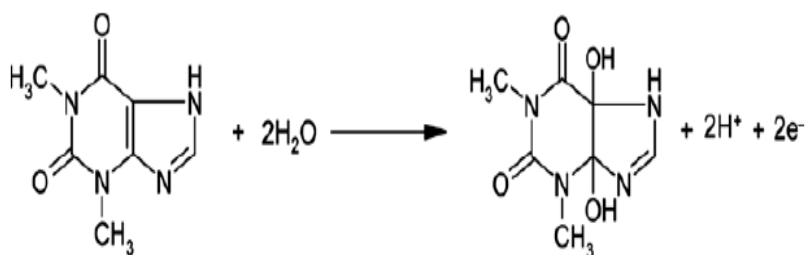


Figure 1.8 Oxidation of theophylline (Adapted from Magdum et al., 2015).

1.4.1.2 Determination of Theophylline

Several analytical methods have been used for the determination of theophylline such as near infrared spectrophotometry (Huck et al., 2005), capillary electrochromatography (Chen et al., 2010), high-performance liquid chromatography/ultraviolet detection (Nirogi et al., 2007), capillary electrophoresis (Haque et al., 1999), LC–MS/MS (Chae et al., 2012b). While these methods involve time-consuming pre-extraction or separation and usage of organic solvents, which pollute the environment, the electrochemical techniques provide simple, time effective procedures with low costs for detection TP with high sensitivity and selectivity. Therefore, up to now, many researchers focused on the electrochemical detection of TP.

Carbon nanotubes were common modifiers as electrode surfaces which was also used for the theophylline determination in pH 3.0 phosphate buffer solution. Multi-wall carbon nanotube paste electrode (MWCNT-PE) was prepared by mixing appropriate amount of carbon nanotube powder and paraffin oil which was homogenized and packed to polytetrafluoro ethylene tube. Two-electron two-proton released oxidation process observed for TP at MWCNT-PE which showed with diffusion controlled irreversible oxidation behaviour. Based on the results of differential pulse voltammetry, the linear calibration range was found as 2.0×10^{-6} to 1.5×10^{-4} M with 1.97×10^{-8} M detection limit for TP. (Malode et al., 2012).

Simultaneous determination of theophylline (TP) and uric acid (UA) successfully achieved by using aminotriazole (AT) functionalized gold nanoparticles (AuNPs) modified glassy carbon and ITO electrode in pH 6 PB solution. The proposed AT-AuNPs film modified electrode provide selective TP and UA detection in the presence of 30 μ M common ions (Na^+ , NH_4^+ , Cl^- , CO_3^{2-} , SO_4^{2-} etc.) and organic interferants (urea, glucose, and oxalate). Limit of detection found as 8.5×10^{-9} M with wide linear calibration range AT-AuNPs film modified electrode. The researchers studied human blood serum and urine sample as real sample analysis that TP and UA contents were found with good recovery values (Kesavan and John, 2014).

Another study described the ferrocene-derivative (1-(4-bromobenzyl)-4-ferrocenyl-1H-[1,2,3]-triazole (1,4-BBFT)) modified-graphene paste electrode for theophylline determination in the presence of isoproterenol and acetaminophen 0.1 M pH 7.0 PBS with chronoamperometry, cyclic voltammetry and square wave voltammetry. Square wave voltammetric analysis represents the successful determination of all three compounds in their mixture solutions. The real sample analysis of theophylline, isoproterenol and acetaminophen was studied by researchers in tea, urine and human blood serum at 1,4-BBFT/IL/GPE with excellent recovery values (Tajik et al., 2014).

Imprinted sol-gel electrode (MIP/CNPs- SO_3H /GCE) prepared by the combination of organofunctional silane (CoG-TEICPS) and coated with carbon nanoparticles containing sulfonic acid groups (CNPs- SO_3H) modified glassy carbon electrode. The comparative studies for theophylline investigation was carry out by cyclic voltammetry and differential pulse anodic stripping voltammetry in 5.0 mL of PBS. Accumulation time, potential and supporting electrolyte pH was studied to obtain best condition for theophylline oxidation.

The LOD value was found as 1.4×10^{-9} M and real sample analysis in pharmaceutical tablets were determined with good recovery values (93.46% - 103.40%) (Güney and Cebeci, 2015).

1.4.2 Caffeine

1.4.2.1 Chemical properties of caffeine

Caffeine (CAF), 1,3,7-trimethyl-1H-purine-2,6(3H,7H)-dione or 1,3,7-trimethylxanthine, is a xhantine derivative which is odorless, white, prismatic crystalline solid. Molecular formula of CAF is $C_8H_{10}N_4O_2$ (MW, $194.19 \text{ g mol}^{-1}$) and molecule structure was shown in Figure 1.9 In case of unusual weakness or drowsiness, caffeine intake was advised which stimulate the central nervous system. Excessive intake of CAF causes restlessness, insomnia, jitters, anxiety, increasing or irregular heart rate (Srdjenovic et al., 2008, Sultan, 2014).

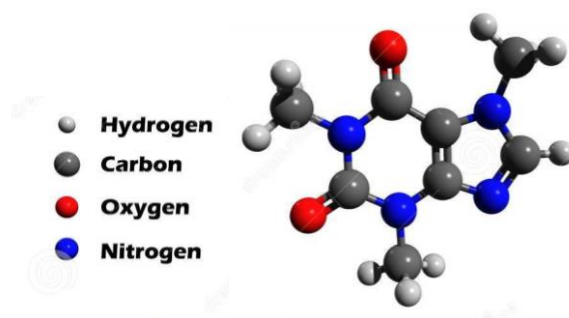


Figure 1.9 Chemical structure of caffeine.

Dose of 200mg/day CAF cause an increase in the rate of basal metabolism that let it called “sports drinks” (Sultan, 2014; Chen et al., 1998). While manufacturers claimed that the caffeine added to baverages for its flavor, only 8% of consumer recognizes its flavor difference with varying amounts. Caffeine cause a physical dependence in long term by its effect on central nervous system, which explains the consuming of caffeinated drinks so much all over the world (Griffiths and Vernotica, 2000).

Caffeine is also an alkaloid, in other word, is an organic compound that contains at least one nitrogen atom in a heterocyclic ring commenly found in the leaves, seeds and fruit of some plants. CAF provide a protection to plants due to where its natural pesticide-like behavior that paralyses and kills insects (Tadesse et al., 2013; Xia et al., 2013).

Tadesse and coworkers proposed an oxidation mechanism to CAF which involves totally four electrons and four protons (Figure 1.10). The first step shows 2H^+ , 2e^- oxidation to form substituted uric acid (8-oxy-caffeine). Then oxidized with 2H^+ , 2e^- to the 4,5-diol analogue of uric acid (Tadesse et al., 2013).

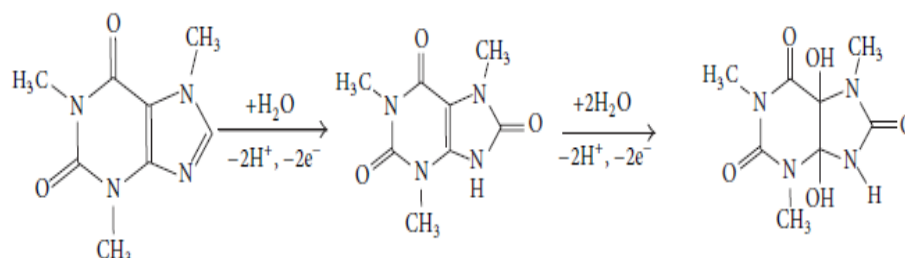


Figure 1.10 Oxidation of caffeine (Adapted from Tadesse et al., 2013).

1.4.2.2 Determination of caffeine

Hitherto, different methods have been reported for CAF determination such as; including capillary electrophoresis, gas chromatography, high-performance liquid chromatography, and electrochemical methods (Marra et al., 2014; Shrivastava and Wu, 2007; Hadad et al., 2012; Habibi et al., 2012). Considering these methods, electrochemical methods preferred due to the high sensitivity, low cost and rapid procedures as compared to the others. However, they have a critical disadvantage on CAF determination with conventional electrode materials due to its high positive oxidation potential, which overlap with the corrosion of electrode material or electrolyte solution. The electrodes are modified with various materials in order to overcome this disadvantage (Güney and Cebeci, 2015; Tadesse et al., 2013). The electrochemical methods for CAF analysis were given in the following paragraphs.

Recently published literature described the preparation of nafion coated lead film electrode for determination of caffeine in H_2SO_4 by adsorptive stripping voltammetry. The modified electrode was prepared by applying constant potential to GCE in Pb containing HNO_3 solution. Then electrode coated with nafion film. Caffeine was determined by following the stripping procedure on nafion modified lead film GCE. First electrode kept at -1.55 V 120 s with stirring then stopped 5 seconds for equilibration. The potential scanned between 0.65 to 1.6 V and finally electrode kept under constant potential at 1 V to clean caffeine residues. Supporting electrolyte, accumulation time, and potential was investigated as well

as DPV parameters to obtain sensitive caffeine determination on modified surface. In addition, caffeine content in coffee, tea, energetic drinks, and pharmaceutical product successfully determined with good recoveries and also compared with standard spectroscopic method which showed coherent results (Tyszczuk-Rotko and Beczkowska, 2015).

Habibi and coworkers studied caffeine (CF) determination in the presence of codeine (CO) by using single-walled carbon nanotubes modified carbon-ceramic electrode (SWCNT/CCE). Caffeine oxidized at 1.38 V vs. SCE on SWCNT/CCE while it oxidized at 1.48 V in 0.01 M H₂SO₄. The linear concentration ranges were found as 0.2–230 and 0.4–300 μ M with detection limits of 0.11 and 0.25 μ M for CO and CF, respectively (Habibi et al., 2014).

Another group employed newly designed electrode for caffeine (CF) investigation in the presence of acetaminophen (AC) and ascorbic acid (AA) by CV and SWV. Manganese(II)ferrite (MnFe₂O₄) nanoparticles which have magnetic property were formed on N-doped carbon nanotube (CNT-N/GCE) by insitu coprecipitation. The resulted MnFe₂O₄@CNT-N/GCE displayed higher electrocatalytic activity toward all three compounds in terms of peak current increase of 52%, 50% and 55% for CF, AC and AA, respectively as compared to the bare GCE in pH 2.5 H₂SO₄/Na₂SO₄ buffer solution. The limit of detection was found as (S/N = 3) 0.83 μ M for CF for simultaneous determination with AA and AC on MnFe₂O₄@CNT-N/GCE (Fernandes et al., 2015).

Also boron doped diamond (BDD) electrode was used for investigation of caffeine in acidic media. Supporting electrolyte type was studied in hydrobromic acid, sulfuric acid, hydrochloric acid, nitric acid, perchloric acid and HClO₄ was found as optimum supporting electrolyte for CAF oxidation at this electrode. They calculated 4.39 protons for caffeine oxidation that was close to the theoretical number (4). The diffusion controlled oxidation mechanism observed from the scan rate studies on BDD electrode. Caffeine content was also found in real samples such as Coca cola, Pepsi-cola, tea and energy drink with BDD electrode which were coherent with HPLC results. Based on DPV studies, detection limit of caffeine was calculated as 1.5×10^{-7} M (Švorc et al., 2012).

TP and CF are naturally found in especially green tea, cacao beans, coffee, cola, etc. (Gao et al., 2013). The similar structure and simultaneous existence of TP and CAF in natural medium let the researchers to investigate these compounds

together. Once the modified electrode surface shows desired response to one of these compounds, it most probably shows same behavior to other compound because of the structure similarity, which contains same electroactive functional groups. This behavior was not resulted in trouble for individual investigation while it present obstacle in simultaneous electrochemical determination due to the close oxidation peak potentials at high positive potentials which result the overlapping of peaks and limited the selective determination. The following paragraphs describe the individual and simultaneous determination of TP and CAF by electrochemical and other methods in literature.

Individual determination of theophylline, caffeine in the presence of theobromine which were xhantine derivatives was studied at boron doped dimond electrode. Electrochemical investigations carry out by cyclic and linear voltammetry in pH 1.8 Britton-Robinson buffer solution. pH, sweep rate and concentration effects were investigated which lead to observe well defined peaks for all compounds. Three commercially caffeine containing real samples, coke and caffee products were determined successfully with the proposed electrode and method (Spataru et al., 2002)

Kinetic spectrophotometric method is one of the methods that used for the simultaneous determination of TP and CAF in food samples. By the help of kinetic characteristics between the reactions of analytes with cerium sulphate in sulphuric acid, TP and CAF determined based on the reaction-absorbance change. The limit of detections was found as $0.30 \mu\text{g mL}^{-1}$ and $0.16 \mu\text{g mL}^{-1}$ for caffeine and theophylline, respectively (Xia et al., 2013). Theophylline and caffeine in the presense of theobromine was also determined in cocoa bean samples with the help of reversed-phase high-performance liquid chromatographic method (Brunetto et al., 2007). In other study, ion chromatography proposed as an alternative to liquid chromatography for simultaneous determination of TP and CAF in the presence of theobromine. The analytes were determined in foods and pharmaceuticals with excellent recoveries (Chen et al., 1998).

While chromatographic methods were more commen for simultaneous determination of TP and CAF, sporadic studies were found in the literature with electrochemical techniques (Rahim et al., 2014; Srdjenovic et al., 2008; Yang et al., 2014; Gao et al., 2013)

An hybride electrode was proposed for the simultaneous determination of TP and CAF which prepared by the combination of chemically reduced gold nanoparticles doped chitosan (CHIT)-ionic liquid (1-butyl-3-methylimidazoliumtetrafluoroborate, [BMIM][BF₄]) with reduced graphene modified glassy carbon electrode. The modified electrode used for the determination of theophylline and caffeine in pH 7.4 phosphate buffer solution. Composition ratios, pH, accumulation time were optimized that excellent peak separation was obtained at multicomponent hybride electrode which provide the selective and sensitive determination of TP and CAF in synthetic and real samples accurately. The real sample analysis of green tea, puer tea, energy drink, TP tablet were carry out successfully with proposed hybride GNP-CHIT-IL/r-GO/GCE/r-GO electrode which confirmed by HPLC technique. The limit of detections is calculated as $1.32 \times 10^{-9} \text{ molL}^{-1}$ and $4.42 \times 10^{-9} \text{ molL}^{-1}$ for TP and CAF, respectively (Yang et al., 2014).

In another study, large mosoporous carbon (LMC) was synthesized by using CaCO₃ nanoparticles and sucrose then appropriate amount was dispersed in Nafion. Five μL of the suspension dropped on the glassy carbon surface and let drying in air. The resulted modified electrode denoted as LMC/Nafion/GCE and applied for simultaneous determination of TP and CAF in 0.1 M sulfuric acid. Electrolyte type, scan rate, accumulation time was optimized and very well separated oxidation peaks observed. TP or/and CAF amount in Pu er tea, coffee and cola samples as well as in human serum were studied successfully. The linear ranges of TP and CF found as 0.8–180.0 μM and 1.3–230.0 μM with 0.37 and 0.47 μM detection limits, respectively (Gao et al., 2013).

1.5 Surface Characterization Techniques

Enormous kind of materials was prepared paralelly with the development of many technological areas. Manufacturers and researchers need to be understand and observed the matrials in order to obtaine surfaces with desired properties. Shape, composition and chemical/physical properties of solid surfaces can be measured by surface characterization techniques. In analytical applications, the composition of the electrode material is crucial for the activity, stability, sensitivity and selectivity the system. Therefore, it is important to undertand the surface which provided by the surface characterization techniques.

Characterization of modified electrodes can be carried out by electrochemical, spectroscopic, and microscopic methods. Generally, cyclic voltammetry (CV), electrochemically impedance spectroscopy (EIS), scanning electron microscopy (SEM), X-Ray Photoelectron Spectroscopy (XPS), X-Ray diffraction (XRD) and transmission electron microscopy (TEM) been useful for imaging electrode surfaces and understanding the materials (Miyoshi, 2002).

1.5.1 Electrochemically impedance spectroscopy (EIS)

Electrochemical impedance spectroscopy (EIS) is generally used in order to meliorate the understanding of multi-step reactions such as diffusion impedance, charge transfer, double-layer capacitance, solution resistance. EIS is used for analysis of corrosion, electrode kinetics, membranes, nanoparticles, conduction polymers, semiconductors, surface treatment, batteries and fuel cells, interfaces, etc. For impedance measurements, a periodic small amplitude sinusoidal AC signal is applied, and the current response is determined. These measurements are carried out at different ac frequencies and, thus, the name impedance spectroscopy was later adopted (Sun, 2008; Uygun and Uygun, 2014).

EIS was used frequently to measure the electrode impedance in the presence of a faradaic reaction to determine the kinetics of electrode processes. In the electrochemical measurement, transformations occurring at the electrode–solution interface can be displayed by using modules of the electronic equivalent circuitry. Particularly useful to model interfacial phenomena is the Randles electronic equivalent-circuit model (Figure 1.11a). R_{ct} is the charge-transfer resistance, which is inversely proportional to the rate of electron transfer; C_{dl} is the double-layer capacitance; R_s is the solution-phase resistance; and, w is the Warburg impedance, which arises from mass-transfer limitations. The impedance of the interface, derived by application of Ohm's law, consists of two parts, a real number Z' and an imaginary one, Z'' :

$$Z(\omega) = R_s + \frac{R_p}{1+(\omega R_p C_{dl})^2} - j \frac{\omega R_p^2 C_{dl}}{1+(\omega R_p C_{dl})^2} = Z' + jZ'' \quad (6)$$

Where $j = \sqrt{-1}$.

At higher frequencies, the typical Nyquist plot consisted of a semicircle portion related to the electron transfer-limited process and at lower frequency range, a linear part express the diffusion-limited process (Figure 1.11b). The charge transfer resistance or polarization resistance (R_{ct}) is equal to the semicircle diameter (Orazem and Tribollet, 2008).

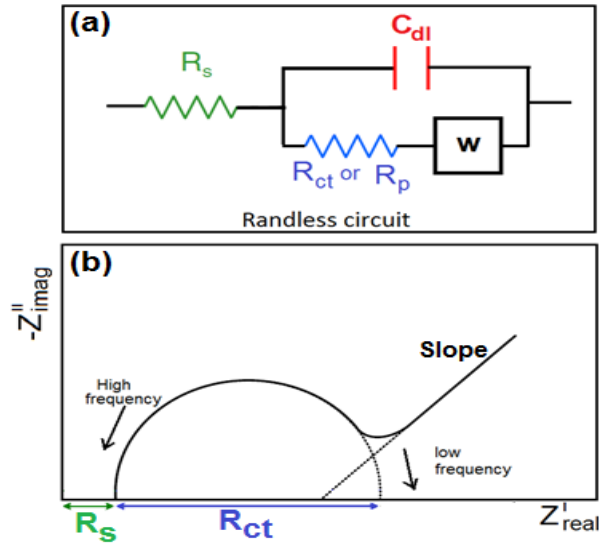


Figure 1.11 Nyquist plot (a) arising from the Randles circuit (b).

1.5.2 X-Ray photoelectron spectroscopy (XPS)

K. Siegbahn has pioneered the use of XPS that gave him a Nobel Prize in 1981 which called as the Electron Spectroscopy Chemical Analysis (ESCA) by Siegbahn. XPS technique does not only provide information about the atomic composition of the sample, but also the structure of the compound of the element and provides information about the oxidation state of elements.

Figure 1.12 shows as schematically physical events related to XPS. K and L show the energy of inner shell electrons of an atom. Two lines on the top level represent the energy of valence shell electrons. As shown in Figure 1.12, one of the photons with $h\nu$ energy in monochromatic X-ray beam is remove an electron of E_b binding energy level in K orbital (Skoog et al., 1998). The kinetic energy of the electrons released, E_k , measured, then the electron binding energy, E_b , calculated according to the equation 7. In equation, w , is called the work function of spectrometer.

$$E_b = h\nu - E_k - w \quad (7)$$

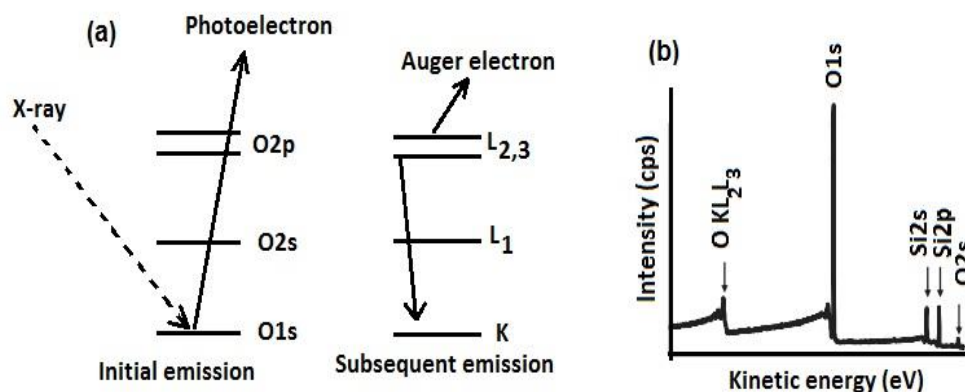


Figure 1.12 a) XPS schematic representation on an oxygen atom, b) XPS spectrum of oxygen in the silicon surface (Adapted from Heide, 2012).

As shown in Figure 1.12b, a XPS spectrum shows the binding energy (E_b) versus as a function of count rate of the electron. The oxygen 1s, 2s and silicon peaks are separately observed in spectrum which correspond to the oxygen onto the silicon surface.

Most of the XPS analyzers are semi-spherical typed and the electron beam was deflected by following the curved path in the electrostatic magnetic field. The radius of the curvature depends on the kinetic energy of electrons and strength of the applied field. The focusing of the electrons on the detector, which have different kinetic energy, can be provided by changing the field (Skoog et al., 1998).

1.5.3 Transmission electron microscopy (TEM)

The first TEMs designed by Max Kroll and Ernst Ruska in 1931 which then commercialized in 1939. TEM is composed from several components such as, a vacuum system, an electron emission source for generation of the electron beam, detectors and lenses and pumping unit. The TEM consists of an emitters that generally made up of tungsten filament or lanthanum hexaboride. After, high voltage source ($\sim 100\text{--}300\text{ kV}$) and passed through a strong magnetic field that acts as a lens into the vacuum. In order to prevent the generation of an electrical arc for the cathode, ultra-high vacuums on the range of 10^{-7} to 10^{-9} Pa were used High-voltage TEMs. The TEM uses a high-energy electron beam transmitted through a very thin sample to image and analyze the structure of materials.

TEM utilizes energetic electrons to provide morphologic, compositional and crystallographic information on samples. TEMs find application in materials science, cancer research, virology, nanotechnology, and semiconductor research. TEM is an ideal characterization tool for micro- and the nano-structures and it can provide information between micron sizes to atomic scale. TEM comprises a variety of methods; TEM comprises a variety of methods;

Bright Field (BF)/Dark Field (DF) methods can provide information as dark and bright images. The thick parts or higher molecular weight containing parts of sample seem dark, while the image seem bright if electron beam does not get through in any substance. **Electron Diffraction (ED)** is obtained by elastically scattered electrons, which provide information about crystallographic structure such as crystal symmetry and orientation. High Resolution Transmission Electron Microscopy (HRTEM) provides size and arrangement of particles in atomic diameter scale. In addition, the technique allows the detection of atomic scale defects as well as gives information about elements in different oxidation states (Zinin, 2015)

1.5.4 Scanning electron microscopy (SEM)

Scanning electron microscopy (SEM) is a technique used for the surface characterization. SEM electrons emerging from tungsten, lanthanum hexaboride cathode or field emission gun (FEG) will examine the interactions sent to the surface of the material. The surface of the sample scanned as raster pattern with a high-energy electron beam by SEM (Figure 1.13). Various types the signals from the surface are emerged. These signals are backscattered electrons, secondary electrons, Auger electrons, X-ray photons, and any other photon florensans. The backscattered and the secondary electrons are constituted commonly the basis of SEM. In the SEM, the electron beams formed with highly advanced optical lens system thst focused on the surface of sample thus the surface morphology imaged.

High capacity vacuum pump is used in order to reach the $<10^{-4}$ torr pressures rapidly. Conductive samples are easier to work with SEM. For non-conductive samples, system is performed with coating. SEM images of living biological systems can be obtained with specific sample holders in the advanced SEM equipment (Skoog et al., 1998).

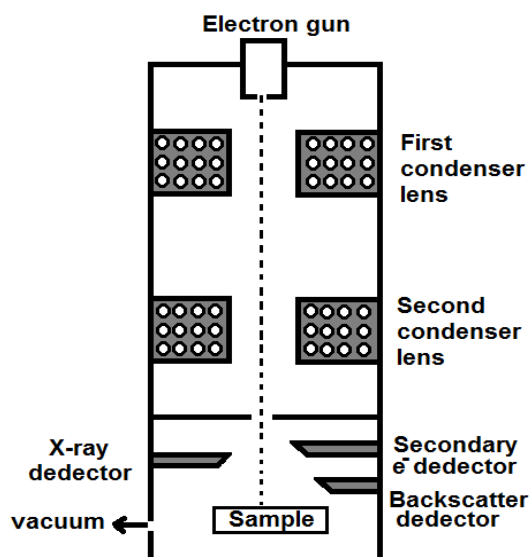


Figure 1.13 Illustration of a SEM.

1.5.5 X-Ray diffraction (XRD)

X-rays were discovered by Wilhelm Roentgen in 1895. He awarded the Nobel prize in 1905. X-rays are generated whenever high-speed electrons by high voltage from the filament hit a target (Mo or Cu are commonly used as target in XRD tubes). X-ray tube must contain a source of electrons, a high accelerating voltage, and a metal target. Because the kinetic energy of the electrons resulted to heating of the target, the anode (metal target) must be water-cooled to prevent its melting. All X-ray tubes contain two electrodes, a cathode, maintained at a high negative potential, for diffraction work (Culluty, 1956).

Determination of the exact three-dimensional arrangement of building blocks (atoms, ions, molecules) in a crystalline chemical compound is employs X-ray radiation. XRD is generally used as applications, geological prospecting, microelectronics, cement, pharma, steel/aluminium, cosmetics, coating, paint and mine. In a powder sample, only a few crystallites have the right orientation. .When the tilt angle changes, other crystallites meet the diffraction condition (Figure 1.14a).

The X-rays come onto the crystal are absorbed by the crystal. The intensity of the reflected X-rays is reduced for absorbed X-rays by atoms in crystal. Amount of violence X-ray absorption depends on the crystal size and the angle between the incident and reflected X- rays. The X-rays scattered from the different (hkl) plane crystal is follow different ways within the crystal (Figure 1.14 b) (Kabak, M., 2004).

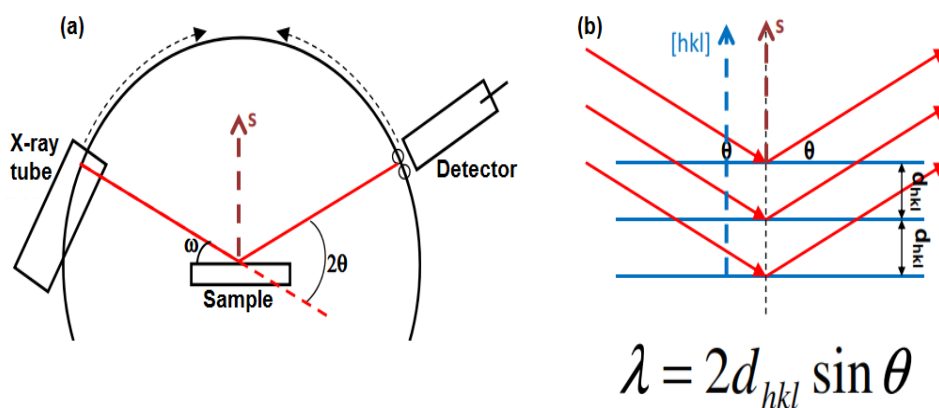


Figure 1.14 a) XRD measurement system, b) Bragg's law and diffraction (Adapted from Speakman, 2015).

In Figure 1.14, between the sources of X-ray and sample was related to incident angle (θ). In addition the incident beam and the detector angle correspond to the diffraction angle (2θ). The vector of diffraction (s) is always normal to the surface of the sample in the Bragg-Brentano geometry. For parallel planes of atoms, with a space d_{hkl} between the planes, constructive interference only occurs when Bragg's law is satisfied. λ is the wavelength of X-ray that is fixed. The vector drawn from the origin of the unit cell is d_{hkl} which intersect the crystallographic plane (hkl) at a 90° angle (Speakman, 2015).

1.6 Voltammetric Techniques

Voltammetry is an electroanalytical technique that current-voltage relationship with concentration investigated by the polarized electrodes. Voltammetry is carried out by three electrode systems in order to accurately measure the applied potential on the working electrode.

Hg/Hg₂SO₄, Ag/AgCl and standart hydrogen electrodes are such examples of generally used electrodes that have a stable and well-known electrode potential that described as reference electrode. Working electrodes have a small surface area, which made with various materials (gold, bismute, glassy carbon,) that helps to investigate the electroactive analyte in the solution. There is a minimum potential needed to start an oxidation or reduction reaction at an electrode. And the last one of three electrode system is called counter (auxiliary) electrode that has a surface area much larger than that of the working electrode which used for the prevent the polarization of reference electrode. Voltammetric techniques were named by the current type or working electrode.

For instance if dropping mercury used as a working electrode this technique called polarography that invented by J. Heyrovsky. On the other hand, the technique called alternating current voltammetry if alternating current chosen during voltammetric experiments (Tural et al., 2006; Protti, 2001).

Voltammetry is used in almost every discipline of chemistry by inorganic, organic, analytical chemists and biochemists in order to investigate the oxidation-reduction reactions in various solutions, adsorption properties and electron mechanism of modified surfaces. The combination of this technique with spectroscopic or chromatographic devices resulted in the simple analysis of complex mixtures (Skoog et al., 1997).

In this thesis, cyclic voltammetry, differential pulse voltammetry, chronoamperometry techniques were used with solid disk, rotating disk and composite materials modified electrodes.

1.6.1 Cyclic voltammetry

Cyclic voltammetry (CV) is a voltammetric technique that the potential scans start from the selected potential to the different end potential, and then scan were reverse from the end potential to the initial potential again. The cyclic scans can be carry out once or repetitive, optionally.

CV facilitate the investigation of the product in the reverse scan which produced by the electrochemical reaction on the forwards scan. Cv is a useful technique to determine kinetics and mechanism of redox systems by changing the parameters such as potential window and scan rate. The dependence of peak potential and currents on scan rate gives information about homogeneous reactions and adsorption behaviours (Tural et al., 2006; Skoog et al., 1997).

In reversible reactions, both anodic and cathodic peaks were observed almost in the same current value with a peak potential relation as shown below in the equation

$$\Delta E_p = E_{p_{\text{anodic}}} - E_{p_{\text{cathodic}}} = 0.0591/n \quad (8)$$

Quantitative information is obtained based on the relation of concentration and peak current which expressed as the Randles–Sevcik equation (at 25°C):

$$i_p = (2.69 \times 10^5) n^{3/2} A C D^{1/2} \nu^{1/2} \quad (9)$$

Where i_p is the peak current in amper, n is the electron number involved in reaction, A is the electrode area (cm^2), C is the concentration in mol.cm^{-3} , D is the diffusion coefficient (cm^2s^{-1}), and ν is the scan rate in V.s^{-1} . If all other variables (A , C , ν) were known, the diffusion coefficient can be calculated by the equation.

The difference in the potential values of the anodic and cathodic peaks wider as compared to a reversible system and peak current increase become unproportional to the scan rate for quasi-reversible systems. In conclusion, CV is used as a useful technique to understand the mechanism of organic and inorganic electroactive species (Tural et al., 2006).

1.6.2 Pulse voltammetry

Pulse techniques in voltammetry, targeted to lower the background (residual) current of the measurement in order to obtain lower detection limits as compared to the conventional voltammetric techniques. The residual current is consisting of two components; charging current and diffusion current. The latter usually occurred by the solution impurities, while charging current occurred in all polarographic measurement that main cause of residual current. Pulse techniques were primarily improved for the dropping mercury electrode and aimed reducing the residual current by synchronizing the pulses with mercury drop growth and sampling at the end. Close to the end of drop lifetime, charging current decreases and faradaic current increases which is the optimum time for measurement.

Two pulse techniques; normal pulse and differential pulse voltammetry differ from each other by their current sampling process. In normal pulse voltammetry; successive pulses with an increasing amplitude combined with direct current potential that applied to the drops close to the end of drop lifetime. Currents are measure only in few seconds after pulse application that results in the increment of faradaic current and reduction of charging current. The limiting currents in normal pulse are the modification of Cottrell equation and voltammograms have sigmoidal shapes.

In differential pulse voltammetry, pulses with constant amplitudes combined with linear increasing potential that applied to the electrode. Currents are measured before and after pulse application which followed by the subtraction of these values. This procedure results in good correction of charging current so on lower detection limits (lower than 10^{-8} M) obtained in analysis of organic and inorganic electroactive species (Wang, 1994; Turan et al., 2006).

1.6.3 Chronoamperometry

Chronoamperometry is the controlled potential technique, which enables the investigation of current-time relation. Chronoamperometry is a useful technique that allows for measuring the surface area of electrode, determining the electron number of electroactive species and giving information about stability of the electrode. Cottrell equation expressed below which enables the estimation of electron number:

$$i = \frac{nFACD^{1/2}}{\pi^{1/2}t^{1/2}} \quad (10)$$

Where i is the current density, n is the number of electrons transferred, F is the Faraday's constant (96500 C.mol^{-1}), A is the electrode area (cm^2), D is diffusion coefficient ($\text{cm}^2.\text{s}^{-1}$) and C is concentration (mol.cm^{-3}) (Wang, 1994; Turan et al., 2006).

1.6.4 Rotating disk electrodes

Voltammetric studies at rotating disk electrode (RDE) are a technique that enables the investigation of the electrode process. RDE system consists of the disk electrode that is attached to the rotating motor. Rotation of the electrode allows the researchers to get information not only about diffusion but also about convection. The convective flow theory is similar with flowing fluids theory at the RDE.

RDE has advantages such as; stability of diffusion layer thickness, minimization of the effect of double layer during measurement and simple application of experimental data to the theoretically solved and expressed equations which give information about mass transport of analytes to the electrode surface.

Levich equation express the mass transfer for the RDE which also enables estimation of number of electrons in redox reaction at a chosen potential can be expressed as:

$$i = -0.62 n F A D^{2/3} \nu^{-1/6} C \omega^{1/2} \quad (11)$$

Where i is the limiting current, n is the number of electron transferred, A is the electrode area (cm^2), F is the Faraday's constant, D is the diffusion coefficient ($\text{cm}^2.\text{s}^{-1}$), ν is the kinematic solution viscosity, ω is the the angular velocity of the electrode (rad.s^{-1}), and C is the concentration (mol.cm^{-3}) (Town et al., 1991; Skoog et al., 1997).

2. EXPERIMENTAL

2.1 Apparatus

Voltammetric and electrochemical impedance measurements were carried out using Autolab/302 N and Bas 100B Electrochemical Analysers with a three electrodes system consisted of a working electrode (bare GCE, Pt disk, Au disk, metal phthaloyanine modified GCE, metal phthalocyanine-carbon nanotube composite modified GCE, various metal nanoparticles modified metal phthalocyanine-carbon nanotube composite GCE, poly(p-aminophenol) film GCE, various metal nanoparticles poly(p-aminophenol) film GCE), a platinum wire counter electrode and an home made Ag/AgCl (sat.KCl) reference electrode, respectively. Cyclic voltammetry (CV), linear sweep voltammetry (LSV), differential pulsed voltammetry (DPV) and chronoamperometry techniques were used for electrochemical measurements. Bandelin Sonorex model ultrasonic bath was used for cleaning of electrodes. MSH-20A magnetic stirrer which produced by Wids Laboratory Instruments was used. Philips XL30 SFEG scanning electron microscopy was used for the characterization of bare and modified electrode surfaces. Surface chemistry of each metal particle modified electrodes was studied by X-Ray-photoelectron Spectroscopy (XPS) using Thermo K-Alpha-monochromated high-performance XPS spectrometer. JEOL JEM-ARM200F transmission electron microscopy was used for metal nanoparticles modified composite electrode surfaces. XRD patterns of the bare ITO and modified ITO were obtained by X-ray diffraction analyses using PANalytical Empyrean diffractometer, Cu-K-Alpha1 radiation (1.5406 Å; 45 kV, 40 mA) and the samples were scanned from 5 to 90 2Theta in step sizes of 0.0130. The XRD patterns were matched by PANalytical X'Pert HighScore database program. The pH measurements were made with WTW handheld 330i ion analyzer meter pH.

2.2 Reagents and Materials

All reagents were of analytical reagent grade. 4-aminophenol ($\text{H}_2\text{NC}_6\text{H}_4\text{OH}$), dimethylamine borane ($(\text{CH}_3)_2\text{NHBH}_3$), theophylline ($\text{C}_7\text{H}_8\text{N}_4\text{O}_2$), caffeine ($\text{C}_8\text{H}_{10}\text{N}_4\text{O}_2$), MWCNT (diam: 110-170 nm, length: 5-9 micron), phthalocyanine ($\text{C}_{32}\text{H}_{18}\text{N}_8$), cobalt phthalocyanine ($\text{C}_{32}\text{H}_{16}\text{CoN}_8$), copper(II) phthalocyanine ($\text{C}_{32}\text{H}_{16}\text{CuN}_8$), manganese(II) phthalocyanine ($\text{C}_{32}\text{H}_{16}\text{MnN}_8$), N,N-dimethylformamide (DMF) ($\text{C}_3\text{H}_7\text{NO}$), sodium dodecyl sulphate ($\text{C}_{12}\text{H}_{25}\text{NaO}_4\text{S}$), perchloric acid (HClO_4), hydrochloric acid (HCl), sulfuric acid

(H₂SO₄), sodium perchlorate (NaClO₄), phosphoric acid (H₃PO₄), boric acid (H₃BO₃), sodium hydroxide (NaOH), ethanol (C₂H₅OH), methanol (CH₃OH), chloroplatinic acid (H₂PtCl₆), chloroauric acid (H₂AuCl₆), copper sulfate (CuSO₄), silver sulfate (AgNO₃), cadmium sulfate (CdSO₄), palladium sulfate (PdSO₄), nickel sulfate (NiSO₄), cobalt sulfate (CoSO₄), ruthenium chloride (RuCl₃), alimuna (Al₂O₃), were supplied from Merck, Sigma or Aldrich.

The solutions of p-aminophenol polymer in SDS and NaClO₄, dimethylamine borane (CH₃)₂NHBH₃, methanol, theophylline, caffeine were freshly prepared by dissolving the required amount of reagent in ultrapure water [Millipore Milli Q system (18.2 MΩ)].

For analytical applications, new synthesized organic groups functionalized phthalocyanines were used. The new phthalocyanines (Tetra-[(5-chloroquinolin-8-yloxy)phthalocyanato]manganese(II)) were synthesized by Ass. Prof. Dr. Asiye NAS and Prof. Dr. Halit KANTEKİN in inorganic research laboratory of science faculty, chemistry department in Karadeniz Technical University.

The standard solutions of metal ions were prepared by dissolution of metal salts with acids. To prepare chloroauric acid (HAuCl₄) solution, a 0.05 g Au wire was dissolved concentrated HNO₃:HCl (1:3) and the solution was boiled until evaporation of the acid. Then, the residual solid was dissolved in 100.0 mL 0.1 mol L⁻¹ HCl solution. Britton-Robinson buffer solutions consist of mixtures of acids of diminishing strength (increasing pK_a) so that the change in pH is approximately proportional to the amount of alkali added. It consists of a mixture of 0.04 M H₃BO₃, 0.04 M H₃PO₄ and 0.04 M CH₃COOH that has been titrated to the desired pH with 0.2 M NaOH.

All experiments were carried out at ambient temperature and high purity nitrogen kept flowing over the solution during electrochemical experiments. In the experiments of oxygen reduction, supporting electrolyte was kept under high purity oxygen until the saturation of solution.

2.3 Methods

2.3.1 Pretreatment of GCE

The cleaning procedure of GCE was carry out by using different grade of Al_2O_3 slurry (0.05-3 micron) for polishing the surface on a synthetic cloth. Then electrode rinsing with pure water and tprocedure was followed by the ultrasonication for 3 minutes in ultra pure water/ethanol mixture. GCE was also electrochemically cleaned by keeping 10 minutes at constant potential at 1.0 V.

2.3.2 Pre-treatment of multiwalled carbon nanotubes

Multiwalled carbon nanotube (CNT) which as received, is pretreated with concentrated HNO_3 . 0.1g. CNT was boiled in approximately 4 mL concantrated HNO_3 . Then it was washed many times with ultrapure water. The asit-treated CNT was dispersed in DMF to get a black suspension after 30 minutes ultrasonication.

2.3.3 Preparation of CNT modified GCE

A 10 μL of MWCNT suspension was injected on the pre-conditioned bare GCE surface. The electrode kept in the drying oven at 60°C for 1/2 hour in order to evaporate the solvent (DMF) of the suspension.

2.3.4 Preparation of phthalocyanine modified GCE

Phthalocyanines (nonmetallic phthalocyanine, cobalt phthalocyanine, copper(II) phthalocyanine, manganese(II) phthalocyanine, copper phthalocyanine), as received and Tetra-[(5-chloroquinolin-8-yloxy)phthalocyanato]manganase(II) as synthesized, were directly dispersed in DMF without using any treatment procedure. An amount of four mg Pc was dispersed in 4 mL DMF to get a blue suspension. A 10 μL sample of Pc suspension was dropped on the bare GCE surface which was followed by the 1/2 hour evaporation of solvent at 60°C to prepare the Pc/GCE.

2.3.5 Preparation of phthalocyanine-carbon nanotube modified GCE

Phthalocyanine-carbon nanotube (Pc-CNT) or metalphthalocyanine-carbonnanotube (MPc-CNT), i.e. CuPc-CNT, suspension was prepared by mixing the various amount of MPc with 30 mg of CNT in 4 mL DMF. The obtained dark blue suspension was ultrosonicated 1 hour. A 10 μL sample of MPc-CNT suspension was dropped on the bare GCE surface and then electrode kept in the drying oven at 60°C for 1/2 hour in order to evaporate the solvent on the electrode surface to prepare the resulted MPc-CNT/GCE.

MPc/CNT/GCE was prepared by dropping 5 μL of CuPc suspension after 5 μL CNT suspension were dropped on the bare glassy carbon electrode and dried at 60°C. CNT/MPc/GC electrode was prepared by following an opposite procedure.

2.3.6 Preparation of poly(p-aminophenol) film modified GCE

Electrochemical polymerization of p-aminophenol was carried out in 0.5 M HClO_4 solution containing 5mM SDS and 5mM p-aminophenol by CV. The polymerization voltammograms were obtained by repetitive 20 potential cycles from -600 mV to 2000 mV (vs. Ag/AgCl (sat. KCl)) at a scan rate of 100 mV.s^{-1} . This electrode donated as PAP/GCE. The obtained electrode was washed with ultra pure water to remove the adsorbed monomer residues on the surface of the electrode.

2.3.7 Preparation of various metal nanoparticles modified Pc and Pc-CNT composite GCE

The metal nanoparticles electrochemically deposited on the Pc/GCE and Pc-CNT/GCE by cyclic voltammetry. Au, Pt, Cu, Ag, Co, Ni, Pd, Ru nano particles deposited on modified electrode surfaces by CV technique with a scan rate of 50 mV.s^{-1} for 10 cycles at particular potential window in HAuCl_4 containing 0.1 mol.L^{-1} HCl, H_2PtCl_6 containing 0.1 mol.L^{-1} HCl, CuSO_4 containing 0.1 mol.L^{-1} H_2SO_4 , AgNO_3 containing 0.1 mol L^{-1} HNO_3 , CoSO_4 containing 0.1 mol.L^{-1} H_2SO_4 , NiSO_4 containing 0.1 mol L^{-1} H_2SO_4 , PdSO_4 containing 0.1 mol.L^{-1} H_2SO_4 and RuCl_3 containing 0.1 mol.L^{-1} HCl solutions, respectively.

Bimetallic nano particles modified Pc/GCE and Pc-CNT/GCE electrodes obtained by applying the same procedure consecutively that mentioned above. In addition, another bimetallic nano particles deposition carried out from their solutions that contains both metals together. To emphasize the difference of step-by-step deposition and deposition from the same solution, different abbreviations were used. For alternate deposition of metals on the electrode surfaces from different solutions, electrodes denoted as M/M/Pc-CNT while the electrodes denoted as M-M/Pc-CNT when metal particles deposited from the same solution together. The all obtained metal nano particles modified electrodes were ready for use after the final wash with ultra pure water.

2.3.8 Preparation of various metal nanoparticles modified polymer film GCE

The metal nanoparticles deposited on the polymer film electrodes by cyclic voltammetry. The electrochemical deposition of metal particles, gold and silver, were carried out in the particular potential window of each metal ion at a sweep rate of 50 mV.s^{-1} using various concentrations of HAuCl_4 in 0.1 mol.L^{-1} HCl solution and AgNO_3 in 0.1 mol.L^{-1} HNO_3 solution. Bimetallic nano particles modified polymer film GC electrodes obtained by applying the same procedure consecutively that mentioned above. The obtained metal nanoparticles modified polymer GC electrodes were ready for use after wash the electrode with ultra pure water to clean the residues that adsorbed on the electrode surface

2.3.9 Preparation of real samples

In order to evaluate the application of designed modified electrodes to real samples, green tea, cola and theophylline serum were studied. Green tea leaves were powdered in electric mixer. Than 5 gram of green tea dissolved in boiling 150 mL water This mixture was then filtered with a membrane filter. The resulted green tea sample was determined under the optimized conditions. Beverage sample of cola studied for CAF content analysis. Containing gas was eliminated by ultrasonication and then sample was diluted by a factor 1:10 (v/v) with the supporting electrolyte. The theophylline were purchased from Hospira (200 mg/100mL). 0.1 mL sample were diluted to 100 mL with $0.1 \text{ M H}_2\text{SO}_4$. ($1.1 \times 10^{-4} \text{ M}$)

3. RESULTS AND DISCUSSIONS

3.1 Electrochemical Reduction of Oxygen at Modified Electrodes

Fuel cells are devices that convert chemical energy, which obtained from fuel and oxidant to electric energy. Although various kinds of fuels such as methanol, ethanol, borohydride, formic acid etc. were used, oxidant is limited that oxygen is the most chosen one for fuel cells. To achieve the thermodynamically prescribed voltage, the high overpotential of oxygen reduction due to the strong double bond of oxygen can not be easily broken, can be reduced. In order to overcome this problem at conventional cathode materials, electrode surfaces were modified with different modifier compounds especially with metal nanoparticles to improve electron transfer kinetic in fuel cells (Barile, C., 2010).

3.1.1 Preparation of metal nanoparticles modified CuPc-CNT composite electrodes

Metal nanoparticles were widely used as an electrode material due to their unique properties, which exactly different from their bulk forms such as enhance the electron transfer and catalyse the reaction. In this thesis, metal nanoparticles were frequently used as a component of composite electrode material that serves to obtain the more catalytic electrode surfaces towards analytes.

Figure 3.1 and 3.2 displays the repetitive cyclic voltammograms of platinum, copper, gold, silver, palladium and nickel nanoparticles electrochemical deposition on CuPc-CNT/GC electrode surfaces in acidic mediums.

Figure 3.1 a shows the platinum nanoparticle formation on CuPc-CNT modified GC electrode surface by cyclic scans between -1100 mV and +500 mV with a scan rate of 50 mV.s^{-1} . A reduction peak at about -300 mV and hydrogen adsorption peak near -1000 mV was observed during the cathodic scan, while an oxidation peak at +100 mV and hydrogen desorption peak near -800 mV were appeared in anodic scan (Sharma and Kar, 2015).

Multiple potential scans were performed between -1100 mV and + 600 mV with 50 mV.s^{-1} scan rates to form copper nanoparticles on composite electrode surface (Figure 3.1b). A small cathodic peak related to reduction of Cu^{2+} ions at approximately -800 mV and sharp increasing oxidation peak copper nanoparticles were observed at -300 mV that shows the redox process is quasi-reversible. Another small peak at about +150 mV suggested as oxidation of oxygen-adsorbed species on the electrode surface (Zheng et al., 2013).

Gold nanoparticles were deposited by the immersion of electrode to HAuCl_4 containing HCl solution and applying the potential scans between -800 mV and + 600 mV (Figure 3.1c). During the consecutive potential cycles, two sharp increasing redox peaks were observed which corresponds to the reduction of Au^{3+} ions at approximately -300 mV during cathodic potential scan and oxidation of Au nanoparticles at +300 mV to cationic form in the potential scanning of anodic direction (Bakır et al., 2011).

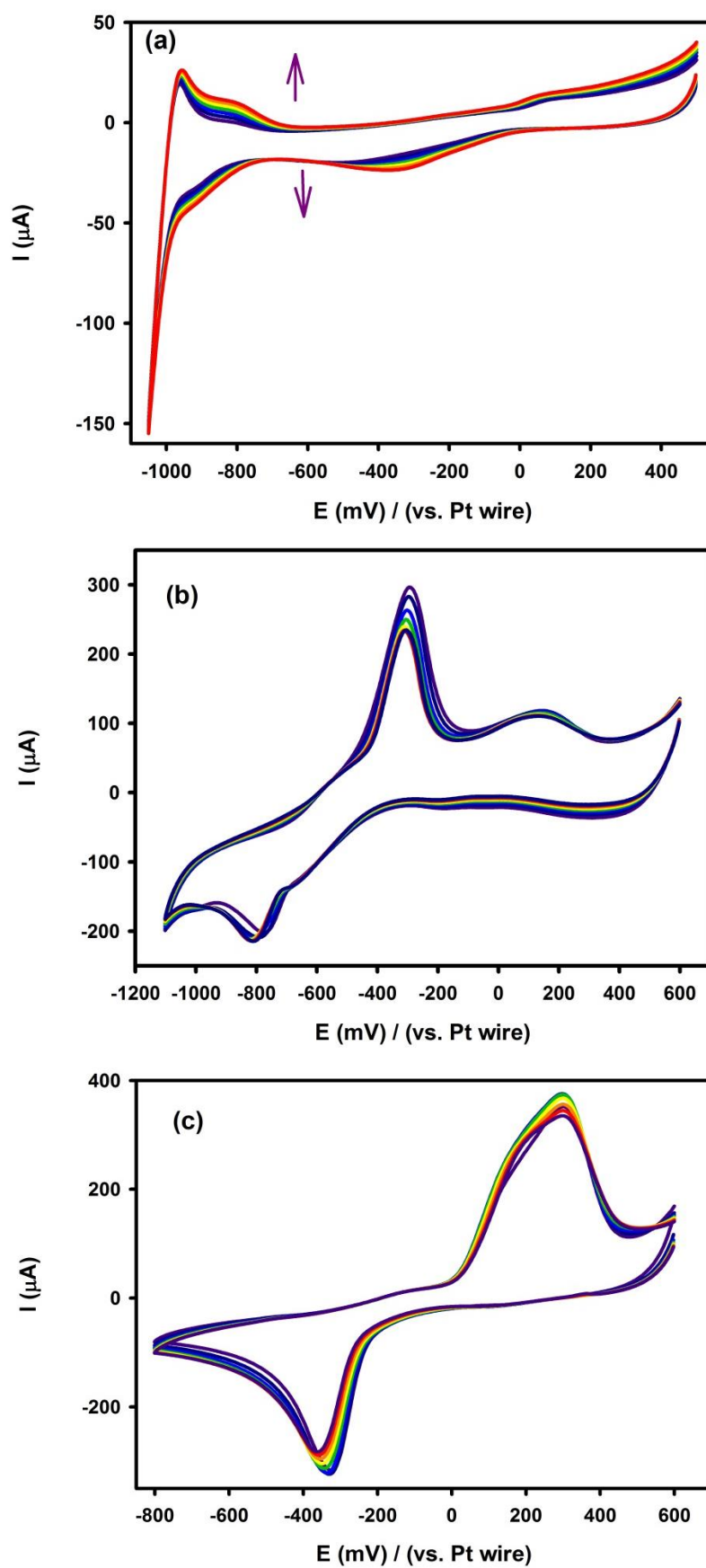


Figure 3.1 Consecutive cyclic voltammograms of a) Pt, b) Cu, c) Au nanoparticles on a CuPc-CNT/GCE in 1 mM metal ion containing acidic solutions.

Figure 3.2a exhibits the 10 CV scans for silver nanoparticle electrochemical deposition in the Ag^+ ions containing 0.1 M HNO_3 solution on CuPc-CNT/GCE surface. Repetitive potential cycles were start from +400 mV to the negative direction until reached the -900 mV. During the cathodic scan sharp and increasing reduction peak of Ag^+ ions to metallic silver observed at -300 mV which fallowed by the anodic dissolution of metallic silver to silver ions in the backward scan at about -150 mV which were coherent with the literatures (Wang, Q. and Zheng, J., 2010; Hernández-Ramírez et al., 2009)

Palladium nanoparticles were another promising electrode material for especially fuel cell applications, which was also studied in this thesis. Palladium nanoparticles formation on composite electrode surface was carry out by applying the consecutive potential cycles between -900 mV and +400 mV (Figure 3.2b). A small sharp reduction peak was observed at about -750 mV that was fallowed by two oxidation peaks at approximately at -600 and -200 mV.

Nickel nanoparticles formation on phthalocyanine-carbon nanotube composite electrode was shown in Figure 3.2c. Multicycle potential scans were performed between -1000 mV and +500 mV with 50 mV.s^{-1} scan rate. A reduction peak was obtained at about -500 mV which was shifted to more positive potentials by consecutive scans that suggested as easier deposition of nickel nanoparticles on the electrode surface. The hydrogen coevolution method used for electrodeposition of nickel with the hydrogen evolution at the same time which observed at -1000 mV. In the backward scan, the peak at about -800 mV that attributed to the oxidation of metallic nickel was in accordance with the literature (Zach, M. P. and Penne, R. M., 2000). In addition, an increasing oxidation peak metallic nickel to ionic form was observed at +300 mV.

Metal nanoparticles modified CNT/GCE, CuPc/GCE or Pc/GCE surfaces were obtained by fallowing the same procedures that described above for CuPc-CNT/GCE. All metal nanoparticles deposited in the same potential range and scan rates that mentioned previously. Therefore, almost same peak characteristics were obtained except for a few minor changes for all composite surfaces.

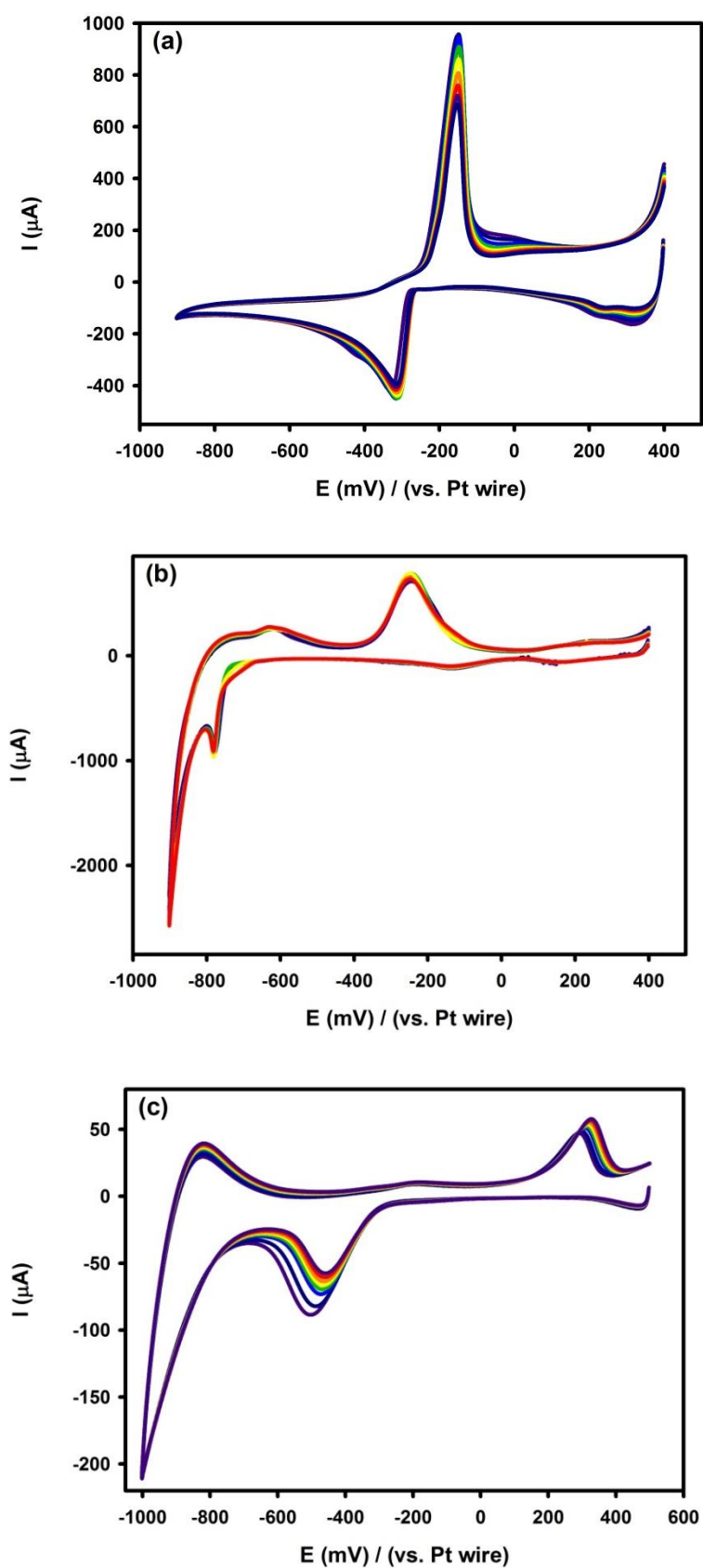


Figure 3.2 Consecutive cyclic voltammograms of a) Ag, b) Pd, c) Ni nanoparticles on a CuPc-CNT/GCE in 1 mM metal ion containing acidic solutions.

3.1.2 Electrochemical behavior of oxygen

The cyclic voltammograms of bare GCE and modified electrodes in 0.1 M NaOH solution with and without oxygen were shown in Figure 3.3. Figure represents the exact effect of modifiers as their individual or composite forms. As described before, CuPc/CNT/GCE and CNT/CuPc/GCE prepared by sequential drop and dry of CuPc and CNT, which differ from the CuPc-CNT/GCE that prepared from the one suspension containing of both CuPc and CNT together.

A small oxygen reduction peak was observed at -436 mV with 32 μ A peak current on bare GCE. Copper phthalocyanine modification on GCE was not improved the signal that oxygen reduction occurred at -471 mV with 34.3 μ A. The reduction peak was observed at -408 mV with a 32.5 μ A peak current and -436 mV with a 36.4 μ A peak current at CuPc/CNT/GCE and CNT/CuPc/GCE, respectively. As can be clearly seen from the figure that meliorated reduction behavior was only obtained at CNT/GCE and CuPc-CNT/GCE that oxygen reduction occurred at -420 mV with 109 μ A and -375 mV with 166 μ A potential and current values, respectively.

All potential and current values of bare and modified electrodes were listed in the Table 3.1. the peak current of oxygen reduction on CNT/GCE was 4.0 times higher than bare GCE. In addition, the results showed that CuPc/CNT/GC and CNT/CuPc/GC electrodes prepared layer by layer had less catalytic activity on ORR compared with the CuPc-CNT/GCE which was prepared at only a single step by mixing the CuPc and CNT at the same suspension. The best catalytic activity for oxygen reduction was obtained on CuPc-CNT/GCE. Significant current enhancement was observed with CuPc-CNT/GCE that was about 5.2 times higher than bare GCE and 1.5 times higher than CNT/GCE.

Table 3.1 Peak potential and current values of bare and modified electrodes.

Electrode	Potential(mV)	Current(μ A)
Bare GCE	-436	32
CuPc/GCE	-471	34.3
CNT/GCE	-420	109
CuPc-CNT/GCE	-375	166.0
CuPc/CNT/GCE	-408	32.5
CNT/CuPc/GCE	-436	36.4

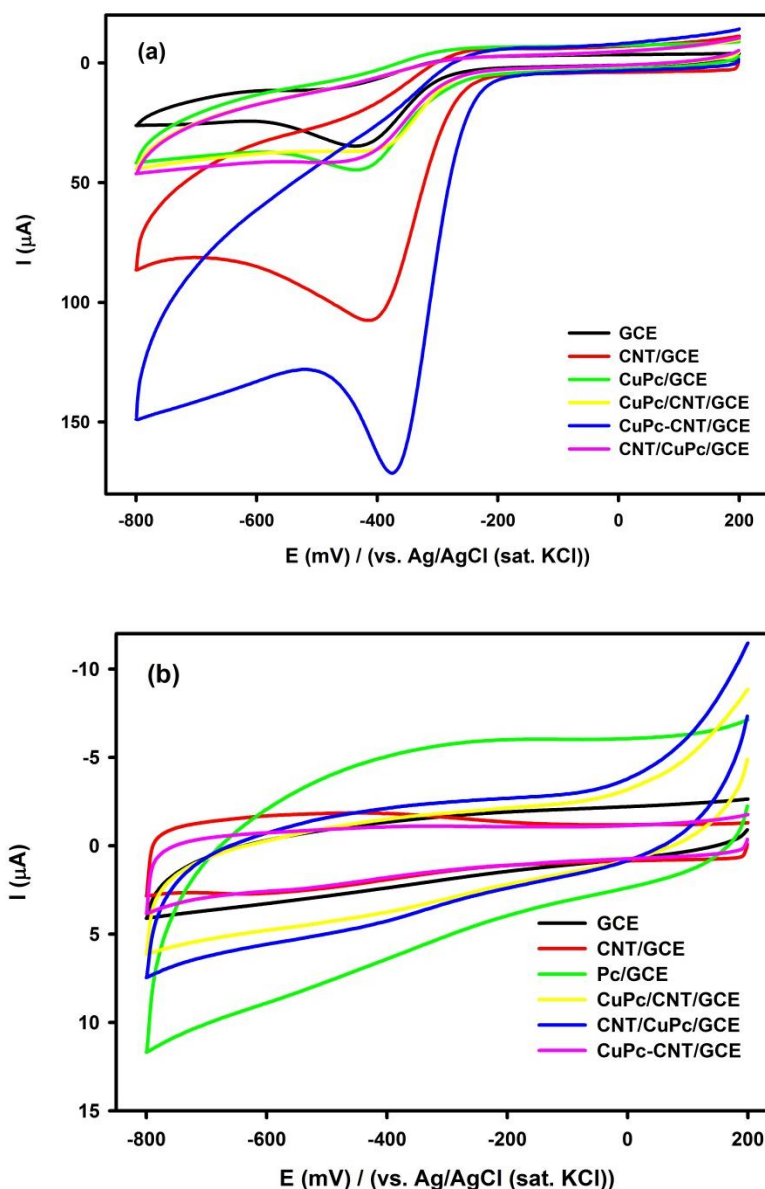


Figure 3.3 Cyclic voltammograms of bare GCE, CNT and CuPc modified different composite electrodes in a) O_2 saturated 0.1 M NaOH and b) N_2 saturated 0.1 M NaOH.

To improve the electrocatalytic activity of composite electrodes toward the reduction of oxygen, the electrodes were modified with different metal nanoparticles (Ni, Ag, Cu, Pd, Au, Pt). Figure 3.4-3.6 depict the cyclic voltammograms of oxygen reduction at CuPc/GC, CNT/GC, and CuPc-CNT/GC electrodes modified with different metal nanoparticles. Peak current and potential values of all modified electrodes for oxygen reduction were given in Table 3.2.

Figure 3.4 shows the responses of modified electrodes in oxygen saturated (Figure 3.4a) and N_2 saturated (Figure 3.4b) NaOH solution. Ni, Cu, Pd and Au modified CuPc/GC electrodes show almost same behavior with metal free-CuPc/GCE. The reduction peak of oxygen was appeared at -415 mV with 38 μA on CuPc/GCE. Ag nanoparticles modified copperphthalocyanine electrode (Ag/CuPc/GCE) has good activity for oxygen reduction reaction due to its highest peak current value (63 μA at -380 mV) among other nanoparticles modified electrodes. According to the results, platinum nanoparticles modified CuPc/GCE chosen as the best electrode due to the most positive potential value (-210 mV). The peak current of oxygen reduction at Pt/CuPc/GCE was about 1.45 times higher than CuPc/GCE and the reduction peak potential was also shifted 205 mV more positive potential value. The supporting electrolyte voltammograms of those electrodes in 0.1 NaOH solutions were shown in Figure 3.4b that platinum modified electrode has more active sites as compared to the other electrodes, which resulted the higher background currents.

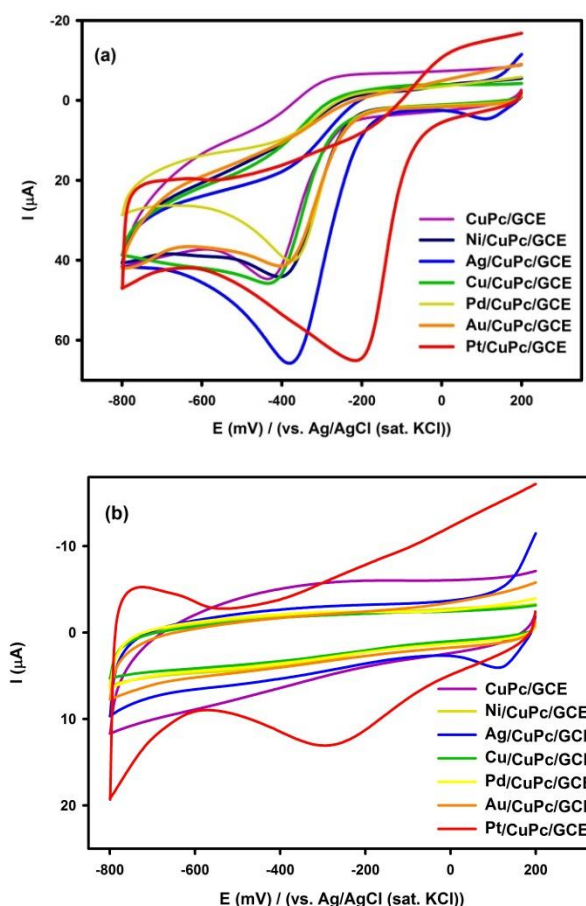


Figure 3.4 Cyclic voltammograms of Ni, Ag, Au, Cu, Pd, Pt nano particles modified CuPc/GCE in a) O_2 saturated 0.1 M NaOH b) N_2 saturated 0.1 M NaOH.

The electrocatalytic activity of Ni, Ag, Cu, Pd, Au, Pt nanoparticles onto CNT/GC electrodes in saturated oxygen solution were also investigated in alkaline solution (Figure 3.5). The reduction peak of oxygen appeared at -420 mV with 109 μ A at CNT/GCE.

Surprisingly, ORR occurred at more negative potential values with lower peak currents at all metal nano particles modified CNT/GCE except Pt/CNT/GCE (-397 mV 101 μ A) and Pd/CNT/GCE (-279 mV 127 μ A). This unpredicted behavior can be attributed to the functionalization procedure of CNTs which produce the active functional groups on CNTs that effect the binding of metals or analytes. The results revealed that the best catalytic activity was observed on the Pd/CNT/GCE due to the most positive peak potential and highest current value in comparison with the CNT/GCE, with a 127 mV shift from -406 mV to -279 mV. The supporting electrolyte voltammograms of those electrodes in 0.1 NaOH solutions were shown at Figure 3. 5b that Pd, Au, Ag, Pt modified surfaces have more active sites that increase the background responses.

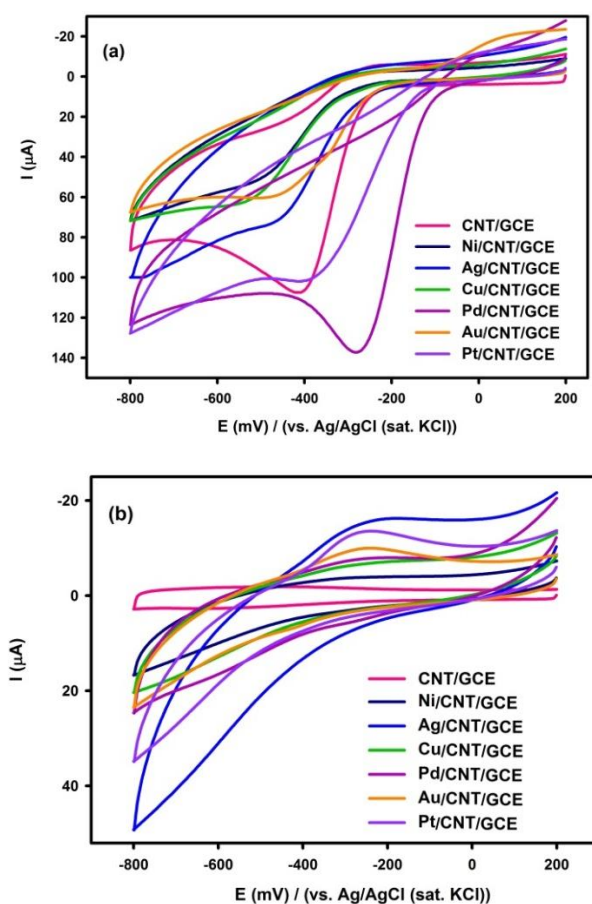


Figure 3.5 Cyclic voltammograms of Ni, Ag, Au, Cu, Pd, Pt nano particles modified CNT/GCE in a) O_2 saturated 0.1 M NaOH b) N_2 saturated 0.1 M NaOH.

Figure 3.6 shows the comparative cyclic voltammograms of the composite electrodes studied in oxygen saturated 0.1 M NaOH solution. The oxygen reduction reaction on the various metal nano particles modified electrodes were compared with CuPc-CNT/GC electrode. Oxygen reduction occurred with two peaks at Ni, Ag, Cu and Au modified CuPc-CNT/GC electrodes. The Pt/CuPc-CNT/GCE showed better response in terms of current, peak potential and less onset potential compared to other electrodes. The best catalytic activity was observed with the Pt/CuPc-CNT/GCE modified electrode in comparison to the CuPc-CNT/GCE, with a 142 mV shift from -375 mV to -233 mV. The peak current at this electrode was about 1.7 times higher than that at CuPc-CNT/GCE. As expected, Pt/CuPc-CNT/GC electrode showed a single peak, which probably related to the 4-electron transferred (one-step) reduction of oxygen. This result agrees with our previously published paper that Cu–Au–MWCNT/GCE catalysts follow the direct 4-electron pathway (Bakır et al., 2011).

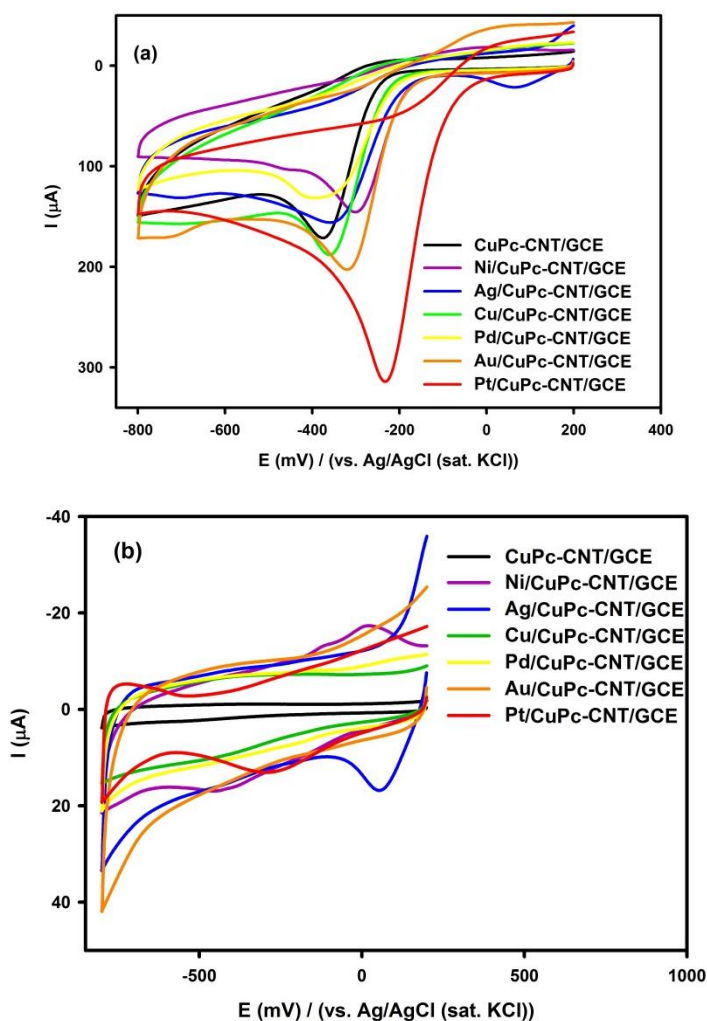


Figure 3.6 Cyclic voltammograms of Ni, Ag, Au, Cu, Pd, Pt nano particles modified CuPc-CNT/GCE in a) O₂ saturated 0.1 M NaOH b) N₂ saturated 0.1 M NaOH.

Table 3.2 represents the peak current and potential values of all metal nano particles modified CNT/GC, CuPc/GC and CuPc-CNT/GC electrodes for comparison. According to the voltammograms and Table 3.2, CuPc-CNT/GC support was meliorated the behavior of the electrode towards ORR for almost all kind of modified metals (except Pd) as compared to the metallated CNT/GC, CuPc/GC electrodes. In addition, Ni, Ag, Cu, Au nanoparticles modified CuPc-CNT/GCEs have more positive reduction peak potentials as compared to the same metals modified CNT/GC and CuPc/GC electrodes.

The overall table depicts that, platinum nanoparticles modified CuPc-CNT/GCE showed best catalytic activity towards oxygen reduction in terms of peak current which also have more positive reduction potential value as compared to the almost all other electrodes. The peak current of oxygen reduction at platinum nanoparticles modified CuPc-CNT/GC electrode was about 1.7, 3.0 and 5.3 times higher than that at CuPc-CNT/GCE, Pt/CNT/GCE and Pt/CuPc/GCE, respectively. Moreover, the reduction peak potential of oxygen on Pt/CuPc-CNT/GC electrode shifted 142 mV and 164 mV to positive values as compared to the CuPc-CNT/GCE and Pt/CNT/GCE, respectively. However the peak potential observed at more positive potential on Pt/CuPc-CNT/GCE.

Table 3.2 Potential and current values of different kind nanoparticles modified CuPc/GC, CNT/GC, CuPc-CNT/GC electrodes towards oxygen reduction.

Nanoparticles	CuPc/GCE		CNT/GCE		CuPc-CNT/GCE	
	Potential (mV)	Current (μ A)	Potential (mV)	Current (μ A)	Potential (mV)	Current (μ A)
-	-415	38	-406	109	-375	166
Ni	-394	42	-558	51	-300	116
Ag	-370	63	-446	62	-356	146
Cu	-433	42	-539	58	-359	177
Pd	-375	37	-279	127	-348	101
Au	-404	39	-484	48	-319	189
Pt	-210	55	-397	98	-233	295

The influence of NaOH concentration on the peak potential and peak current of oxygen reduction at Pt/CuPc-CNT/GCE were examined in the concentration range between 0.01 to 1.0 M that shown in Figure 3.7. Figure 3.8 plotted from the cyclic responses that obtained from Figure 3.7. The low concentration value, 0.01 M NaOH, gave an exceptional bahviour as compared to other concentrations in terms of current and potential with poor shaped peak. As the NaOH concentration increases, the oxygen reduction peak was shifted to more positive potentials with a decrease in peak current. The peak potential shifted to -233 mV with a current increase in 0.1 M NaOH solution. Overall results showed that the best catalytic activity observed at a Pt/CuPc-CNT/GC electrode was obtained in 0.1 M NaOH solution that was chosen as an optimum supporting electrolyte for the future studies.

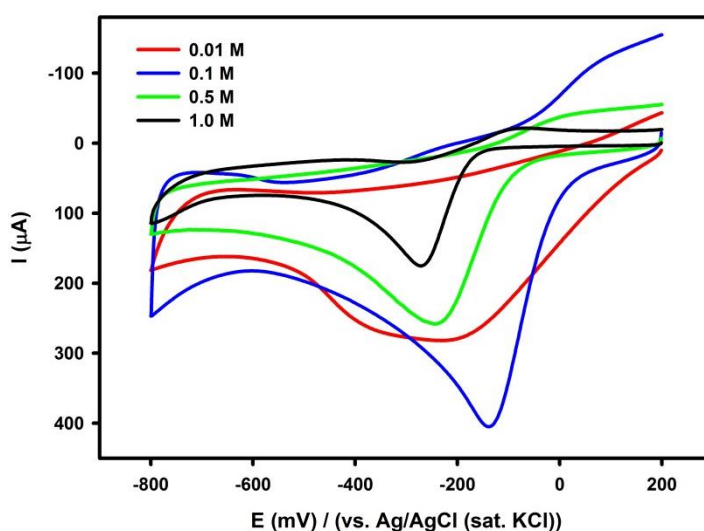


Figure 3.7 Cyclic voltammograms for oxygen reduction on Pt/CuPc-CNT/GC electrodes at different NaOH concentrations.

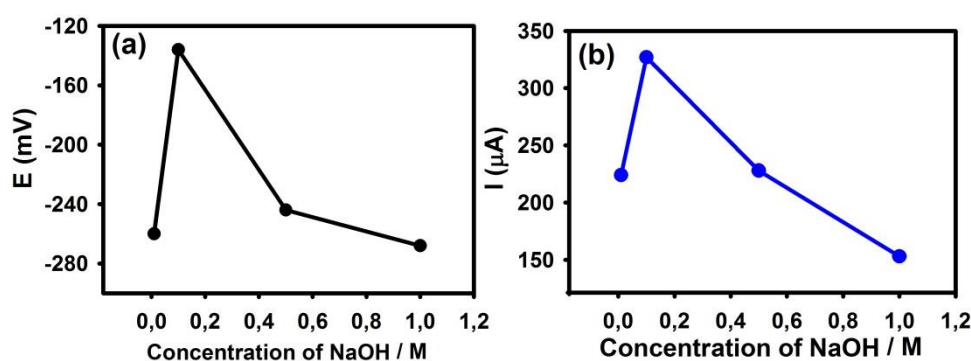


Figure 3.8 a) Peak potential and b) peak current changes of Pt/CuPc-CNT/GCE by the change of NaOH concentration for oxygen reduction reaction.

To observe the best catalytic effect with Pt nanoparticles modified CuPc-CNT/GCE on the oxygen reduction, the platinum solution concentration was changed by using cyclic voltammetry in the concentration range from 0.5 mM to 5 mM (Figure 3.9). As the Pt^{4+} concentration increases, the peak related to the oxygen reduction was shifted to positive potentials until reach to 3 mM. At higher concentration of platinum solutions, platinum particles covered the all surface that behave like platinum disk surface which explain the negative shift in peak potential. In addition, at first, peak current of ORR was increased up to 1 mM which then remains almost stable. The results showed that the best catalytic activity was observed at a Pt/CuPc-CNT/GC electrode that was prepared with 3 mM chloroplatinic acid solution due to the more positive peak potential value. Therefore, the future studies will be performed in 3 mM chloroplatinic acid solution.

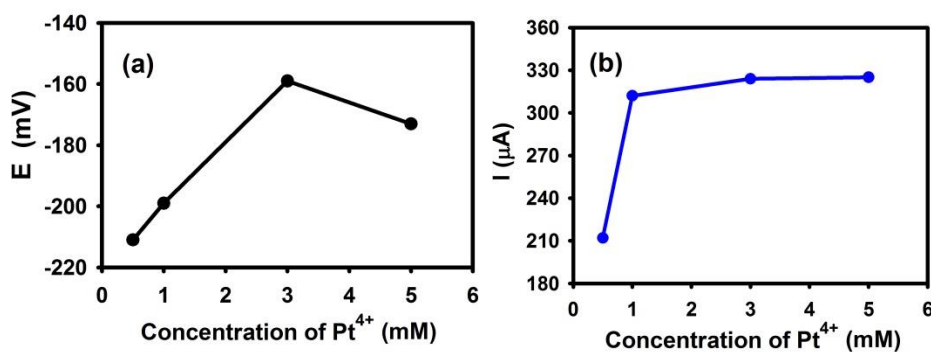


Figure 3.9 Concentration of Pt^{4+} vs. oxygen reduction a) peak potential, b) peak current at CuPc-CNT/GCE.

Another parameter to be optimized is the CuPc:CNT mass ratio that can also affect the peak characteristic of oxygen reduction. Figure 3.10 shows the effect of mass ratio on the oxygen reduction peak. The amount of CuPc was changed to maintain the mass ratio of 1:15, 1:6, 1:2 and 1:1 CuPc:CNT, respectively. The peak characteristics obtained from the resulting voltammograms were shown in Figure 3.11. The best response towards dissolved oxygen was obtained with a mole ratio of 1:6 CuPc:CNT. Above this ratio value, peak potential of oxygen reduction shifted back to negative values with decreased currents which not desired for catalytic surfaces.

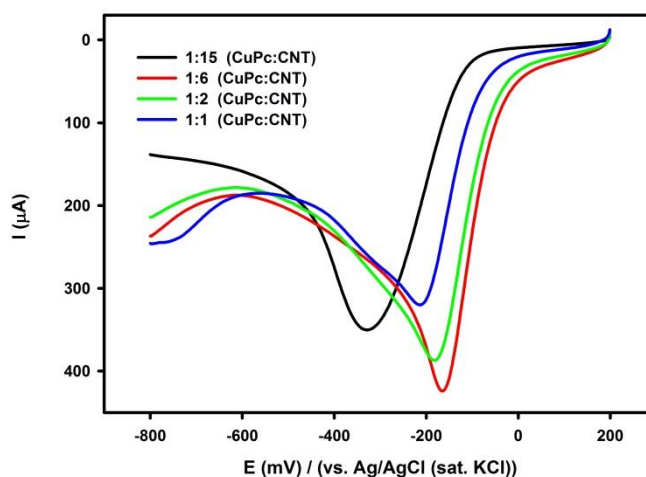


Figure 3.10 Linear sweep voltammograms of oxygen reduction at Pt/CuPc-CNT/GC electrode with different CuPc:CNT mass ratios.

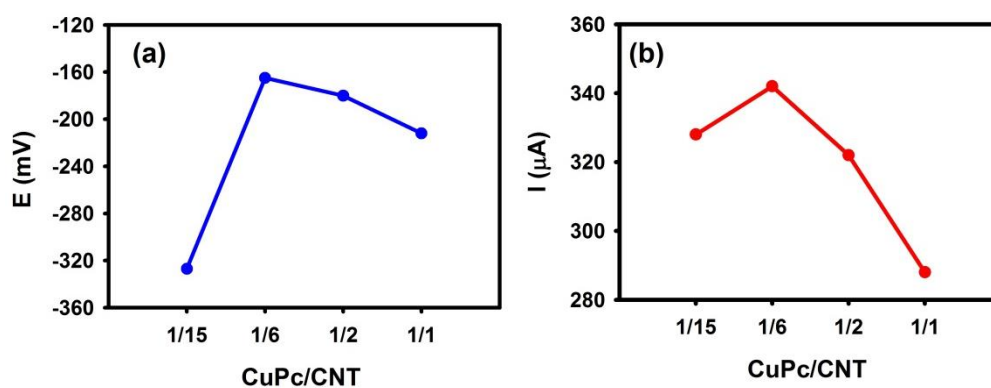


Figure 3.11 Effect of CuPc:CNT mass ratio on oxygen reduction a) peak potential and b) peak current at Pt/CuPc-CNT/GCE.

In Figure 3.12, the oxygen reduction behavior on Pt nanoparticles modified composite CuPc-CNT/GCE was compared with Pt disk, bare GCE, CuPc-CNT and the other platinum modified electrodes. Only one reduction signal as peak form was observed at all electrodes in oxygen saturated NaOH solution. Oxygen reduction occurred with a sluggish peak at -436 mV on GCE while it occurred at -207 mV on Pt disk electrode. The ORR occurred at a more negative potential on CuPc-CNT/GCE compared with the Pt/CuPc/GCE and Pt/CuPc-CNT/GCE, while the peak current (166 μA) was higher than Pt/CuPc/GCE (55.3 μA) and Pt/CNT/GCE (101 μA). In addition, Pt/CuPc-CNT/GCE showed best catalytic activity towards ORR in terms of both more positive reduction potential (-156 mV) and higher peak current value (327 μA) as compared to all the other electrodes.

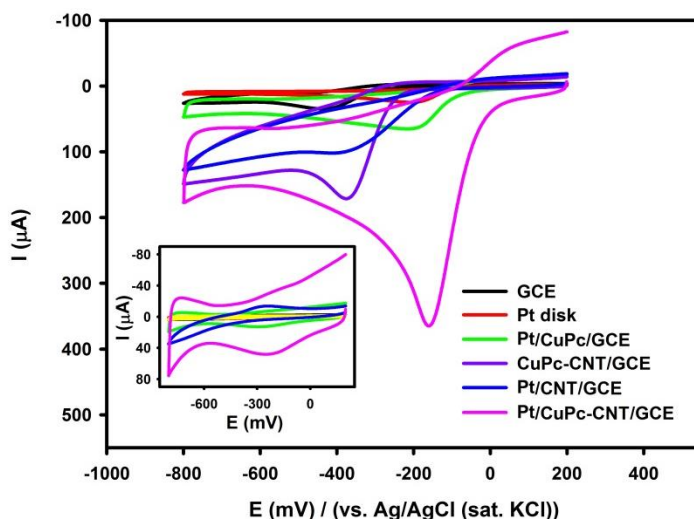


Figure 3.12 Cyclic voltammograms of oxygen reduction reaction on bare GCE, Pt disk, Pt/CuPc/GCE, CuPc-CNT/GCE, Pt/CNT/GCE and Pt/CuPc-CNT/GC electrodes. Insets: on right side; with arrow, the zoomed view of voltammograms and on left side; background voltammograms of electrodes.

The effect of scan rate on the peak current of oxygen reduction at bare GCE, Pt disk, Pt/CuPc/GCE, CuPc-CNT/GCE, Pt/CNT/GCE and Pt/CuPc-CNT/GC electrodes were studied in a range of 5-250 mVs^{-1} . Figure 3.13 shows the cyclic voltammograms of Pt/CuPc-CNT/GCE with a various scan rate in oxygen saturated 0.1 M NaOH solution. As the scan rate increases, the electrocatalytic oxygen reduction potential shifted negatively. Oxygen reduction peak current vs. $(\text{scan rate})^{1/2}$ for bare GCE, Pt disk, Pt/CuPc/GCE, CuPc-CNT/GCE, Pt/CNT/GCE and Pt/CuPc-CNT/GC electrodes were shown in Figure 3.14. The peak currents have shown a linear increase with the square root of the scan rate indicating that oxygen reduction reaction at all electrodes were controlled by diffusion.

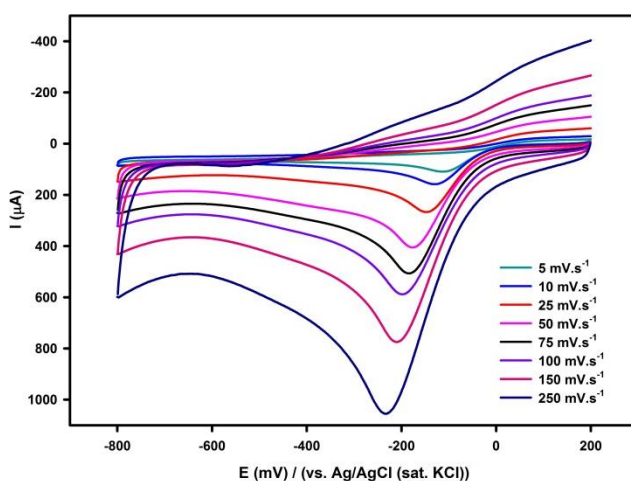


Figure 3.13 Cyclic voltammograms of different scan rates of oxygen reduction on Pt/CuPc-CNT/GCE

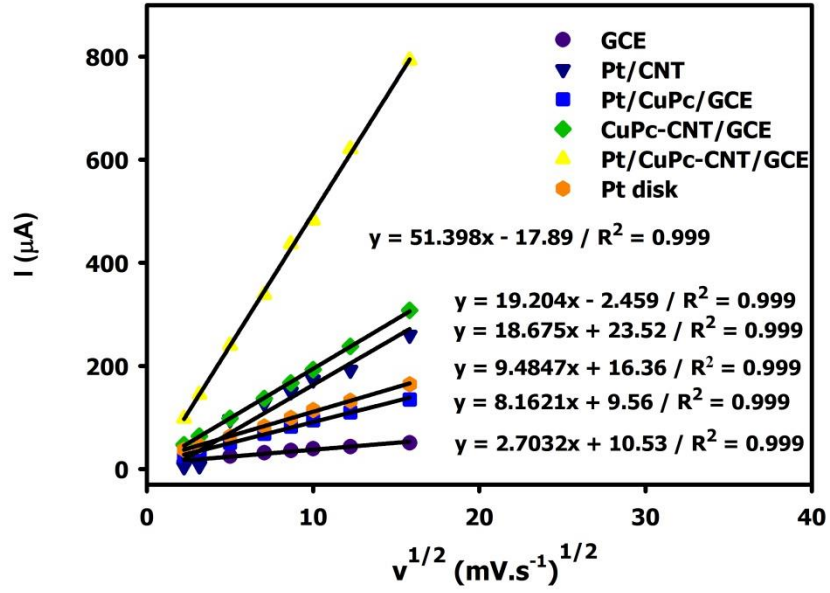


Figure 3.14 Square root of the scan rate vs. current plots from scan rate studies of GCE, Pt disk, Pt/CuPc/GCE, CuPc-CNT/GCE, Pt/CNT/GCE and Pt/CuPc-CNT/GCE in oxygen saturated NaOH.

Hydrodynamic voltammetric studies were also performed on rotating GC electrodes modified with Pt/CuPc-CNT in the oxygen saturated 0.1 M NaOH to determine the kinetic parameters more quantitatively (Figure 3.15). The RDE data were analyzed using the Koutecky–Levich (K–L) equation, which in the case of a thin Pt/CuPc-CNT film on the electrode can be expressed as follows:

$$\frac{1}{j} = \frac{1}{j_k} + \frac{1}{B\omega^{1/2}} \quad (12)$$

Where j is the measured current density, j_k is the kinetic current density, The theoretical value of the Levich slope (B) is evaluated from Eq. (12)

$$B = 0.62nFC_{O_2}D_{O_2}^{2/3}\gamma^{-1/6} \quad (13)$$

Where n is the number of electrons transferred per oxygen molecule, F is Faraday constant ($96485.333 \text{ C mol}^{-1}$), C_{O_2} is the concentration of oxygen in 0.1 M NaOH ($1.2 \times 10^{-6} \text{ mol cm}^{-3}$), D_{O_2} is the diffusion coefficient of oxygen ($1.9 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$), γ is the kinematic viscosity of the solution ($0.01 \text{ cm}^2 \text{ s}^{-1}$). According to Eq. (12), the plots of j^{-1} vs. $\omega^{-1/2}$ should be linear. From the slope of the K–L plots (inset of Figure 3.15), the value of n was calculated. For the Pt/CuPc-CNT/GC electrode, the value of n was calculated as 3.7, indicating that O_2 is reduced by direct almost four-electron pathway to produce water.

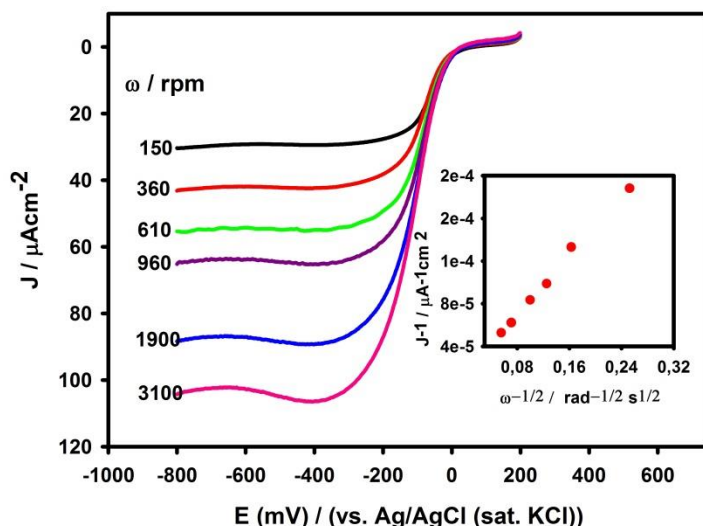


Figure 3.15 RDE voltammetry results for O_2 reduction on a Pt/CuPc-CNT/GC electrode in O_2 -saturated 0.1 M NaOH. Inset: Koutecky–Levich plot for O_2 reduction.

Mass-transport currents were used to examine the Tafel behavior of the mixed kinetic diffusion region (Figure 3.16). A Tafel slope varies from $-0.056 \text{ V dec}^{-1}$ at lower current densities to -0.11 V dec^{-1} in the higher current density region. Changing the coverage of surface by adsorbed oxygen species give rise to two Tafel slope regions that attributed to the change from Temkin to Langmiur conditions. This behavior was found very similar to that observed with Cu-Au-MWCNT/GCE in our previous study (Bakır et al., 2011).

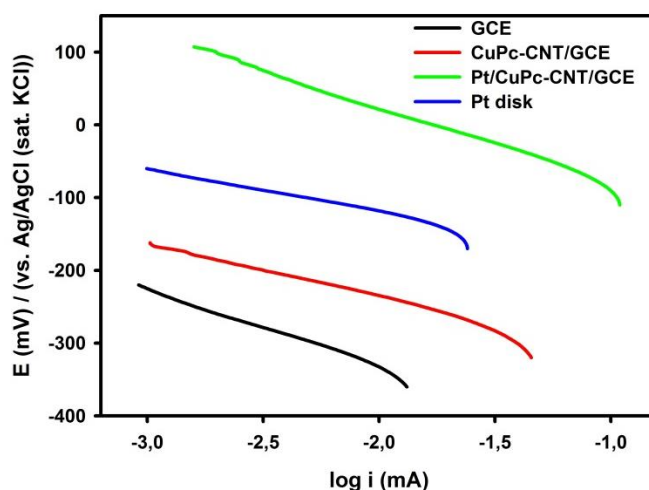


Figure 3.16 Tafel slopes of oxygen reduction on different electrode surfaces for a 5 mVs^{-1} scan rate.

The stability of the Pt/CuPc-CNT film modified electrode was studied by cyclic voltammetric measurements. No remarkable change was observed in the current response of modified electrode stored in the vapor of 0.1 M NaOH solution for 10 days. A good reproducibility was observed in modified electrode

for oxygen reduction reaction. The response of the electrode in the O₂ saturated solution maintained 87.5% of the original peak current value after 10 days. Also a series of 10 modified electrodes was prepared and OR behavior was investigated. According to the results, relative standard deviation was found only 3.5%. These experiments show that the GC electrodes modified with Pt/CuPc-CNT films have good repeatability and stability that related with the synergistic effect of the nano particles, CuPc and CNT.

3.1.3 Characterization of modified electrodes

The surface morphology of all electrodes was characterized using scanning electron microscope (SEM). As it is expected, smooth and homogeneous electrode surface observed for bare GCE. As shown in Figure 3.17, SEM image of acid-treated CNT (Figure 3.17b) shows the distribution of tubular like carbon nanotubes on the GCE surface with a smooth and rather uniform pattern. Figure 3.17c shows the cotton like shaped surface for CuPc/GCE that was different from the bare GCE and carbon nanotube containing surfaces. The composition of CuPc on the CNT/GCE in Figure 3.17d shows both tubular forms and cotton like areas on electrode surface that was exactly the image that it is expected which was compatible with the individual images of CNT and CuPc. The scanning electron microscopy images of Pt/CuPc-CNT/GCE in Figure 3.17e displayed many bright dots due to the deposition of Pt nanoparticles on the CuPc-CNT surface. Pt nanoparticles calculated on the surface of the composite electrode with a diameter ranging between 100 and 150 nm. Pt nanoparticles appeared brighter than Cu particles in the backscattered image due to a higher molecular weight of Pt (Figure 3.17e). Comparison between the Figure 3.17d and e before and after Pt nanoparticles deposition revealed an obvious change in distribution of particle size on the CuPc-CNT surface.

In order to qualitatively confirmation of the composite electrode surface composition, the prepared CuPc/GCE, CuPc-CNT/GCE and Pt/CuPc-CNT/GCE characterized with EDX (Figure 3.18) which proved the Cu content of modifier and successful electrodeposition of Pt nanoparticles on CuPc-CNT/GC surface. Comparison of Figure 3.18a and b shows that the weight gain of copper decreased from 8.35% to 1.54% due to the addition of high carbon containing carbon nanotube in to modifier composition. The weight gain of the CuPc-CNT due to the Pt loading was about 9.7%. N and Cu atoms were found in the structure of copper phthalocyanine molecule.

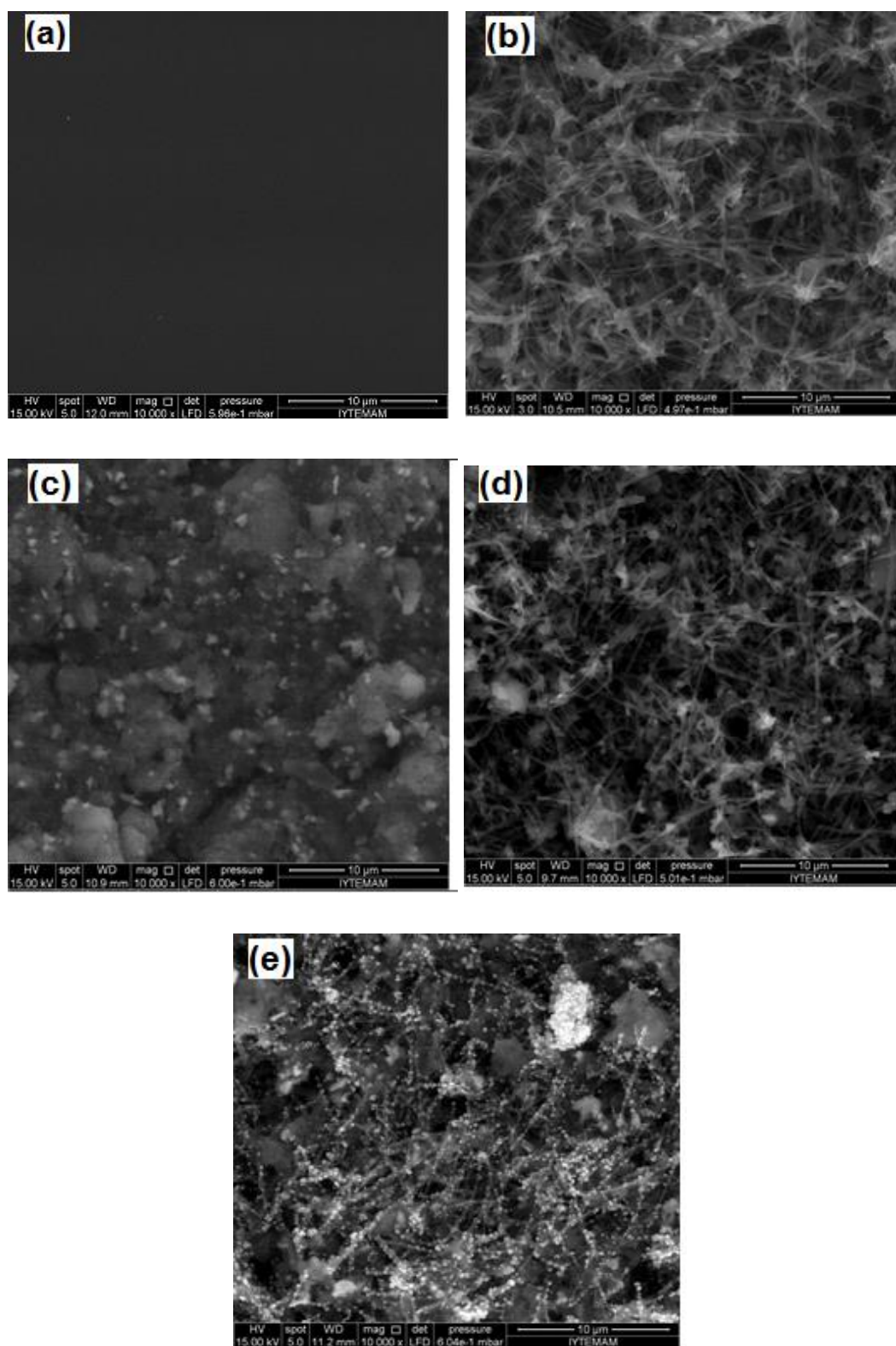


Figure 3.17 SEM images of the a) Bare GCE, b) CNT/GCE c) CuPc/GCE, d) CuPc-CNT/GCE, e) Pt/CuPc-CNT/GCE surfaces.

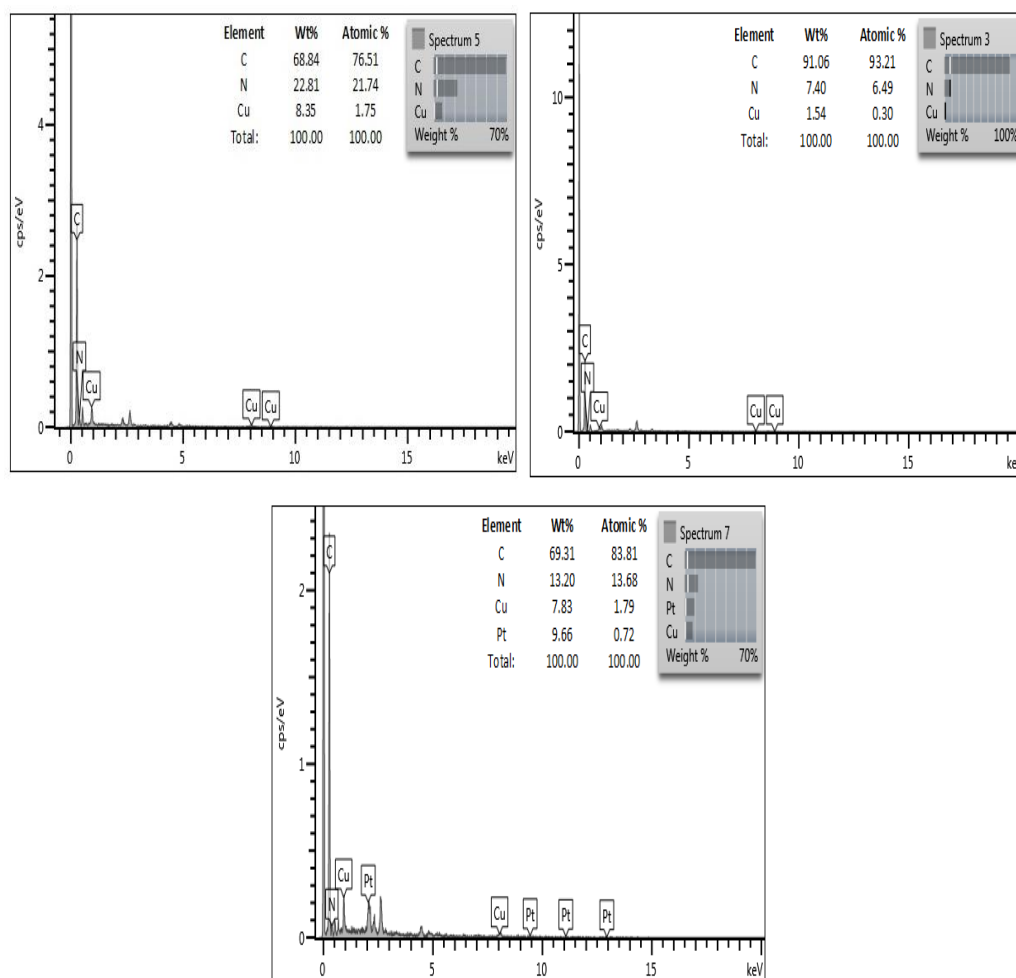


Figure 3.18 EDX results of the a) CuPc/GCE, b) CuPc-CNT/GCE, c) Pt/CuPc-CNT/GCE surfaces.

TEM images of CuPc-CNT/GCE and Pt/CuPc-CNT/GCE catalyst were shown in Figure 3.19. The typical TEM images, can help to understand the morphology and particle size differences before and after the platinum nanoparticles modification. Figure 3.19 (a-f) show micrographs of CuPc-CNT/GCE in the decreasing focus areas from 0.5 μm to 5 nm that shows surface with evenly dispersed CuPc particles on the carbon nanotubes. We can see that, most of the Pt nanoparticles were uniformly dispersed in the range of 3-6 nm on the CuPc-CNT/GCE support, while some aggregates like Pt-containing cluster compounds appear on the CuPc modified carbon nanotubes (Figure 3.19 (g-l)). Compared with CuPc precursor, there are some Pt-containing cluster compounds distributed uniformly on the carbon nanotubes. These results imply that the immobilization of copper phthalocyanine on the carbon nanotubes produces the uniform distribution of surface functional groups, which are beneficial to the deposition of Pt nanoparticles. These results were consistent with the literatures (Qing et al., 2014; Chen et al., 2010; Jin et al., 2012).

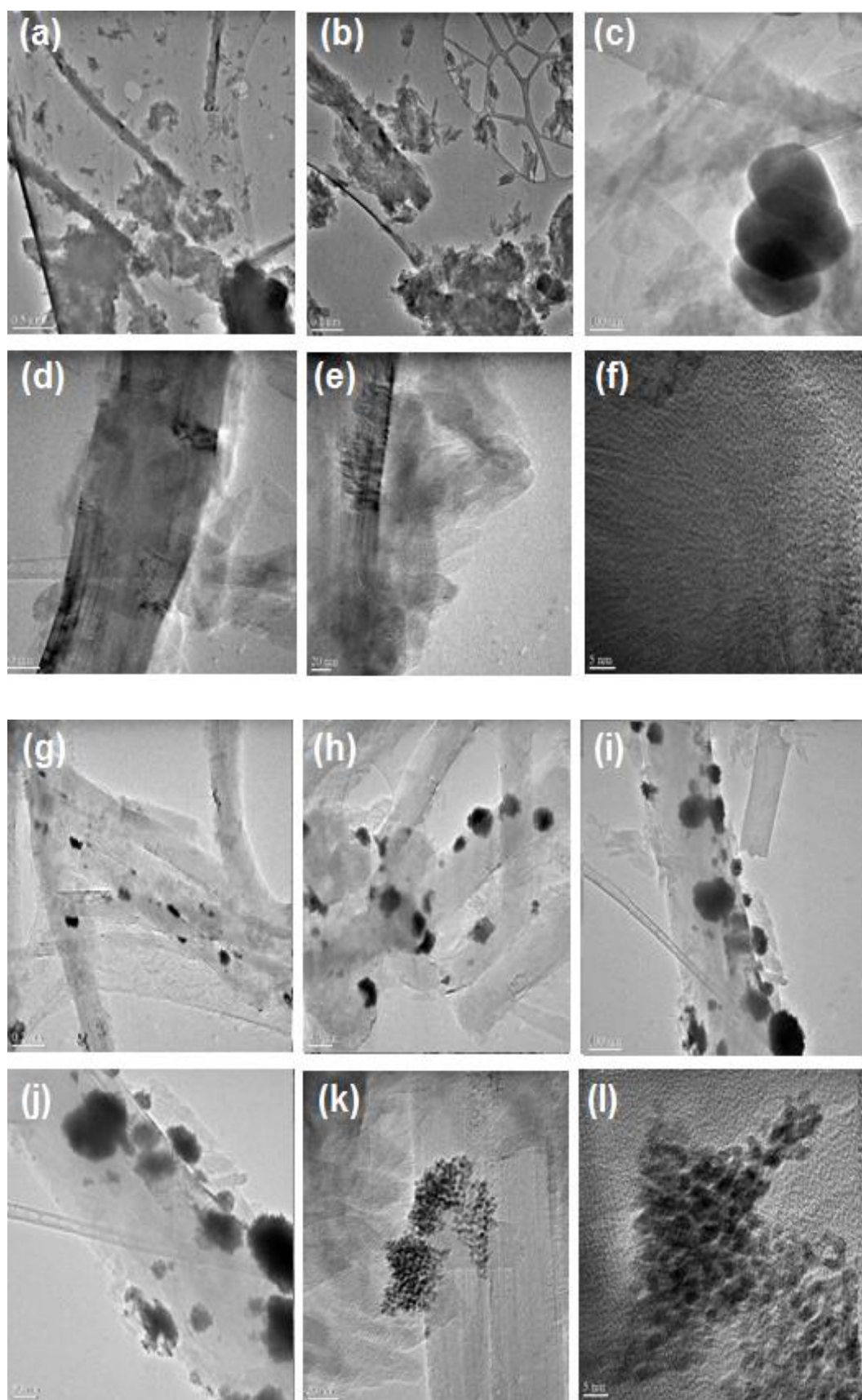


Figure 3.19 TEM images of samples at different magnifications: (a-f) CuPc-CNT/GCE and (g-l) Pt/CuPc-CNT/GCE.

The formation of platinum nanoparticles on the copper phthalocyanine-carbon nanotube also characterized with XPS as shown in Figure 3.20. Composition analysis of the electrochemically deposited films carried out by XPS in order to identify the material quality. The signals of Cu2p at 933.79 eV, O1s at 533.12 eV, N1s at 399.45 eV, C1s at 285.19 eV and Pt4f at 73.54 eV were also observed due to the surface modification of carbon nanotubes and copper phthalocyanine (Figure 3.20a). Figure 3.20b shows Pt 4f region of the XPS spectra of Pt/CNT/GCE catalysts. The 4f_{5/2} and 4f_{7/2} spectra of Pt existed at 74.77 eV and 71.56 eV, respectively, corresponding to the Pt⁰ state. The 4f_{5/2} and 4f_{7/2} peaks have separation energies close to 3.21 eV. These findings were compatible with literature (Acharya et al., 2009; Ji et al., 2001). In the literature, the peaks of Pt 4f_{7/2} at 72.8 eV and Pt 4f_{5/2} at 76.5 eV are attributed to the Pt²⁺ chemical state on PtO or Pt(OH)₂. However, the binding energy of Pt⁰ of Pt/CuPc-CNT/GCE observed as 75.42 eV and 72.31 eV revealing that a negative shift in the binding energy of Pt species on the Pt/CuPc-CNT/GCE surface (Figure 3.20c). The peaks have separation energies close to 3.11 eV. This doublet can be attributed to the metallic platinum.

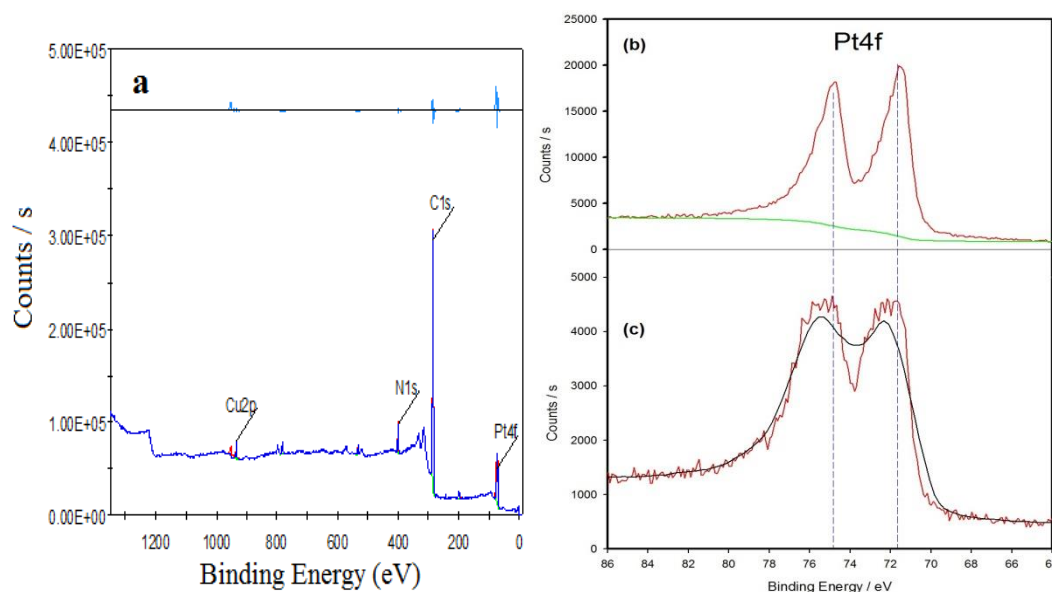


Figure 3.20 XPS spectra for a) survey of all elements, b) Pt/CNT/GCE, c) Pt/CuPc-CNT/GCE.

X-ray diffraction (XRD) is used widely to analyze the configuration of molecules and their crystallographic structures. The XRD patterns of CuPc-CNT and Pt/CuPc-CNT on the indium tin oxide (ITO) glass were analysed. The samples were scanned from 5 to 90 2Theta in step sizes of 0.0130. To phase identification the contents of samples were used the HighScore database program.

HighScore is the ideal software for phase identification, semi-quantitative phase analysis, pattern treatment, profile fitting. Figure 3.21 shows the comparative XRD patterns of bare ITO, CuPc-CNT and Pt/CuPc-CNT/ITO. The characteristic ITO peaks were determined with a broad form at about 22° , sharp peak at 30.6° and weak peaks at $2\theta = 35.5^\circ, 50.9^\circ, 60.6^\circ$ that correspond to the reflections of (211), (222), (400), (440), (622) cubic structured ITO. The obtained results were coherent with the literatures. (koseoglu et al., 2015; Koo et al., 2015)

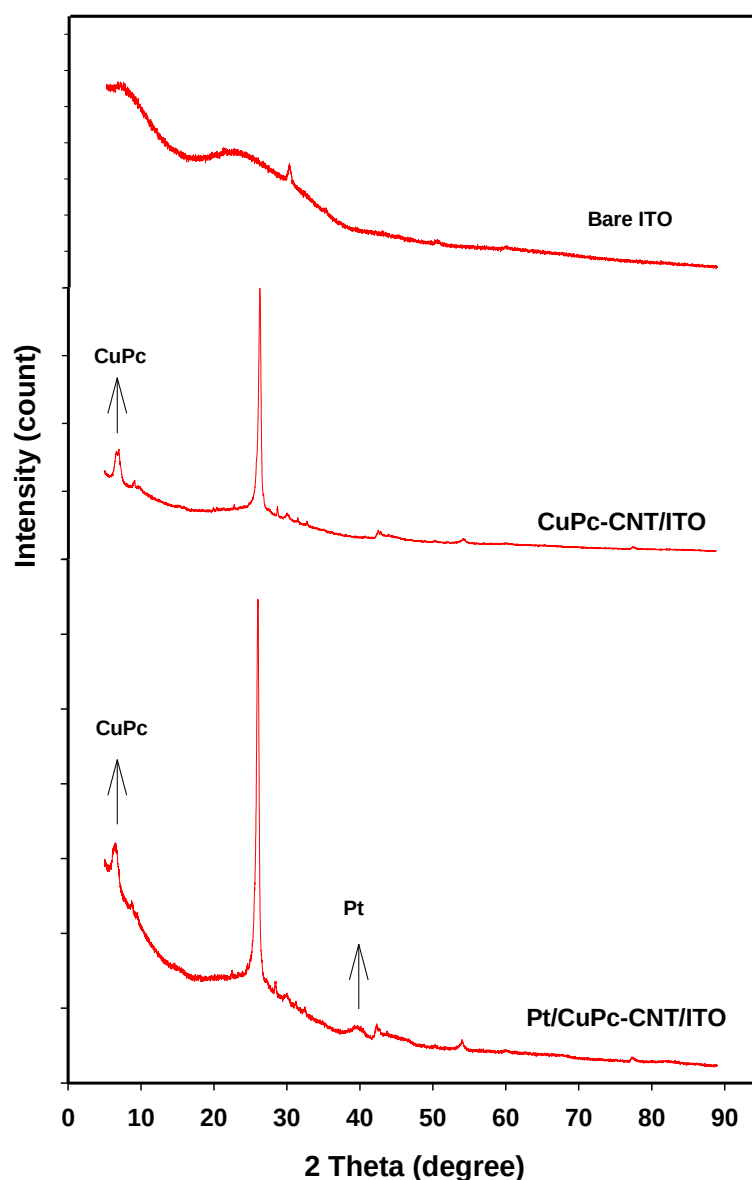


Figure 3.21 Comparative XRD patterns of bare and modified ITO electrodes.

In the XRD pattern in Figure 3.22 and inset, for CuPc, the characteristic peaks were determined at $2\theta = 6.78^\circ, 6.86^\circ, 9.18^\circ, 9.74^\circ, 15.62^\circ$. These peaks were corresponding to the (200) and (002) planes of the α -phase, (101) plane of β -phase, α phase and polymorphic phase, respectively (Topuz et al., 2013; Afify et al., 2015). The other major peaks are at 26.28° and 26.35° indicated 50% and 13% intensities, respectively. The sharp diffraction peak at 26.35° indicates the characteristic hexagonal structure of carbon (ICSD, card no. 98-002-9123). In addition, the weak peaks around $43^\circ, 54^\circ$ and 78° can be indicated as C(100), C(004) and C(110) reflection of the hexagonal graphite structure. These datas were well agreement with previous studies (Atchudan et al., 2015; Zeng et al., 2014; Tatar et al., 2014).

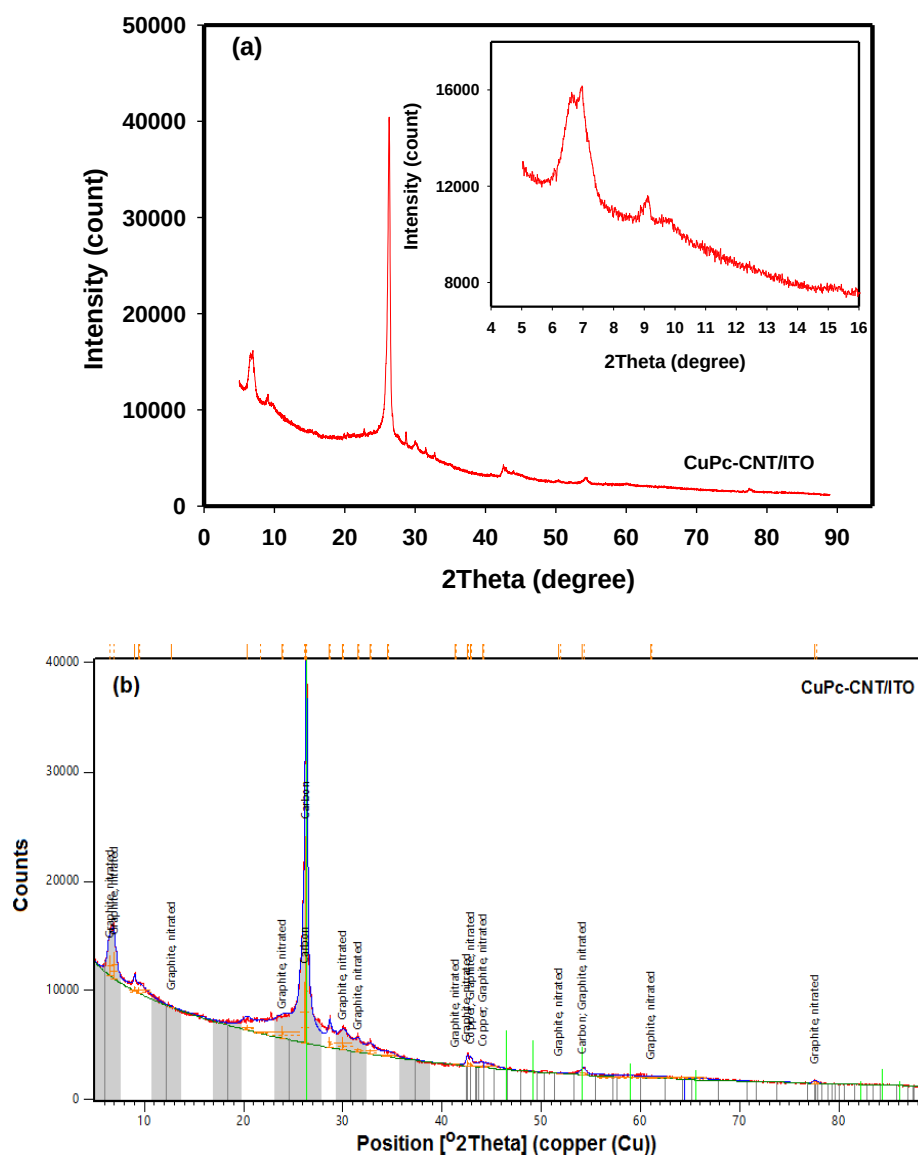


Figure 3.22 a) XRD pattern and b) matching XRD pattern of the CuPc-CNT/ITO.

The formation of Pt nanoparticles on the CuPc-CNT/ITO surface, XRD diffraction was scanned in the range between 5 to 90, 2 θ degree. Pt nanoparticles on the CuPc-CNT surface were confirmed as pure metal nanoparticles by XRD analysis and related pattern was shown in Figure 3.23 and inset. Also, the simulated X-ray pattern were matched by using HighScore database program (Figure 3.23b). In the pattern (indicated with line and arrows), sharp diffraction peak at 39.7° and weak broad diffraction peaks at 46.2° and 67.6° were observed which correspond to the (111), (200) and (220) crystalline planes of face-centered cubic Pt crystal, respectively. Finally, it can be claimed that the Pt nanoparticles are formed of pure crystalline Pt. These results are also in good agreement with the published data (Sharma and Kar, 2015, Kakaei, 2015). In the Figure 3.23b, the simulated X-ray diffraction pattern for Pt/CuPc-CNT/ITO matched well with the measured one (ICSD, card no. 98-064-9490).

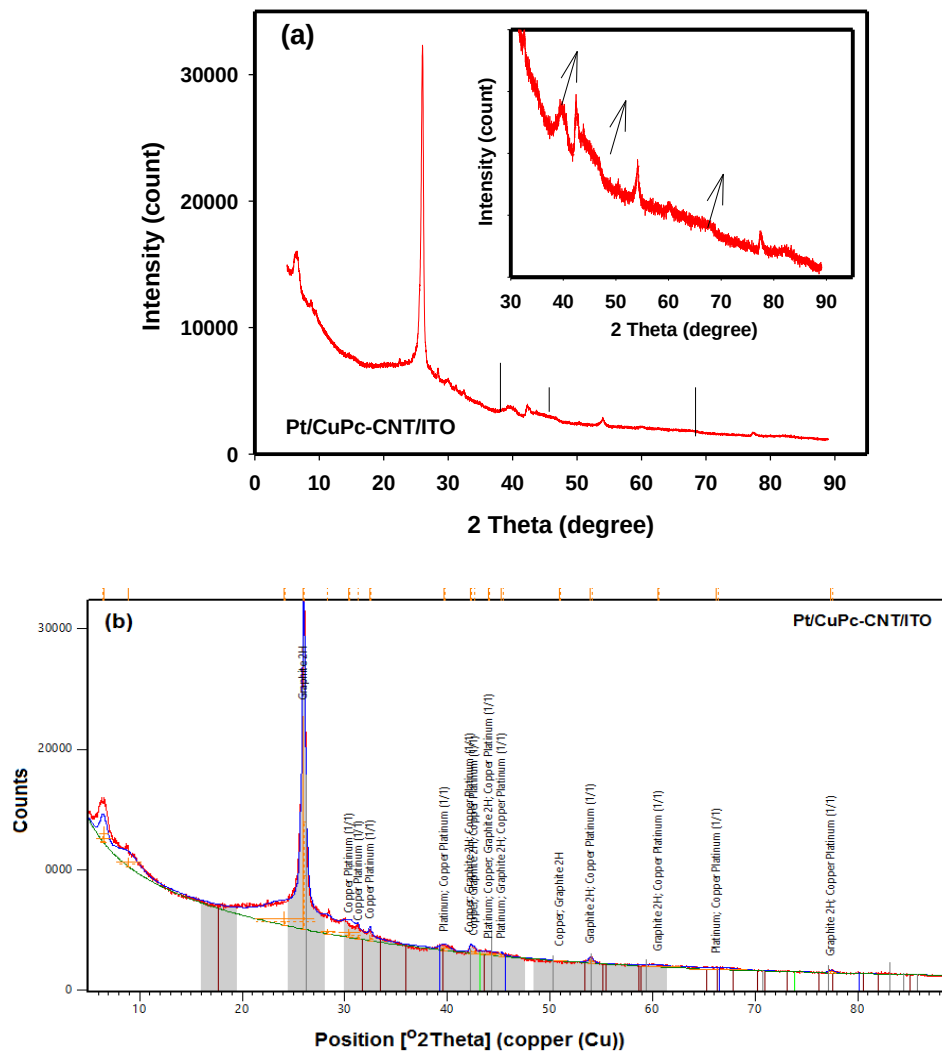


Figure 3.23 a) XRD pattern and b) matching XRD pattern of the Pt/CuPc-CNT/ITO.

Figure 3.24 shows the results of electrochemical impedance spectroscopy (EIS) on bare GCE, CNT/GCE, CuPc/GCE, CuPc-CNT/GCE and Pt/CuPc-CNT/GCE in the presence of 5 mM $K_3[Fe(CN)_6]/K_4[Fe(CN)_6]$ containing 0.1 M KCl solution at varying frequencies from 0.05 to 50 000 Hz. The impedance circuit contains the solution resistance R_s , Warburg impedance (W), constant phase element (CPE or Q), and the charge transfer resistance R_{ct} . R_{ct} value was obtained from a semicircle diameter at high frequencies that were related with dielectric and insulating characteristics of the electrode/electrolyte interface (Mugadza and Nyokong, 2011). In Nyquist diagrams, a straight line with a slope of nearly 45° related to mass transport process via electroactive compound diffusion. It clearly seen in Figure 3.24 that bare glassy carbon electrode shows a large charge transfer resistance of about 548 Ω . The R_{ct} value for the bare GCE is higher than the R_{ct} values obtained for other modified electrodes. This low R_{ct} value (1.7 Ω) for the Pt/CuPc-CNT/GCE implies the relatively fast charge transfer compared to the CNT/GCE (270 Ω), CuPc/GCE (62.3 Ω), CuPc-CNT/GCE (15.8 Ω), and bare GCE (548 Ω). These results suggested that the synergistic effect of CNTs with Pcs and Pt nano particles effectively increased the conductivity of the electrode and promoted the electron transfer rate.

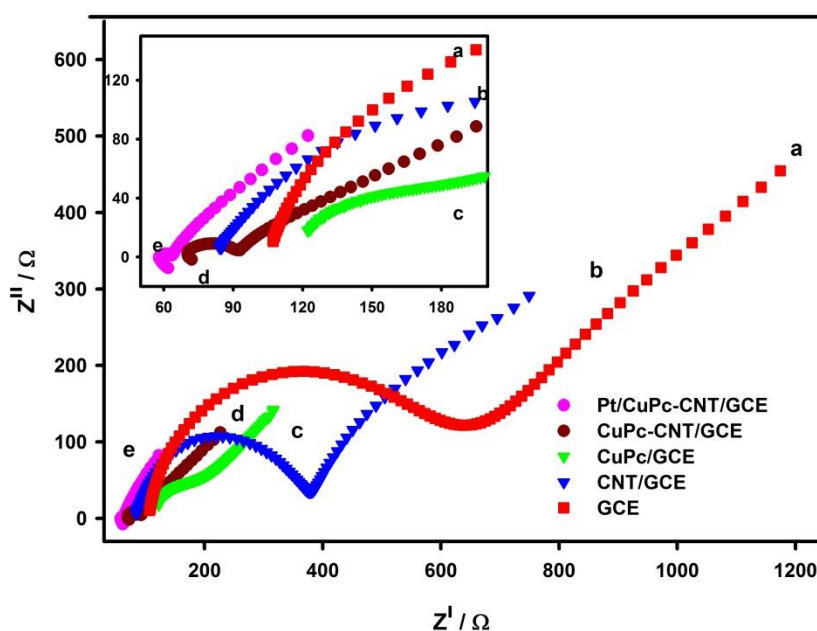


Figure 3.24 Electrochemical impedance spectrum of a) GCE, b) CNT/GCE, c) CuPc/GCE, d) CuPc-CNT/GCE, e) Pt/CuPc-CNT/GCE in the presence of 5 mM $K_3[Fe(CN)_6]/K_4[Fe(CN)_6]$ containing 0.1 M KCl solution with a frequency range of 0.05 to 50000 Hz.

3.2 Electrochemical Oxidation of Methanol at Modified Electrodes

Electrochemical oxidation of methanol has attracted great interest especially due to its potential in fuel cell applications. Unlike the supply and storage problems of hydrogen, methanol is a second best choice for fuel cells due to its high energy content, easy production, safely transport and storage property which directly fed to the direct methanol fuel cell (DMFC) system as a fuel. Although methanol has an advantages compared with the hydrogen, some difficulties can be overcome for fuel cell applications. Such as formation of various intermediates during methanol oxidation, which resulted the need of more catalytically active surfaces that generally obtained with metal nanoparticles incorporation to electrode surface (Jusys, Z. and Behm, R. J., 2001; Vielstich, W., 2003; Tapan et al., 2004; Li, L. and Xing, Y., 2009).

In this thesis, methanol oxidation was studied by various metal nanoparticles modified phthalocyanine-carbon nanotube composite GCE which described in the next section.

3.2.1 Preparation of metal nanoparticles modified CuPc-CNT composite electrodes

To improve the catalytic effect of copper phthalocyanine-carbon nanotube composite electrode, Au, Cu, Pt, Ag, Ni, Pd, Co and Ru nanoparticles were formed on the electrode surfaces by cyclic voltammetry technique.

Electrochemical preparation of Au, Cu, Pt, Ag, Ni and Pd nanoparticles were described in section 3.1.1 in detailed before. The previously explained Figure 3.1 and 3.2 shows the redox peaks related to the formation of metal nanoparticles on the composite electrode surfaces. Methanol oxidation reaction was investigated also by CuPc-CNT/GC electrodes, which Co and Ru nanoparticles modified on their surfaces.

Figure 3.25a exhibits the cyclic voltammograms for ruthenium nanoparticles formation in the potential scan range of -800 mV to +200 mV. An increasing reduction peak at about -500 mV and oxidation peak nearly -100 mV were observed for ruthenium oxide type nanoparticle preparation that was in accordance with the published literatures. (Gorski et al., 1997; Hong Yu-H. and Tsai, Yu-C., 2009)

Cobalt nanoparticles were formed on the composite electrode surface by the repetitive cyclic voltammograms in the potential range between -1200 and +500 mV which shown in Figure 3.25b. Three small reduction peaks at 0 mV, -600 mV and -900 mV and oxidation peak at +300 mV were observed that related to redox behavior of cobalt nanoparticle formation (Long et al., 2015). The effect of metal nanoparticles modified electrodes towards methanol oxidation were compared with each other and nonmetallic surfaces in the following voltammograms Figure 3.27 – Figure 3.30.

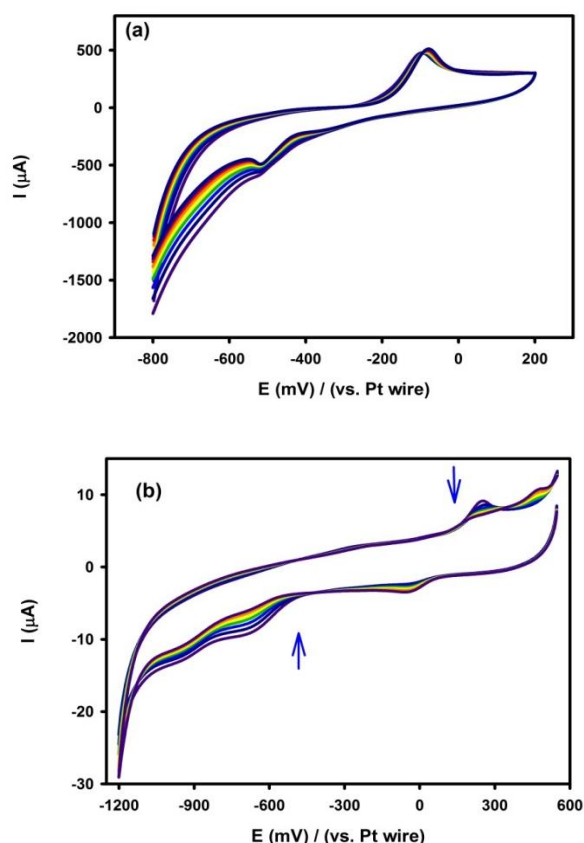


Figure 3.25 Consecutive cyclic voltammograms of a) Ru and b) Co nanoparticles on a CuPc-CNT/GCE in 1 mM metal ion containing acidic solutions.

In addition bimetallic nanoparticles modified electrode surfaces studied for methanol oxidation which prepared with different procedures. For instance, different steps that explained in the following sentences can prepare Au and Pt bimetallic nanoparticles. Pt nanoparticles formed by electrochemical technique using cyclic voltammetry for 5 repetitive cycles. Then Pt/CuPc-CNT/GCE rinsed with water and dipped in Au solution and again 5 repetitive potential cycles were applied to form Au nanoparticles. Resulting electrode was denoted as Au/Pt/CuPc-CNT/GCE. Pt/Au/CuPc-CNT/GCE was prepared by following the opposite of that procedure. Another route to make bimetallic nanoparticle

formation is using the mixture solution of both Au and Pt presence together. The CuPc-CNT/GCE was immersed in the 3 mM Au and Pt containing 0.1 M HCl and 10 repetitive potential cycles were applied by CV technique.

3.2.2 Electrochemical behavior of methanol

Methanol oxidation on CuPc and CNT composite electrodes

To obtain the reliable comparison data in order to exhibit the real effect of metal nanoparticles modified CuPc-CNT composite electrodes, methanol oxidation on bare GCE, CNT/GCE and CuPc-CNT/GCE were need to be studied. The electrochemical behavior of bare GCE, CuPc/GCE, CNT/GCE, CuPc-CNT/GCE was studied in the absence and presence of 50 mM methanol in 1 M NaOH. Figure 3.26 depicts that there was no electrocatalytic oxidation takes place for methanol at bare and modified electrodes in the potential range between -900 mV and 400 mV.

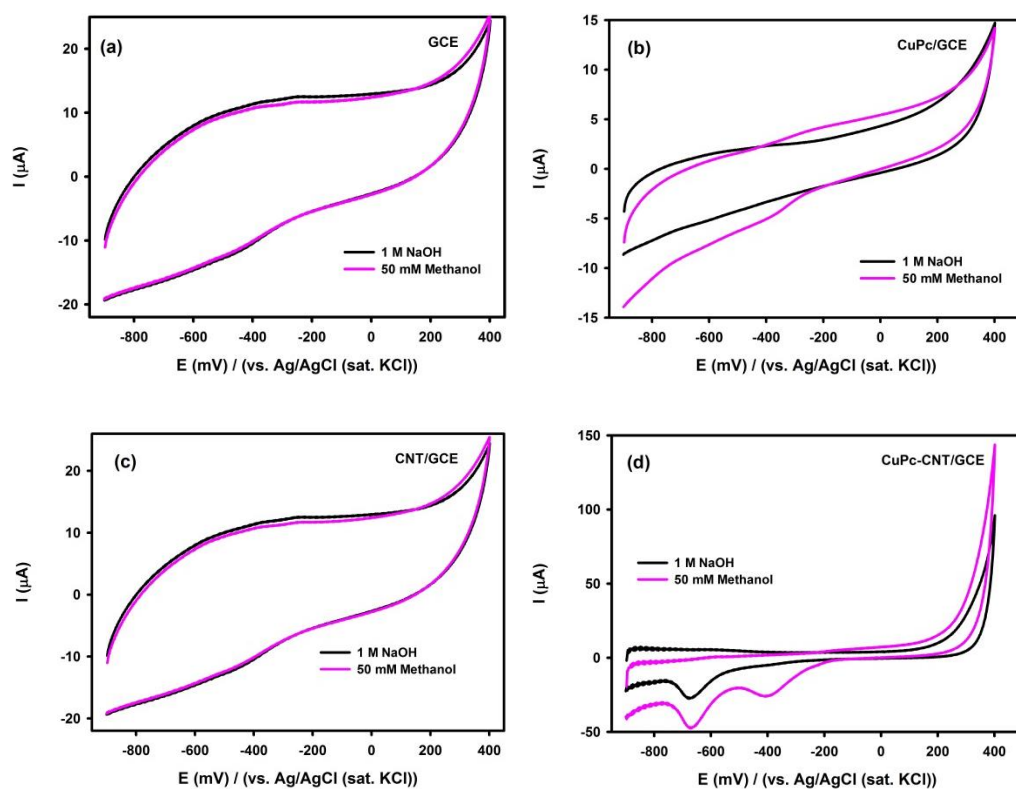


Figure 3.26 Cyclic voltammetric responses of a) Bare GC, b) CuPc/GC, c) CNT/GC, d) CuPc-CNT/GC electrodes towards methanol in 1 M NaOH.

Methanol oxidation on metal nano particles modified CuPc-CNT composite electrodes

It is understood from the previous study that bare GCE, CuPc and CNT based composite electrodes without metal nano particles were inappropriate modifiers for methanol oxidation in alkaline solution. In order to improve the methanol oxidation signals, CuPc-CNT/GCE was modified with various nano particles (Ag, Co, Cu, Ni, Pd, Ru, Au, Pt). Figure 3.27 and 3.28 show the response of metal nano particles modified Pc-CNT/GC electrodes in the absence and presence of 50 mM methanol containing NaOH solution in the potential range of -900 mV to +400 mV with a scan rate of 50 mV.s^{-1} .

Figure 3.27 shows the behavior of Ag, Co, Cu, Ni, Pd, Ru nanoparticles modified CuPc-CNT/GC composite electrodes for methanol oxidation in alkaline media. There was no electrocatalytic oxidation takes place for methanol at Co, Cu, Ni, Ru and Pd nanoparticles modified electrodes. The Ag nano particles modified CuPc-CNT/GCE shows poor activity to methanol oxidation. The small and broad oxidation peak was observed at -100 mV for Ag/CuPc-CNT/GCE while its not noteworthy to take into consideration as a modifier. In addition, gold and platinum metals containing electrodes have been shown electrocatalytic activity towards methanol oxidation reaction and as fuel in fuel cell applications (Koçak et al., 2011; Lu et al., 2015; Ma et al., 2013; Wang et al., 2015). Therefore, gold and platinum were prescinding from other metals and studies were shown in Figure 3.28. While Pt nanoparticles modified CuPc-CNT/GCE shows promising results as expected, only a small increase occurred at high potentials for Au/CuPc-CNT/GCE without peak form.

Table 3.3 was comprised by the results obtained from Figure3.28b that shows the peak potential and current values of increasing concentrations (12, 25, 50, 100 mM) of methanol oxidation at Pt/CuPc-CNT/GCE. The catalytic activity of methanol oxidation was increased with Pt nanoparticles deposition on the CuPc-CNT/GCE while it needs more improvement in terms of peak current and linearity with the concentration increase.

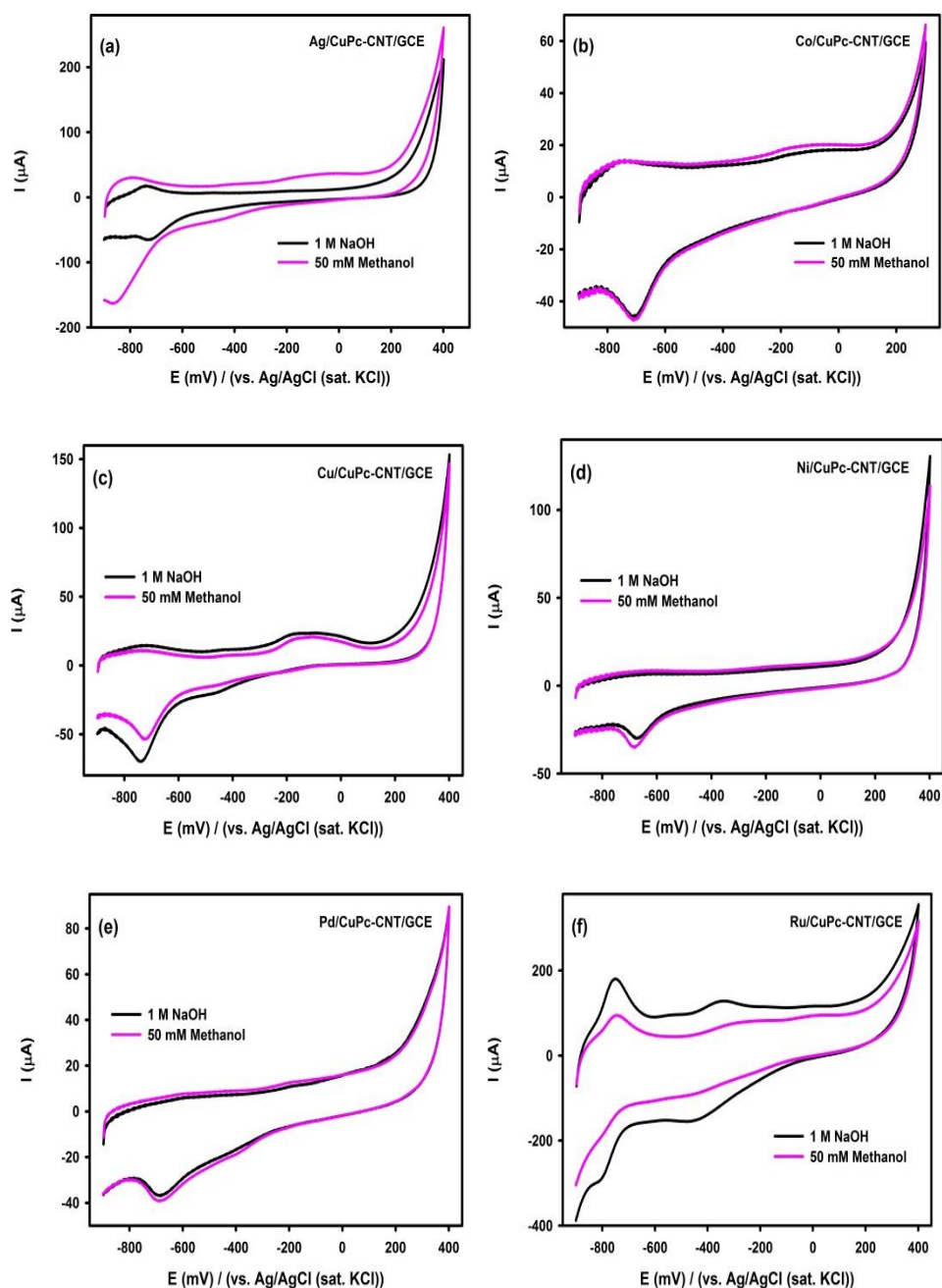


Figure 3.27 CVs of different metal nano particles modified CuPc-CNT/GC electrodes towards 50 mM methanol oxidation in alkaline solution with 50 mV/s. a) Ag, b) Co, c) Cu, d) Ni, e) Pd, f) Ru nanoparticles. Black colored plots are background response of the electrodes.

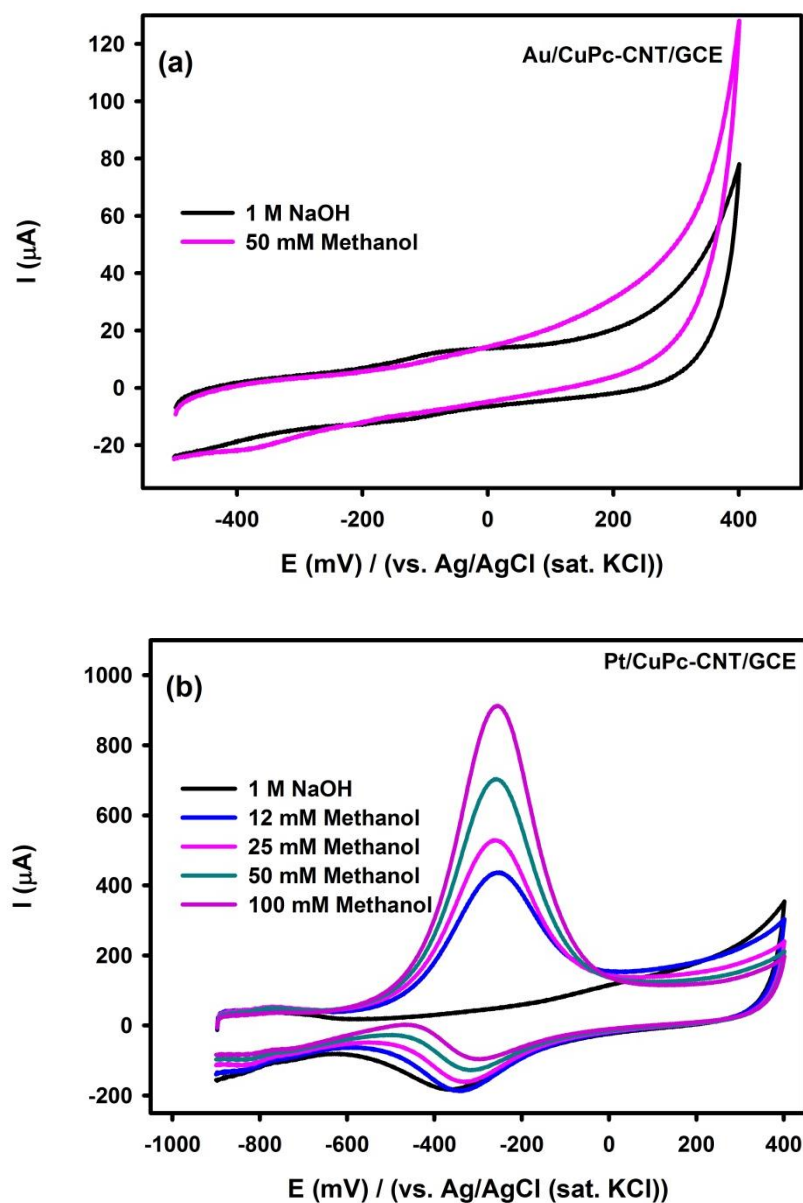


Figure 3.28 CVs of methanol oxidation at a) Au/CuPc-CNT/GCE and b) Pt/CuPc-CNT/GCE in 1 M NaOH solution.

Table 3.3. Potential and current values of methanol oxidation on Pt/CuPc-CNT/GCE at various concentrations.

Concentration (mM)	Potential (mV)	Current (μ A)
12	-253	335
25	-257	552
50	-252	673
100	-252	832

Methanol oxidation at bimetallic Pd-metal(M) nano particles modified CuPc-CNT composite electrodes

The binary or ternary composition of metals represents the higher electrocatalytic activity than the single forms, which explained as synergistic effect of metals (Mao et al., 2015; Jurzinsky et al., 2015; Lee et al., 2015). Pd-based modifiers attracted a great attention due to their even better behavior in alkaline solution compared with Pt containing catalysts (Bianchini et al., 2009; Cui and Yu, 2013; Yin et al., 2013). This knowledge was form an opinion to investigate the electrochemical behavior of methanol on Pd containing bimetallic nanoparticles modified CuPc-CNT/GCE.

Figure 3.29 shows the behavior of metal nano particles which prepared by combination of various metals (Au, Co, Cu, Ni) with palladium in the absence and presence of 0.5 and 1.0 M methanol containing NaOH. Indistinct difference obtained in the absece and presence of methanol on Pd-Co, Pd-Cu and Pd-Ni bimetallic nanoparticles modified CuPc-CNT/GCE while relatively high results obtained at Pd-Au modified CuPc-CNT/GCE. Methanol oxidation peak current was increase by the increasing of the methanol concentration, still the low current values was less preferred for fuel cell applications.

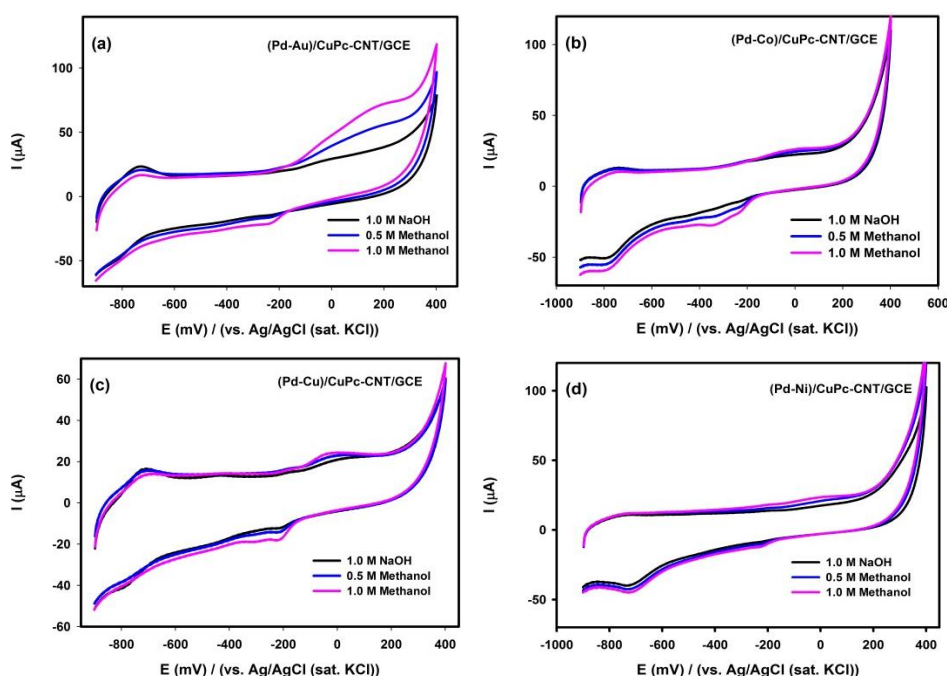


Figure 3.29 CVs of different bimetallic a) Pd-Au, b) Pd-Co, c) Pd-Cu, d) Pd-Ni nano particles modified CuPc-CNT/GC electrodes towards methanol oxidation in alkaline solution. Black colored plots are background response of electrodes.

Methanol oxidation at bimetallic Au and Pt nano particles modified CuPc-CNT composite electrodes

Enormous efforts have been go at to escalate the catalytic efficiency of electrodes towards methanol oxidation. As it mentioned before Pt nanoparticles have good activity towards methanol oxidation. The most common strategy to improve the catalytic activity of Pt-based catalysts is to combine one or two metals with platinum (Serrà et al., 2015; Zhang et al., 2015).

According to this knowledge, bimetallic gold and platinum nanoparticles were prepared on CuPc-CNT/GCE. Figure 3.30 shows the voltammetric behavior of Au/Pt/CuPc-CNT/GCE, Pt/Au/CuPc-CNT/GCE and (Au-Pt)/CuPc-CNT/GCE in the absence and presence of 12, 25, 50, 100 mM methanol.

The different abbreviated modified electrodes were explained in detailed in Section 3.2.1. Oxidation peak current were increase by the increment of concentration on all electrodes. Comparison of the potential and current values for all modified electrodes was listed in the Table 3.4. While the oxidation peak slightly shifted to positive values, (Au-Pt)/CuPc-CNT/GCE showed high current response compared to the others. The methanol oxidation peak current of (Au-Pt)/CuPc-CNT/GCE was 3 times higher than the Pt/Au/CuPc-CNT/GCE and 46 times higher than the Au/Pt/CuPc-CNT/GCE. Therefore, (Au-Pt)/CuPc-CNT/GCE was chosen as a best working electrode for further studies due to the practical preparation and higher current value for methanol oxidation.

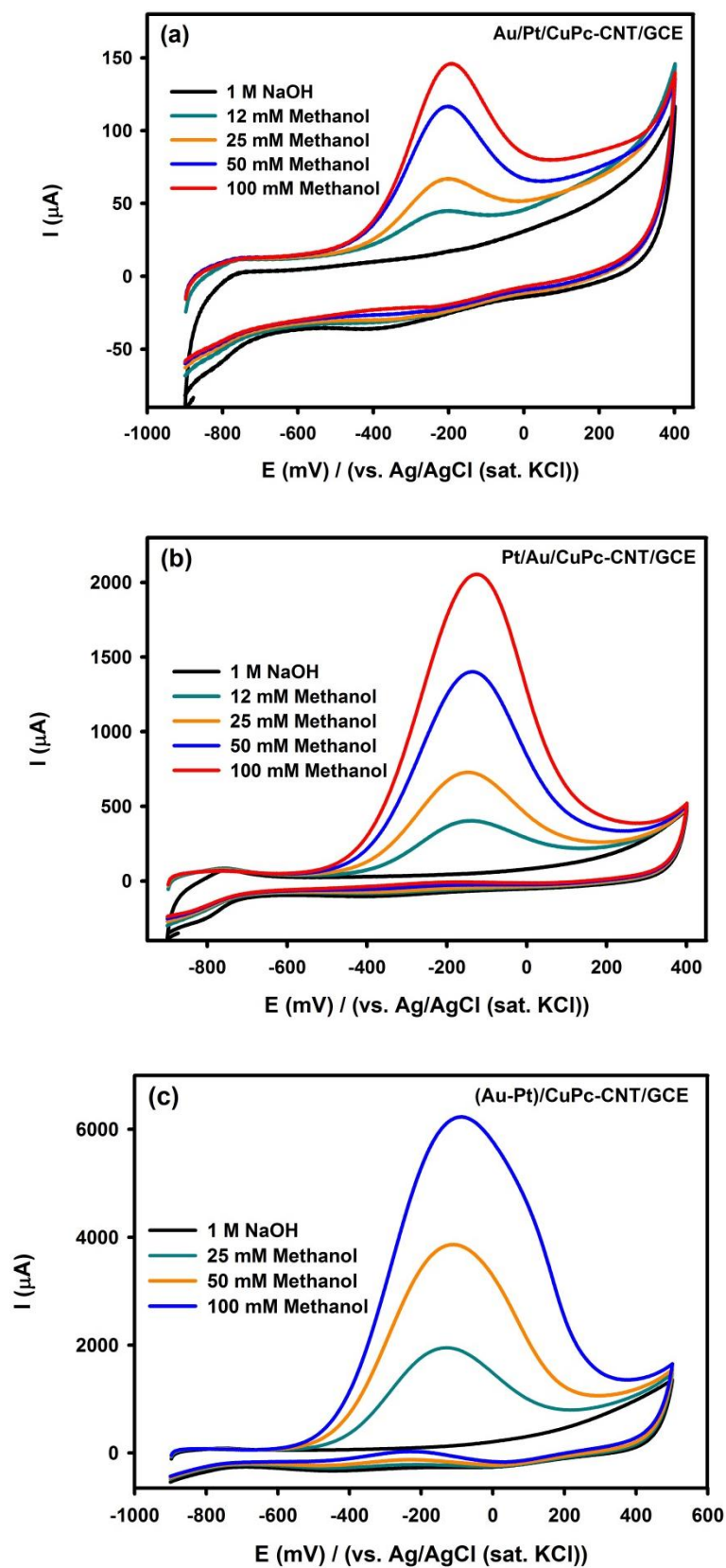


Figure 3.30 CV behavior of a) Au/Pt/CuPc-CNT/GCE, b) Pt/Au/CuPc-CNT/GCE and (Au-Pt)/CuPc-CNT/GCE towards increasing methanol concentrations in 1 M NaOH solution.

Table 3.4. Potential and current values for methanol oxidation at Au and Pt bimetallic nanoparticles modified CuPc-CNT/GCE.

Concentration	Au/Pt/CuPc-CNT/GCE		Pt/Au/CuPc-CNT/GCE		(Au-Pt)/CuPc-CNT/GCE	
(M)	Pot.(mV)	Current	Pot.(mV)	Current	Pot.(mV)	Current
0.025	-221	29.85	-150	571	-170	1492
0.05	-214	72.4	-140	1205	-143	3277
0.1	-199	96.81	-130	1830	-118	5499

Figure 3.31 shows the comparison of Au, Pt and their bimetallic combinations as a modifier on CuPc-CNT/GCE for 25 mM methanol oxidation in 1 M NaOH solution with 50 mV.s^{-1} scan rate. The potential and current values of related electrodes were shown in Table 3.5 which presents the electrode activity. The faintest results obtained at Au/CuPc-CNT/GCE not only for poor peak current but also for most positive peak potential value. Pt modification before Au deposition on the electrode surface (Au/Pt/CuPc-CNT/GCE), bring about 155 mV peak shift to more positive values with a peak escalation. Mono metallic platinum nanoparticle subsistence on CuPc-CNT/GCE shows behave more active than the Au/Pt/CuPc-CNT/GCE in terms of peak current and peak potential. The deposition of Pt particles on Au-CuPc-CNT/GCE (Pt/Au/CuPc-CNT/GCE) was offered higher peak current while the peak potential slightly shifted to more positive values compared to the Pt/CuPc-CNT/GCE. Finally, the simultaneous deposition of Au and Pt nanoparticles from the same solution on the CuPc-CNT/GCE shows the best current value among all others. The methanol oxidation peak current of (Au-Pt)/CuPc-CNT/GCE was about 3 times higher than the Pt/CuPc-CNT/GCE and 330 times higher than the Au/CuPc-CNT/GCE.

Table 3.5 Potential and current values of modified electrodes towards 25 mM methanol oxidation.

Electrode	Potential (mV)	Current (μA)
Au/CuPc-CNT/GCE	-55	4.4
Au/Pt/CuPc-CNT/GCE	-221	33.3
Pt/CuPc-CNT/GCE	-265	436
Pt/Au/CuPc-CNT/GCE	-150	571
(Au-Pt)/CuPc-CNT/GCE	-170	1492

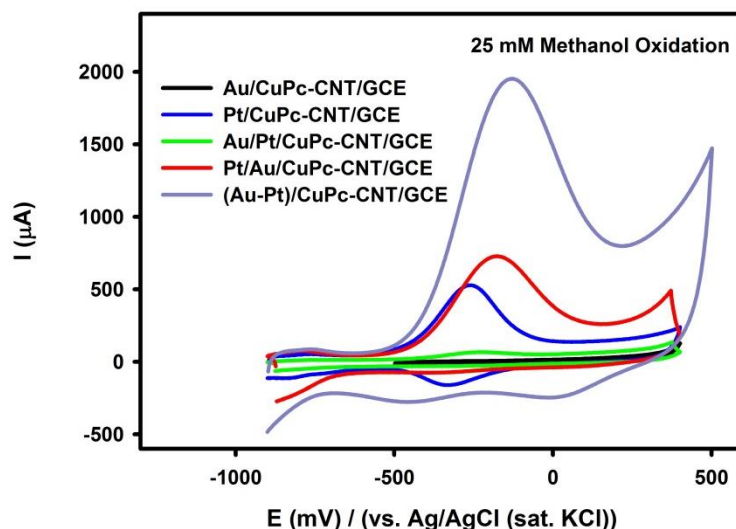


Figure 3.31 Comparative CV scans of Au, Pt and Au-Pt bimetallic nanoparticles modified CuPc-CNT electrodes towards 25 mM Methanol oxidation in alkaline solution.

Optimization of Au-Pt concentration of composite electrode

Enormous efforts have been go at to increase the efficiency of Pt catalysts such as synthesis type to control the size and composition of Pt catalysts. In this respect, bimetallic Au-Pt modified surfaces prepared by variate the deposition cycle number, Au concentration, Pt concentration and mixture concentration.

Figure 3.32 shows the effect of variation of Au-Pt mixture concentration on the 25 mM methanol oxidation in the potential range of -900 mV to +400 mV. The background currents were increase by the increment of mixture concentration that can be ascribed to the inceasing thickness of electrode surface (Figure 3.32b). While poor response obtained at 0.5 mM solution concentration, it increase by the increment of the molarity. Maximum current value and most negative peak potential was obtained in condition of 2 mM Au-Pt modification on CuPc-CNT/GCE. The current was decrease and peak form was wider at 3 mM Au-Pt deposited composite electrode as compared to the 2 mM. This decrease can be attributed to the bulk like surface characterization of the electrode at higher concentrations. The effect of concentration was clearly seen in Table 3.6 that 2mM was chosen as an optimum mixture concentration for further studies.

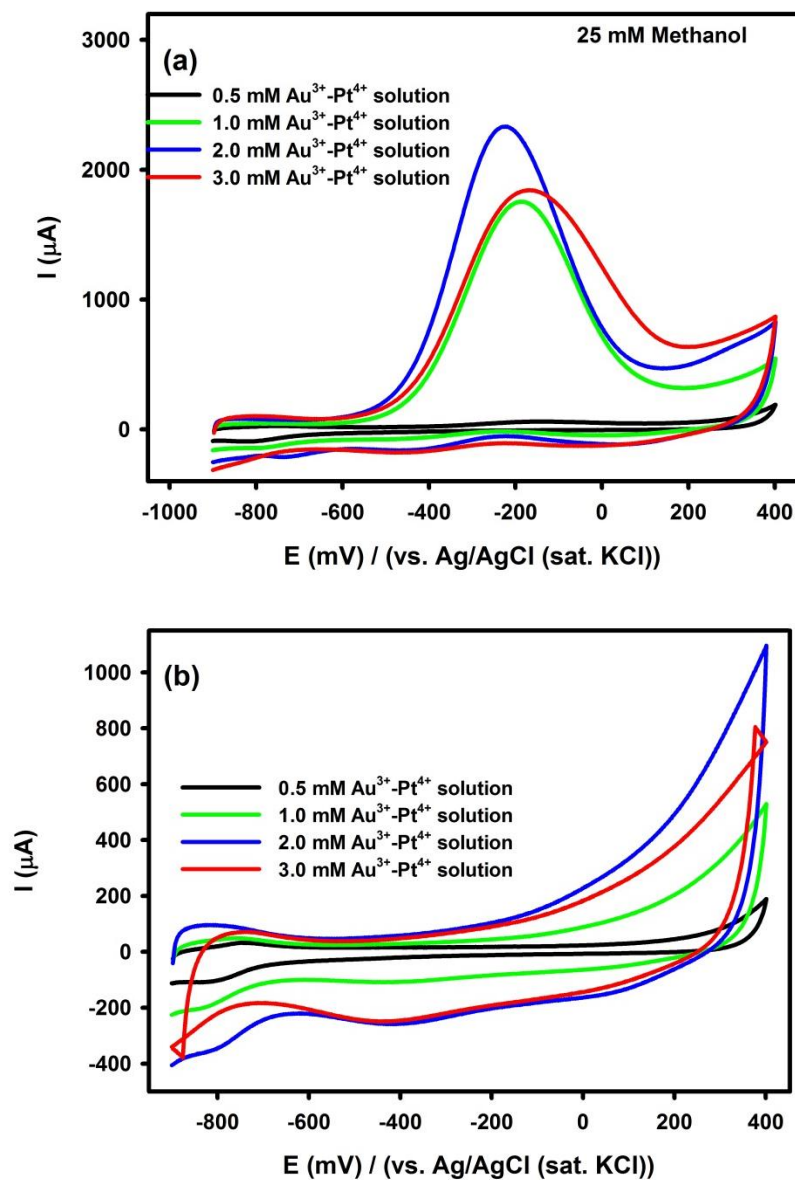


Figure 3.32 Concentration effect of bimetallic $\text{Au}^{3+}\text{-Pt}^{4+}$ modification solution on 25 mM methanol oxidation in 1 M NaOH solution. Scan rate 50 mV.s^{-1} .

Table 3.6 25 mM methanol oxidation peak current and potential at $(\text{Au-Pt})(\text{XmM})/\text{CuPc-CNT/GCE}$.

Concentration of $\text{Au}^{3+}\text{-Pt}^{4+}$ bimetallic solution (mM)	E (mV)	i (μA)
0.5	-167	25.97
1.0	-187	1567
2.0	-226	2542
3.0	-170	1484

Optimization of Au concentration of bimetallic solution for methanol oxidation at Au(XmM)-Pt(2mM)/CuPc-CNT/GCE

Figure 3.33 demonstrates the cyclic voltammograms of Au(XmM)-Pt(2mM)/CuPc-CNT/GCE in the presence and absence of 25 mM methanol in 1 M NaOH. New Au-Pt mixtures were prepared which contain same amount of Pt^{4+} (2 mM) and various concentrations of Au^{3+} (0.1, 1.0, 2.0, 3.0 mM) in the same solution.

The background currents were represented in Figure 3.33b that a reduction peak at about +350 observed for 0.1 mM Au^{3+} and 2.0 mM Pt^{4+} containing mixture. This peak can be ascribed as hydrogen adsorption/desorption peak of platinum which was decrease by the increment of Au^{3+} concentration that cause the decrease of Pt^{4+} ratio on the electrode surface as expexted (Plana and Dryfe, 2011).

The peak characteristics, in other word peak currents and potentials were shown in Table 3.7. 2 mM Au^{3+} and 2 mM Pt^{4+} containing HCl solution was chosen as an optimum deposition solution for methanol oxidation.

Table 3.7 The values of peak current and potential of 25 mM methaol oxidation at Au(XmM)-Pt(2mM)/CuPc-CNT/GCE.

<i>Au(XmM)-Pt(2mM)/CuPc-CNT/GCE</i>	E (mV)	I (μA)
0.1	-238	960
1.0	-223	1489
2.0	-226	2542
3.0	-155	580

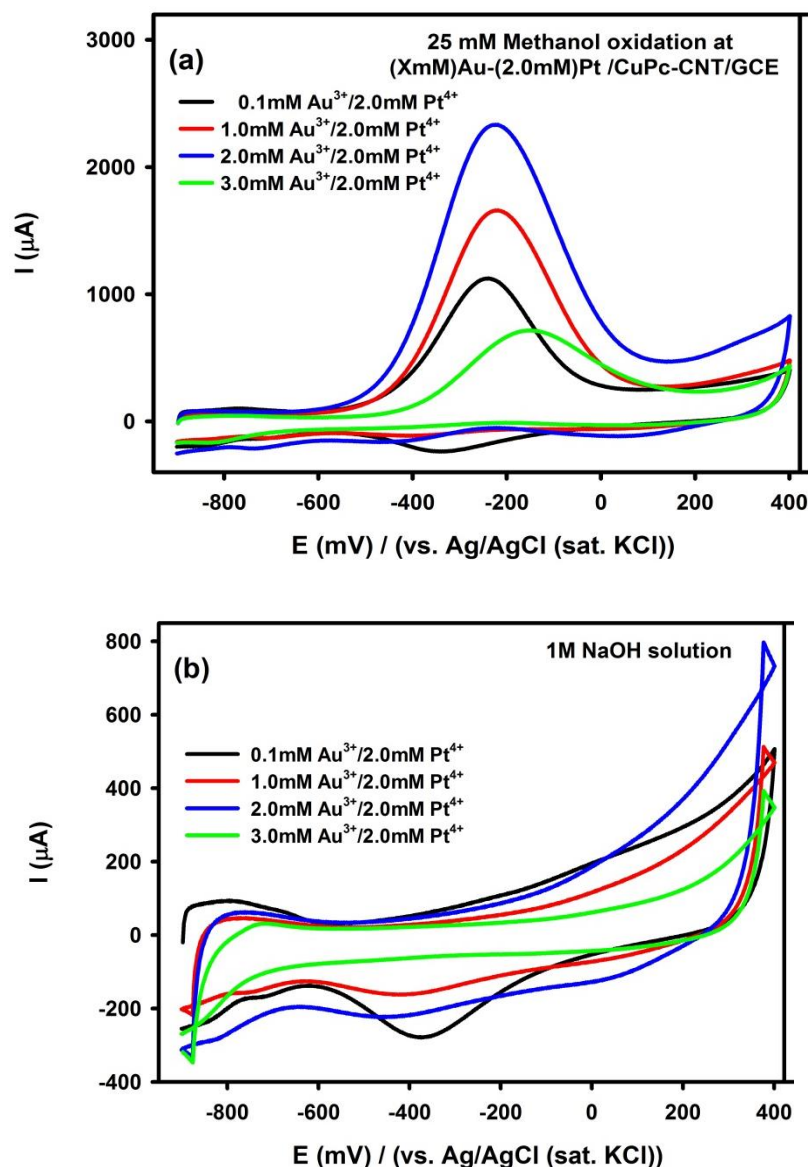


Figure 3.33 Effect of Au^{3+} concentration in the bimetallic mixture solution on methanol oxidation at (Au-Pt)/CuPc-CNT/GCE. CVs of electrodes a) with and b) without 25 mM methanol.

Optimization of cycle number for metal nanoparticles preparation

To optimize the Au-Pt nanoparticles deposition on the CuPc-CNT/GCE surface, cycle number of deposition varies from 5 to 30. The amount, the size even the shape of the deposited Au-Pt nanoparticles can be controlled by changing the cyclic number in electrodeposition process which really affect the activity of the electrode. Figure 3.34 shows the effect of cycle number (5, 10, 15, 20, 30) on the methanol oxidation. As can be clearly seen from the Table 3.8 that highest peak current obtained at 15 cycles of metal deposited CuPc-CNT/GC electrode.

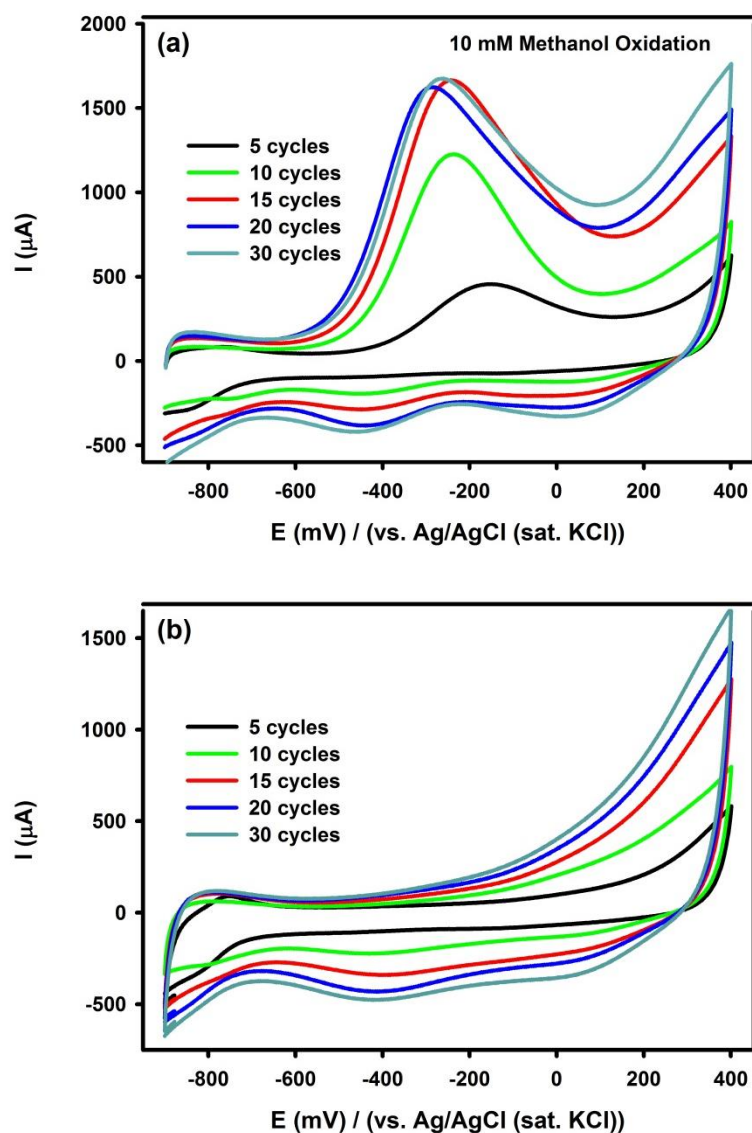


Figure 3.34 Effect bimetallic mixture cycle number on methanol oxidation at (Au-Pt)/CuPc-CNT/GCE. CVs of electrodes a) with and b) without 10 mM methanol.

Table 3.8 Peak current and peak potential values of methanol oxidation for different nanoparticles formation cycle number.

Nanoparticle formation cycle number	E (mV)	i (μA)
5	-165	295
10	-226	991
15	-253	1201
20	-270	1189
30	-272	1106

Scan rate study of Methanol on (Au-Pt)/CuPc-CNT/GCE

The relationship between peak current-potential and scan rate usually provide information about electrochemical mechanism. The effect of scan rate on the anodic peak current of methanol was investigated in 1.0 M NaOH at (Au-Pt)/CuPc-CNT/GCE using cyclic voltammetry. These cyclic voltammograms were shown in Figure 3.35. The graphs were obtained from peak current with various scan rate. The results indicated that the i_{pa} was not linearly changed with the square root of scan rate over the range of 5–150 mV.

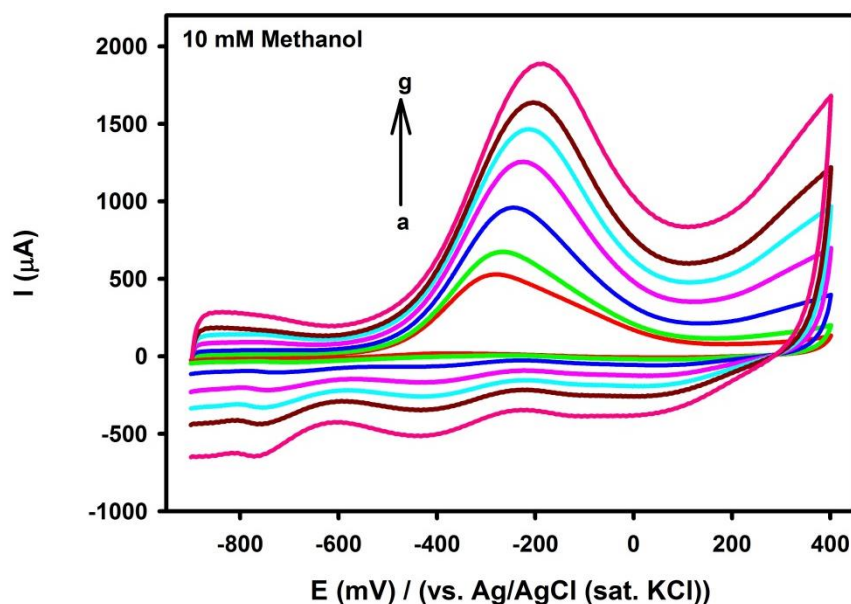


Figure 3.35 CVs for the oxidation of methanol at (Au-Pt)/CuPc-CNT/GCE. Scan rates: 5–150 mV.s⁻¹.

Figure 3.36 was represented the datas that obtained from the voltammograms of Figure 3.35 for methanol oxidation. The affiliation between the square root of scan rate and peak currents was in linear with an equation of $i_{pa} (\mu A) = 86.231v^{1/2} ((mV.s^{-1})^{1/2}) + 349.19$, $R^2 = 0.9902$ that shown in figure 3.36a pointed the diffusion controlled process at (Au-Pt)/CuPc-CNT/GC electrode. The oxidation peak shifts to more positive potentials with the increasing logarithm of scan rate values that indicate the irreversible electrode process (Figure 3.36b).

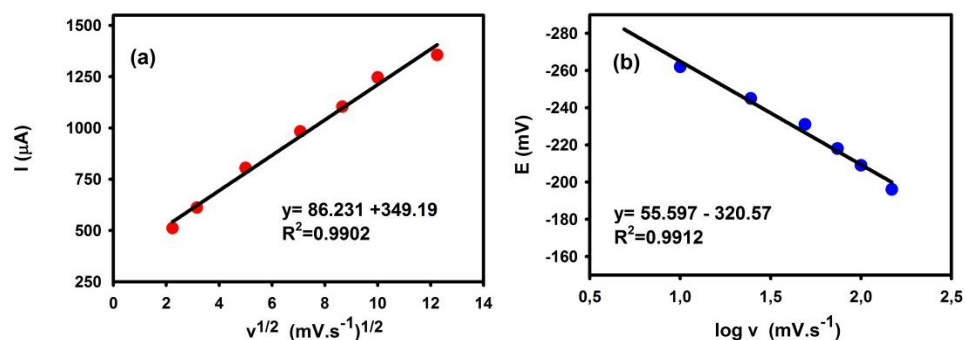


Figure 3.36 Dependence of a) peak current to square root of scan rate and b) logarithm of scan rate to peak potential for methanol oxidation on (Au-Pt)/CuPc-CNT/GCE.

Chronoamperometric study of methanol oxidation at (Au-Pt)/CuPc-CNT/GCE

Chronoamperometric (CA) measurements, under long-term operation condition, were used in order to investigate the (Au-Pt)/CuPc-CNT/GCE performance for methanol oxidation. was carried out by The applied potentials in CA were chosen inside the methanol oxidation potential region (-170, -253 and -275 mV vs. Ag/AgCl(Sat.KCl)) for 1200 s.

Figure 3.37 shows the chronoamperometric curves for the (Au-Pt)/CuPc-CNT/GCE in 0.05M CH₃OH/1M NaOH at different potential steps. In all CA curves the currents dropped rapidly at first, which can be explained by fast surface poisoning by adsorbed intermediates such as; CO, COOH and CHO (Zhou, et al., 2013; Ali et al., 2015), and then became relatively stable. The initial high current corresponds mainly to double layer charging. As shown in Figure 3.37, -253 mV step potential is the most suitable and stable as compared to the other potentials in terms of plateau current.

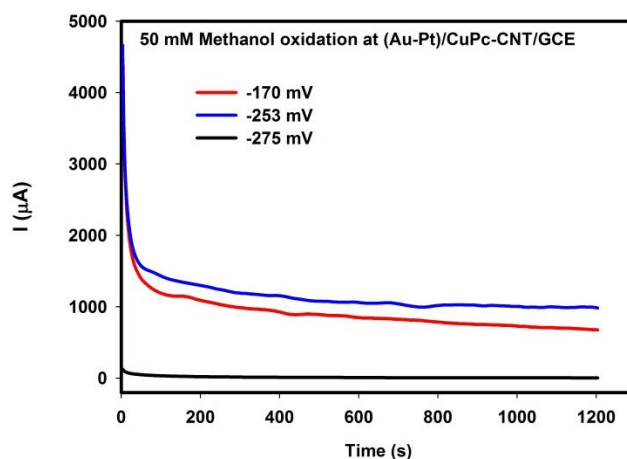


Figure 3.37 Chronoamperometric study of 50 mM methanol oxidation at (Au-Pt)/CuPc-CNT/GCE with various potentials.

Thermal gravimetric analysis of (Au-Pt)/CuPc-CNT/GCE

The thermal stability of CuPc-CNT and (Au-Pt)/CuPc-CNT composites were investigated by TGA under a nitrogen protection. Figure 3.38 demonstrates the thermogram of CuPc-CNT and (Au-Pt)/CuPc-CNT. While the thermogram of the CuPc-CNT shows a weight loss of 37.1% at 1000 °C, (Au-Pt)/CuPc-CNT thermogram depicts only 11.2% weight loss at same temperature. According to the results bimetallic nanoparticles deposition highly improve the thermal stability of the composite, which is crucial parameter for the catalyst material in fuel cells (Zhong et al., 2013b).

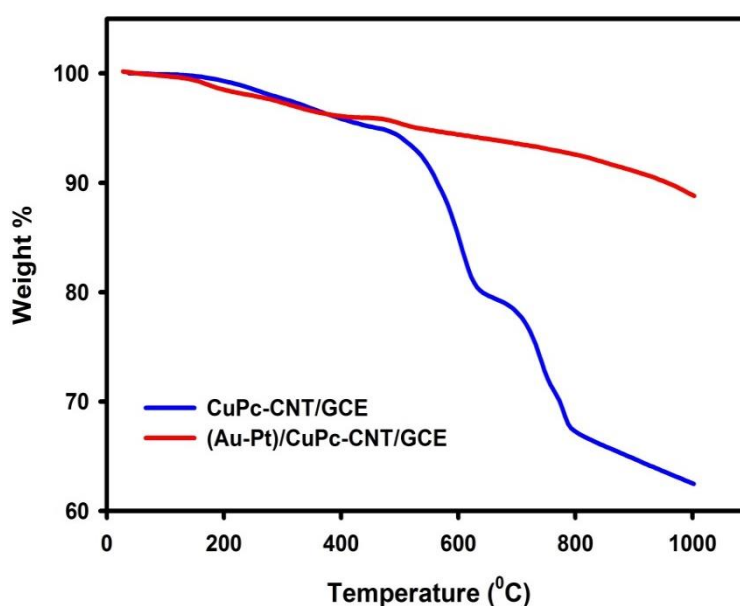


Figure 3.38 TGA curves of CuPc-CNT and (Au-Pt)/CuPc-CNT under the protection of N₂.

3.2.3 Characterization of modified electrodes

(Au-Pt)/CuPc-CNT/GC electrode was successfully prepared and optimized in previous section that was a candidate for an efficient anode electrode surface for fuel cell applications. In order to identify the electrode surface characteristic and prove the existence of modifiers; SEM, EDX, TEM, XRD and EIS techniques were used.

Figure 3.39 shows the scanning electron microscopy (SEM) images of CuPc-CNT/GCE, Pt/CuPc-CNT/GCE, Au/CuPc-CNT/GCE, Pt/Au/CuPc-CNT/GCE and (Au-Pt)/CuPc-CNT/GCE.

As shown in Figure 3.39a, distribution of tubular forms represents the acid-treated CNTs and cotton like areas on electrode surface related with the CuPc existence. Figure 3.39a shows exactly the expected image that was compatible with the individual images of CNT and CuPc (shown in previous section in Figure 3.17).

The scanning electron microscopy images of Pt/CuPc–CNT/GCE in Figure 3.39b displays many bright dots especially on the sidewalls of CNTs due to the deposition of Pt nanoparticles on the CuPc–CNT surface. Pt nanoparticles calculated on the surface of the composite electrode with a diameter ranging between 100 and 150 nm.

Figure 3.39c and 3.39d represent the detailed SEM images of Au/CuPc–CNT/GCE with 1000x and 10000x magnifications. As its seen, small bright homogeneous dots were related with the Au nanoparticles which distribute all over the CuPc–CNT/GCE surface. As compared to the Pt nanoparticles, gold nanoparticles sparcely deposited on the surface with smaller diameters.

Figure 3.39e represents the sequentially deposited Au and Pt nanoparticles in order to show the distribution difference of deposition from the mixture and individual metal containing solutions. Figure 3.39e shows different image as compared to the single Au (Figure 3.39d) and Pt (Figure 3.39b) deposition. Clannish parts in the image let us to think that platinum nanoparticles prefer to deposite on Au nanoparticles as well as individual deposition on the CNT and CuPc surface.

Pt nanoparticles appeared brighter than Au particles in the backscattered image due to a higher molecular weight of Pt (Figure 3.39f). Comparison between the Figure 3.39e and f, bimetallic nanoparticles deposition revealed an obvious change in distribution of particle as well as their size on the CuPc–CNT surface. As we suppose, coexistence of Au and Pt in same solution catalysis the deposition of eachother which seen in the SEM image clearly. Both Au and Pt nanoparticles deposited all over the sidewalls CNTs as well as CuPcs which also formed some aggregated parts supposed as Pt act as a core to deposition of Au nanoparticles.

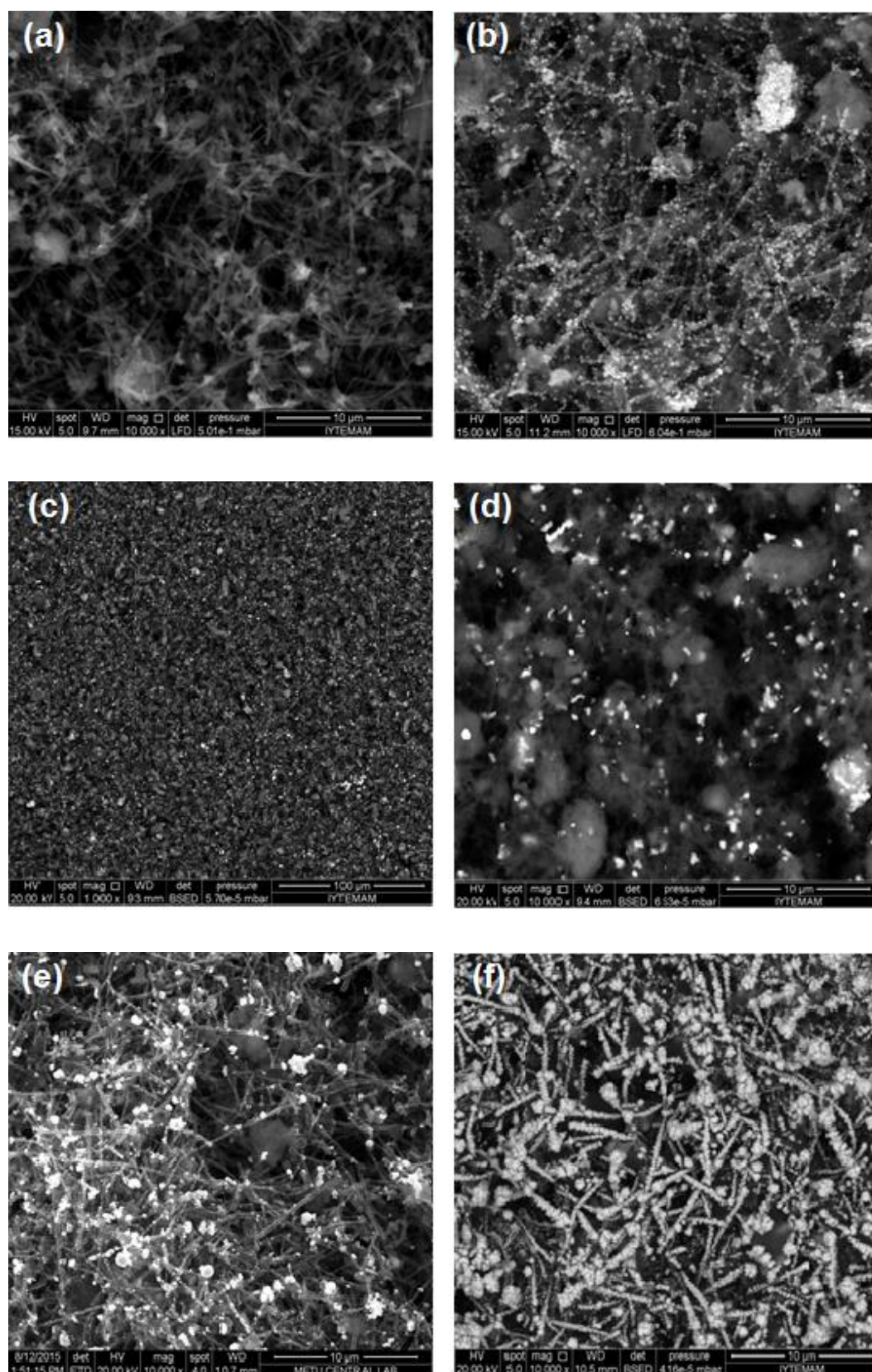


Figure 3.39 SEM images of the a) CuPc-CNT/GCE, b) Pt/CuPc-CNT/GCE c) Au/CuPc/GCE 1000x magnification, d) Au/CuPc/GCE 10000x magnification, e) Pt/Au/CuPc-CNT/GCE and f) (Au-Pt)/CuPc-CNT/GCE surfaces.

In order to qualitatively confirm the composite electrode surface composition, the prepared Au/CuPc-CNT/GCE, Pt/CuPc-CNT/GCE and (Au-Pt)/CuPc-CNT/GCE characterized with EDX (Figure 3.40) which proved the Cu content of modifier and successful electrodeposition of Pt, Au or both Pt and Au nanoparticles on CuPc-CNT/GC surface. N and Cu atoms have been in the structure of copper phthalocyanine molecule. Comparison of Figure 3.40a and b shows that the weight of Pt on the surface much more higher than Au content even if they deposited by the same number of cycles. This results from the higher molecular weight of Pt and high interaction of Pt with CNT-CuPc surface which facilitate the Pt deposition. Interestingly, the Au weight percentage in the codeposited (Au-Pt)/CuPc-CNT/GCE almost 3 times higher than Pt. This behavior supposed that Pt existence catalysis the Au deposition which coherent with the SEM image in 3.39f.

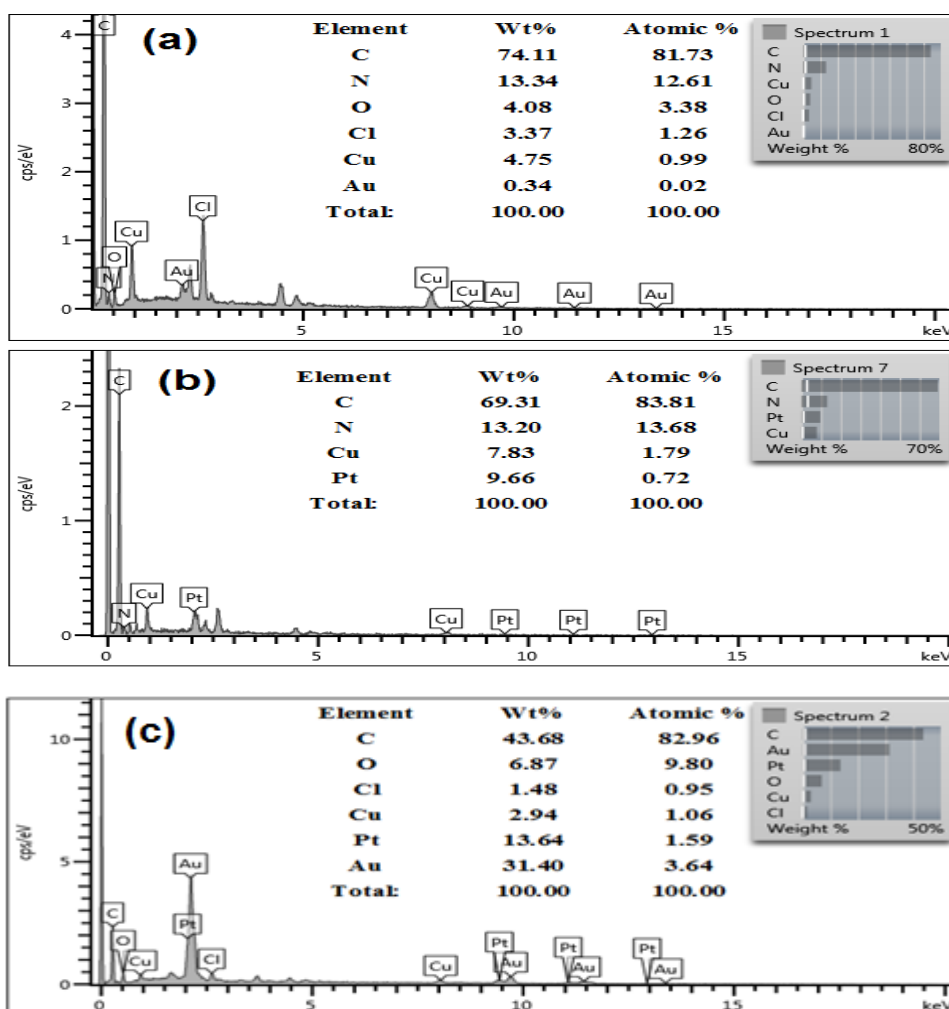


Figure 3.40 EDX results of the a) Au/CuPc-CNT/GCE, b) Pt/CuPc-CNT/GCE, c) (Au-Pt)/CuPc-CNT/GCE surfaces.

Figure 3.41 shows typical TEM images of (Au-Pt)/CuPc-CNT composite surfaces from low to high magnifications. The tubular structure of CNTs and jelly like forms that related with CuPc were obviously seen in TEM images. In addition, attachment of metal nanoparticles on both carbon nanotube and CuPc surface clearly seen from the image which distributed with narrow sized on all surface. It also possible to say that, the outer diameter of carbon nanotubes were between 100 and 200 nm. The spherical gold nanoparticles with an average diameter of approximately 3 nm were formed on the composite electrode surface. Au and Pt NPs were deposited also edges of the tubular structures of CNT as well as their sidewalls. Moreover, Linescan shows the individual gold atoms in nanocrystal. The intensity increases according to the number of atoms in the columns by the gold and platinum atoms move into the nanocrystal (Pennycook et al., 2006)

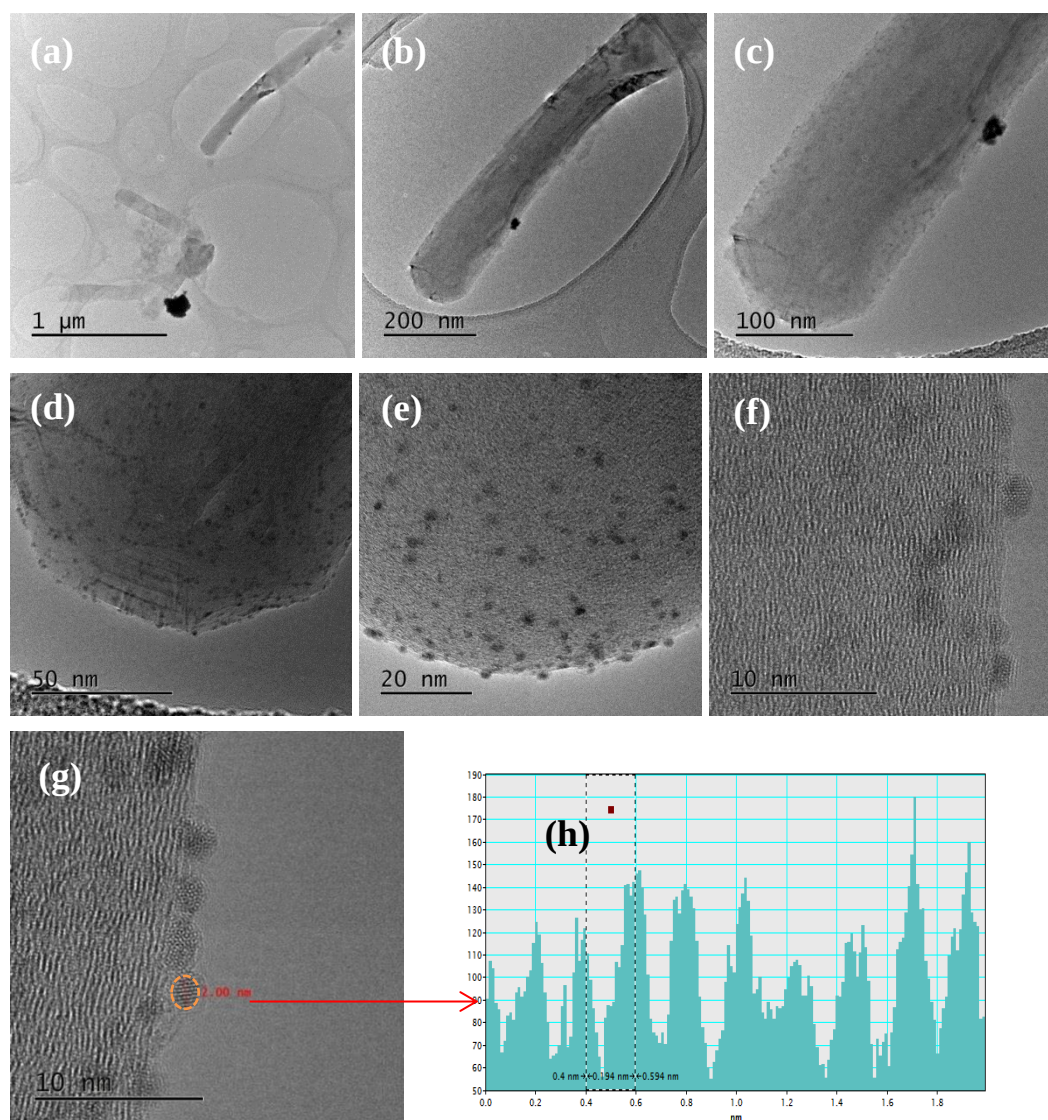


Figure 3.41 TEM images of (Au-Pt)/CuPc-CNT composite from low to high magnifications.

Scanning transmission electron microscopy (STEM) images of (Au-Pt)/CuPc-CNT/GCE at different scales were shown in Figure 3.42. We can see that, most of the Pt and Au nanoparticles were uniformly dispersed on the CuPc-CNT/GCE support especially on the sidewalls of CNTs. Small spherical nanoparticles with a diameter of lower than 5 nm (average size of bimetallic particles $\sim 2\text{-}3$ nm) observed on the composite surface. Figure 3.42 exhibits the dark field (a, c) and bright field (b, d) images, which were complementary for each other to clearly identify the surface. There was no inducement of a core-shell structure. The small size and homogeneous distribution of nanoparticles on CuPc-CNT/GCE explains the high catalytic activity of modified electrode towards methanol oxidation.

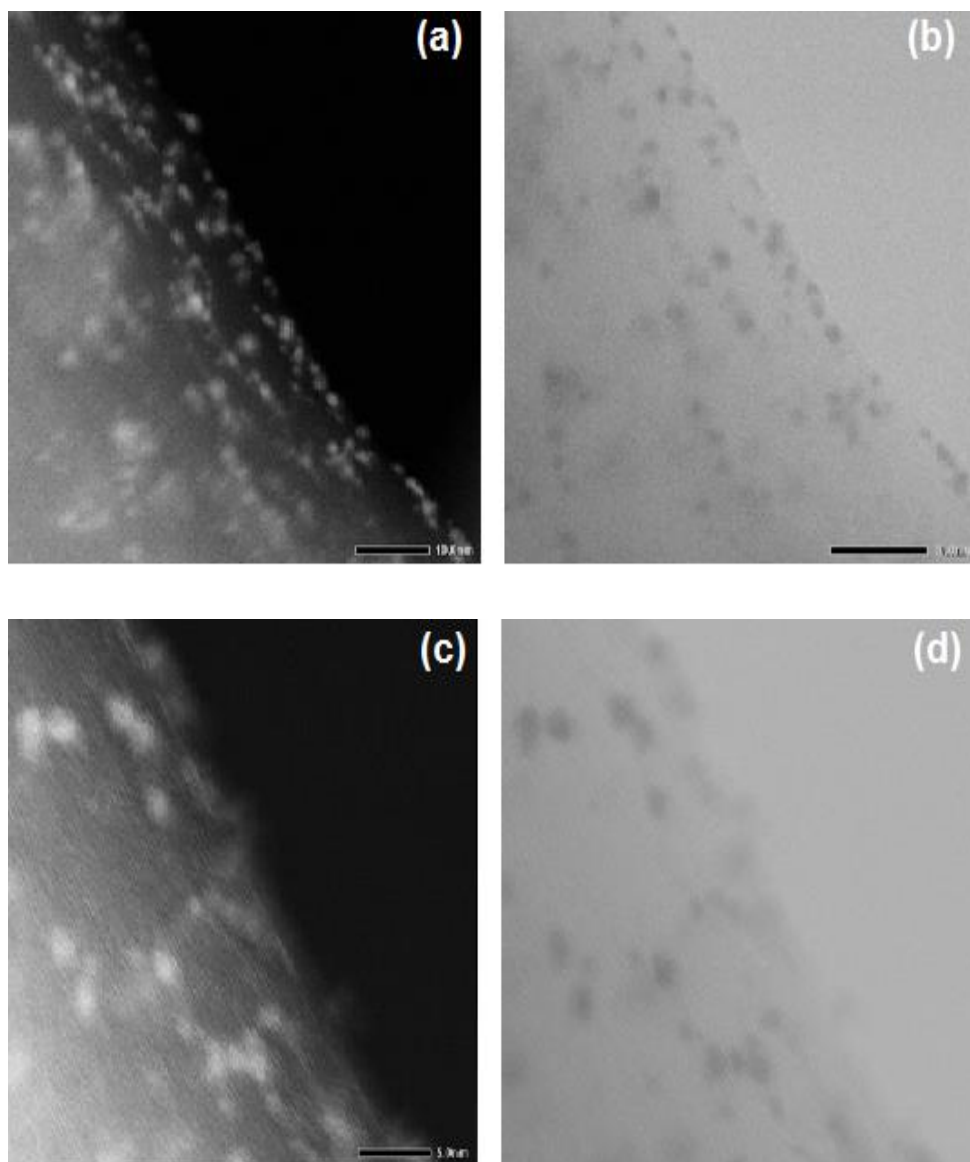


Figure 3.42 STEM images of (Au-Pt)/CuPc-CNT at narrow focus areas.

STEM image of (Au-Pt)/CuPc-CNT represented in Figure 3.43a that shows spherical nanoparticles on tubular structure. Figure 3.43b, c and d display the elemental maps of Pt, Au and Au-Pt elements, respectively. These maps show that Au and Pt elements were not only distributed on the nanotube but also were placed on CuPcs (colored spots observed outside of the tubules). Moreover, Au and Pt NPs were homogeneously distributed all over the surface individually with very narrow diameter sizes which clearly seen from the color of elements. The energy-dispersive X-ray spectrum (EDS) used for the elemental analysis of STEM samples that EDS of (Au-Pt)/CuPc-CNT shown in Figure 3.43e. C, Cu, Pt and Au signals were represented in EDS that prove the existence of AuNPs, PtNPs, CuPc and CNT on the surface.

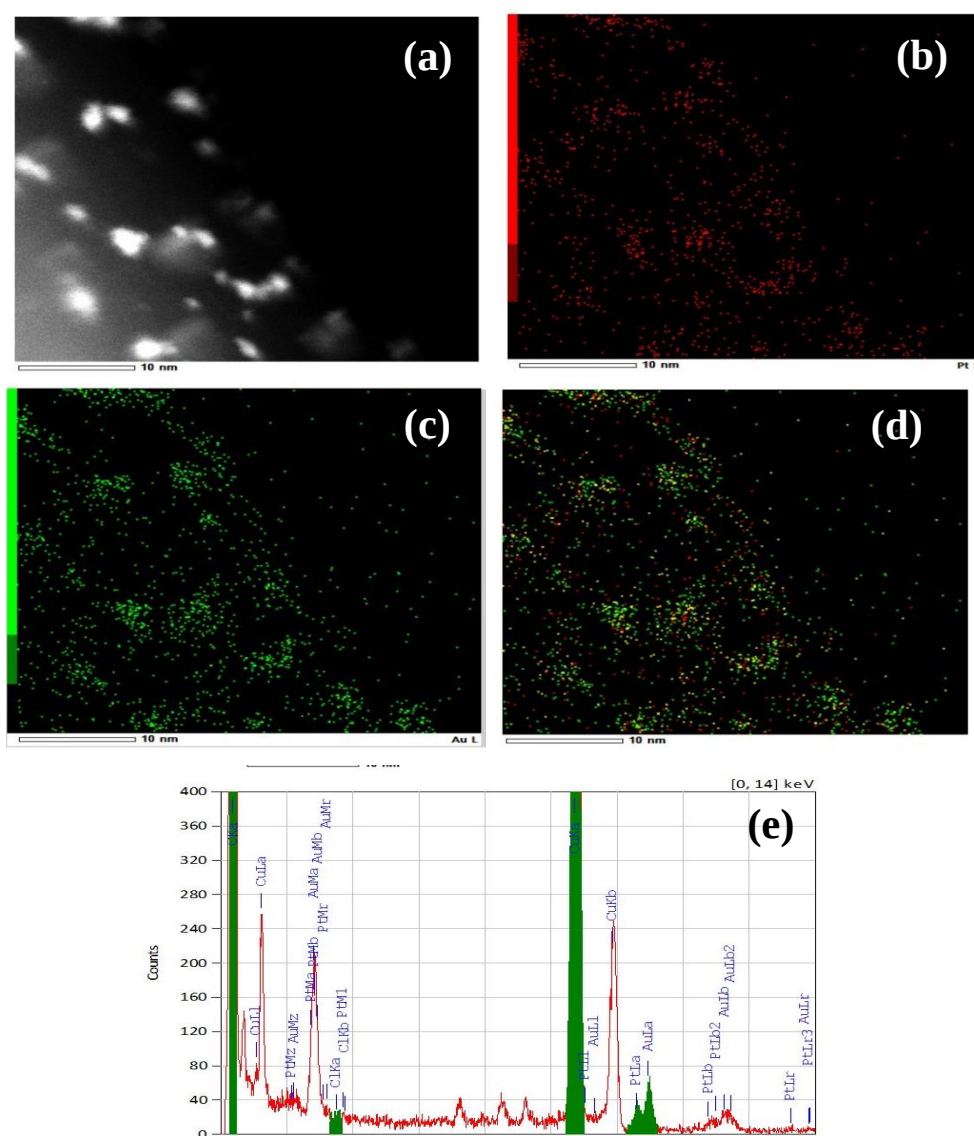


Figure 3.43 STEM elements mapping of Au, Pt and Cu composite (a-d) and EDS of (Au-Pt)/CuPc-CNT.

X-Ray diffraction is also used for analyzing the configuration and crystallographic structure of (Au-Pt)/CuPc-CNT/ITO. The comparison of the XRD pattern of ITO, CuPc-CNT/ITO, Au/CuPc-CNT/ITO, Pt/CuPc-CNT/ITO and (Au-Pt)/CuPc-CNT/ITO obtained under the same experimental conditions was shown in Figure 3.44 which obviously proved the change of surface modification and existence of Au and Pt on the surface with defined crystallographic forms.

The characteristic ITO peaks were determined with a broad form at about 22° , sharp peak at 30.6° and weak peaks at $2\theta = 35.5^\circ, 50.9^\circ, 60.6^\circ$ that correspond to the cubic structured ITO. The characteristic CuPc peaks were determined at $2\theta < 16^\circ$ both for CuPc-CNT. The sharp diffraction peak at 26.35° and small peaks around $43^\circ, 54^\circ$ indicates characteristic hexagonal structure of carbon (ICSD, card no. 98-002-9123). The detailed explanation with extra images of ITO and CuPc-CNT/ITO surfaces can be found in the previous section in Figure 3.22 and Figure 3.23.

It is clear that the Au/CuPc-CNT/ITO show excellent crystallographic quality, and predominate diffraction peaks could be determined from the gold crystal planes according to the simulated XRD pattern. The characteristic gold 100% peak is determined at 38.18° , and other major peaks are at $44.38^\circ, 64.57^\circ, 77.56^\circ, 81.72^\circ$ indicated 48%, 30%, 34% and 10% intensities, respectively. The peaks without any impure peaks were attributed to the reflections of (111), (200), (220), (311) and (222) of face-centered cubic Au, respectively. These results are also in good agreement with the published data (Narayanan et al., 2015; Chiu et al., 2008; Khurana et al., 2014, Atar et al., 2015;).

In the pattern of Pt/CuPc-CNT/ITO, sharp diffraction peak at 39.7° and weak broad diffraction peaks at 46.2° and 67.6° were observed which correspond to the (111), (200) and (220) crystalline planes of face-centered cubic Pt crystal, respectively. It can be claimed that the Pt nanoparticles are formed of pure crystalline Pt. These results are also in good agreement with the published data (Sharma and Kar, 2015, Kakaei, 2015).

The XRD spectrum of (Au-Pt)/CuPc-CNT/ITO contains all peaks that explained above with higher densities as compared to the others. In conclusion, XRD prove the existence of elements on the composite surface in detail. The modified electrode was exactly containing the all components that we prepared.

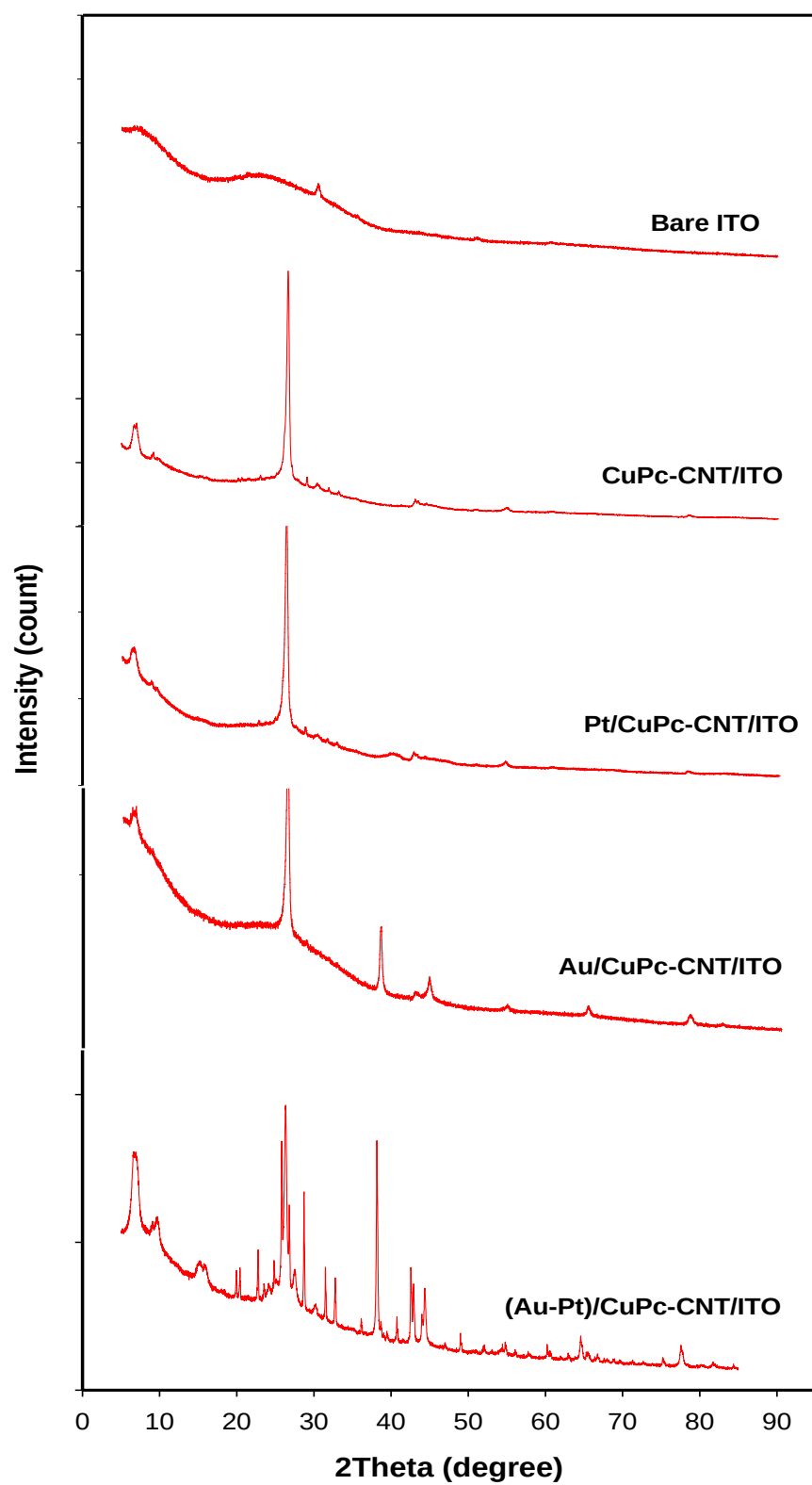


Figure 3.44 Comparative XRD patterns of bare ITO, CuPc-CNT/ITO and Pt/CuPc-CNT/ITO, Au/CuPc-CNT/ITO and (Au-Pt)/CuPc-CNT/ITO.

Electrochemical impedance spectroscopy (EIS) is a measurement technique to examine the heterogeneous electron-transfer capability and electrode kinetics and electrode analyte interface. The electrochemical impedance spectroscopy results of (Au-Pt)/CuPc-CNT/GCE in different methanol concentrations (25-200 mM) containing 2.0 M NaOH demonstrated in Figure 3.45. The frequency applied in the range of 0.05 to 50 000 Hz at the formal potential.

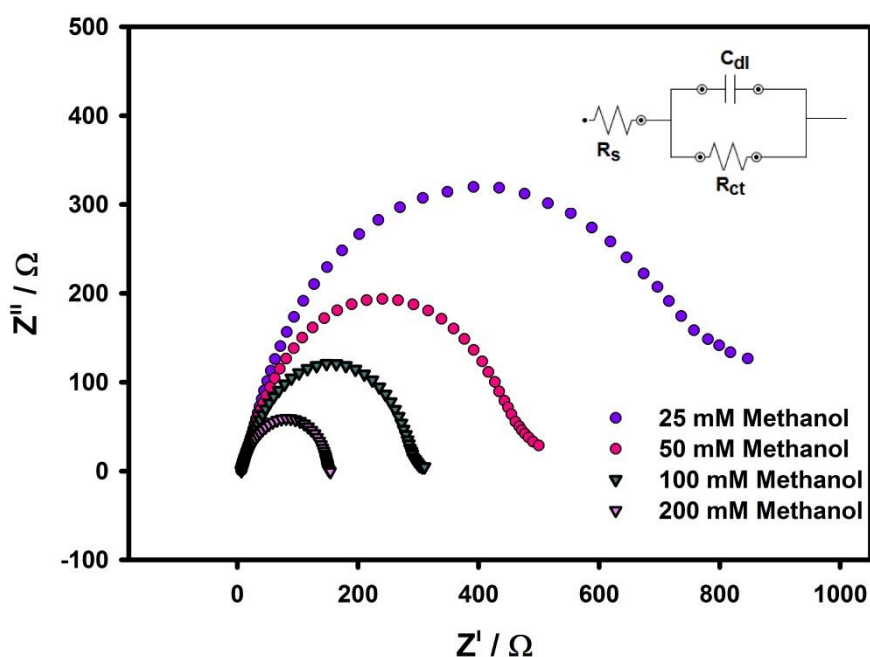


Figure 3.45 Nyquist plots of (Au-Pt)/CuPc-CNT/GCE in different methanol concentrations (25-100 mM) at 1.0 M NaOH. The frequencies ranged from 0.05 to 50000 Hz at the formal potential.

As shown in Figure 3.45, Nyquist plots shows only a semi-circle that Warburg element does not exist or it can not give signal. A large semicircle was obtained for (Au-Pt)/CuPc-CNT/GCE in the presence 25 mM methanol solution containing 1 M NaOH, indicating the high electron transfer resistance. $R(C(R))$ circuit design compatible with the Nyquist diagram that responsible for the interface between an electrode and its surrounding electrolyte. R_{ct} values of (Au-Pt)/CuPc-CNT/GCE were decreased by the increment of methanol concentration. The EIS data were fitted with this equivalent circuit and values were shown in Table 3.9. This phenomenon indicated that the excellent electroconductibility was proved by (Au-Pt)/CuPc-CNT/GCE bimetallic surface. These results are also in good agreement with the published papers (Yuan et al., 2015; Chen, et al., 2012; Ren et al., 2015).

Table 3.9 The R_s , R_{ct} and C_{dl} values of (Au-Pt)/CuPc-CNT/GCE in different methanol concentrations.

Methanol	R_s (Ω)	C_{dl} (μF)	$R_{ct}(\Omega)$
25 mM	7.12	339	663
50 mM	7.43	283	410
100 mM	7.63	237	260
200 mM	7.57	196	130

3.3 Electrochemical Oxidation of Dimethylamine Borane at Modified Electrodes

Fuel cells are devices that convert chemical energy obtained from fuel supply to electrical energy, which basically starts with the reaction between hydrogen in the anode and oxygen or air in the cathode. Since hydrogen has a carriage and storage problems, hydrogen rich chemicals such as formic acid, borohydride, ammino borane and dimethylamine borane chemicals were widely used as a storage method (Nash et al., 2014; Eberle et al., 2009; Bulushev and Ross, 2011). Among all chemicals, DMAB attracted an attention due to its high energy density, easily and cheap production and relatively less toxic structure (Plana et al., 2011).

DMAB oxidation behavior was studied in this thesis to investigate the ability of prepared catalytic surfaces as an anode material for fuel cells. For this purpose, mono and bimetallic nanoparticles modified polymer film electrodes and metal nanoparticles modified phthalocyanine-carbon nanotube composite electrodes for DMAB oxidation.

Electrooxidation of dimethylamine borane on Au disk electrode

Although fuel cells have been studied in a long period, sporadic literatures were found about DMAB oxidation. In order to obtain information about DMAB oxidation behavior Au disk electrode was studied in the absence and presence of DMAB. Figure 3.46 shows the behavior of Au disk electrode in the potential range of -1200 mV to +600 mV in alkaline solution in the absence and presence of 2 mM DMAB. Multiple peaks were observed at Au disk that were related to an irreversible oxidation peak of BH_3OH^- at -812 mV, followed by the broad peak of

Au oxide formation. Sequential and homogenous peaks at about +250 and +350 were corresponds to the $\text{BH}_2(\text{OH})_2^-$ and $\text{BH}(\text{OH})_3^-$, respectively. On the reverse scan, sharp reactivation peak was observed which was corresponds to the potential of gold oxide reduction peak observed in the background voltammogram. DMAB oxidation on Au disk electrodes can cause passivation of the electrode. If this gold oxide layer was removed by the reduction resulted the re-appearance of DMAB, the peak defined as reactivation peak. All obtained peak characteristics were coherent with the published papers by other researchers (Finkelstein et al., 2009; Sadik et al., 2005).

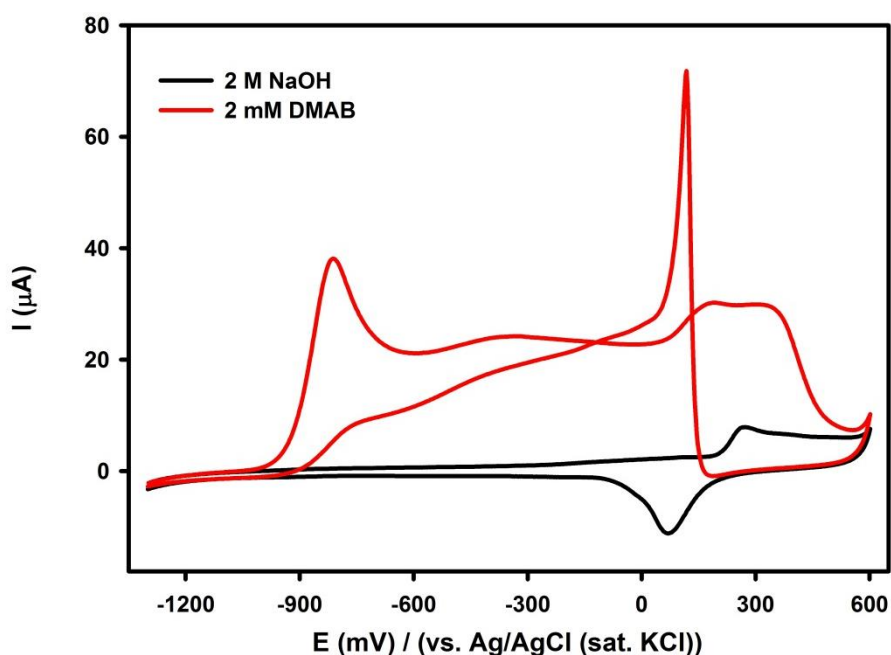


Figure 3.46 Cyclic voltammograms of Au disk electrode in 2 M NaOH in the absence and presence of 2 mM DMAB.

DMAB oxidation was investigated at various concentrations of NaOH (0.5 - 4.0 M) supporting electrolyte. Figure 3.47 shows the redox behavior of Au disk electrode in the presence and absence of 1 mM DMAB. Characteristic peaks of Au disk and DMAB oxidation peak at negative potentials were observed in all NaOH concentrations (Figure 3.47a). In Figure 3.47b, the anodic peak currents that correspond to the adsorbed hydroxyl species on gold electrode at about +300 mV and gold oxide reduction peak at about +100 mV were increased by the upswing of NaOH concentration as expected.

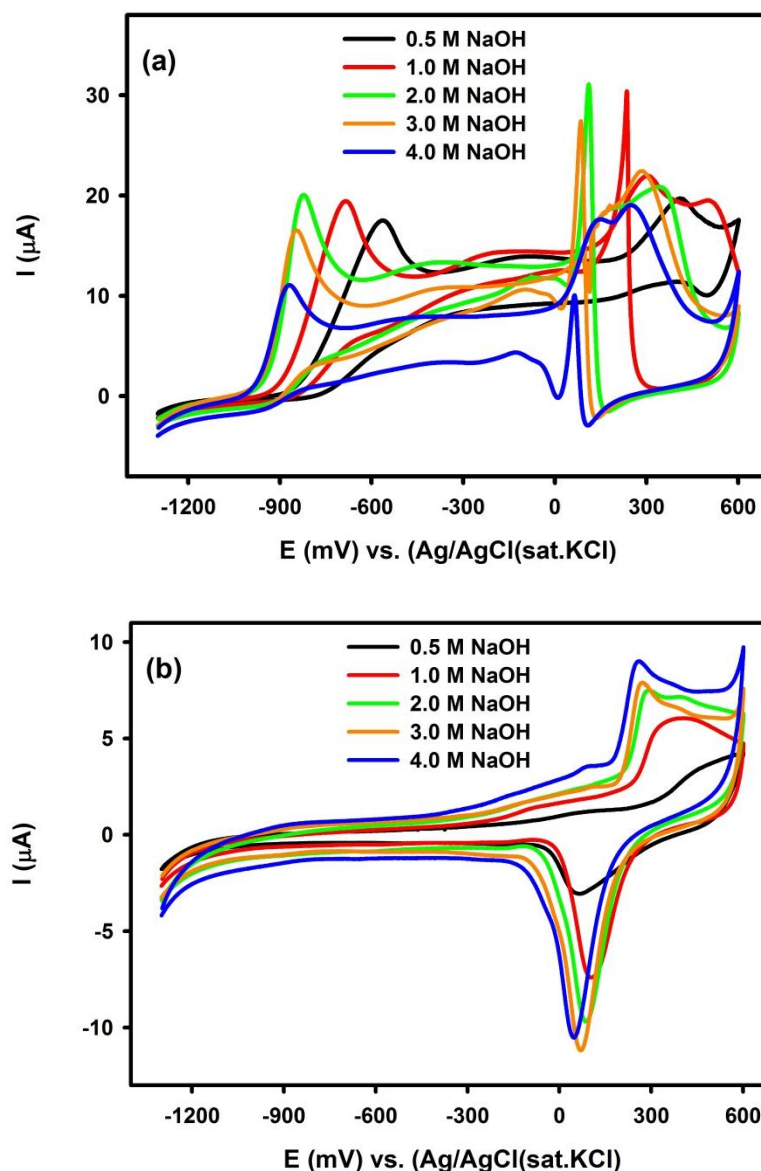


Figure 3.47 Cyclic voltammograms of Au disk electrodes a) with and b) without 1 mM DMAB in various NaOH concentrations: 0.5-4.0 M.

Detailed consideration of NaOH effect on peak potential and current values of DMAB oxidation, Figure 3.48 were plotted. DMAB oxidation peak currents increased from 0.5 M up to 2.0 M NaOH, which was followed by the decrease until reached the 4.0 M NaOH. DMAB oxidation peak potentials were shifted to values that are more negative by the upswing of NaOH concentration (Figure 3.48b). In the light of results obtained from Figure 3.47 and 3.46, 2 M NaOH concentration was chosen as an optimum electrolyte medium. Also other researchers preferred high NaOH concentration for investigation of DMAB oxidation (Finkelstein et al., 2009; Martins and Nunes, 2008). These results provide us prevision for suitable medium for other modified electrode surfaces that we prepared and discussed in following sections.

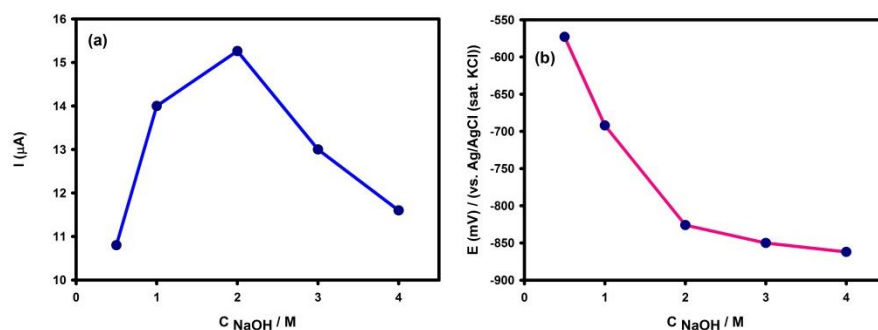


Figure 3.48 a) Peak potential and b) peak current changes of Au disk by the change of NaOH concentration for DMAB oxidation reaction.

The effect of scan rate on the electrooxidation of DMAB at Au disk electrode was investigated by cyclic voltammetry between the 5 mV.s^{-1} and 250 mV.s^{-1} range that exhibited in Figure 3.49. DMAB oxidation peak at negative potentials and characteristic peaks of Au disk at positive potentials were observed in all scan rates with different current values.

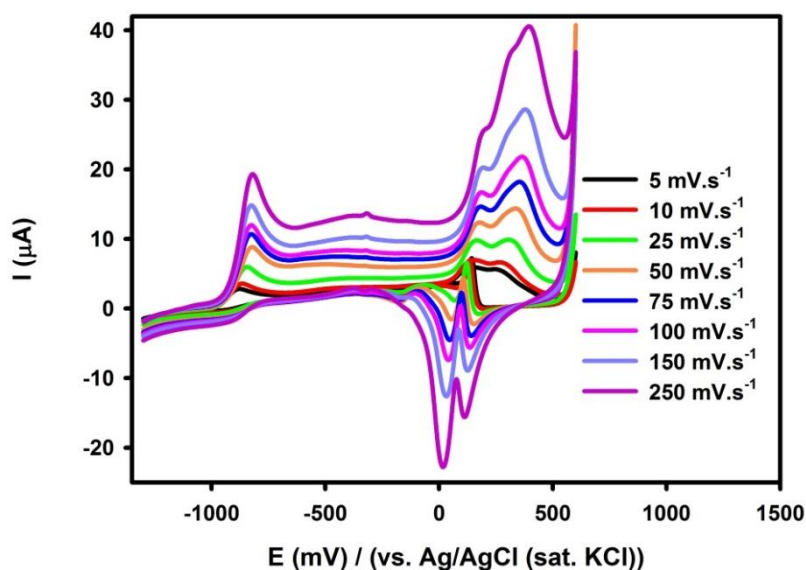


Figure 3.49 Cyclic voltammograms of Au disk electrode for DMAB oxidation with different scan rates: 5-250 mV.s^{-1} .

Figure 3.50 represents the data obtained from the voltammograms of Figure 3.49 for the first peak which corresponds to the DMAB oxidation. The affiliation between the square root of scan rate and peak currents was in linear with an equation of $i_{\text{pa}} (\mu\text{A}) = 0.8533v^{1/2} ((\text{mV.s}^{-1})^{1/2}) + 0.1812$, $R^2 = 0.9937$ that shown in Figure 3.50a pointed the diffusion controlled process at Au disk electrode. The oxidation peak shifts to more positive potentials with the increasing logarithm of scan rate values that indicate the irreversible electrode process (Figure 3.50b).

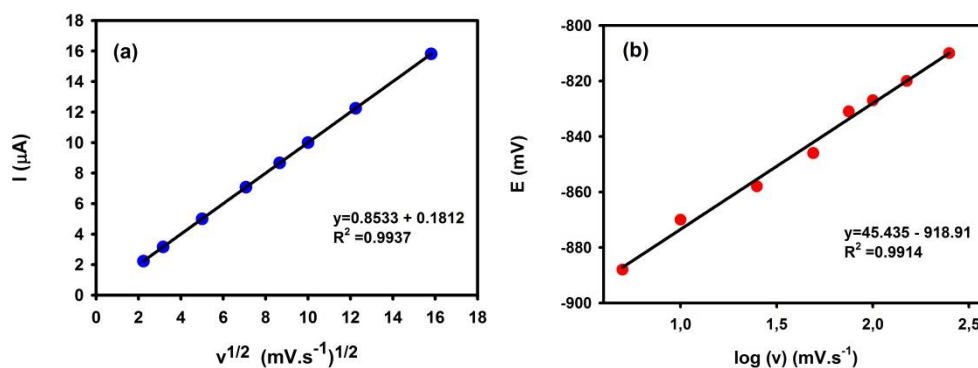


Figure 3.50 a) Square root of the scan rate vs. current and b) Logoritm of scan rate vs. potential graphics from scan rate study of Au disk electrode.

Figure 3.51 exhibits the cyclic voltammograms of Au disk electrode in the absence and presence of DMAB. Concentration of DMAB varies between 0.5 mM to 3mM. DMAB oxidation peak potential was faintly shifted to more positive values that suggested the slow reaction kinetic on Au disk surface. Peak currents of DMAB oxidation and other characteristic Au disk peaks were ascend with the increasing concentrations as expected. The dependence of peak current on the DMAB concentration was in linear that shown in the inset of the Figure 3.51.

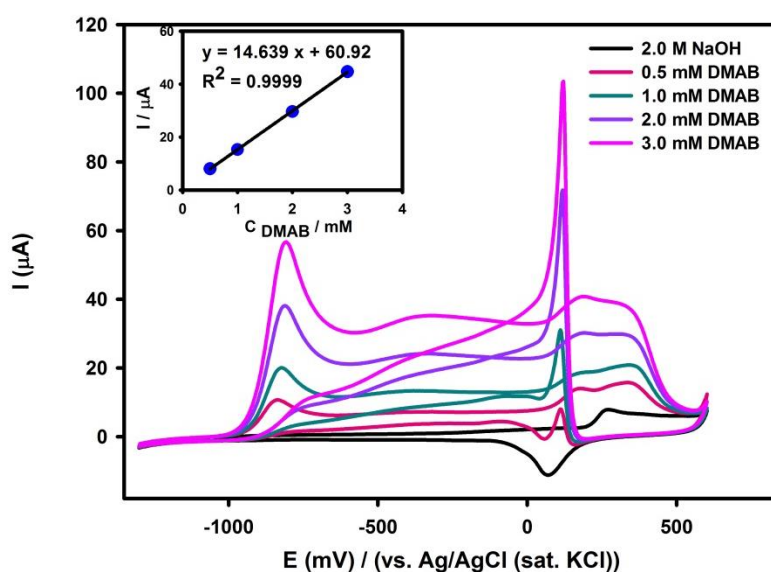


Figure 3.51 Cyclic voltammograms of Au disk electrode in 2 M NaOH in the absence and presence of different DMAB concentration: 0.5-3.0 mM. Inset: Anodic peak currents vs. DMAB concentrations on Au disk electrode.

3.3.1 Dimethylamine borane oxidation at polymer based modified electrodes

Polymers are promising materials for the preparation of nanocomposites. Conducting polymers have attracted significant attention because of their chemical, mechanical, optical, and electrical properties (Porrás-Gutiérrez et al., 2013; Guimard et al., 2007; Kuilla et al., 2010). Due to their unique properties, a variety of conducting polymers are used in catalytic surfaces in fuel cells (Kuwahara et al., 2008; Wang et al., 2009; Ehsani et al., 2012). In order to improve the activity of polymer film electrodes, metal nanoparticles were widely used due to their effect on promoting the electron transfer kinetic and catalysis the reaction (Sağlam et al., 2015; Hui et al., 2015).

3.3.1.1 Preparation of metal nanoparticles modified p-aminophenol film electrodes

Figure 3.52 shows multisweep cyclic voltammograms of p-aminophenol electropolymerization on GCE surface in 0.5 M HClO_4 solution containing 5mM SDS and 5mM p-aminophenol by cycling the potential from -0.5 to 2 V vs. Ag/AgCl (sat. KCl) at a scan rate of 100 mV /s for 20 cycles. p-aminophenol oxidation can be easily occurred on the electrode surface in the presence of SDS which is leading more monocation radicals formation on the electrode surface. The conductivity of PAP was increased due to the SDS behave as an anionic dopant of the polymer.

During the p-aminophenol polymerization in acidic medium, an irreversible oxidation peak was observed at 1600 mV without the corresponding cathodic processes in the reverse scan. After the second cycle, a single cathodic peak at -100 mV and reversible oxidation and reduction peaks were seen at around +550 and +500 mV, respectively. The generation of the peaks might be attributed to the intermediate species during the aminophenol oxidation process (Ojani, 2009). The increasing peak currents for all oxidation and reduction peaks were show that an electropolymerization takes place and polymer was formed on the GCE surface.

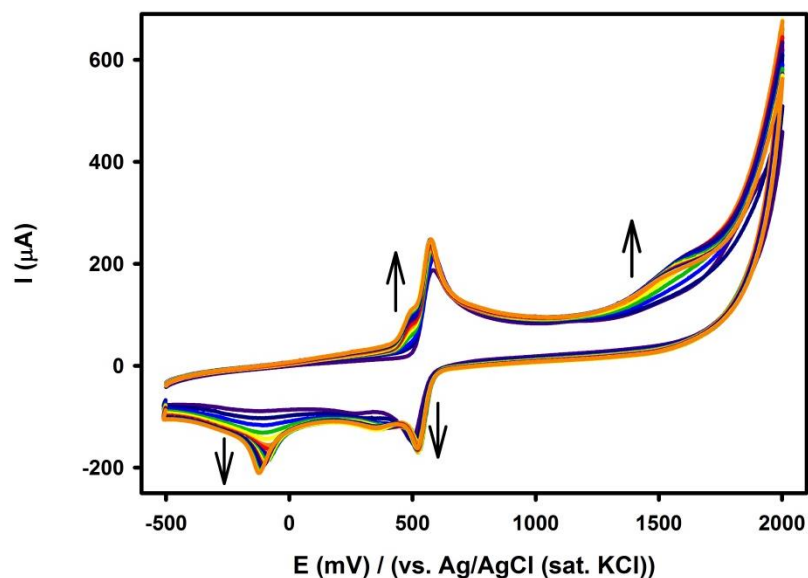


Figure 3.52 Cyclic voltammogram of p-aminophenol electropolymerization in a 5.0 mM p-AP monomer and 5.0 mM SDS containing 0.5 M HClO_4 solution on the surface of the glassy carbon electrode at a scan rate of 100 mVs^{-1} . The arrows indicate the trends of current during CVs.

Ag nanoparticles preparation was performed in 2 mM AgNO_3 containing 0.1 M HNO_3 . Figure 3.53 shows the preparation of Ag nano particles in the potential range of 300 mV to -900 mV on the PAP/GCE. There is a cathodic peak at about -400 mV related with Ag^+ ions and at -150 mV for oxidation of Ag nano particles. Peak currents of both reduction and oxidation peaks were increase during the Ag nano particles deposition on PAP/GCE surface.

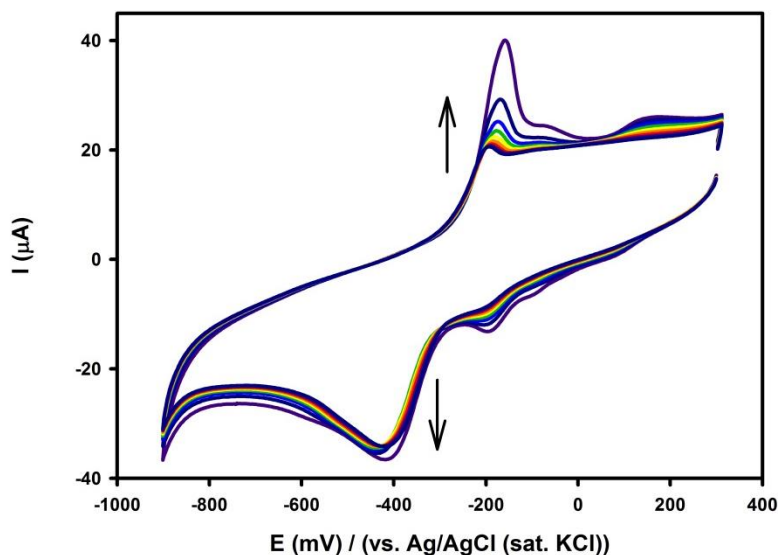


Figure 3.53 Multicycle cyclic voltammogram for the electrodeposition of Ag nanoparticles on PAP/GCE from 2 mM AgNO_3 containing 0.1 M HNO_3 solution.

Gold nanoparticles deposition on the polymer film modified GC electrodes was carried out between 100 mV to -900 mV potential range in HAuCl_4 containing 0.1 M HCl solution (Figure 3.54). Au (III) ions reduction observed at -450 mV in the cathodic scan while two small oxidation peaks were occurred at -200 mV and -400 mV suggested as the Au (I) and Au (III) reoxidation peaks.

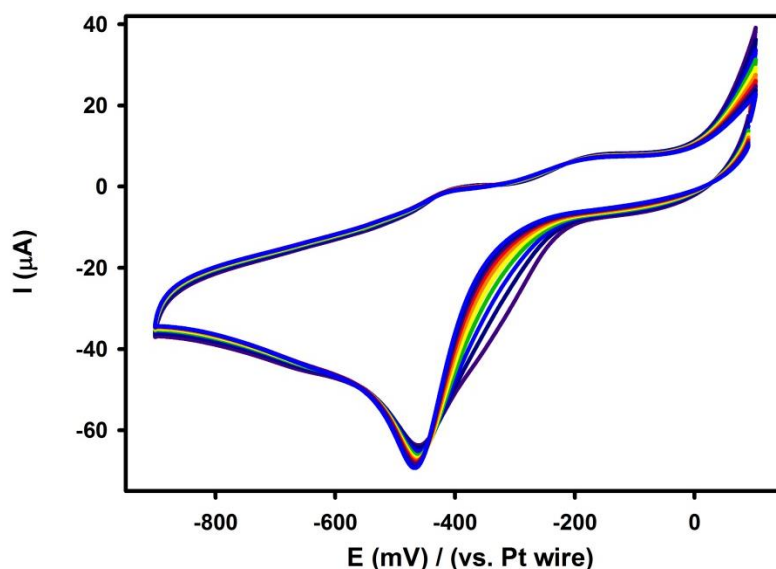


Figure 3.54 Multicycle cyclic voltammogram for the electrodeposition of Au nanoparticles on PAP/GCE from 5 mM HAuCl_4 containing 0.1 M HCl solution.

3.3.1.2 Electrochemical behavior of dimethylamine borane

Oxidation of dimethylamine borane on Ag nanoparticles modified poly(p-aminophenol) film GCE

Electrochemical oxidation of DMAB was investigated at bare and polymer based modified electrodes within the context of this section. Figure 3.55a clearly demonstrates the distinction in the performances of the bare, PAP/GCE and Ag/PAP/GCE for DMAB oxidation in alkaline media. While there is no response obtained at bare and PAP/GCE for DMAB oxidation, Ag/PAP/GCE showed well defined, sharp peak at -916 mV with 27.2 μA current value. Background response of bare and modified electrodes was shown in Figure 3.55b in 2 M NaOH solution. It was obviously seen that bare GCE and PAP/GCE showed same behavior in 2 M NaOH with and without DMAB. According to the literature that published by Plana and Dryfe (2011), an irreversible oxidation peak was observed at high positive potential (1280 mV) for glassy carbon electrode which Au disk was not studied in that potential range due to the passivation of its surface.

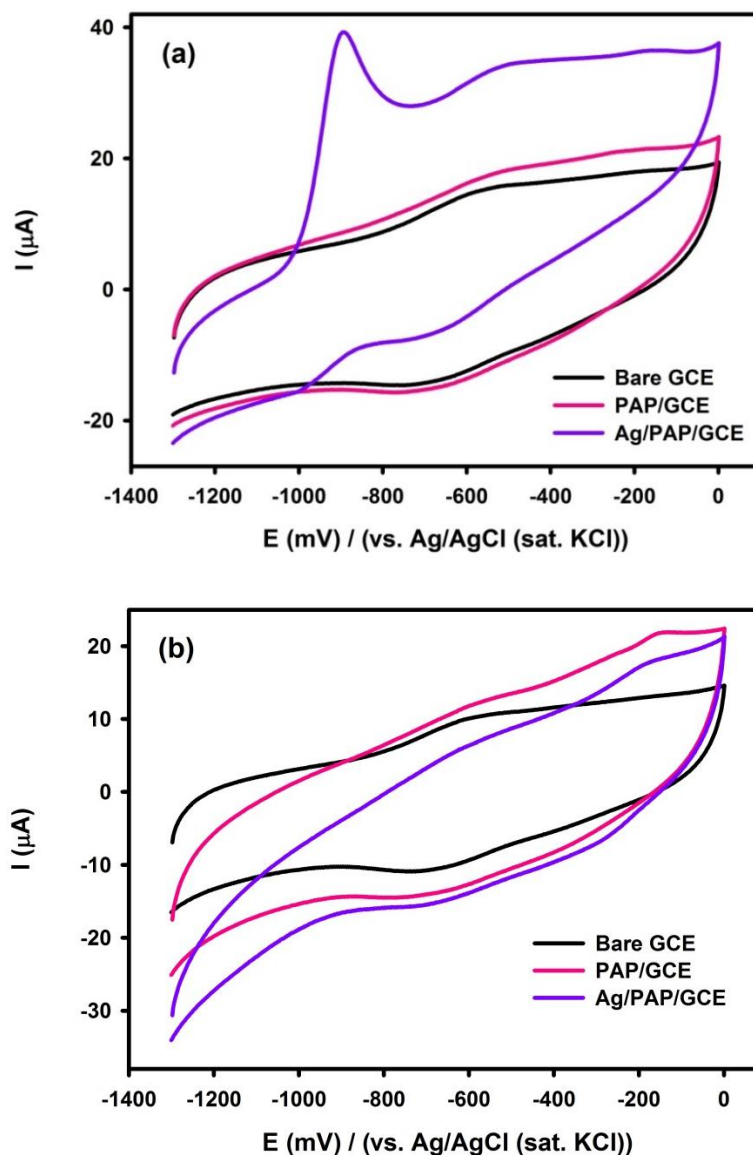


Figure 3.55 Cyclic voltammetric behavior of bare GCE, PAP/GCE and Ag/PAP/GCE in 2 M NaOH A) with 1 mM DMAB, B) without DMAB.

In order to obtain the best electrode surface towards DMAB oxidation, some parameters such as polymer cycle number, cycle number of nanoparticle deposition, AgNO_3 concentration, and concentration of supporting electrolyte should be optimized. Chosen of the optimum conditions were decided by the valuing the peak current and peak potential of DMAB. Related optimizations discussed in the following paragraphs.

Optimization of polymerization cycle number for preparation of Ag/PAP/GCE

PAP/GC electrodes prepared with different coverage that examined by changing the cycle numbers of polymerization to obtain catalytically active surface towards DMAB oxidation. For this purpose, various cycle numbers (30, 35, 40, and 50) applied for polymerization and modified electrodes investigated in the presence (Figure 3.56a) and absence (Figure 3.56b) of 1 mM DMAB in 2.0 M NaOH.

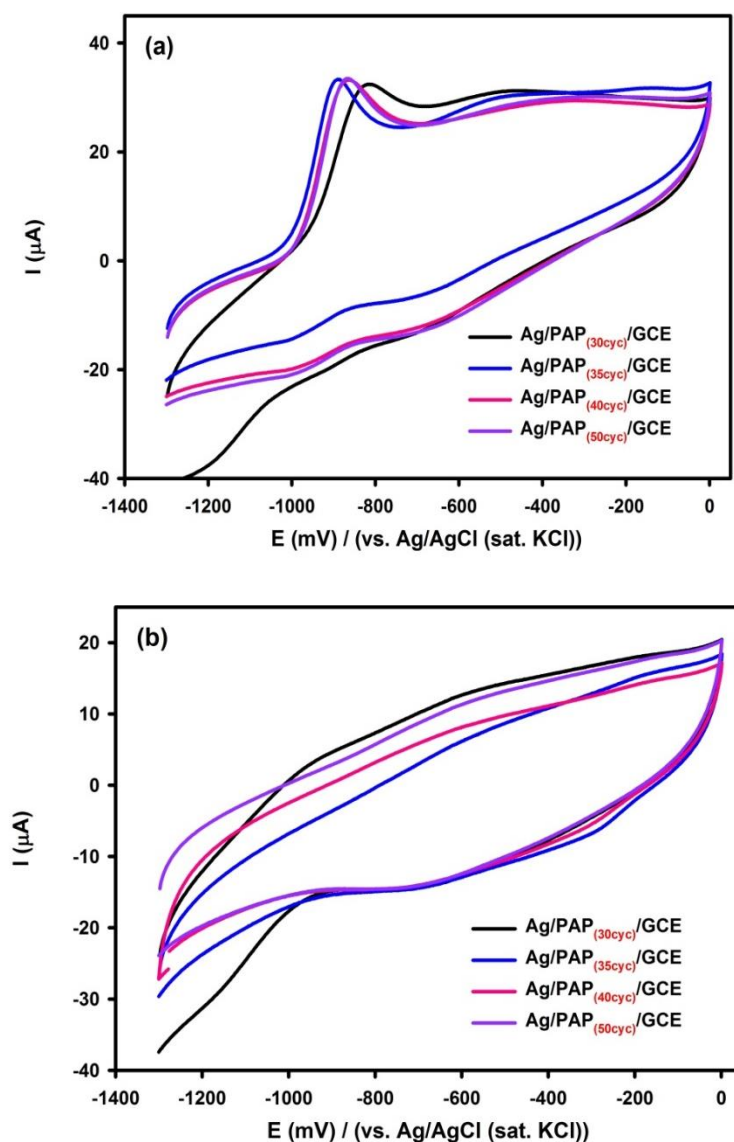


Figure 3.56 Cyclic voltammograms of Ag/PAP/GCE that prepared with various polymerization cycle number of p-aminophenol a) with and b) without 1 mM DMAB in 2 M NaOH.

Effect of polymerization cycle number on peak characteristics were shown in Figure 3.57. By the increment of cycle number, slight increase observed in terms of peak current while the peak potential shifted negative value up to 35 and higher than that value, peak shift back to positive. Overall results showed that 35 cycles of p-AP polymerization provides good enhancement in peak characteristics of DMAB.

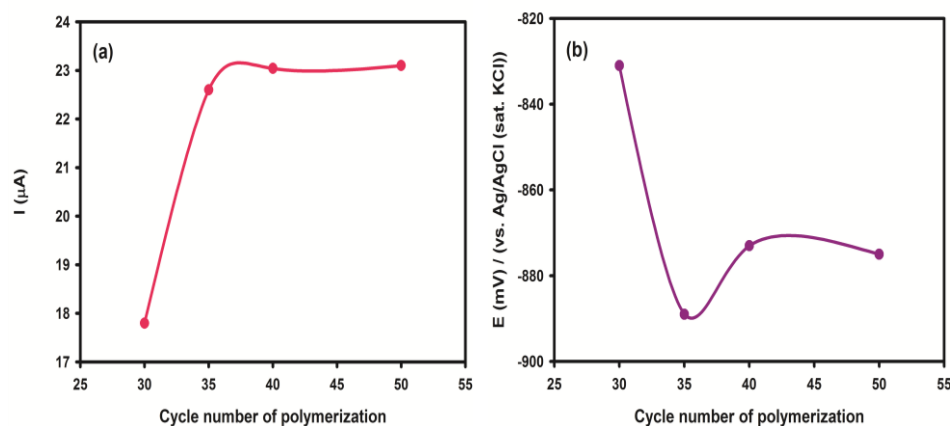


Figure 3.57 Plots for the effect of p-aminophenol polymerization cycle number on a) peak current and b) peak potential of 1 mM DMAB oxidation at Ag/PAP/GCE.

Optimization of AgNO_3 concentration for preparation of Ag/PAP/GCE

In order to improve the response of Ag nanoparticles modified PAP/GCE, AgNO_3 concentration also optimized. Figure 3.58 represents the current and potential change of DMAB oxidation peak by the change of AgNO_3 concentration that varies between 0.5 mM and 5 mM. By the increasing of Ag^+ concentration, DMAB oxidation peak current increase from 24 to 27 μA and the peak potential shift from -870 mV to -928 mV. The change in peak current with the Ag^+ concentration was not significant. Although oxidation potential was shifted to more negative values at higher concentrations, electrode surface was covered fully by silver at high AgNO_3 concentrations and act like bulk Ag electrode. As a result, 2 mM AgNO_3 concentration chosen as an optimum value for Ag nanoparticles deposition that DMAB oxidation occurred at -911 mV with 26.1 μA .

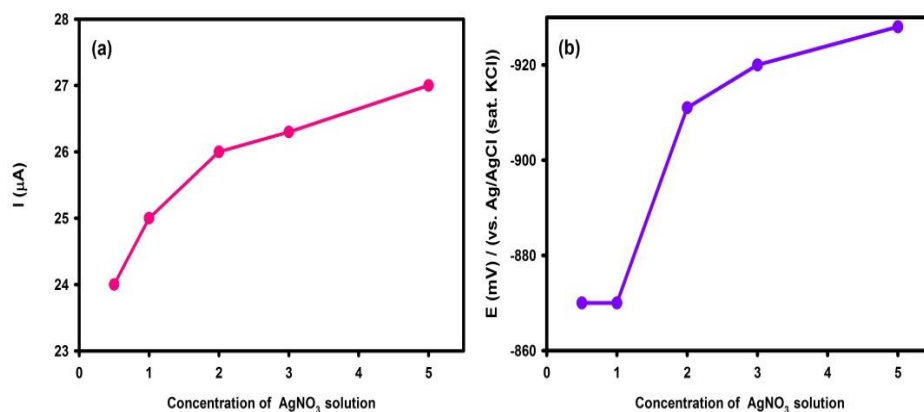


Figure 3.58 Plots for the effect of AgNO_3 concentration on a) peak current and b) peak potential of 1 mM DMAB oxidation at Ag/PAP/GCE.

Optimization of Ag nanoparticle deposition cycle number for preparation of Ag/PAP/GCE

Figure 3.59 represents the change in peak current and peak potential of DMAB oxidation by the change of Ag nanoparticles formation cycle number in alkaline medium. Ag deposition cycle number varies between 5 to 20 cycles. Oxidation peak current of DMAB was increase up to 10 cycles. Then decrease again probably due to the high surface coverage that behaves like bulk Ag electrode. In addition, peak potential showed parallel behavior like current that most negative value obtained at 10 cycles. In this regard, 10 cycles of Ag nanoparticles deposition chosen as an optimum for DMAB in alkaline medium at Ag/PAP/GCE.

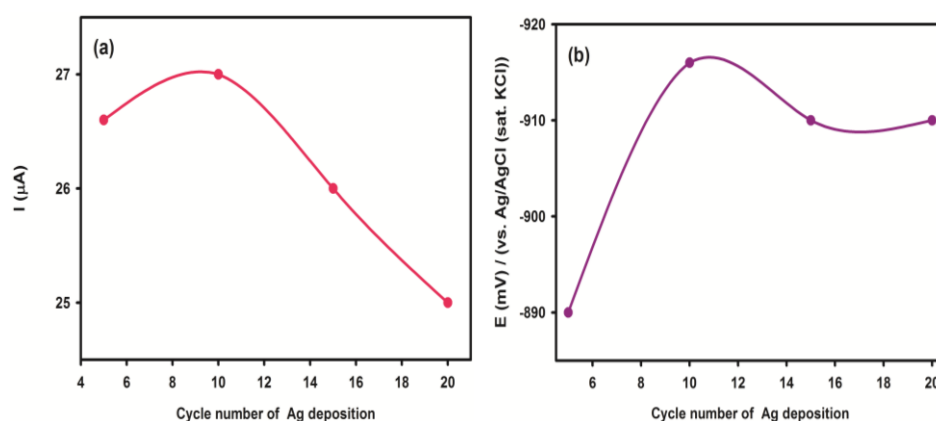


Figure 3.59 Plots for the effect of Ag nanoparticles formation cycle number on a) peak current, b) peak potential of 1 mM DMAB oxidation at Ag/PAP/GCE.

Optimization of NaOH concentration

The effect of NaOH concentrations to DMAB oxidation was investigated in Figure 3.60. NaOH concentration varies between 0.5 to 4.0 M, which studied at Ag/PAP/GCE in the presence (Figure 3.60a), and absence (Figure 3.60b) of DMAB. Background responses of Ag/PAP/GC electrodes increase with the increase of NaOH concentration. As shown in Figure 3.60, peak characteristics of DMAB were affected by the NaOH concentration as expected.

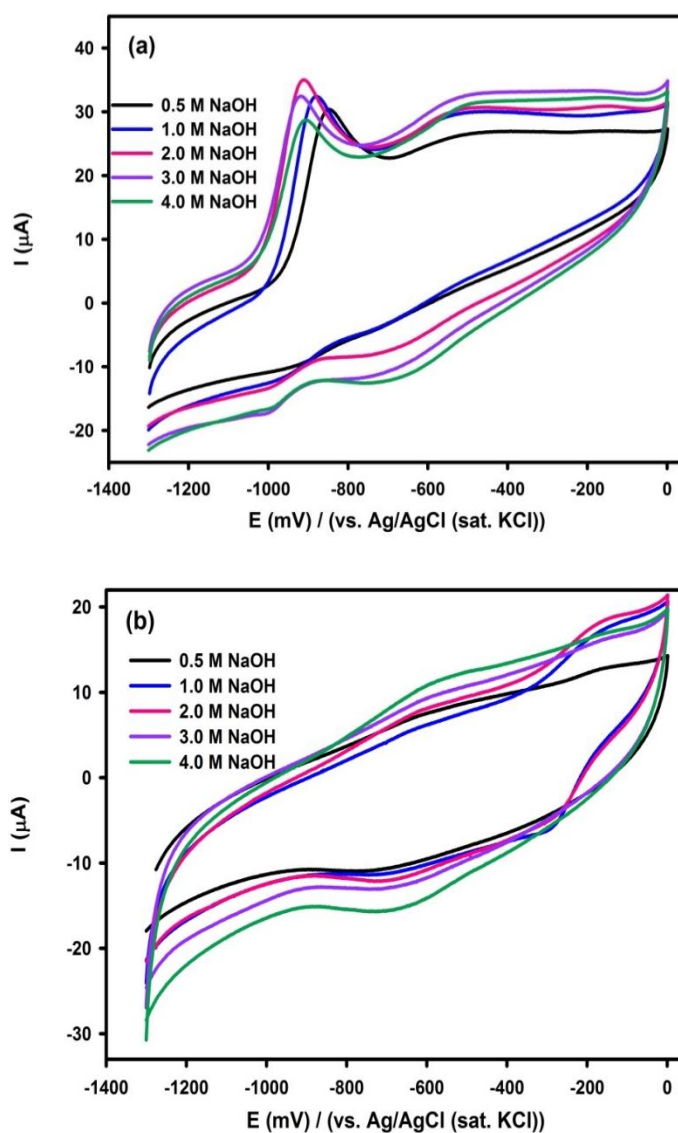


Figure 3.60 Cyclic voltammograms of Ag/PAP/GCE in various NaOH concentrations (0.5-4.0 M) a) with and b) without 1 mM DMAB.

The current and potential behavior versus NaOH concentration represented in Figure 3.61. The current values of oxidation peak were increase until the concentration reached to 2 M and then decrease to low current values until 4 M

NaOH concentration. In addition, DMAB oxidation peak potential was affected by the NaOH concentration that peak potentials shifted to values that are more negative by the increasing of concentration up to 3 M. It has been known that DMAB is relatively stable at high pH values that DMAB oxidation (Plana and Dryfe, 2011). There was not any significant change in peak potential at concentration higher than the 3 M. According to the results, 2 M NaOH medium was selected as an optimum supporting electrolyte due to the high peak current and adequate negative peak potential value.

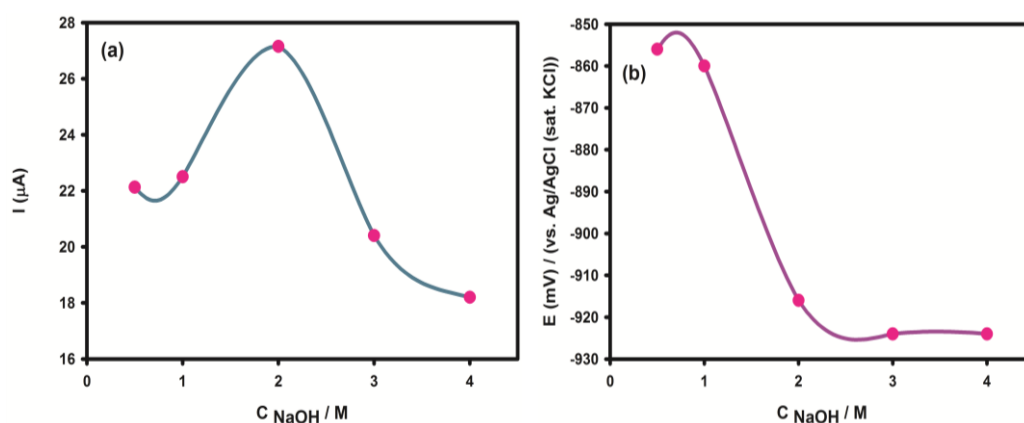


Figure 3.61 Plots for the effect of NaOH concentration on a) peak current, b) peak potential of 1 mM DMAB oxidation at Ag/PAP/GCE

Scan rate study of DMAB oxidation on Ag/PAP/GCE

Cyclic voltammetric response of Ag/PAP/GCE in 1mM DMAB containing 2 M NaOH with various scan rates were shown in Figure 3.62. Scan rates were changed in the range of 3 mVs^{-1} to 1000 mVs^{-1} in the 1 mM DMAB containing 2 M NaOH solution.

Figure 3.63 exhibits the dependence of peak current to square root of scan rate and logarithm of scan rate to peak potential for DMAB oxidation on Ag/PAP/GCE. The peak current of DMAB was directly proportional to the scan rate in the range of $3\text{--}1000 \text{ mVs}^{-1}$. These data show that the electrode reaction controlled by diffusion of DMAB to electrode surface (Figure 3.63a). In addition, plot of peak potential vs logarithm of scan rate was shown in Figure 3.63b. In reversible reactions, peak potentials are not dependent on scan rate, whereas the logarithm of the square root of the scan rate has a linear dependence with peak potential reaction is irreversible.

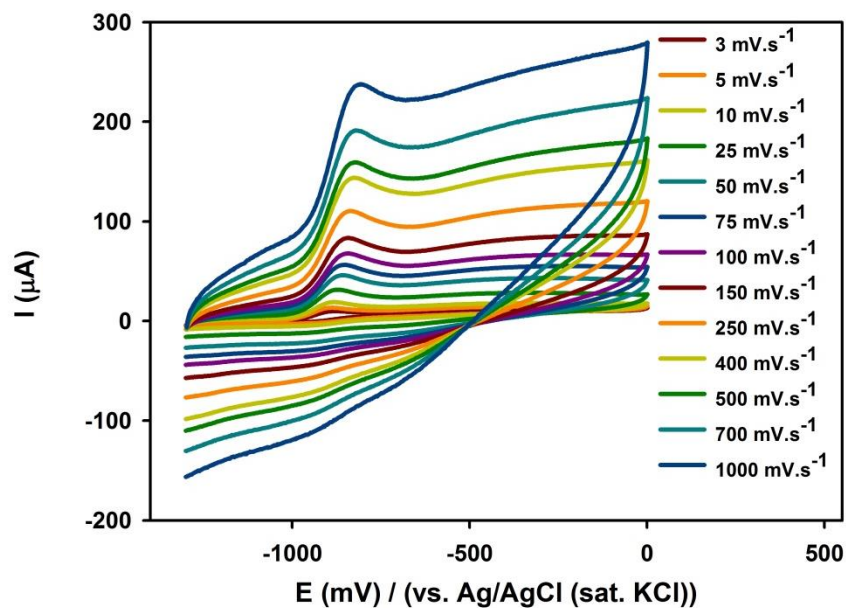


Figure 3.62 Cyclic voltammograms of Ag/PAP/GCE for DMAB oxidation with different scan rates: 3-1000 mV.s^{-1} .

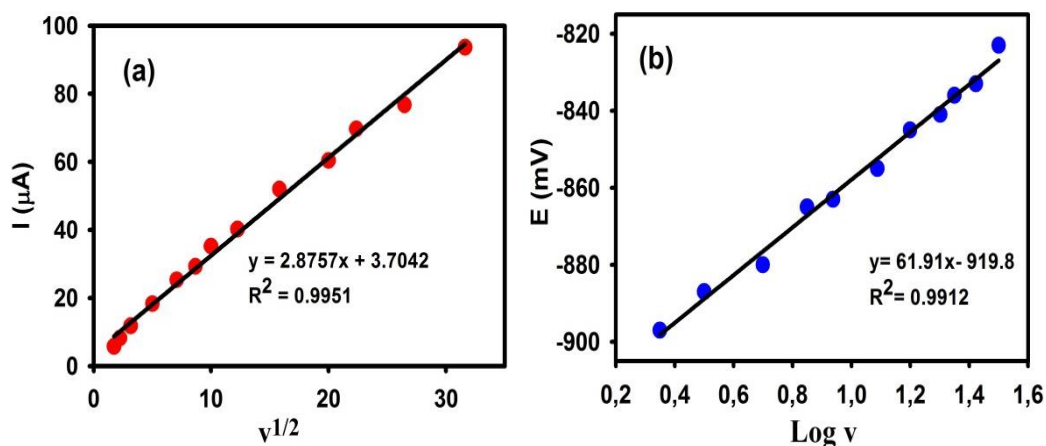


Figure 3.63 Dependence of a) peak current to square root of scan rate and b) logarithm of scan rate to peak potential for DMAB oxidation on Ag/PAP/GCE.

The voltammetric response and corresponding calibration plot of peak currents vs. concentrations shown in Figure 3.64. The curve (a) corresponds to the background response of Ag/PAP/GCE in 2 M NaOH solution. The curves (b–e) correspond to the DMAB concentrations of 1, 3, 5, and 8 mM, respectively. By the increasing of DMAB concentration, oxidation peak currents increase from 27.15 to 177 μA and the peak potential shift from -916 mV to -911 mV. The peak current value were directly proportional with the increasing concentrations of DMAB with a correlation of 0.9975.

Concisely, DMAB was investigated at Ag/PAP/GCE in alkaline medium that some optimization studies were carrying out in order improves the catalytic activity. Result from the optimization studies, the best catalytic activity obtained at an electrode that modified electrochemically with 10 cycles in 2 mM AgNO₃ containing solution after 35 cycles polymer modification on GCE surface in 2 M NaOH solution.

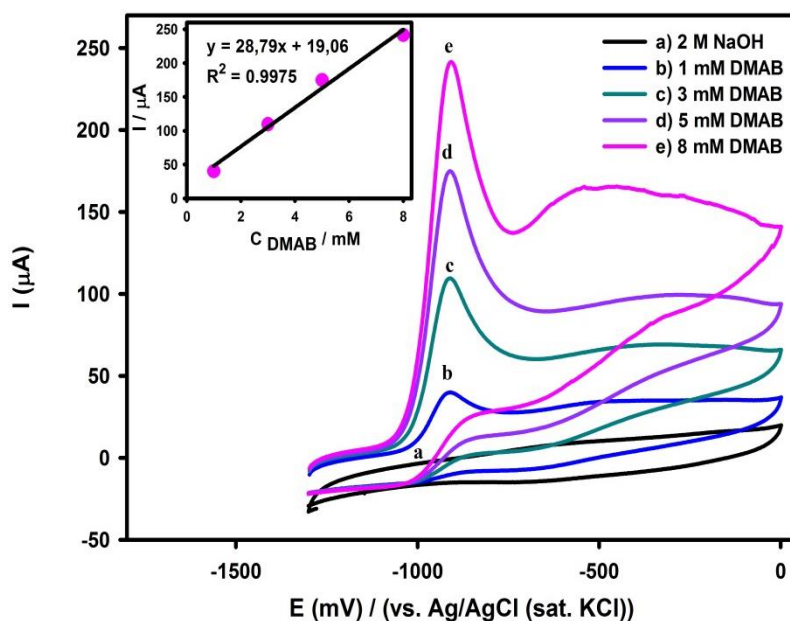


Figure 3.64 Cyclic voltammograms of a) background response in 2M NaOH. b) 1 mM, c) 3 mM, d) 5 mM, e) 8 mM DMAB oxidation at Ag/PAP/GCE. Inset: Plot of the peak current versus DMAB concentration.

Oxidation of dimethylamine borane on Au-Ag bimetallic nanoparticles modified poly(*p*-aminophenol) film GCE

Figure 3.65 shows the comparison of the Au disk, Au nanoparticles and bimetallic Au and Ag nanoparticles modified electrodes towards DMAB oxidation in 2 M NaOH. Polymer film electrode first modified with Ag nanoparticles and then dipped in Au solution in order to prepare Au nanoparticles. This electrode abbreviated as Au/Ag/PAP/GCE. Ag/Au/PAP/GC electrode was prepared by following the opposite of this procedure. As it mentioned before, GCE and PAP/GCE have no response towards DMAB oxidation that did not shown for comparison.

According to the CV results, peak current and potential values of modified electrodes listed in Table 3.10. A small oxidation peak observed at Au disk electrode for DMAB oxidation as compared to the other electrodes. Individual existence of Au nanoparticles on PAP/GCE surface was not give promising results due to positive peak potential as compared to other electrodes. Bimetallic Au and Ag nanoparticles show meliorated catalytic activity in terms of both peak current and potential in comparison with the Au disk and Au/PAP/GCE. Finally, Au/Ag/PAP/GC electrode was chosen as a working electrode for further DMAB oxidation studies due to the relatively negative peak potential.

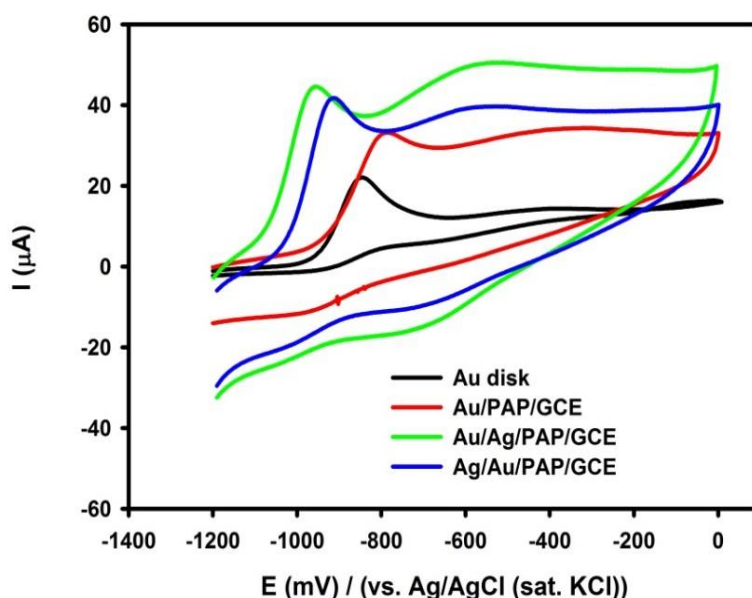


Figure 3.65 CV plots for 1.0 mM DMAB oxidation in 2.0 M NaOH at Au disk electrode, Au/PAP/GCE, Au/Ag/PAP/GCE, Ag/Au/PAP/GCE.

Table 3.10 Comparison of DMAB oxidation peak characteristics at modified electrodes in alkaline solution.

Electrode	Potential (mV)	Current (μA)
Au disk	-812	13
Au/PAP/GCE	-792	15
Au/Ag/PAP/GCE	-960	27
Ag/Au/PAP/GCE	-888	23

Optimization of polymerization cycle number for preparation of Au/Ag/PAP/GCE

Electrochemical polymerization provides an advantage of tuning the polymeric film thickness, nanoparticle size and distribution, which are important for catalytic activity. The surface coverage of PAP/GC electrodes were adjusted by changing the cycle numbers used in polymerization from 20 to 50 in the potential range studied. Figure 3.66 demonstrates the effect of cycle number for formation of PAP film from p-aminophenol monomer, which modified with Au/Ag nanoparticles. Behavior of the modified electrodes investigated in 1 mM DMAB containing 2 M NaOH solution. As can be seen clearly in Figure 3.66, the highest peak current obtained at 40 cycles while there is no significant change shown for peak potential. Therefore, the 40 consecutive scans from -0.5 to 2 V with a rate of 100 mVs^{-1} used as polymerization procedure in further studies.

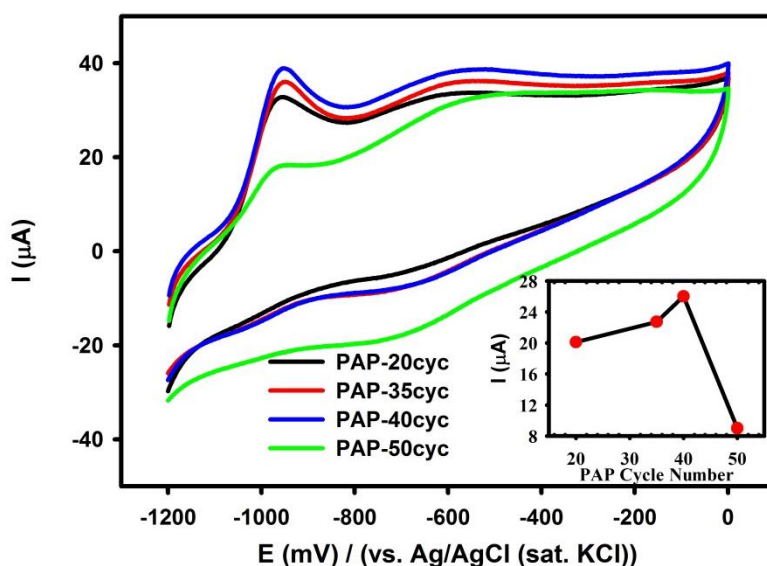


Figure 3.66 Effect of p-aminophenol polymerization cycle number on 1 mM DMAB oxidation at Au(10cyc)-Ag(10cyc)/PAP/GC electrode.

Optimization of Au nanoparticle deposition cycle number for preparation of Au/Ag/PAP/GCE

In order to improve the catalytic activity of modified electrodes, metal content is an important issue. Electrochemical techniques provide the easy control of metal content by changing the cycle number. In this regard, Au nanoparticles were deposited with various cycle number (5, 10, 15, 20) on Ag(10cyc)/PAP(40cyc)/GCE surface.

Figure 3.67a depicts the cyclic voltammograms of modified electoredes in 1 mM DMAB containing NaOH. The oxidation peak potential of DMAB remains almost same. However, the peak current increase up to 15 cycles which decrease again for higher cycle numbers. The detailed current vs cycle number plot shown in Figure 3.67b. Au(15cyc)-Ag(10cyc)/PAP/GCE was chosen as an optimum electrode for electro oxidation of 1 mM DMAB in 2 M NaOH supporting electrolyte.

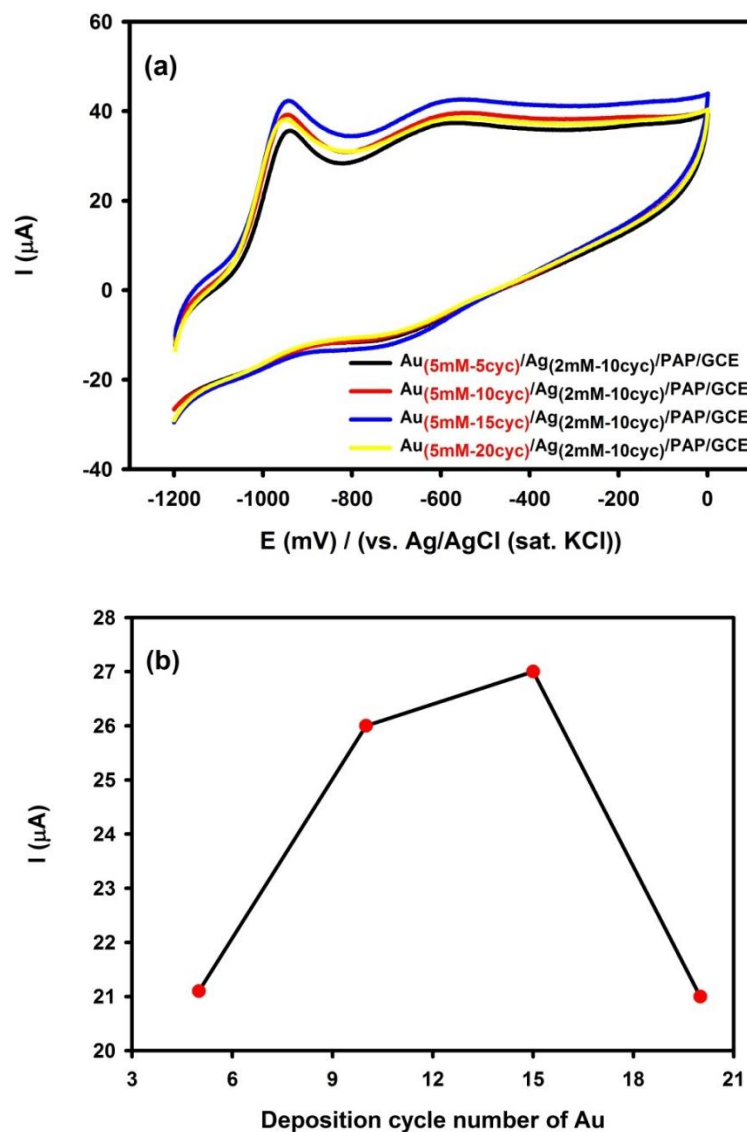


Figure 3.67 a) CVs of 1 mM DMAB oxidation at Au(Xcyc)-Ag(10cyc)/PAP/GCE b) Effect of cycle number on peak current.

Optimization of Ag nanoparticle deposition cycle number for preparation of Au/Ag/PAP/GCE

Ag nanoparticles were deposited with various cycle numbers (5, 7, 10, 15, 20) on PPAPGCE surface which then Au deposited with 15. Figure 3.68 represents the current and potential change of DMAB with Ag nanoparticle deposition cycle number. The potential shifted to more negative up to 10 cycles as desired, which then shifted to positive with the increasing cycle number. Peak currents of DMAB oxidation on Au(15cyc)-Ag(10cyc)/PAP/GCE increase up to 10 cycles and decrease again above that cycle number. In conclusion, 10 cycles of Ag deposition show the best catalytic activity towards DMAB oxidation in alkaline solution. Finally Au(15cyc)-Ag(10cyc)/PAP/GCE was chosen as an optimum electrode for further studies.

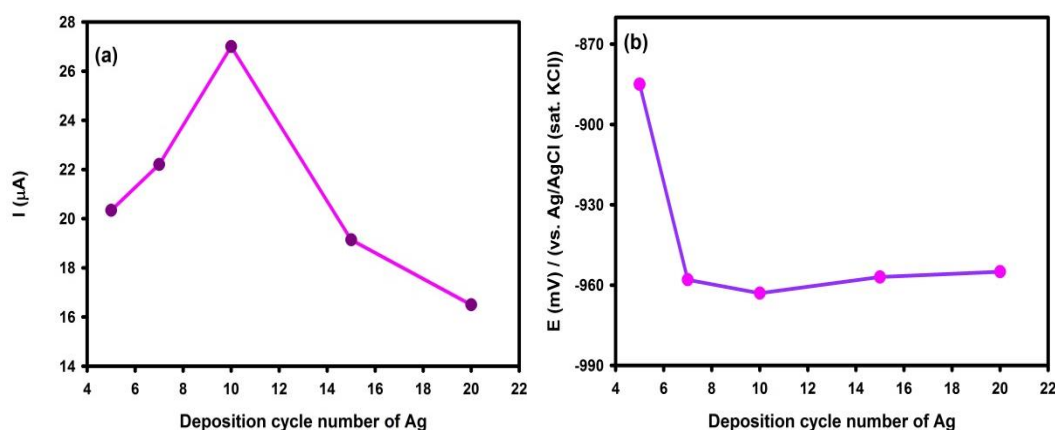


Figure 3.68 Plots for the effect of Ag nanoparticles deposition cycle number on a) peak current and b) peak potential of 1 mM DMAB oxidation at Au/Ag/PAP/GCE.

Optimization of NaOH concentration

In fuel cell studies, alkaline media is preferred for operational purposes. The effect of NaOH concentrations on the DMAB oxidation investigated in the concentration range of 0.5 to 3.0 M Au/Ag/PAP/GCE that represented in Figure 3.69.

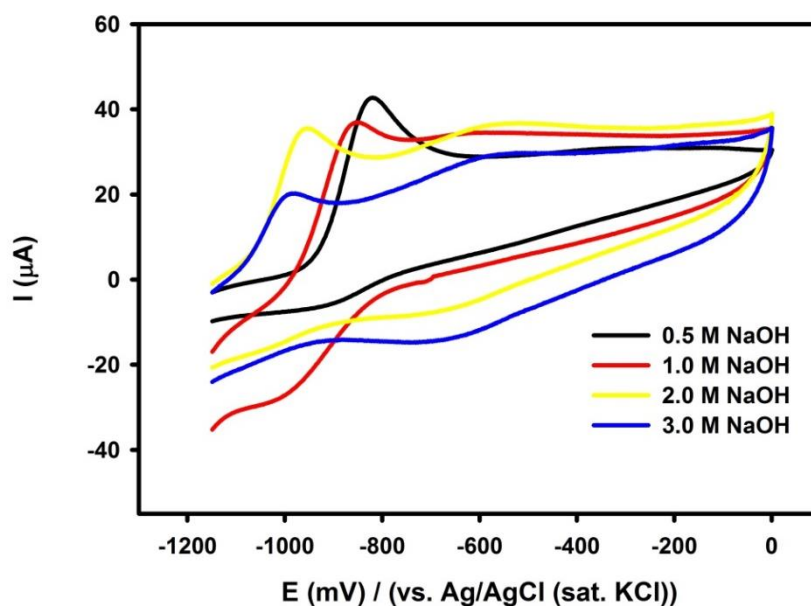


Figure 3.69 Effect of supporting electrolyte concentration on 1 mM DMAB oxidation at Au/Ag/PAP/GCE.

Dependence of peak current and potential on NaOH concentration plotted in Figure 3.70. The peak potential was shifted to negative values by increasing NaOH concentrations. However, the peak current remains almost same until reached to 2 M that decrease above that value. It is known that DMAB is relatively stable at high pH values. Therefore, 2 M NaOH medium was selected as the optimum supporting electrolyte since it provides a satisfactory shift in the peak potential.

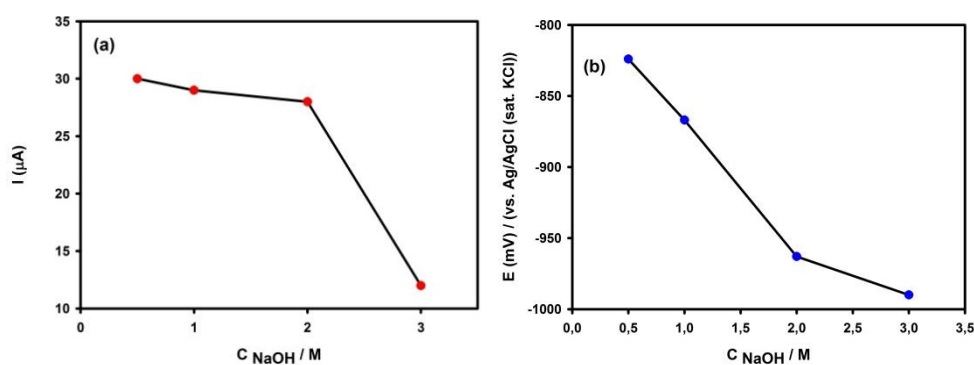


Figure 3.70 Plots for the effect of NaOH concentration on a) peak current and b) peak potential of 1 mM DMAB oxidation at Au/Ag/PAP/GCE.

Scan rate study for DMAB oxidation on Au/Ag/PAP/GCE

Cyclic voltammetric response of Au/Ag/PAP/GCE in 1 mM DMAB containing 2 M NaOH with various scan rates (3 mVs^{-1} - 1000 mVs^{-1}) were shown in Figure 3.71. DMAB oxidation peak current increases with the increase of scan rate and peak potential slightly shifted to positive potentials.

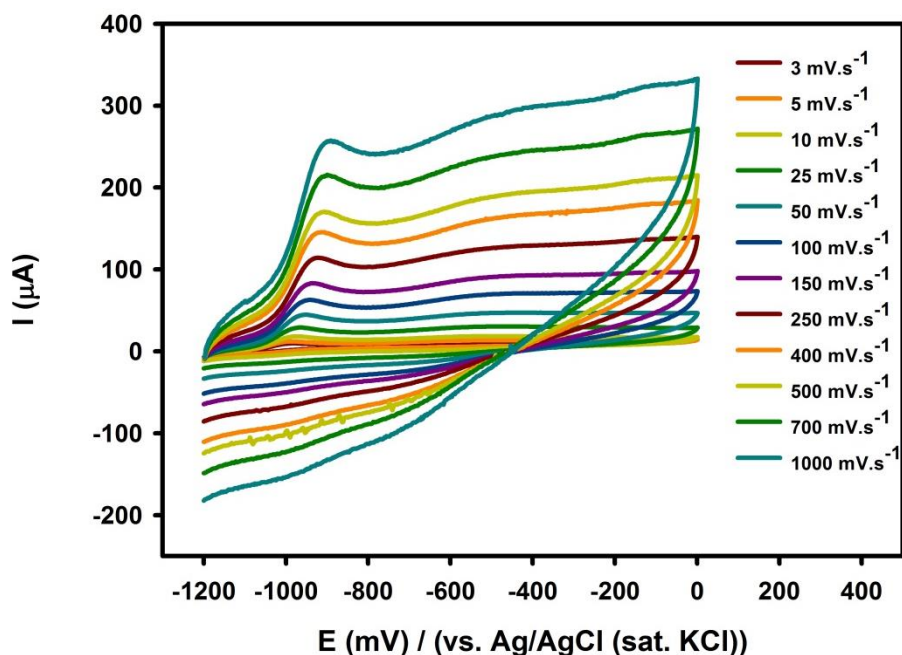


Figure 3.71 Cyclic voltammograms of Au/Ag/PAP/GCE for DMAB oxidation with different scan rates: 3-1000 mV.s^{-1} .

Figure 3.72 represents the dependence of peak current to square root of scan rate and logarithm of scan rate to peak potential for DMAB oxidation on Au/Ag/PAP/GCE. The peak current of DMAB was directly proportional to the scan rate in the range of 3–1000 mVs^{-1} . The linear regression equation was $i_p (\mu\text{A}) = 3.2529v^{1/2} (\text{mVs}^{-1})^{1/2} + 0.8643$ with a correlation coefficient of $R^2 = 0.9981$. These datas show that the electrode reaction controlled by diffusion of DMAB to electrode surface (Figure 3.72a). In addition, plot of peak potential vs logarithm of scan rate was shown in Figure 3.72b. In reversible reactions, peak potentials are not dependent on scan rate, whereas the logarithm of the square root of the scan rate has a linear dependence with peak potential reaction is irreversible.

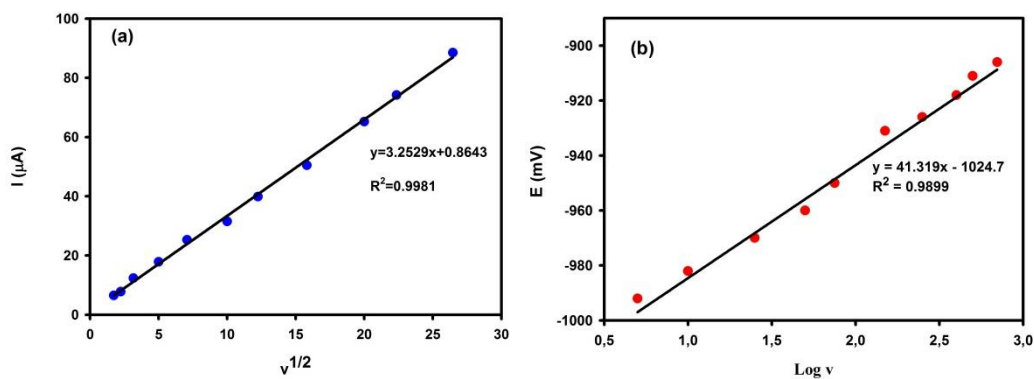


Figure 3.72 a) Square root of the scan rate vs. current and b) Logarithm of scan rate vs. potential graphics from scan rate study of Au/Ag/PAP/GC electrode.

The voltammetric response and corresponding calibration plot of peak currents vs. concentrations shown in Figure 3.73. The responses of background and increasing concentrations (1, 3, 5, 8 and 10 mM) of DMAB on Au/Ag/PAP/GCE in 2 M NaOH solution shown in the same figure. By the increasing of DMAB concentration, oxidation peak currents increase from 27 to 270 μA and the peak potential remains almost stable. The peak current value were directly proportional with the increasing concentrations of DMAB with a correlation of 0.9973. The results indicated the possible use of Au/Ag/PAP/GCE as amperometric sensor for DMAB. In addition, the stable peak characteristics at wide concentration range, especially higher concentrations, prove that this modified electrode can be successfully used in fuel cell applications for every concentration value.

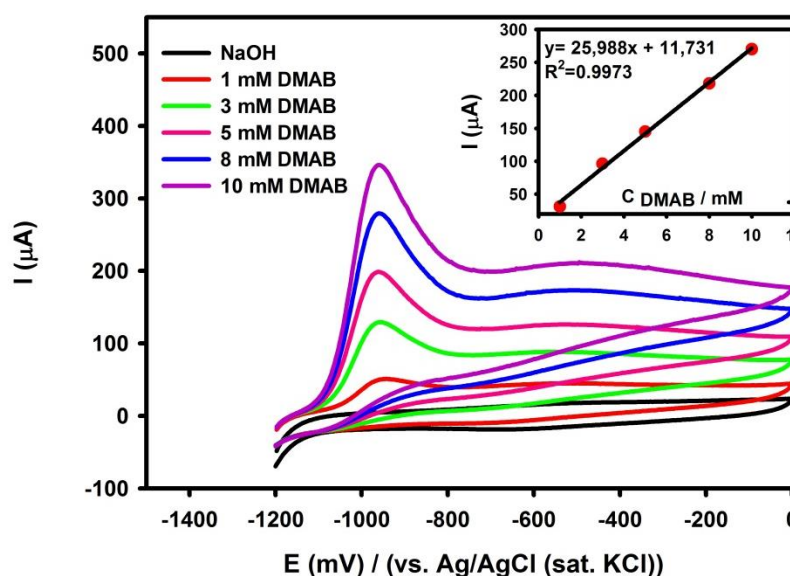


Figure 3.73 Cyclic voltammograms of Au/Ag/PAP/GCE in the absence and presence of 1-10 mM DMAB in 2M NaOH. Inset: Plot for the peak current of Au/Ag/PAP/GCE vs. DMAB concentration.

Breifly, DMAB was investigated at Au/Ag/PAP/GCE in alkaline medium that some optimization studies were carrying out in order meliorates the catalytic activity. Result from the optimization studies, the best catalytic activity obtained at an electrode that sequentially modified with electrochemical technique by following the order; 40 cycles polymer modification on GCE then 10 cycles applied in 2 mM AgNO_3 solution which followed by 15 consecutive cycles in 5 mM HAuCl_4 solution to obtained reduced form of metal particles. The resulted Au/Ag/PAP/GCE used for the investigation of DMAB oxidation in 2 M NaOH solution.

Electroactive surface areas of GCE, Ag/PAP/GCE and Au/Ag/PAP/GCE

The electroactive surface area (ESA) was generally determined by CV with ferrocyanide-ferricyanide redox couple which involves one electron per molecule with a reversible redox characteristic (Prasad et al., 2012; Ndlovu et al., 2012). CVs were recorded at various scan rates in ferro-ferricyanide redox couple containing solution and square root of scan rate versus peak current was plotted. After then ESA can be calculated based on the Randles–Sevcik equation:

$$i_p = (2.69 \times 10^5) n^{3/2} A C D^{1/2} \nu^{1/2}$$

n is the number of electrons transferred in the redox process, A is the active area of the electrode (cm^2), D is the diffusion coefficient ($\text{cm}^2 \text{s}^{-1}$), C is the concentration of electroactive species (mol cm^{-3}), and ν is the scan rate value (V s^{-1}). The ferro-ferricyanide system involves one electron therefore n value was taken as 1, D was taken as $6.70 \times 10^{-6} \text{ cm}^2 \cdot \text{s}^{-1}$ (Lu et al., 2007), ferro-ferricyanide concentration (C) was taken as $10^{-6} \text{ mol} \cdot \text{cm}^{-3}$ and scan rate studies were carry out for all bare and modified electrodes ($10\text{-}350 \text{ mV} \cdot \text{s}^{-1}$). If the slope value of square root of scan rate versus peak current plot put in the equation, the only unknown component of equation (A) can be calculated. To investigate the ESA of bare and modified electrodes the CVs were recorded with different scan rates and related equations and calculated ESA values were summarized in Table 3.11. According to the table, the all geometric area of the bare GCE is not electrochemically active which often happens that was observed same as in the related literature (Carvalho et al., 2010). In the presence of polymer film and MNPs modified polymer film electrodes lead to an increase of the electroactive area. The larger electroactive surface area justifies the higher current values that obtained for DMAB oxidation in the same order.

Table 3.11 Equation of square root of scan rate versus peak current and ESA of various electrodes from CVs in 1 mM $\text{K}_4\text{Fe}(\text{CN})_6/0.1 \text{ M KCl}$.

Electrode	Equation	ESA(cm^2)
GCE	$y = 4.10^{-5}x + 5.10^{-7}$	0.056
PAP/GCE	$y = 2.10^{-4}x + 1.10^{-5}$	0.290
Ag/PAP/GCE	$y = 4.10^{-4}x + 2.10^{-5}$	0.574
Au/Ag/PAP/GCE	$y = 5.10^{-4}x + 6.10^{-5}$	0.743

Investigation of DMAB oxidation on rotating Au disk,
Ag/PAP/GCE and Au/Ag/PAP/GC electrodes

The rotating disk electrode (RDE) technique is a convenient technique to determine of kinetics and the mechanism of electrochemical electrode reactions. Linear sweep voltammetric studies were performed on rotating gold disk, Ag/PAP and Au/Ag/PAP with modified GC electrodes in the absence and presence of dimethylamine borane at the 2.0 M NaOH to determine the kinetic parameters more quantitatively. In linear sweep voltammetry, the number of electrons involved in an oxidation reaction at a chosen potential can be obtained from the Koutecky–Levich (K–L) equation (Bard and Faulkner, 2001). The RDE datas were analyzed using the Koutecky–Levich equation, which in case of a thin Ag/PAP, Au/Ag/PAP on the GCE can be expressed as follows:

$$\frac{1}{j} = \frac{1}{j_k} + \frac{1}{B\omega^{1/2}}$$

where j is the measured current density, j_k is the kinetic current density, ω is the electrode rotation rate (rad/s). The theoretical value of the Levich slope (B) is evaluated from Eq.

$$B = 0.62nFC_{DMAB}D_{DMAB}^{2/3}\gamma^{-1/6}$$

where n is the number of electrons transferred for DMAB, F is Faraday constant (96485 C mol^{-1}), C_{DMAB} is the concentration of DMAB in 2.0 M NaOH ($5\times 10^{-6}\text{ mol cm}^{-3}$), D_{DMAB} is the diffusion coefficient of DMAB ($7.48\times 10^{-6}\text{ cm}^2\text{ s}^{-1}$), γ is the kinematic viscosity of the solution ($0.0117\text{ cm}^2\text{ s}^{-1}$). Kinematic solution viscosity is $1.17\times 10^{-2}\text{ cm}^2\text{ s}^{-1}$ determined with Oswald viscosimeter at $25\text{ }^{\circ}\text{C}$. According to Equations, the n was calculated from the slope of the Koutecky–Levich plot j^{-1} vs. $\omega^{-1/2}$ at different electrode potentials. In RDE experiment, D_{DMAB} , the diffusion coefficient for DMAB in alkaline solution was used as $7.48\times 10^{-6}\text{ cm}^2\text{ s}^{-1}$ and $8.55\times 10^{-6}\text{ cm}^2\text{ s}^{-1}$, respectively, reported in earlier literature (Nagle and Rohan, 2005, Sargent et al, 2001). In addition, diffusion coefficient for DMAB oxidation on polycrystalline Au was founded as $1.7\times 10^{-5}\text{ cm}^2\text{ s}^{-1}$ (Plana, D. and Dryfe, 2011).

Rotating Au disk electrode

The linear sweep voltammograms (LSV) of 5.0 mM DMAB in 2.0 M NaOH at Au disc electrode is shown in Figure 3.74. In voltammogram, the peak oxidation potentials of DMAB is -0.86 V on Au disc electrode. As shown in Figure 3.74, during the sweep in the anodic direction, DMAB oxidation appeared at two steps. Two steps are located at about -800 mV and -200 mV in 2.0 M NaOH. In the literature, the oxidation of DMAB on Au electrodes at alkali media have described by Nagle and Rohan. According to their published work, the first step of voltammogram involves three electrons and the second step involves a further three-electron transfer too. Totally, six-electron transfer is occurred by a supposed mechanism (Nagle and Rohan, 2005).

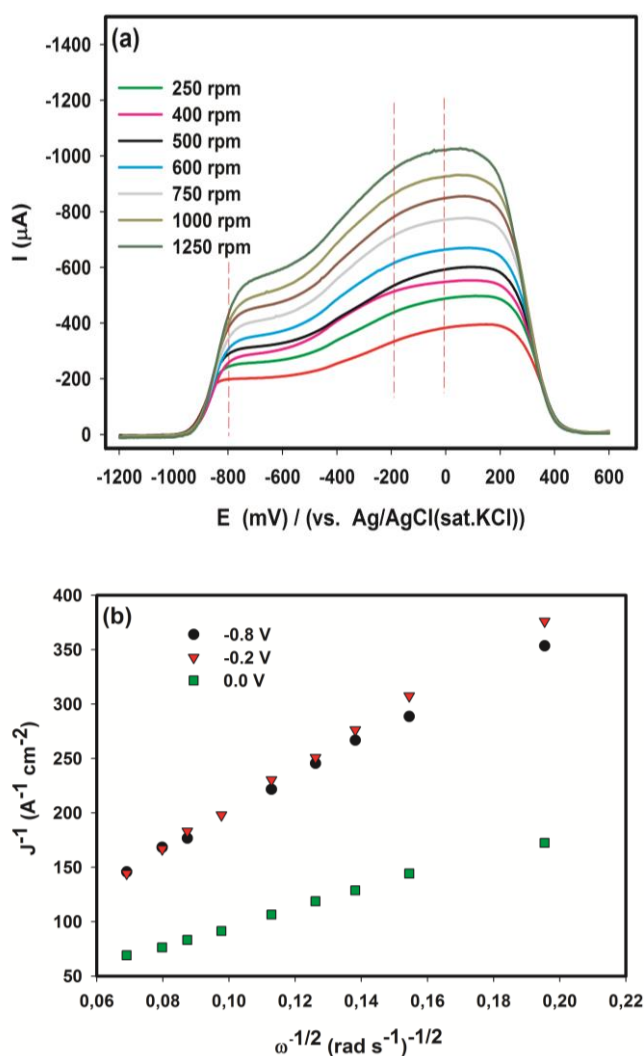


Figure 3.74 a) LSVs of rotating Au disk electrode in the presence of 5.0 mM DMAB solution in 2.0 M NaOH at different rotation rates (250 to 1250 rpm). b) Koutecky–Levich (K-L) plots of Au disk electrode at different potentials obtained from I–E Figure 3.74a.

In order to determine the number of electrons during DMAB oxidation, LSV's (Figure 3.74a) was obtained at different electrode rotation rates (50 rpm - 1250 rpm) with Au disk electrode. The transferred electron number (n) of DMAB oxidation on the Au disk electrode was calculated based on the K-L plots ($j^{-1} - \omega^{-1/2}$) in Figure 3.74b.

According to the K-L equation, behaviour of the limiting current densities of 5.0 M DMAB in 2.0 M NaOH varied with rotation rates at (Figure 3.74b). From the calculated slope of the so-called B factor (B^{-1}), the number of electron transferred at Au disk electrode during the DMAB oxidation is determined for each potential. These values are summarized in Table 3.12. The K-L plots at -800 mV, -200 mV, and 0.0 mV, in Figure 3.74b, exhibit a good linearity with the slope. Therefore, the electron number value was calculated as 2.52 in the first step and 2.25 in the second step that total electron transfer found as 4.77. In addition, electron number during oxidation of DMAB was calculated as 4.89 at high potential (0.0 mV).

Table 3.12 Equation components of the Kotecky-Levich plots and calculated electron numbers for the 5.0 mM DMAB oxidation at Au disk electrode in 2.0 M NaOH solutions.

Peak	I _{peak} (-800 mV)	II _{peak} (-200 mV)	(0 mV)
Slope of plot	1642.9	1836.7	846.69
Intercept of plot	35.497	20.42	10.288
R ²	0.9984	0.9988	0.9965
n	2.52	2.25	4.89

Rotating Ag/PAP/GC electrodes

The linear sweep voltammograms of 5.0 M DMAB in 2.0 M NaOH at Ag/PAP/GCE is shown in Figure 3.75a. In order to determine the number of electrons during DMAB oxidation, voltammograms were obtained at different rotation rates (250 rpm - 1500 rpm). DMAB oxidation was occurred in two steps. The K-L graphs (j^{-1} vs. $\omega^{-1/2}$) of various potentials were shown in Figure 3.75b to calculate the number of electrons involved in the DMAB. From the calculated slope of K-L plot, the number of electron transferred during the DMAB oxidation at Ag/PAP/GC electrode is determined for each potential. These values summarized in Table 3.13.

The slope of K-L plots at -800 mV, -200 mV, and 0 mV, in Figure 3.76b, exhibit a good linearity. The transferred electron number (n) value was calculated as 2.33 in the first step (at -800 mV) and 2.50 in the second step (at -200 mV) that total electron transfer found as 4.83. In addition, electron number during oxidation of DMAB was calculated as 5.06 at high potential (0.0 mV). The electron transference number of Ag/PAP/GC electrode was almost same with gold electrode.

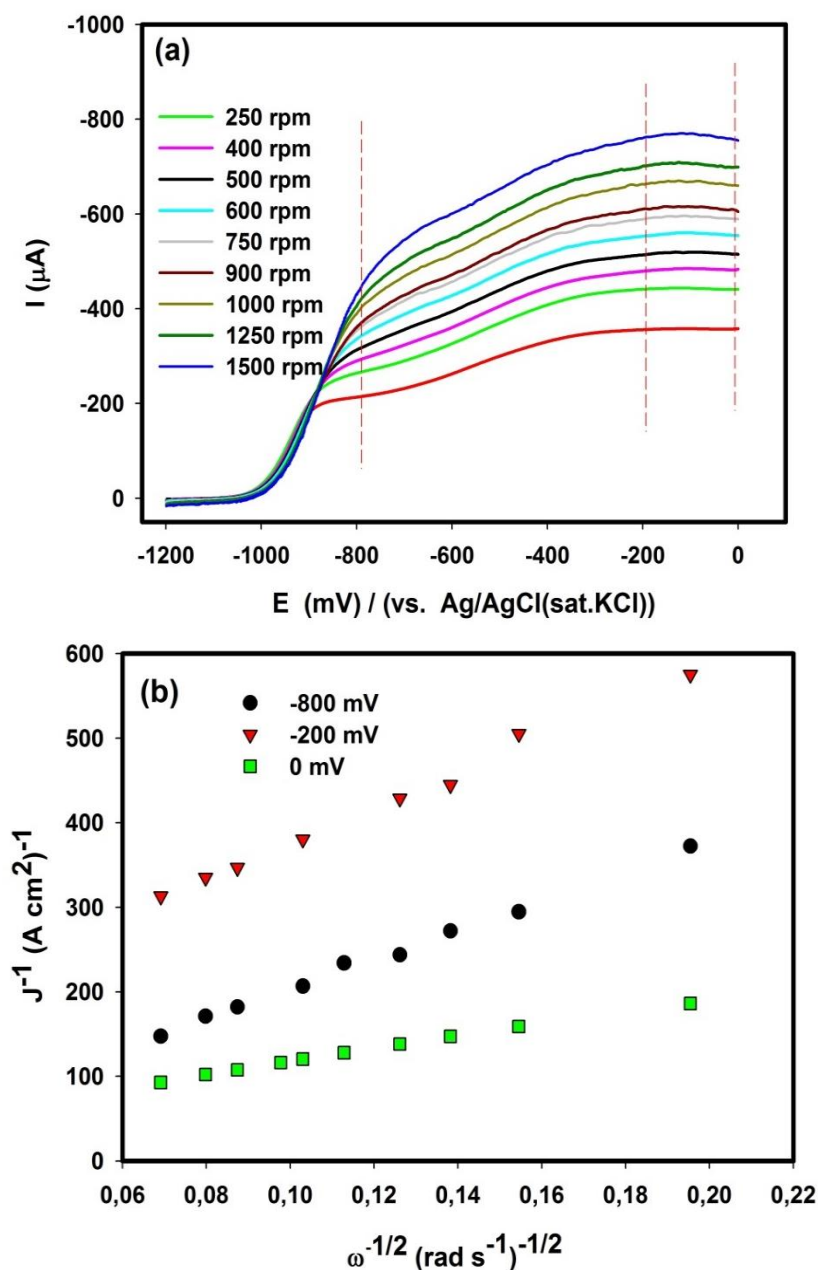


Figure 3.75 a) LSVs of rotating Ag/PAP/GC electrode in the presence of 5.0 mM DMAB solution in 2.0 M NaOH at different rotation rates (250 to 1500 rpm). b) Koutecky–Levich (K-L) plots of Ag/PAP/GC electrode at different potentials obtained from I–E Figure 3.75a.

Table 3.13 Equation components of the Kotecky-Levich plots and calculated electron numbers for the 5.0 mM DMAB oxidation at Ag/PAP/GC electrode in 2.0 M NaOH solutions.

Peak	I.peak (-800 mV)	II.peak (-200 mV)	(0 mV)
Slope of plot	1743.3	1654	741.31
Intercept of plot	29.368	188.65	43.444
R^2	0.9966	0.9903	0.9980
n	2.33	2.50	5.60

Rotating Au/Ag/PAP/GC electrodes

Owing to the excellent catalytic effect of bimetallic nanoparticles, DMAB oxidation was investigated at Ag and Au nanoparticles modified PAP/GCE. This electrode was prepared by dipping the Ag/PAP/GCE into HAuCl_4 solution and performed by repetitive potential cycles. The LSV of 5.0 M DMAB in 2.0 M NaOH at Au/Ag/PAP/GCE is shown in Figure 3.77a. In voltammetric study, voltammograms were obtained at different rotation rates (250 rpm - 1500 rpm). As shown in Figure 3.76a, DMAB oxidation was occurred in two steps. The K-L graphs (j^{-1} vs. $\omega^{-1/2}$) of various potentials were shown in Figure 3.76b to calculate the number of electrons involved in the DMAB oxidation.

The number of electron transferred during the DMAB oxidation at Au/Ag/PAP/GC electrode in 2.0 M NaOH is determined for each potential that calculated from the slope of K-L plot. These values are summarized in Table 3.14. In Figure 3.76b, K-L plot slopes at -800 mV, -200 mV, and 0 mV exhibit a good linearity. The transferred electron number (n) value was calculated as 3.20 in the first step (at -800 mV) and 2.67 in the second step (at -200 mV). Moreover, the total electron number during oxidation of DMAB was calculated as 5.93 at high potential (0 mV). The total value of first and second step electron number was close to the obtained high potential electron number as suggested. DMAB oxidation followed 6.0 e⁻ pathway on Au surfaces that obtained results are compatible with previous studies (Nagle and Noyan, 2005; Sadik et al., 2005).

The Au/Ag/PAP/GC electrode displays an excellent electrocatalytic activity for DMAB oxidation than that of an Ag/PAP/GCE and Au disk electrode. The synergistic effect of electrodes prepared by incorporation of Au and Ag modified PAP at glassy carbon electrode surface can significantly improve the electrode activity for DMAB oxidation. According to our knowledge, there have been no report published about the development of Au and Ag bimetallic nanoparticles modified PAP film glassy carbon electrode towards DMAB oxidation.

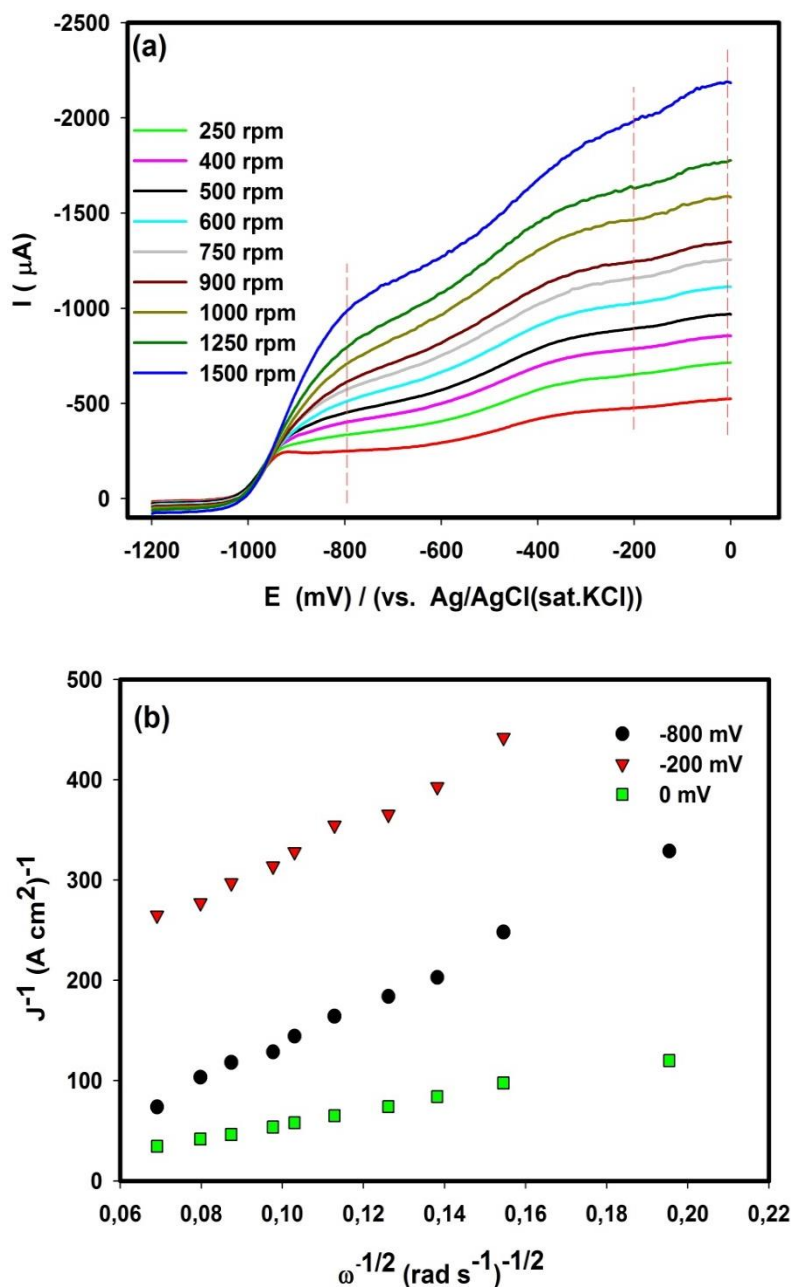


Figure 3.76 a) LSVs of rotating Au/Ag/PAP/GC electrode in the presence of 5.0 mM DMAB solution in 2.0 M NaOH at different rotation rates (250 to 1500 rpm). b) Koutecky–Levich (K-L) plots of Au/Ag/PAP/GC electrode at different potentials obtained from I–E Figure 3.76a.

Table 3.14 Equation components of the Kotecky-Levich plots and calculated electron numbers for the 5.0 mM DMAB oxidation at Au/Ag/PAP/GC electrode in 2.0 M NaOH solutions.

Peak	I.peak (-800 mV)	II.peak (-200 mV)	(0 mV)
Slope of plot	1295.8	1550.8	697.53
Intercept of plot	-1.8368	148.58	-13.803
R ²	0.9805	0.985	0.9964
n	3.20	2.67	5.93

3.3.1.3 Characterization of polymer film electrodes

In order to understand the morphology and prove the existence of modifiers on the prepared surfaces, characterization techniques used. For this purpose, metal nanoparticles modified polymer film GC electrodes characterized with SEM, EDX, TEM, XPS and EIS techniques.

Figure 3.77 shows the SEM images of bare GCE, PAP/GCE, Ag/PAP/GCE and Au/Ag/PAP/GCE. The smooth electrode surface image obtained for bare GCE in Figure 3.77a. The polymer film modification on bare surface obviously change the surface image that sheet like illustration proves the polymer coverage (Figure 3.77b). Figure 3.77c represents the spherical Ag nanoparticles that distributed on all over the polymer sheets. In case of Au nanoparticles deposition on Ag/PAP/GCE surface, surface image obviously change. This difference between bare, PAP/GCE, Ag/PAP/GCE and Au/Ag/PAP/GCE, helps to clarify the different catalytic activity of electrodes towards DMAB oxidation. Au nanoparticles were deposited on the Ag nanoparticles modified PAP surface with round shaped that seen bright. The dense deposition of gold nanoparticles on polymer surface may be resulted from the catalytic effect of Ag nanoparticles existence, which probably facilitates the Au nanoparticles deposition. Some growing clannish parts observed in Figure 3.77d that supported this suggestion.

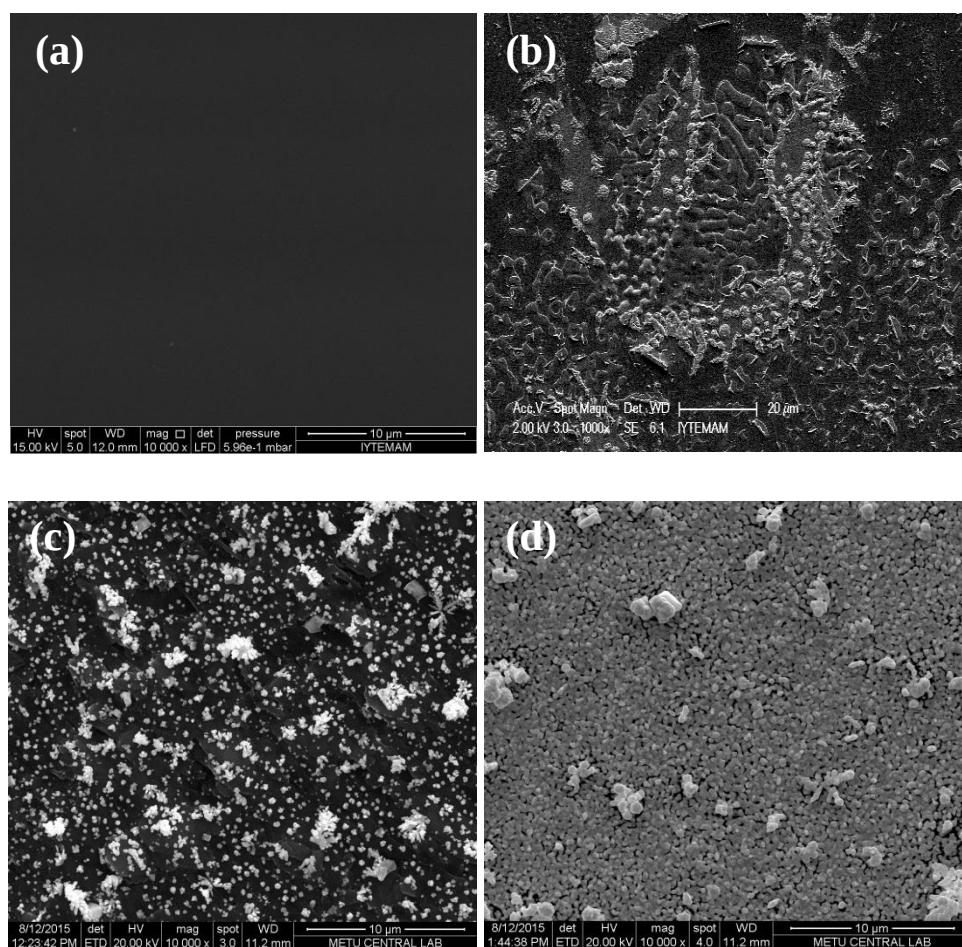


Figure 3.77 SEM image of the a) Bare GCE, b) PAP/GCE, c) Ag/PAP/GCE and d) Au/Ag/PAP/GCE.

EDX results of Ag/PAP/GCE and Au/Ag/PAP/GCE shown in Figure 3.78. The weight percentages that obtained from EDX study were prove the existence of nano gold and silver on polymer modified surface.

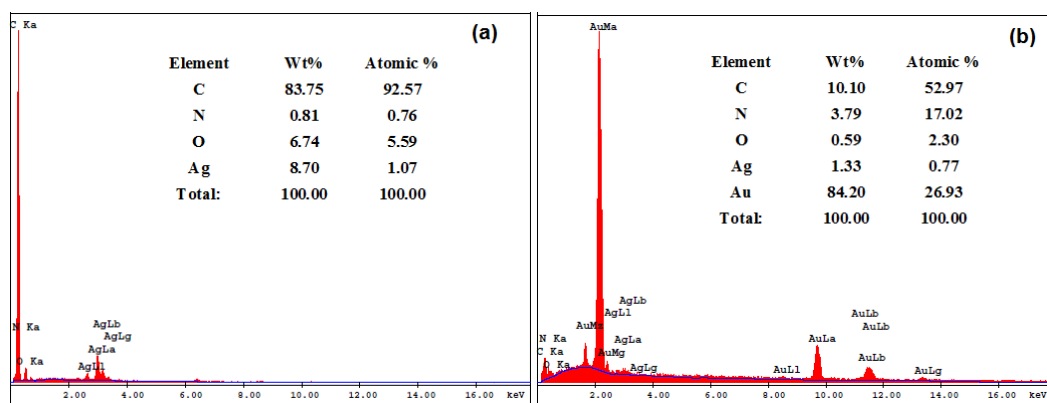


Figure 3.78 EDX results of the a) Ag/PAP/GCE and b) Au/Ag/PAP/GCE.

TEM images of Au/Ag/PAP/GCE were shown in Figure 3.79. The typical TEM images, can help to understand the morphology and particle size differences nanoparticles modification. Figure represents micrographs of Au/Ag/PAP/GCE in the decreasing focus areas from 50 nm to 20 nm. We can see that, most of the Au and Ag nanoparticles were uniformly dispersed in the range of 5-15 nm on the polymer, while some flower like clannish parts appear on the surface. These results imply the individual existence of gold and silver nanoparticles on polymer surface that there was no indication of core-shell structure.

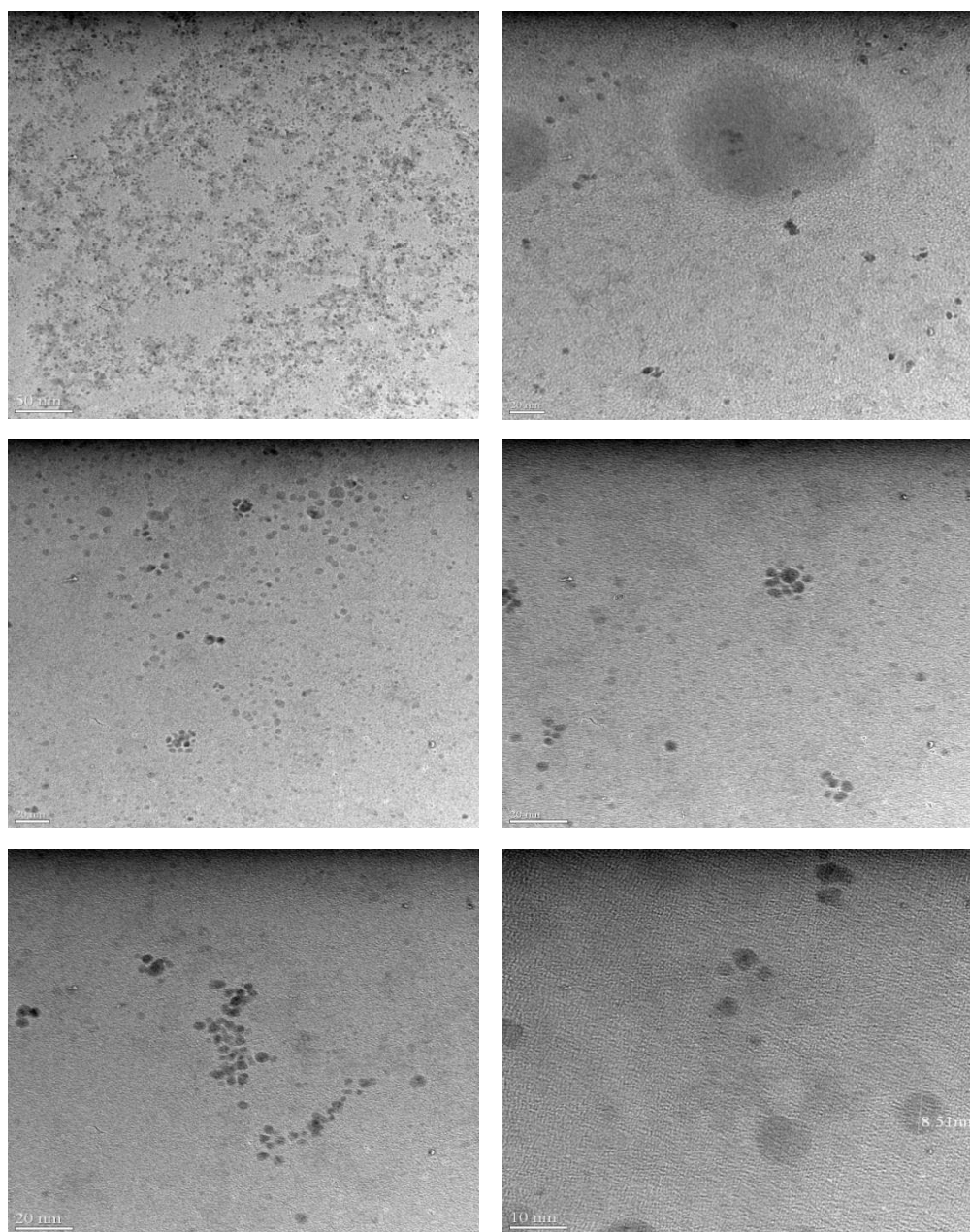


Figure 3.79 TEM images of Au/Ag/PAP/GCE with different magnifications.

XPS technique provides important information about bonding characteristics of the film and oxidation states of Au and Ag nanoparticles. Figure 3.80a and b shows the XPS survey spectra and narrow range spectrum of the sample which indicates the presence of C, O, Au and Ag, as expected. The binding energies of the Au doublets (Au 4f_{7/2} and Au 4f_{5/2}) were at about 84.14 and 88.08 eV, respectively, showing that the metallic Au was the dominant component (Figure 3.80c). The results were coherent with our previously published literature (Bakır et al., 2011). Figure 3.80d exhibits the binding energies of Ag doublets (Ag 3d_{5/2} and Ag 3d_{3/2}) at about 368.39 and 374.08 eV, respectively, which verify that the Ag species on the aminophenol polymer film are chiefly dispersed as metallic Ag. Therefore, XPS results prove the metallic gold and silver nanoparticles on modified surface.

Figure 3.81a shows the electrochemical impedance spectroscopy results of bare GCE, PAP/GCE, Ag/PAP/GCE and Au/Ag/PAP/GCE in the presence 5.0 mM DMAB solution at 2.0 M NaOH at a frequency range of 0.05 to 50 000 Hz at the formal potential. A large semicircle was obtained for bare GCE in the presence 5.0 mM DMAB solution at 2.0 M NaOH, indicating that there was a high electron transfer resistance. Dots represent the experimental data points, and continuous lines represent simulated curve using the equivalent circuit (Figure 3.81b).

The equivalent circuit responsible for the electrode and its surrounding electrolyte interface that fits with the R(R(C)) circuit design (Figure 3.81 inset). As shown in Figure 3.81a, Nyquist plots shows only a semi-circle that Warburg element does not exist or it cannot give signal (Uygun at al. 2014). The results of simulated curves also show that R_{ct} values are in well agreement with the circuit when Warburg impedans does not exist. The EIS data were fitted with this equivalent circuit and obtained values were shown in Table 3.15. The Au/Ag/PAP/GCE shows a lower interfacial electron transfer resistance (960 Ω) than that of the Ag/PAP/GCE (1490 Ω) and of PAP/GCE (6150 Ω). This phenomenon indicated that the excellent electroconductibility of Au/Ag/PAP/GCE bimetallic surface. Moreover, prove the successfully formation of Au/Ag/PAP/GCE film on the GCE surface.

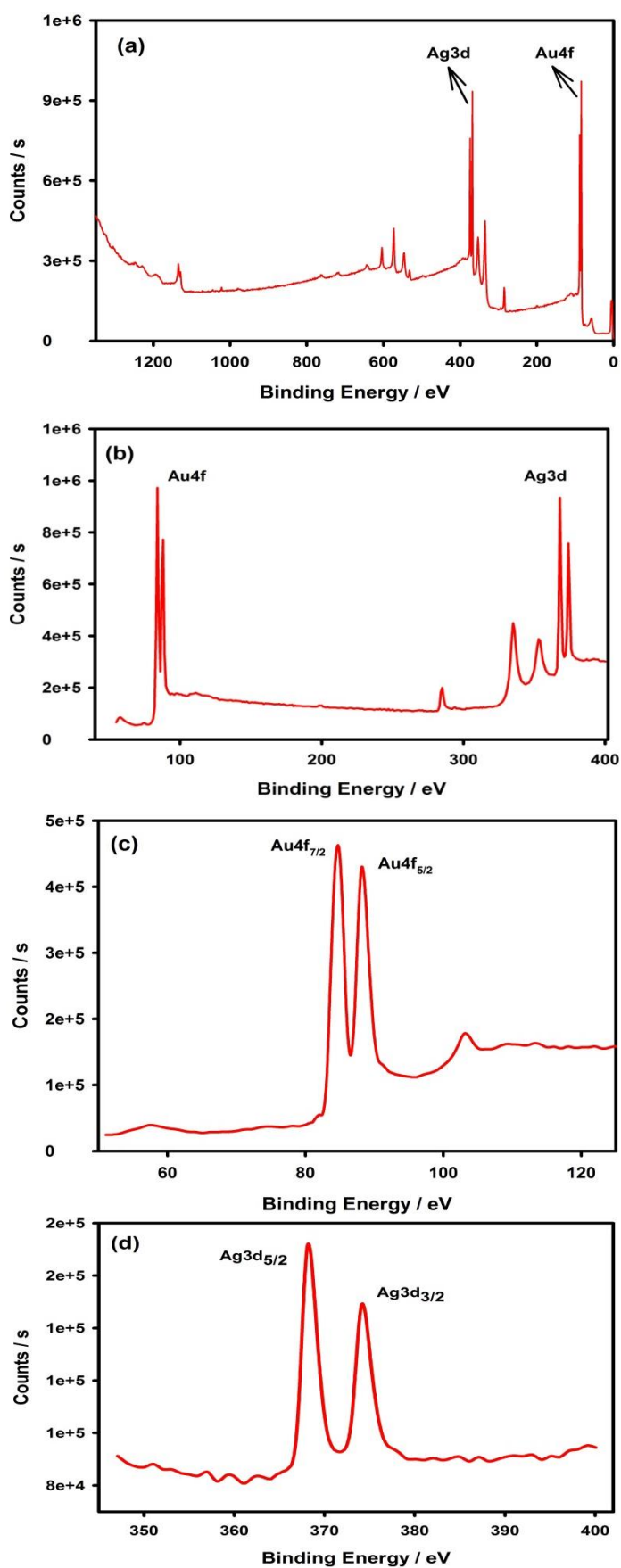


Figure 3.80 XPS results. a) survey spectrum b) narrow range survey spectrum c) Au 4f binding energies and d) Ag 3d binding energies of the Au/Ag/PAP/GCE.

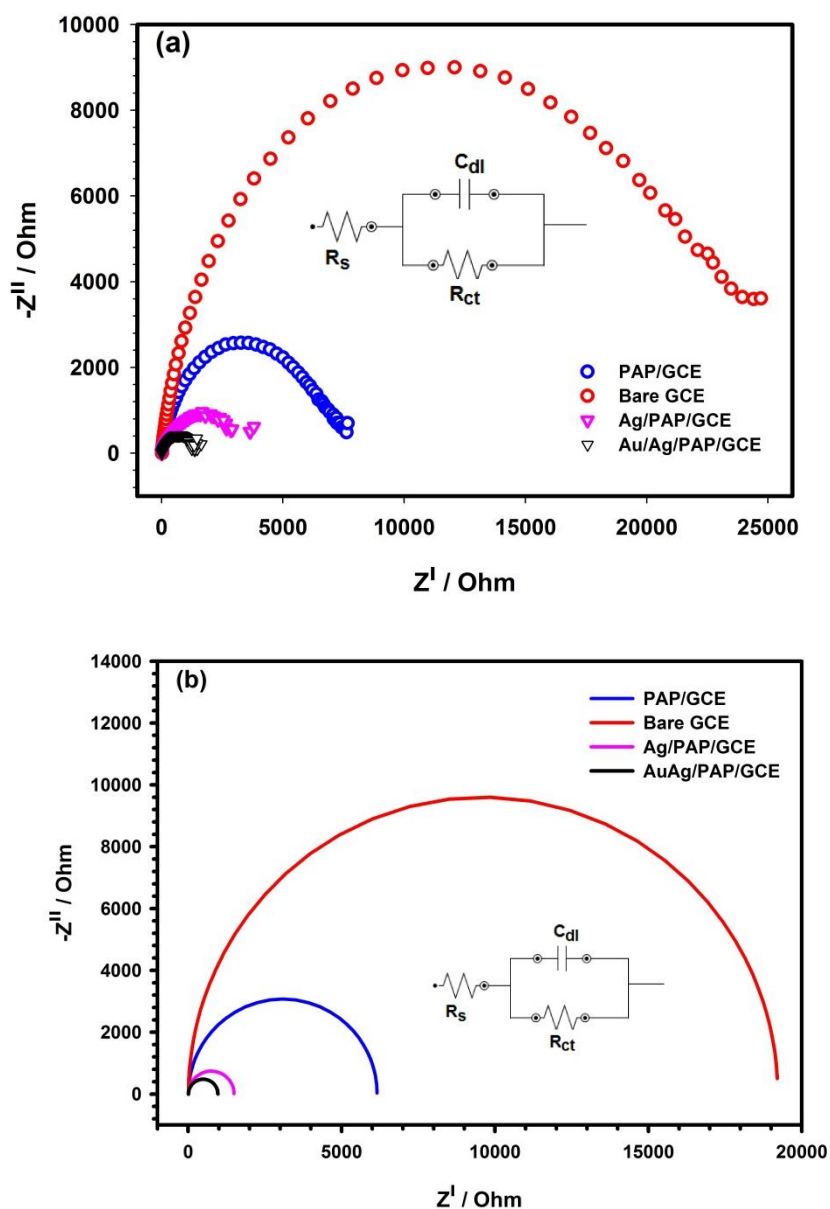


Figure 3.81 a) Nyquist plots of bare GCE, PAP/GCE, Ag/PAP/GCE and Au/Ag/PAP/GCE in 5.0 mM DMAB solution in 2.0 M NaOH. The frequencies ranged from 0.05 to 50 000 Hz. b) simulated curves using the equivalent circuit for the same electrodes.

Table 3.15 The R_s , R_{ct} and C_{dl} values of bare and modified electrodes.

Electrode	R_s (Ω)	C_{dl} (μF)	R_{ct} (Ω)
Bare GCE	11.9	4.3	19200
PAP/GCE	10.7	3.0	6150
Ag/PAP/GCE	11.0	25.2	1490
Au/Ag/PAP/GCE	10.8	14.2	960

3.3.2 Dimethylamine borane oxidation at Pc and CNT based composite electrodes

Phthalocyanines were two dimensional aromatic macromolecules that used as an electrode material for various kinds of applications due to their physicochemical properties (Zuo et al., 2012). Carbon nanotubes are special form of carbon with a tubular shape were important materials due to their extraordinary strength, high surface area, thermal and electrical conductivity (Wang et al., 2004). Because of their special properties, CNTs were found various application fields such as fuel cells. CNTs were given preference in fuel cells not only by their ability to hydrogen storage but also being a good candidate for catalyst support that used as an electrode. As hydrogen storage material, hydrogen adsorbed and stored in the interstitial parts and inside of the tubular forms of carbon nanotubes by physisorption. In addition, CNTs are excellent supporting materials for platinum and nonplatinum modified catalyst surfaces (Zhang and Silva, 2011; Miller et al., 2015; Huang et al., 2015). In this thesis, carbon nanotubes were combined with phthalocyanines that used as an electrode material especially as a support for metal nanoparticles.

3.3.2.1 Preparation of metal nanoparticles modified Pc and Pc-CNT composite electrodes

To improve the catalytic effect of copper phthalocyanine-carbon nanotube composite electrode towards DMAB oxidation, Au, Cu, Pt, Ag, Ni, Pd, Co, and Ru nano particles were formed on the electrode surfaces by cyclic voltammetry technique.

Electrochemical preparation of Au, Cu, Pt, Ag, Ni and Pd nano particles were described in section 3.1.1 and also Co and Ru nano particles were described in section 3.2.1 in detailed before. The previously explained Figure 3.1 and Figure 3.2 show the redox peaks related to the formation of metal nano particles on the composite electrode surfaces.

3.3.2.2 Electrochemical behavior of dimethylamine borane

DMAB oxidation on metal nano particles modified Pc/GCE

Electrooxidation of DMAB was investigated on the Pc modified GCE and their metal nano particles deposited forms. Figure 3.82 shows the response of the Pc/GC electrode in the absence and presence of 5 mM to 30 mM increasing DMAB in 1 M NaOH. Broad oxidation peak of DMAB take place at approximately -300 mV with poor current value about 1 μ A.

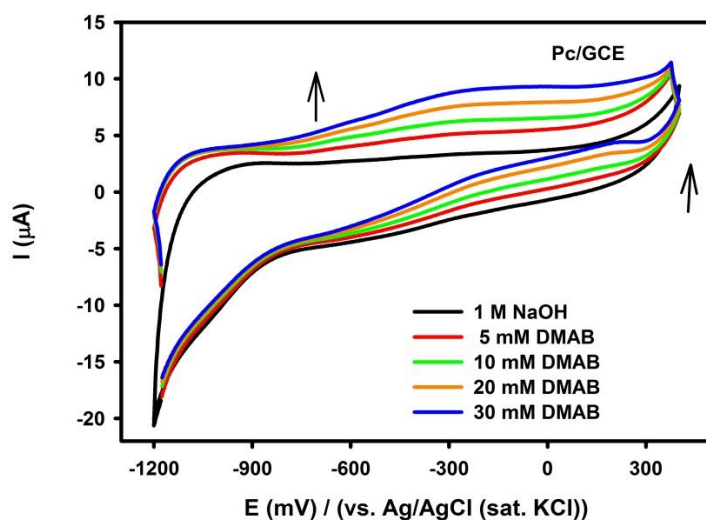


Figure 3.82 Cyclic voltammograms of increasing concentrations of DMAB at CuPc/GCE.

The weak oxidation reaction behavior of Pc modified glassy carbon electrode was giving an impression of metal nanoparticle need to improve the response of the electrode. Au, Pt, Co, Ni, Pd, Ru nano particles were prepared on the Pc/GCE surface by electrochemical techniques and their effect on various concentration of DMAB was investigated in alkaline solution. Figure 3.83 exhibits the behavior of Au, Pt and Co nano particles modified Pc/GC electrodes in the absence and presence of 5, 10, 20 mM DMAB.

In Figure 3.83a, a broad peak, starts from -950 mV and ends at +300 mV was observed for DMAB oxidation at -297 mV on Au/Pc/GCE. In the backward scan, a reactivation (reverse oxidation) peak was observed at about -200 mV. All peak currents related for DMAB oxidation were increase by the increase of DMAB concentration as unsurprisingly. DMAB oxidation occurred at 49 mV at Pt/Pc/GCE (Figure 3.83b).

Reactivation peak was observed at more negative potentials (-500 mV) compared with the Au containing surfaces which was coherent with the behavior of Pt disk electrode (Plana and Dryfe, 2011). A broad and multiple oxidation peaks were observed for DMAB oxidation on Co nano particles modified Pc/GCE that shown in Figure 3.83c. The peak at about +100 mV with an anodic current was suggested as reactivation peak as observed for gold and platinum surfaces. The current of reactivation peak was higher than the main oxidation peak. All defined peak currents were rised by the increment of DMAB concentration.

Figure 3.84 shows the behavior of nickel, palladium and ruthenium nano particles modified Pc/GC electrodes in the absence and presence of 5, 10, 20 mM DMAB. A broad and multiple oxidation peaks were observed for DMAB oxidation on nickel nano particles modified Pc/GCE that shown in Figure 3.84a. Reactivation peak was observed at about +100 mV with an anodic current, which was become higher than the main oxidation peak of DMAB by the increment of concentration. The nickel NPs modified electrode was not suitable for DMAB oxidation due to the ambiguous peak shapes and unstable peak characteristic.

In Figure 3.84b, a small peak at nearly -850 mV which followed by the broad peak at -122 mV was observed for DMAB oxidation Pd/Pc/GCE. In the backward scan, a reactivation peak was observed at about -200 mV. All peak currents related for DMAB oxidation were increase by the increase of DMAB concentration as expected.

DMAB oxidation was investigated also at ruthenium nano particles modified Pc/GCE which shows two sluggish, broad oxidation peaks followed by a high reactivation peak in the reverse scan (Figure 3.84c). The oxidation peak currents were not proportional with the increasing DMAB concentration.

Peak potential and current values of unmodified and metal nano particles modified Pc/GC electrodes towards 20 mM DMAB oxidation in alkaline solution were summarized in Table 3.16 which extracted from voltammograms of Figure 3.83 and 3.84. If the overall results were interpreted, platinumium nano particles modified Pc/GCE was showed better activity in terms of high peak current values, albeit the positive oxidation potential, compared to the Au, Co, Ni, Pd, Ru nano particles modified Pc/GC electrodes. Au, Co, Ni, Pd, Ru was not appropriate modifiers for DMAB oxidation on Pc/GC electrodes due to their ambiguous peak forms and unstable peak characteristics.

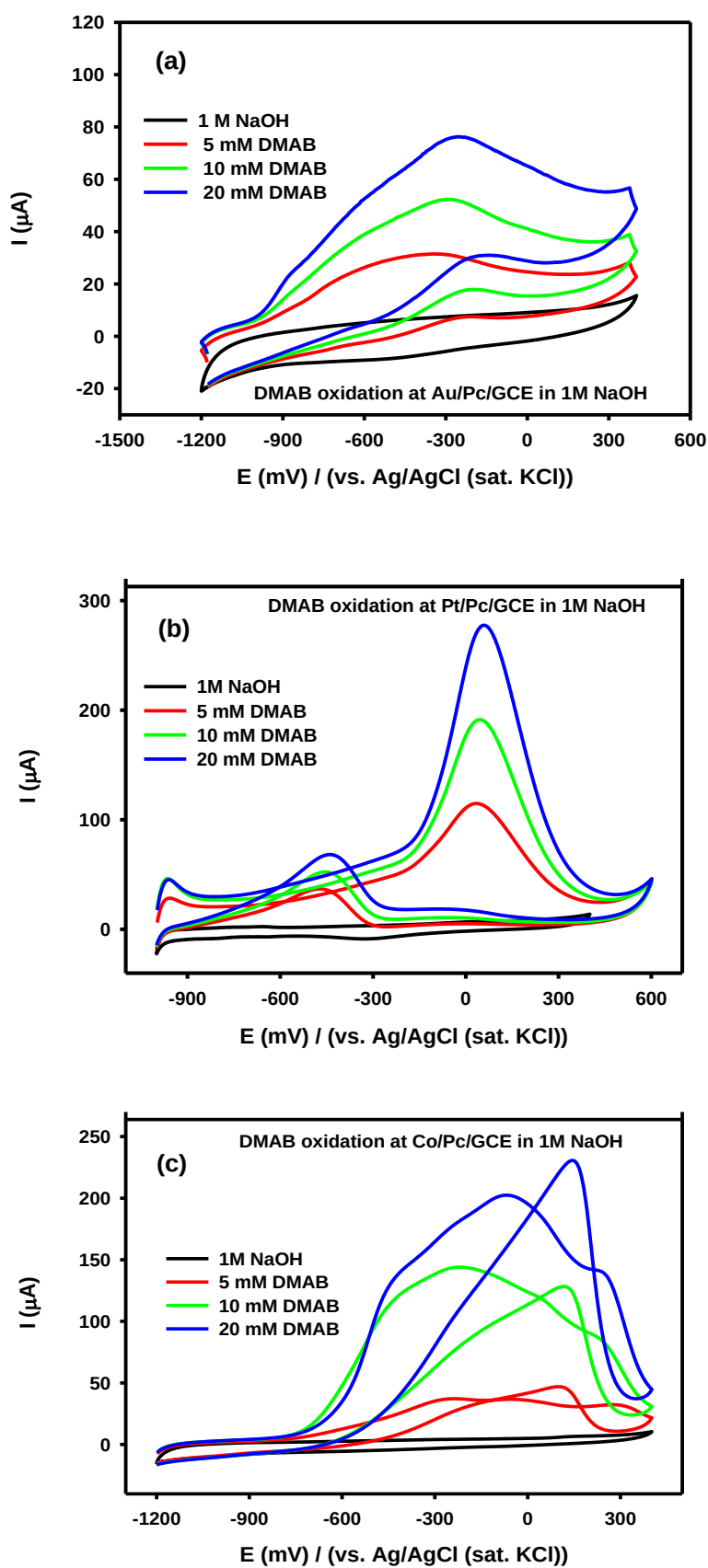


Figure 3.83 Cyclic voltammograms for increasing concentrations of DMAB at M/Pc/GCE. a) Au/Pc/GCE, b) Pt/Pc/GCE, c) Co/Pc/GCE in 1 M NaOH.

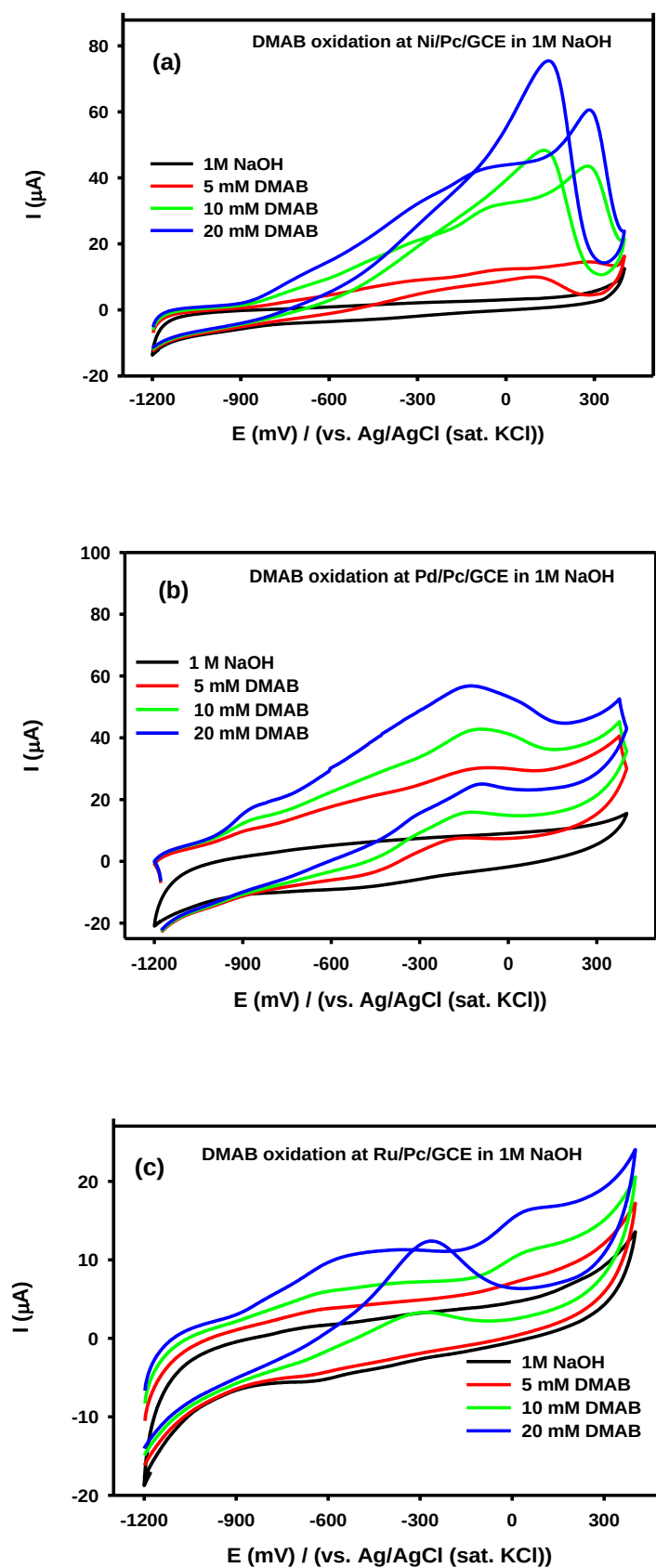


Figure 3.84 Cyclic voltammograms of increasing concentrations of DMAB at M-Pc/GCE. a) Ni/Pc/GCE, b) Pd/Pc/GCE, c) Ru/Pc/GCE in 1 M NaOH.

Table 3.16 Potential and current values of modified electrodes towards 20 mM DMAB oxidation.

Electrode	Potential (mV)	Current (μA)
<i>Pc/GCE</i>	-279	1.14
<i>Ru/Pc/GCE</i>	43	0.51
<i>Pd/Pc/GCE</i>	-122	20.9
<i>Co/Pc/GCE</i>	142	201
<i>Ni/Pc/GCE</i>	125	41

Since the higher catalytic activity of bimetallic nano particles compared to their individual modification, bimetallic nano particles modified surfaces was used in various applications. Au and Pt nano particles were studied previously for DMAB oxidation reaction. To improve the activity of the electrodes towards DMAB oxidation, Pt-Au bimetallic nano particles which deposited from the 1 mM Au and 1 mM Pt containing HCl solution were prepared on the Pc/GCE surface. Figure 3.85 depicts the comparison of Au, Pt and (Pt-Au) bimetallic nano particles modified Pc/GC electrodes. Detailed analysis of peak potential and currents were shown in Table 3.17. A broad oxidation peak on the anodic scan and sharp reactivation peak same as obtained for gold disk surface on the cathodic scan were observed at (Pt-Au)/Pc/GCE. The initial potential of the oxidation peak with high peak current values in the presence of DMAB, let us to think competitive hydrogen evolution and DMAB oxidation take place at negative potentials on (Pt-Au)/Pc/GCE.

In order to improve the catalytic activity of electrodes towards DMAB oxidation, metal nano particles were used as modifier on Pcs. While promising results obtained from the studies that explained above, current and potential values need to be improved to more negative and higher values, respectively. In this context, carbon nanotubes were chosen as another component as composite surface design which followed by metal nano particles deposition towards DMAB oxidation.

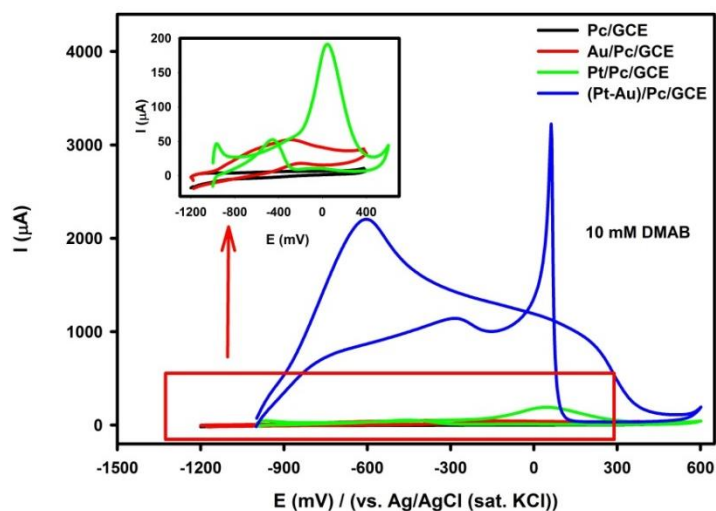


Figure 3.85 Cyclic voltammograms of 10 mM DMAB oxidation at M-Pc/GCE in 1 M NaOH.

Table 3.17 Potential and current values of 10 mM DMAB oxidation peak at CuPc/GCE and metal nano particles modified CuPc/GCEs.

Electrode	Potential (mV)	Current(μA)
<i>Pc/GCE</i>	-279	0.8
<i>Au-Pc/GCE</i>	-297	30.2
<i>Pt-Pc/GCE</i>	49	167
<i>(Pt-Au)/Pc/GCE</i>	-619	1452

DMAB oxidation on Pc and CNT composite modified GCE

In the light of the results that obtained from the nano particles modified Pc/GCE, carbon nanotubes were included in the composite structure of the electrode to improve the catalytic activity towards DMAB oxidation. To obtain the reliable comparison data to exhibit the real effect of metal nano particles modified Pc-CNT composite electrodes, DMAB oxidation on bare GCE, CNT/GCE and Pc-CNT/GCE were need to be studied.

Figure 3.86 shows the CV response of these electrodes in the absence and presence of 3 mM DMAB in 2 M NaOH solution in the potential range of -1200 mV to +600 mV. There is no obvious change obtained in the signals related with the oxidation of DMAB on GCE, CNT/GCE and Pc-CNT/GCE. Compared with the GCE and CNT/GCE, Pc-CNT/GCE has high background current and also two small reduction peaks at nearly -600 mV and - 800 mV which suggested as the

characteristics functional groups of Pc in alkaline medium. It was clearly seen in Figure 3.86b that there was no obvious change observed at Pc-CNT/GCE compared with the baseline and DMAB added signals.

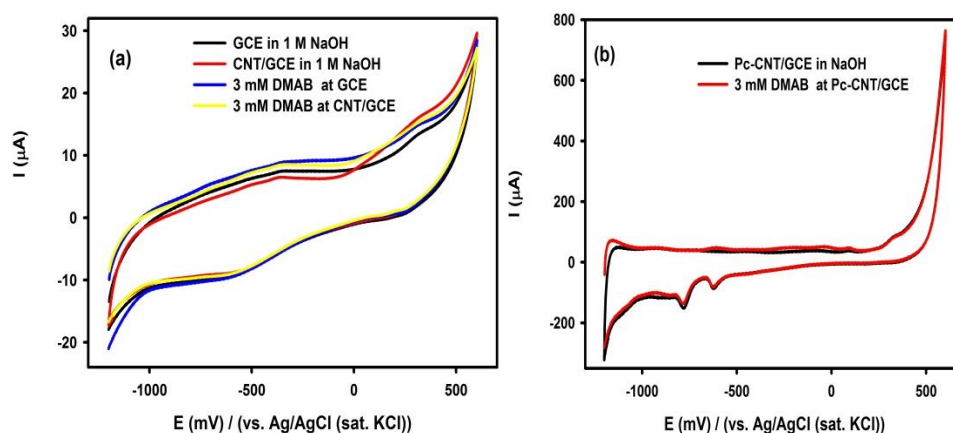


Figure 3.86 Cyclic voltammograms of a) GCE and CNT/GCE, b) Pc-CNT/GCE electrodes with and without 3 mM DMAB. Scan rate: 50 mV.s^{-1} .

DMAB oxidation on metal nano particles modified Pc and CNT composite GCE

It is understood that Pc and CNT based composite electrodes without metal nano particles are not suitable modifiers for DMAB oxidation in alkaline medium. To improve the DMAB oxidation signals, Pc-CNT/GCE was modified with various nano particles (Au, Pt, Ag, Zn, Pd, Ni, Co). Figure 3.87 and Figure 3.88 shows the response of metal nano particles modified Pc-CNT/GC electrodes in the absence and presence of 1mM DMAB containing NaOH solution.

Figure 3.87 shows the CVs of Zn, Pd, Ni, Co nano particles modified Pc-CNT/GCEs with and without 1 mM DMAB containing NaOH solution. The background response of electrodes was quite similar without remarkable peaks except Pd/Pc-CNT/GCE, which shows a peak at about -700 mV supposed as oxidation of Pd nano particles (Figure 3.87b). While there is no peak found at Co/Pc-CNT/GCE and Zn/Pc-CNT/GCE, a small oxidation peak was observed at Ni/Pc-CNT/GCE at -219 mV $12.7 \mu\text{A}$. Two peaks were observed at Pd/Pc-CNT/GCE at -699 mV and -125 mV with 95 and $97 \mu\text{A}$ current values, respectively. A peak was observed in the reverse scan with an anodic high current values (-211 mV with $56 \mu\text{A}$) supposed as the reactivation peak formed due to the reaction of DMAB and Pd oxide surface like observed at Pt and Au disk electrodes.

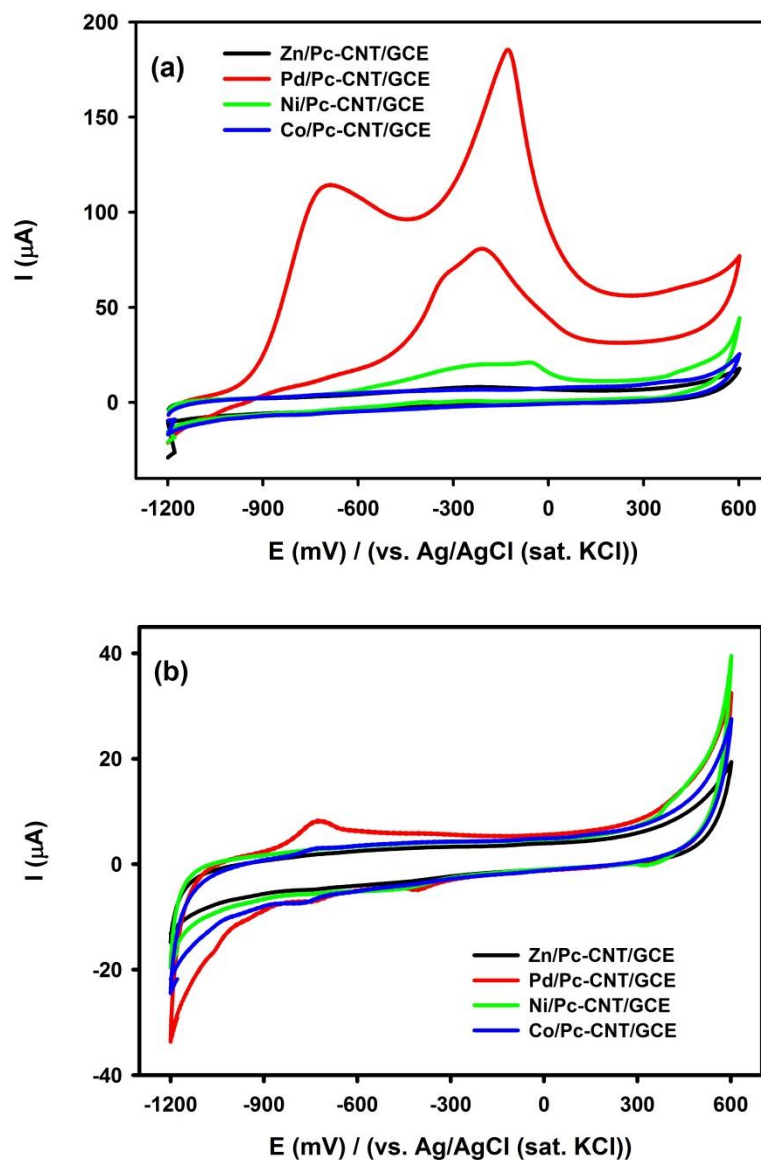


Figure 3.87 Cyclic voltammograms of Zn, Pd, Ni, Co nano particles modified Pc-CNT/GC electrodes in NaOH a) with and b) without 1 mM DMAB. Scan rate 50 mV.s^{-1} .

Au, Pt, Ag and oxidized Ag nano particles modified Pc-CNT/GC electrodes were depicted in Figure 3.88. All electrodes except Pt nano particles modified Pc-CNT/GC were studied in the potential range between -1200 mV and +600 mV in the presence (Figure 3.88a) and absence (Figure 3.88b) of DMAB. All metal nano particles modified electrodes give response to the DMAB oxidation.

The hydrogen evolution was observed at Pt nano particles modified Pc-CNT/GCE which followed by wide oxidation peak at -33 mV and high reactivation peak in -460 mV in 1 mM DMAB containing NaOH solution. The potential window needs to be narrowed due to the hydrogen evolution on Pt/Pc-CNT/GCE.

DMAB oxidation occurred at -778 mV with 51.5 μ A current value at Ag nano particles modified Pc-CNT/GCE. While the Ag/Pc-CNT/GCE shows good response to DMAB oxidation, the peak current was unstable that it decreases by the repeated cycles. Ag(ox)/Pc-CNT/GCE prepared by the same procedure of Ag/Pc-CNT/GCE but with a small difference. After Ag/Pc-CNT/GCE preparation, electrode immersed in the NaOH solution and three repetitive CVs taken in the wide potential range (-1200 mV to 1100 mV). This procedure improve the DMAB oxidation peak both as peak potential (-794 mV) and current (104 μ A) but the Ag(ox)/Pc-CNT/GCE has unstable peak current which was decrease with the consecutive scans.

DMAB oxidation observed at -758 mV with 102 μ A current value followed by the wide reverse peak at Au/Pc-CNT/GCE. While oxidation occurs in more positive potentials than Ag/Pc-CNT/GCE, the peak shows very good stability in consecutive cycles. According to the results, Au/Pc-CNT/GCE shows the best catalytic towards DMAB oxidation in alkaline medium.

All peak current and peak potential values of Au, Pt, Ag, Zn, Pd, Ni, Co, Ru, Cu, Ce and Mn nano particles modified Pc-CNT/GC electrodes were listed in Table 3.18 to clearly seen the comparison of the electrode responses towards DMAB oxidation. To view all modified electrodes from a potential and current values perspective, the most negative potential values obtained in the existence of Ag and Ag(ox) modified Pc-CNT/GC electrodes, while peak forms were unstable and decrease with the repetitive scans which was not desired for the electrodes. Au nano particles modified Pc-CNT/GCE was chosen as the best electrode due to the stable peak characteristic at negative potential with high peak current value towards DMAB oxidation. Therefore, the following studies were designed for Au nanoparticle containing modified electrodes.

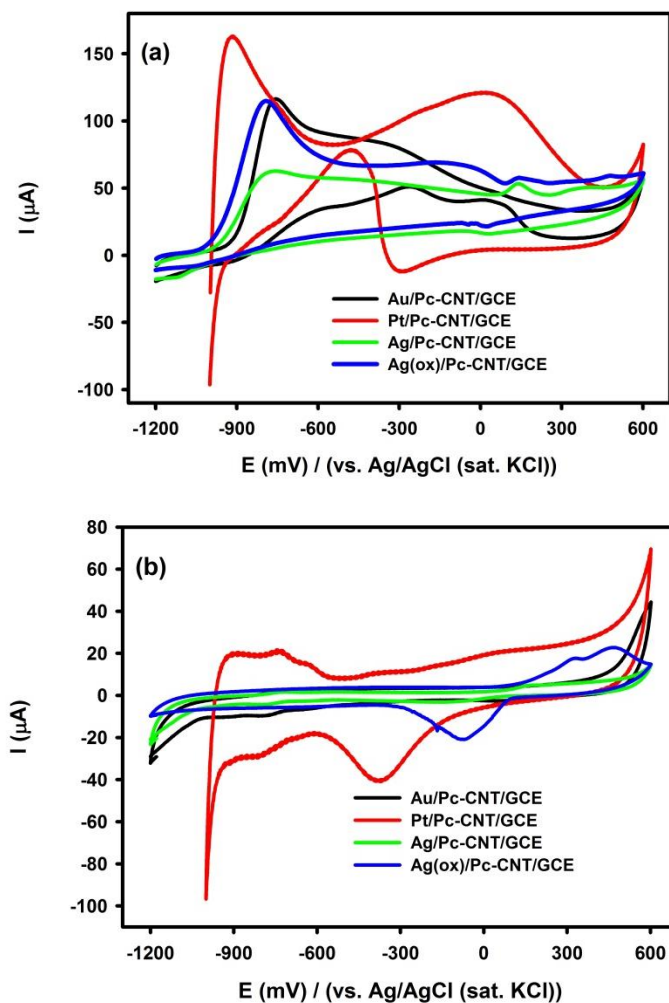


Figure 3.88 Cyclic voltammograms of Au, Pt, Ag, oxidized Ag nano particles modified Pc-CNT/GC electrodes in NaOH a) with and b) without 1 mM DMAB. Scan rate: 50 mV.s^{-1} .

Table 3.18 Potential and current values of 1 mM DMAB oxidation peak on various metal nano particles modified Pc-CNT/GCEs.

Electrode	E (mV)	Current (μA)
<i>Au/Pc-CNT/GCE</i>	-758	102
<i>Pt/Pc-CNT/GCE</i>	Compete with hydrogen evolution	
<i>Ag/Pc-CNT/GCE</i>	-778	51.5 (decrease with repetitive cycles)
<i>Ag(ox)/Pc-CNT/GCE</i>	-794	104 (decrease with repetitive cycles)
<i>Zn/Pc-CNT/GCE</i>	---	---
<i>Pd/Pc-CNT/GCE</i>	-699/-125	95/97 Two peaks observed
<i>Ni/Pc-CNT/GCE</i>	-219	12.7
<i>Co/Pc-CNT/GCE</i>	---	---

DMAB oxidation on Au nano particles modified different Pc types composed CNT GCE

Pcs are macro molecules that can be contain central metal which affect the activity of molecule. In light of the foregoing, DMAB oxidation was investigated by Au nano particles modified Pc-CNT/GC, MnPc-CNT/GC, CoPc-CNT/GC and CuPc-CNT/GC electrodes in alkaline media. Figure 3.89 shows the cyclic voltammograms of these electrodes with and without 1 mM DMAB. Related current and potential values were summerized in Table 3.19.

According to the Figure 3.89b background currents of Au/CoPc-CNT/GCE and Au/CuPc-CNT/GCE were higher than other modified electrodes. This can be attributed to the more active functional structure of electrode material. The small various oxidation and reduction peaks at these electrodes in NaOH solution were suggested as structural peaks.

Figure 3.89a clearly demonstrates that Au nano particles modified CuPc-CNT/GCE show best catalytic activity towards DMAB oxidation at -870 mV with 268 μ A. DMAB oxidation was shifted to 112 mV negative potential while accompanied twice current increasing compared with the Au/Pc-CNT/GCE. This can be attributed to the synergistic effect of copper and gold existence on the composite electrode surface. Au/CoPc-CNT/GCE was not preferred as an electrode material due to the wide, multiple peak characteristic at more positive peak potential towards DMAB oxidation.

In addition, Au/MnPc-CNT/GCE was not chosen as an optimum electrode due to the low peak current value at more positive oxidation potential for DMAB oxidation as compared to the Au/CuPc-CNT/GCE and Au/Pc-CNT/GCE. In conclusion, Au/CuPc-CNT/GCE was chosen as an optimum electrode due to the highest peak current and most negative peak potential value towards DMAB oxidation.

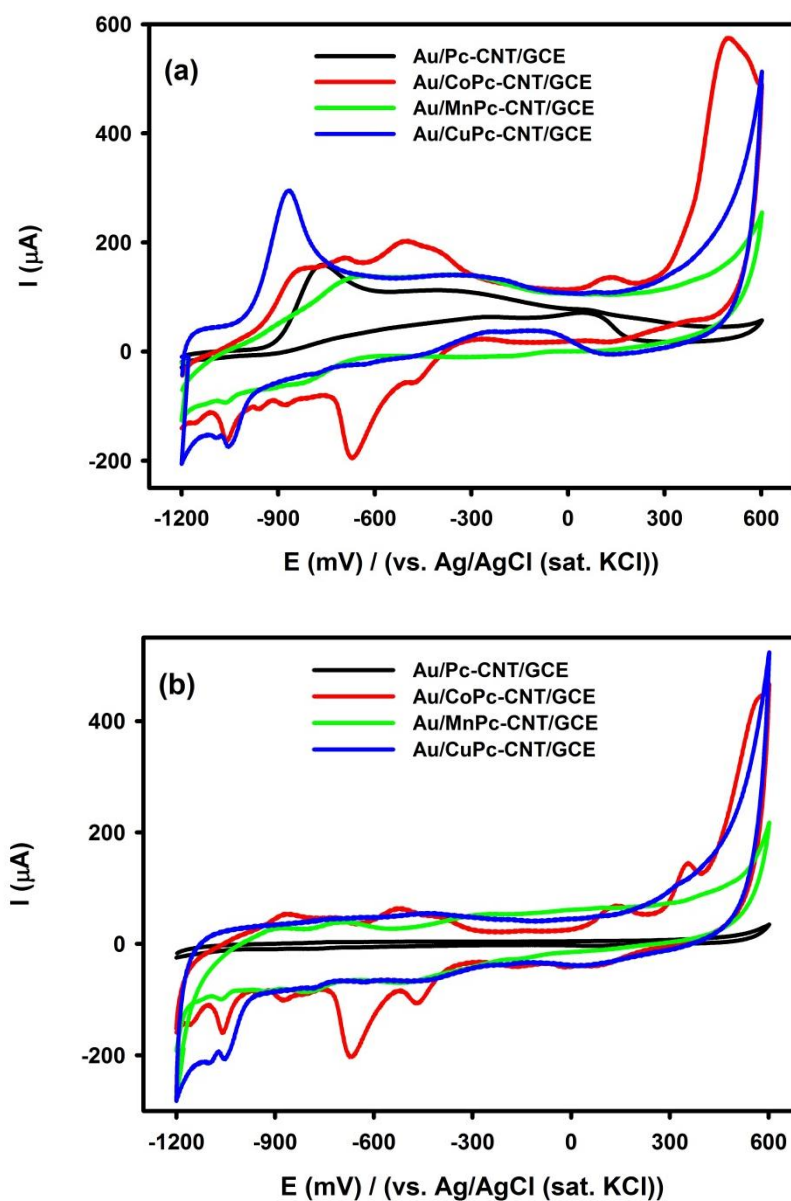


Figure 3.89 CV behaviour of Au nano particles modified Pc and metallated (Co, Mn, Cu) Pc-CNT/GC electrodes in NaOH solution a) with and b) without 1 mM DMAB.

Table 3.19 Potential and current values of 1 mM DMAB oxidation peak at Au nano particles modified Pc/GCE and MPc/GCEs.

Electrode	Potential (mV)	Current(μA)
<i>Au/Pc-CNT/GCE</i>	-758	102
<i>Au/CoPc-CNT/GCE</i>	-513	148
<i>Au/MnPc-CNT/GCE</i>	-697	42
<i>Au/CuPc-CNT/GCE</i>	-870	268

Effect of NaOH concentration on DMAB Oxidation peak

The effect of supporting electrolyte concentration on electrooxidation of DMAB at Au/CuPc-CNT/GCE was studied in the concentration range of 0.5 to 4 M NaOH that shown in Figure 3.90. DMAB oxidation peak at negative potentials were observed in all NaOH concentrations (Figure 3.90a).

The potential and current varied by the changing of NaOH concentration was plotted and shown in Figure 3.91. The potential sharply shifted to the negative values by the change of NaOH concentration from 0.5 to 1 M. After 1 M NaOH concentration, the shift rate was decrease and reached almost the same value for 3 M and 4 M NaOH.

In addition, it can be clearly seen from the Figure 3.91b that oxidation peak current was increase by the increasing of NaOH concentration from 0.5 to 2 M. Then current was turn to decrease by the increasing concentrations. According to the results, 2 M NaOH was chosen as an optimum concentration for DMAB oxidation at Au/CuPc-CNT/GCE. This choice was coherent with other studies in which high NaOH concentration was chosen for investigation of DMAB oxidation (Finkelstein et al., 2009; Martins and Nunes, 2008). These results provide us prevision for suitable medium for other modified electrode surfaces that we prepared and discussed in following sections.

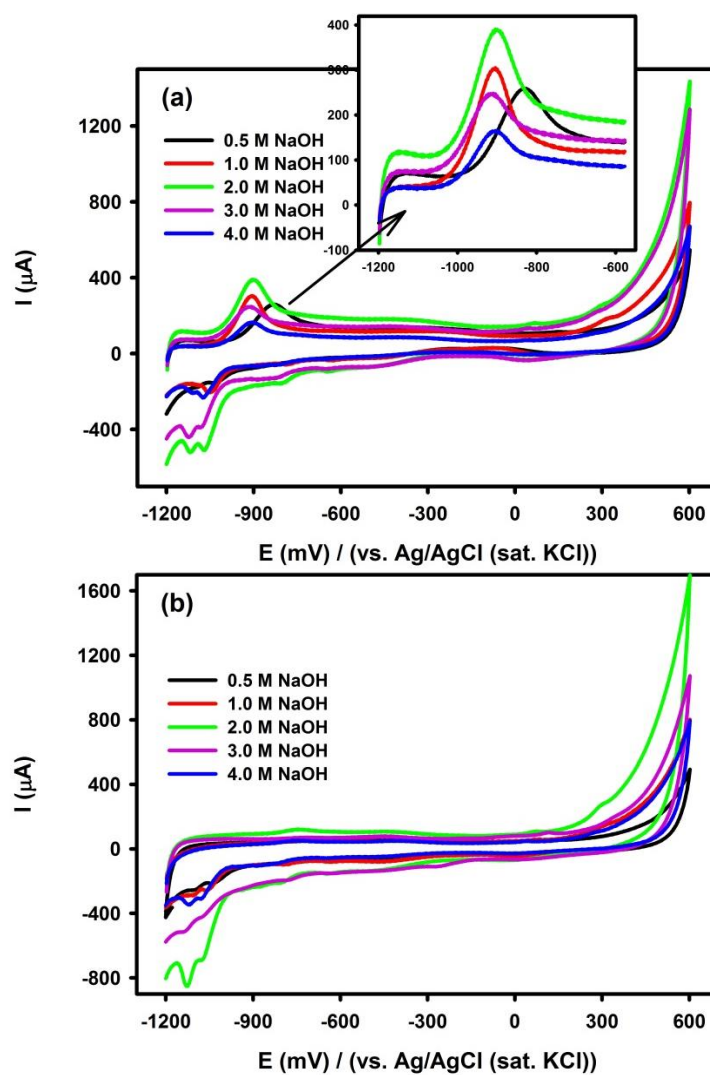


Figure 3.90 a) Cyclic voltammograms of 1 mM DMAB oxidation on Au/CuPc-CNT/GCE with various concentrations of NaOH solution (0.5 - 4 M), b) supporting electrolyte solution response.

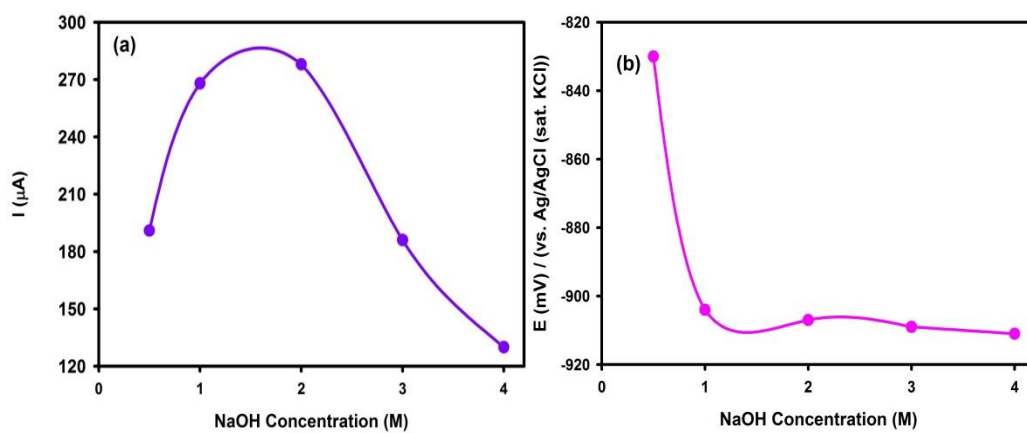


Figure 3.91 Plots for the change in a) peak current and b) peak potential of DMAB oxidation versus NaOH concentration change.

Effect of CuPc/CNT ratio on DMAB oxidation

CuPc and CNT are both an important components of composite electrode which strongly change the activity of electrode towards DMAB oxidation in alkaline media. As it mentioned before only one component was not provide enough activity to DMAB oxidation so they can be compose together. Figure 3.92 shows the cyclic voltammograms of Au/CuPc-CNT/GC electrodes in 2 M NaOH solution with (Figure 3.92a) and without (Figure 3.92b) 1 mM DMAB. It was expected before the experiments that the ratio of CuPc and CNT possible change the activity of electrode towards DMAB oxidation. Figure 3.92c clearly shows the current changes of DMAB oxidation peaks by the change of CuPc to CNT ratios. The ratio was changed between %5 to %20 and peak current was increase until the ratio reached the %15 value. Then current decrease when the ratio was %20. According to the results % 15 CuPc-CNT ratio was chosen as an optimum composite ratio towards DMAB oxidation in 2 M NaOH.

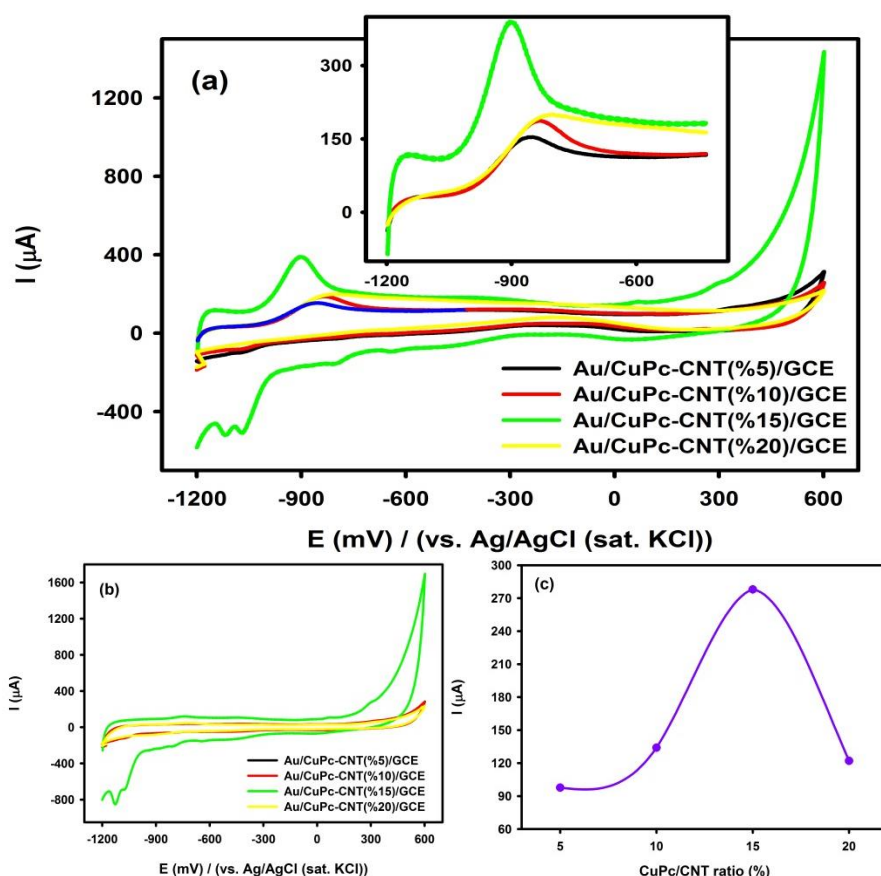


Figure 3.92 a) Cyclic voltammograms of 1 mM DMAB oxidation at Au/CuPc-CNT/GC electrodes prepared with various CuPc/CNT ratios (%5-%20) b) supporting electrolyte solution response, c) plot of CuPc/CNT ratios versus DMAB oxidation peak current.

Optimization of HAuCl_4 concentration for Au nano particles modified CuPc/CNT/GCE

To obtain best catalytic activity to DMAB oxidation, various parameters such as composite ratio, NaOH concentration, metal phthalocyanine type and various nano particles were studied.

As it mentioned before, composite electrodes without metal nano particles have lack of activity towards DMAB oxidation. Therefore, the chosen metal (gold) nanoparticle concentration was an important parameter to obtain the most active electrode surface. Electrochemical technique gives a chance to control the nano particle formation by changing the metal solution concentration and cycle number. In this respect, various concentrations (0.5 to 3 mM) of gold solution were studied and related cyclic voltammograms were illustrated in Figure 3.93a-b.

Peak characteristics of the modified electrodes were listed in Table 3.20 to exhibit the comparison of the electrode responses towards DMAB oxidation. The peak potential was shifted to the negative values by the change of concentration from 0.5 to 1 mM and then it was stabilized at same potential for increasing concentrations.

Peak current value of DMAB oxidation in 2 M NaOH was first increase by the increasing concentration and then almost same currents were obtained for 1 and 2 mM Au solution. The peak current was decrease again when the Au concentration reached at 3 mM. This behavior can be attributed to the formation of bulk like electrode surface when the gold concentration was increased that lead to the decrease in current.

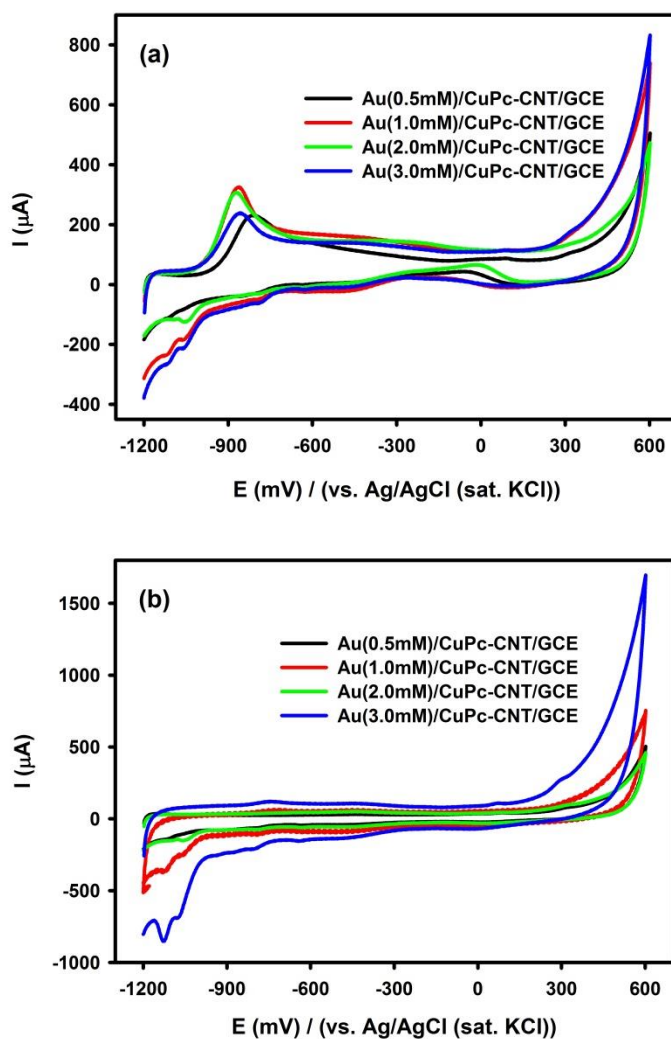


Figure 3.93 a) Cyclic voltammograms of 1 mM DMAB oxidation on Au(XmM)/CuPc-CNT/GC electrodes b) supporting electrolyte solution response.

Table 3.20 Potential and current values of 1 mM DMAB oxidation peak at Au(XmM)/CuPc-CNT/GCE.

Electrode	Potential (mV)	Current(μA)
<i>Au(0.5mM)/CuPc-CNT/GCE</i>	-814	200
<i>Au(1mM)/CuPc-CNT/GCE</i>	-868	281
<i>Au(2mM)/CuPc-CNT/GCE</i>	-870	268
<i>Au(3mM)/CuPc-CNT/GCE</i>	-858	188

DMAB Oxidation at Au disk and Au nano particle modified composite electrodes

Nano particles were used for their special properties that were different from their bulk form. Bulk form of metals was not suitable electrode materials due to their high costs. We expected to obtain more catalytically active surfaces than bulk materials by using nano particles, cheap form of metal use. Figure 3.94 shows the comparative cyclic voltammograms of Au disk, Au/GC, Au/CNT/GC, Au/CuPc-CNT/GC and CuPc-CNT/GC electrodes in NaOH solution with and without 1 mM DMAB. Oxidation peak potential and current values can be found in Table 3.21 for clearly understand the activity of the electrodes.

As it's mentioned before, carbon based composite electrodes were not suitable electrode materials without metal nano particles modification. CuPc-CNT/GCE prove this suggestion with the positive potential value (-201 mV) with low current (11.5 μ A) towards DMAB oxidation. DMAB oxidation was occurred at -600 mV with 3.3 μ A Au/CNT/GCE. This low current value shows that CNTs are not suitable modifiers without phthalocyanines towards DMAB oxidation. So this can be proving the necessity of copper phthalocyanine as an electrode material. The same lack of activity obtained at Au/GCE by the same reasons of Au/CNT/GCE.

Neither carbon based materials nor metal nano particles highly catalysis the DMAB oxidation. Both metal nano particles and CuPc-CNTs can be found together to obtain the synergistic effect that results the best active electrode surfaces towards DMAB oxidation. Au disk electrode showed good activity towards DMAB oxidation as negative peak potential value (-806 mV) but current value (19.43 μ A) was lower than Au/CuPc-CNT/GCE. The best catalytic activity was obtained at Au/CuPc-CNT/GCE due to the highest peak current and most negative peak potential value towards DMAB oxidation. At Au/CuPc-CNT/GCE, the potential was shifted to 64 mV negative and the obtained current was 13 times higher than bare Au disk electrode. The experimental results proved the improved activity of designed composite electrodes.

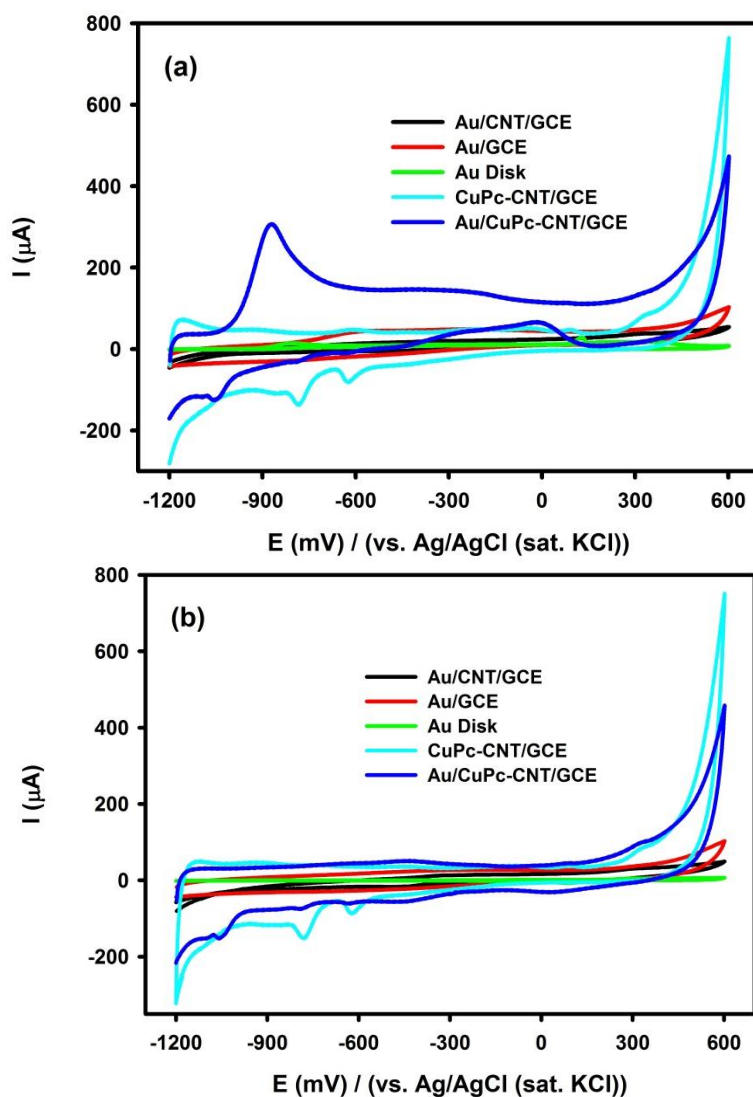


Figure 3.94 CV behaviour of Au disk, CuPc-CNT/GC, Au/GC, Au/CNT/GC, Au/CuPc-CNT/GC electrodes in NaOH solution a) with and b) without 1 mM DMAB.

Table 3.21 Potential and current values of 1 mM DMAB oxidation peak at CuPc-CNT/GCE, Au disk and Au nano particles doped modified GCEs.

Electrode	Potential (mV)	Current(μ A)
<i>Au/CNT/GCE</i>	-600	3.3
<i>Au/GCE</i>	-577	21.5
<i>Au Disk</i>	-812	13
<i>CuPc-CNT/GCE</i>	-201	11.5
<i>Au/CuPc-CNT/GCE</i>	-868	281

Scan rate study of Au/CuPc-CNT/GCE

The effect of different scan rate ($3\text{--}500\text{ mV.s}^{-1}$) on the anodic peak current of 1 mM DMAB was investigated in NaOH at Au/CuPc-CNT/GCE using cyclic voltammetry. These cyclic voltammograms were showed in Figure 3.95.

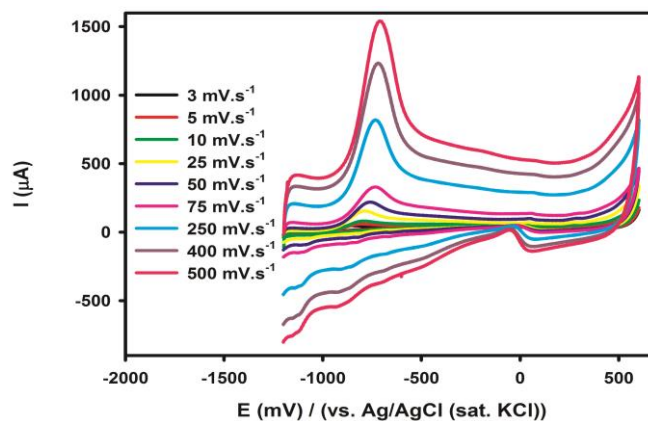


Figure 3.95 Cyclic voltammograms of Au/CuPc-CNT/GC electrode for 1 mM DMAB oxidation with different scan rates: $3\text{--}500\text{ mV.s}^{-1}$.

The Figure 3.96 was obtained from peak current and peak potential of DMAB oxidation with various scan rate. The results indicated that the peak current was linearly changed with the square root of scan rate in the range of $3\text{--}500\text{ mV.s}^{-1}$ (Figure 3.96b). The linear regression equation was $i_{\text{Pa}}(\mu\text{A}) = 52.319 v^{1/2} ((\text{mV.s}^{-1})^{1/2}) + 105.13$ with a correlation coefficient of $R^2 = 0.9902$. this modified electrode showing a diffusion-controlled process in the solution. The peak potential shifted to potential that is more positive by the increment of the logarithmic scan rates. The linear relation between peak potential and logarithm of scan rate (Figure 3.96b) indicated that an irreversible electrode process.

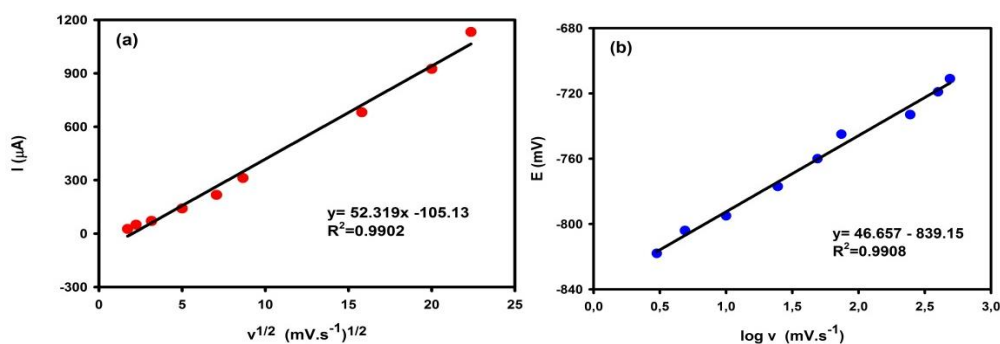


Figure 3.96 a) Square root of the scan rate vs. current and b) logarithm of scan rate vs. potential graphics from scan rate study of Au/CuPc-CNT/GC electrode.

Figure 3.97 shows the cyclic voltammograms for Au/CuPc-CNT/GC electrode as a function of DMAB concentration between 0.5 and 3 mM. The dependence of peak current on the concentration of DMAB was linear which predicted The stable peak characteristics at wide concentration range, especially higher concentrations, prove that this modified electrode can be successfully used in fuel cell applications for every concentration value.

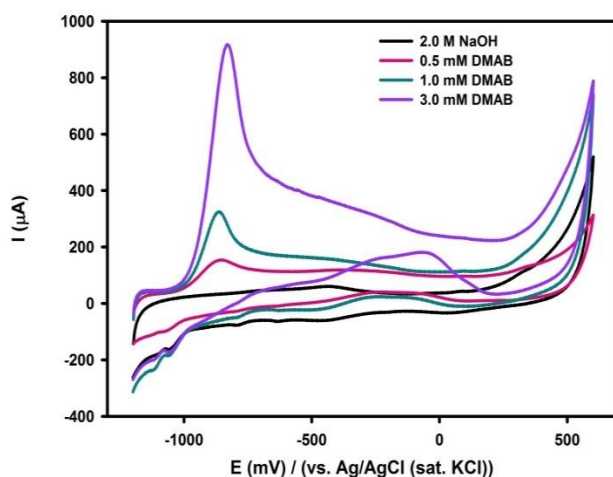


Figure 3.97 Cyclic voltammograms of Au/CuPc-CNT/GC electrodes in 2 NaOH with increasing DMAB concentrations. Scan rate 50 mV.s^{-1} .

Investigation of DMAB oxidation on rotating Au/CuPc-CNT/GC electrodes

The linear sweep voltammograms were recorded at Au/CuPc-CNT/GCE in different rotation rates (50 rpm - 1000 rpm) to investigate the transferred electron number of DMAB oxidation in 2.0 M NaOH (Figure 3.98a). In this experiment, Au/CuPc-CNT/GCE was not study at the rotation rates higher than 1000 rpm due to the responsive structure of physically attached CuPc-CNT. DMAB oxidation peak potential was observed at about -750 mV on Au/CuPc-CNT/GCE. As shown in Figure 3.98a, DMAB oxidation occurred by multi-step electron transfer mechanism. The electron number involved in the DMAB oxidation was calculated from the K-L plots (j^{-1} vs. $\omega^{-1/2}$) at various potentials in Figure 3.98b. These values are represented in Table 3.22 The slope of K-L plots at -800 mV, -200 mV, and 0 mV, shows good linearity. The transferred electron number (n) value was calculated as 2.99 in the first step (at -800 mV) and 2.97 in the second step (at -200 mV). Moreover, electron number during oxidation of DMAB was calculated as 5.97 at high potential (0 mV). The results were in agreement with the

previously published literature datas (Plana at al, 2011, Nagle and Noyan, 2005, Sadik at al, 2005).

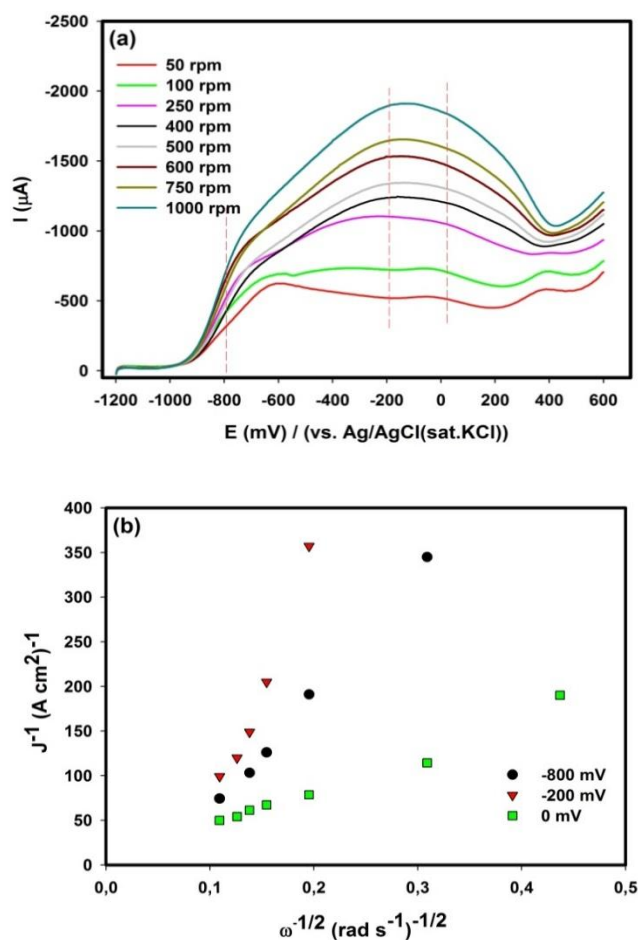


Figure 3.98 a) LSVs of rotating Au/CuPc-CNT/GCE in the presence of 5.0 mM DMAB solution in 2.0 M NaOH at different rotation rates (250 to 1500 rpm). b) Koutecky–Levich (K-L) plots of Au/CuPc-CNT/GCE at different potentials obtained from I–E Figure 3.99a.

Table 3.22 Equation components of the Koutecky-Levich plots and calculated electron numbers for the 5.0 mM DMAB oxidation at Au/CuPc-CNT/GCE in 2.0 M NaOH solutions.

Peak	I.peak (-800 mV)	II.peak (-200 mV)	Total (0.0 mV)
Slope of plot	1383.2	1393.7	693.81
Intercept of plot	-82.85	-71.43	-24.645
R ²	0.9979	0.9982	0.9958
n	2.99	2.97	5.97

3.3.3 Characterization of modified electrodes

An active electrode for DMAB oxidation reaction was prepared and optimized in previous section. Au/CuPc-CNT/GC electrode can be used as an efficient anode electrode surface for fuel cell applications. To identify the electrode surface characteristic, SEM, EDX, TEM, XPS, XRD and EIS techniques were used. SEM images and EDX results of Au/CuPc-CNT/GC electrode was given already in section 3.2.3 for the explanation (Au-Pt)/CuPc-CNT/GCE and Au/CuPc-CNT/GCE difference which was found as an optimum electrode for methanol oxidation. See Figure 3.39 for detailed SEM images with 1000x and 10000x magnifications. EDX study confirmed the presence of nano Au particles on CuPc-CNT composite electrode surface with the electrochemical deposition that can be seen in previously explained Figure 3.40. In addition, XRD patterns of Au/CuPc-CNT/GCE can be found also in previous section in Figure 3.44 that explained for exhibits the difference of (Au-Pt)/CuPc-CNT/GCE and Au/CuPc-CNT/GCE.

Figure 3.99 shows typical TEM images of Au/CuPc-CNT composite surfaces from low to high magnifications. The tubular structure of CNTs and jelly like forms that related with CuPc were obviously seen in TEM images. In addition, attachment of metal nano particles on both carbon nanotube and CuPc surface clearly seen from the image which distributed with narrow sized on all surface. It also possible to say that, the outer diameter of carbon nanotubes were between 100 and 200 nm. The spherical gold nano particles with an average diameter of approximately 8 nm were formed on the composite electrode surface which found coherent with previously published literatures (Segura et al., 2015; Vinoth et al., 2015). Moreover, Linescan shows the individual gold atoms in nanocrystal. The intensity increases according to the number of atoms in the columns by the gold atoms move into the nanocrystal (Pennycook et al., 2006)

Scanning transmission electron microscopy (STEM) images of Au/CuPc-CNT at different scales were shown in Figure 3.100. The first two images of the STEM (first line), prove that gold nano particles not only modified on the sidewalls of carbon nanotube, but also modified on the surface of CuPcs. In addition these first two images in Figure 3.100 were correspond to the dark field and bright field images, respectively which were complementary for each other to clearly identify the surface.

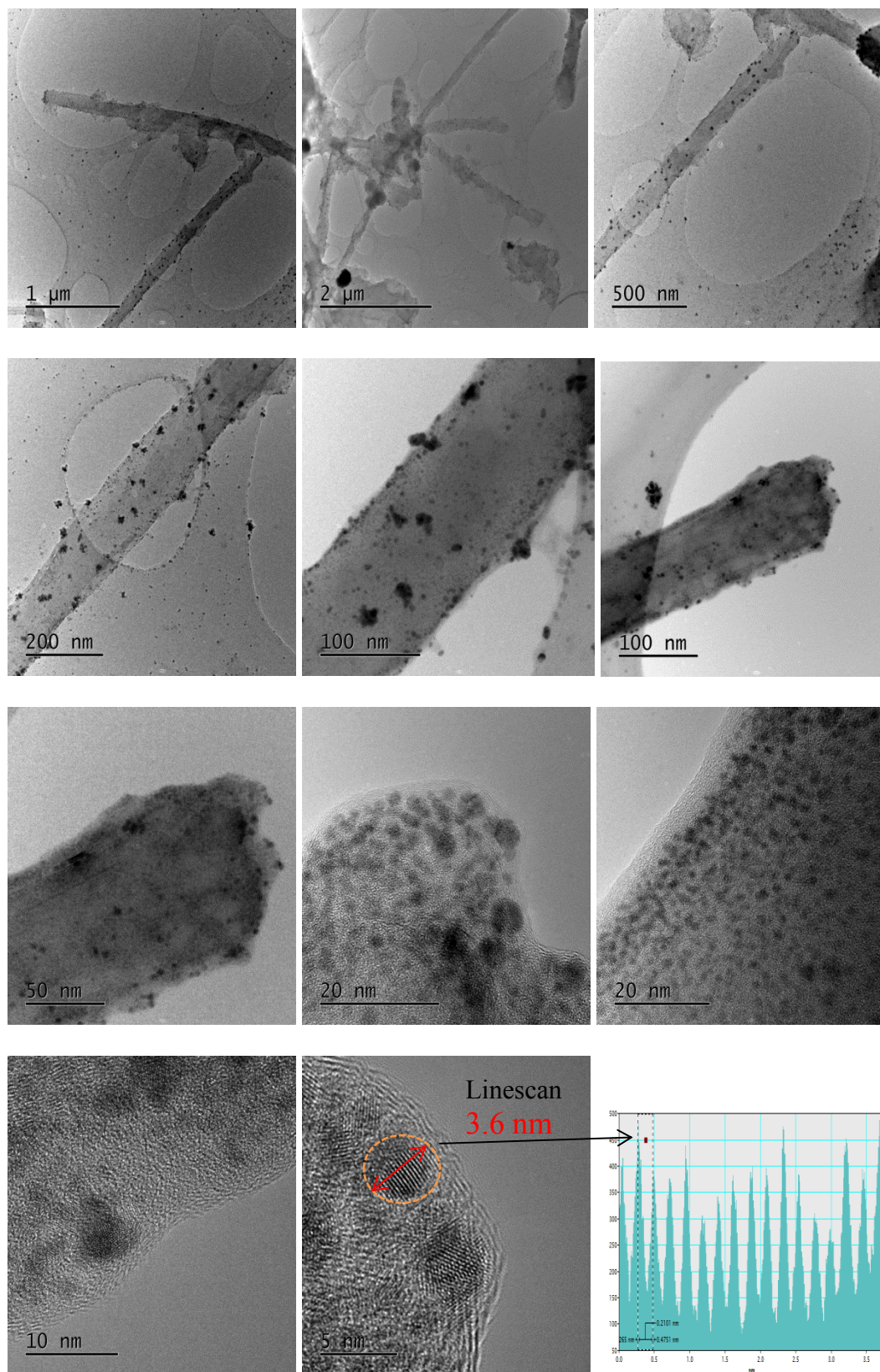


Figure 3.99 TEM images of Au/CuPc-CNT composite from low to high magnifications.

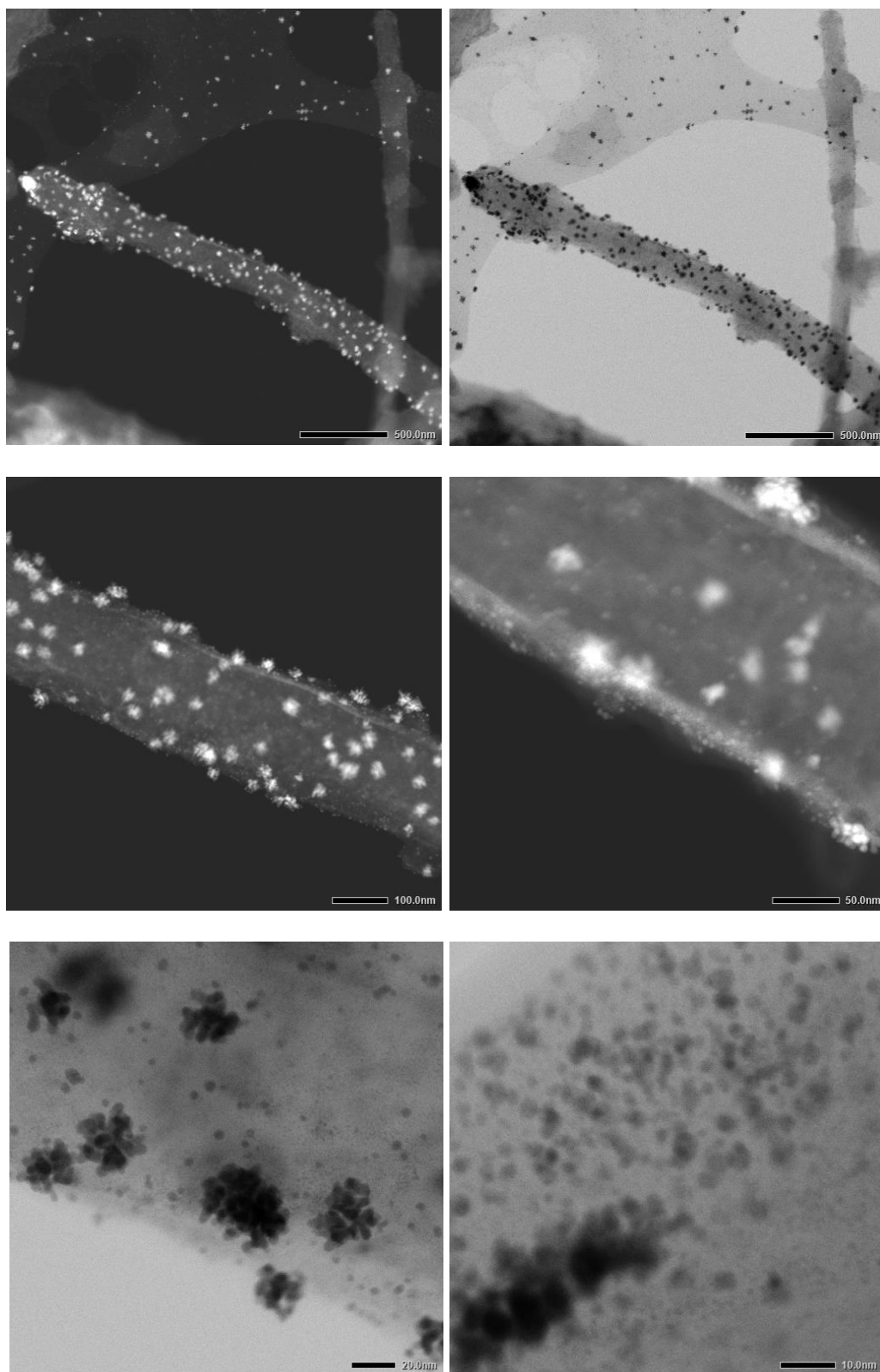


Figure 3.100 STEM images of Au/CuPc-CNT composite from low to high magnifications.

STEM image of Au/CuPc-CNT represented in Figure 3.101a, that shows spherical nano particles on tubular structure. Figure 3.101b, c and d display the elemental maps of Cu, Au and Au-Cu elements. These maps display that not only Au elements were distributed on the nanotube as nano particles but also CuPcs (form of Cu elements) attached on the nanotube which clearly seen from the color of elements. The energy-dispersive X-ray spectrum (EDS) used for the elemental analysis of STEM samples that EDS of Au/CuPc-CNT shown in Figure 3.101e. Carbon, copper and gold signals were represented in EDS that prove the existence of AuNPs, CuPc and CNT on the surface.

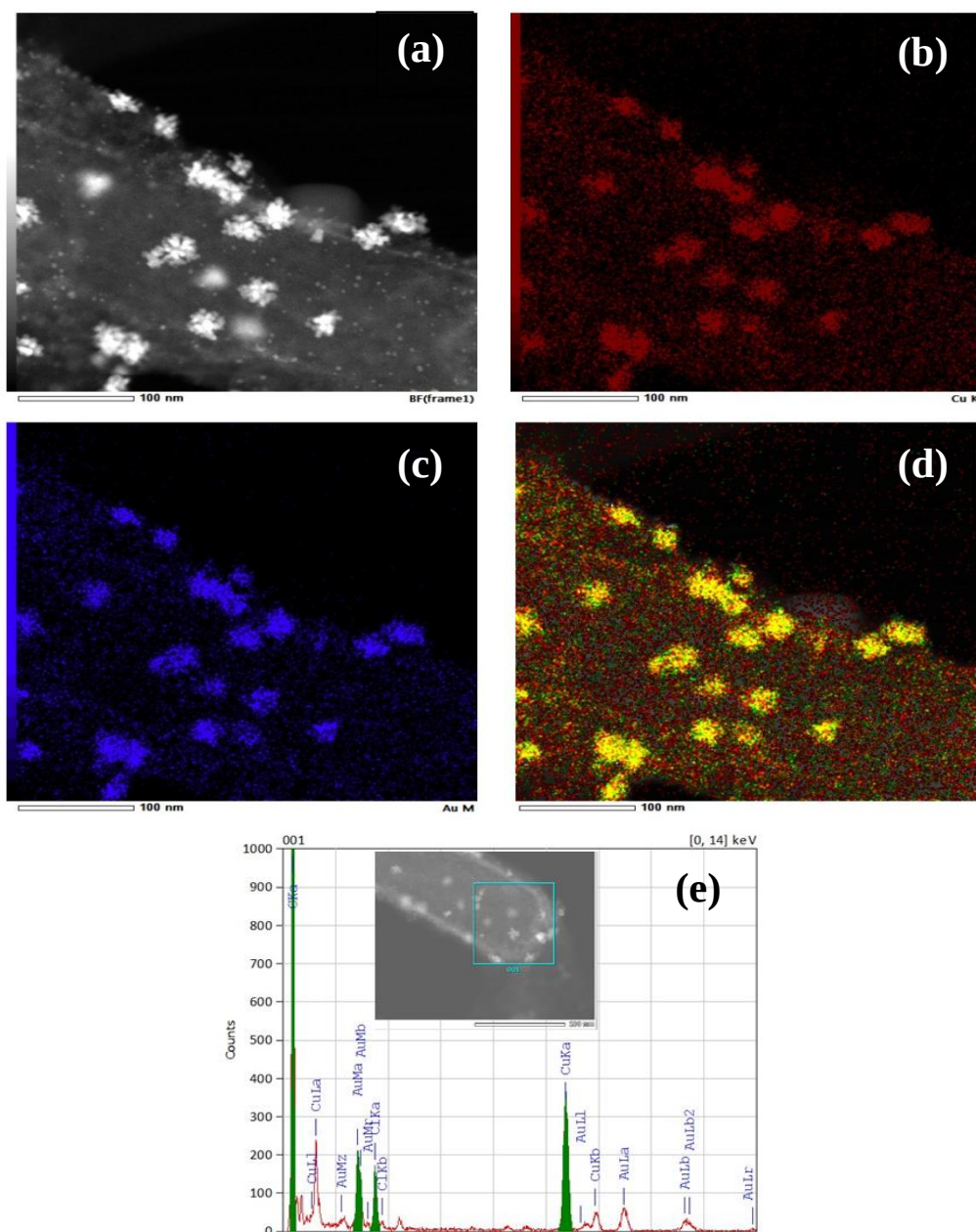


Figure 3.101 a) STEM image of Au/CuPc-CNT/GCE, (b-d) STEM-EDX element mappings of Cu, Au and Au-Cu, e) EDS of Au/CuPc-CNT.

XPS is a valuable technique that gives important information about bonding characteristics of the film and oxidation states of nano particles. Figure 3.102 shows the XPS survey spectra and narrow range spectrum of Au/CuPc-CNT/GCE the sample. Spectrums indicates the presence of C, O, Au and Cu, as expected. The binding energies of the Au doublets (Au 4f_{7/2} and Au 4f_{5/2}) were at about 84.47 and 88.15 eV, respectively, showing that the metallic Au was the found in the composite structure. The results were coherent with our previously published literature (Bakır et al., 2011).

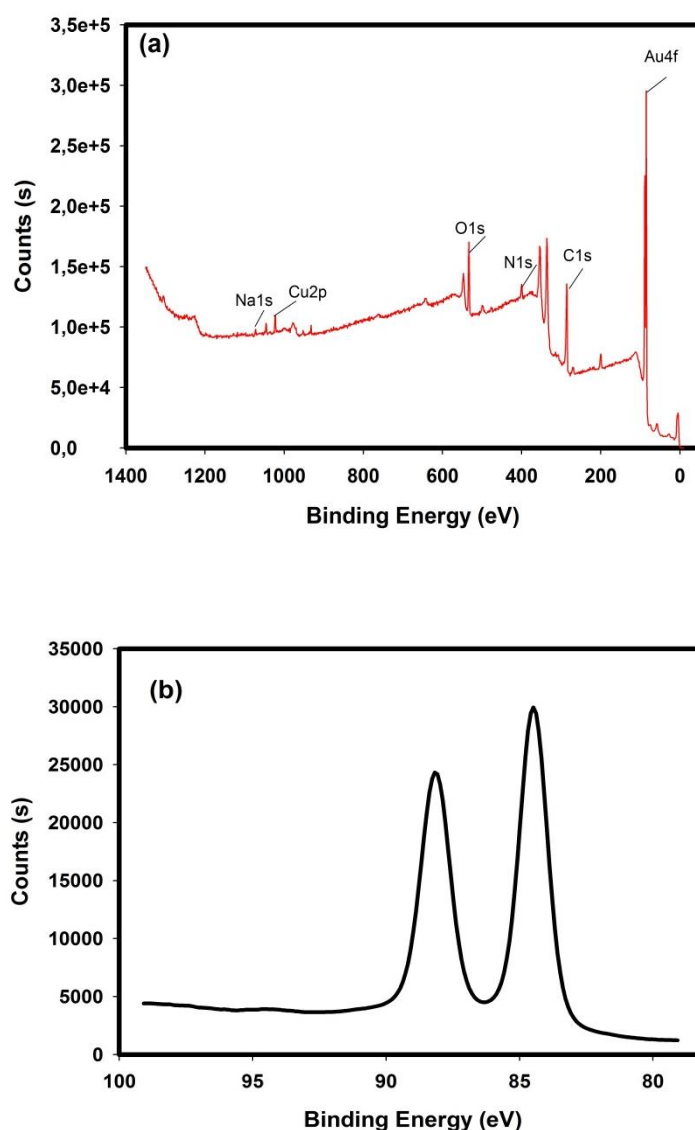


Figure 3.102 a) XPS survey spectrum and b) narrow range spectrum of Au/CuPc-CNT/GCE.

Figure 3.103 shows the electrochemical impedance spectroscopy results of bare GCE, CuPc-CNT/GCE and Au/CuPc-CNT/GCE in the presence 5.0 mM DMAB and 2.0 M NaOH solution at a frequency range of 0.05 to 50 000 Hz. The EIS data were fitted with the equivalent circuit (Figure 3.103 inset) and values were shown in Table 3.23. The Au/CuPc-CNT/GCE shows a lower interfacial electron transfer resistance (403 Ω) than that of the CNT/GCE (738 Ω) and of bare GCE (19100 Ω). This results show that the Au/CuPc-CNT/GCE surface has good electroconductibility.

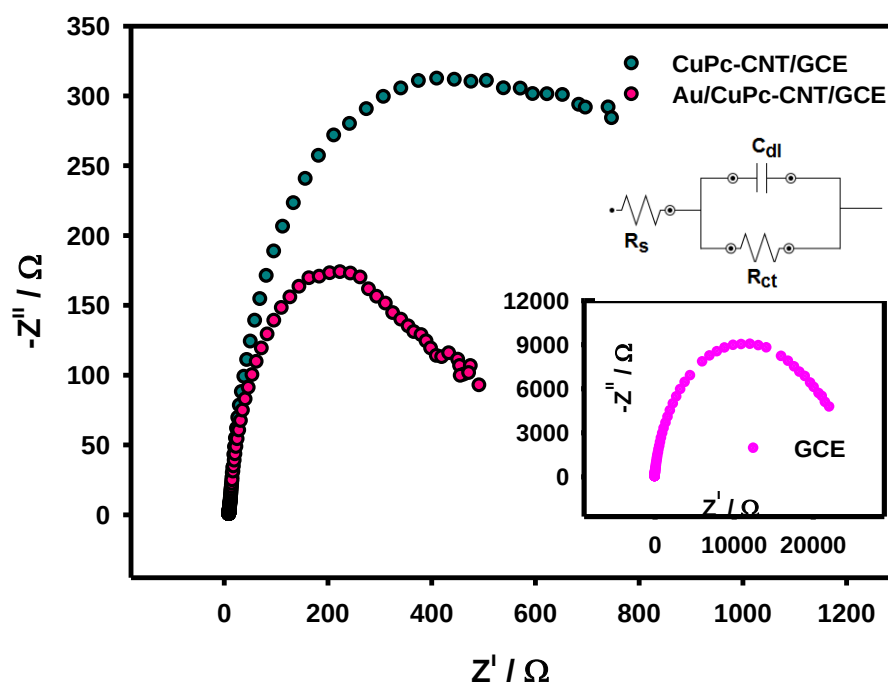


Figure 3.103 Nyquist plots of bare GCE, CuPc-CNT/GCE and Au/CuPc-CNT/GCE in 5.0 mM DMAB containing 2.0 M NaOH. The frequencies ranged from 0.05 to 50 000 Hz.

Table 3.23 The R_s , R_{ct} and C_{dl} values of bare and modified electrodes.

Electrode	R_s (Ω)	C_{dl} (μF)	R_{ct} (Ω)
Bare GCE	11.3	105	21000
CuPc-CNT/GCE	10.6	142	738
Au/CuPc-CNT/GCE	10.5	133	403

Figure 3.104 shows the Nyquist plots of bare GCE, CuPc-CNT/GCE and Au/Pc-CNT/GCE in the presence of 5.0 mM $[\text{Fe}(\text{CN})_6]^{-3/2}$ containing 0.1 M KCl solution at a frequency range of 0.05 to 50 000 Hz at the formal potential. The zoomed views of CuPc-CNT/GCE and Au/Pc-CNT/GCE were placed in inset to showed the R_{ct} values clearly. The EIS data were fitted with the equivalent circuit (Figure 3.104 inset) and related values were shown in Table 3.24. The Au/Pc-CNT/GCE shows a lower interfacial electron transfer resistance ($9\ \Omega$) than that of the CuPc-CNT/GCE ($22\ \Omega$) and of bare GCE ($548\ \Omega$). These results proved the excellent electroconductibility of Au/Pc-CNT/GCE surface.

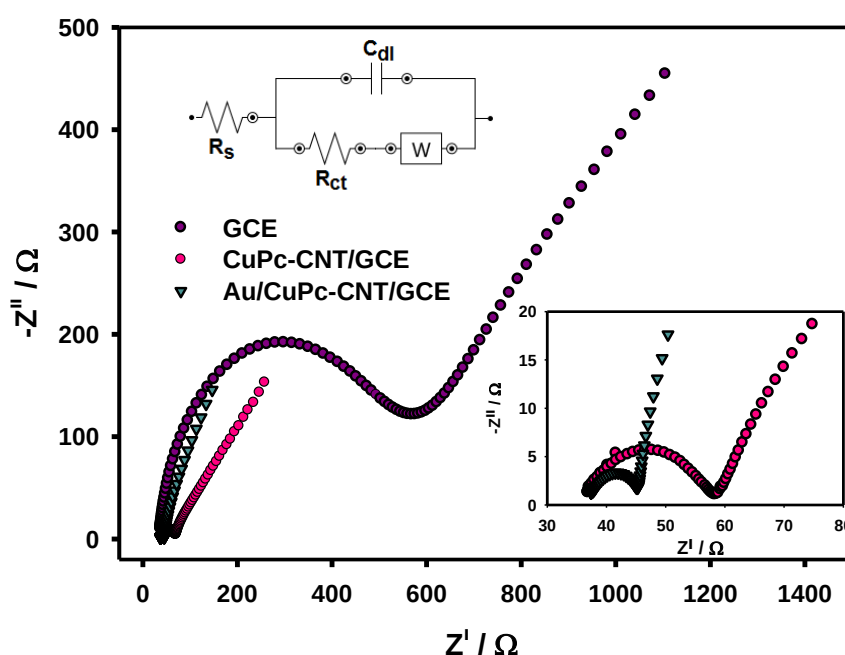


Figure 3.104 Nyquist plots of bare GCE, CuPc-CNT/GCE and Au/Pc-CNT/GCE in the presence of 5.0 mM $[\text{Fe}(\text{CN})_6]^{-3/2}$ containing 0.1 M KCl solution. The frequencies were ranged from 0.05 to 50 000 Hz. Insets: Equivalent circuit and zoomed views of CuPc-CNT/GCE and Au/Pc-CNT/GCE.

Table 3.24 The R_s , R_{ct} and C_{dl} values of bare and modified electrodes.

Electrodes	$R_s\ (\Omega)$	$C_{dl}\ (\mu\text{F})$	$R_{ct}\ (\Omega)$
Bare GCE	87.3	3.3	548
CuPc-CNT/GCE	37.0	2.5	22
Au/CuPc-CNT/GCE	38.1	2.4	9

The EIS measurements were studied not only in the presence of DMAB in NaOH, but also in $[\text{Fe}(\text{CN})_6]^{-3/-2}$ containing 0.1 M KCl solution. In each solution or analyte type, Au/CuPc-CNT/GC electrode show better conductivity and improved electron transfer rate as compared to the CuPc-CNT/GCE and GCE. The two EIS measurements were coherent with each other as we expected.

3.4 Composite Electrodes for Electroanalytical Applications

Theophylline and caffeine are methylxanthine derivatives that are generally found in food and drinks, which have an effect on cardiovascular, neurological and respiratory systems (Xia et al., 2013; Hedge et al., 2009). Their voltammetric analysis was difficult due to their high oxidation potentials and similar structures, which causes limited peak separation (Khoo et al., 2013). To obtain suitable peak separation and selectively determination of TP and CAF, electrodes were needed to be modified. Therefore, CNT that have an active functional groups and high surface area were composed with newly synthesized functionalized manganese phthalocyanines to obtain more active surfaces towards selective and sensitive determination of TP and CAF.

3.4.1 Preparation of 2eOHMnPc-CNT composite electrodes

Novel synthesized Tetra-[(5-chloroquinolin-8-yloxy) phthalocyanato] manganese (II) (2eOHMnPc) and acid treated CNT dispersion was prepared by the same procedure as described above in section 2.3.5. 30 mg pretreated CNT and appropriate amount of 2eOHMnPc mixed and dispersed in 4mL DMF to form a green-black suspension. A 10 μL of CNT suspension was injected on the pre-conditioned bare GCE surface. The solvent (DMF) of the suspension on the GCE surface was evaporated at 60°C for ½ hour.

To improve the catalytic effect of 2eOHMnPc-CNT composite electrode, Au, Pt, Pd and bimetallic Au-Pt nano particles were formed on the electrode surfaces by cyclic voltammetry technique. Electrochemical preparation of Au, Pt, Pd nano particles was described in detail in section 3.1.1 before. The previously explained Figure 3.1 and 3.2 show the redox peaks related to the formation of metal nano particles on the composite electrode surfaces.

3.4.2 Electrochemical behavior of theophylline and caffeine

Investigation of individual theophylline and caffeine oxidations on 2eOHMnPc-CNT/GC electrodes by CV

The individual electrochemical behavior of caffeine and theophylline was investigated before their simultaneous behavior, in order to obtain the characteristic information about analytes in supporting electrolyte. Firstly, electrochemical behavior of caffeine was investigated at 2eOHMnPc-CNT/GC electrode in 0.01 M H₂SO₄ solution with wide potential scan in order to observe the all redox peaks of caffeine which shown in Figure 3.105. Caffeine was known of its high over potential which was oxidized at 1418 mV with 30.2 μ A at 2eOHMnPc-CNT/GC electrode as expected (Amare and Admassie, 2012b). There is no other peak was observed for CAF oxidation during the CV scan in acidic solution.

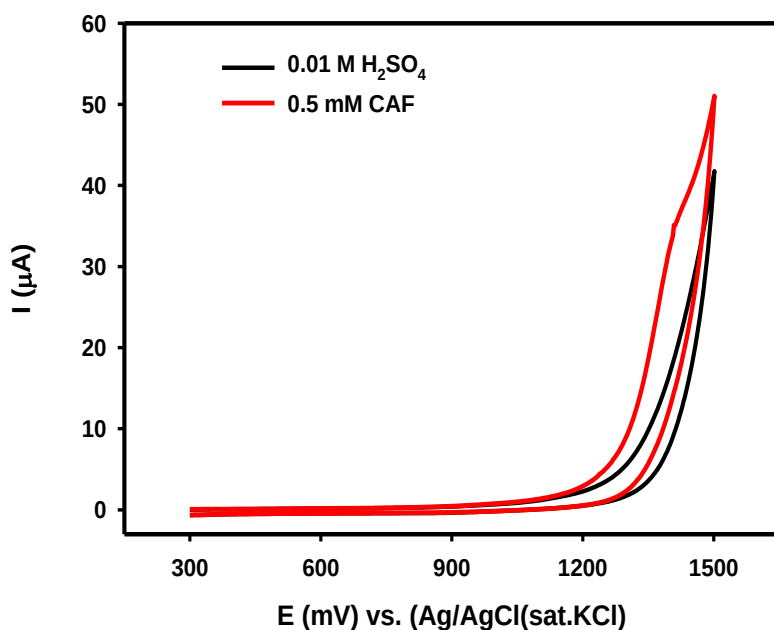


Figure 3.105 Cyclic voltammograms of 2eOHMnPc-CNT/GCE with and without CAF in 0.01 M H₂SO₄.

The cyclic voltammetric behavior of theophylline at the 2eOHMnPc-CNT/GC electrode was investigated in H₂SO₄ solution in a wide potential scan range between 300 mV and 1600 mV. Figure 3.106 shows the CVs of 2eOHMnPc-CNT/GC electrode in the absence and presence of 50 μ M TP that recorded under similar conditions. The obtaining voltammograms were promising

that TP was oxidized at 1272 mV with 12.2 μA current value. According to the results, 2eOHMnPc-CNT/GCE can be used for the TP determination. In addition, the individual oxidation peak potentials of TP and CAF were enable the simultaneous determination of these compounds with appropriate peak potential separation of ~ 145 mV.

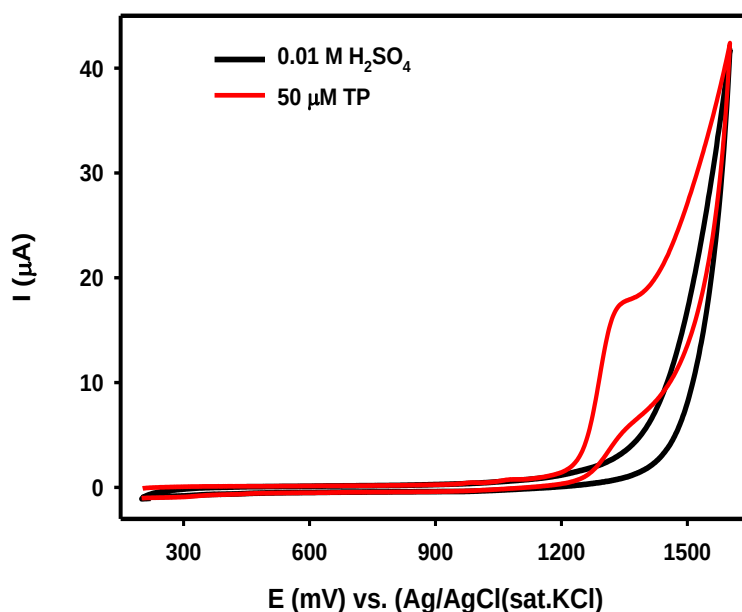


Figure 3.106 Cyclic voltammograms of 2eOHMnPc-CNT/GCE with and without 50 μM theophylline in 0.01 M H_2SO_4 .

Investigation of simultaneous theophylline and caffeine oxidations on XPc-CNT/GC electrodes by DPV

Individual determination of TP and CAF investigated in previous studies that their oxidation potential was suitable for simultaneous determination. According to this suggestion, simultaneous oxidation of TP and CAF was investigated at CNT/GC, 2eOHTiPc-CNT/GC and 2eOHMnPc-CNT/GC electrodes with DPV in the absence and presence of TP and CAF (Figure 3.107a-b). The central metal of Pc, provide different behaviour to the electrode material that need to be investigate for designing the best electrode surface for electroanalysis. The potential window narrowed between 700 and 1600 mV based on the above CV results that there were no oxidation/reduction peak were observed before that potential. As all three modified electrodes compared to each other, both TP and CAF oxidation peaks observed.

The highest peak current obtained on 2eOHMnPc-CNT/GCE both for TP and CAF, while TP and CAF oxidation peaks were observed at more positive potentials on same electrode as compared to the CNT/GCE and 2eOHTiPc-CNT/GCE. The potential and current values were represented in Table 3.25 that the best electrode was selected as 2eOHMnPc-CNT/GCE for TP and CAF oxidation due to its higher current value, which was associate with the lower detection limit. In addition, the best peak separation of TP and CAF obtained on 2eOHMnPc-CNT/GCE with 170 mV potential difference that was higher than other modified electrodes (125 mV). IN conclusion, 2eOHMnPc-CNT/GCE was chosen as an suitable electrode surface for selective TP and CAF determination.

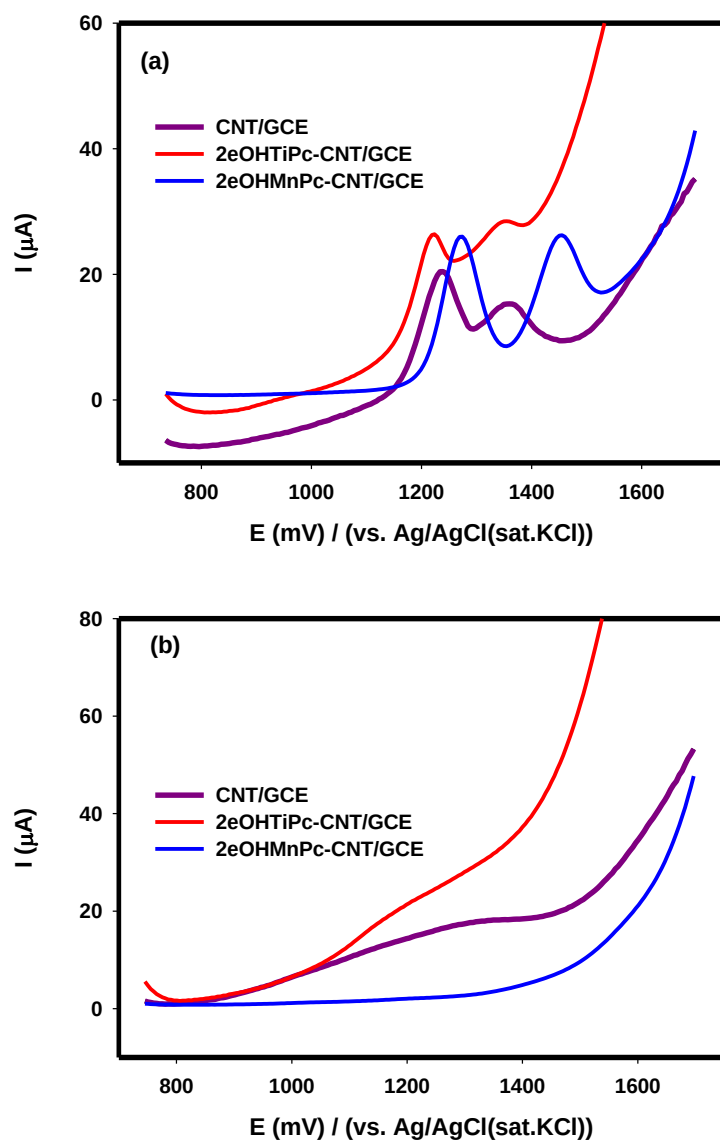


Figure 3.107 Differential puls voltammograms of CNT/GCE, 2eOHTiPc-CNT/GCE and 2eOHMnPc-CNT/GCE a) with and b) without 2 μM theophylline and 20 μM caffeine in 0.01 M H₂SO₄.

Table 3.25 Peak values of theophylline and caffeine oxidation at modified electrodes.

Electrode	Theophylline		Caffeine	
	E (mV)	I (μ A)	E (mV)	I (μ A)
CNT/GCE	1234	9.1	1359	3.0
2eOHTiPc-CNT/GCE	1225	6.6	1350	2.2
2eOHMnPc-CNT/GCE	1263	15.34	1435	8.46

Effect of supporting electrolyte type on theophylline and caffeine oxidation

In order to improve the analytical signal of compounds, some parameters need to optimize. As mentioned in the introduction section, proton participated in oxidation reaction of the analytes that pH changes of supporting electrolyte affect their oxidation behavior. Therefore, simultaneous TP and CAF oxidation was investigated in various supporting electrolytes such as Britton Robinson buffer (BR) solution and acidic solutions.

Figure 3.108 exhibits the simultaneous oxidation of TP and CAF that was investigated at GC, CNT/GC and 2eOHMnPc-CNT/GC electrodes with CV in the presence of TP and CAF in britton robinson buffer solution (pH: 2-4-6). All electrodes show oxidation peaks with different potential and current values.

Figure 3.109 was plotted based on the current values of all electrodes towards TP and CAF oxidation that shown in Figure 3.108. Figure 3.109a represents the TP current change by the increasing pHs. The higher current values were obtained at acidic pHs for all electrodes while the oxidation peak potentials were shift to more negative values for TP oxidation. The equation of the plot found as $E/V = 1.421 - 0.059 \text{ pH}$, $R^2 = 0.996$. A slope of 59 mV/pH can be attributed to the equal number of electron and hydrogen ions transfer occurred in the oxidation reaction of TP on 2eOHMnPc-CNT/GCE.

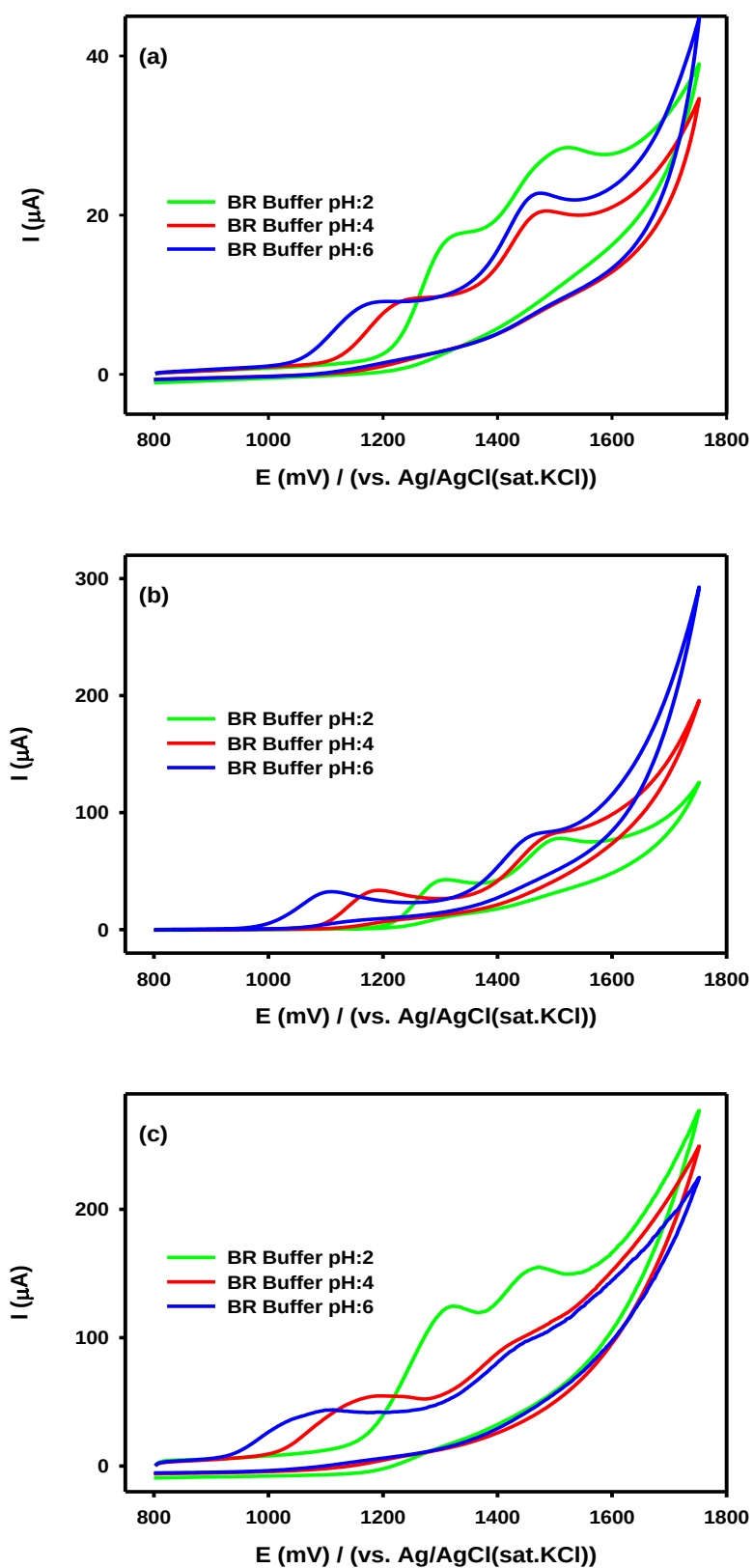


Figure 3.108 CVs of 0.5 mM TP and CAF oxidation at a) GCE, b) CNT/GCE, c) 2eOHMnPc-CNT/GCE in BR buffer pH: 2-6.

CAF oxidation behaviour was investigated and related oxidation current values were plotted in Figure 3.109b. These high current values in lower pHs gave an idea for choosing the electrolyte in acidic media. In addition, the potential changes versus increasing pHs were not proportional while many published work proposed potential shift with about 59 mV slope value (Habibi et al, 2012; Goyal et al, 2011). This interesting behaviour can be attributed to the simultaneous existence of TP and CAF. They possibly affect the electrochemical response of each other.

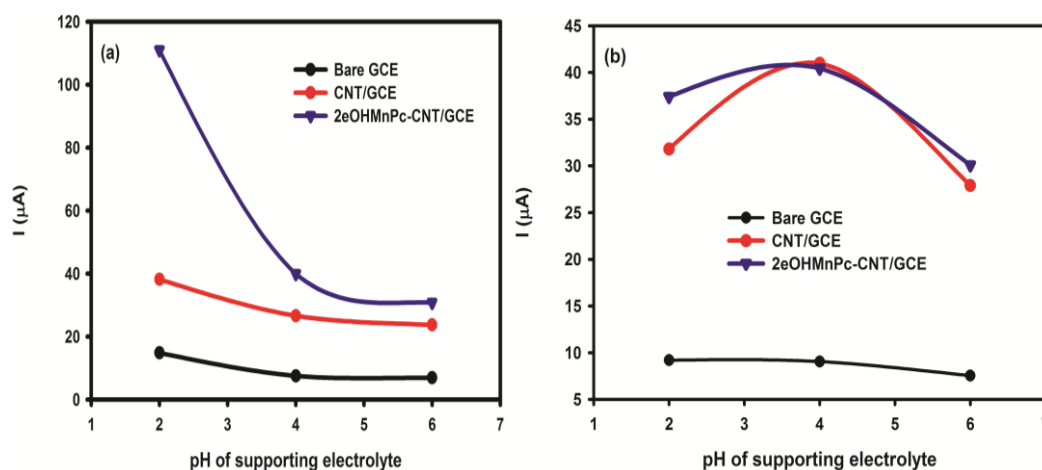


Figure 3.109 Plots of current change versus supporting electrolyte pH for TP (a) and CAF (b) oxidation.

In Figure 3.110, GCE, CNT/GCE and 2eOHMnPc-CNT/GCE were studied in four different acid solutions that were prepared for investigation of TP and CAF oxidation behavior. 0.01 M of HNO_3 , HCl , HClO_4 , H_2SO_4 were investigated in the absence and presence of TP and CAF as they studied in the published literatures (Habibi et al., 2012; Gao et al., 2013) on these three electrodes. The potential and current values of TP and CAF at different electrodes and different medias were written in Table 3.26. H_2SO_4 solution was chosen as an optimum supporting electrolyte due to the highest current value with more negative potential for all electrodes.

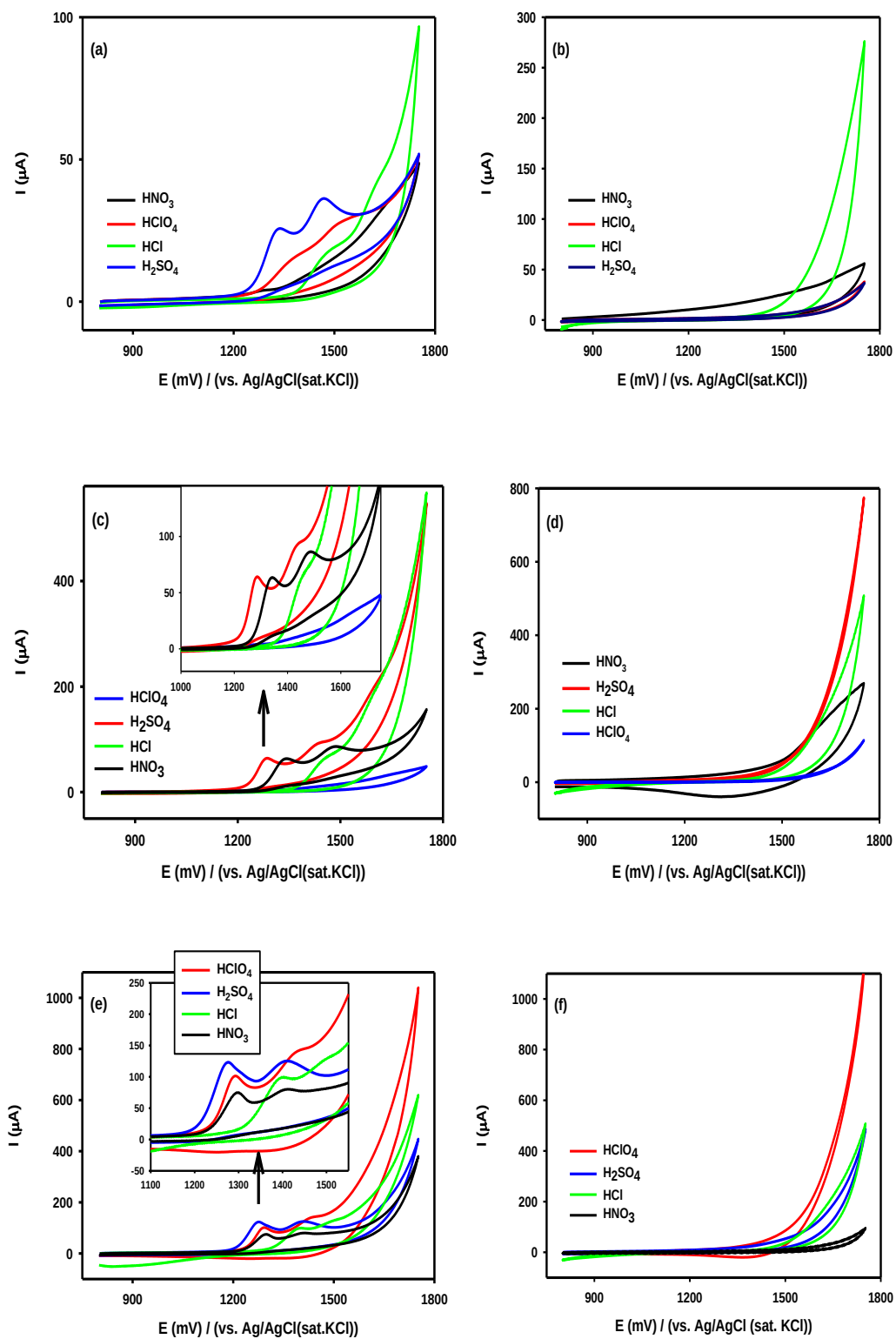


Figure 3.110 Cyclic voltammograms of GCE (a, b), CNT/GCE (c, d), 2eOHMnPc-CNT/GCE (e, f) with (a, c, e) and without (b, d, f) 0.5 mM TP and CAF in various acidic supporting electrolytes.

Table 3.26 0.5 mM TP and CAF oxidation peak values at GCE, CNT/GCE and 2eOHMnPc-CNT/GCE in acidic electrolytes.

Acid	Electrode	TP		CAF	
		E (mV)	I (μ A)	E (mV)	I (μ A)
HNO ₃	GCE	1293	1.63	-	-
	CNT/GCE	1337	61.47	1469	16
	2eOHMnPc-CNT/GCE	1290	86.49	1435	20.92
HCl	GCE	1472	14.7	1620	7.1
	CNT/GCE	1464	25.64	1591	33.3
	2eOHMnPc-CNT/GCE	1388	76.1	1495	33.1
HClO ₄	GCE	1359	9.84	1513	3.5
	CNT/GCE	1284	50.42	1435	33.79
	2eOHMnPc-CNT/GCE	1276	93	1408	30.6
H ₂ SO ₄	GCE	1334	21.8	1469	11.65
	CNT/GCE	1342	59.6	1488	30.76
	2eOHMnPc-CNT/GCE	1298	120	1400	29

Optimization of DPV scan rate

Scan rate is an important parameter for differential pulse voltammetric studies which was need to be determined for sensitive determination for analytes. Figure 3.111 shows the behaviour of TP and CAF at 2eOHMnPc-CNT/GC electrode with different scan rates (10-50 mV.s⁻¹). Peak potentials were not affected by the scan rate while peak currents increase by the increasing of scan rate. 40 and 50 mV.s⁻¹ scan rate values was not significantly different that 40 mV.s⁻¹ was chosen as the optimum scan rate due to the peak shape and high current value.

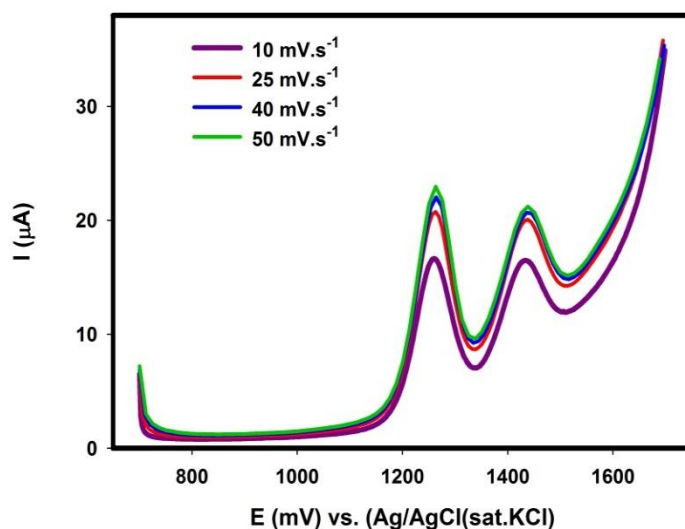


Figure 3.111 DP voltammograms of 2 μM TP and 20 μM CAF at 2eOHMnPc-CNT/GCE in 0.01 M H_2SO_4 with scan rates of 10, 25, 40, 50 mV.s^{-1} .

Optimization of DPV accumulation time

Figure 3.112 shows the accumulation time effect on oxidation of TP and CAF in 0.01 M H_2SO_4 . 5 s to 100 s accumulation times were applied before the DPV scan on 2eOHMnPc-CNT/GCE. According to the literatures, TP and CAF were accumulated mostly in open circuit potential. Therefore, different accumulation times between 5 and 100 seconds were investigated for open circuit conditions. According to the results, peak current values were decrease by the increase of accumulation time that 5 s was chosen as an optimum time for accumulation for DPV measurements on 2eOHMnPc-CNT/GCE.

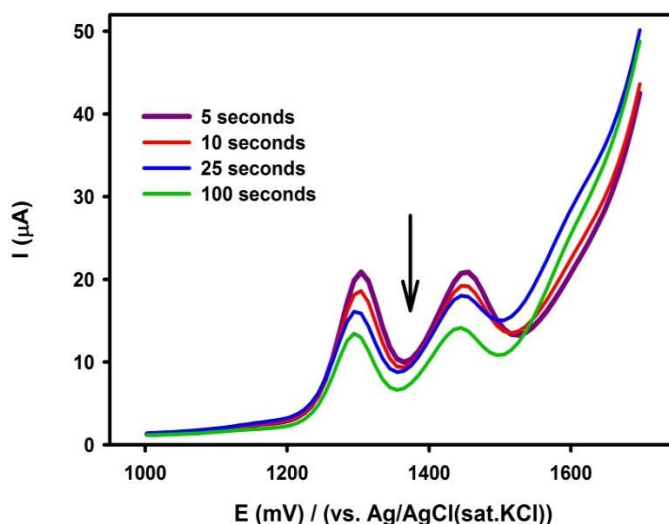


Figure 3.112 DP voltammograms of 2 μM TP and 20 μM CAF at 2eOHMnPc-CNT/GCE in 0.01 M H_2SO_4 with open circuit accumulation time range of 5-100 s.

Optimization of 2eOHMnPc/CNT ratio

In order to improve the analytical signal, which provide the sensitive determination of analytes that electrode surface characteristic was crucial. The main components of composite electrode materials are 2eOHMnPc and CNT that their ratio variation may possibly affect the response to analytes. The ratios were change between 3% and 15%. The oxidation potential was independent from the surface ratio towards oxidation of TP and CAF. In addition, both TP and CAF oxidation peak current was first increase to reach maximum value at 6%. Then it decreased again and remains stable after 10%. The highest peak current was obtained at the ratio of 6% 2eOHMnPc/CNT was chosen as an optimum electrode surface which can be clearly seen in Figure 3.113.

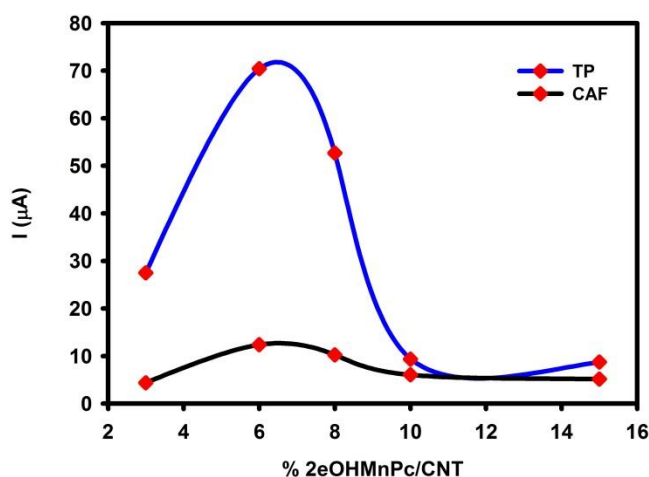


Figure 3.113 Plots for current changes of TP and CAF versus 2eOHMnPc/CNT ratios.

Effect of metal nano particles towards TP and CAF oxidation

In many studies, metal nano particles modification increased the analytical response of the electrodes due to its unique properties. In the light of this, Au, Pt, Pd and Au-Pt bimetallic nano particles were formed on 2eOHMnPc-CNT/GC electrode surface. Effect of metal nano particles deposition was investigated by DPV in 0.01 M H₂SO₄ in Figure 3.114. It was clearly shown in figures that metal nano particles deposition decrease the current values of both TP and CAF oxidation which also show unstable characteristics. It was suggested that, metal nano particles were get out of the surface during the potential scan to high positive potentials which resulted to low current values. In conclusion, metal nano particles were not used as electrode modifiers for TP and CAF oxidation.

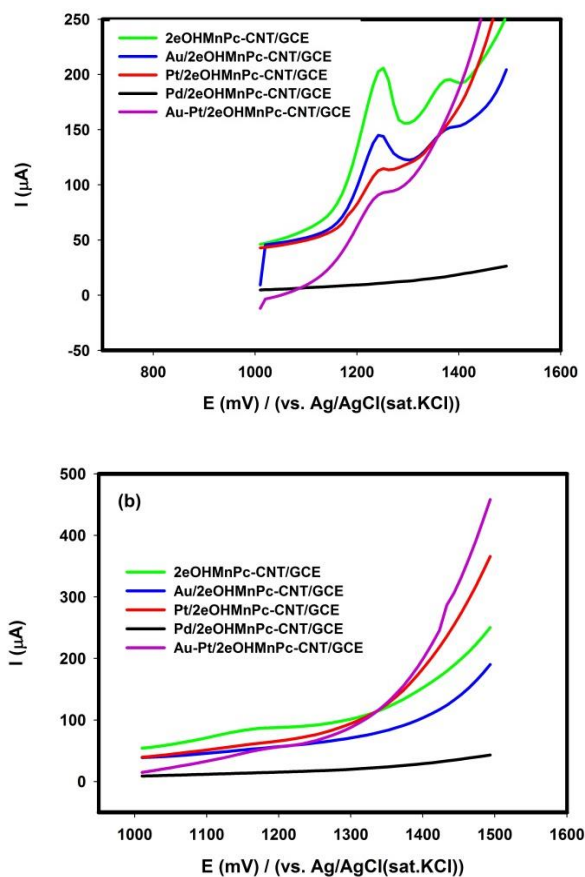


Figure 3.114 DP voltammograms of metal (M: Au, Pt, Pd, Au-Pt) nano particles modified 2eOHMnPc-CNT/GC electrodes with a) and without b) 20 μ M TP and CAF in 0.01 M H_2SO_4 .

Differential pulse voltammetric determination of theophylline and caffeine

The simultaneous determination of caffeine and theophylline at conventional solid electrodes generally struggles due to the overlapping of oxidation peaks. Differential pulse voltammetry has high current density and better peak separation as compared to the cyclic voltammetry. Therefore, the individual and simultaneous determination of TP and CAF on GCE, CNT/GCE and 2eOHMnPc-CNT/GCE was studied by DPV in acidic solution.

The differential pulse voltammetric results were obtained under following conditions; step potential: 10 mV, amplitude: 50 mV, modulation time: 0.05 s, interval time: 0.25 s and scan rate 40 mV.s^{-1} .

Limit of detection values were calculated from (S/N:3) and calibration curves. The average value of background current estimated from 10 different

measurements. LOQ values were calculated for estimation of linear ranges for all electrodes.

In analytical method, the linear range is the analyte concentration range over that response is proportional to concentration. Dynamic range is the concentration range over which there is a measurable response to analyte, even if the response is not linear. To determine limit of linearity, the following equation is used:

$$\%S = \left| \left[\frac{y_i}{\hat{y}} \right] - 1 \right| \times 100 = \left| \frac{y_i}{mx_i + b} - 1 \right| \times 100$$

In equation, y_i is measured value, $\hat{y}$ is calculated value from the calibration equation. If the %s is $\leq 5\%$, the linearity is accepted. If the %s is $\geq 5\%$, this concentration (y_i) was not included in the linear range.

Initial studies were focused on the electrochemical response of increasing TP concentrations on GCE, CNT/GCE and 2eOHMnPc-CNT/GCE. Figure 3.115 shows that differential pulse voltammetric response of bare GC electrodes in H_2SO_4 solution in the absence and presence of increasing concentrations of TP. The dynamic concentration range and linear range of TP on bare GCE was shown in Figure 3.116 According to the equation, if the limit of linearity point chosen as $400 \mu M$, the linear range of TP on bare GCE is found between 20 and $400 \mu M$ with an equation of $I_p = 0.0116 C_{TP} + 0.4674$ ($R^2 = 0.9912$).

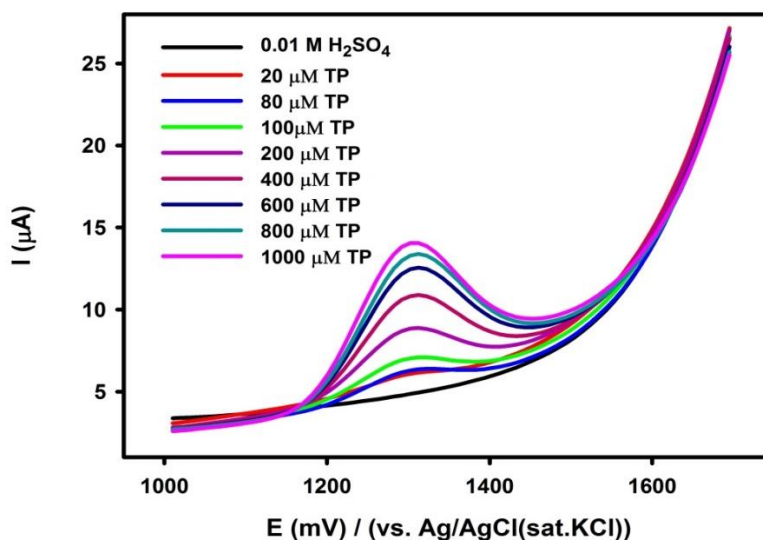


Figure 3.115 Differential pulse voltammograms at GCE for increasing concentrations of TP in $0.01 M H_2SO_4$ with $40 mV.s^{-1}$ scan rate and $50 mV$ pulse amplitude.

If the limit of linearity extended to 600 μM , the equation found as $I_p = 0.0098 C_{\text{TP}} + 0.6832$ ($R^2 = 0.9776$). The calculated $s\%$ for 600 μM was found as 5.22% which is larger than 5.0 that means unacceptable linearity limit. If the calculation was based on 400 μM TP concentration, the $s\%$ found as 2.10% which was an acceptable value for determine the limit of linearity point. In the light of these results, the linear range was found as 20-400 μM .

The detection limit of TP at bare GCE was calculated as 1×10^{-6} M ($S/N=3$). Relative standard deviations (RSD) are 1.91% (5×10^{-5} M, $n=5$).

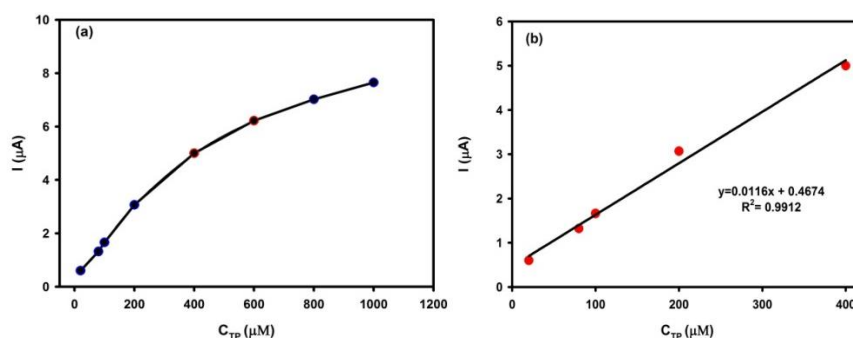


Figure 3.116 Plots for TP oxidation peak currents versus TP concentration. a) dynamic range (20, 80, 100, 200, 400, 600, 800, 1000 μM TP) and b) linear calibration range (20-400 μM TP) for TP oxidation on bare GCE.

Figure 3.117 shows that differential pulse voltammetric response of CNT/GC electrodes in H_2SO_4 solution in the absence and presence of increasing concentrations of TP.

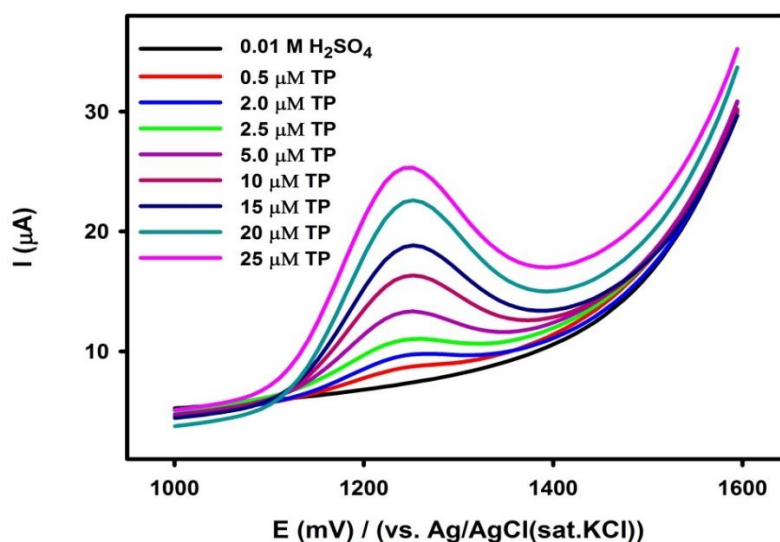


Figure 3.117 Differential pulse voltammograms at CNT/GCE for increasing concentrations of TP in 0.01 M H_2SO_4 with 40 mV.s^{-1} scan rate and 50 mV pulse amplitude.

The dynamic concentration range and linear range of TP on CNT/GCE was shown in Figure 3.118. According to the equation, if the limit of linearity point chosen as 15 μM , the linear range of TP on CNT/GCE is found between 0.5 and 20 μM with an equation of $I_p = 0.5814 C_{\text{TP}} + 0.8808$ ($R^2 = 0.9943$). If the limit of linearity extended to 20 μM , the equation found as $I_p = 0.5082 C_{\text{TP}} + 1.1732$ ($R^2 = 0.9781$). The calculated s% for 20 μM was found as 7.09% which is larger than 5.0 that means unacceptable linearity limit. If the calculation was based on 15 μM TP concentration, the s% found as 2.83% which was an acceptable value for determine the limit of linearity point. In the light of these results, the linear range was found as 0.5-20 μM .

The detection limit of TP at CNT/GCE was calculated as 8×10^{-8} M ($S/N=3$). Relative standart deviations (RSD) are 2.10% (1×10^{-6} M, $n=5$).

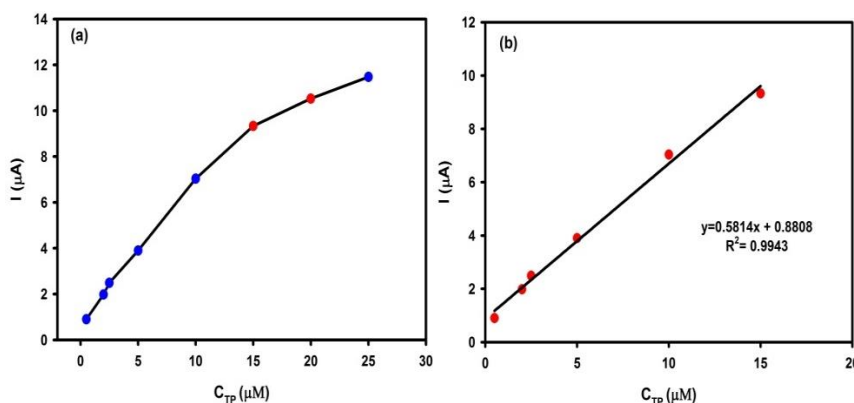


Figure 3.118 Plots for TP oxidation peak currents versus TP concentration. a) dynamic range (0.5, 2, 2.5, 5, 10, 15, 20, 25 μM TP) and b) linear calibration range (0.5-15 μM TP) for TP oxidation on CNT/GCE.

Figure 3.119 shows that differential pulse voltammetric response of 2eOHMnPc-CNT/GC electrode in H_2SO_4 solution in the absence and presence of increasing concentrations of TP.

The dynamic concentration range and linear range of TP on 2eOHMnPc-CNT/GCE was shown in Figure 3.119. According to the equation, if the limit of linearity point chosen as 12 μM , the linear range of TP on bare GCE is found between 0.04 and 12 μM with an equation of $I_p = 9.8485 C_{\text{TP}} + 1.5645$ ($R^2 = 0.9941$).

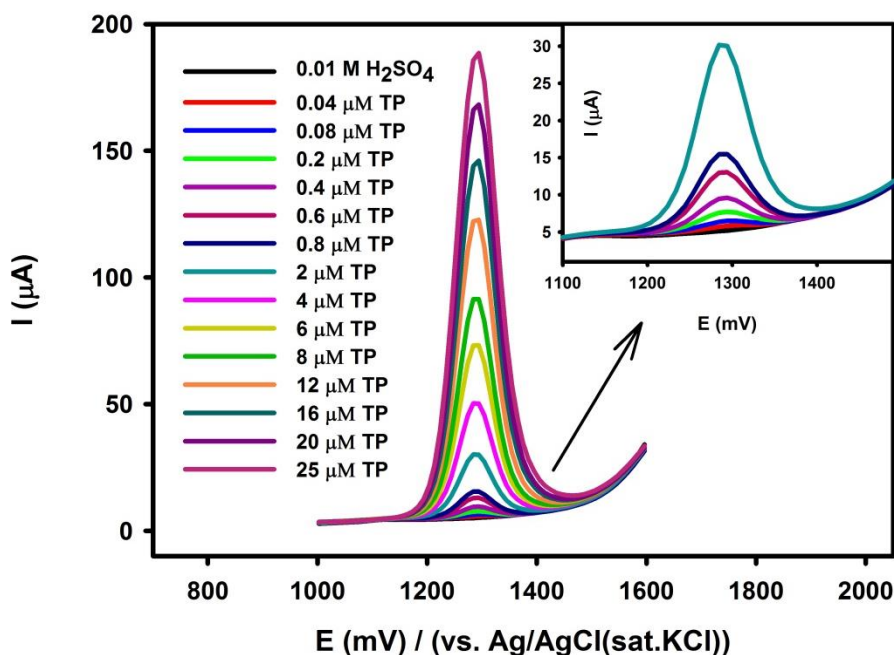


Figure 3.119 Differential pulse voltammograms at 2eOHMnPc-CNT/GCE for increasing concentrations of TP in 0.01 M H_2SO_4 with $40 \text{ mV} \cdot \text{s}^{-1}$ scan rate and 50 mV pulse amplitude.

If the limit of linearity extended to 16 μM , the equation found as $I_p = 9.0091C_{\text{TP}} + 3.2252$ ($R^2 = 0.9875$). The calculated s% for 16 μM was found as 7.04% which is larger than 5.0 that means unacceptable linearity limit. If the calculation was based on 12 μM TP concentration, the s% found as 4.79% which was an acceptable value for determine the limit of linearity point. In the light of these results, the linear range was found as 0.04-12 μM .

The detection limit of TP at 2eOHMnPc-CNT/GCE was calculated as $6.6 \times 10^{-9} \text{ M}$ ($S/N=3$). Relative standard deviations (RSD) are 2.51% ($1 \times 10^{-7} \text{ M}$, $n=5$)

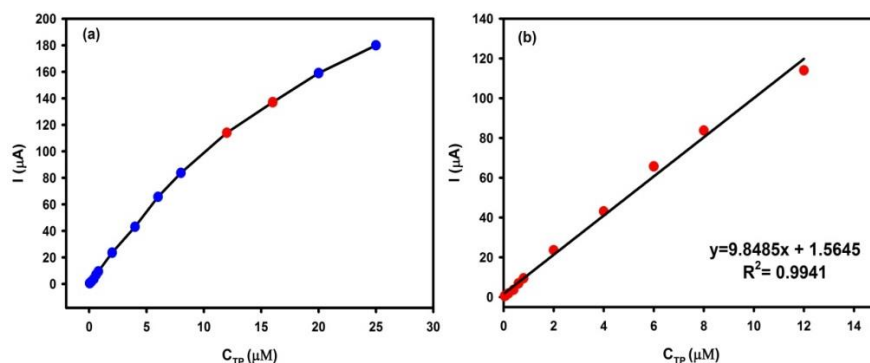


Figure 3.120 Plots for TP oxidation peak currents versus TP concentration. a) dynamic range (0.04, 0.08, 0.2, 0.4, 0.6, 0.8, 2, 4, 6, 8, 12, 16, 20, 25 μM TP) and b) linear calibration range (0.04-12 μM TP) for TP oxidation on bare GCE.

Figure 3.121 shows that DPV response of bare GC electrodes in H_2SO_4 solution in the absence and presence of increasing concentrations of CAF. The dynamic concentration range and linear range of CAF on bare GCE was shown in Figure 3.122. According to the equation, if the limit of linearity point chosen as 600 μM , the linear range of CAF on bare GCE is found between 8 and 600 μM with an equation of $I_p = 0.0381C_{\text{CAF}} + 0.4245$ ($R^2 = 0.9981$). If the limit of linearity extended to 800 μM , the equation found as $I_p = 0.0341C_{\text{CAF}} + 0.869$ ($R^2 = 0.9861$). The calculated $s\%$ for 800 μM was found as 7.63% which is larger than 5.0 that means unacceptable linearity limit. If the calculation was based on 600 μM CAF concentration, the $s\%$ found as 2.08% which was an acceptable value for determine the limit of linearity point. In the light of these results, the linear range was found as 8-600 μM . The detection limit of CAF at bare GCE was calculated as 1×10^{-6} M ($S/N=3$). RSD is 1.75% (1×10^{-5} M, $n=5$).

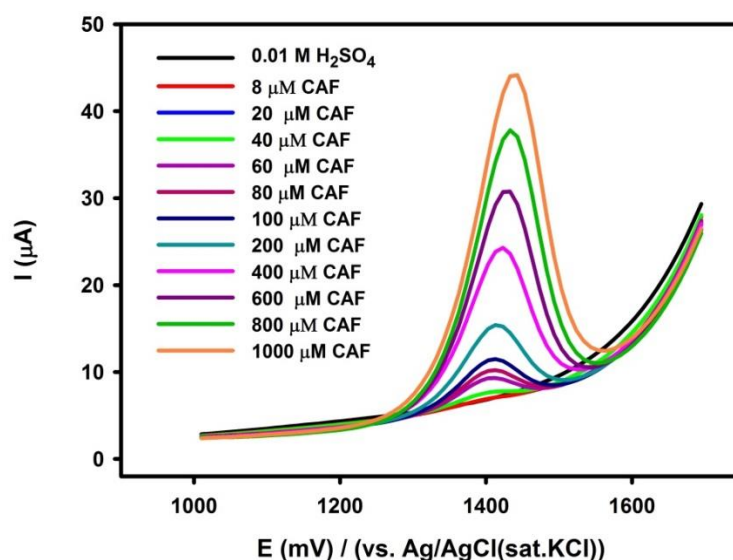


Figure 3.121 Differential pulse voltammograms at GCE for increasing concentrations of CAF in 0.01 M H_2SO_4 with 40 mV.s^{-1} scan rate and 50 mV pulse amplitude.

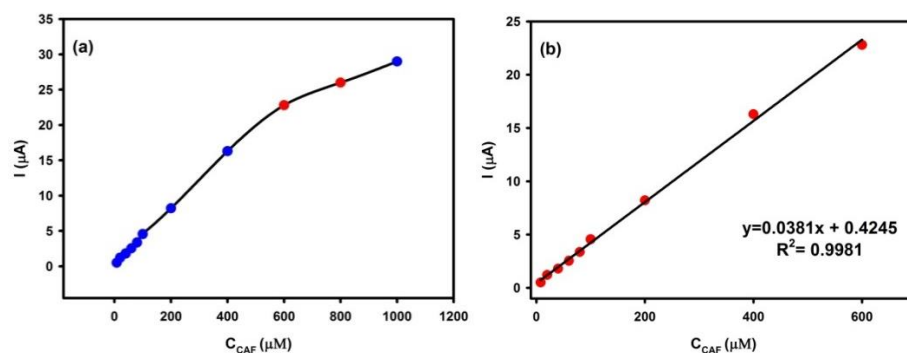


Figure 3.122 Plots for CAF oxidation peak currents versus CAF concentration. a) dynamic range (8, 20, 40, 60, 80, 100, 200, 400, 600, 800, 1000 μM CAF) and b) linear calibration range (8-600 μM CAF) for CAF oxidation on bare GCE.

Figure 3.123 shows that differential pulse voltammetric response of CNT/GC electrodes in H_2SO_4 solution in the absence and presence of increasing concentrations of CAF.

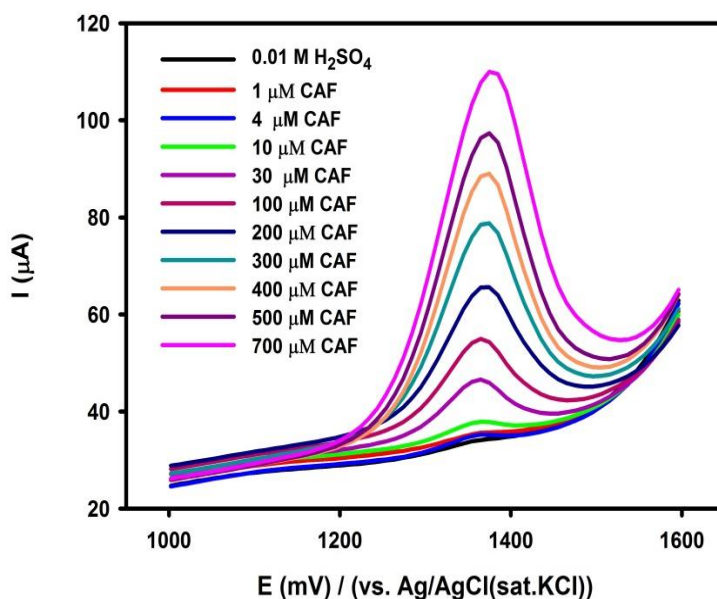


Figure 3.123 Differential pulse voltammograms at CNT/GCE for increasing concentrations of CAF in 0.01 M H_2SO_4 with 40 mV.s^{-1} scan rate and 50 mV pulse amplitude.

The dynamic concentration range and linear range of CAF on CNT/GCE was shown in Figure 3.124. According to the equation, if the limit of linearity point chosen as 500 μM , the linear range of CAF on CNT/GCE is found between 1 and 500 μM with an equation of $I_p = 0.1084C_{\text{CAF}} + 2.9126$ ($R^2 = 0.9914$). If the limit of linearity extended to 600 μM , the equation found as $I_p = 0.1016C_{\text{CAF}} + 3.5773$ ($R^2 = 0.9861$). The calculated s% for 600 μM was found as 7.03% which is larger than 5.0 that means unacceptable linearity limit. If the calculation was based on 500 μM CAF concentration, the s% found as 4.57% which was an acceptable value for determine the limit of linearity point. In the light of these results, the linear range was found as 1-500 μM . The detection limit of CAF at CNT/GCE was calculated as $5 \times 10^{-7} \text{ M}$ ($S/N=3$). Relative standard deviations (RSD) are 2.15% ($5 \times 10^{-6} \text{ M}$, $n=5$).

Figure 3.125 shows the calibration curves for caffeine oxidation at bare GCE, CNT/GCE and 2eOHMnPc-CNT/GCE. The best activity towards CAF oxidation obtained at 2eOHMnPc-CNT/GCE due to its higher slope value as compared to the bare GCE and CNT/GCE in acidic solution. The compared slope values of TP at those electrodes were not shown due to its different concentration scale on different electrodes.

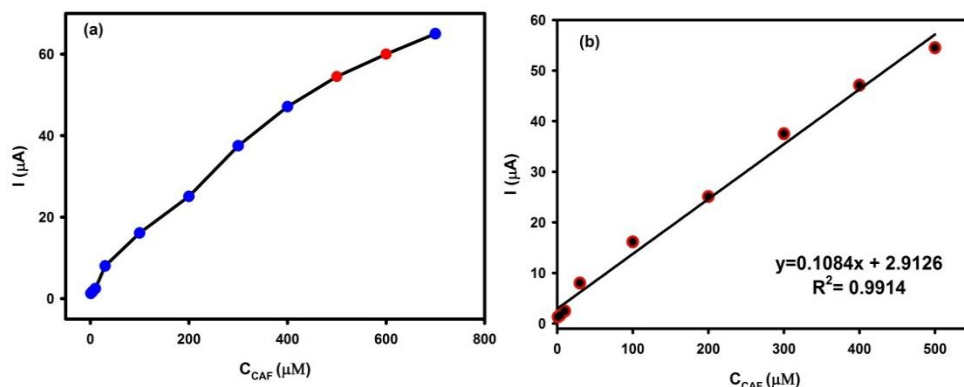


Figure 3.124 Plots for TP oxidation peak currents versus CAF concentration. a) dynamic range (1, 4, 10, 30, 100, 200, 300, 400, 500, 600, 700 μM CAF) and b) linear calibration range (1-500 μM CAF) for CAF oxidation on CNT/GCE.

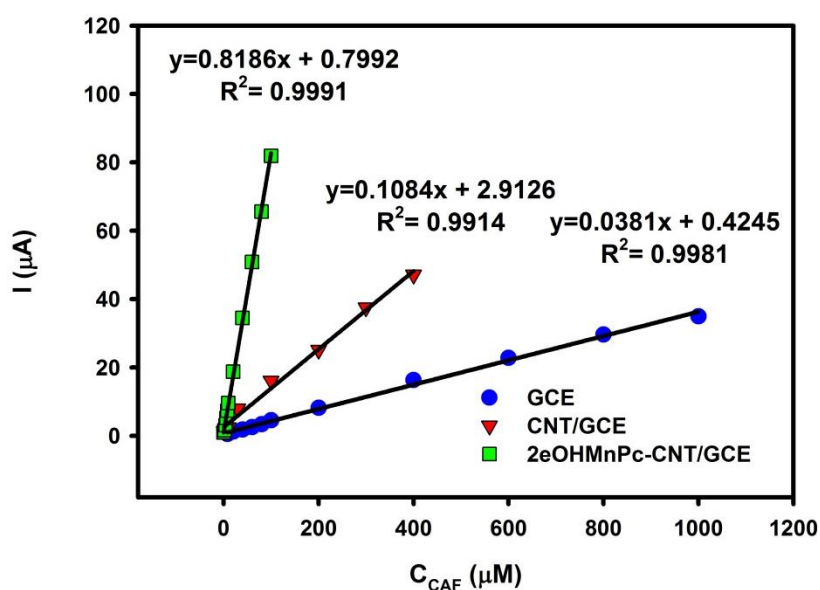


Figure 3.125 Calibration curves and related equations for caffeine oxidation at bare GCE, CNT/GCE and 2eOHMnPc-CNT/GCE.

Figure 3.126 shows that differential pulse voltammetric response of 2eOHMnPc-CNT/GCE in H_2SO_4 solution in the absence and presence of increasing concentrations of CAF.

The dynamic concentration range and linear range of CAF on 2eOHMnPc-CNT/GCE was shown in Figure 3.127. According to the equation, if the limit of linearity point chosen as 100 μM , the linear range of CAF on 2eOHMnPc-CNT/GCE is found between 0.2 and 100 μM with an equation of $I_p = 0.8186C_{CAF} + 0.7992$ ($R^2 = 0.9991$). If the limit of linearity extended to 150 μM , the equation found as $I_p = 0.7218C_{CAF} + 2.4431$ ($R^2 = 0.9826$). The calculated s% for 150 μM was found as 9.67% which is larger than 5.0 that means unacceptable linearity limit.

If the calculation was based on 100 μM TP concentration, the s% found as 2.0% which was an acceptable value for determine the limit of linearity point. In the light of these results, the linear range was found as 0.2-100 μM .

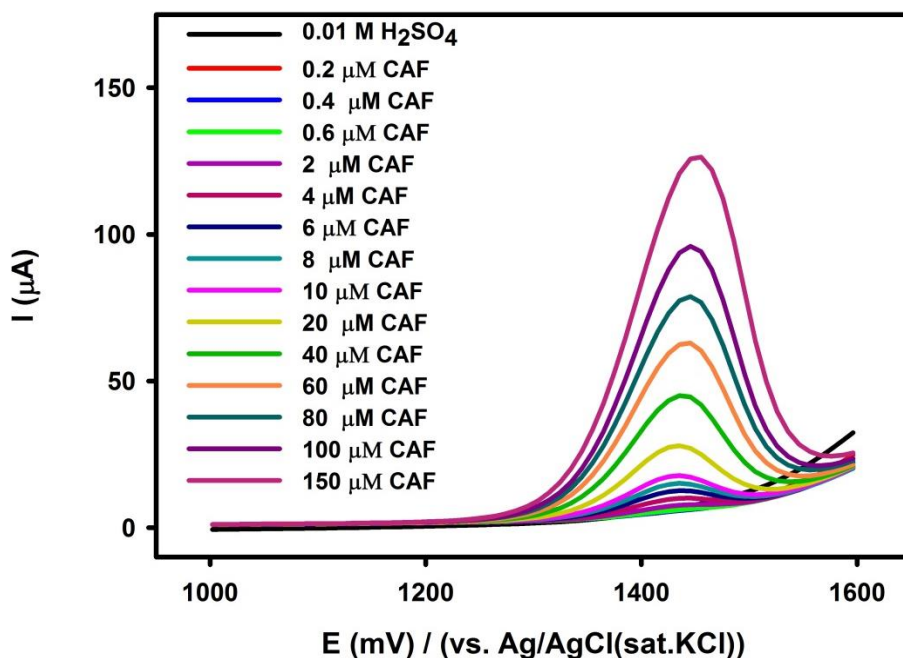


Figure 3.126 Differential pulse voltammograms at 2eOHMnPc-CNT/GCE GCE for increasing concentrations of CAF in 0.01 M H_2SO_4 with 40 mV.s^{-1} scan rate and 50 mV pulse amplitude.

The detection limit of CAF at 2eOHMnPc-CNT/GCE was calculated as 5×10^{-8} M (S/N=3). Relative standard deviations (RSD) are 2.64% (2×10^{-7} M, $n=5$).

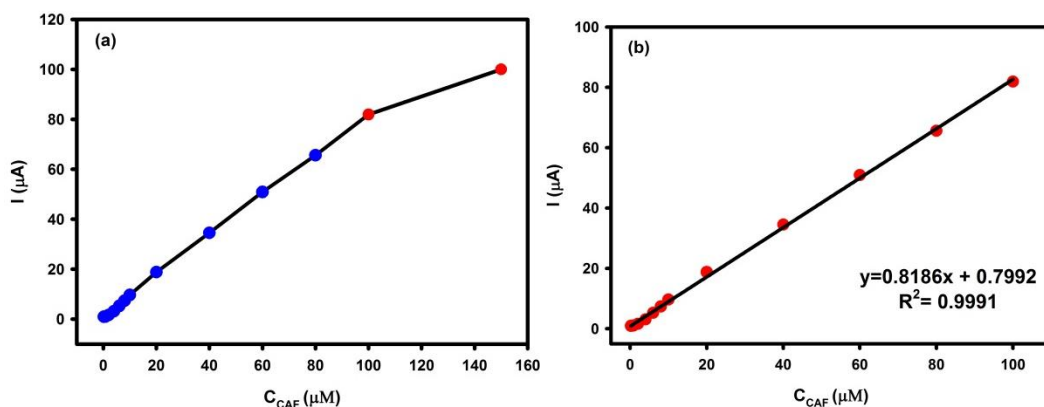


Figure 3.127 Plots for TP oxidation peak currents versus CAF concentration. a) dynamic range (0.2, 0.4, 0.8, 2, 4, 6, 8, 10, 20, 40, 60, 80, 100, 150 μM CAF) and b) linear calibration range (0.2-100 μM CAF) for CAF oxidation 2eOHMnPc-CNT/GCE.

Simultaneous determination of caffeine and theophylline was also investigated 2eOHMnPc-CNT/GCE. Determination of one component presence of another was carry out by addition of increasing concentrations of the analyte while keeping the other analyte's concentration constant. Figure 3.128 exhibits the differential pulse voltammograms obtained for increasing concentrations of TP, while the concentration of CAF was kept constant at a value of 20 μM on 2eOHMnPc-CNT/GCE in H_2SO_4 solution.

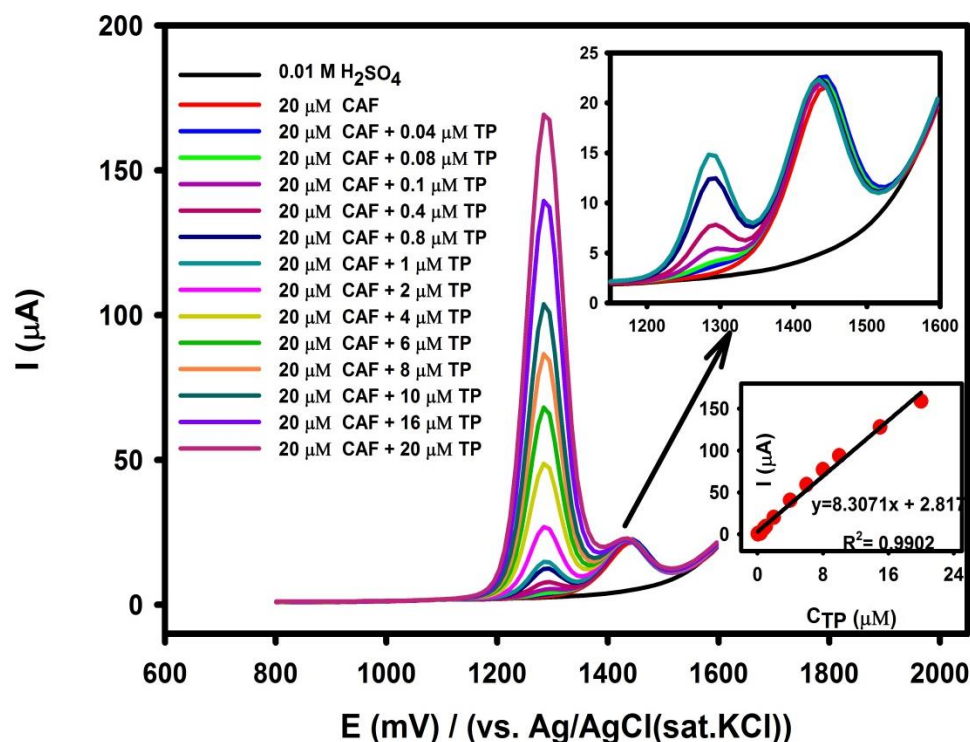


Figure 3.128 Differential pulse voltammograms at 2eOHMnPc-CNT/GCE in the presence of CAF (20 μM) for increasing concentrations of TP in 0.01 M H_2SO_4 with 40 mV.s^{-1} scan rate and 50 mV pulse amplitude. Inset: Corresponding calibration curve of increasing TP concentration.

The linear range of TP was found as 0.2-100 μM by the same way that mentioned above previously. The linear regression equation can be expressed as $I_p = 0.8186C_{\text{TP}} + 0.7992$ ($R^2 = 0.9991$) that shown as an inset in the related voltammogram. The detection limit of TP at 2eOHMnPc-CNT/GCE was calculated as 8.1×10^{-9} M ($S/N=3$). Relative standart deviations (RSD) are 2.78% (5×10^{-7} M, $n=5$).

Figure 3.129 shows the differential pulse voltammograms obtained for increasing concentrations of CAF, while the concentration of TP was kept constant at a value of 1 μM on 2eOHMnPc-CNT/GCE in H_2SO_4 solution. The linear range of CAF was found as 2-200 μM by the same way that mentioned above previously. The peak current of TP was decreased only slightly with the increasing CAF concentrations. The linear regression equation can be expressed as $I_p = 0.4988C_{\text{CAF}} - 0.1678$ ($R^2 = 0.9970$) that shown as an inset in the related voltammogram. The detection limit of CAF at 2eOHMnPc-CNT/GCE was calculated as 3×10^{-7} M ($S/N=3$). Relative standart deviations (RSD) are 3.13% (5×10^{-6} M, $n=5$).

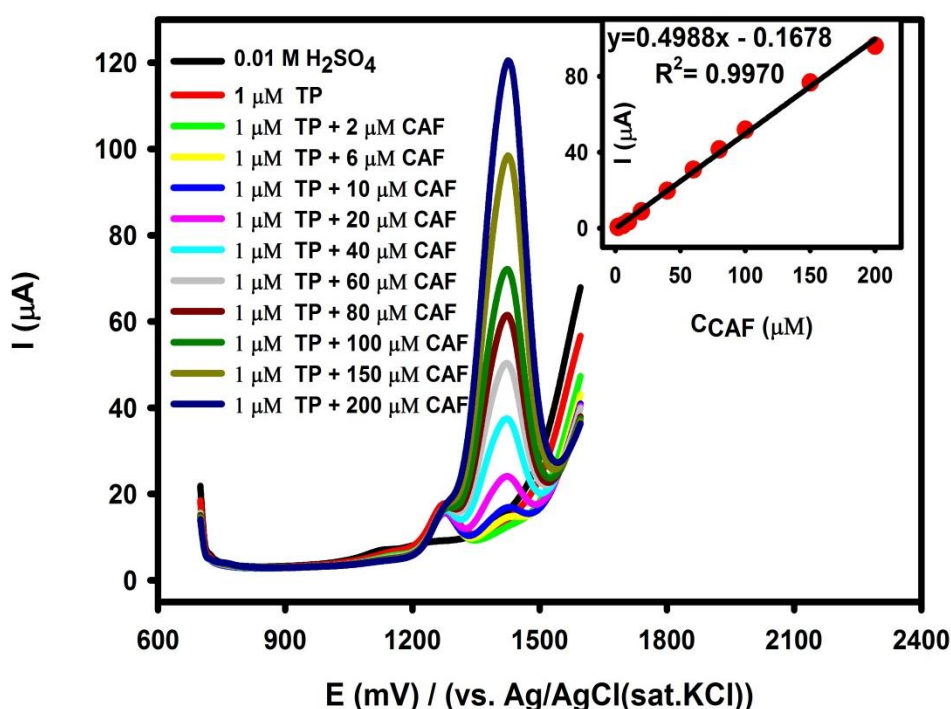


Figure 3.129 Differential pulse voltammograms at 2eOHMnPc-CNT/GCE in the presence of TP (1 μM) for increasing concentrations of CAF in 0.01 M H_2SO_4 with 40 mV.s^{-1} scan rate and 50 mV pulse amplitude. Inset: Corresponding calibration curve of increasing CAF concentration.

Comparison of the bare and modified electrodes in terms of sensitivity, LOD and linear range were listed in Table 3.27. High sensitivity that related with the low detection limits were obtained for TP as compared to the CAF at almost all electrodes (except bare GCE). The results show that 2eOHMnPc-CNT/GCE provide selective and sensitive determination of TP and CAF.

Table 3.27 Analytical characteristics for determination of theophylline, caffeine and their mixtures at bare and modified electrodes.

Analytes	Theophylline	Caffeine
Electrode	Bare GCE	
Calibration Equation^a	$ip=0.00116C_{TP}+0.4674$	$ip=0.0381C_{CAF}+0.4245$
Linear Range	$2 \times 10^{-5} \text{ M} - 4 \times 10^{-4} \text{ M}$	$8 \times 10^{-6} \text{ M} - 6 \times 10^{-4} \text{ M}$
LOD	$1.0 \times 10^{-6} \text{ M}$	$1.0 \times 10^{-6} \text{ M}$
R²	0.9912	0.9981
Electrode	CNT/GCE	
Calibration Equation^a	$ip=0.5814C_{TP}+0.8808$	$ip=0.1084C_{CAF}+2.9126$
Linear Range	$5 \times 10^{-7} \text{ M} - 1.5 \times 10^{-6} \text{ M}$	$1 \times 10^{-6} \text{ M} - 5 \times 10^{-4} \text{ M}$
LOD	$8.0 \times 10^{-8} \text{ M}$	$5.0 \times 10^{-7} \text{ M}$
R²	0.9943	0.9914
Electrode	2eOHMNPc-CNT/GCE	
Calibration Equation^a	$ip=9.8485C_{TP}+1.4674$	$ip=0.00116C_{CAF}+0.4674$
Linear Range	$4 \times 10^{-8} \text{ M} - 1.2 \times 10^{-6} \text{ M}$	$2 \times 10^{-7} \text{ M} - 1 \times 10^{-4} \text{ M}$
LOD	$6.6 \times 10^{-9} \text{ M}$	$5.0 \times 10^{-8} \text{ M}$
R²	0.9941	0.9991
Analytes	Mixture of TP and CAF at 2eOHMNPc-CNT/GCE	
	20 μM CAF + TP$\uparrow$	1 μM TP + CAF $\uparrow$
Calibration Equation^a	$ip=8.3071C_{TP}+2.817$	$ip=0.4988C_{CAF}-0.1678$
Linear Range	$4 \times 10^{-8} \text{ M} - 2 \times 10^{-5} \text{ M}$	$2 \times 10^{-6} \text{ M} - 2 \times 10^{-4} \text{ M}$
LOD	$8.1 \times 10^{-9} \text{ M}$	$3.0 \times 10^{-7} \text{ M}$
R²	0.9902	0.9970

^a ip is microampere and C is micromolar concentration

Table 3.28 represents the comparison of linear range and LOD values of different modified electrodes that were used for determination of caffeine. The 2eOHMnPc-CNT/GCE electrode in the present study is a promising alternative for TP sensor due to its high selectivity and low detection limit.

Table 3.28 Comparison of linear range and limit of detection values of various modified electrodes for determination of theophylline.

Electrode	Linear range (M)	LOD	Ref.
Multi-wall carbon nanotube modified glassy carbon electrode	$3 \times 10^{-7} - 1 \times 10^{-5}$	5.0×10^{-8}	Zhu et al., 2005
Multi-wall carbon nanotube paste electrode	$2 \times 10^{-6} - 1.5 \times 10^{-4}$	1.97×10^{-8}	Malode et al., 2012
CdSe microparticles modified GCE	$1 \times 10^{-6} - 4 \times 10^{-5}$	4×10^{-7}	Yin et al., 2012
GC/Chit/NH₂-IL/MnOx modified GCE	$1 \times 10^{-7} - 1.2 \times 10^{-4}$	5×10^{-8}	MansoriMajd et al., 2013
AT-AuNPs film modified GCE	$4 \times 10^{-8} - 1 \times 10^{-4}$	8.5×10^{-9}	Kesavan et al., 2014
2eOHMnPc-CNT/GCE	$4 \times 10^{-8} - 1.2 \times 10^{-5}$	6.6×10^{-9}	Present study

Table 3.29 exhibits the comparison of linear range and LOD values of different modified electrodes that were used for determination of caffeine. The 2eOHMnPc-CNT/GCE electrode in the present study is a promising alternative for CAF sensor due to its high selectivity and low detection limit.

Table 3.29 Comparison of linear range and limit of detection values of various modified electrodes for determination of caffeine.

Electrode	Linear range (M)	LOD (M)	Ref.
4-Amino-3-hydroxynaphthalene sulfonic acid modified GCE	$6 \times 10^{-8} - 4 \times 10^{-5}$	1.37×10^{-7}	Gupta et al., 2013
Edge plane pyrolytic graphite electrode	$2 \times 10^{-8} - 10^{-4}$ M	8×10^{-9}	Goyal et al., 2011
4^a-Cu^{II}TAPc SAM modified GCE	$5 \times 10^{-6} - 1.410^{-3}$	3.04×10^{-8}	Jeevagan et al., 2012
Boron-doped diamond electrode	$4 \times 10^{-7} - 2.5 \times 10^{-5}$	1.5×10^{-7}	Švorc et al., 2012
2eOHMnPc-CNT/GCE	$2 \times 10^{-7} - 1 \times 10^{-5}$	5.0×10^{-8}	Present study

Interference studies of TP and CAF oxidation

The influence of various potentially interfering compounds in determination of theophylline and caffeine was studied. The potential interferences were investigated by addition of interferent to a solution containing fixed amount of caffeine and theophylline. The various organic molecules such as glucose, dopamine, ascorbic acid and various anions and cations can be present in beverage samples, pharmaceuticals and/or in biological fluids so they were investigated under the same optimized conditions.

The tolerance limit was estimated to be less than 5% of the relative error. The experiments showed that more than 100-fold excess of ascorbic acid, dopamine and glucose; 500-fold of K^+ , Na^+ , Ca^{2+} , Fe^{3+} , Cl^- , SO_4^{2-} , NO_3^- , CO_3^{2-} have no influences on the signals of the caffeine and theophylline.

Stability, repeatability and reproducibility of modified electrode

Repeatability, reproducibility and stability studies were evaluated using CV technique. Five different modified electrodes were prepared by the same way and their responses toward the theophylline and caffeine were studied to test the reproducibility of the modified electrodes. As a result, the relative standard deviation (RSD) of the peak currents was 3.4% and 4.1% for theophylline and caffeine, respectively ($n=5$). This indicates that the electrode had good reproducibility.

In order to study repeatability of the electrode, the same electrode was used for every hours within a day and the RSD of the peak current was 2 % and 3.9% for theophylline and caffeine, respectively ($n=5$).

The stability of the 2eOHMnPc-CNT/GC electrode was also examined. The modified electrode was stored in the supporting electrolyte during the stability experiments. The current response of electrode retained about 98% and 95 % of its initial current after 7 days for TP and CAF, respectively. Also after stored over the period of 3 weeks the current response decreased only by 8% and 9% for TP and CAF, respectively. The results of the modified electrodes demonstrate the electrodes have good stability and can be used as long life voltammetric sensor.

Electroanalysis of theophylline and caffeine in real samples

In order to assess the practical applicability of 2eOHMnPc-CNT/GC electrode, determination of TP and CAF were carry out in the real samples by the standard addition method. Green tea, cola and epinephrine serum samples were studied by the same method. The all samples were treated as described in experimental section.

Figure 130 shows the standart addition graph of TP and CAF in green tea sample. As can be seen from the figure, standart addition graph was constructed and related calibration curves were found linear which expressed with equations of $i_p = 5.923C + 7.308$, $R^2 = 0.9929$ and $i_p = 0.482C + 5.02$, $R^2 = 0.9911$ ($i_p: \mu A$ and $C: \mu M$) for TP and CAF, respectively. By the extrapolation of the calibration graph, the TP and CAF contents were found as $1.23 \pm 0.04 \mu M$ and $10.41 \pm 0.08 \mu M$, respectively.

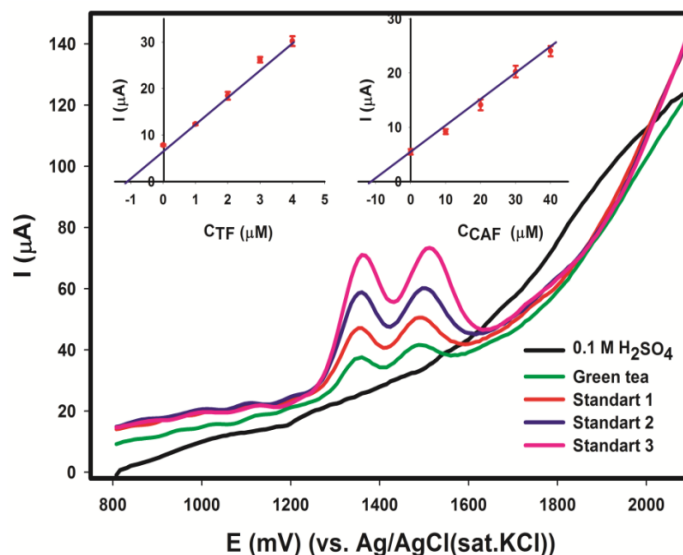


Figure 3.130 DPVs for standart addition method of theophylline and caffeine determination in green tea ($1\mu\text{M}$ TP+ $10\mu\text{M}$ CAF added to sample for each standart addition). Insets: Related calibration curves for TP and CAF.

Cola beverage sample was also analyzed for its caffeine content. Maximum caffeine was declared as maximum 0.15 gL^{-1} (maximum $77.2\mu\text{M}$) by the firm. According to the Figure 3.131, the peak currents in standart addition voltammograms were increase with the addition of CAF. The calibration curve for CAF samples on 2eOHMnPc-CNT/GCE was found linear which expressed as an equation of $i_p = 0.1325C + 8.5833$, $R^2 = 0.9999$ ($i_p: \mu\text{A}$ and $C: \mu\text{M}$). CAF content was found as $64.8 \pm 0.3\mu\text{M}$ by the extrapolation. The result was compatible with the caffeine content given by the company.

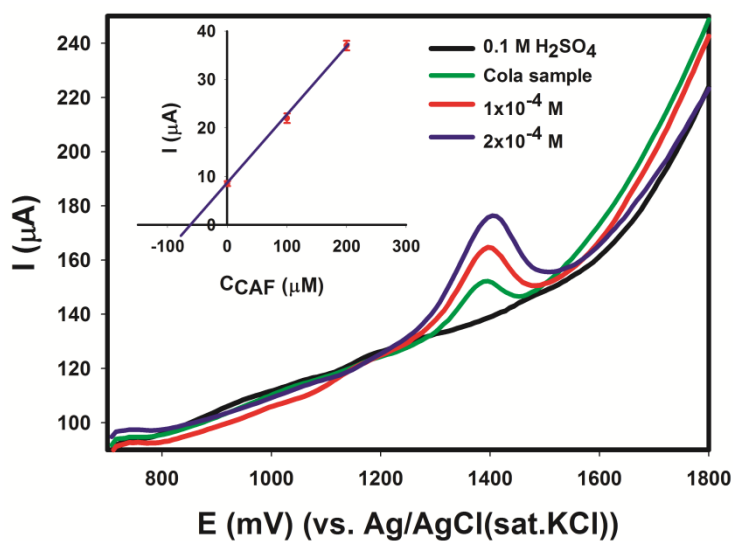


Figure 3.131 DPVs for standart addition method of caffeine determination in cola sample. Inset: Related calibration curve for CAF.

Theophylline serum sample was analyzed for its theophylline content. The concentration of TP was calculated from the declaration of pharmaceutical company as 0.111 mM. According to the Figure 3.132, the peak currents in standart addition voltammograms were increase with the addition of TP. The calibration curve for TP samples on 2eOHMnPc-CNT/GCE was found linear which expressed as an equation of $i_p = 2.232C + 2.442$, $R^2 = 0.9946$ ($i_p: \mu A$ and $C: \mu M$). TP content was found as 0.109 ± 0.003 mM by the extrapolation. The result was compatible with the theophylline content given by the company.

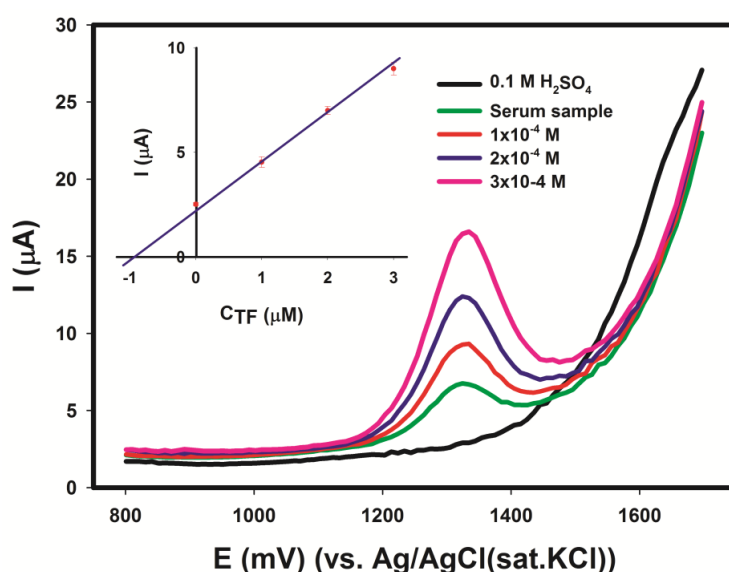


Figure 3.132 DPVs for standart addition method of theophylline determination in theophylline serum sample. Inset: Related calibration curve for TP.

Table 3.30 represents the recovery values of CAF and TP in green tea samples, TP recovery in serum samples and finally CAF recovery in cola samples for three measurements. 0.2 mL green tea sample was added to N_2 saturated 0.01 M H_2SO_4 with a total volume of 10 mL. First, sample signal was measured and then 0.1 mL from the 10^{-4} M TP+ 10^{-3} M CAF standart was added to the sample and measured which was repeated three times. Recoveries were found as 97.8% and 102.8% for TP and CAF, respectively. 2 mL sonicated cola sample was added to N_2 saturated 0.01 M H_2SO_4 with a total volume of 10 mL. First, sample signal was measured and then 0.1 mL from the 10^{-2} M CAF standart was added to the sample and measured. The recovery value was found as 98.7% for three measurements. 0.1 mL TP serum sample was added to N_2 saturated 0.01 M H_2SO_4 with a total volume of 10 mL. First, sample signal was measured and then 0.1 mL from the 10^{-2} M TP standart was added to the sample and measured. The recovery was found as 101.9%.

Table 3.30 Recovery percentages of TP and CAF in different samples using 2eOHMnPc-CNT/GCE by DPV (n=3).

Sample	Analyte	Determined (μM)	Added (μM)	Found (μM)	Recovery (%)	RSD (n=3)
Serum	TP	109.0	100.0	213.0	101.9	2.1
Cola	CAF	64.8	50.0	116.3	98.7	4.3
Green tea	TP	1.23	1.00	2.18	97.8	5.2
	CAF	10.4	10.0	21.3	102.8	4.9

3.4.3 Characterization of modified electrodes

Surface characterization techniques were important techniques that help to understand the morphology and prove the existence of prepared modifiers on electrode surfaces. For this regard, 2eOHMnPc and carbon nanotube composed GC electrodes characterized with SEM, EDX and EIS techniques. Typical SEM images were represented in Figure 3.133. Figure 133a and b correspond to the 2eOHMnPc/GCE surface images in different magnifications. It is clearly seen from the images that cloudy like images related with 2eOHMnPc was found on the GCE surface. In addition, composed 2eOHMnPc and CNT surface imaged with different magnifications that shown in Figure 3.133c and d. The tubular forms were corresponding to the CNT structure. The cotton like structures on all over the tubules were correspond 2eOHMnPc that represent the attachment of CNTs and 2eOHMnPcs. 2eOHMnPc-CNT/GCE SEM images were coherent with the 2eOHMnPc/GCE images.

Figure 3.134 depicts the EDX spectrums of 2eOHMnPc/GCE and 2eOHMnPc-CNT/GCE, which gave qualitative confirmation about composite electrode surfaces. Figure 3.135a and b prove the Mn existence in modifier. N and O atoms have been in the structure of Tetra-[(5-chloroquinolin-8-yloxy) phthalocyanato] manganese (II) (2eOHMnPc) molecule. Based on the results of Figure 3.135a and b, weight percentage of Mn on 2eOHMnPc/GCE and 2eOHMnPc-CNT/GCE surfaces were found as 0.26% and 0.31%, respectively.

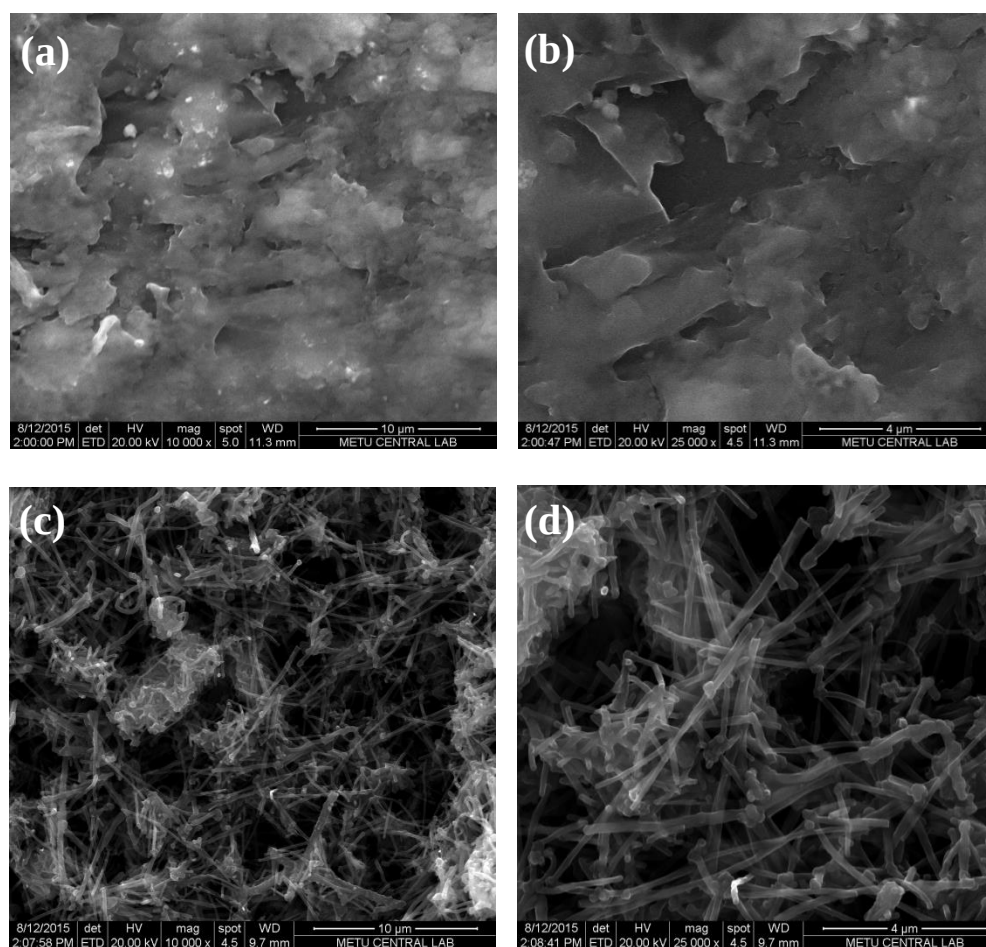


Figure 3.133 SEM images of a) 2eOHMnPc/GCE and b) 2eOHMnPc-CNT/GCE

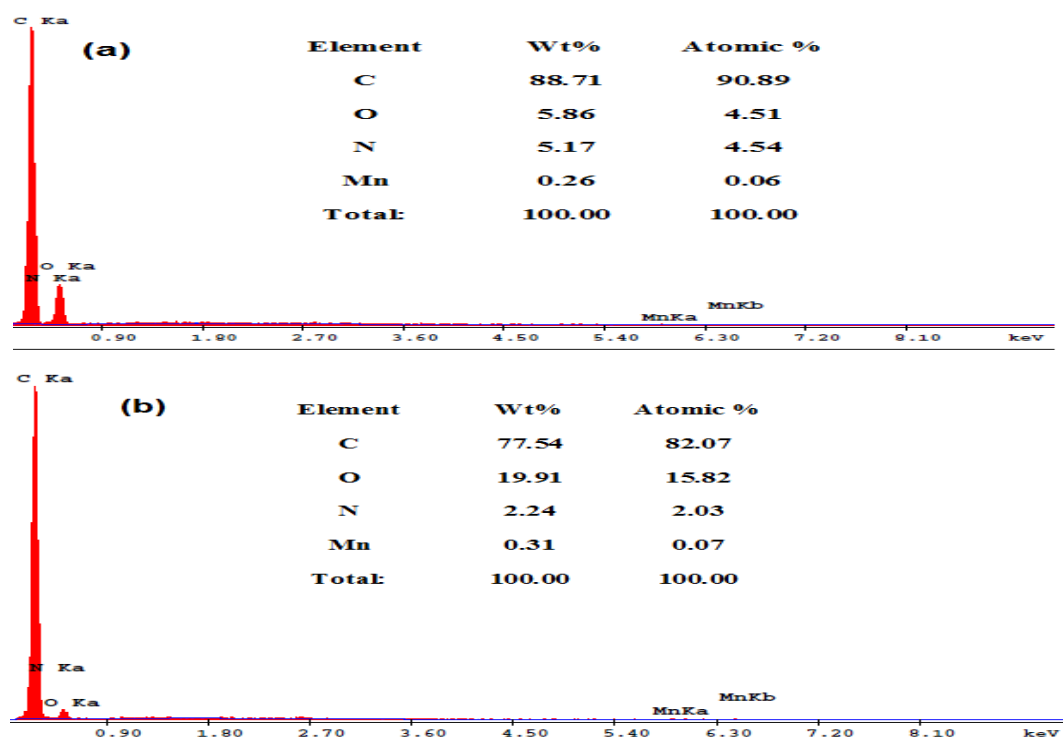


Figure 3.134 EDX result of the 2eOHMnPc-CNT/GCE.

Figure 3.135 shows the electrochemical impedance spectroscopy results of bare GCE, CNT/GCE and 2eOHMnPc-CNT/GCE in the presence 5.0 mM $[\text{Fe}(\text{CN})_6]^{3-/2-}$ solution at a frequency range of 0.05 to 50 000 Hz at formal potential. A large semicircle was obtained for bare GCE, indicating that there was a high electron transfer resistance. The experimental data points, and continuous lines represent simulated curve using the equivalent circuit (Figure 3.135 inset). The EIS data were fitted with this equivalent circuit and values were shown in Table 3.31. The 2eOHMnPc-CNT/GCE shows a lower interfacial electron transfer resistance (187 Ω) than that of the CNT/GCE (296 Ω) and of bare GCE (548 Ω). This results show that the good electroconductibility was proved by 2eOHMnPc-CNT/GCE surface. These results suggested that the synergistic effect of CNTs and functionalized manganese phthalocyanine composite which improve the conductivity of the electrode and promoted the electron transfer rate.

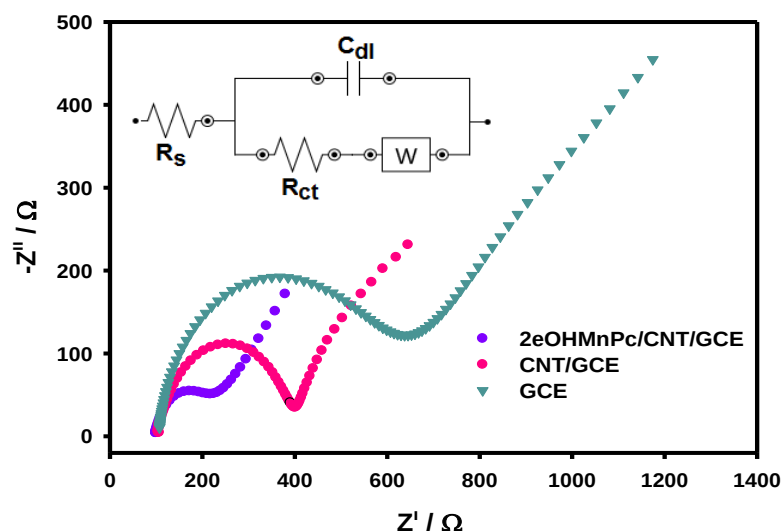


Figure 3.135 Nyquist plots of bare GCE, CNT/GCE and 2eOHMnPc-CNT/GCE in 5.0 mM $[\text{Fe}(\text{CN})_6]^{3-/2-}$ containing KCl solution. The frequencies ranged from 0.05 to 50 000 Hz at formal potential.

Table 3.31 The R_s , R_{ct} and C_{dl} values of bare and modified electrodes.

	R_s (Ω)	C_{dl} (μF)	R_{ct} (Ω)
Bare GCE	116	0.32	548
CNT/GCE	111	3.08	296
2eOHMnPc-CNT/GCE	106	10	187

4. GENERAL DISCUSSIONS AND CONCLUSIONS

4.1 Fuel cell Applications

Renewable energy sources especially fuel cells are important alternative for energy production. A promising alternative to the hydrogen-based problems in fuel cells, such as deposition and transportation drawbacks, is to use fuel in liquid form. For this purpose, various kinds of fuels (e.g. methanol, ethanol, formaldehyde and dimethylamine borane etc.) were studied on different modified surfaces. Methanol attracting great interest as a fuel due to the simple and cheaply synthesis, easy storage, relatively reduced system weight, high energy density, and low emission profile. Dimethylamine borane is a borane derivative that has amine groups which was used recently by the researchers as a fuel. In fuel cell technology, oxygen is a critical component that cathodic reaction all based on it. Air or pure oxygen feed to the cell and chemical reaction between anode and cathode generate the power of the cell.

In the first section of this thesis polymer or phthalocyanine-carbon nanotube based modified surfaces were prepared and then modified with different metal nanoparticles which used for investigation of methanol, dimethylamine borane oxidation and oxygen reduction. Oxidation/reduction peak potential and current values were compared with both bare and modified surfaces in order to evaluate the performance of the prepared electrodes. To obtain best catalytic activity towards fuels and oxygen, experimental parameters such as; concentration of supporting electrolyte, deposition cycle number and concentration of polymer and metal nanoparticles, Pc-CNT ratio and scan rate were optimized.

In order to investigate the oxygen reduction, CuPc and CNT composed and physically adsorbed on the GE surface with drop-dry technique. Bare GCE, CuPc/GCE, CNT/GCE, CuPc-CNT/GCE, CuPc/CNT/GCE and CNT/CuPc/GCE studied in oxygen saturated alkaline medium. The best results in terms of significant current enhancement was observed with CuPc-CNT/GCE that was about 5.2 times higher than bare GCE and 1.5 times higher than CNT/GCE. To improve the electrocatalytic activity of composite electrodes toward the reduction of oxygen, the CuPc/GC, CNT/GC, and CuPc-CNT/GC electrodes were modified with different metal nanoparticles (Ni, Ag, Cu, Pd, Au, Pt). The peak current of oxygen reduction at PtNPs modified CuPc-CNT/GC electrode was about 1.7, 3.0 and 5.3 times higher than that at CuPc-CNT/GCE, Pt/CNT/GCE and

Pt/CuPc/GCE, respectively. Moreover, the reduction peak potential of oxygen on Pt/CuPc-CNT/GC electrode shifted 142 mV and 164 mV to positive values as compared to the CuPc-CNT/GCE and Pt/CNT/GCE, respectively. On the basis of the results, Pt/CuPc-CNT/GCE was chosen as the best electrode for oxygen reduction in alkaline medium in terms of high peak current and relatively positive potential value.

PtNPs amount effect the electrode behavior which could be controlled by the changing the concentration of chloroplatinic acid. 3 mM was chosen as an optimum concentration which provide the highest peak current. In addition, the best response towards dissolved oxygen was obtained with a mole ratio of 1:6 CuPc:CNT. Scan rate studies between 5-250 mV.s^{-1} represent that the peak currents have shown a linear increase with the square root of the scan rate on all bare and modified electrodes indicating that oxygen reduction reaction were controlled by diffusion. Rotating disk electrode studies help to calculate the tranfered electron number during reduction of oxygen on Pt/CuPc-CNT/GC electrode. From the slope of the K–L plots, the value of electron for the Pt/CuPc-CNT/GC electrode was calculated as 3.7, indicating that O_2 is reduced by direct almost four-electron pathway to produce water. In addition, Tafel slope varies from $-0.056 \text{ V dec}^{-1}$ at lower current densities to -0.11 V dec^{-1} in the higher current density region on Pt/CuPc-CNT/GCE. Changing the coverage of surface by adsorbed oxygen species give rise to two Tafel slope regions that attributed to the change from Temkin to Langmiur conditions. The response of the electrode in the O_2 saturated solution maintained 87.5% of the original peak current value after 10 days. The experiments show that the GC electrodes modified with Pt/CuPc-CNT films have good repeatability and stability that related with the synergistic effect of the nano particles, CuPc and CNT.

Characterization of Pt/CuPc-CNT/GCE surface with SEM, EDX, XPS, XRD and EIS techniques were clearly identify the modified surface. SEM images of different modified electrodes clearly show the coverage difference compared with GCE. According to the EDX, the weight gain of the CuPc–CNT due to the Pt loading was found about 9.7%. N and Cu atoms have been in the structure of copper phthalocyanine molecule. TEM images coherent with SEM images that most of the Pt nanoparticles were uniformly dispersed in the range of 3-6 nm on the CuPc-CNT/GCE support. XPS results prove the metallic Pt nanoparticles on electrode surface. In addition, sharp diffraction peak at 39.7° and weak broad diffraction peaks at 46.2° and 67.6° were observed which correspond to the (111),

(200) and (220) crystalline planes of face-centered cubic pure Pt crystal. Comparative EIS studies of GCE, CNT/GCE, CuPc/GCE, CuPc-CNT/GCE and Pt/CuPc-CNT/GCE clearly demonstrate the charge transfer resistances of all electrodes with different diametered semicircles in 5 mM $K_3[Fe(CN)_6]/K_4[Fe(CN)_6]$ containing 0.1 M KCl solution. The R_{ct} value for the bare GCE is higher than the R_{ct} values obtained for other modified electrodes while the smallest R_{ct} value obtained for the Pt/CuPc-CNT/GCE. These results suggested that the synergistic effect of CNTs with Pcs and Pt nano particles effectively increased the conductivity of the electrode and promoted the electron transfer rate.

Methanol oxidation was studied also in this thesis with MNPs modified CuPc-CNT composite electrodes. Various kinds of metallic and bimetallic NPs studied, while Au-Pt bimetallic NPs modified CuPc-CNT showed best catalytic activity towards methanol. The sequential and one step deposition from Au-Pt mixture was compared with each other. Au and Pt nanoparticles from the same solution on the CuPc-CNT/GCE show the best current value among all others. The methanol oxidation peak current of (Au-Pt)/CuPc-CNT/GCE was about 3 times higher than the Pt/CuPc-CNT/GCE and 330 times higher than the Au/CuPc-CNT/GCE. 2mM Au and Pt containing solution was used for MNP deposition with optimized 15 repetitive cycles. According to the TGA results bimetallic nanoparticles deposition highly improve the thermal stability of the composite, which is crucial parameter for the catalyst material in fuel cells.

SEM, EDX, XPS, XRD and EIS techniques were clearly identify the modified surfaces. Au and Pt NPs found in metallic form with small diametered spherical shapes on CuPc-CNT. EIS studies support the high catalytic activity of electrode with conductivity datas. In brief, highly active and practical composite electrodes were prepared which could be a great candidate as anode material in DMFC applications.

For DMAB electrocatalytic oxidation, not only Pc-CNT composite modified electrodes but also bimetallic nanoparticles modified polymer film electrodes were prepared. It can be attributed to the synergistic effect of Au/Ag bimetallic nanoparticles, which jointly improves the electrocatalytic oxidation of DMAB. The electron transfer number during oxidation of DMAB on Au disk, Au/PAP, Ag/PAP and Au/Ag/PAP/GCE surface was calculated from RDE studies as 4.89, 5.60 and 5.93, respectively.

The number of electron indicated that a completely direct electrochemical oxidation of DMAB take place on the Au/Ag bimetalli particles modified PAP surfaces due to the number of electrons close to the theoretically expected value as six electrons. The electroactive surface areas of Ag, Au and Au/Ag bimetallic NPs modified PAP/GCE were calculated from Randles-Sevcik equation that highest active surface areas obtained at bimetallic surface as expected from its high catalytic activity.

The formation of Au and Ag nanoparticles on polymer films were confirmed by SEM, EDX, TEM, XPS and EIS. SEM images demonstrate the different surface covarages and EDX prove the Au and Ag existence on PAP surface. TEM results in decreased focus areas indicated that most of the Au and Ag nanoparticles were uniformly dispersed in the range of 5-15 nm on the polymer, while some flower as clannish parts appear on the surface. XPS results prove the metallic gold and silver nanoparticles on modified surface in metallic forms which were determined by characteristic Ag and Au doublets. The semicircles without warburg element and linear part, are typical nyquist plots for DMAB containing alkaline mediums. The smallest Rct value that means the highest electroconductibility was obtained at Au/Ag/PAP/GCE.

In addition, DMAB investigated with MNPs modified Pc and PC-CNT surfaces. The unstable results with lower current values obtained for Pc modified electrode, while CNT existence with Pc improve the signals and catalysis the oxidation reaction. Zn, Pd, Ni, Co, Au, Pt, Ag, oxidized Ag nano particles modified Pc-CNT composite electrodes investigated and best catalytic activity obtained on Au/Pc-CNT/GCE. The peak characteristics changed also with type of central metals of Pc. The highest peak current and most negative oxidation potential value obtained at Au/CuPc-CNT/GCE. 2 M NaOH medium and %15 CuPc-CNT ratio was chosen as an optimum values towards DMAB oxidation. The best catalytic activity was obtained at Au/CuPc-CNT/GCE as compared to the Au disk, Au/CNT/GCE and Au/CuPc/GCE due to the highest peak current and most negative peak potential value towards DMAB oxidation. At Au/CuPc-CNT/GCE, the potential was shifted to 64 mV negative and the obtained current was 13 times higher than bare Au disk electrode. The mass transfer to the electrode was diffusion controlled and transferred electrons during oxidation reaction were calculated as 5.97 on Au/CuPc-CNT/GCE.

SEM, TEM, XPS and EIS studies confirm the composite and metal content on CuPc-CNT surface. XPS prove the metallic Au existence on composite surface. Detailed TEM and STEM analysis obviously represent the tubular structure of CNTs, jelly like forms that related with CuPc and spherical gold nano particles with an average diameter of approximately 8 nm which were found on the composite electrode surface. The outer diameter of carbon nanotubes were found between 100 and 200 nm. Impedance spectrums in ferri/ferro system and DMAB containing NaOH medium were studied with different electrodes. In each solution or analyte type, Au/CuPc-CNT/GC electrode show better conductivity and improved electron transfer rate as compared to the CuPc-CNT/GCE and GCE.

The DMAB oxidation studies show that catalytically active, easy prepared and relatively cheape anode composite electrode could be fabricated by using very small amount Au/Ag bimetallic nanoparticles on polymer films and AuNPs on CuPc-CNT films for DMAB based fuel cells.

4.2 Analytical Application

Caffein is an xanthine derivative that its intake was advised which stimulate the central nervous system. However, excessive intake of CAF causes restlessness, insomnia, jitters, anxiety, increasing or irregular heart rate. Theophylline founding a place in the top three drugs which mostly watching clinically is commenly used as bronchodilator medicine and cures the cronic /acute obstructive pulmonary disease, neonatal apnea. In addition, TP and CF are naturally found in especially green tea, cacao beans, coffee, cola, etc together. However, the similar structure of TP and CAF in natural medium resulted in difficulties for their selective determination. The improved catalytic surfaces required in order to investigate the selective and sensitive simultaneous determination of TP and CAF.

In this thesis, TP and CAF investigated in acidic medium by CV and DPV with phthalocyanine modified glassy carbon electrode. The best catalytic activity and selective determination of TP and CAF was obtained at new synthesized tetra-[(5-chloroquinolin-8-yloxy)phthalocyanato]manganase(II) composed multiwalled carbon nanotube modified GCE in 0.01 M H₂SO₄. This electrode compared with CNT/GCE, its metal nanoparticles modified forms and its other synthesized form with Ti that 2eOHMnPc-CNT/GCE showed better catalytic activity than other electrodes.

Britton Robinson buffer (2-6) and different acidic mediums investigated for selective determination of TP and CAF that best peak separation and high peak currents obtained at 0.01 M H₂SO₄ medium. Open circuit accumulation time studies represents that TP and CAF were not have adsorptive characteristic on 2eOHMnPc-CNT/GCE. In addition, 2eOHMnPc/CNT ratio affect the catalytic behavior that 2eOHMnPc must be only found in surface of the electrode with the ratio of 6%.

Moreover, DPV studies were carried out for individual and simultaneous determination of both TP and CAF on GCE, CNT/GCE and 2eOHMnPc-CNT/GCE. The dynamic range and linear calibration ranges plotted for all electrodes. The lowest detection limit and wider calibration range for TP and CAF were obtained at 2eOHMnPc-CNT/GCE as compared to the GCE and CNT/GCE. The detection limits of individual TP and CAF were established as 6.6×10^{-9} M ve 5.0×10^{-8} M, respectively. In case of the constant concentration of one analyte with increasing concentration of other, the limit of detection values were calculated as 8.1×10^{-9} M ve 3.0×10^{-7} M for TP and CAF, respectively.

In addition, the relative standard deviation of the peak currents that obtained from reproducibility studies were found as 3.4% and 4.1% for theophylline and caffeine, respectively (n=5). The measurements with the same electrode for every hour during the day, represents the high repeatability of the electrode with 2% and 3.9% RSD values for theophylline and caffeine, respectively (n=5). Also, the long term stability studies in the period of three weeks exhibits that this modified 2eOHMnPc-CNT/GCE can be used as long life voltammetric sensor with only current decrease of 8% and 9% for TP and CAF, respectively.

The various organic molecules such as glucose, dopamine, ascorbic acid and various anions and cations can be present in beverage samples, pharmaceuticals and/or in biological fluids so they were investigated on 2eOHMnPc-CNT/GCE under optimized conditions. The tolerance limit was estimated to be less than 5% of the relative error for 100-fold excess of ascorbic acid, dopamine and glucose; 500-fold of K⁺, Na⁺, Ca²⁺, Fe³⁺, Cl⁻, SO₄²⁻, NO₃⁻, CO₃²⁻ on the signals of the caffeine and theophylline.

The TP and CAF content in real sample analysis of green tea, cola and medicine was determined with the prepared 2eOHMnPc-CNT/GC electrodes. The results were coherent with the contents that claimed by the manufacturers. The modified 2eOHMnPc-CNT/GCE can be easily used for the cheap, fast, accurate and selective determination of TP and CAF in real samples.

SEM, EDX and EIS were used for the characterization of 2eOHMnPc-CNT/GCE surface. The comparison of individual and composed forms of CNT and 2eOHMnPc obviously prove the existence of components on the modified surface. EDX revealed the content of C, Mn, O, N elements which found in the structure of the 2eOHMnPc-CNT composite surface. Impedance studies with GCE, CNT/GCE and 2eOHMnPc-CNT/GCE in 5.0 mM $[\text{Fe}(\text{CN})_6]^{-3/-2}$ containing KCl solution. The smallest semicircle that means lowest resistance and highest conductivity obtained at 2eOHMnPc-CNT/GCE as compared to the GCE and CNT/GCE.

The overall results represent that CNT composition with newly synthesized 2eOHMnPc on GCE generate the catalytically active surface towards individual and simultaneous determination of TP and CAF with high selectivity and sensitivity both synthetic and real samples.

REFERENCES

- Acharya, C.K., Li, W., Liu, Z., Kwon, G., Turner, C.H. Lane AM, Nikles, D., Klein, T. and Weaver, M.**, 2009, Effect of boron doping in the carbon support on platinum nanoparticles and carbon corrosion, *Journal of Power Sources*, 192(2):324-329 pp.
- Afify, H.A., Gadallah, A.S., El-Nahass, M.M. and Atta Khedr, M.**, 2015, Effect of thermal annealing on the structural and optical properties of spin coated copper phthalocyanine thin films, *Journal of Molecular Structure*, 1098:161-166 pp.
- Afkhami, A., Soltani-Felehgari, F., Madrakian, T. and Ghaedi, H.**, 2014, Surface decoration of multi-walled carbon nanotubes modified carbon paste electrode with gold nanoparticles for electro-oxidation and sensitive determination of nitrite, *Biosensors and Bioelectronics*, 51:379–385 pp.
- Alexeyeva, N., Matisen, L., Saar, A., Laaksonen, P., Kontturi, K. and Tammeveski, K.**, 2010, Kinetics of oxygen reduction on gold nanoparticle/multi-walled carbon nanotube hybrid electrodes in acid media, *Journal of Electroanalytical Chemistry*, 642:6-12 pp.
- Ali, S., Ahmed, R., Sohail, M., Khan, S.A. and Ansari, M.S.**, 2015, Co@Pt core–shell nanoparticles supported on carbon nanotubes as promising catalyst for methanol electro-oxidation, *Journal of Industrial and Engineering Chemistry*, 28:344–350 pp.
- Al-Oqla, F.M., Sapuan, S.M., Anwer, T., Jawaid, M. and Hoque, M.E.**, 2015, Natural fiber reinforced conductive polymer composites as functional materials: A review, *Synthetic Metals*, 206:42–54 pp.
- Amare, M. and Admassie, S.**, 2012a, Differential pulse voltammetric determination of theophylline at poly(4-amino-3-hydroxynaphthalene sulfonic acid) modified glassy carbon electrode, *Bulletin of the Chemical Society of Ethiopia*, 26(1):73-84 pp.
- Amare, M. and Admassie, S.**, 2012b, Polymer modified glassy carbon electrode for the electrochemical determination of caffeine in coffee, *Talanta*, 93:122– 128 pp.
- Antunes, R.A., Oliveira, M.C.L., Ett, G. and Ett, V.**, 2010, Corrosion of metal bipolar plates for PEM fuel cells: A review, *International Journal of Hydrogen Energy*, 35:3632–3647 pp.

REFERENCES (Continued)

- Ariga, K., Yamauchi, Y., Mori, T. and Hill, J.P.**, 2013, What can be done with the langmuir-blodgett method? Recent developments and its critical role in materials science, *Advance. Materials*, 25:6477–6512 pp.
- Ashrafia, A.M., Cerovac, S., Mudric', S., Guzsvány, V., Husáková, L., Urbanová, I. and Vytras, K.**, 2014, Antimony nanoparticle-multiwalled carbon nanotubes composite immobilized at carbon paste electrode for determination of trace heavy metals, *Sensors and Actuators B*, 191:320–325 pp.
- Atar, N., Eren T. and Yola, M.L.**, 2015, Ultrahigh capacity anode material for lithium ion battery based on rod gold nanoparticles decorated reduced graphene oxide, *Thin Solid Films*, 590:156–162 pp.
- Atchudan, R., Perumal, S., Immanuel Edison, T.N.J., Pandurangan, A. and Lee Y.R.**, 2015, Synthesis and characterization of graphenated carbon nanotubes on IONPs using acetylene by chemical vapor deposition method, *Physica E*, 74:355–362 pp.
- Ates, M.**, 2013, A review study of (bio)sensor systems based on conducting polymers, *Materials Science and Engineering C*, 33:1853–1859 pp.
- Atilgan, B. and Azapagic, A.**, 2015, Life cycle environmental impacts of electricity from fossil fuels in Turkey, *Journal of Cleaner Production*, 106:555-564 pp.
- Ayan, E.M., Karabiberoğlu, Ş.U. and Dursun, Z.**, 2013, Electrochemistry of 2,6-diaminopurine on multiwall carbon nanotube modified glassy carbon electrode, *Turkish Journal of Chemistry*, 37:325–334 pp.
- Bakır, Ç.C., Şahin, N. Polat, R. and Dursun, Z.**, 2011, Electrocatalytic reduction of oxygen on bimetallic copper–gold nanoparticles–multiwalled carbon nanotube modified glassy carbon electrode in alkaline solution, *Journal of Electroanalytical Chemistry*, 662:275-280 pp.
- Balint, R., Cassidy, N.J. and Cartmell, S.H.**, 2014, Conductive polymers: Towards a smart biomaterial for tissue engineering, *Acta Biomaterialia*, 10:2341–2353 pp.

REFERENCES (Continued)

- Baltruschat, H.**, 2004, Differential electrochemical mass spectrometry, *Journal of the American Society for Mass Spectrometry*, 15:1693–1706 pp.
- Bard, A.J. and Faulkner, L.R.**, 2001, *Electrochemical Methods Fundamentals and Applications*, John Wiley & Sons, Inc, 833p.
- Barile, C.**, 2010, Oxygen reduction catalysts for fuel cells, <http://large.stanford.edu/courses/2010/ph240/barile1/> (Available: 02 August 2015)
- Batista, E.A., Malpass, G.R.P., Motheo, A J. and Iwasita, T.**, 2003, New insight into the pathways of methanol oxidation, *Electrochemistry Communications*, 5:843–846 pp.
- Becerik, İ. Süzer, Ş. and Kadirgan, F.**, 2001, Electrooxidation of methanol on doped polypyrrole films in acidic Media, *Journal of Electroanalytical Chemistry*, 502:118–125 pp.
- Bianchini, C. and Shen, P.K.**, 2009, Palladium-based electrocatalysts for alcohol oxidation in half cells and in direct alcohol fuel cells, *Chemical Reviews*, 109:4183–4206 pp.
- Brushett, F.R., Naughton, M.S., Ng, J.W.D., Yin, L. and Kenis P.J.A.**, 2012, Analysis of Pt/C electrode performance in a flowingelectrolyte alkaline fuel cell, *International Journal of Hydrogen Energy*, 37:2559-2570 pp.
- Budde, B., Alkemade, F. and Hekkert, M.**, 2015, On the relation between communication and innovation activities: A comparison of hybrid electric and fuel cell vehicles, *Environmental Innovation and Societal Transitions*, 14:45–59 pp.
- Bulushev, D.A. and Ross, J.R.H.**, 2011, Vapour phase hydrogenation of olefins by formic acid over a Pd/C catalyst, *Catalysis Today*, 163(1):42-46 pp.
- Çakar, I., Özdokur, K.V., Demir, B., Yavuz, E., Demirkol, D.O., Koçak, S., Timur S. and Ertas, F.N.**, 2013, Molybdenum oxide/platinum modified glassy carbon electrode: A novel electrocatalytic platform for the monitoring of electrochemical reduction of oxygen and its biosensing applications, *Sensors and Actuators B*, 185:331–336 pp.

REFERENCES (Continued)

- Carvalho, R.C., Gouveia-Caridade, C. and Brett, C.M.A.**, 2010, Glassy carbon electrodes modified by multiwalled carbon nanotubes and poly(neutral red): A comparative study of different brands and application to electrocatalytic ascorbate determination, *Analytical and Bioanalytical Chemistry*, 398:1675–1685 pp.
- Cerovac, S., Guzsvány, V., Kónya, Z., Ashrafi, A.M., Švancara, I., Rončević, S., Kukovecz, Á., Dalmacija, B. and Vytrás, K.**, 2015, Trace level voltammetric determination of lead and cadmium in sediment pore water by a bismuth-oxychloride particle-multiwalled carbon nanotube composite modified glassy carbon electrode, *Talanta*, 134:640–649 pp.
- Chae, J.W. Baek, I.H. and Kwon, K.I.**, 2012a, Effect of decursin on the pharmacokinetics of theophylline and its metabolites in rats, *Journal of Ethnopharmacology*, 144:248–254 pp.
- Chae, J.W., Kim, D.H., Lee, B.Y., Kim, E.J. and Kwon, K.I.**, 2012b, Development and validation of a sensitive LC–MS/MS method for the simultaneous quantitation of theophylline and its metabolites in rat plasma, *Journal of Chromatography B*, 889:44–49 pp.
- Chen, K.J., Lee, C.F., Ricka, J., Wang, S.H., Liu, C.C. and Hwang, B.J.**, 2012, Fabrication and application of amperometric glucose biosensor based on a novel PtPd bimetallic nanoparticle decorated multi-walled carbon nanotube catalyst, *Biosensors and Bioelectronics*, 33:75–81 pp.
- Chen, M.L., Zheng, M.M. and Feng, Y.Q.**, 2010, Preparation of organic–inorganic hybrid silica monolith with octyl and sulfonic acid groups for capillary electrochromatography and application in determination of theophylline and caffeine in beverage, *Journal of Chromatography A*, 1217:3547–3556 pp.
- Chen, Q.C., Mou, S.F., Hou, X.P. and Ni, Z.M.**, 1998, Simultaneous determination of caffeine, theobromine and theophylline in foods and pharmaceutical preparations by using ion chromatography, *Analytica Chimica Acta*, 371:287–296 pp.
- Chen, Y., Zhang, G., Ma, J., Zhou, Y., Tang, Y. and Lu, T.**, 2010, Electro-oxidation of methanol at the different carbon materials supported Pt nanoparticles, *International Journal of Hydrogen Energy*, 35(19):10109–10117 pp.

REFERENCES (Continued)

- Chiu, K.C., Juey, L.T., Su, C.F., Tang, S.J., Jong, M.N., Wang, S.S., Wang, J.S., Yang, C.S. and Chou, W.C.**, 2008, Effects of source and substrate temperatures on the properties of ITO/CuPc/C60 heterostructure prepared by physical vapor deposition, *Journal of Crystal Growth*, 310:1734–1738 pp.
- Choudhary, V. and Gupta, A.**, 2011, Carbon Nanotubes-polymer nanocomposites, Edited by Yellampalli S., Publisher: InTech, Polymer/Carbon Nanotube Nanocomposites, chapter 4. ISBN 978-953-307-498-6, 410p.
- Ciucu, A.A.**, 2014, Chemically modified electrodes in biosensing, *Journal of Biosensors & Bioelectronics*, 5(3):154 pp.
- Claessens, C.G., Hahn, U. and Torres, T.**, 2008, Phthalocyanines: From outstanding electronic properties to emerging applications, *The Chemical Record*, 8:75–97 pp.
- Cote, L.J., Teja, A.S., Wilkinson, A.P. and Zhang, Z.J.**, 2003, Continuous hydrothermal synthesis of CoFe_2O_4 nanoparticles, *Fluid Phase Equilibria*, 210(2):307-317 pp.
- Cui, C.H. and Yu, S.H.**, 2013, Engineering interface and surface of noble metal nanoparticle nanotubes toward enhanced catalytic activity for fuel cell applications, *Accounts of Chemical Research*, 46:1427–1437 pp.
- Cullity, B.D.**, 1956, Elements of X-ray diffraction, addison-wesley publishing, Wesley Publishing Company, Inc., Massachusetts, 531 pp.
- Dafydd, H., Worsley, D.A. and McMurray, H.N.**, 2005, The kinetics and mechanism of cathodic oxygen reduction on zinc and zinc–aluminium alloy galvanized coatings, *Corrosion Science*, 47(12):3006-3018 pp.
- Dallas, P. and Georgakilas, V.**, 2015, Interfacial polymerization of conductive polymers: Generation of polymeric nanostructures in a 2-D space, *Advances in Colloid and Interface Science*, 224:46-61 pp.
- Del Rosario Brunetto, M., Gutiérrez, L., Delgado, Y., Gallignani, M., Zambrano, A., Gómez, Á., Ramos, G. and Romero, C.**, 2007, Determination of theobromine, theophylline and caffeine in cocoa samples by a high-performance liquid chromatographic method with on-line sample cleanup in a switching-column system, *Food Chemistry*, 100:459–467 pp.

REFERENCES (Continued)

- Devasenathipathy, R., Mani, V., Chen, S.M., Kohilarani, K. and Ramaraj, S.,** 2015, Determination of L-cysteine at iron tetrasulfonated phthalocyanine decorated multiwalled carbon nanotubes film modified electrode, *International Journal of Electrochemical Science*, 10:682 – 690 pp.
- Deyab, M.A.,** 2014, Corrosion protection of aluminum bipolar plates with polyaniline coating containing carbon nanotubes in acidic medium inside the polymer electrolyte membrane fuel cell, *Journal of Power Sources*, 268:50-55 pp.
- Dicu, D., Muresan, L., Popescu, I.C., Cristea, C., Silberg, I.A. and Brouant, P.,** 2000, Modified electrodes with new phenothiazine derivatives for electrocatalytic oxidation of NADH, *Electrochimica Acta*, 45:3951–3957 pp.
- Do Nascimento, R.F., Selva, T.M.G., Ribeiro, W.F., Belian, M.F., Angnes, L. and do Nascimento, V.B.,** 2013, Flow-injection electrochemical determination of citric acid using a cobalt(II)–phthalocyanine modified carbon paste electrode, *Talanta*, 105:354–359 pp.
- Dohle, H., Divisek, J., Mergel, J., Oetjen H.F., Zingler, J., and Stolten, D.,** 2002, Recent developments of the measurement of methanol permeation in a direct methanol fuel cells, *Journal of Power Sources*, 105:274-282 pp.
- Duan, D., You, X., Ren, W., Wei, H., Liu, H. and Liu, S.,** 2015, Oxygen reduction reaction of different electrodes in dimethyl sulfoxide solvent for Li-air batteries *International Journal of Hydrogen Energy*, 40:10847-10855 pp.
- Duman, S. and Özkar, S.,** 2013, Oleylamine-stabilized ruthenium(0) nanoparticlescatalyst in dehydrogenation of dimethylamineborane, *International Journal of Hydrogen Energy*, 38:10000–10011 pp.
- Dursun, Z. and Gelmez, B.,** 2010, Simultaneous determination of ascorbic acid, dopamine and uric acid at Pt nanoparticles decorated multiwall carbon nanotubes modified GCE, *Electroanalysis*, 22(10):1106–1114 pp.
- Dursun, Z., Ulubay Karabiberoğlu, Ş., Gelmez, B. and Ertaş, F.N.,** 2011, Electrocatalytic reactivity of Pt ad-layer modified Au(111) single crystal electrodes on reduction of oxygen, *Turkish Journal of Chemistry*, 35:513–521 pp.

REFERENCES (Continued)

- Dursun, Z. Ulubay, Ş. Gelmez, B. and Ertaş, F.N.**, 2009, Electrocatalytic reduction of oxygen on a Pd ad-layer modified Au(111) electrode in alkaline solution, *Catalysis Letter*, 132:127–132 pp.
- Eberle, U., Felderhoff M. and Schth, F.**, 2009, Chemical and physical solutions for hydrogen storage, *Angewandte Chemie International Edition*, 48(36):6608-6630 pp.
- Edwards, P.P., Kuznetsov, V.L., David, W.I.F. and Brandon, N.P.**, 2008, Hydrogen and fuel cells: Towards a sustainable energy future, *Energy Policy*, 36:4356-4362 pp.
- Ehsani, A., Mahjani, M. G., Jafarian, M. and Naeemy, A.**, 2012, Electrosynthesis of polypyrrole composite film and electrocatalytic oxidation of ethanol, *Electrochimica Acta*, 71:128–133 pp.
- Erdinc, O. and Uzunoglu, M.**, 2010, Recent trends in PEM fuel cell-powered hybrid systems: Investigation of application areas, design architectures and energy management approaches, *Renewable and Sustainable Energy Reviews*, 14:2874–2884 pp.
- Esparza, R., Rosas, G., López Fuentes, M., Sánchez Ramírez, J.F., Pal, U., Ascencio, J.A. and Pérez, R.**, 2007, Synthesis of gold nanoparticles with different atomistic structural characteristics, *Materials Characterization*, 58:694-700 pp.
- Fagan-Murphy, A., Allen, M.C. and Patel, B.A.**, 2015, Chemically modified multiwall carbon nanotube composite electrodes: An assessment of fabrication strategies, *Electrochimica Acta*, 152:249–254 pp.
- Fernandes, D.M., Silva, N., Pereira, C., Mourac, C., Magalhães, J.M.C.S., Bachiller-Baeza, B., Rodríguez-Ramos, I., Guerrero-Ruiz, A., Delerue-Matos, C. and Freire, C.**, 2015, MnFe₂O₄@CNT-N as novel electrochemical nanosensor for determination of caffeine, acetaminophen and ascorbic acid *Sensors and Actuators B*, 218:128–136 pp.
- Finkelstein, D.A., Da Mota, N., Cohen, J.L. and Abruna, H.D.**, 2009, Rotating disk electrode (rde) investigation of BH₄⁻ and BH₃OH⁻ electro-oxidation at Pt and Au: implications for BH₄⁻ fuel cells, *Journal of Physical Chemistry C*, 113:19700–19712 pp.

REFERENCES (Continued)

- Flink, S. van Veggel, F.C.J.M. and Reinhoudt, D.N.**, 2000, Sensor Functionalities in Self-Assembled Monolayers, *Adv. Mater.* 12(18):1315-1328 pp.
- Gao, Y. Wang, H. and Guo, L.**, 2013, Simultaneous determination of theophylline and caffeine by large mesoporous carbon/Nafion modified electrode, *Journal of Electroanalytical Chemistry*, 706:7–12 pp.
- Garcia-Serrano, J. and Pa, U.**, 2003, Synthesis and characterization of Au nanoparticles in Al₂O₃ matrix, *International Journal of Hydrogen Energy*, 28:637–640 pp.
- Gendron, D., Ansaldo, A., Bubak, G., Ceseracciu, L., Vamvounis, G., Ricci, D.**, 2015, Poly(ionic liquid)-carbon nanotubes self-supported, highly electroconductive composites and their application in electroactive devices, *Composites Science and Technology*, 117:364-370 pp.
- Ghanbari, K. and Hajheidari, N.**, 2015, ZnO–Cu_xO/polypyrrole nanocomposite modified electrode for simultaneous determination of ascorbic acid, dopamine, and uric acid, *Analytical Biochemistry*, 473:53–62.
- Ghanema, M.A., Al-Mayouf, A.M., Shaddad, M.N. and Marken, F.**, 2015, Selective formation of hydrogen peroxide by oxygen reduction on TiO₂ nanotubes in alkaline media, *Electrochimica Acta*, 174:557–562 pp.
- Gorski, W., Aspinwall, C.A., Lakey, J.R.T. and Kennedy, R.T.**, 1997, Ruthenium catalyst for amperometric determination of insulin at physiological pH, *Journal of Electroanalytical Chemistry*, 425:191-199 pp.
- Goyal, N.R., Bishnoi, S. and Agrawal, B.**, 2011, Electrochemical sensor for the simultaneous determination of caffeine and aspirin in human urine samples, *Journal of Electroanalytical Chemistry*, 655:97–102 pp.
- Griffiths, R.R. and Vernotica, E.M.**, 2000, Is caffeine a flavoring agent in cola soft drinks?, *Archives of Family Medicine*, 9:727–734 pp.
- Guimard, N.K., Gomez, N. and Schmidt, C.E.**, 2007, Conducting polymers in biomedical engineering, *Progress in Polymer Science*, 32:876–921 pp.
- Güney, S. and Cebeci, F.**, 2015, Selective electrochemical sensor for theophylline based on an electrode modified with imprinted sol–gel film immobilized on carbon nanoparticle layer, *Sensors and Actuators B*, 208:307–314 pp.

REFERENCES (Continued)

- Guo, S. and Wang, E.**, 2007, Synthesis and electrochemical applications of gold nanoparticles, *Analytica Chimica Acta*, 598:181–192 pp.
- Gupta, V.K., Jain, A.K. and Shoor, S.K.**, 2013, Multiwall carbon nanotube modified glassy carbon electrode as voltammetric sensor for the simultaneous determination of ascorbic acid and caffeine, *Electrochimica Acta*, 93:248–253 pp.
- Habibi, B., Abazari, M. and Pournaghi-Azar, M.H.**, 2012, A carbon nanotube modified electrode for determination of caffeine by differential pulse voltammetry, *Chinese Journal of Catalysis*, 33:11 pp.
- Habibi, B., Abazari, M. and Pournaghi-Azar, M.H.**, 2014, Simultaneous determination of codeine and caffeine using single-walled carbon nanotubes modified carbon-ceramic electrode, *Colloids and Surfaces B: Biointerfaces*, 114:89–95 pp.
- Hadad, G.M., Abdel Salam, R.A., Soliman, R.M. and Mesbah, M.K.**, 2012, Rapid and simultaneous determination of antioxidant markers and caffeine in commercial teas and dietary supplements by HPLC-DAD, *Talanta*, 101:38–44 pp.
- Haque, A., Xu, X., and Stewart, J.T.**, 1999, Determination of ephedrine, theophylline and phenobarbital in a tablet dosage form by capillary electrophoresis, *Journal of Pharmaceutical and Biomedical Analysis*, 21:1063–1067 pp.
- Hegde, R.N., Hosamani, R.R. and Nandibewoor, S.T.**, 2009, Electrochemical oxidation and determination of theophylline at a carbon paste electrode using cetyltrimethyl ammonium bromide as enhancing agent, *Analytical Letters*, 42:2665–2682 pp.
- Hernández-Ramírez, V.A., Alatorre-Ordaz, A., Yopez-Murrieta, M.L., Ibanez, J.G., Ponce-de-León, C. and Walsh, F.C.**, 2009, Oxidation of the borohydride ion at silver nanoparticles on a glassy carbon electrode using pulsed potential techniques, *Electrochemical Transactions*, 20:211–225 pp.
- Hong Y.H. and Tsai, Y.C.**, 2009, Electrodeposition of platinum and ruthenium nanoparticles in multiwalled carbon nanotube-nafion nanocomposite for methanol electrooxidation, *Journal of Nanomaterials*, Article ID 892178, 2009:6 pp.

REFERENCES (Continued)

http://download.springer.com/static/pdf/635/chp%253A10.1007%252F978-0-387-39620-6.pdf?originUrl=http%3A%2F%2Flink.springer.com%2Fchapter%2F10.1007%2F978-0-387-39620-0_6&token2=exp=1443296912~acl=%2Fstatic%2Fpdf%2F635%2Fchp%25253A10.1007%25252F978-0-387-39620-0_6.pdf [available: 25 September 2015]

Huang, J., Zhu, N., Yang, T., Zhang, T., Wu, P. and Dang Z., 2015, Nickel oxide and carbon nanotube composite (NiO/CNT) as a novel cathode non-precious metal catalyst in microbial fuel cells, *Biosensors and Bioelectronics*, 72:332–339 pp.

Huang, M., Jin, Y., Jiang, H., Sun, X., Chen, H., Liu, B., Wang E. and Dong, S., 2005, Designed Nanostructured Pt Film for Electrocatalytic Activities by Underpotential Deposition Combined Chemical Replacement Techniques, *Journal of Physical Chemistry, B*, 109(32):15264–15271 pp.

Huck, C.W., Guggenbichler, W. and Bonn, G.K., 2005, Analysis of caffeine, theobromine and theophylline in coffee by near infrared spectroscopy (NIRS) compared to high-performance liquid chromatography (HPLC) coupled to mass spectrometry, *Analytica Chimica Acta*, 538:195–203 pp.

Hui, N., Wang, S., Xie, H., Xu, S., Niu, S. and Luo, X., 2015, Nickel nanoparticles modified conducting polymer composite of reduced graphene oxide doped poly(3,4-ethylenedioxythiophene) for enhanced nonenzymatic glucose sensing, *Sensors and Actuators B*, 221:606–613 pp.

Ikhsan, N.I., Rameshkumar, P., Pandikumar, A., Shahid, M.M., Huang, N.M., Kumar, S.V. and Lim, H.N., 2015, Facile synthesis of graphene oxide–silver nanocomposite and its modified electrode for enhanced electrochemical detection of nitrite ions, *Talanta* 144 (2015) 908–914 pp.

Inoue, H., Yamazaki, T., Kitamura, T., Shimada, M., Chiku, M. and Higuchi, E., 2012, Electrochemical hydrogen production system from ammonia borane in methanol solution, *Electrochimica Acta*, 82:392–396 pp.

Inzelt, G., 2008, Conductive polymers, Springer, Germany, 262p.

Iwasita T., 2002, Electrocatalysis of methanol oxidation, *Electrochimica Acta*, 47:3663–3674 pp.

REFERENCES (Continued)

- Jeevagan, A.J. and John, S.A.**, 2013, Electrochemical determination of guanosine 5-monophosphate using the electropolymerized film of non-peripheral amine substituted nickel(II) phthalocyanine modified electrode, *Electrochimica Acta*, 95:246–250 pp.
- Jeevagan, J.A. and John, A.S.**, 2012, Electrochemical determination of caffeine in the presence of paracetamol using a self-assembled monolayer of non-peripheral amine substituted copper(II) phthalocyanine, *Electrochimica Acta*, 77:137–142 pp.
- Jeon, D.H., Lim, T.J. and Park, S.J.**, 2015, Role of microporosity of carbon produced from rice husks on electrochemical performance of Pt-Ru catalyst for direct methanol fuel cells, *Journal of Industrial and Engineering Chemistry*, 31:244–250 pp.
- Jeong, H.T., Kim, B.C., Higgins, M.J. and Wallace, G.G.**, 2015, Highly stretchable reduced graphene oxide (rGO)/single-walled carbon nanotubes (SWNTs) electrodes for energy storage devices, *Electrochimica Acta*, 163:149–160 pp.
- Ji, Z.G., Wong, K.W., Wang, M., Tse, K.P.K., Kwok, R.W.M. and Lau, W.M.**, 2001, X-ray photoemission study of low-energy ion beam induced changes on copper phthalocyanine film. *Nuclear Instruments & Methods in Physics Research Section B-Beam Interactions with Materials and Atoms*, 174(3):311–316 pp.
- Jin, X., He, B., Miao, J., Yuan, J., Zhang, Q. and Niu, L.**, 2012, Stabilization and dispersion of PtRu and Pt nanoparticles on multiwalled carbon nanotubes using phosphomolybdic acid, and the use of the resulting materials in a direct methanol fuel cell, *Carbon*, 50(8):3083–91 pp.
- Joseph, A., Subramanian, S., Ramamurthy, P.C., Sampath, S., Kumar, R.V. and Schwandt, C.**, 2014, Iminodiacetic acid functionalized polypyrrole modified electrode as Pb(II) sensor: Synthesis and DPASV studies, *Electrochimica Acta*, 137:557–563 pp.
- Jukk, K., Kongi, N., Tarre, A., Rosental, A., Treshchalov, A.B., Kozlova, J., Ritslaid, P., Matisen, L., Sammelselg, V. and Tammeveski, K.**, 2014, Electrochemical oxygen reduction behaviour of platinum nanoparticles supported on multi-walled carbon nanotube/titanium dioxide composites, *Journal of Electroanalytical Chemistry*, 735:68–76 pp.

REFERENCES (Continued)

- Jurzinsky, T., Bär, R., Cremers, C., Tübke, J. and Elsner, P.**, 2015, Highly active carbon supported palladium-rhodium PdXRh/C catalysts for methanol electrooxidation in alkaline media and their performance in anion exchange direct methanol fuel cells (AEM-DMFCs), *Electrochimica Acta*, 176:1191–1201 pp.
- Jusys, Z. and Behm, R.J.**, 2001, Methanol oxidation on a carbon-supported Pt fuel cell catalysts: a kinetic and mechanistic study by differential electrochemical mass spectrometry, *Journal of Physical Chemistry B*, 105:10874–10883 pp.
- Kabak, M.**, 2004, X-ışınları kristalografisi, Bıçaklar Kitabevi. Ankara, 234s.
- Kakaei, K.**, 2015, Decoration of graphene oxide with Platinum Tin nanoparticles for ethanol oxidation, *Electrochimica Acta*, 165:330–337 pp.
- Kanoun, O., Müller, C., Benchirouf, A., Sanli, A., Dinh, T.N., Al-Hamry, A., Bu, L., Gerlach C. and Bouhamed, A.**, 2014, Flexible Carbon Nanotube Films for High Performance Strain, Sensors, *Sensors*, 14(6):10042–10071 pp.
- Karabiberoğlu, Ş.**, 2014, Preparation of metal nanoparticles modified polymer film electrodes; their characterizations and applications, PhD. Thesis, Ege University, 328 pp.
- Karimi, M., Mohsen-Nia, M. and Akbari, A.**, 2014, Electro-separation of synthetic azo dyes from a simulated wastewater using polypyrrole/polyacrylonitrile conductive membranes, *Journal of Water Process Engineering*, 4:6–11 pp.
- Kesavan, S. and John, A.S.**, 2014, Fabrication of aminotriazole grafted gold nanoparticles films on glassy carbon electrode and its application towards the simultaneous determination of theophylline and uric acid, *Sensors and Actuators B*, 205:352–362 pp.
- Khoo, W. Y. H., Pumera, M. and Bonanni, A.**, 2013, Graphene platforms for the detection of caffeine in real samples, *Analytica Chimica Acta*, 804:92–97 pp.
- Khurana, P., Thatai, S., Chaure, N.B., Mahamuni, S. and Kulkarni, S.**, 2014, Solution-processed copper phthalocyanine–gold nanoparticle hybrid nanocomposite thin films, *Thin Solid Films*, 565:202–206 pp.

REFERENCES (Continued)

- Kiran, V., Kalidindi, S.B., Jagirdar, B.R. and Sampath, S.,** 2011, Electrochemical oxidation of boron containing compounds on titanium carbide and its implications to direct fuel cells, *Electrochimica Acta*, 56:10493–10499 pp.
- Kissinger, P.T. and Heineman, W.R. (Eds),** 1996, Laboratory Techniques in Electroanalytical, Marcel Dekker Inc., New York, 990 pp.
- Koçak, Ç.C. and Dursun, Z.,** 2013, Simultaneous determination of ascorbic acid, epinephrine and uric acid at over-oxidized poly(p-aminophenol) film modified electrode, *Journal of Electroanalytical Chemistry*, 694:94–103 pp.
- Koçak, S., Dursun, Z. and Ertaş, F.N.,** 2011, Electrocatalytic oxidation of methanol at Pd and Pt ad-layer modified Au(111) electrodes in alkaline solution, *Turkish Journal of Chemistry*, 35:711–722 pp.
- Koo, J., Jung, J.Y., Lee, S., Lee, M. and Chang, J.,** 2015, Development of waterborne oil spill sensor based on printed ITO nanocrystals, *Marine Pollution Bulletin*, <http://dx.doi.org/10.1016/j.marpolbul.2015.07.005> (in press).
- Koseoglu, H., Turkoglu, F., Kurt, M., Yaman, M.D., Akca, F.G., Aygun, G. and Ozyuzer, L.,** 2015, Improvement of optical and electrical properties of ITO thin films by electro-annealing, *Vacuum*, <http://dx.doi.org/10.1016/j.vacuum.2015.06.027> (in press).
- Kuilla, T., Bhadra, S., Yao, D., Kim, N.H., Bose, S. and Lee, J.H.,** 2010, Recent advances in graphene based polymer composites, *Progress in Polymer Science*, 35:1350–1375 pp.
- Kumara Swamy, B.E. and Jill Venton, B.,** 2007, Carbon nanotube-modified microelectrodes for simultaneous detection of dopamine and serotonin in vivo, *Analyst*, 132:876-884 pp.
- Kuwahara, T., Ohta, H., Kondo, M. and Shimomura, M.,** 2008, Immobilization of glucose oxidase on carbon paper electrodes modified with conducting polymer and its application to a glucose fuel cell, *Bioelectrochemistry*, 74:66–72 pp.

REFERENCES (Continued)

- Lane, R.F. and Hubbard, A.T.**, 1973, Electrochemistry of Chemisorbed Molecules. I. Reactants Connected to Electrodes through Olefinic Substituents, *The Journal of Physical Chemistry*, 77(11):1401–1410 pp.
- Larminie, J. and Dicks, A.**, 2003, Fuel Cell Systems Explained Wiley, England, 418 pp.
- Lasia, A.**, 1999, Electrochemical Impedance Spectroscopy and its Applications, Kluwer Academic/Plenum Publishers, New York, 523 pp.
- Lee, H.Y., Kim, S.W. and Lee, H.Y.**, 2001, Expansion of active site area and improvement of kinetic reversibility in electrochemical pseudocapacitor electrode, *Electrochem. Solid-State Lett.* 4(3):A19-A22 pp.
- Lee, Y.W., Lee, J.Y., Kwak, D.H., Hwang, E.T., Sohn, J.I. and Park, K.W.**, 2015, Pd@Pt core-shell nanostructures for improved electrocatalytic activity in methanol oxidation reaction, *Applied Catalysis B: Environmental*, 179:178–184 pp.
- Li, L. and Xing, Y.**, 2009, Methanol electro-oxidation on pt-ru alloy nanoparticles supported on carbon nanotubes, *Energies*, 2:789-804 pp.
- Li, T., Peng, Y., Li, K., Zhang, R., Zheng, L., Xia, D. and Zuo, X.**, 2015, Enhanced activity and stability of binuclear iron (III) phthalocyanine on graphene nanosheets for electrocatalytic oxygen reduction in acid, *Journal of Power Sources*, 293:511-518 pp.
- Liao, Y., Zhang, S. and Dryfe, R.**, 2012, Electroless copper plating using dimethylamine borane as reductant, *Particuology*, 10:487– 491 pp.
- Lin, Y., Peng, Y. and Di, J.**, 2015, Electrochemical detection of Hg(II) ions based on nanoporous gold nanoparticles modified indium tin oxide electrode, *Sensors and Actuators B*, 220:1086–1090 pp.
- Liu, H. and Iglesia, E.**, 2004, Effects of support on bifunctional methanol oxidation pathways catalyzed by polyoxometallate Keggin clusters, *Journal of Catalysis*, 223:161–169 pp.
- Liu, J., Lin, W., Alsaadi, F. and Hayat, T.**, 2015, Nonlinear observer design for PEM fuel cell power systems via second order sliding mode technique, *Neurocomputing*, 168:145–151 pp.

REFERENCES (Continued)

- Liu, L.P., Yin, Z.J. and Yang, Z.S.**, 2010, A L-cysteine sensor based on Pt nanoparticles/poly(o-aminophenol) film on glassy carbon electrode, *Bioelectrochemistry*, 79:84–89 pp.
- Liu, S., Dong, Y., Zhao, C., Zhao, Z., Yu, C., Wang, Z. and Qiu, J.**, 2015, Nitrogen-rich carbon coupled multifunctional metal oxide/graphene nanohybrids for long-life, lithium storage and efficient oxygen reduction, *Nano Energy*, 12:578–587 pp.
- Long, F. Zhang, Z., Wang, J., Yan, L. and Zhou, B.**, 2015, Cobalt-nickel bimetallic nanoparticles decorated graphene sensitized imprinted electrochemical sensor for determination of octylphenol, *Electrochimica Acta*, 168:337–345 pp.
- Lou, X., Chen, J., Wang, M., Gu, J., Wu, P., Sun, D. and Tang, Y.**, 2015, Carbon nanotubes supported cerium dioxide and platinum nanohybrids: Layer-by-layer synthesis and enhanced electrocatalytic activity for methanol oxidation, *Journal of Power Sources*, 287:203–210 pp.
- Lu, C. Kong, W. Zhang, H. Song, B. and Wang, Z.**, 2015, Gold platinum bimetallic nanotubes templated from tellurium nanowires as efficient electrocatalysts for methanol oxidation reaction, *Journal of Power Sources*, 296:102–108 pp.
- Lu, J., Drzal, L.T., Worden, R.M. and Ilsoon L.**, 2007, Simple fabrication of a highly sensitive glucose biosensor using enzymes immobilized in exfoliated graphite nanoplatelets nafion membrane, *Chemistry of Materials*, 19:6240–6246 pp.
- Ma, W., Lv, X., Han, D., Li, F., Dong, X. and Niu, L.**, 2013, Decoration of electro-reduced graphene oxide with uniform gold nanoparticles based on in situ diazonium chemistry and their application in methanol oxidation, *Journal of Electroanalytical Chemistry*, 690:111–116 pp.
- Magdum, P.A., Pattar V.P. and Nandibewoor, S.T.**, 2015, Electrochemical Characterization and Determination of Theophylline at a Graphite Pencil Electrode using Cetyltrimethyl Ammonium Bromide as an Enhancing Agent, *Analytical & Bioanalytical Electrochemistry*, 7:426–438 pp.
- Malode, S.J., Shetti, P.N. and Nandibewoor, T.S.**, 2012, Voltammetric behavior of theophylline and its determination at multi-wall carbon nanotube paste electrode, *Colloids and Surfaces B: Biointerfaces*, 97:1–6 pp.

REFERENCES (Continued)

- Mansouri M.S., Teymourian, H., Salimi, A. and Hallaj, R.**, 2013, Fabrication of electrochemical theophylline sensor based on manganese oxide nanoparticles/ionic liquid/chitosan nanocomposite modified glassy carbon electrode, *Electrochimica Acta*, 108:707–716 pp.
- Mao, H., Huang, T. and Yu, A.**, 2015, Surface Palladium rich Cu_xPd_y /carbon catalysts for methanol and ethanol oxidation in alkaline media, *Electrochimica Acta*, 174:1–7 pp.
- Marra, M.C., Cunha, R.R., Vidal, D.T.R., Munoz, R.A.A., do Lago, C.L. and Richter, E.M.**, 2014, Ultra-fast determination of caffeine, dipyrone, and acetylsalicylic acid by capillary electrophoresis with capacitively coupled contactless conductivity detection and identification of degradation products, *Journal of Chromatography A*, 1327:149–154 pp.
- Martin, C.R. and Foss, Jr. C.A.**, 1996, Chemistry, Chemically Modified Electrodes, Marcel Dekker Inc., New York, 986 pp.
- Martins, J.I. and Nunes M.C.**, 2008, Comparison of the electrochemical oxidation of borohydride and dimethylamine borane on platinum electrodes: Implication for direct fuel cells, *Journal of Power Sources*, 175:244–249 pp.
- Martins-Júnior, P.A., Alcântara, C.E., Resende, R.R. and Ferreira, A.J.**, 2013, Carbon Nanotubes: Directions and Perspectives in Oral Regenerative Medicine, *Journal of dental research*, 92(7):575-583 pp.
- Mehmood, A., Scibioh, M.A., Prabhuram, J., An, M.G. and Ha, H.Y.**, 2015, A review on durability issues and restoration techniques in long-term operations of direct methanol fuel cells, *Journal of Power Sources*, 297:224-241 pp.
- Melo, E.I., Franco, D.L., Afonso, A.S., Rezende, H.C., Brito-Madurro, A.G., Madurro J.M. and Coelho, N.M.M.**, 2011, A Biosensor Using Poly(4-Aminophenol)/Acetylcholinesterase Modified Graphite Electrode for the Detection of Dichlorvos, *Brazilian Archives of Biology And Technology*, 54:1217-1222 pp.
- Merle, G., Wessling, M. and Nijmeijer, K.**, 2011, Anion exchange membranes for alkaline fuel cells: A review, *Journal of Membrane Science*, 377:1–35 pp.

REFERENCES (Continued)

- Miller, T.S., Sansuk, S.E.S.P., Lai, S.C.S., Macpherson, J.V. and Unwin, P.R.**, 2015, Pt nanoparticles modified single walled carbon nanotube network electrodes for electrocatalysis: Control of the specific surface area over three orders of magnitude, *Catalysis Today*, 244:136-145 pp.
- Miyake, J., Sakai, M., Sakamoto, M., Watanabe, M. and Miyatake, K.**, 2015, Synthesis and properties of sulfonated block poly(arylene ether)s containing m-terphenyl groups as proton conductive membranes, *Journal of Membrane Science*, 476:156–161 pp.
- Miyoshi, K.**, 2002, Surface Characterization Techniques: An Overview, Glenn Research Center, Ohio, <http://ntrs.nasa.gov/archive/nasa/casi.ntrs.nasa.gov/20020070606.pdf> [available: 20 August 2015].
- Mohanty, U.S.**, 2011, Electrodeposition: a versatile and inexpensive tool for the synthesis of nanoparticles, nanorods, nanowires, and nanoclusters of metals, *Journal of Applied Electrochem*, 41:257–270 pp.
- Moraesa, F.C., Golinelli, D.L.C., Mascaroa, L.H. and Machado, S.A.S.**, 2010, Determination of epinephrine in urine using multi-walled carbon nanotube modified with cobalt phthalocyanine in a paraffin composite electrode, *Sensors and Actuators B*, 148:492–497 pp.
- Moses, P.R. Wier, L. and Murray, R.W.**, 1975, Chemically Modified Tin Oxide Electrode, *Analytical Chemistry*, 47:1882-1886 pp.
- Muench, F., Eils, A., Toimil-Molares, M.E., Hossain, U.H., Radetinac, A., Stegmann, C., Kunz, U., Lauterbach, S., Kleebe H.-J. and Ensinger, W.**, 2014, Polymer activation by reducing agent absorption as a flexible tool for the creation of metal films and nanostructures by electroless plating, *Surface & Coatings Technology*, 242:100–108 pp.
- Mugadza, T. and Nyokong, T.**, 2010, Electrocatalytic oxidation of amitrole and diuron on iron(II) tetraaminophthalocyanine-single walled carbon nanotube dendrimer, *Electrochimica Acta*, 55:2606–2613 pp.
- Mugadza, T. and Nyokong, T.**, 2011, Synthesis, characterization and application of monocarboxy-phthalocyanine-single walled carbon nanotube conjugates in electrocatalysis, *Polyhedron*, 30(11):1820-1829 pp.

REFERENCES (Continued)

- Muraviev, D.N.**, 2005, Inter-matrix synthesis of polymer stabilised metal nanoparticles for sensor applications, *Contributions to Science*, 3:19-32 pp.
- Murray R.W.**, 1980, Chemically Modified Electrodes, *ACC Chem. Res.*, 13:135-141 pp.
- Nagle, L.C. and Rohan, J.F.**, 2005, Investigation of DMAB Oxidation at a Gold Microelectrode in Base, *Electrochemistry Solid-State Letters*, 8(5):C77-C80 pp.
- Narayana, P.V., Madhusudana Reddy, T., Gopal, P., Mohan Reddy, M. and Ramakrishna Naidu, G.**, 2015, Electrocatalytic boost up of epinephrine and its simultaneous resolution in the presence of serotonin and folic acid at poly(serine)/multi-walled carbon nanotubes composite modified electrode: A voltammetric study, *Materials Science and Engineering C*, 56:57–65 pp.
- Narayanan, K.B., Park, H.H. and Han, S.S.**, 2015, Synthesis and characterization of biomatrixed-gold nanoparticles by the mushroom *Flammulina velutipes* and its heterogeneous catalytic potential, *Chemosphere*, 141:169–175 pp.
- Nas, A., Kahrman, N., Kantekin, H., Yaylı, N. and Durmus, M.**, 2013, The synthesis of novel unmetallated and metallated phthalocyanines including (E)-4-(3-cinnamoylphenoxy) groups at the peripheral positions and photophysical properties of their zinc phthalocyanine derivatives, *Dyes and Pigments*, 99:90-98 pp.
- Nash, S., Andrieux, F., Dawson, R., Sutherland, H. and Lewis, G.**, 2014, Direct fuel oxidation alkaline fuel cells; the kinetics of borohydride oxidation, *Chemical Engineering Transactions*, 41:247-252 pp.
- National Toxicology Program**, “Chemical Information Profile for Dimethylamine Borane”, july, 2008, https://ntp.niehs.nih.gov/ntp/htdocs/chem_background/exsumpdf/dimethylamineborane508.pdf [available: 30 August 2015].
- National Toxicology Program**, “NTP technical report on the toxicology and carcinogenesis studies of theophylline”, 1998, http://ntp.niehs.nih.gov/ntp/htdocs/lt_rpts/tr473.pdf [available: 30 August 2015].

REFERENCES (Continued)

- Navaee, A., Salimi, A., Soltanian, S. and Servati, P.**, 2015, Facile one-pot synthesis of platinum nanoparticles decorated nitrogen-graphene with high electrocatalytic performance for oxygen reduction and anodic fuels oxidation, *Journal of Power Sources*, 277:268-276 pp.
- Ndlovu, T., Arotiba¹, O.A., Sampath, S., Krause¹, R.W. and Mamba, B.B.**, 2012, Reactivities of modified and unmodified exfoliated graphite electrodes in selected redox systems, *International Journal of Electrochemical Science*, 7:9441-9453 pp.
- Nikolic, V.M., Perovic, I.M., Gavrilov, N.M., Pasti, I.A., Saponjic, A.B., Vulic, P.J., Karic, S.D. Babic, B.M. and Kaninski, M.P.M.**, 2014, On the tungsten carbide synthesis for PEM fuel cell application e Problems, challenges and advantages, *International Journal of Hydrogen Energy*, 39:11175-11185 pp.
- Nirogi, R.V.S., Kandikere, V.N., Shukla, M., Mudigonda, K. and Ajjala, D.R.**, 2007, A simple and rapid HPLC/UV method for the simultaneous quantification of theophylline and etofylline in human plasma, *Journal of Chromatography B*, 848:271–276 pp.
- Nkosi, D. and Ozoemena, K.I.**, 2008, Interrogating the electrocatalytic properties of coordination self-assembled nanostructures of single-walled carbon nanotube–octa(hydroxyethylthio)phthalocyaninatoiron(II) using thiocyanate as an analytical probe, *Journal of Electroanalytical Chemistry*, 621:304–313 pp.
- Ohma, A., Fushinobu, K. and Okazaki, K.**, 2010, Influence of Nafion® film on oxygen reduction reaction and hydrogen peroxide formation on Pt electrode for proton exchange membrane fuel cell, *Electrochimica Acta*, 55:8829–8838 pp.
- Orazem, M.E. and Tribollet, B.**, 2008, *Electrochemical Impedance Spectroscopy*, John Wiley & Sons, Inc., Hoboken, New Jersey, 325p.
- Özcan, L., Şahin, Y. and Türk, H.**, 2008, Non-enzymatic glucose biosensor based on overoxidized polypyrrole nanofiber electrode modified with cobalt(II) phthalocyanine tetrasulfonate, *Biosensors and Bioelectronics*, 24:512–517 pp.

REFERENCES (Continued)

- Özdokur, K.V., Demir, B., Yavuz, E., Ulus, F., Erten, Ç., Aydın, I., Demirkol, D.O., Pelit, L., Timur, S. and Ertas, F.N., 2014, Pyranose oxidase and Pt–MnOx bionanocomposite electrode bridged by ionic liquid for biosensing applications *Sensors and Actuators B* 197:123–128 pp.
- Paulus, U.A., Wokaun, A., Scherer, G.G., Schmidt, T.J., Stamenkovic, V., Radmilovic, V., Markovic, N.M. and Ross, P.N., 2002, Oxygen Reduction on Carbon-Supported Pt–Ni and Pt–Co Alloy Catalysts, *Journal of Physical Chemistry B*, 106:4181–4191 pp.
- Pennycook, S.J., Lupini, A.R., Varela, M., Borisevich, A.Y., Peng, Y., Oxley, M.P., van Benthem, K. and Chisholm, M.F., 2006, Scanning Transmission Electron Microscopy for Nanostructure Characterization (Chapter of Scanning Microscopy for Nanotechnology), Springer, 152–191 pp.
- Pillay, J. and Ozoemena, K.I., 2009, Layer-by-layer self-assembled nanostructured phthalocyaninatoiron(II)/SWCNT-poly(m-aminobenzenesulfonic acid) hybrid system on gold surface: Electron transfer dynamics and amplification of H₂O₂ response, *Electrochimica Acta*, 54:5053–5059 pp.
- Plana, D. and Dryfe, R. A.W., 2011, The electro-oxidation of dimethylamine borane: Part 1, polycrystalline substrates, *Electrochimica Acta*, 56:3835–3844 pp.
- Plana, D., Rodriguez, P., Koper, M.T.M. and Dryfe, R. A.W., 2011, The electro-oxidation of dimethylamine borane: Part 2, in situ FTIR on single-crystal gold electrodes, *Electrochimica Acta*, 56:7637–7643 pp.
- Porras-Gutiérrez, A. G., Frontana-Uribe, B. A., Gutiérrez-Granados, S., Griveau, S. and Bedioui, F., 2013, In situ characterization by cyclic voltammetry and conductance of composites based on polypyrrole, multi-walled carbon nanotubes and cobalt phthalocyanine, *Electrochimica Acta*, 89:840–847 pp.
- Prakash, J. and Joachin, H., 2000, Electrocatalytic activity of ruthenium for oxygen reduction in alkaline solution, *Electrochimica Acta*, 45:2289–2296 pp.

REFERENCES (Continued)

- Prasad, K. S., Chuang, M.-C. and Ho, J. A.**, 2012, Synthesis, characterization, and electrochemical applications of carbon nanoparticles derived from castor oil soot, *Talanta*, 88:445–449 pp.
- Protti, P.**, 2001, AMEL electrochemistry-Introduction to Modern Voltammetric and Polarographic Analysis Techniques, IV. Edition, http://www.amelchem.com/wp-content/uploads/2011/10/VPAT_manual_eng.pdf [available: 11 July 2015].
- Puguan, J.M.C., Chinnappan, A., Kostjuk, S.V. and Kim, H.**, 2015, Zirconium dioxide nanofilled poly(vinylidene fluoride-hexafluoropropylene) complexed with lithium trifluoromethanesulfonate as composite polymer electrolyte for electrochromic devices, *Materials Research Bulletin*, 69:104–111 pp.
- Qing, X., Shi, J, M,a C, Fan, M., Bai, Z., Chen, Z., Qiao, J. and Zhang J.**, 2014, Simultaneous formation of nitrogen and sulfur-doped transition metal catalysts for oxygen reduction reaction through pyrolyzing carbon-supported copper phthalocyanine tetrasulfonic acid tetrasodium salt, *Journal of Power Sources*, 266:88-98 pp.
- Rahim, A.A., Nofrizal, S. and Saad, B.**, 2014, Rapid tea catechins and caffeine determination by HPLC using microwave-assisted extraction and silica monolithic column, *Food Chemistry*, 147:262-268 pp.
- Rajabzadeh, S., Rounaghi, G.H., Arbab-Zavar, M.H. and Ashraf, N.**, 2014, Development of a dimethyl disulfide electrochemical sensor based on electrodeposited reduced graphene oxide-chitosan modified glassy carbon electrode, *Electrochimica Acta*, 135:543–549 pp.
- Ren, F., Zhai, C., Zhu, M., Wang, C., Wang, H., Bin, D., Guo, J., Yang, P. and Du, Y.**, 2015, Facile synthesis of PtAu nanoparticles supported on polydopamine reduced and modified graphene oxide as a highly active catalyst for methanol oxidation, *Electrochimica Acta*, 153:175–183 pp.
- Sadik, O.A., Xu, H. and Sargent, A.**, 2005, Multi-electron transfer mechanism of dimethylamine borane in electroless gold deposition, *Journal of Electroanalytical Chemistry*, 583:167–175 pp.

REFERENCES (Continued)

- Sağlam, Ş., Üzer, A., Tekdemir, Y., Erçağ, E. and Apak, R.,** 2015, Electrochemical sensor for nitroaromatic type energetic materials using gold nanoparticles/poly(o-phenylenediamine–aniline) film modified glassy carbon electrode, *Talanta*, 139:181–188 pp.
- Sakamoto, K. and Ohno-Okumura, E.,** 2009, Syntheses and Functional Properties of Phthalocyanines, *Materials*, 2:1127-1179 pp.
- Salimi, A., Pourbahram, B., Mansouri-Majd, S. and Hallaj, R.,** 2015, Manganese oxide nanoflakes/multi-walled carbon nanotubes/chitosan nanocomposite modified glassy carbon electrode as a novel electrochemical sensor for chromium (III) detection, *Electrochimica Acta*, 156:207–215 pp.
- Sargent, A., Sadik, O.A. and Matienzo, L.J.,** 2001, Probing the mechanism of electroless gold plating using an electrochemical quartz crystal microbalance I. Elucidating the nature of reactive intermediates in dimethylamine borane, *Journal of The Electrochemical Society*, 148(4):C257-C265 pp.
- Sastre, C.M., González-Arechavala, Y. and Santos, A.M.,** 2015, Global warming and energy yield evaluation of Spanish wheat straw electricity generation – A LCA that takes into account parameter uncertainty and variability, *Applied Energy*, 154:900–911 pp.
- Segura, R., Pizarro, J., Díaz, K., Placencio, A., Godoy, F., Pino, E. and Recio, F.,** 2015, Development of electrochemical sensors for the determination of selenium using gold nanoparticles modified electrodes *Sensors and Actuators B*, 220:263–269 pp.
- Serrà, A., Gómez, E. and Vallés, E.,** 2015, Novel electrodeposition media to synthesize CoNi-Pt Core@Shell stable mesoporous nanorods with very high active surface for methanol electro-oxidation, *Electrochimica Acta*, 174: 630–639 pp.
- Shang, C., Hong, W., Wang, J. and Wang, E.,** 2015, Carbon supported trimetallic nickelpalladiumgold hollow nanoparticles with superior catalytic activity for methanol electrooxidation, *Journal of Power Sources*, 285:12-15 pp.

REFERENCES (Continued)

- Sharma, R. and Kar, K.K.**, 2015, Particle size and crystallographic orientation controlled electrodeposition of platinum nanoparticles on carbon nanotubes, *Electrochimica Acta*, 156:199–206 pp.
- Shipovskov, S. and Ferapontova, E.E.**, 2008, Biocatalysis of theophylline oxidation by microbial theophylline oxidase in the presence of non-physiological electron acceptors, *Biocatalysis and Biotransformation*, 26(6):508-518 pp.
- Shrivastava, K. and Wu, H.F.**, 2007, Rapid determination of caffeine in one drop of beverages and foods using drop-to-drop solvent microextraction with gas chromatography/mass spectrometry, *Journal of Chromatography A*, 1170:9–14 pp.
- Skoog, D.A., Holler, F.J. and Nieman, T.A.**, 1997, Enstrümantal Analiz İlkeleri (Transl. Kılıç, E., Köseoğlu, F. and Yılmaz, H.), Bilim yayıncılık, Ankara, 849s.
- Snell, K.D. and Keenan, A.G.**, 1979, Surface modified electrodes, *Chemical Society Reviews*, 8:259-282 pp.
- Spataru, N., Sarada, B.V., Tryk, D.A. and Fujishima, A.**, 2002, Anodic voltammetry of xanthine, theophylline, theobromine and caffeine at conductive diamond electrodes and its analytical application, *Electroanalysis*, 14:11721-11728 pp.
- Speakman, S.A.**, Basics of X-Ray Powder Diffraction, <http://prism.mit.edu/xray> [available: 13 August 2015].
- Srdjenovic, B., Djordjevic-Milic, V., Grujic, N., Injac, R. and Lepojevic, Z.**, 2008, Simultaneous HPLC Determination of Caffeine, Theobromine, and Theophylline in Food, Drinks, and Herbal Products, *Journal of Chromatographic Science*, 46:144-149 pp.
- Subsingha, W. and Sarakarn, P.**, 2012, 4 Phase interleaved DC boost converter for PEMFC applications, *Procedia Engineering*, 32:1127–1134 pp.
- Sultan, M.**, 2014, Simultaneous HPLC determination and validation of amphetamine, methamphetamine, caffeine, paracetamol and theophylline in illicit seized tablets, *International Journal of Pharmacy and Pharmaceutical Sciences*, 6:294-298 pp.

REFERENCES (Continued)

- Suni, I.I.**, 2008, Impedance methods for electrochemical sensors using nanomaterials, *Trends in Analytical Chemistry*, 27(7):604-611 pp.
- Sverdlov, Y. and Shacham-Diamand, Y.**, 2003, Electroless deposition of Co(W) thin films, *Microelectronic Engineering*, 70:512–518 pp.
- Švorc, L., Tomčík, P., Svítková, J., Rievaj, M. and Bustin, D.**, 2012, Voltammetric determination of caffeine in beverage samples on bare boron-doped diamond electrode, *Food Chemistry*, 135(3):1198-1204 pp.
- Tadesse, Y., Tadesse, A., Saini, R.C. and Pa, R.**, 2013, Cyclic Voltammetric Investigation of Caffeine at Anthraquinone Modified Carbon Paste Electrode, *International Journal of Electrochemistry*, 7 pp.
- Taei, M. and Ramazani, G.**, 2014, Simultaneous determination of norepinephrine, acetaminophen and tyrosine by differential pulse voltammetry using Au-nanoparticles/poly(2-amino-2-hydroxymethylpropane-1,3-diol) film modified glassy carbon electrode, *Colloids and Surfaces B: Biointerfaces*, 123:23–32 pp.
- Tajik, S., Taher, M.A. and Beitollahi, H.**, 2014, Application of a new ferrocene-derivative modified-graphene paste electrode for simultaneous determination of isoproterenol, acetaminophen and theophylline, *Sensors and Actuators B*, 197:228–236 pp.
- Tammeveski, K., Kontturi, K., Nichols, R.J., Potter, R.J. and Schiffrin, D.J.**, 2001, Surface redox catalysis for O₂ reduction on quinone-modified glassy carbon electrodes, *Journal of Electroanalytical Chemistry*, 515:101–112 pp.
- Tapan, N.A., Mustain, W.E., Gurau, B., Sandi, G. and Prakash, J.**, 2004, Investigation of methanol oxidation electrokinetics on Pt using the asymmetric electrode technique, *Journal of New Materials for Electrochemical Systems*, 7:281-286 pp.
- Tatar, B., Demiroglu, D. and Ürgen, M.**, 2014, Investigation of structural and electrical properties of p-CuPc/c-Si and p-CuPc/a-Si/c-Si hybrid photodiodes prepared by CSP technique, *Microelectronic Engineering*, 126:184–190 pp.
- Thenmozhi, G., Jaya, K.D., Mohanraj, G. and Jaya, S.R.**, 2011a, Synthesis, characterisation and biological applications of conducting poly (p- amino phenol) and its nano compound, *Der Pharma Chemica*, 2011a, 3(4):116-126 pp.

REFERENCES (Continued)

- Thenmozhi, G, Jaya, K.D, Mohanraj, G. and Jaya, S.R.**, 2011b, Synthesis, characterization and biological applications of poly meta amino phenol and its nano compound, *Der Pharma Chemica*, 3(6):325-333 pp.
- Tiburcio-Silver, A. and Sánchez-Juárez, A.**, 2004, SnO₂:Ga thin films as oxygen gas sensor, *Materials Science and Engineering B*, 110:268–271 pp.
- Topuz, B.B., Gündüz, G., Mavis, B. and Çolak, Ü.**, 2013, Synthesis and characterization of copper phthalocyanine and tetracarboxamide copper phthalocyanine deposited mica-titania pigments, *Dyes and Pigments*, 96:31-37 pp.
- Town, J.L., MacLaren, F. and Dewald, H.D.**, 1991, Rotating Disk Voltammetry Experiment, *Journal of Chemical Education*, 68(4):352-354 pp.
- Transmission electron microscopy**, https://en.wikipedia.org/wiki/Transmission_electron_microscopy, [available: 18 August 2015].
- Transmission electron microscope**, TEM materials applications, http://www.weizmann.ac.il/Chemical_Research_Support/EM_Unit/transmission-electron-microscope-tem-materials-applications [available: 18 August 2015].
- Tural, H., Gökçel, H.İ. and Ertaş, F.N.**, 2006, Enstrümental analiz I elektroanalitik yöntemler, Ege Üniversitesi Yayınları Fen Fakültesi, 186, İzmir, 339s.
- Tysczuk-Rotko, K. and Beczkowska, I.**, 2015, Nafion covered lead film electrode for the voltammetric determination of caffeine in beverage samples and pharmaceutical formulations, *Food Chemistry*, 172:24–29 pp.
- Ulubay, Ş. and Dursun, Z.**, 2010, Cu nanoparticles incorporated polypyrrole modified GCE for sensitive simultaneous determination of dopamine and uric acid, *Talanta*, 80:1461–1466 pp.
- Uygun, Z.O. and Uygun, H.D.E.**, 2014, A short footnote: Circuit design for faradaic impedimetric sensors and biosensors, *Sensors and Actuators, B*, 202:448–453 pp.

REFERENCES (Continued)

- Vaik, K., Schiffrin, D.J. and Tammeveski, K.**, 2004, Electrochemical reduction of oxygen on anodically pre-treated and chemically grafted glassy carbon electrodes in alkaline solutions, *Electrochemistry Communications*, 6:1–5 pp.
- Van der Heide, P.**, 2012, X-Ray Photoelectron Spectroscopy, A John Wiley & Sons, Inc., Hoboken, New Jersey, 236 pp.
- Vashist, S.K., Zheng, D., Al-Rubeaan, K., Luong, J.H.T. and Sheu, F.-S.**, 2011, Advances in carbon nanotube based electrochemical sensors for bioanalytical applications, *Biotechnology Advances*, 29:169–188 pp.
- Ventra, M.D., Evoy, S. and Heflin, J.R.**(Eds), 2004, Introduction to nanoscale science and technology, Kluwer Academic Publishers, Boston, 611 pp.
- Vielstich, W.**, 2003, Electrochemical Energy Conversion – Methanol Fuel Cell as Example, *Journal of Brazilian Chemical Society*, 14(4):503-509 pp.
- Vinoth, V., Wu, J.J., Asiri, A.M. and Anandan, S.**, 2015, Simultaneous detection of dopamine and ascorbic acid using silicate network interlinked gold nanoparticles and multi-walled carbon nanotubes, *Sensors and Actuators B*, 210:731–741 pp.
- Wallace G.G., Spinks, G.M., Kane-Maguire, L.P., Teasdale, P.R.**, 2009, Conductive Electroactive Polymers, CRC Pres, Taylor & Francis Group, New York, 263 pp.
- Wang, C., Waje, M., Wang, X., Tang, J. M., Haddon, R. C. and Yan, Y.**, 2004, Proton exchange membrane fuel cells with carbon nanotube based electrodes, *Nano Letters*, 4(2):345-348 pp.
- Wang, J.**, 1994, Analytical electrochemistry, Wiley-VCH, Canada, 198p.
- Wang, M., He, Y., Li, R., Ma, Z., Zhang, Z. and Wang, X.**, 2015, Electrochemical activated PtAuCu alloy nanoparticle catalysts for formic acid, methanol and ethanol electro-oxidation, *Electrochimica Acta*, <http://dx.doi.org/10.1016/j.electacta.2015.07.157> (in press)
- Wang, Q. and Zheng, J.**, 2010, Electrodeposition of silver nanoparticles on a zinc oxide film: improvement of amperometric sensing sensitivity and stability for hydrogen peroxide determination, *Microchim Acta*, 169:361–365 pp.

REFERENCES (Continued)

- Wang, Y., Hu, N., Zhou, Z., Xu, D., Wang, Z., Yang, Z., Wei, H., Kong E.S.W. and Zhang, Y.**, 2011, Single-walled carbon nanotube/cobalt phthalocyanine derivative hybrid material: preparation, characterization and its gas sensing properties, *Journal of Material Chemistry*, 21:3779–3787 pp.
- Wang, Z., Gao, G., Zhu, H., Sun, Z., Liu, H. and Zhao, X.**, 2009, Electrodeposition of platinum microparticle interface on conducting polymer film modified nichrome for electrocatalytic oxidation of methanol, *International Journal of Hydrogen Energy*, 34:9334–9340 pp.
- Webb, P.A.**, 2003, Introduction to Chemical Adsorption Analytical Techniques and their Applications to Catalysis, *Micromeritics Instrument Corporation Technical Publications*, 1-12 pp.
- Wee, J.H., Lee, K.Y. and Kim, S.H.**, 2007, Fabrication methods for low-Pt-loading electrocatalysts in proton exchange membrane fuel cell systems, *Journal of Power Sources*, 165 (2007) 667–677 pp.
- Wu, H., Yuan, T., Huang, Q., Zhang, H., Zou, Z., Zheng, J. and Yang, H.**, 2014, Polypyrrole nanowire networks as anodic micro-porous layer for passive direct methanol fuel cells, *Electrochimica Acta*, 141:1–5 pp.
- Xia, Z., Ni, Y. and Kokot, S.**, 2013, Simultaneous determination of caffeine, theophylline and theobromine in food samples by a kinetic spectrophotometric method, *Food Chemistry*, 141:4087-4093 pp.
- Yang, B., Lu, N., Huang, C., Qi, D., Shi, G., Xu, H., Chen, X., Dong, B., Song, W., Zhao, B. and Chi, L.**, 2009, Electrochemical deposition of silver nanoparticle arrays with tunable density, *Langmuir*, 25:55-58 pp.
- Yang, G., Zhao, F. and Zeng, B.**, 2014, Facile fabrication of a novel anisotropic gold nanoparticle–chitosan–ionic liquid/graphenemodified electrode for the determination of theophylline and caffeine, *Talanta*, 127:116–122 pp.
- Yang, G., Zhou, Y., Pan, H.B., Zhu, C., Fu, S., Du, D., Zhu, J.J. and Lin, Y.**, 2016, Ultrasonic-assisted synthesis of Pd–Pt/carbon nanotubes nanocomposites for enhanced electro-oxidation of ethanol and methanol in alkaline medium, *Ultrasonics Sonochemistry*, 28:192–198 pp.
- Yang, J., Li, X., Liu C. and Ma, G.**, 2015, Changes of structure and electrical conductivity of multi-walled carbon nanotubes film caused by 3 MeV proton irradiation, *Applied Surface Science*, 325:235–241 pp.

REFERENCES (Continued)

- Yang, J., Sudik, A., Wolverton, C. and Siegel, D.J.**, 2010, High capacity hydrogen storage materials: attributes for automotive applications and techniques for materials discovery, *Chemical Society Reviews*, 39:656–675 pp.
- Yin, H., Meng, X., Su, H., Xu, M. and Ai, S.**, 2012, Electrochemical determination of theophylline in foodstuff, tea and soft drinks based on urchin-like CdSe microparticles modified glassy carbon electrode, *Food Chemistry*, 134:1225–1230 pp.
- Yin, J., Shan, S., Ng, M.S., Yang, L., Mott, D., Fang, W., Kang, N., Luo, J. and Zhong C.J.**, 2013, Catalytic and Electrocatalytic Oxidation of Ethanol over Palladium-Based Nanoalloy Catalysts, *Langmuir*, 29:9249–9258 pp.
- Yuan, L.S., Zheng, Y.X., Jia, M.L., Zhang, S.J., Wang, X.L. and Peng, C.**, 2015, Nanoporous nickel-copper-phosphorus amorphous alloy film for methanol electro-oxidation in alkaline medium, *Electrochimica Acta*, 154:54–62 pp.
- Zach, M.P. and Penne, R.M.**, 2000, Nanocrystalline nickel nanoparticles, *Advanced Materials*, 12:878-883 pp.
- Zahmakiran, M. and Özkar, S.**, 2009, Dimethylammonium Hexanoate Stabilized Rhodium(0) Nanoclusters Identified as True Heterogeneous Catalysts with the Highest Observed Activity in the Dehydrogenation of Dimethylamine–Borane, *Inorganic Chemistry*, 48:8955–8964 pp.
- Zare, H.R. and Nasirizadeh, N.**, 2010, Simultaneous determination of ascorbic acid, adrenaline and uric acid at a hematoxylin multi-wall carbon nanotube modified glassy carbon electrode. *Sensors and Actuators B*, 143:666–672 pp.
- Zen, J.M., Kumar, A.S. and Tsai, D.M.**, 2003, Recent Updates of Chemically Modified Electrodes in Analytical Chemistry, *Electroanalysis*, 15(13):1073-1087 pp.
- Zeng, J.Q., Sun, S.N., Zhong, J.P., Li, X.F., Wang, R.X., Wu, L.N., Wang, L. and Fan, Y.J.**, 2014, Pd nanoparticles supported on copper phthalocyanine functionalized carbon nanotubes for enhanced formic acid electrooxidation, *International Journal of Hydrogen Energy*, 39:15928-15936 pp.

REFERENCES (Continued)

- Zewde, B.W. and Admassie, S.**, 2012, Electrocatalysis of oxygen reduction at poly (4-amino-3-hydroxynaphthalene sulfonic acid) and platinum loaded polymer modified glassy carbon electrodes, *Journal of Power Sources*, 216:502-507 pp.
- Zhang, J.**, 2008, PEM Fuel Cell Electrocatalysts and Catalyst Layers Fundamentals and Applications, Springer, Canada, 1137 pp.
- Zhang, M. Li, Y. Yan, Z. Jing, J. Xie, J. and Chen, M.**, 2015, Improved catalytic activity of cobalt core–platinum shell nanoparticles supported on surface functionalized graphene for methanol electro-oxidation, *Electrochimica Acta*, 158:81–88 pp.
- Zhang, R., Liu, S., Wang, L. and Yang, G.**, 2013, Electroanalysis of ascorbic acid using poly(bromocresol purple) film modified glassy carbon electrode, *Measurement*, 46:1089–1093 pp.
- Zhang, W. and Silva, S.R.P.**, 2011, Application of carbon nanotubes in polymer electrolyte based fuel cells, Application of carbon nanotubes in polymer electrolyte based fuel cells, *Reviews on Advanced Materials Science*, 29:1-14 pp.
- Zhen, X. and Wang, Y.**, 2015, An overview of methanol as an internal combustion engine fuel, *Renewable and Sustainable Energy Reviews*, 52:477–493 pp.
- Zheng, S., Huang, Y., Cai, J., and Guo, Y.**, 2013, Nano-copper-MWCNT-modified glassy carbon electrode for selective detection of dopamine, *International Journal of Electrochemical Science*, 8:12296-12307 pp.
- Zhong, J.P., Fan, Y.J., Wang, H., Wang, R.X., Fan, L.L., Shen, X.C. and Shi, Z.J.**, 2013a, Copper phthalocyanine functionalization of graphene nanosheets as support for platinum nanoparticles and their enhanced performance toward methanol oxidation, *Journal of Power Sources*, 242:208-215 pp.
- Zhong, J.P., Fan, Y.J., Wang, H., Wang, R.X., Fan, L.L., Shen, X.C. and Shi, Z.J.**, 2013b, Highly active Pt nanoparticles on nickel phthalocyanine functionalized graphene nanosheets for methanol electrooxidation, *Electrochimica Acta*, 113:653–660 pp.

REFERENCES (Continued)

- Zhou, Y., Hu, X., Xiao, Y. and Shu, Q.**, 2013, Platinum nanoparticles supported on hollow mesoporous tungsten trioxide microsphere as electrocatalyst for methanol oxidation, *Electrochimica Acta*, 111:588–592 pp.
- Zhu, Y.H., Zhang, Z.L. and Pang, D.W.**, 2005, Electrochemical oxidation of theophylline at multi-wall carbon nanotube modified glassy carbon electrodes, *Journal of Electroanalytical Chemistry*, 581:303–309 pp.
- Zi, L., Li, J., Mao, Y., Yang, R. and Qu, L.**, 2012, High sensitive determination of theophylline based on gold nanoparticles/l-cysteine/Graphene/Nafion modified electrode, *Electrochimica Acta*, 78:434–439 pp.
- Zinin, P.**, Transmission Electron Microscope, <http://www.soest.hawaii.edu/HIGP/Faculty/sksharma/GG711/GG711Lec15TEM.pdf>, [available: 30 August 2015].
- Zuo, X., Zhang, H., Li, N.**, 2012, An electrochemical biosensor for determination of ascorbic acid by Co(II) phthalocyanine–multi-walled carbon nanotubes modified glassy carbon electrode, *Sensors and Actuators B*, 161:1074–1079 pp.

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