

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

**(MSc THESIS)**

**PREPARATION AND CHARACTERIZATION OF**  
**GRAPHENE BASED NANOCOMPOSITE**  
**ELECTRODES AND THEIR ELECTROCHEMICAL**  
**APPLICATIONS**

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**Müge Şatır** tarafından **Yüksek Lisans** tezi olarak sunulan “**Preparation and characterization of graphene based nanocomposite electrodes and their electrochemical applications**” başlıklı bu çalışma E.Ü. Lisansüstü Eğitim ve Öğretim Yönetmeliği ile E.Ü. Fen Bilimleri Enstitüsü Eğitim ve Öğretim Yönergesi’nin ilgili hükümleri uyarınca tarafımızdan değerlendirilerek savunmaya değer bulunmuş ve **14.01.2015** tarihinde yapılan tez savunma sınavında aday oybirliği/oyçokluğu ile başarılı bulunmuştur.

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# EGE ÜNİVERSİTESİ FEN BİLİMLERİ ENSTİTÜSÜ

## ETİK KURALLARA UYGUNLUK BEYANI

E.Ü. Lisansüstü Eğitim ve Öğretim Yönetmeliğinin ilgili hükümleri uyarınca Yüksek Lisans Tezi olarak sunduğum “**Preparation and characterization of graphene based nanocomposite electrodes and their electrochemical applications**” başlıklı bu tezin kendi çalışmam olduğunu, sunduğum tüm sonuç, doküman, bilgi ve belgeleri bizzat ve bu tez çalışması kapsamında elde ettiğimi, bu tez çalışmasıyla elde edilmeyen bütün bilgi ve yorumlara atıf yaptığımı ve bunları kaynaklar listesinde usulüne uygun olarak verdiğimi, tez çalışması ve yazımı sırasında patent ve telif haklarını ihlal edici bir davranışımın olmadığını, bu tezin herhangi bir bölümünü bu üniversite veya diğer bir üniversitede başka bir tez çalışması içinde sunmadığımı, bu tezin planlanmasından yazımına kadar bütün safhalarda bilimsel etik kurallarına uygun olarak davrandığımı ve aksinin ortaya çıkması durumunda her türlü yasal sonucu kabul edeceğimi beyan ederim.

14 / 01 / 2015

Müge ŞATIR



**ÖZET****GRAFEN TEMELLİ NANOKOMPOZİT ELEKTROTLARIN  
HAZIRLANMASI, KARAKTERİZASYONU VE  
ELEKTROKİMYASAL UYGULAMALARI**

ŞATIR, Müge

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Metal nano parçacıkların grafen, karbon nano tüp, iletken polimerler ve bunların karışımlarından oluşan kompozit elektrot yüzeylerinin elektrokimyasal yöntemlerle kontrollü bir şekilde oluşturulması konusunda giderek artan sayıda çalışma yapılmaktadır.

Üç bölümden oluşan bu tez çalışmasının ilk kısmında metal nanoparçacıklar ile modifiye edilmiş grafen oksit (GO) kaplı elektrotlar hazırlanarak metanolün elektrokimyasal davranışı incelenmiştir. GO kaplı elektrot üzerine Au-Pt bimetalik nanoparçacıklar oluşturulmuştur. Pt-Au-GO/GC elektrot ile pik akımlarında artış gözlenmiştir. İkinci kısımda ise metal nanoparçacıklar ile modifiye, poli-anilin (PANI) polimer film elektrotlar hazırlanarak, metanolün elektrokatalitik yükseltgenmesine olan etkileri incelenmiştir. Pt and Cu bimetalik nano parçacık modifiye polimer elektrot ile hem yüksek akım değerinde hem de daha negatif potansiyelde bir yükseltgenme piki elde edilmiştir. Son kısımda ise metal nanoparçacık ile modifiye PANI-MWCNT (çok duvarlı karbon nanotüp) kompozit elektrotlar hazırlanarak, katekolün elektrokimyasal davranışı incelenmiştir. En yüksek katalitik etkinlik, Ni-MWCNT-PANI yüzeyinde birarada olduğu koşullarda saptanmıştır. Tüm polimer, grafen oksit ve çok duvarlı karbon nanotüp ile modifiye edilmiş elektrot yüzeyleri ve onların metal nano parçacık kaplı formları taramalı elektron mikroskopu, enerji dağılımlı X-ışını spektroskopisi, elektrokimyasal impedans spektroskopisi ile karakterize edilmiştir.

**Anahtar sözcükler:** çok duvarlı karbon nanotüp, grafen oksit, katekol, metal nano parçacık, metanol, polimer film elektrotlar, voltammetri.



**ABSTRACT****PREPARATION AND CHARACTERIZATION OF GRAPHENE BASED  
NANOCOMPOSITE ELECTRODES AND THEIR ELECTROCHEMICAL  
APPLICATIONS**

ŞATIR, Müge

MSc in Chemistry Department  
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An effort has been made to control size and morphology of nanoparticles on graphene, carbon nano tube, conducting polymers and their composite based electrode surfaces generating and growing by electrochemical technique.

In the first part of this thesis which consisted of three different sections, metal nano particles modified graphene oxide covered electrodes were prepared and their effect on electrochemical behaviour of methanol. Au-Pt nanoparticles were consisted of the GO/GCE surface. Pt-Au-GO/GCE indicated high catalytic effect for methanol. Second part of this thesis, metal nano particles modified poly-aniline (PANI) electrodes were prepared and their effect on methanol oxidation reaction was investigated. Cu-Pt nano particles modified polymer electrodes was obtained both higher the peak current and the negative oxidation potential for methanol. Finally poly (aniline)-MWCNT-MNP film modified electrodes were used for electrochemical reaction of catechol. The best catalytic activity towards electrochemical reaction of catechol was obtained with Ni-MWCNT-PANI/GCE. All polymer, graphene oxide and multi-walled carbon nanotube modified electrode surfaces were characterized by scanning electron microscopy, energy disperse x-ray spectroscopy and electrochemical impedance spectroscopy.

**Keywords:** catethol, graphene oxide, methanol, metal nano particles, multi-walled carbon nanotube, polymer film electrode, voltammetry.



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## ABBREVIATIONS

| <u>Symbol</u>    | <u>Explanation</u>                     |
|------------------|----------------------------------------|
| A                | Electrode area                         |
| C                | Analyte concentration                  |
| CE               | Capillary Electrophoresis              |
| CFC              | Carbon reinforced material             |
| CFME             | Carbon fibre micro electrophoresis     |
| CL               | Chemiluminescence                      |
| CNT              | Carbon Nanotubes                       |
| C <sub>ox</sub>  | Concentration of oxidized form         |
| C <sub>red</sub> | Concentration of reduced form          |
| CV               | Cyclic Voltammetry                     |
| D                | Diffusion coefficient                  |
| DPV              | Differential Pulse Voltammetry         |
| E <sup>0</sup>   | The standart potential                 |
| E <sub>p</sub>   | Peak potential                         |
| E <sub>pa</sub>  | Anodic peak potential                  |
| E <sub>pc</sub>  | Cathodic peak potential                |
| E <sub>q</sub>   | Equation                               |
| EIS              | Electrochemical impedance spectroscopy |
| GCE              | Glassy carbon electrode                |
| GO               | Graphene oxide                         |
| i <sub>l</sub>   | Limiting current                       |
| i <sub>pa</sub>  | Anodic peak current                    |
| i <sub>pc</sub>  | Cathodic peak current                  |
| LOD              | Limit of Detection                     |
| LR               | Lineer range                           |
| MNP              | Metal nano particle                    |
| MWCNT            | Multiwalled Carbon Nanotubes           |
| Ox               | Oxidized form                          |
| Red              | Reduced form                           |
| SAM              | Self-assembled monolayer               |
| SEM              | Scanning Electron Microscopy           |
| SPE              | screen printed electrode               |
| SWCNT            | Single Walled Carbon Nanotubes         |
| V                | Scan rate                              |



## 1. INTRODUCTION

The application of nano-materials in various fields of science and technology has been widely studied due to their unique optical, electrical and magnetic properties of these materials. These types of materials, possesses some interesting properties such as high specific area, subtle electronic characteristics, strong adsorptive ability and promote the electron-transfer reactions of electroactive molecules. The property of these materials is usually different from that of their bulk counterparts due to their extremely small size, special structure and large surface-to-bulk ratio. The increasing surface area to volume ratio provides to an increase in the dominance of the surface atoms of the nanoparticle over those in its inside structure (Abid et al., 2013).

In recent years, metal/metal oxide nanoparticles, carbon based nanomaterials, nano composites and hybride structures have been used for preparation of novel electrode materials. In the beginning of nano systems, generally one compound based nano particles have been studied because such particles have several better properties than the bulk materials. Later, the studies showed that heterogeneous, composite or hybride nano material particles have better efficiency than their corresponding single particles. Thus, nanomaterials have potential applications in field of electronics and photonics, catalysis, information storage, chemical sensing and imaging, environmental remediation, drug delivery and biological labelling (Guo et al., 2005).

Composite material can be describes as a combination of two or more materials which has better properties than their individual forms used alone. In composite materials, each material retains its separate chemical, physical, and mechanical properties on contrary to metallic alloys. In technical terms, it can define a composite as a multiphase material from a combination of materials (Campbell, 2010). The most of composite nanomaterials are based on the use of carbon materials. Among these nanoparticles graphene is, basically, a single atomic layer of graphite; an abundant mineral which is an allotrope of carbon that is made up of very tightly bonded carbon atoms organised into a hexagonal lattice. The other nanoparticles type used in nanoscience and nanotechnology is metal

nanoparticles. Metal nanoparticles among the nanomaterials have played an important role in applications such as optics, electronics, magnetism, catalysis and biology because of various unusual chemical and physical properties compared with those of metal atoms or bulk metal. It is well known that the optical, electronic and catalytic properties of metal nanoparticles are mostly affected from their size, shape, composition and crystal structure (Ghosh and Pal, 2007). Metal nanoparticles generally exhibit small sizes in a narrow size distribution, and well defined, regular shapes. Thus, metal nanoparticles of different forms may catalyze the reactions with different efficiencies due to nanocrystals of different shape and sizes. Furthermore, the nanoparticles provide very fast kinetics and enhanced sorption capacity due to their high surface to volume ratio (Sarkar et al., 2012). On the other hand, both metal and metal oxide nanoparticles such as silver, gold, copper, palladium and platinum, iron and its oxides have found applications in catalytic reactions (Nair et al., 2007).

Nanoparticles can be classified as single or multiple materials into simple and composite or hybrid nanoparticles, respectively. In general, simple nanoparticles are made of a single material, whereas, composite and hybrid nanoparticles are composed of two or more materials. These mixture nanoparticles can consist of a wide range of different combinations in close interaction, including inorganic/inorganic, inorganic/organic, organic/inorganic and organic/organic materials. In electrochemical studies, the typical composite and hybrid nanoparticles are based on mixture of carbon and metal nanoparticles. Polymer films can be formed on an electrode surface via dip coating, spin coating, electrodeposition, and covalent attachment. From these methods, the electrochemically modified polymer film electrodes have received extensive interest in the detection of analytes because the electrochemical deposition offers a thin and uniform structure, homogeneity and strong adherence. Conducting polymers also offer a chemically stable film to electrode surface which offer a selective and sensitive opportunity for the analyte to determine many biologically and pharmaceutically important molecules. Polymer film surface was also used as host material for the preparation of homogeneously distributed metal nanoparticles for electrocatalytic electrode reactions (Biallozor and Kupniewska, 2005).

Conducting Polymers (CPs) have received much attention due to their high surface area, high stability and low resistance. Porous structure improve their use as supporting material for the development of new catalytic and electrocatalytic materials. Because of the high electric conductivity of some polymers, it is possible to shuttle the electrons through polymer chains between the electrode and dispersed metal particles, where the electrocatalytic reaction forms. For this reason, these composite materials can achieve an efficient electrocatalysis and offer the use of conducting polymers as supporting matrices for the immobilization of catalytically active noble metal particles. The most common CPs used as supporting materials are conjugated polymers with heteroatoms in main chain as polyaniline (PANI), polythiophene (PTh) and their derivatives (Antolini, et al.,2009).

### **1.1 The Aim of The Thesis**

This thesis mainly comprises in three parts. The first part include that the preparation of graphene oxide and modified with Au-Pt metal nano particles for the electrocatalytic oxidation of methanol in alkaline solution. To increase the catalytic activity of the bimetallic Au-Pt on methanol, different concentration and ratio of metal deposition on graphene oxide procedure was optimized by following the oxidation of methanol in alkaline solution.

The second part include that the poly-aniline (PANI) film was prepared on GCE and then modified with different metal nano particles (Cu and Pt bimetallic forms) by electrochemical deposition. The modified electrode surfaces were characterized with cyclic voltammetry, scanning electron microscopy and EDX detector. Eventually, the metal nano particles modified electrodes were utilized as the catalytic surface for electrocatalytic oxidation of methanol in alkaline media and to compare the electrocatalytic activity of each MNP modified PANI/GCE with PANI/GCE and bare electrodes from their corresponding voltammetric curves.

In third part, multiwall carbon nanotube was purified and functionalized using pretreated procedure with concentrated  $\text{HNO}_3$  and then poly-aniline

(PANI)-MWCNT composite electrode was prepared and finally the MWCNT-PANI composite electrode was modified with Ni metal nano particles by electrochemical deposition. The metal nano particles modified electrode was used for investigation of electrochemical behaviour and determination of catechol in phosphate buffer solution. The surface morphologies and chemistry of all electrodes were characterized by cyclic voltammetry (CV), Scanning Electron Microscopy (SEM), Energy Disperse X-ray Spectroscopy (EDX) and Electrochemical Impedance Spectroscopy (EIS).

## 1.2 Graphene Oxide

Elemental carbon in its chemical allotropes of graphite and diamond occurs in a great variety of species and has been developed to a large number of highly specialised applications as structural and functional materials. The underlying reason for this unique manifold of species is two fold: The coordination chemistry of carbon is flexible in allowing continuous mixtures of C=C and C-C bonding in one structure. This leads to an infinite possibility of 3-dimensional structures and to continuous tunability of electronic properties from wide-gap semiconductor (diamond) to metallic (graphite). Carbon based materials plays a major role in nano-sciences. Fullerenes, nanotubes, carbon onions are typical representatives of nano-structured carbons to which all the above mentioned variables also apply in addition to the small scale of each object.

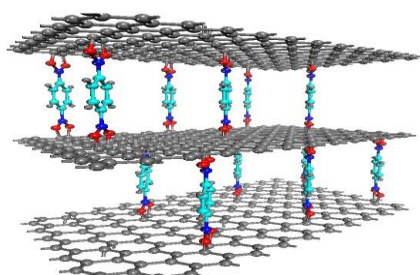


**Figure 1.1** Images of graphene oxide.

Graphene is the latest sensation with unusual properties, such as half-integer quantum hall effect and ballistic electron transport (Rao, 2009). Graphene, as defined, is a 2D crystal of  $sp^2$ -hybridized carbon atoms arranged in six-membered rings. The discovery of graphene was first achieved in 2004, and rapidly earned Geim and Novoselov the 2010 Nobel Prize in Physics. It is the thinnest known and the strongest ever measured material in the universe.

The long-range 2D  $\pi$ -conjugation in graphene yields extraordinary physical properties including large theoretical specific area ( $2630 \text{ m}^2 \text{ g}^{-1}$ ), high Young's modulus and elasticity, unparalleled thermal and electricity conductivity, plus fascinating electronic properties such as ambipolar electric field effect along with ballistic conduction of charge carriers, which have become an exciting area for both theoretical and experimental studies in recent years (Wei and Qu, 2012).

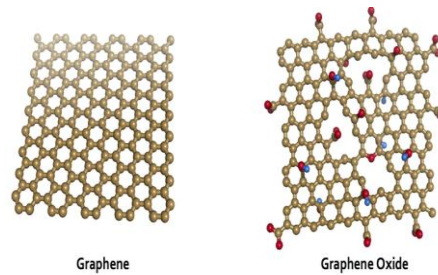


**Figure 1.2** A graphene and graphene oxide structures

The first physical properties of graphene to be studied were its unprecedentedly electronic properties, which have thus been the focus of the majority of research to date. The electronic properties in graphene are really due to delocalized  $\pi$  bonds above and below the basal plane, which arise from the  $sp^2$  hybridization responsible for graphene's layered structure.

### 1.3 Types of GO And Their Synthesis

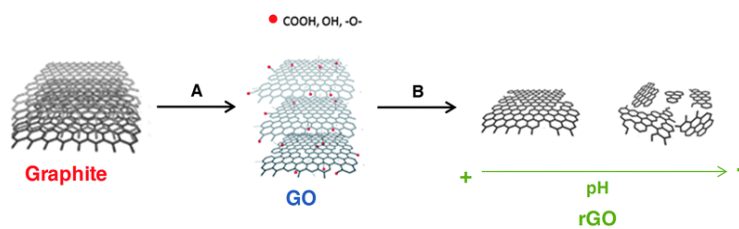


**Figure 1.3** The schematic representation of the processes occurring during the experiment.

Graphite oxide sheets, now called graphene oxide (GO), can be made from chemical exfoliation of graphite by reactions that have been known for more than 150 years with the first instance carried out by B.C. Brodie in 1859.

The synthesis of graphene can be broadly categorized into bottom-up methods (chemical vapor deposition and epitaxial growth on SiC) and top-down methods (mechanical exfoliation and chemical exfoliation).

### **Chemical vapor deposition (CVD)**

Graphene sheets can also be prepared on transition metal substrates such as Ni, Pd, Ru, Ir or Cu. The carbon solubility in the metal and the cooling rate strongly affect the final thicknesses of the graphene films. In the beginning, Ni was generally used as a metal catalyst to grow graphene, but multi layers were dominant because of carbon segregation on the Ni surface owing to its high carbon solubility. At moderate cooling rates, C atoms segregate and form a graphene film, whereas C atoms also segregate out of Ni at higher rates but form a weakly crystalline, less defective graphitic structure. In contrast to Ni substrates, copper has the lowest affinity to carbon among the transition metals and has very low carbon solubility compared with Ni. As copper has minimal reciprocal repulsions due to the fully filled 3D-electron shell, it shows very low reactivity toward carbon, which results in good graphitic carbon formation.

### **Mechanical exfoliation**

The ‘Scotch tape’ method has limitations in terms of scale-up, but it is used to create the best graphene samples for various fundamental studies. Recently, direct milling of graphite has been reported to fabricate graphene in cost effective ways. W. Zhao et al. have demonstrated a feasible way to produce graphene from graphite flakes using wet ball milling exfoliation. Using shear-force-dominated grinding, single-layer and few-layer graphene sheets were readily prepared and homogeneously and stably suspended in a solvent medium such as ethanol, formamide, acetone, tetrahydrofuran, tetramethylurea, N, N-dimethylformamide (DMF), or N-methylpyrrolidone (NMP) with a concentration up to  $0.08 \text{ mg ml}^{-1}$  and a yield greater than 32.0 wt%. Due to the weak van der Waals forces between graphite layers, the graphene sheets in graphite can be easily exfoliated by the application of simple mechanical shear forces, creating isolated graphene sheets in the solvent media.

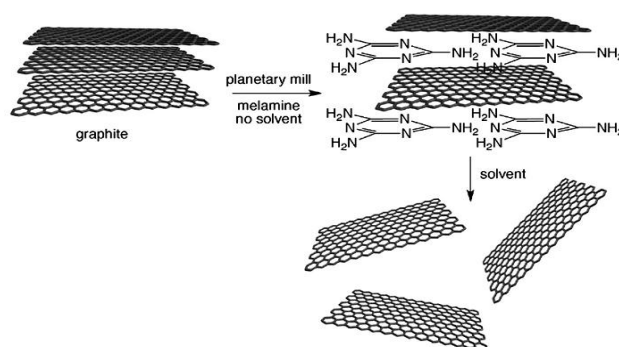


**Figure 1.4** Synthesis of graphene oxide by mechanical exfoliation method.

### Chemical exfoliation

In 2003, R. Kaner et al. reported the synthesis of ‘expanded’ graphite by intercalation of graphite using a stage-1 potassium intercalation compound ( $KC_8$ ) with various solvents, followed by thermal expansion. Recently, S. Jeon et al. reported high quality, exfoliated monolayer graphene sheets using stable alkali metal salt intercalation compounds as shown at Fig.1.5. This approach is fully commercializable and is regarded as suitable to obtain graphene sheets with fewer defects. However, it also requires further development as only submicron size graphene can currently be obtained. Another approach uses graphite oxide (GO) as a precursor for graphene synthesis. GO can be produced by the oxidative treatment of graphite using the methods developed by either Brodie, Hummers or Staudenmeier.

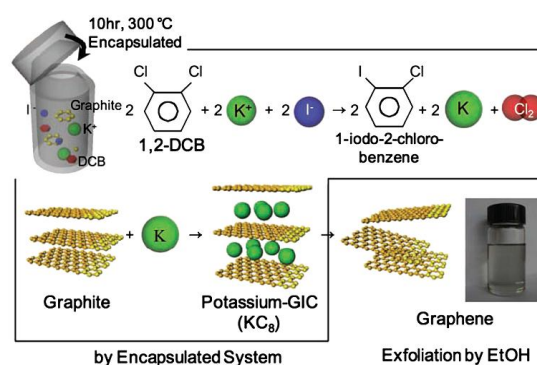


**Figure 1.5** Synthesis of graphene oxide by chemical exfoliation method.

## **Epitaxial growth**

High quality graphene can be obtained by the thermal desorption of Si on the Si-terminated (0001) face of single-crystal 6H-SiC wafers. Graphene sheets were formed when the H<sub>2</sub>-etched surface of 6H-SiC was heated to 1250–1450 °C for 1–20 min. The number of layers depends on the decomposition temperature, but generally 2–3 layers of graphene were dominant, and monolayer graphene was rarely observed. Moreover, because the size of the graphene sheet is controlled by the SiC wafer size, it is very difficult to obtain large area graphene films by this approach. Recently, K. Emtsev et al. showed much larger domain sizes of monolayer graphene film than previously attainable by using ex situ graphitization of Si-terminated SiC (0001) in an argon atmosphere of about 1 bar. Electronic mobilities were measured as high as 2000 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> at T = 27 K.

### **1.4 Carbon Nanotubes**

Elemental carbon in its chemical allotropes of graphite and diamond occurs in a great variety of species and has been developed to a large number of highly specialised applications as structural and functional materials. The underlying reason for this unique manifold of species is twofold: The co-ordination chemistry of carbon is flexible in allowing continuous mixtures of C=C and C-C bonding in one structure. This leads to an infinite possibility of 3-dimensional structures and to continuous tunability of electronic properties from wide-gap semiconductor (diamond) to metallic (graphite). Carbon based materials play a major role in nano-sciences. Fullerenes, nanotubes, carbon onions are typical representatives of nano-structured carbons to which all the above mentioned variables also apply in addition to the small scale of each object.

The new carbon materials of fullerenes, are closed cage carbon molecules with three-coordinate carbon atoms tiling the spherical or nearly-spherical surfaces, the best known example is C<sub>60</sub>, with a truncated icosahedral structure formed by twelve pentagonal rings and twenty hexagonal rings.

Examples of larger molecular weight fullerenes are C<sub>70</sub>, C<sub>76</sub>, C<sub>78</sub>, C<sub>80</sub> and higher mass fullerenes, which possess different geometric structure e.g. C<sub>70</sub> has a rugby ball-shaped symmetry (Dresselhaus, et al.,1996).

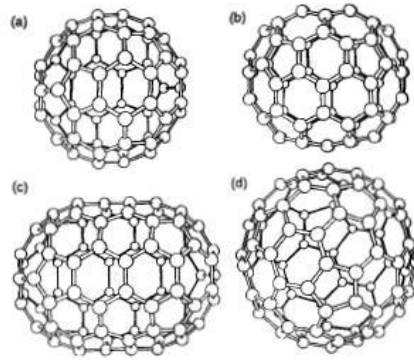


**Figure 1.6** Structure and geometry of different fullerene molecules. (a) The icosahedral C<sub>60</sub> molecule, (b) C<sub>70</sub> molecule, (c) a C<sub>80</sub> molecule as an extended rugby ball-shaped molecule, (d) C<sub>80</sub> molecule as in icosahedran.

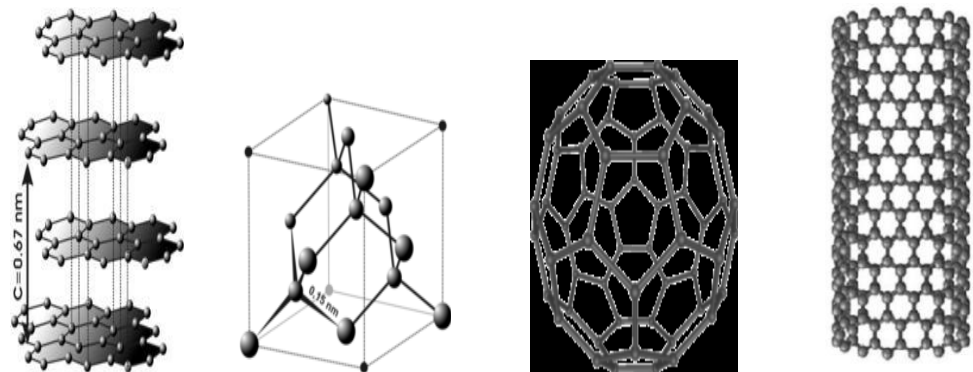


**Figure 1.7** Different allotropes of the carbon element; grafite, diamond, fullerene and carbon nanotube, respectively.

Carbon nanotubes were discovered by Iijima in 1991, observed that nanotubules of graphite were deposited on the negative electrode during the direct current arcing of graphite for the preparation of fullerenes.

Although carbon nanotube streuctures were characterized with transmission electrone microscopy (TEM) in 1991 by Ijima, the first report on the carbon based material called later CNTs came from Radushkevich and Lukyauovich in 1952.

CNTs are one dimensional well-ordered, hollow graphitic nanostructure made of  $sp^2$ -hybridized carbon atoms. These long hollow cylindrical carbon molecules have revealed being remarkable nanostructures for several aspects from they discovered. Carbon nanotubes are composed of carbon, and they can be easily produced by several techniques. A carbon nanotube can bend easily but still is very robust. These nanotubes are concentric graphitic cylinders closed at either end due to the presence of five-membered rings (Ijima, 2002).

SWCNTs were discovered by Ijima and Ichihashi in 1993 and most of these nanostructures have a diameter close to 1 nm, with a tube length that may be many thousands of times larger and up to orders of centimeters (Zhu, 2002). The electrical conductivity of SWCNTs depends on their chirality and diameter while for MWCNTs such dependence is not observed. SWCNTs possess a cylindrical nanostructure. The carbon atoms are arranged in a single sheet called a grapheme layer in a hexagonal repeating pattern (Figure 1.8). The sheet is rolled into a seamless, tube hence the name SWCNT. Therefore, SWCNT are considered as molecular wire with every carbon atom on the surface.

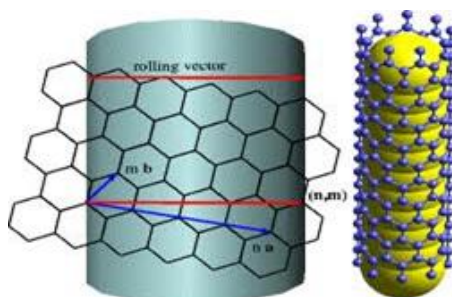


**Figure 1.8** A single walled carbon nanotube structure.

A grapheme sheet can be rolled more than one way, producing different types of CNTs and the three main types are armchair, zig-zag and chiral (Figure 1.9).

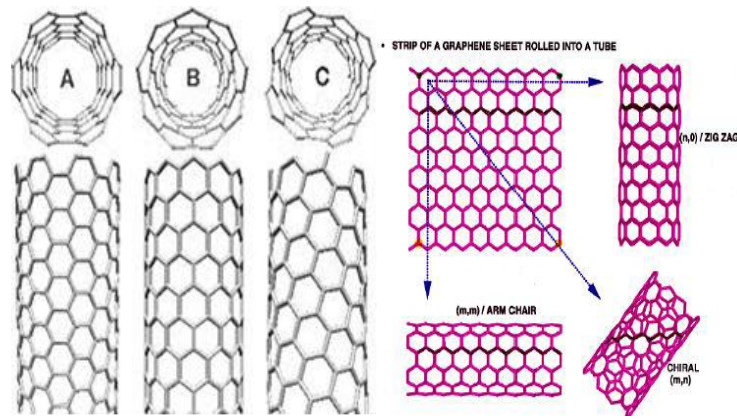


**Figure 1.9** Three basic geometric structure of carbon nanotubes (a) armchair, (b) zig-zag, (c) chiral.

### 1.5 Types of CNTs And Their Synthesis

Carbon nanotubes were immediately studied by different group of researchers because of their relative simplicity, their unique properties, and their promise for practical applications.

In 1993, single-walled carbon nanotubes (SWNTs), new type of carbon nanotube in nanotube family, were reported by again Iijima. The report of this new type of carbon fiber triggered intense research focused on harnessing the unique properties of these nanostructures. This form was the pioneered fort he discovery of other special forms of carbon nanotubes. There are many kinds of carbon nanotubes, including single wall carbon nanotubes, double wall carbon nanotubes, multi-wall carbon nanotubes, intercalated nanotubes, and nanotubes filled with various species constituting internal nanowires including fullerenes and even fullerenes filled with metal species (endohedral fullerenes) (see Figure 1.6) (Dresselhaus, et al., 2003).

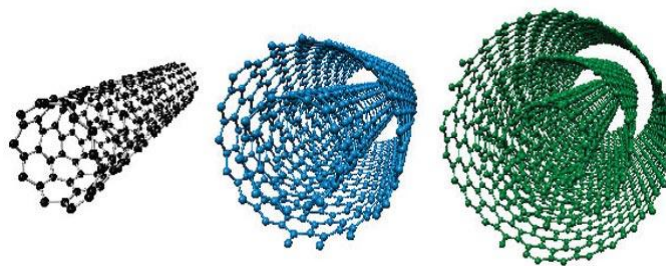


**Figure 1.10** Schematic diagram of a single wall carbon nanotube (SWCNT), a multi-wall carbon nanotube (MWCNT) and doublewalled carbon nanotube.

CNTs have two different structure as multi-walled carbon nanotubes (MWCNTs) and single-walled carbon nanotubes (SWCNTs). MWCNT is composed of several concentric tubes of graphite sharing a common longitudinal axis whereas SWCNTs are composed of a single layer of graphene rolled into a tube.

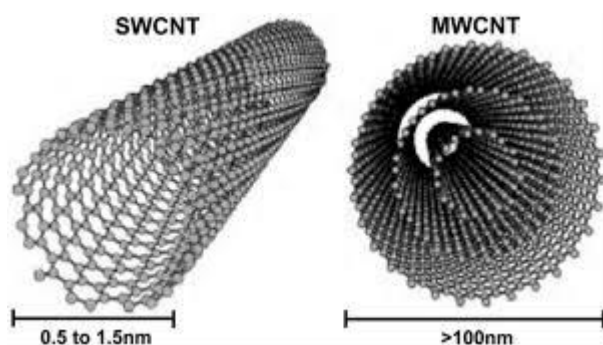


**Figure 1.11** Structures of a) Single-walled carbon nanotube b) Multi-walled carbon nanotube.

Because of its structure, SWCNTs display excellent chemical stability, good mechanical strength and a range of electrical conductivity. They are at least ten times stronger than steel, around six times lighter and, depending on their chirality and diameter, can behave as metals, semiconductors or insulators. In a typical sample, around one third can be thought as metallic. Due to their high surface energies, SWCNTs are usually found in bundles composed of tens to hundreds of tubes in parallel and in contact with each other. Thus, SWCNTs exhibit important electric properties that are not shown by MWCNTs. The most basic building block of these systems is the electric wire and these are excellent conductors. MWCNTs consist of multiple layers of graphene rolled on themselves to form a tube shape with an interlayer spacing of  $3.4 \text{ \AA}$ . The outer diameter of MWCNTs may range from 1 to 50 nm while the inner diameter is usually of several nanometers.

CNTs are regarded entirely as metallic conductors, which in some respects makes them more suitable for electrochemical applications. However, SWCNTs are more well-defined systems, making their electrochemical properties easier to understand. Because of their electrical properties, the electrochemical properties of both multi-walled (MWCNT) and single-walled (SWCNT) carbon nanotubes

have been examined and still gone on to be examine. These materials should serve as excellent candidates for nanoelectrodes and platforms for nanoelectrochemical cells and amperometric biosensor devices (Lyons and Keeley, 2008).

There are several ways or methods on preparing them have been developed. Carbon nanotubes are readily prepared in that;

- i. by using plasma arc-jets and in large quantities, optimizing the quenching process in an arc between a graphite anode and a cooled copper electrode,
- ii. by carrying out electrolysis in molten halide salts with carbon electrodes in an argon atmosphere,
- iii. by striking an arc between graphite electrodes in 2/3 atm (~500 torr) of helium, considerably higher than the pressure of helium used in the production of fullerene soot. The arcing process can be optimized such that the major portion of the carbon anode is deposited on the cathode in the form of carbon nanotubes and graphitic nanoparticles,
- iv. MWNTs with well-ordered graphitic structures have been synthesized under hydrothermal conditions using a polyethylene and water mixture in the presence of nickel catalyst at around 800 °C under 60–100 MPa pressure,
- v. Besides the conventional arc-evaporation technique, carbon nanotubes are produced by the decomposition of hydrocarbons such as C<sub>2</sub>H<sub>2</sub> under inert conditions at around 700 °C, over Fe/ graphite, Co/graphite or Fe/silica catalysts.

Recently, the number of literatures shows the use of carbon nanotubes as sensitive electrodes for small molecules such as hydrogen peroxide, glucose, methanol, neurotransmitters, nucleic acids and also oxygen reduction reaction.

For instance, Dursun et.al., studied multiwalled carbon nanotubes (MWCNTs) functionalized with acid treatment and gold–copper nanoparticles were electrodeposited on the MWCNTs by applying several repetitive scans, thus forming a Cu–Au–MWCNT/GCE. The electrochemical reduction of oxygen was studied on this modified electrode in 0.1 M NaOH solution. The electrocatalytic

activity on the Cu–Au–MWCNT/GCE showed a tendency towards the O<sub>2</sub> reduction. The peak potential of O<sub>2</sub> reduction on the Cu–Au–MWCNT/GCE shifted ca. 70 mV higher positive potentials as compared to that of a polished glassy carbon electrode. A significant current enhancement was obtained on the Cu–Au–MWCNT/GCE compared to that of bare GCE, MWCNT/GCE, Cu–MWCNT/GCE and Au–MWCNT/GCE (Dursun, et al., 2011).

Recent experiments have shown that carbon nanotube surfaces provide enhanced electron transfer rates when used as electrodes in electrochemical reactions. The role of MWCNT in the electrocatalysis of oxygen reduction has been demonstrated, and charge transfer on CNTs is seen to occur faster compared to graphite (Qu et al., 2004).

In other study, the reduced graphene oxide and multiwall carbon nanotubes (RGO–MWNTs) hybrid materials provide a strategy for detecting environmental contaminations. Due to the excellent catalytic activity, enhanced electrical conductivity and high surface area of the RGO–MWNTs, the simultaneous measurement of hydroquinone (HQ), catechol (CC), p-cresol (PC) and nitrite (NO<sub>2</sub><sup>–</sup>) with four well-separate peaks was achieved at the RGO–MWNTs modified electrode. The fabricated sensor was applied for the simultaneous determination of HQ, CC, PC and NO<sub>2</sub><sup>–</sup> in the river water sample (Hu et al., 2012).

## 1.6 Conductive Electroactive Polymers

Metal nanoparticle can be unstable, fragile and losing their special shape and properties in the absence of any special porous surface containing material. The stabilization of metal nanoparticle is required for a number of reasons: 1) to prevent the uncontrollable growth of particles, 2) to prevent particle aggregation; 3) to control the particles growth rate; 4) to control particle size, and finally 5) to allow particle solubility in various solvents.

The stabilizing agent can be either some ligands, capping agents and passivating agents or surfactants, carbon nanotubes, graphene and conducting

polymers. Among these materials, conducting polymers as the support for catalytic active metal particles provide good electron and ion conductivity and in some cases also good proton conductivity (Muraviev, 2005). Moreover, the porous structure of conducting polymer allows dispersing the metal nano particles into the polymer matrix and generates additional electrocatalytic sites. However conducting electroactive polymers were discovered in the mid-1970s, their impact was recognized in 2000 by the awarding of the Nobel Prize for Chemistry to the three discoverers of conducting polymers: Alan MacDiarmid, Alan Heeger and Hideki Shirakawa. CEPs provide a wide searching area for many researchers. The industrial development of conducting polymer products and has provided the fundamental understanding of the chemistry, physics and material science of these materials (Wallace et al., 2009).

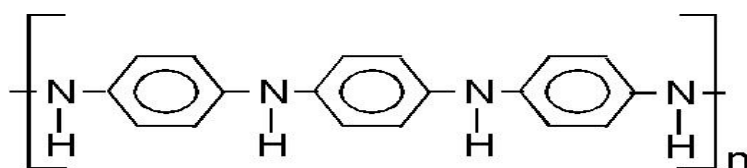
Conducting polymers can be classified in two which are electron-conducting polymers and proton-conducting polymers. Much of current understanding of conjugated polymers is based on the two-band model, such as that appropriate for the  $\pi$ -electronic structure of polyacetylene. Studies on the two-band model system have led to a rather detailed understanding of the electronic structure, including the effects of  $\pi$ -band alteration and electron-electron interactions on the photophysics (Inzelt, 2008).

Conducting polymers are obtained by chemical oxidation and electrochemical polymerization, it is also possible to produce the anion salts of the highly conjugated polymers using electrochemical reduction or chemical reduction with reagents such as sodium naphthalide. An oxidized conducting polymer has electrons removed from the backbone, resulting in a cationic radical. On the other hand, a reduced conducting polymer has electrons added to the backbone, resulting in an anionic radical. However, this reduced conducting polymer is much less stable than the cation counterpart. In general, there are two synthetic methods of conducting polymers: chemical polymerization and electrochemical polymerization (Jang, 2006). CPs can be synthesized either chemically or electrochemically, with each having advantages and disadvantages as summarized in Table 1.

**Table 1.** Comparison of chemical and electrochemical CP polymerization.

| Polymerization approach        | Advantages                                                                                                                          | Disadvantages                                                                                         |
|--------------------------------|-------------------------------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------------|
| Chemical polymerization        | Larger-scale production possible<br>Post-covalent modification of bulk CP possible<br>More options to modify CP backbone covalently | Can not make thin films<br>Synthesis more complicated                                                 |
| Electrochemical polymerization | Thin film synthesis possible<br>Ease of synthesis<br>Entrapment of molecules in CP doping issimultaneous                            | Difficult to remove film from electrode surface<br>Post-covalent modification of bulk CP is difficult |

Among all conductive polymers poly aminophenol, polythiophene, polypyrrole and polyaniline has an attractive place. Aminophenols are interesting members of the class of substituted anilines which gave a surface film of interesting electrochemical and electrochromic properties when their's electropolymerized in acidic solution. As in the many organic molecules, the electropolymerization reaction of PAP is initiated by oxidizing the respective monomer to a radical cation (Wallace, et al., 2009).

**Figure 1.12** Structure of p-aniline.

### 1.6.1 Applications of CEPs

Conducting polymers are important material for technology because of their wide range application in sensors, actuators, batteries, solar cells molecular electronic devices, energy storage/conversion and modified electrodes. They have been studied increasigly after 1980 and Figure 1.9 shows the main areas of interest for papers published on CEPs that listed below. A further breakdown of

the areas of application of CEPs are greatly used in this fields such as; batteries, sensors, membrans, and polymer light-emitting diodes (PLEDs). There has been a distinct move in recent years toward biological/biomedical applications of CEPs (Gerard, et al., 2002).

- a) Polymer Photovoltaics
- b) Display Technologies
- c) Electrochromics
- d) Electromechanical Actuators
- e) Seperation Technologies
- f) Corrosion Protecion
- g) Chemical Sensors
- h) Biomedical Applications
- i) Communication and Characterization Tools
- j) Electrochemical Methods

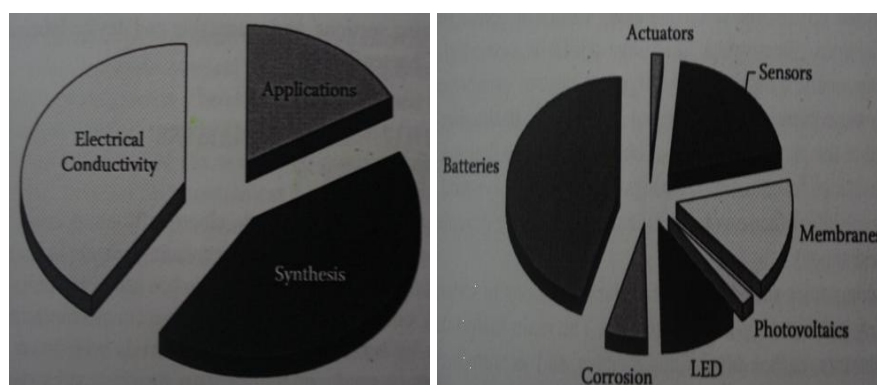


**Figure 1.13** Scientific papers published on conducting polymers (1990-2000) categorized into various topics.

### 1.6.2 Studies at polymer modified electrodes

Polymer films obtained by different methods such as vapor deposition, dip coating, and spin-coating that all of them required toxic solvents and special equipments. Besides these methods electrochemical techniques are simple methods that provide a uniform, strongly adherent conducting polymer films with better conducting properties at the electrode surfaces without any expensive equipments (MacDiarmid, 1997).

A polyaniline (PANI) network structure was fabricated on a poly(o-aminophenol) (POAP) modified glassy carbon electrode (GCE) by using a three-step electrochemical deposition procedure, and applied to the electrocatalytic oxidation of ascorbic acid (AA) and uric acid (UA). Scanning electron microscopy (SEM), electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV) have been studied to investigate the PANI network structure on a POAP modified GCE (PANI-OAP/GCE), which reveal the formation of a 3-dimensional (3D) non-periodic PAN network with good electrical contact and the maintenance of the electro-activity of PAN in neutral and in alkaline media. Due to its different catalytic effect towards the electro-oxidation of AA and UA, the PAN-OAP/GCE could resolve the overlapped voltammetric response of AA and UA into two sharp and well-defined voltammetric peaks with both CV and differential pulse voltammetry (DPV), which could be applied for the selective and simultaneous determination of AA and UA in their binary mixture. Besides good stability and reproducibility, the PAN-OAP/GCE also exhibited good sensitivity and selectivity (Zhang, et al., 2012). Li-Ping, L. et al., 2010, was studied the determination of L-cysteine at electrochemically polymerized poly(o-aminophenol) (POAP) film. Then modified electrode was decorated with platinum again by electrochemical method. The resultant nano-Pt/POAP/GCE was showed excellent electrochemical response to L-cysteine at low oxidative potential in BR buffer solution (pH=3.0), with good stability and sensitivity. The detection limit ( $0.08\ \mu\text{M}$ , S/N=3) and wide linear range ( $0.4\ \mu\text{M}$ – $6.3\ \text{mM}$ ) (Liu, et al., 2010).

## 1. 7 Metal Nano Particles

Nanometer-sized metal particles or metal nano particles (MNP) are objects of great interest in modern chemical research due to their unique electrical, magnetic, optical and other properties, which are distinct from both those of the bulk metal and those of isolated atoms and molecules. They improve the catalytic activity of the surfaces where they attached (Haudy, et al., 2006).

However metal nanoparticles play a significant role in many applications such as sensors, catalysts, field-emitters, they can be so fragile and unstable that if their surfaces touch, they will fuse together, losing their special shape and properties. The stabilization of MNP is required to prevent the uncontrollable growth of particles, but also to prevent particle aggregation, to control the particles growth rate, to control particle size, and finally to allow particle solubility in various solvents (Muraviev, 2005).

Metal particles can be divided into three following groups:

- 1) Nanometric or ultradispersed: from 1 to 30–50nm;
- 2) Submicrometric or highly dispersed: from 30–50 to 100-500nm, and
- 3) Micrometric: from 100–500 to 1000 nm (Muraviev, 2005).

Metal nano particles can be synthesized with different techniques. Such as synthesis of semiconductor nanoparticles in solutions of the corresponding salts by controlled addition of anions (cations) or by hydrolysis another one is preparation of nanoparticles as a result of phase transformations, third one is the synthesis of nanoparticles in aerosol and finally by electrochemical methods.

In above methods, the electrochemically synthesis of metal nanoparticles is one of the most reliable uniformly dispersed nano particle preparation technique on the stabilized conducting material covered electrode surface. The advantage of electrodeposition method offer low cost, taken short time, a high purity of the particles, more easily control the nano particules dimensions, lower particle size distribution compare to chemical and physical methods. In addition to other advantages of the electrodeposition method includes the ability to uniformly coat non-planar substrates, to plate over wide areas, and to deposit a nanocomposite to an overall thickness much larger than can be generally achieved with vacuum deposition methods (Heflin, et al., 2004).

Metal nano particles modified electrodes have been used in modern chemical research due to their unique electrical, magnetic, optical and other properties to improve catalytic activity and the analytical sensitivity and selectivity.

The electrochemical detection of ammonia in drinking water was carried out on MWCNT-copper nanoparticle composite paste electrodes. The optimized electrodes showed significantly better performance than simple CNT or Cu paste electrodes, in terms of linear range of concentrations (3-100  $\mu\text{M}$ ), lower detection limit (3.47  $\mu\text{M}$ ), higher sensitivity. The sensors were applied to the determination of ammonia in real samples of tap water (Valentini, et al., 2007).

Recently, many researches in the areas of catalysis had focused on the evaluation and preparation of metal nanoparticles as nanostructured materials on glassy carbon and CNTs modified glassy carbon for the catalytic electrooxidation of methanol. The metallic nanoparticles (MNPs) modified electrodes like MNP modified MWCNT/GCE and bare electrodes have been used as the catalytic surface for electrocatalytic reduction of oxygen in alkaline media (Bakır, 2010).

## **1. 8 Methanol**

### **1.8.1 Chemical properties of methanol and importance of fuel cell and medical applications**

The investigation of methanol electrochemical behaviour in presence of new catalyst system is important to obtain high efficiency in fuel cell. Among the fuel used in fuel cells, alcohols have an important place. Because, it is liquids to easy storage and their mass energy density is rather high, almost close to that of gasoline (Vigier et al., 2006). Methanol is mostly used as a fuel. In the case of methanol, the methanol is converted to carbon dioxide and hydrogen at the anode. Then, the hydrogen ions act with oxygen to form the water. Each fuel has particular advantages and disadvantages (Wongyao et al., 2011). Methanol is more efficiently oxidized than other alcohols. The disadvantage of methanol as a fuel is methanol crossover through Nafion<sup>TM</sup> membrane to the oxygen electrode, and anode poisoning by strongly adsorbed intermediates (mainly CO). The fuel

cell efficiency is decreased by the methanol crossover. Moreover, methanol is relatively toxic for human beings, and especially for optical nerve, easily volatile and inflammable.

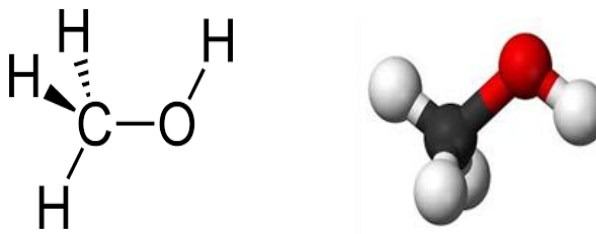
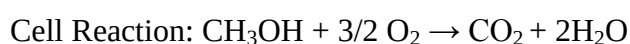
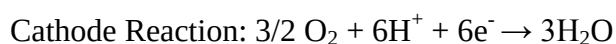
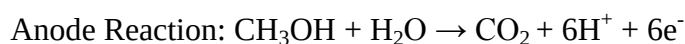


**Figure 1.14** Structure of methanol.

The methanol as fuel was oxidized on the anode in the anodic compartment of direct methanol fuel cell (DMFC). At the anode, alcohol molecules combine with water to give up electrons, forming hydrogen ions. In the case of methanol, the methanol is converted to carbon dioxide and hydrogen at the anode. The hydrogen ions then go on to react with oxygen. These reactions for methanol at the electrodes are shown as follows:



The catalyst is not required for methanol as a fuel because methanol has good kinetics of oxidation compared to other alcohols at low temperatures. It oxidizes completely to  $\text{CO}_2$ , meaning the maximum transfer of electrons is occurring (Rao et al., 2007). However it has very low oxidation rate. The problem of the slow methanol oxidation rate has been solved to some extent by alloying Pt with other elements such as Ru, Sn, Mo etc. (Lee, 2010). However, the CO poisoning of the anode catalysts is one of the most important drawbacks for the application of direct methanol fuel cell (DMFC) (Hall et al., 2004). Besides, methanol as a fuel has drawbacks because of its poor electrochemical activity on the cathode reaction. The complete electrooxidation of alcohol to  $\text{CO}_2$  involving

carbon-carbon bond rupture is not carried out by insufficient catalyst performance of present electrode systems. This limitation reduces the cell voltage of its, almost 0,4 V.

Thus, in the electrochemical oxidation of liquid fuel like methanol, the electrode material is a crucial factor to obtain power densities from the fuel cells. It is required to prepare catalyst material with high activity and develop new catalyst preparation method for the electrooxidation of methanol. More studies are needed, however, to further enhance the electrocatalytic activity, stability and CO tolerance of the catalyst.

Due to these requirements explained above, until now, most of the research in methanol oxidation has been focused on the electrooxidation mechanism of alcohol and development of suitable catalyst.

The electrocatalytic oxidation of methanol was carried out on iron and nickel modified manganese oxide electrodes. The oxide layer is produced as a thin film in situ by thermal decomposition of the precursors on a platinum substrate. The electrochemical activity is investigated as a function of the nature of the dopant, the amount of dopant and the effect of the heat treatment of electrode strips. It is found that nickel modified manganese oxide is significantly active for the electro-oxidation of methanol (Samant, 1999). In the other study, the electrochemical oxidation of methanol was investigated on non-covalently functionalized graphene with copper phthalocyanine-3,4',4'',4'''-tetrasulfonic acid tetrasodium salt (TSCuPc) as a promising catalyst support for Pt nanoparticles. As-prepared Pt/TSCuPc-graphene catalyst exhibits much higher electrocatalytic activity and stability than the Pt/graphene and commercial Pt/C catalysts for methanol oxidation (Zhong, 2013).

## 1. 9 Catechol

Phenolic compounds are ubiquitous in nature since they are formed during biological degradation processes. In addition, phenolic compounds are used in a large number of industries, such as coal mining, oil refinery,

paint, polymer and pharmaceutical preparation (Mu, 2006) and released into the environment in either large or small quantities. When present above certain concentration limits, they will result in an acute environmental problem and show harmful effects on human health, animals, plants and aquatic life (Chen, 2009). Furthermore, some phenolic compounds are reported carcinogenic (Notsu, 2004).

Catechol is a model molecule for bisphenol compounds, which usually coexist in plants, tea, fruits, wines, beers, juices, etc. Catechol has been widely studied due to the biological importance such as anti-oxidation, anti-virus and affecting the activities of some enzymes. Therefore, it is important to establish a sensitive, rapid and convenient method for the determination of catechol (Chambers, 1988).

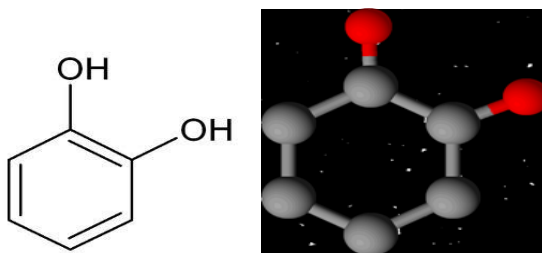


**Figure 1.15** Structure of catechol.

It has been also proven that catechol is generated endogenously in biological systems from adrenaline, noradrenaline, and dopamine (Mansoor et al., 2010). Catechol is also widely used in medicine as a precursor of drugs in Parkinson disease (DOPA), drugs decreasing blood pressure (methyldopa) and bronchodilators (isoproterenol) (Adnan, 2011)

Catechol also known as pyrocatechol or 1,2-dihydroxybenzene is formed endogenously in the organism from neurotransmitters including adrenaline, noradrenaline, and dopamine. It is also a metabolite of many drugs like DOPA, isoproterenol or aspirin and it is also formed in the environment during transformation of various xenobiotics (Bukowska, 2014).

Hydroquinone (HQ) and catechol (CC) are two isomers of phenolic compounds which are important contaminants in medical, food and environmental matrices. Reliable analytical procedures are required for simultaneous

determination of HQ and CC in various matrices with high sensitivity. So far, many methods have been established for their determination, including liquid chromatography, synchronous fluorescence, chemiluminescence, spectrophotometry, gas chromatography/mass spectrometry, pH based-flow injection analysis, electrochemical methods etc. However, most of the above-mentioned methods have some disadvantages, such as time consuming, high cost, low sensitivity and complicate pretreatment. Electrochemical methods provide an easy and fast way in environmental analysis. Hence, some carbon or carbon nanotubes (CNTs) modified electrodes with electrocatalysis property were used for the determination of dihydroxybenzene isomers.

Du et al., 2011 studied a voltammetric sensor for simultaneous determination of hydroquinone (HQ) and catechol (CC) at a glassy carbon electrode modified with graphene (GR/GCE). The separation of oxidation and reduction peak (DE) is decreased from 281 to 31 mV for HQ and from 250 to 26 mV for CC at GR/GCE, respectively. Separation of the oxidation peak potentials for HQ and CC was about 112 mV in 0.10 M acetate buffer solution (pH 4.5), and the anodic currents for the oxidation of both HQ and CC are greatly increased at GR/GCE, which makes it suitable for simultaneous determination of these compounds. In the other study was the simultaneous determination of catechol (CC) and hydroquinone (HQ) at electrodeposited Pt-MnO<sub>2</sub> particles on glassy carbon electrode. Well defined voltammetric peaks were obtained for a mixture of equal concentrations of HQ and CC in pH 7 with a peak potential separation of 0.12 V. The linear range of detection of CC is 15  $\mu$ M to 0.447 mM and HQ is 3  $\mu$ M to 0.481 mM (Unnikrishnan, 2012).

Another study, the reduced graphene oxide and multiwall carbon nanotubes hybrid materials (RGO-MWNTs) were prepared and a strategy for detecting environmental contaminations was proposed on the basis of RGO-MWNTs modified electrode. Due to the excellent catalytic activity, enhanced electrical conductivity and high surface area of the RGO-MWNTs, the simultaneous measurement of hydroquinone (HQ), catechol (CC), p-cresol (PC) and nitrite (NO<sub>2</sub><sup>-</sup>) with four well-separate peaks was achieved at the RGO-MWNTs modified electrode. The linear response ranges for HQ, CC, PC and NO<sub>2</sub><sup>-</sup> were 8.0–391.0  $\mu$ M, 5.5–540.0  $\mu$ M, 5.0–430.0  $\mu$ M and 75.0–

6060.0  $\mu\text{M}$ , correspondingly, and the detection limits ( $S/N = 3$ ) were 2.6  $\mu\text{M}$ , 1.8  $\mu\text{M}$ , 1.6  $\mu\text{M}$  and 25.0  $\mu\text{M}$ , respectively (Hu, 2012).

### 1.9.1 Chemical properties of catechol and importance of human healthy

Catechols can undergo a variety of chemical reactions. In the presence of heavy metals, such as iron or copper, stable complexes can be formed. In the presence of oxidizing agents, catechols can be oxidized to semiquinone radicals and in a next step to o-benzoquinones. Heavy metals may catalyse redox reactions in which catechols are involved. Further chemical properties like the acidity constant and the lipophilicity of different catechols are shortly described as well. As a consequence of the chemical properties and the chemical reactions of catechols, many different reactions can occur with biomolecules such as DNA, proteins and membranes, ultimately leading to non-repairable damage. Reactions with nucleic acids such as adduct formation and strand breaks are discussed among others. Interactions with proteins causing protein and enzyme inactivation are described.

The membrane-catechol interactions discussed here are lipid peroxidation and uncoupling. The deleterious effect of the interactions between catechols and the different biomolecules is discussed in the context of the observed toxicities, caused by catechols (Schweigert, 2001).

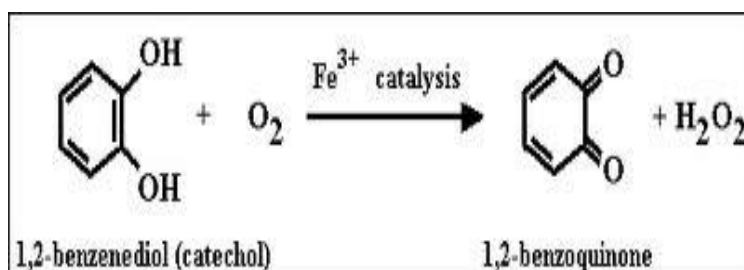


**Figure 1.16** Electrochemical interconversion of 1,2-benzoquinone and catechol.

Exposure to catechol may occur during its manufacture and use. Skin contact with catechol causes eczematous dermatitis in humans. In humans, absorption through the skin results in an illness resembling that induced by phenol, except convulsions are more pronounced. Large doses of catechol can

cause depression of the central nervous system (CNS) and a prolonged rise of blood pressure in animals. Due to the lack of information regarding the duration of exposure in the above studies, it is not clear whether these health effects were observed following acute (short-term) or chronic (long-term) exposure.

### **Sources and potential exposure**

Catechol may be released into the environment during its manufacture and use. The major routes of human exposure are consumption of contaminated drinking water and ingestion of contaminated food (Bethesda, 1993). Catechol occurs naturally in fruits and vegetables. It has been detected in cigarette smoke ((Lyon, 1999).

### **Acute effects**

Skin contact causes eczematous dermatitis in humans. In humans, absorption through the skin results in an illness resembling that induced by phenol, except convulsions are more pronounced (Sittig, 1985). Large doses of catechol can cause depression of the CNS and a prolonged rise of blood pressure in animals. The rise of blood pressure appears to be due to peripheral vasoconstriction (Clayton, 1981). Due to the lack of information regarding the duration of exposure in the above studies, it is not clear whether these health effects were observed following acute or chronic exposure. Acute animal tests in rats, mice, guinea pigs, and rabbits have demonstrated catechol to have high acute toxicity by oral or dermal exposure (Bethesda, 1993).

## **1.10 Voltammetry And Voltammetric Techniques**

Historically, the branch of electrochemistry we now call voltammetry developed from the discovery of polarography in 1922 by the Czech chemist Jaroslav Heyrovsky, received the 1959 Nobel Prize in chemistry. The early voltammetric methods experienced a number of difficulties, making them less than ideal for routine analytic use.

Voltammetry is one of the most important electroanalytical methods used in analytical chemistry and various industrial processes. Voltammetry is the name of

a group of electrochemical techniques. In voltammetry, information about an analyte is obtained by measuring the current as the potential is varied.

The common characteristic of all voltammetric techniques is that they involve the application of a potential ( $E$ ) to an electrode and the monitoring of the resulting current ( $i$ ) flowing through the electrochemical cell. In many cases the applied potential is varied or the current is monitored over a period of time ( $t$ ). Thus, voltammograms are obtained as some function of  $E$ ,  $I$  and  $t$ . Voltammetric techniques are considered active techniques because the applied potential does a change in the concentration of an electroactive species at the electrode surface by the electrochemically reducing or oxidizing it.

Voltammetry is an electrochemical technique in which the current-potential behaviour at an electrode surface is measured. The potential is varied in some systematic manner to cause electroactive chemical species to be reduced or oxidized at the electrode. The resultant current is proportional to the concentration of the electrochemical species. The voltammetric techniques are based on Faraday's Law and Fick's Laws. In voltammetry the current corresponding to the quantity of material transported by diffusion and reacting at the electrode surface is usually measured. This current is proportional to the concentration of the electroactive component (analyte) present in the test solution. The current measured is usually the current due to a specific oxidation or reduction process involving the analyte species at the surface of one of the electrodes.

In voltammetry, the applied potential, as calculated by the Nernst equations, controls the concentrations of the redox species at the electrode surface ( $c_O^0$  and  $c_R^0$ ).

For a reversible electrochemical reaction, which can be described by Oxidation (Ox) +  $ne \leftrightarrow$  Reduction (Red), the application of a potential  $E$  forces the respective concentrations of Ox and Red at the surface of the electrode (that is,  $c_{Ox}^0$  and  $c_{Red}^0$ ) to a ratio in compliance with the Nernst equation:

$$E = E^0 + 2.3 RT / n F \log c_{Ox}^0 / c_{Red}^0$$

R is the molar gas constant ( $8.3144 \text{ J mol}^{-1} \text{ K}^{-1}$ ), T is the absolute temperature (K), n is the number of electrons transferred, F=Faraday constant ( $96,485 \text{ C/equiv}$ ), and  $E^0$  is the standard reduction potential for the redox couple. If the potential applied to the electrode is changed, the ratio  $c_{\text{Red}}^0/c_{\text{Ox}}^0$  at the surface will also change so as to satisfy. If the potential is made more negative the ratio becomes larger (that is, Ox is reduced) and conversely, if the potential is made more positive the ratio becomes smaller (that is, Red is oxidized).

### 1.10.1 Polarography

**Polarography** is a subclass of voltammetry in which the working electrode is dropping mercury. Because of the special properties of this electrode, is wide cathodic range. Polarography has been widely used for the determination of many important reducible species.

This classical technique was invented by J. Heyrovsky in Czechoslovakia in 1922. The excitation signal used in conventional (DC) polarography is a linearly increasing potential ramp. We can obtain the Ilkovic equation for the limiting diffusion current:

$$(i_d)_l = 708nD^{1/2}m^{2/3}t^{1/6}C$$

Here,  $(I_d)_l$  will have microamperes ( $\mu\text{A}$ ), when D is in  $\text{cm}^2/\text{s}$ , m is in  $\text{mg/s}$ , t in second, C is  $\text{mmol/L}$ . In equal, the current can be taken 607 instead of 708 when taking mean of oscillations. When all the device parameters are kept constant, this equation becomes as given below; and this equation is used in quantitative analysis

$$i_d = KC$$

The relationship between current and potential is derived by the Nernst equation (Wang, 2001).

$$E = E_{1/2} + \frac{0.059}{n} \log \frac{i_d - i}{i}$$

### 1.10.2 Pulse voltammetry

The potential step is the basis of pulse voltammetry. Pulse techniques were initially developed for the dropping mercury electrode, the objective being to synchronize the pulses with drop growth and reduce the capacitive current contribution by current sampling at the end of drop life. After applying a pulse of potential, the capacitive current dies away faster than the faradaic current; thus the current is measured at the end of the pulse (Bard and Faulkner, 2001).

**Normal pulse voltammetry** uses a series of potential pulses of increasing amplitude. Between the pulses the electrode is kept at a constant potential at which no reaction of the analytes occurs. The amplitude of the pulse increases linearly with each drop. The current is measured about 40 ms after the pulse is applied, at which time the contribution of the charging current is nearly zero. In addition, because of the short pulse duration, the diffusion layer is thinner than that of DC polarography and hence the faradaic current is increased and normal-pulse polarography will be 5–10 times more sensitive than DC polarography. The limit of detection is about  $10^{-7}$  to  $10^{-8}$  (mol/L) for NPV technique. NPV is also a very good technique for determining diffusion coefficient.

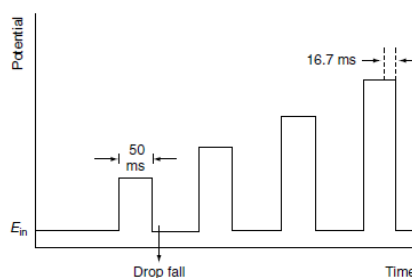


**Figure 1.17** The schematic representation of waveform of normal pulse voltammetry.

**Differential pulse voltammetry (DPV)** is an extremely useful technique for measuring trace levels of organic and inorganic species. DPV is similar to NPV but with two important differences: The base potential is incremented between pulses, these increments being equal and the current is measured immediately

before pulse application and at the end of the pulse: the difference between the two currents is registered.

Two current samples are taken during each drop's life time. One is taken immediately before applying the potential pulse, and the second the drop is dislodged. For each cycle the first current difference value is instrumentally subtracted from the second. A plot of this current difference versus applied (dc ramp) potential produces a stepped peak-shaped incremental derivative voltammogram (Figure 1.18).

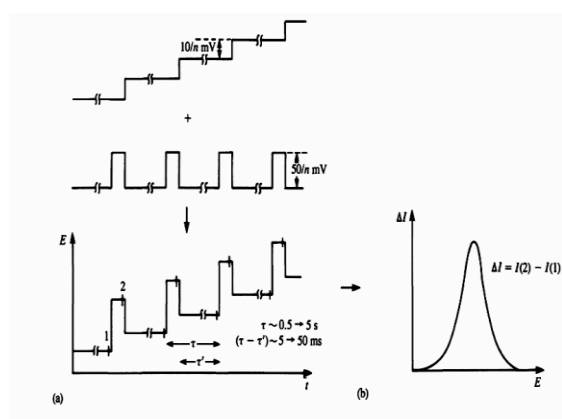


**Figure 1.18** Differential pulse voltammetry. (a) Scheme of application of potentials (sometimes superimposed on a ramp rather than a staircase), (b) Schematic I-E profile.

### 1.10.3 Cyclic voltammetry

Cyclic voltammetry (CV) is a simple, rapid and powerful method for characterizing the electrochemical behavior of analytes that can be electrochemically oxidized or reduced. It is mostly used for the study of redox processes, for understanding reaction intermediates, and for obtaining stability of reaction products (Kounaves, 1997).

This technique is based on varying the applied potential at a working electrode in both forward and reverse directions (at some scan rate) while monitoring the current. For example, the initial scan could be in the negative direction to the switching potential. At that point the scan would be reversed and run in the positive direction. Usually the scan is reversed at a specific switching potential, hence the name cyclic voltammetry.

The important parameters in a cyclic voltammogram are the peak potentials ( $E_{p,c}$ ,  $E_{p,a}$ ) and peak currents ( $i_{p,c}$ ,  $i_{p,a}$ ) of the cathodic and anodic peaks, respectively.

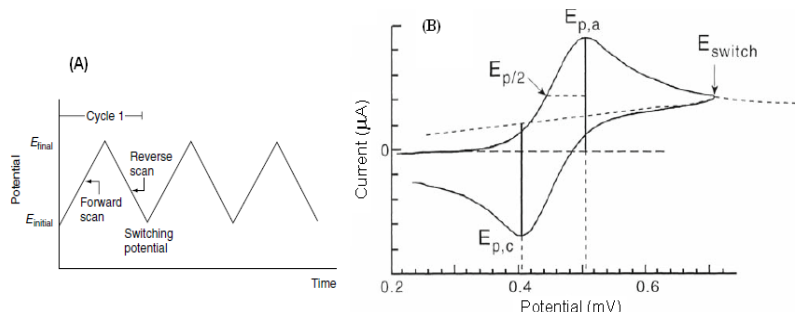


**Figure 1.19** A) potential waveform B) current-potential representations.

If the electron transfer process is fast compared with other processes (such as diffusion), the reaction is said to be electrochemically reversible, and the peak separation is

$$\Delta E_p = E_{p,a} - E_{p,c} = 2.303 RT/nF$$

Thus, for a reversible redox reaction at 25 °C with  $n$  electrons  $\Delta E_p$  should be  $0.0592/n$  V or about 60 mV for one electron. In practice this value is difficult to attain because of such factors as cell resistance. Irreversibility due to a slow electron transfer rate results in  $\Delta E_p > 0.0592/n$  V, than 70 mV for a one-electron reaction. The formal reduction potential ( $E^o$ ) for a reversible couple is given by

$$E^o = \frac{E_{p,c} + E_{p,a}}{2}$$

For a reversible reaction, the concentration is related to peak current by the Randles–Sevcik expression (at 25 °C):

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

where  $i_p$  is the peak current in amper,  $A$  is the electrode area ( $\text{cm}^2$ ),  $D$  is the diffusion coefficient ( $\text{cm}^2 \text{s}^{-1}$ ),  $C_0$  is the concentration in  $\text{mol cm}^{-3}$ , and  $v$  is the scan rate in  $\text{V s}^{-1}$ . For irreversible processes (those with sluggish electron

exchange), the individual peaks are reduced in size and widely separated totally irreversible systems are characterized by a shift of the peak potential with the scan rate (Wang et al.,2006).

For quasi-reversible systems the kinetics of the oxidation and reduction reactions have to be considered simultaneously. As a general conclusion, the extent of irreversibility increases with increase in sweep rate, while at the same time there is a decrease in the peak current relative to the reversible case and an increasing separation between anodic and cathodic peaks (Gosser, 1994).

### **1. 11 Surface Characterization Techniques**

The developments in material sciences have increased demand for surface characterization techniques to improve the function and quality of target surface. Characterization of surface properties is important in many research fields of material science, including heterogeneous catalysis, activity of metal surfaces, semiconductor thin-film technology, corrosion resistance and studies of the behavior and functions of biological membranes.

Desired surface properties such as optical, electrical, chemical or mechanical are affected from the surface structure and composition. In this connection, also, surface characterization techniques such as scanning electron microscopy (SEM), transmission electron microscopy (TEM), scanning tunneling microscopy (STM) and atomic force microscopy (AFM) and X-Ray Photoelectron Spectroscopy (XPS) are very usefull instruments for the understanding of catalytic activities of modified electrode surface having a important place in electrochemical studies.

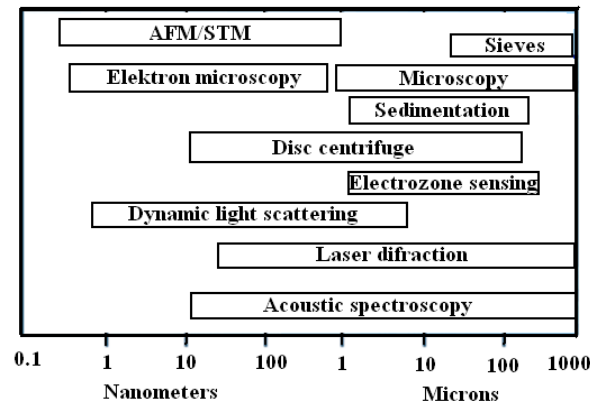


**Figure 1.20** Comparison of the imaging of many types 2D and 3D profiling and imaging instruments.

### 1.11.1 Scanning electron microscope (SEM)

Scanning electron microscope (SEM) is the most important electron-optical instrument for the investigation of bulk specimens. An electron probe is produced by two- or three-stage demagnification of the smallest cross section of the electron beam after acceleration.

The SEM consists a source of electrons; lenses for focusing them to a fine beam; facilities for sweeping the beam in a raster; arrangements for detecting electrons (and possibly other signals) emitted by the specimen; and an image-display system (Figure 1.21).

The most important signals are those produced by secondary electrons (SE) with most probable exit energies of 2-5 eV and by backscattered electrons (BSE) with energies that range from the energy of the primary electrons to about 50 eV. The secondary-electron yield and the backscattering coefficient depend on the angle of electron incidence (topographic contrast), the mean atomic number (material contrast), the crystal orientation (channeling contrast) and electrostatic and magnetic fields near the surface (potential and magnetic contrast). A signal can also be produced by the specimen current and by electron-beam-induced currents in semiconductors. Analytical information is available from the X-Ray spectrum and Auger electrons or from light quanta emitted by cathodoluminescence. The patterns, electron-backscattering patterns and X-Ray Kossel

diagrams. An environmental SEM can be work with a high partial pressure between the specimen and the objective lens diaphragm.

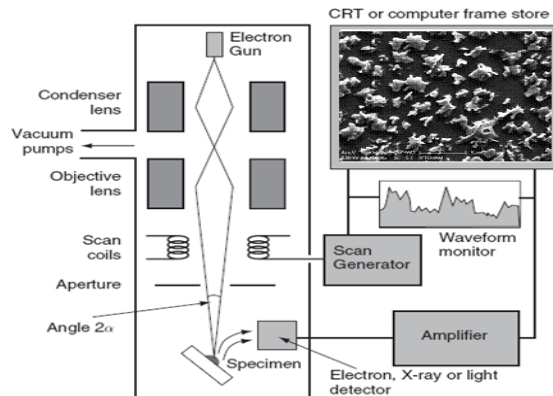


**Figure 1.21** Schematic diagram of the layout of a SEM (Kelsall, 2005).

**Secondary electrons (SE)** are emitted from very near the surface of the sample, with energies of a few electron volts. The SE yield increases with decreasing angle between beam and specimen surface. **Backscattered electrons (BSEs)** have very high energies and low yields compared to secondary electrons. The ET detector may be used to collect only BSEs by making the grid bias slightly negative so as to exclude secondary electrons. However, only those electrons travelling in line-of-sight towards the detector will contribute to the relatively low signal and therefore images will show very strong shadowing contrast and a low signal-to-noise ratio (Kelsall, 2005).

### 1.11.2 X-Ray photoelectron spectroscopy (XPS)

X-Ray Photoelectron Spectroscopy (XPS) provides a great deal of information about elemental distributions, layer or coating structure and thicknesses, surface functionality, and even particles sizes on the 1-20 nm scale for sample types that may not be readily analyzed by other methods. This information is important for both synthetic nanostructured or nanosized materials and a variety of natural materials with nanostructure.

The surface analysis technique called XPS is also known as ESCA, electron spectroscopy for chemical analysis. It is the most widely used surface analysis technique because of its relative simplicity in use and data interpretation. XPS is

chosen when the samples are insulating or when chemical state information is desired.

XPS analysis is usually conducted in two parts. During the first portion, a complete surface elemental analysis is obtained. XPS detects atomic number range 3-92, within 50 Å of the surface. There is good light element sensitivity, with a detectability limit of approximately 0.1 atomic percent. The second portion of a typical XPS experiment is used to determine the chemical binding energy of the surface elements. This portion is the true strength of XPS in that the binding energy furnishes some information about compounds present on the surface. Argon profiling is also available to determine concentration as a function of depth.

The kinetic energy,  $E_k$ , of these photoelectrons are determined by the energy of the X-Ray radiation,  $h\nu$ , and the electron binding energy,  $E_b$ , as given by:

$$E_k = h\nu - E_b$$

The experimentally measured energies of the photoelectrons are given by:

$$E_k = h\nu - E_b - E_w$$

$E_w$  is the work function of the spectrometer.

The electron binding energies are dependent on the chemical environment of the atom, making XPS useful to identify the oxidation state and ligands of an atom.

### 1.11.3 Electrochemical impedance spectroscopy (EIS)

Impedance spectroscopy is an effective technique for probing the features of chemically-modified electrodes and for understanding electrochemical reaction rates. EIS is a very sensitive technique and it must be used with great care. Besides, it is not always well understood. This may be connected with the fact that existing reviews on EIS are very often difficult to understand by non-specialists and, frequently, they do not show the complete mathematical developments of equations connecting the impedance with the physico-chemical parameters. It should be stressed that EIS cannot give all the answers. It is a complementary technique and other methods must be used to elucidate the interfacial processes. Electrochemical transformations occurring at the electrode–solution interface

can be modeled using components of the electronic equivalent circuitry that correspond to the experimental impedance spectra. Particularly useful to model interfacial phenomena is the Randles and Ershler electronic equivalent circuit model (Fig. 1.22). This includes the double-layer capacitance  $C_d$ , the ohmic resistance of the electrolyte solution  $R_s$ , the electron transfer resistance  $R_p$ , and the Warburg impedance  $W$  resulting from the diffusion of ions from the bulk solution to the electrode surface. The impedance of the interface, derived by application of Ohm's law, consists of two parts, a real number  $Z'$  and an imaginary one,  $Z''$ :

$$Z(\omega) = R_s + R_p / (1 + \omega^2 R_p^2 C_d^2) - j \omega R_p^2 C_d / (1 + \omega^2 R_p^2 C_d^2) = Z' + jZ''$$

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

Impedance spectroscopy involves the application of a small-amplitude perturbing sinusoidal voltage signal (at a  $\omega$  frequency) to the electrochemical cell and measuring the current response. The resulting faradaic impedance spectrum, known as a Nyquist plot, corresponds to the dependence of the imaginary number on the real number (e.g., Figure 1.21), and contains extensive information about the electrified interface and the electron transfer reaction. Nyquist plots commonly include a semicircle region lying on the axis followed by a straight line. The semicircle portion (observed at higher frequencies) corresponds to the electrontransfer-limited process, while the straight line (characteristic of the low frequency range) represents the diffusion-limited process. Such spectra can be used for extracting the electron transfer kinetics and diffusional characteristics. In the case of very fast electron transfer processes the impedance spectrum includes only the linear part, while very slow electron transfer processes are characterized by a large semicircular region. The diameter of the semicircle equals the electron transfer resistance. The intercepts of the semicircle with the  $Z_{re}$  axis correspond to those of  $R_s$ .

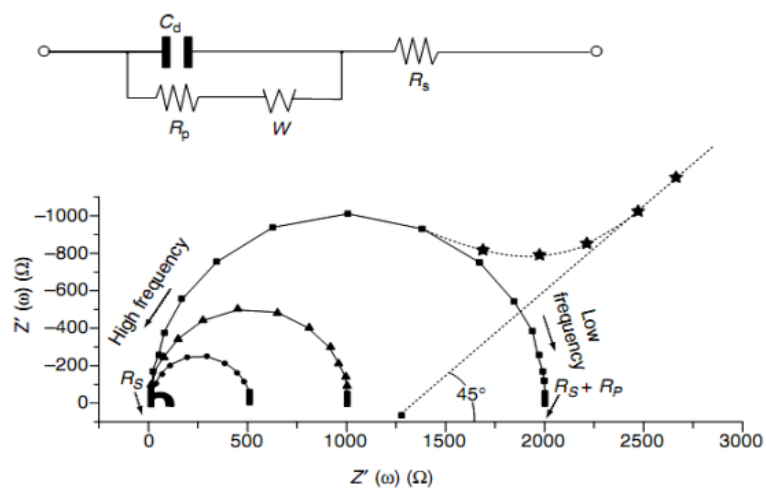


**Figure 1.22** Faradaic impedance spectra presented in the form of Nyquist plots, along with the electronic equivalent circuit of the electrified interface.

## 2. EXPERIMENTAL

### 2. 1 Instrumentation

Voltammetric measurements were carried out using Autolab 101 Potentiostat Electrochemical Analyser equipped with a three electrode system consisted of a working electrode (GCE, GO-GCE, MNP-GO-GCE, PANI/GCE, MNP-PANI/GCE MWCNT-PANI/GCE, MNP-MWCNT-PANI/GCE), an auxiliary a platinum electrode and an Ag/AgCl (sat.KCl) used as reference electrode. Cyclic and differential pulse (dp) mode were used throughout the electroanalytical studies. The pH measurements were made with WTW handheld 330i ion analyzer meter pH. Philips XL30 SFEG and Micro Tech Polar 10 Sputter Coater Scanning Electron Microscopy were used for the characterization of bare and modified electrode surfaces. Bandelin Sonorex model ultrasonic bath was used for preparation of solutions and cleaning the electrodes.

### 2. 2 Reagents and Solutions

All reagents were of analytical reagent grade. Methanol ( $\text{CH}_3\text{OH}$ ), Aniline ( $\text{C}_6\text{H}_5\text{NH}_2$ ), graphene oxide (GO), carbon nanotube (CNT), catechol, sodium hydroxide (NaOH), copper sulphate ( $\text{Cu}(\text{SO}_4)_2 \cdot 5\text{H}_2\text{O}$ ), chloroauric acid ( $\text{HAuCl}_4$ ), chloroplatinic acid ( $\text{H}_2\text{PtCl}_6$ ), hydrochloric acid (HCl), sulfuric acid ( $\text{H}_2\text{SO}_4$ ), alumina ( $\text{Al}_2\text{O}_3$ ), nickel sulphate hepta hydrate ( $\text{Ni}(\text{SO}_4) \cdot 7\text{H}_2\text{O}$ ),  $\text{Na}_2\text{HPO}_4$ - $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$  (PBS), *N,N*-dimethylformamide (DMF) were supplied from Merck, Sigma or Aldrich. Aniline was purified three times and then kept in a refrigerator before use.

Stock standard solutions of methanol ( $10 \text{ mol.L}^{-1}$ ) in ultrapure water, PANI ( $0.1 \text{ mol.L}^{-1}$ ) in  $\text{H}_2\text{SO}_4$  ( $0.1 \text{ mol.L}^{-1}$ ), Graphene oxide (0.05 g) in DMF (3 mL), catechol ( $0.1 \text{ mol.L}^{-1}$ ) in PBS (pH=7), Carbon nanotube (0.0196 g) in DMF (2.5 ml) were freshly prepared by dissolving the required amount of reagent. The metal solutions ( $0.1 \text{ mol.L}^{-1} \text{ Ni}^{+2}$  and  $\text{Cu}^{+2}$ ) in  $\text{H}_2\text{SO}_4$  ( $0.1 \text{ mol.L}^{-1}$ ) were prepared by dissolution of metal salt with acids. All experiments were carried out at ambient temperature and high purity nitrogen kept flowing over the solution during electrochemical experiments.

## **2.3 Methods**

### **2.3.1 Pre-conditioning of GCE**

GCE was activated by polishing with different grade of  $\text{Al}_2\text{O}_3$  slurry (0.05-3 micron) on a synthetic cloth then rinsing with pure water and ultrasonicated for 3 minutes in ethanol and ultra pure water (1:1 v/v) mixture. GCE was also electrochemically cleaned by keeping 10 minutes at constant potential at 1.0 V.

### **2.3.2 Preparation of graphene oxide**

Graphene oxide is obtained with Brodie Method by using spectroscopically grade pure graphite (Merck). In this method, 2.0 g spectroscopically grade pure graphite and 17.0 g  $\text{NaClO}_3$  were mixed in a beaker. Then, 50 mL  $\text{HNO}_3$  was added in to the mixture slowly during the ice bath process. Obtained mixture was continuously mixed in room temperature for 24 hours. At the end of this process, 500 mL distilled water was added to decante. Washing with distilled water goes on until the washing water has the value of pH 7. Finally, it is dried in a 110 °C incubator. A 0.05 g graphene oxide was pretreated with 3 mL N,N-dimethyl formamide (DMF). As a result, a black colored suspense mixture is obtained.

### **2.3.3 Preparation of graphene oxide modified GCE**

A 20  $\mu\text{L}$  of graphene oxide 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 more then one hour.

### **2.3.4 Pre-treatment of multiwalled carbon nanotubes**

A 0.08 g multiwalled carbon nanotube was pretreated with 7.5 mL concentrated  $\text{HNO}_3$  by boiling and then washed many times with ultrapure water. The asit-treated MWCNT was dispersed in DMF to get a black suspension after 30 minutes ultrasonication.

### **2.3.5 Preparation of MWCNT modified PANI/GCE**

A 10  $\mu\text{L}$  of MWCNT suspension was injected on PANI/GCE surface. The solvent (DMF) of the suspension on the PANI/GCE surface was evaporated at  $60^\circ\text{C}$  for more than one hour.

### **2.3.6 Preparation of polyaniline film modified GCE**

Electrochemical polymerization of aniline was carried out in 0.1 M  $\text{H}_2\text{SO}_4$  solution containing  $5 \times 10^{-4}$  M aniline for electrochemical polymerization by cyclic voltammetry. The polymerization voltammograms were obtained by repetitive 10 potential cycles from -0.3 to 0.9 V at a scan rate of 50 mV/s. The electrode was rinsed with water. The obtained electrode was ready for use after the final wash with ultra pure water and denoted as PANI/GCE.

In the other study, electrochemical polymerization of aniline was carried out in 0.1 M  $\text{H}_2\text{SO}_4$  solution containing  $10^{-3}$  M aniline for determination of catechol by cyclic voltammetry. The polymerization voltammograms were obtained by repetitive 5 potential cycles from -0.3 to 0.9 V at a scan rate of 50 mV/s. The electrode was rinsed with water. The obtained electrode was ready for use after the final wash with ultra pure water and denoted as PANI/GCE.

### **2.3.7 Preparation of various metal nanoparticles modified PANI/GCE, MWCNT-PANI/GCE and GO/GCE**

The metal nanoparticles were electrochemically deposited on the PANI/GCE, MWCNT-PANI/GCE and GO/GCE by cyclic voltammetry (CV). For PANI/GCE modification, Pt nano particles deposited by CV scanning between -0.900 and 0.600 V in  $\text{H}_2\text{PtCl}_6$  with a scan rate of 50 mV/s for 10 cycles and for PANI/GCE modification Cu nano particles deposited by CV scanning between -0.800 and 0.500 V in  $\text{CuSO}_4$  with a scan rate of 50 mV/s for 7 cycles.

For MWCNT-PANI/GCE modification, Ni nanoparticles deposited by CV scanning between -1.00 and 0.900 V  $\text{Ni}^{+2}$  solution with a scan rate of 50 mV/s for 15 cycles. Bimetallic nano particles modified GO/GC electrodes were prepared by

applying the same procedure consecutively that mentioned above. For GO/GCE modification, Au nano particles deposited by CV scanning between -0,900 and 0.600 V in  $\text{HAuCl}_4$  with a scan rate of 50 mV/s for 10 cycles and for GO/GCE modification, Pt nano particles deposited by CV scanning between -0,900 and 0.600 V in  $\text{H}_2\text{PtCl}_6$  with a scan rate of 50 mV/s for 3 cycles respectively. The obtained metal nano particles modified electrodes were ready for use after the final wash with ultra pure water and denoted as Pt-Au-GO/GCE, Ni-MWCNT-PANI/GCE and Cu-Pt-PANI/GCE.

### 3. RESULTS AND DISCUSSION

This thesis was composed of three different study. The first one was that fabricate and characterize a highly electrocatalytic active nanocomposite electrode for methanol oxidation.

Second studies was developed a catalytic active metal nanoparticles modified polymer film electrodes for methanol oxidation.

Finally the third study was related with developed a metal nanoparticles modified MWCNT/PANI/GCE for sensitive determination of catethol and applied to the real samples.

#### 3.1 Preparation of Graphene Oxide Modified GCE

A 20  $\mu\text{L}$  of graphene oxide 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 more then one hour.

#### 3.2 Deposition of Pt-Au Nanoparticles on GO/GC Electrode from Natrium Hydroxide Solution

GO was improved the catalytic activity of GCE toward the electrooxidation of methanol. It is well known that, metal nano particles modified graphene oxide electrodes exhibited higher catalytic activity for electrochemical reaction of many organic compounds.

Electrochemically deposition of Au nanoparticles on the GO/GCE surface was carried out from 1mM chloroauric acid solution + 0.1 M HCl solution mixture by concecutive potential scans from -0.9 to 0.6 V (Figure 3.1.A). Figure 3.1 (A) of CV showed that, Au nanoparticles obtained by Au (III) ions reduction at -0.42 V and partially reoxidation at +0.3 V. For the following potential scans only a slight increase of the reduction peak current at -0.42 V was observed, and

the peak potential slightly moved to less negative values. These data are well agreement with previous studies.

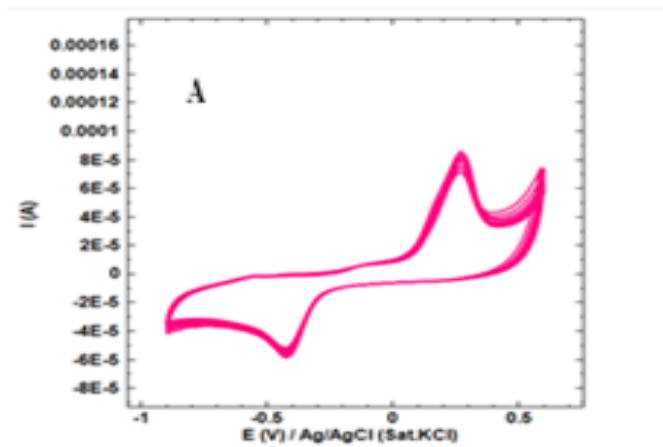


**Figure 3.1** Au deposition on GO/GCE, at 50 mV/s for 10 cycles in 1 mM  $\text{HAuCl}_4$ .

Deposition of Pt nanoparticles on Au-GO/GC electrodes in  $\text{H}_2\text{PtCl}_6 + 0.1$  mol/L HCl solution was obtained in potential range between -0.900 V to 0.600 V. Figure 3.1.B of CV showed that, Pt nanoparticles obtained by  $\text{Pt}^{4+}$  ions reduction at 0.12 V and partially reoxidation at 0.48 V.

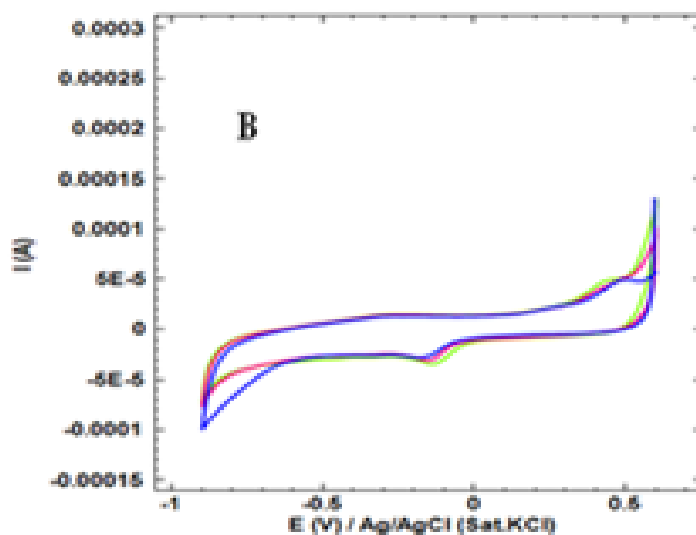


**Figure 3.2 B)** Pt deposition on Au-GO/GCE, at 50 mV/s for 3 cycles in 1 mM  $\text{H}_2\text{PtCl}_6$ .

### 3.3 SEM and EDX Characterization of Graphite Powder, GO/GCE, Au-GO/GCE and Pt-Au-GO/GCE

Figure 3.3 shows the SEM images of GO/GCE and Pt-Au-GO/GCE. Comparison Figure 3.3.B which was corresponding to almost homogeneously distributed porous GO/GCE surface. Nano Au and Pt particles were formed as bright round-shaped which homogeneously dispersed particles decorating on the electrode surface were seen in Figure 3.3.D. To obtained SEM images of Pt-Au-GO/GCE was calculated approximately 20-50 nm.

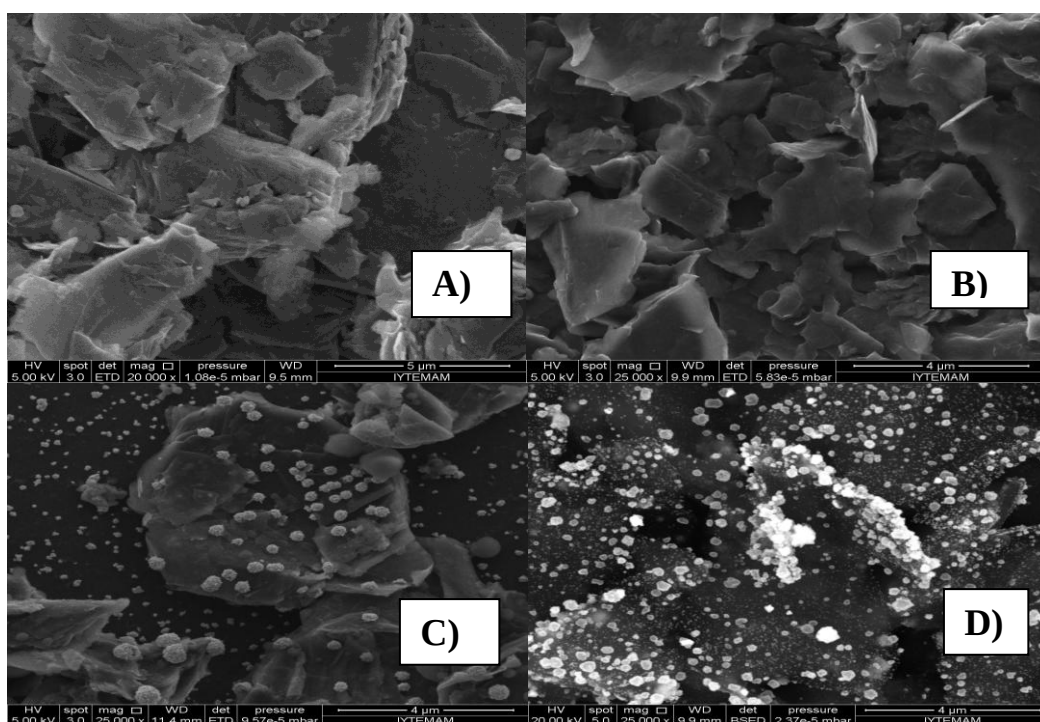


**Figure 3.3** SEM images of (A) Graphite powder, (B) GO/GCE, (C) Au-GO/GCE and (D) Pt-Au-GO/GCE.

Energy dispersive X-Ray spectroscopy (EDX) study confirmed the presence of nano Pt and Au particles decorating GO/GCE, with the electrochemical deposition. Figure 3.4 shows the EDX images of Pt-Au-GO/GCE.

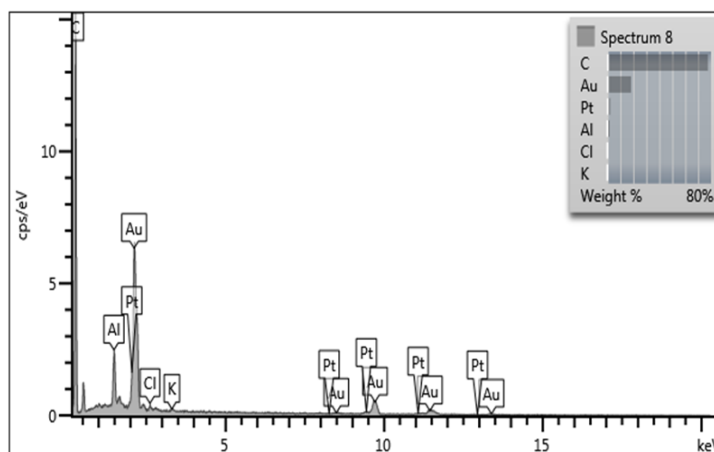


**Figure 3.4** EDX results of the Pt-Au-GO/GCE.

The weight gain of the GO due to the Au and Pt loading were about 18.26 % and 2.14 %, respectively, which was prepared consequently deposition Au and Pt.

### 3.4 Voltammetric Behaviour of Methanol at Bare and Modified Electrode

Figure 3.5 shows the cyclic voltammograms of Ag-Au-GO/GCE, Cu-Au-GO/GCE, Au-Cu-GO/GCE, Au-Pt-GO/GCE and Pt-Au-GO/GCE in 0.1 M NaOH solution in the presence of 1.0 M methanol between the range of 0.8V - (-0.8) V. There was not observe any electrochemical signal for methanol at Ag-Au-GO/GCE, Cu-Au-GO/GCE and Au-Cu-GO/GCE, but a well defined irreversible oxidation peak was appeared at -102 mV and 147 mV on Au-Pt-GO/GCE and Pt-Au-GO/GCE respectively. The maximum peak observed for Pt-Au-GO/GCElectrode that it was chosen for further studies.

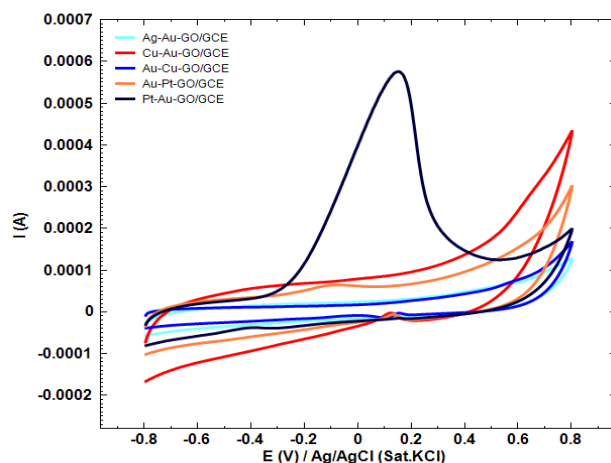


**Figure 3.5** Cyclic Voltammetric behaviors of a) Ag-Au-GO/GC, b) Cu-Au-GO/GC, c) Au-Cu-GO/GC, d) Au-Pt-GO/GC and e) Pt-Au-GO/GC electrodes in 0.1 M NaOH in the presence of 1.0 M methanol.

Figure 3.6 shows the cyclic voltammograms of bare GCE, GO/GCE, Au-GO/GCE, Pt-GO/GCE, Au-Pt-GO/GCE and Pt-Au-GO/GCE in 0.1 M NaOH solution in the presence of 1.0 M methanol between the range of 0.8V - (-0.8) V. There was not observe any electrochemical signal for methanol at both bare GCE and GO/GCE, but a well defined irreversible oxidation peak was appeared at 0.4 V and -0.10 V on Au-GO/GCE and Au-Pt-GO/GCE respectively in the case of narrow potential scan.

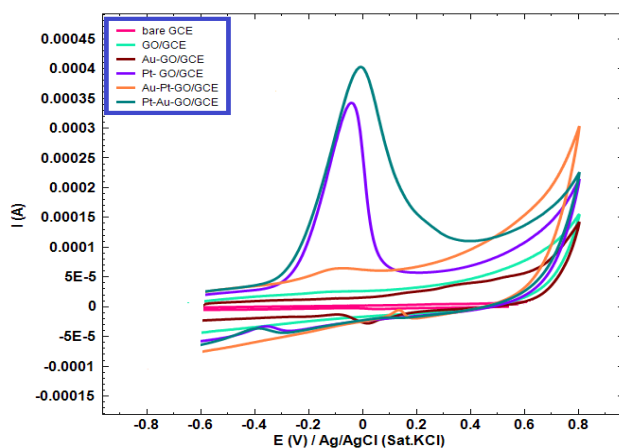


**Figure 3.6** Cyclic Voltammetric behaviors of a) GC, b) GO/GC, c) Au-GO/GC d) Pt-GO/GC, e) Au-Pt-GO/GC and f) Pt-Au-GO/GC electrodes in 0.1 M NaOH in the presence of 1.0 M methanol .

On the other hand, substantial increases in the peak current was also observed at Pt nanoparticles modified GO/GCE due to the catalytic property gain

to GO by Pt nanoparticles. A higher catalytic activity in both peak current and oxidation potential manner for methanol was observed at Pt modified Au-GO/GCE compare to Pt-GO/GCE. Also the electrochemical oxidation of methanol oxidative peak was observed at -0.1 V in the presence of 1.0 M methanol in 0.1 M NaOH solution.

### **3. 5 Optimization Studies of Methanol Oxidation at Pt-Au-GO/GCE**

#### **3.5.1 The influence of chloroauric acid concentration for Au nanoparticles formation and their effect on methanol oxidation**

The effect of chloroauric acid concentrations during the Au nanoparticles formation on the GO/GCE and their effect on the methanol oxidation reaction was investigated in the concentration range of  $10^{-4}$  M -  $2 \times 10^{-3}$  M at 10 cyc Au MNP modified GO/GCE. The maximum peak and negative potential observed for  $10^{-3}$  M that it was chosen for further studies. Au nano particles formed with Au (III) ions reduction at -0.42 V and oxidation at 0.3 V. Increasing of both reduction and oxidation peaks by increasing the cycle numbers of current potential cycling showed that nano Au particles were formed on the electrode surface.

#### **3.5.2 The influence of chloroplatinic acid concentration for Pt nanoparticles formation and their effect on methanol oxidation**

Figure 3.7 shows the effect of chloroplatinic acid concentration on the response of 1.0 M methanol at 0.1 M NaOH. Methanol oxidation reaction was investigated in the concentration range of  $1.0 \times 10^{-4}$  -  $1.0 \times 10^{-3}$  M. Variation of Pt nanoparticles concentration cause a desirable change on peak current of methanol

and the optimum peak characteristics were obtained for  $10^{-3}$  M of Pt nanoparticles

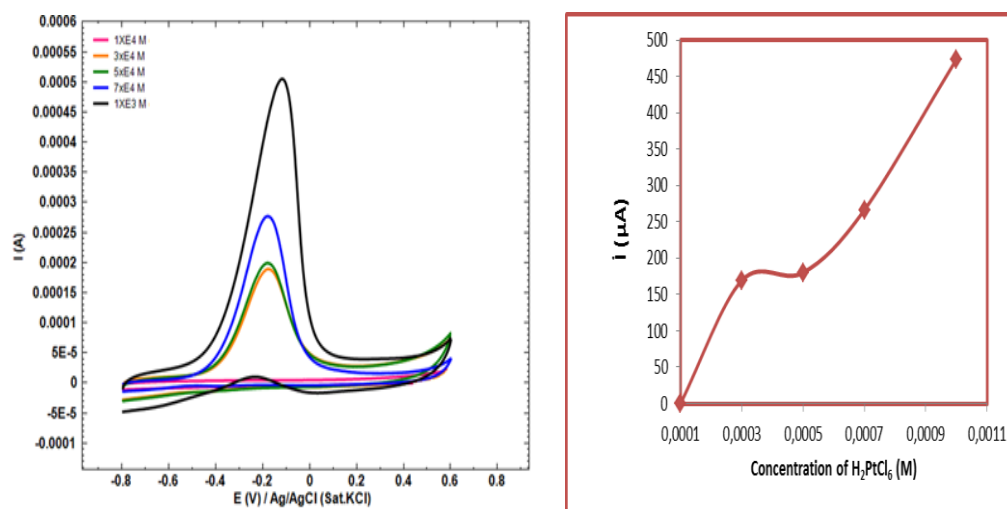


**Figure 3.7** The Influence of chloroplatinic acid concentration for Pt nanoparticles formation and their effect on methanol oxidation.

### 3.5.3 The influence of Au and Pt nanoparticles cycle numbers on methanol oxidation

The effect of potential scan cycle number on the electrodeposition of metal nanoparticles on GO/GCE investigated for 1.0 M methanol oxidation in 0.1 M NaOH solution. For Au and Pt nanoparticles cycle number were observed at in 10 cycles and 3 cycles respectively.

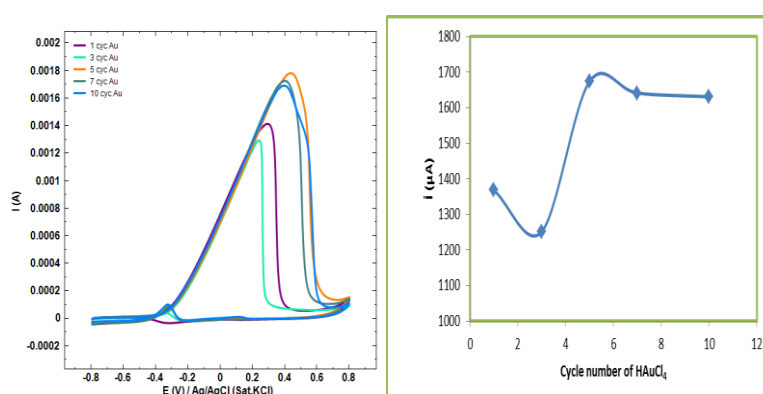


**Figure 3.8** The influence of Au nanoparticle cycle numbers on methanol oxidation.

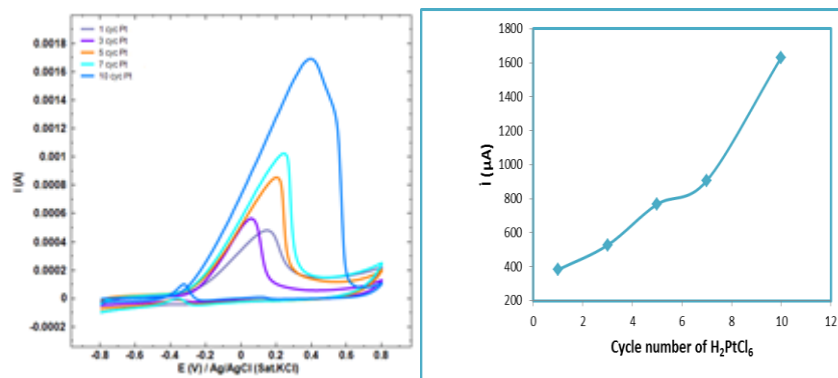


**Figure 3.9** The influence of Pt nanoparticle cycle numbers on methanol oxidation.

### 3.5.4 Optimization of sodium hydroxide concentration at Pt-Au-GO/GC electrode

The effect of NaOH concentrations on the methanol oxidation reaction was investigated in the concentration range of 1.0-4.0 M at Pt-Au-GO/GC electrode. As shown at Figure 3.10 the best catalytic activity and peak current was observed at in 3.0 M NaOH solution.

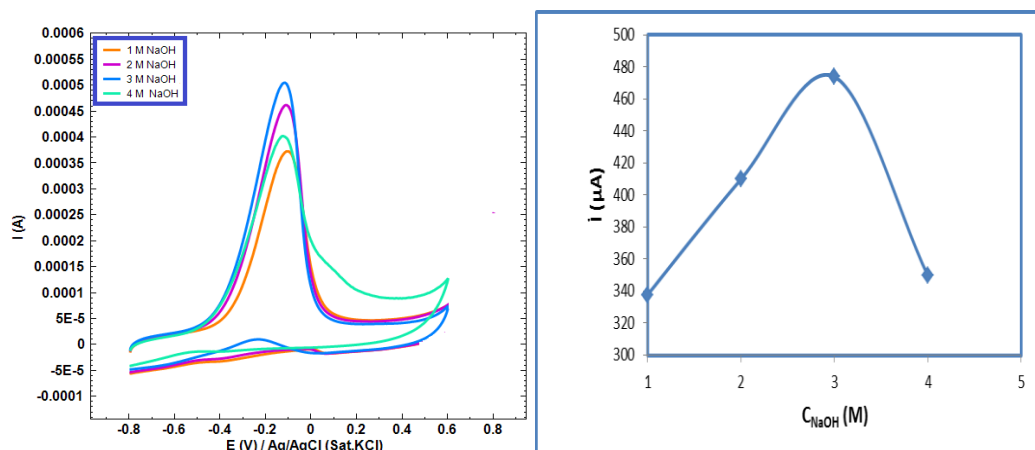


**Figure 3.10** Cyclic voltammograms for methanol oxidation on Pt-Au-GO/GC electrode at different NaOH concentrations.

### 3.5.5 Scan rate study at Pt<sub>(3cyc)</sub>-Au<sub>(10cyc)</sub>-GO/GCE

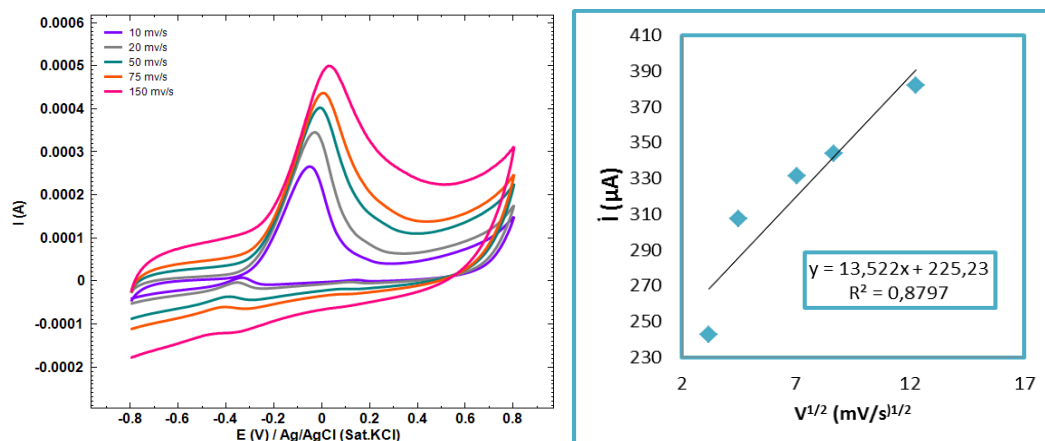


**Figure 3.11** Cyclic voltammogram for methanol oxidation of Pt<sub>(3cyc)</sub>-Au<sub>(10cyc)</sub>-GO/GC electrode at different scan rates. (10, 20, 50, 75, 150, 200, 250, 300, 350, 400 and 500 mV/s).

In order to confirm the electrode behaviour on the oxidation of methanol, a series of cyclic voltammograms were recorded at Pt<sub>(3cyc)</sub>-Au<sub>(10cyc)</sub>-GO/GC electrode by varying potential scan rate. The oxidation peak current increased linearly with the square root of the scan rate (Figure 3.11), suggesting that methanol oxidation reaction at this modified electrode was controlled by diffusion. The oxidation peak potential of methanol shifted positive values with increasing the scan rate, indicating that the electron transfer was irreversible.

The dependence of peak current on the concentration of methanol was obtained as linear while accompanied by the peak potential shift to positive values (Figure 3.12).

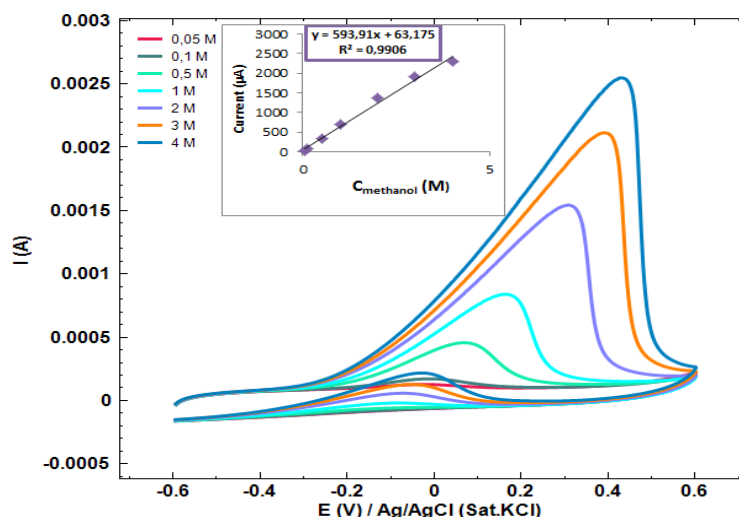


**Figure 3.12** Cycling voltammograms at Pt-Au-GO/GCE for increasing concentrations of methanol in 3.0 M NaOH solution with scan rate 50 mV/s. (Inset: Corresponding calibration curve of increasing methanol concentrations). Methanol concentrations 0.05, 0.1 M, 0.5 M, 1.0 M, 2.0 M, 3.0 M, 4.0 M.

### 3. 6 Preparation of Poly(aniline)(PANI) Film Modified GCE

Figure 3.13 shows the cyclic voltammograms of polyaniline film growth during electrolysis of the solution consisting of  $5 \times 10^{-4}$  M aniline and 0.1 M  $\text{H}_2\text{SO}_4$  by cyclic voltammetry at 50 mV/s between -0.3 and 0.8 V. In an anodic scan, there are three distinct well-defined peaks located at approximately 0.20, 0.45 and 0.7 V for the first, second and third anodic peaks, respectively. Whereas the height of the first and third peaks were nearly the same with some tendency to be higher than second peak. All the three peaks have their cathodic counterparts, observable in the back potential scan.

Their peak currents increase quickly by increasing in the number of potential cycles. This indicates that polyaniline film grows very quickly as the electrolysis proceeds, which was caused by the autocatalytic polymerization (Mu and Kan, 1996).

The oxidation peaks at around 0.2 V are attributed to the transformation of PANI from the reduced leucoemeraldine (LE) state to the partly oxidized emeraldine (EM) state, the second oxidation peak at 0.7 V corresponds to

transition of the PANI, from LE to pernigraniline (PE) state. As the reaction intermediates such as p-benzoquinone, p-aminophenol and some dimers during the polymerization are known to be trapped in the polymer, the anodic hump at 0.45 V, is generally attributed to redox reaction of p-benzoquinone (Niu et.al., 2003; Gomes, 2012; Hand and Nelson, 1974; Pournaghi-Azar and Habibi, 2007). Subsequent cycles indicate a successive growth of the polyaniline film as evidenced by the increase in the redox currents.

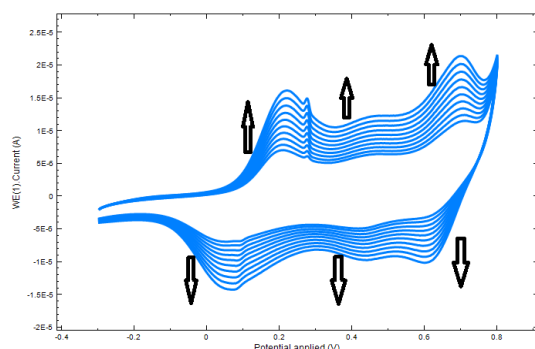


**Figure 3.13** Cyclic voltammograms during electro-polymerization of aniline from a solution containing 0.1 M sulfuric acid and  $5 \times 10^{-4}$  M aniline on GC electrode (sweep rate: 50 mV/s, room temperature).

### 3.7 Electrochemical Deposition of Pt and Cu Nanoparticles on the PANI/GC Electrode from in the Presence of $\text{Cu}^{2+}$ and $\text{Pt}^{4+}$ Solutions

Voltammetric behaviour of PANI/GCE was studied in the presence of  $\text{H}_2\text{PtCl}_6 + 0.1$  M HCl and  $\text{CuSO}_4 + 0.1$  M  $\text{H}_2\text{SO}_4$  in Figure 3.14. The growth of Pt nano particles on the PANI/GCE surface corresponds to a reduction peak at -0.75 V and oxidation peak at -0.35 V in Figure 3.14.A. Stable peak currents were observed for both reduction and oxidation on the electrode reaction after the 10 CV cycles. The peak potentials of both anodic and cathodic manner were shifted by consecutive scan. The Cu metal nanoparticles were electrochemically deposited on the Pt/PANI/GCE surface by cycling the potential from -0.8 to 0.5 V in 1.0 mmol/L  $\text{CuSO}_4 + 0.1$  mol/L  $\text{H}_2\text{SO}_4$  solution at a scan rate of 50 mV/s for 7 times (Figure 3.14.B). A cathodic peak was observed at -0.271 V by reduction of  $\text{Cu}^{2+}$  to Cu metal. A partially re-oxidation of metallic formed Cu was seen at -0.534 V

during the anodic potential scan. These peaks are attributed to the oxidation and reduction of the oxygen-containing species adsorbed on the electrode surface, which can promote the catalytic oxidation of organic molecules. In the continuous cycles, the redox peaks of the copper nanoparticles become higher and higher. It is interesting to find that both reduction peak potentials shift in the positive direction with cycling, suggesting that the reduction of  $\text{Cu}^{2+}$  ions into the Cu nanoparticles becomes easier in the cycles.

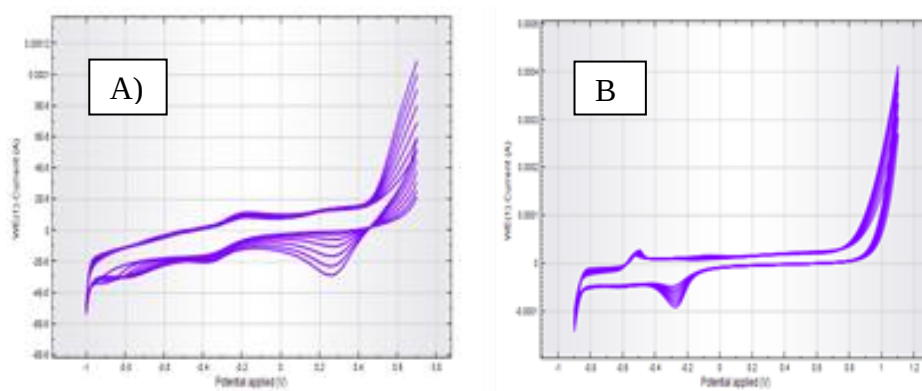


**Figure 3.14** A) Pt deposition, B) Cu deposition on Pt-PANI/GCE, at 50 mV/s for 10 and 7 cycles in 1 Mm  $\text{H}_2\text{PtCl}_6$  and  $\text{CuSO}_4$  respectively.

### 3.8 Surface Characterization of PANI/GCE, Pt-PANI/GCE and Cu-Pt-PANI/GCE

#### 3.8.1 SEM and EDX characterization PANI/GC and metal nanoparticles modified PANI/GC electrode

Figure 3.15 shows the SEM images of PANI/GCE, Pt-PANI/GCE and Cu-Pt-PANI/GCE. The morphology of the PANI on GC electrode showed in Figure 3.15.A almost homogenously distributed porous polymer surface. This porous polymer allow easily electrodeposited of metal nanoparticles on electrode surface. The SEM image of Pt-PANI/GCE shows many observable particles on the PANI surface. The distribution of platinum nanoparticles on polymer shows a few bright round-shaped aggregates (Figure 3.15.B). In particular, the comparison of single metal nanoparticle decorated polymer with bimetallic nanoparticles modified was important. Because the catalytic effect of bi-metallic nanoparticles modified

electrodes is better than that of single metal nanoparticle. Figures 3.15.C show that SEM image of Pt and Cu nanoparticles was deposited on PANI/GC electrode with two different electrodeposition ways, which are consequently. As can be seen these SEM image, the bimetallic surface was obtained after consequently deposition of Pt and Cu on PANI/GCE surface. The average particle size on Cu-Pt/PANI/GCE was 88 nm.

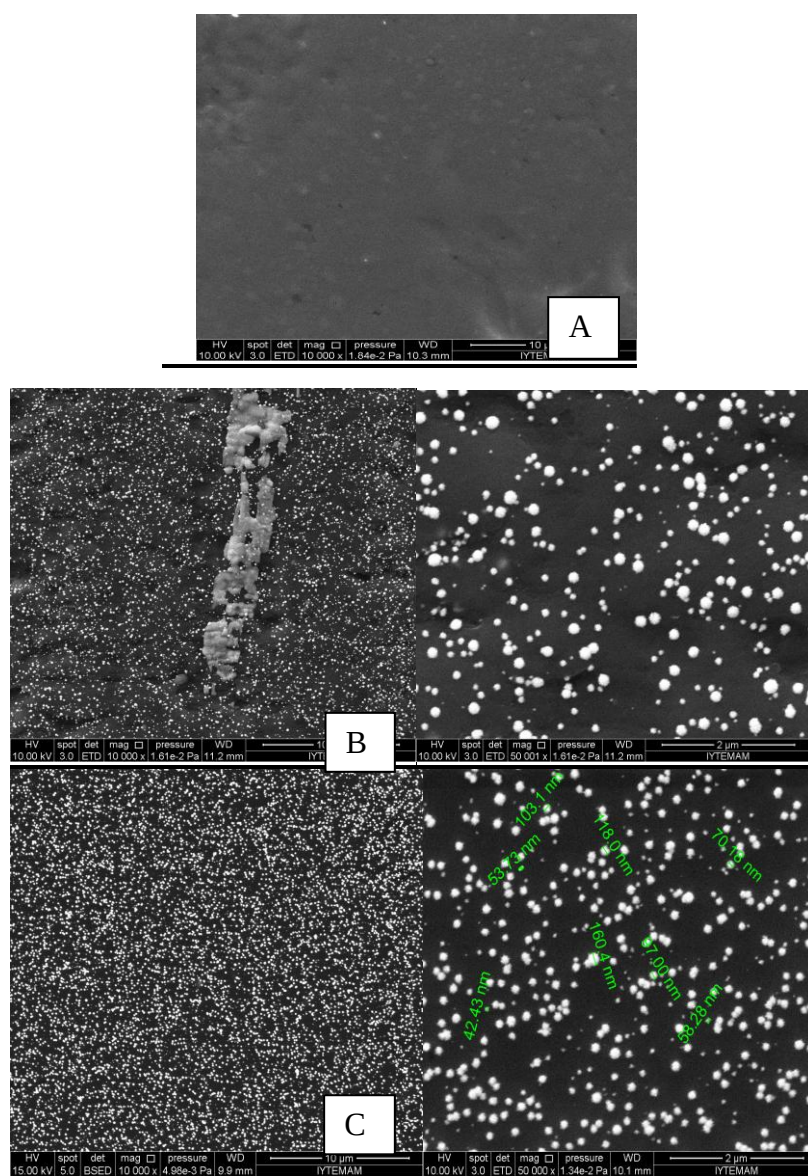


**Figure 3.15** SEM images of the A) PANI/GCE, B) Pt-PANI/GCE, C) Cu-Pt-PANI/GCE.

Energy dispersive X-Ray spectroscopy (EDX) study confirmed the presence of nano Cu and Pt particles decorating PANI/GCE, with the electrochemical deposition. Figure 3.16 shows the EDX images of Cu-Pt-PANI/GCE.

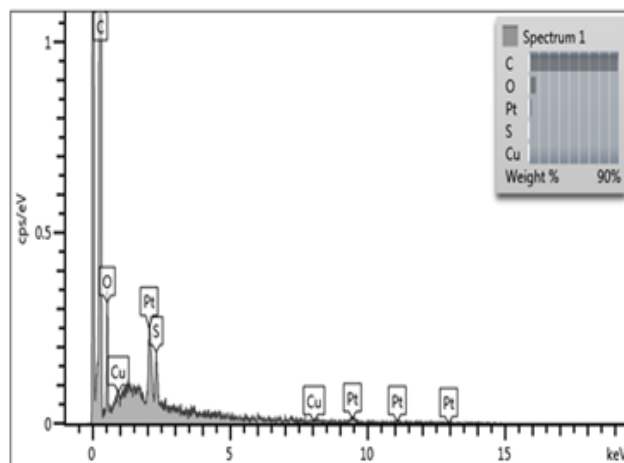


**Figure 3.16** EDX results of the Cu-Pt-PANI/GCE.

The weight gain of the PANI due to the Pt and Cu loading were about 2.87 % and 0.22 %, respectively, which was prepared consequently deposition Pt and Cu.

### 3.8.2 EIS chemical analysis of Pt and Cu nanoparticles modified PANI/GC electrode

Electrochemical impedance spectroscopy (EIS) is a method consisting of the application of a small current or voltage to an electrochemical system and monitoring the response of the system. Electrode properties were characterized using Nyquist plots from EIS measurements to better elucidate the interaction between the electrolyte, electrode surface and the charge transfer within catalytic structure. In impedance measurements, a sinusoidal potential variation is applied to the under studied electrodes such as; bare GCE, PANI/GCE, Pt-PANI/GCE and Cu-Pt-PANI/GCE. The Nyquist plots were obtained by 0.1 M  $\text{KNO}_3$  as a supporting electrolyte including 5.0 mM for both  $\text{K}_4\text{Fe}(\text{CN})_6$  and  $\text{K}_3\text{Fe}(\text{CN})_6$  at varying frequencies from 0.15 to 75000 Hz. The  $R_{ct}$  for the bare GCE is 927 ohm, which was higher than the  $R_{ct}$  values obtained for PANI/GCE (653 ohm). The  $R_{ct}$

values of Pt-PANI/GC and Cu-Pt-PANI/GC electrodes are 374 and 369  $\Omega$ , respectively.

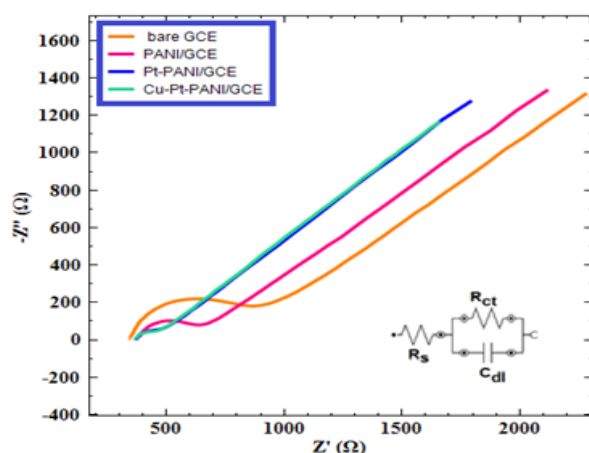


**Figure 3.17** The Nyquist plots of the Bare GCE, PANI/GCE, Pt-PANI/GCE and Cu-Pt-PANI/GCE. The frequency range was from 0.15 to 75000 Hz at the formal potential about 0.23 V.

This phenomenon indicated that the excellent electroconductibility of Cu-Pt bimetallic surface. These results obtained from EIS were in agreement with standard Randles equivalent-model circuit in the high frequency range (inset of Fig.3.17). This equivalent circuit consists of the ohmic resistance ( $R_s$ ) of the electrolyte solution, the double layer capacitance ( $C_{dl}$ ), electron-transfer resistance ( $R_{ct}$ ) resulting from the diffusion of ions from the bulk of the electrolyte to the interface. This low  $R_{ct}$  value for Cu-Pt/PANI/GCE implies that the charge transfer process is relatively fast compared to all other electrodes.

### 3.9 Voltammetric Behaviour of Methanol at Bare and Modified Electrodes

Figure 3.18 shows the cyclic voltammograms of bare GCE, PANI/GCE, Cu-PANI/GCE, Pt-PANI/GCE, Pt-Cu-PANI/GCE and Cu-Pt-PANI/GCE in 1M NaOH solution in the presence of 1.0 M methanol between the range of 0.8V - (-0.8)V. There was not observe any electrochemical signal for methanol at bare GCE, PANI/GCE, Cu-PANI/GCE and Pt-Cu-PANI/GCE but a low-defined

irreversible oxidation peak was appeared at -0.214 V on Pt-PANI/GCE in the case of narrow potential scan.

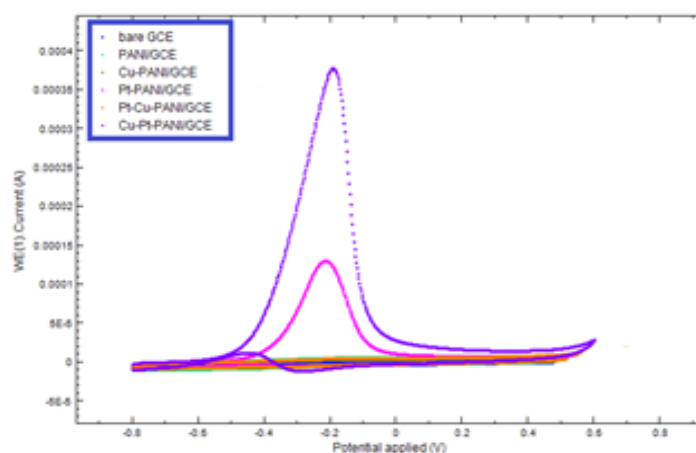


**Figure 3.18** Cyclic Voltammetric behaviors of a) bare GC, b) PANI-GC, c) Cu-PANI-GC d) Pt-PANI-GC ve e) Pt-Cu-PANI-GC ve f) Cu-Pt-PANI-GC electrodes in 1 M NaOH in the presence of 1.0 M methanol.

On the other hand, substantial increases in the peak current was also observed at Pt nanoparticles modified PANI/GCE due to the catalytic property gain to PANI by Pt nanoparticles. A higher catalytic activity in both peak current and negative potential manner for methanol oxidation was observed at Cu-Pt-PANI/GCE compare to Pt-PANI/GCE.

### 3.10 Optimization Studies of Methanol Oxidation at Cu-Pt-PANI/GCE

#### 3.10.1 Optimization of p-aniline concentration

To prepare optimum polymer film on the GCE surface, aniline monomer concentration was changed in the concentration range from  $1 \times 10^{-4}$  M to  $1 \times 10^{-2}$  M. The prepared polymer films electrodes were used for 1.0 M methanol oxidation in 1.0 M NaOH (Figure 3.19). Variation of aniline concentration during the electropolymerization caused a desirable change on peak current of methanol and the optimum peak characteristics were obtained for  $5 \times 10^{-4}$  M of aniline

monomer. Therefore it was chosen optimum monomer concentration  $5 \times 10^{-4}$  M for preparation of PANI/GCE for further studies.

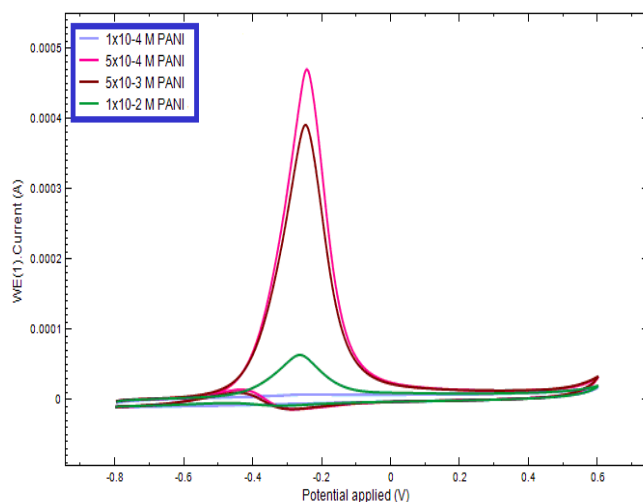


**Figure 3.19** Effect of p-aniline concentration of methanol oxidation.

**Table 3.1** The effect of PANI concentration of methanol oxidation.

| Aniline concentration (mol/L) | Peak current ( $\mu$ A) | Peak potential (mV) |
|-------------------------------|-------------------------|---------------------|
| $1 \times 10^{-4}$            | 2.398                   | -255.58             |
| $5 \times 10^{-4}$            | 464                     | -243.38             |
| $1 \times 10^{-3}$            | 99.381                  | -262.91             |
| $1 \times 10^{-2}$            | 59.085                  | -265.35             |

### 3.10.2 Optimization of cycle number during the polymerization of p-aniline

Figure 3.20 demonstrated the effect of potential scan cycle number on the electropolymerization of p-aniline on GCE for 1.0 M methanol oxidation in 1.0 M NaOH solution. Figure 3.20 inset shows the oxidation peak currents of methanol increased from 5 to 15 cycles of formation of PANI and then decreased for higher cycle numbers. This decrease can be explained to increase the electrode resistance and capacitance by increasing the polymer content on the GCE surface. The optimum polymerization cycle number was chosen as 10 cycle for future studies.

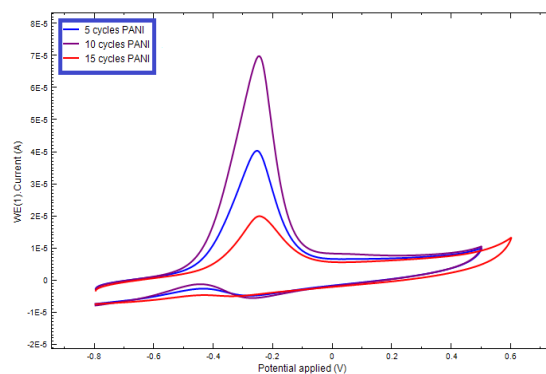


**Figure 3.20** Cyclic voltammograms of 1.0 M methanol in 1.0 M NaOH solution at different cycle polymerization number of PANI .

**Table 3.2** The effect of PANI cycle number on methanol oxidation.

| p-aniline cycle numbers | Peak Current ( $\mu\text{A}$ ) | Peak Potential (mV) |
|-------------------------|--------------------------------|---------------------|
| 5 cycles                | 37.056                         | -253.14             |
| 10 cycles               | 66.328                         | -245.82             |
| 15 cycles               | 16.925                         | -248.26             |

### 3.10.3 Optimization of sodium hydroxide concentration

The effect of NaOH concentrations on the methanol oxidation reaction was investigated in the concentration range of 0.1-2.0 M at Cu-Pt-PANI/GC electrode. As shown at Figure 3.21 the best catalytic activity and peak current was observed at in 1.0 M NaOH solution.

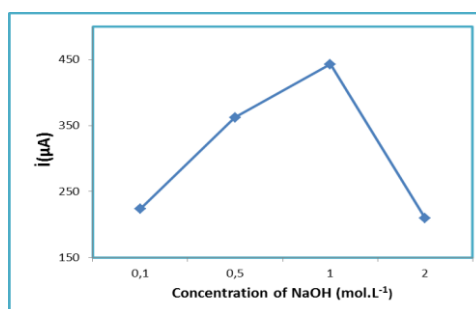


**Figure 3.21** The calibration curve of concentration of sodium hydroxide at Cu-Pt-PANI/GCE.

**Table 3.3** The effect of NaOH concentration on methanol oxidation.

| $C_{\text{NaOH}}$ (mol/L) | Peak current ( $\mu\text{A}$ ) | Peak potential (mV) |
|---------------------------|--------------------------------|---------------------|
| 0.1                       | 223.37                         | -101.93             |
| 0.5                       | 362.59                         | -140.99             |
| 1.0                       | 443.17                         | -143.43             |
| 2.0                       | 209.35                         | -226.44             |

### 3.10.4 The influence of chloroplatinic acid concentration for Pt nanoparticles formation and their effect on methanol oxidation

PANI was improved the catalytic activity of GCE toward the electrooxidation of methanol. It is well known that, metal nano particles modified polymer film electrodes exhibited higher catalytic activity for electrochemical reaction of many organic compounds.

Figure 3.22 shows the effect of chloroplatinic acid concentration for Pt nanoparticles formation on 1.0 M methanol oxidation in 1.0 M NaOH solution. The chloroplatinic acid concentration was investigated in the concentration range of  $5.0 \times 10^{-4}$  -  $2.0 \times 10^{-3}$  M. The optimum peak characteristics were obtained for  $2 \times 10^{-3}$  M of Pt nanoparticles.

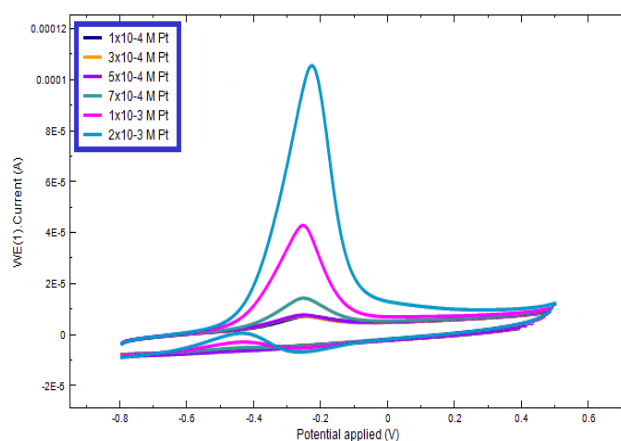


**Figure 3.22** Cyclic voltammograms for methanol oxidation in the presence of different concentration chloroplatinic acid.

**Table 3.4** The effect of Pt nanoparticles concentration on methanol oxidation.

| Pt Nanoparticles Concentration (mol/L) | Peak Current ( $\mu\text{A}$ ) | Peak Potential (mV) |
|----------------------------------------|--------------------------------|---------------------|
| $5 \times 10^{-4}$                     | 4.664                          | -258.03             |
| $7 \times 10^{-4}$                     | 11.419                         | -253.14             |
| $1 \times 10^{-3}$                     | 39.376                         | -255.58             |
| $2 \times 10^{-3}$                     | 101.73                         | -226.29             |

### 3.10.5 The influence of nano Pt particles cycle number on methanol oxidation

The effect of potential scan cycle number during the electrodeposition of Pt metal nanoparticles on PANI/GCE investigated for 1.0 M methanol oxidation in 1.0 M NaOH solution. As seen in Figure 3.23, higher peak current was obtained with 15cycles deposition of Pt metal. Bu the optimum cycle number was choosen as 10 cycles for future studies.

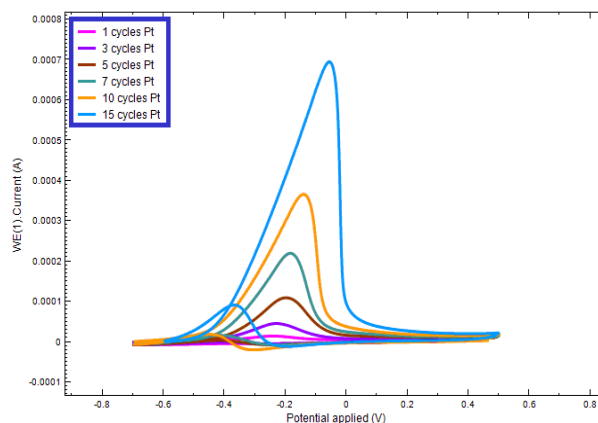


**Figure 3.23** Cyclic voltammogram for methanol oxidation at different cycle number of Pt particle deposition.

**Table 3.5** The effect of Pt nanoparticles cycle number on methanol oxidation.

| Pt nanoparticles cycle numbers | Peak current ( $\mu\text{A}$ ) | Peak potential (mV) |
|--------------------------------|--------------------------------|---------------------|
| 1 cycles                       | 12.161                         | -245.82             |
| 3 cycles                       | 42.143                         | -231.17             |
| 5cycles                        | 104.9                          | -197.14             |
| 7 cycles                       | 214.45                         | -182.5              |
| 10 cycles                      | 357.78                         | -140.99             |
| 15 cycles                      | 684.38                         | -55.542             |

### 3.10.6 The influence of copper sulphate solution concentration for Cu nanoparticles formation and their effect on methanol oxidation

The effect of copper sulphate concentrations during the Cu nanoparticles formation on the PANI/GCE and their effect on the methanol oxidation reaction was investigated in the concentration range of  $10^{-4}$  M -  $10^{-3}$  M at 7 cycles Cu MNP modified PANI/GCE. The maximum peak and negative potential observed for  $3 \times 10^{-4}$  M that it was chosen for further studies.

**Table 3.6** The effect of Cu nanoparticles concentration on methanol oxidation

| Cu Nanoparticles Concentration (mol/L) | Peak Current ( $\mu\text{A}$ ) | Peak Potential (mV) |
|----------------------------------------|--------------------------------|---------------------|
| $1 \times 10^{-4}$                     | 245.38                         | -170.29             |
| $3 \times 10^{-4}$                     | 315.81                         | -170.29             |
| $5 \times 10^{-4}$                     | 291.06                         | -167.85             |
| $1 \times 10^{-3}$                     | 287.5                          | -165.41             |

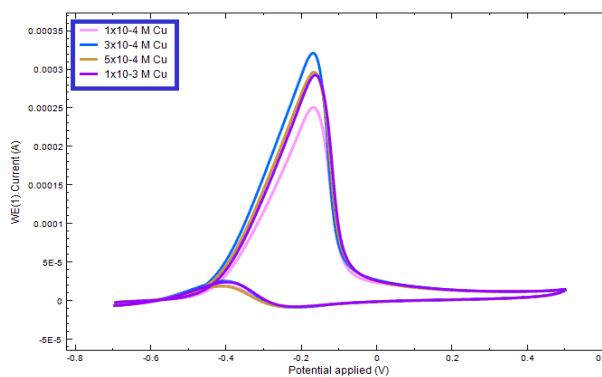


**Figure 3.24** The effect of Cu nanoparticles concentration on Pt-PANI/GCE for methanol oxidation.

### 3.10.7 The influence of Cu nanoparticles cycle number on methanol oxidation

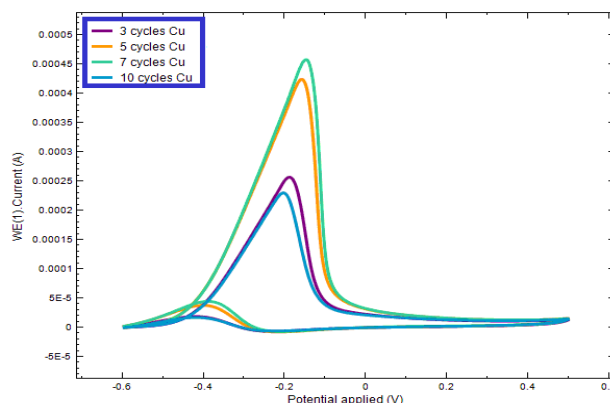


**Figure 3.25** The effect of Cu ( $3 \times 10^{-4}$  M) nanoparticles cycle number on Pt-PANI/GCE for methanol oxidation.

For the optimization of Cu deposition on the Pt-PANI/GCE surface, the cycle number effect on the electrochemical oxidation of methanol was also investigated (Figure 3. 25). The amount, the size even the shape of the deposited Cu nano particles were controlled by changing the cyclic number (n) in electrodeposition process. The maximum peak current was obtained for methanol oxidation Cu-Pt-PANI/GCE which was prepared after 7 cycling Cu deposition.

**Table 3.7** The effect of Cu nanoparticles cycle number on methanol oxidation

| Cu nanoparticles cycle number | Peak current ( $\mu\text{A}$ ) | Peak potential (mV) |
|-------------------------------|--------------------------------|---------------------|
| 3 cycles                      | 252.24                         | -187.38             |
| 5 cycles                      | 418.11                         | -158.08             |
| 7 cycles                      | 451.32                         | -148.32             |
| 10 cycles                     | 225.07                         | -204.47             |

### 3.10.8 Scan rate study at $\text{Cu}_{(7\text{cyc})}\text{-Pt}_{(10\text{cyc})}\text{-PANI}_{(10\text{cyc})}/\text{GCE}$

In order to confirm the electrode behaviour on the oxidation of methanol, a series of cyclic voltammograms were recorded at  $\text{Cu}_{(7\text{cyc})}\text{-Pt}_{(10\text{cyc})}\text{-PANI}/\text{GC}$  electrode by varying potential scan rate. The oxidation peak current increased linearly with the square root of the scan rate (Figure 3.26), suggesting that methanol oxidation reaction at this modified electrode was controlled by diffusion. The oxidation peak potential of methanol shifted positive values with increasing the scan rate, indicating that the electron transfer was irreversible.

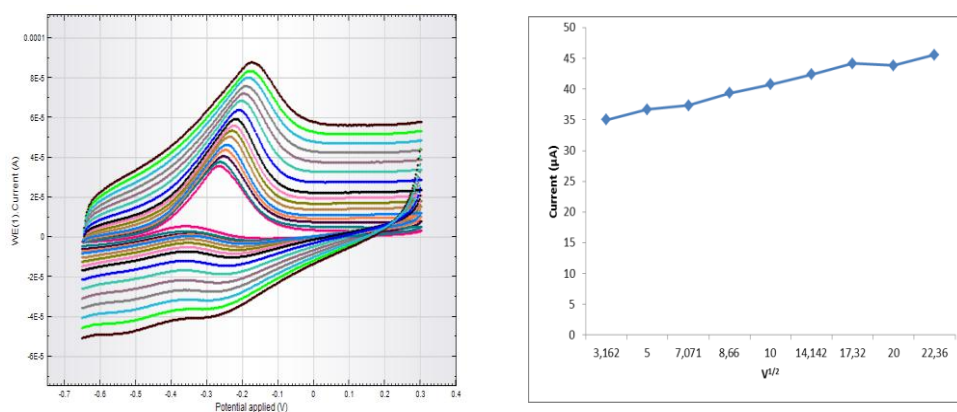


**Figure 3.26** Cyclic voltammogram for methanol oxidation of  $\text{Cu}_{(7\text{cyc})}\text{-Pt}_{(10\text{cyc})}\text{-PANI}/\text{GC}$  electrode at different scan rates (10, 25, 50, 75, 100, 150, 200, 250, 300, 400, 500, 600, 700, 800, 900, 1000 mV/s ).

The dependence of peak current on the concentration of methanol was obtained as linear while accompanied by the peak potential shift to positive values (Fig.3.27).

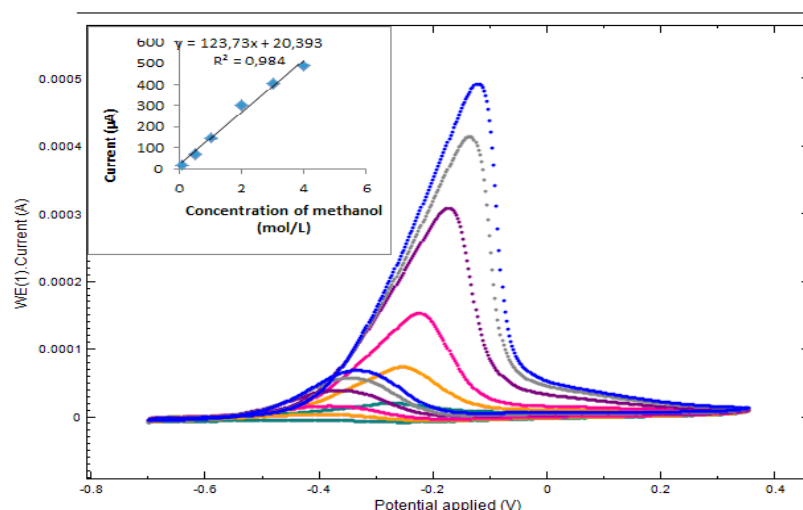


**Figure 3.27** Cycling voltammograms at Cu-Pt-PANI/GCE for increasing concentrations of methanol in 1.0 M NaOH solution with scan rate 50 mV/s. (Inset: Corresponding calibration curve of increasing methanol concentrations). Methanol concentrations 0.1 M, 0.5 M, 1.0 M, 2.0 M, 3.0 M, 4.0 M.

### 3.11 Preparation of Poly (aniline) (PANI) Film Modified GCE

Fig.3.28 shows the cyclic voltammograms of polyaniline film growth during electrodeposition from the solution consisting of  $10^{-3} \text{ mol L}^{-1}$  aniline and  $0.1 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$  by cyclic voltammetry at  $50 \text{ mV s}^{-1}$ , between -0.2 and 0.9 V. At the anodic scan, an irreversible oxidation peak was observed at 0.23 V depending on oxidation of aniline. The peak current increasing with cycles of CV showed that, an electropolymerization takes place easily the content of polymer on the GCE surface.

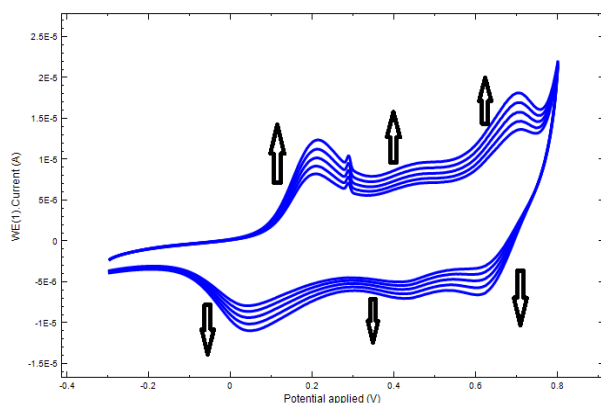


**Figure 3.28** Shows multisweep cyclic voltammograms of Poly(aniline) electropolymerization on GCE surface in  $\text{H}_2\text{SO}_4$  solution containing  $10^{-3}$  M aniline by cycling the potential from -0,200 to +0,900 V vs. Ag / AgCl (sat. KCl) at a scan rate of 50 mV /s for 5 cycles.

### 3.12 Electrochemical Deposition of Ni Nanoparticles on the MWCNT-PANI/GC Electrode from in the Presence Of $\text{Ni}^{2+}$ Solution

Voltammetric behaviour of MWCNT-PANI/GCE was studied in the presence of  $\text{NiSO}_4 + 0.1$  M  $\text{H}_2\text{SO}_4$  in Figure 3.29. The growth of Ni nano particles on the MWCNT-PANI/GCE surface corresponds to a reduction peak at -0.276 V and oxidation peak at -0.237 V in Figure 3.29. The increasing of the reduction peaks depending on cycle number showed that electrodeposition of metal nano particles were carried out on the MWCNT-PANI/GCE surfaces. Stable peak currents were observed for both reduction and oxidation on the electrode reaction after the 15 CV cycles.

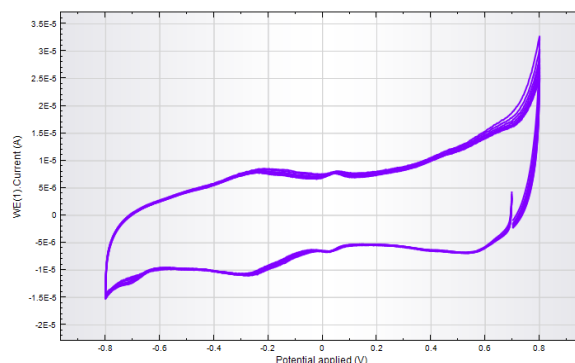


**Figure 3.29** Ni nanoparticles deposition on MWCNT-PANI/GCE, at 50 mV/s for 15 cycles in 1 mM NiSO<sub>4</sub> solution.

### 3.13 Surface Characterization of PANI/GCE, MWCNT-PANI/GCE and Ni Nano Particles Modified MWCNT-PANI/GCE

#### 3.13.1 SEM and EDX characterization Ni nanoparticles modified MWCNT-PANI/GC electrode

Figure 3.30 shows the SEM images of PANI/GC, MWCNT-/PANI/GC and MWCNT-PANI/GC electrodes modified with Ni nano particles. The morphology of MWCNT on PANI-GCE showed a network-like structure in Figure 3.30 B.

On the other hand, the SEM image of Ni-MWCNT-PANI/GCE shows many observable light dots on network-like structure in SEM image of MWCNT-PANI/GCE given in Figure 3.30.C. This SEM image confirms that nickel nanoparticles were bounded to MWCNT-PANI with almost uniform distribution.

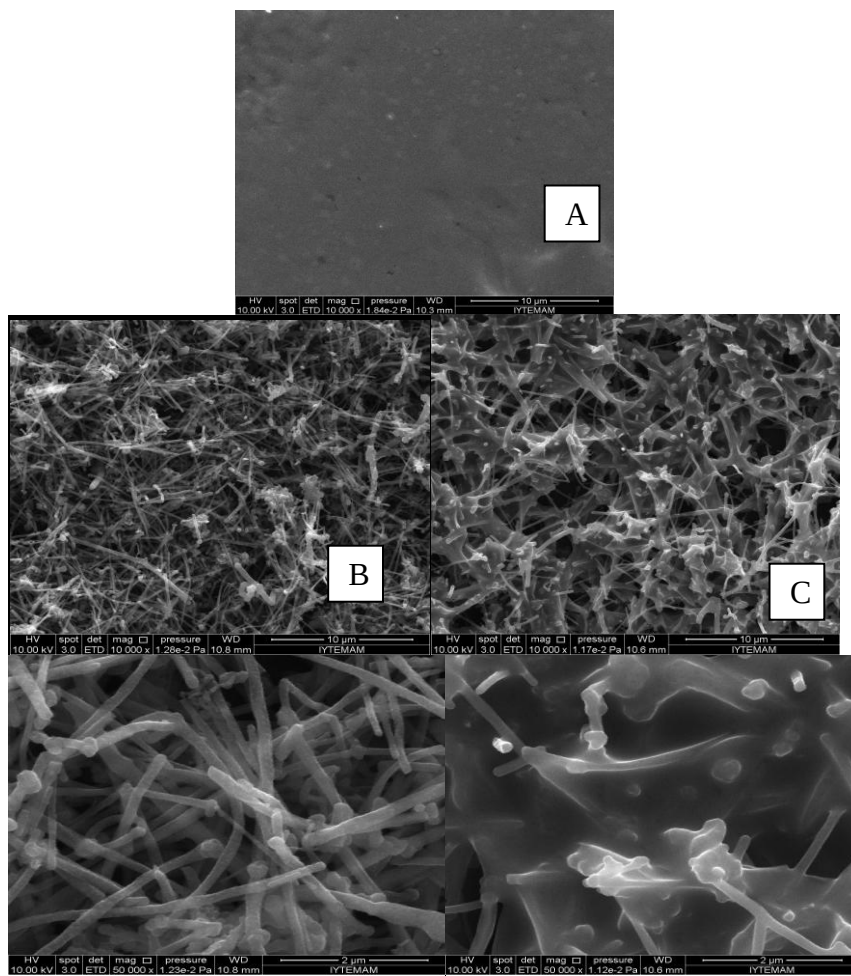


**Figure 3.30** SEM images of A) PANI/GCE B) MWCNT-PANI/GCE C) Ni-MWCNT-PANI/GCE.

Energy dispersive X-ray (EDX) spectroscopy study confirmed the presence of nano Ni particles on MWCNT-PANI/GCE. The weight gain of the MWCNTs due to the Ni loading was about 0.33% (Figure 3.31).

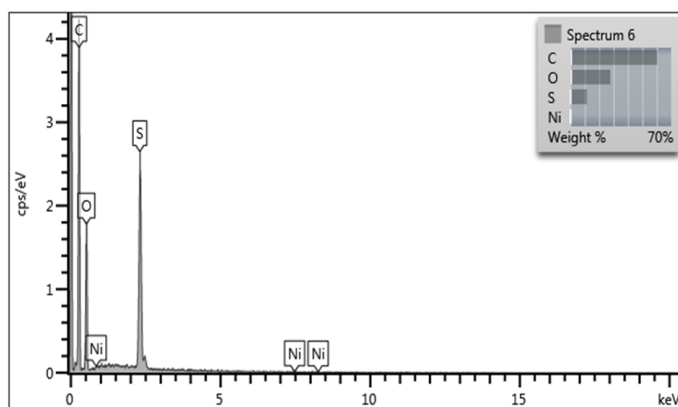


**Figure 3.31** EDX spectrum of Ni-MWCNT-PANI/GCE

### 3.13.2 EIS chemical analysis of Ni nanoparticles modified MWCNT-PANI/GC electrode

Fig.3.32 illustrates the results of electrochemical impedance spectroscopy (EIS) on bare GCE, PANI/GCE, MWCNT/GCE, MWCNT-PANI/GCE and Ni-MWCNT-PANI/GCE in the presence 5.0 mM  $K_3[Fe(CN)_6]/K_4[Fe(CN)_6]$  containing 0.1 M  $KNO_3$  solution at varying frequencies from 0.15 to 75000 Hz. It can be seen that all electrodes represents a semicircular and a linear portion. The semicircle corresponds to the charge transfer process through the GCE and polymer films at high frequencies, whereas the second one was due to the diffusion process in the low frequencies. The diameter of the semicircle represents the magnitude of  $R_{ct}$  at the electrode surface. The obtained EIS data were fitted with an equivalent circuit as given in Fig. 3.32 inset. This equivalent circuit consists of the ohmic resistance ( $R_s$ ) of the electrolyte solution, the double layer capacitance ( $C_{dl}$ ), electron-transfer resistance ( $R_{ct}$ ) resulting from the diffusion of ions from the bulk of the electrolyte to the interface. This equivalent circuit was used to fit the impedance spectra and extract the values of  $R_{ct}$  (Fig. 3.32 inset). The  $R_{ct}$  for the bare GCE is 927 ohm, which was higher than the  $R_{ct}$  values obtained for PANI/GCE (653 ohm) and MWCNT/GCE (902.06). The  $R_{ct}$  values MWCNT-PANI/GC electrode is 512  $\Omega$ . The  $R_{ct}$  values of Ni metallic surface was obviously decreased (449  $\Omega$ ). This phenomenon indicated that the excellent electroconductibility of Ni metallic surface. Moreover, the Ni-MWCNT-PANI film was successfully formed on the GCE surface. These results obtained from EIS were in agreement with standard Randles equivalent-model circuit in the high frequency range (inset of Fig.3.32). This equivalent circuit consists of the ohmic resistance ( $R_s$ ) of the electrolyte solution, the double layer capacitance ( $C_{dl}$ ), electron-transfer resistance ( $R_{ct}$ ) resulting from the diffusion of ions from the bulk of the electrolyte to the interface. This low  $R_{ct}$  value for Ni-MWCNT-PANI/GCE implies that the charge transfer process is relatively fast compared to all other electrodes.

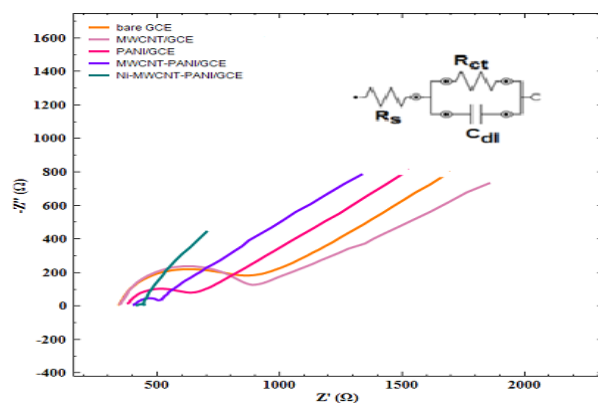


**Figure 3.32** The Nyquist plots of the Bare GCE, PANI/GCE, MWCNT/GCE, MWCNT-PANI/GCE and Ni-MWCNT-PANI/GCE. The frequency range was from 0.15 to 75000 Hz at the formal potential about 0.23 V.

### 3.14 Voltammetric Behaviour of Catechol at Bare and Modified Electrodes

Figure 3.33 shows the cyclic voltammograms of bare GCE, PANI/GCE, MWCNT-PANI/GCE and Ni nano particles modified MWCNT-PANI/GC electrodes in pH=7 PBS in the presence of  $5 \times 10^{-4}$  mol catechol between the potential range of 1V - (-0.3) V. An reversible electrochemical behaviour was observed at bare GC MWCNT/GC and Ni-MWCNT-PANI/GC electrodes for catechol. There was not observe any electrochemical signal for catechol at PANI/GCE. The oxidation of catechol to benzoquinone was observed at 257, 274, 270 mV and the reduction of benzoquinone was appeared at 184, 159, 170 mV at bare GCE, MWCNT-PANI/GCE and Ni-MWCNT-PANI/GCE, respectively.

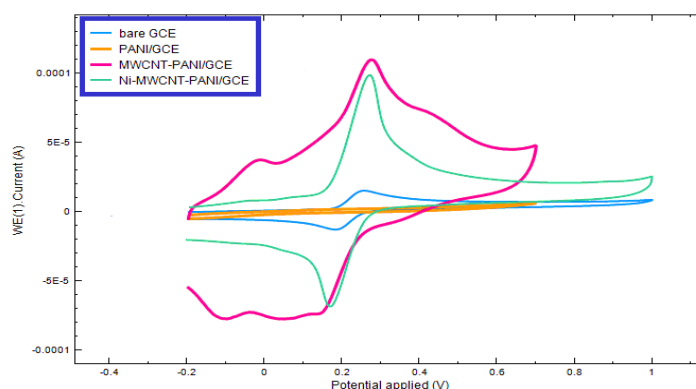


**Figure 3.33** Cyclic Voltammetric behaviors of bare GC, PANI/GC, MWCNT-PANI/GC and Ni nano particles modified MWCNT-PANI/GC electrodes in pH=7 PBS in the presence of  $5 \times 10^{-4}$  mol catechol between the range of 1V - (-0.3) V.

On the other hand, substantial increases in the peak current was also observed at Ni nanoparticles modified MWCNT-PANI/GCE due to the catalytic property gain to MWCNT-PANI by Ni nanoparticles. A higher catalytic activity in both peak current and potential manner for catechol was observed at Ni modified MWCNT-PANI/GCE compare to bare GCE. Also the electrochemical oxidation of catechol oxidative peak was observed at +0,270 V in the presence of  $5 \times 10^{-4}$  M catechol in pH=7 PBS (Ni-MWCNT-PANI/GCE). The remarkably enhanced signal of catechol electrochemical behaviour at Ni-MWCNT-PANI/GC electrode can be attributed increasing the effective surface area and improve the conductivity of the modified electrode surfaces which can be played important role to accelerate the electron transfer.

### 3.15 Optimization Studies for Catechol at Ni-MWCNT-PANI/GCE

#### 3.15.1 Effect of supporting electrolyte pH on cyclic voltammetric behavior of catechol

The effect of pH on the peak currents and peak potentials of the electrocatalytic oxidation of catechol were investigated for  $5 \times 10^{-4}$  M catechol at bare GCE (Figure 3. 34) by CV techniques in the pH range of 3.76-10.15.

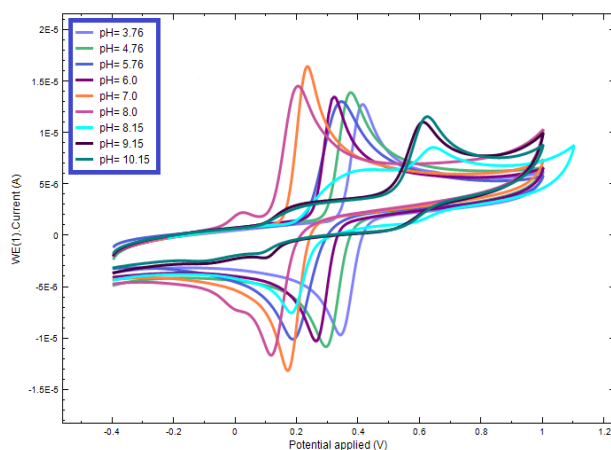


**Figure 3.34** Cyclic Voltammograms of electrooxidation of catechol at bare electrode in various pH (3.76 to 10.15) at a scan rate of 50 mV/s.

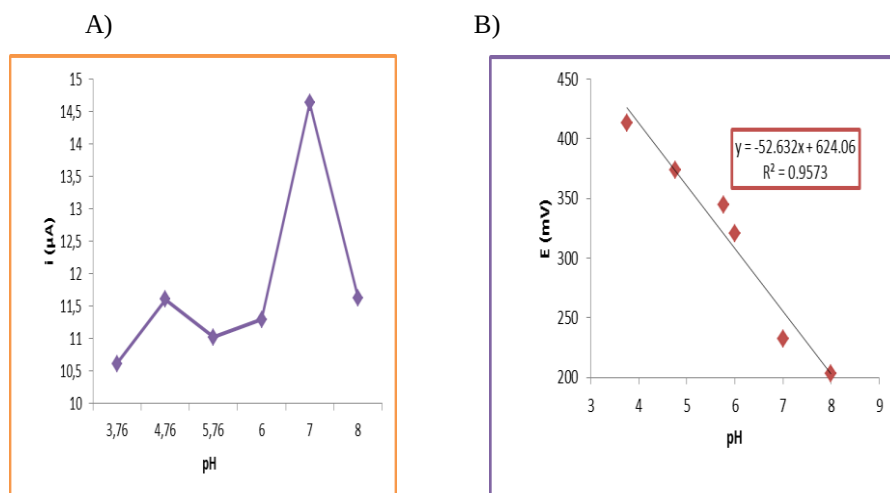


**Figure 3.35** Influence of the pH on A) peak current and B) peak potential for catechol on the Ni-MWCNT-PANI/GCE with cyclic voltammetry (pH: 3.76 to 8).

The peak potentials for catechol showed same trend and shift almost linearly towards negative potentials when pH was increased in the range of 3.76- 8, indicating that proton ions were directly involved in the rate determination step of the oxidation of the analytes. The results showed that the oxidation process of catechol can be occurred by two-electron transfer thus the proton numbers can be also suggested as two for catechol oxidation. As seen the Figure 3.35 optimum pH for catechol future study was observed at pH 7.0 PBS.

### 3.15.2 Optimization of p-Aniline concentration

The effect of p-anilin concentration on catechol voltammetric behaviour was shown in Fig. 3.36 during poly aniline film formation and then prepared MWCNT/PANI composite electrode modified with Ni nano particles. A higher catechol oxidation peak current was obtained in the presence of  $1 \times 10^{-3}$  M p-aniline concentration compare the others. Therefore,  $1 \times 10^{-3}$  M p-aniline concentration was preferred as optimum concentration for further studies.

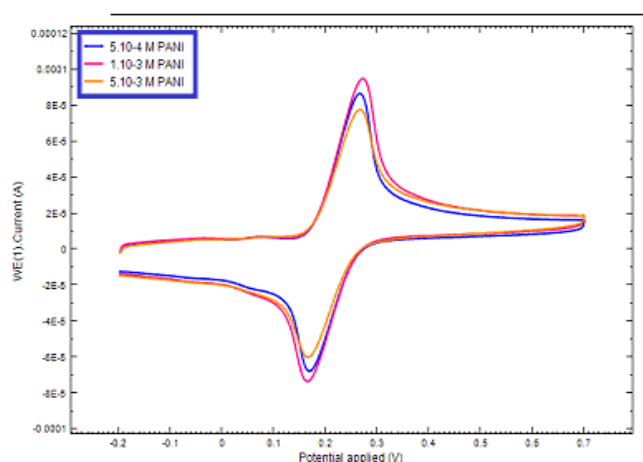


**Figure 3. 36** The effect of PANI concentration of catechol.

**Table 3.8** The effect of PANI concentration on electrochemical of catechol

| PANI concentration<br>(mol/L) | Peak current<br>( $\mu$ A) | Peak potential<br>(mV) |
|-------------------------------|----------------------------|------------------------|
| $5 \times 10^{-4}$            | 78.357                     | 266.27                 |
| $1 \times 10^{-3}$            | 85.517                     | 271.15                 |
| $5 \times 10^{-3}$            | 67.806                     | 266.27                 |

### 3.15.3 Optimization of cycle number for electropolymerization of p-aniline

Figure 3.37 demonstrated the effect of  $1 \times 10^{-3}$  M aniline cycle number during the polymerization process on the response of on  $5 \times 10^{-4}$  M catechol electrochemical behaviour at pH 7.0 of PBS. Figure 3.37 shows the oxidation

peak currents for catechol increased from 3 to 5 cycles of PANI and then decreased for higher cycle numbers. This decrease can be explained to increase the electrode resistance and capacitance by increasing the polymer content on the GCE surface. Therefore 5 cycles number as optimum cycle number for future studies.

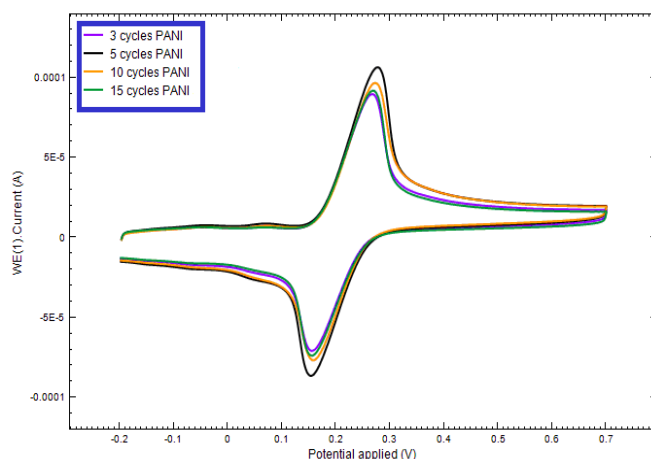


**Figure 3.37** The effect of PANI ( $10^{-3}$  M) cycle number of catechol.

**Table 3.9** The effect of PANI cycle number on electrochemical of catechol

| Cycle number of PANI | Peak current ( $\mu\text{A}$ ) | Peak potential(mV) |
|----------------------|--------------------------------|--------------------|
| 3 cycles             | 80.945                         | 266.27             |
| 5 cycles             | 95.833                         | 276.03             |
| 10 cycles            | 86.938                         | 271.15             |
| 15 cycles            | 83.364                         | 268.71             |

#### 3.15.4 The influence of nickel sulphate concentration for Ni nanoparticles formation and their effect on catechol oxidation

The effect of  $\text{Ni}^{+2}$  concentrations for Ni nano particles modification on the MWCNT-PANI/GCE and their effect on the catechol electrochemical reaction was investigated in the concentration range of  $5 \times 10^{-4}\text{M}$  -  $5 \times 10^{-3}\text{M}$  at 10 cycles Ni MNP modified MWCNT-PANI/GCE. The maximum peak observed for  $10^{-3}\text{M}$  that it was chosen for further studies.

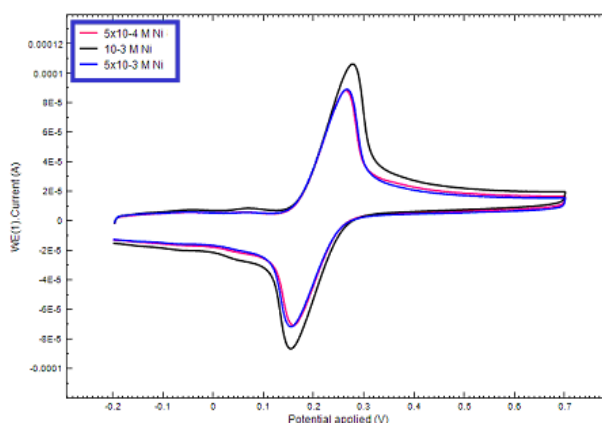


**Figure 3.38** The effect of Ni nanoparticles concentration on catechol.

**Table 3.10** The effect of Ni nanoparticles concentration on electrochemical of catechol

| Ni nanoparticles concentration (M) | Peak current ( $\mu\text{A}$ ) | Peak potential (mV) |
|------------------------------------|--------------------------------|---------------------|
| $5 \times 10^{-4} \text{ M}$       | 80.549                         | 263.82              |
| $1 \times 10^{-3} \text{ M}$       | 95.833                         | 276.03              |
| $5 \times 10^{-3} \text{ M}$       | 81.360                         | 266.27              |

### 3.15.5 The influence of nano Ni particles cycle number on catechol

Ni nanoparticles modified MWCNT-PANI/GC electrodes prepared with different coverage depending on the cycle number of CV that was examined by changing the cycle numbers Ni deposition to obtain most appropriate surface toward catechol electrochemical behaviour. The amount and the size of the deposited Ni nanoparticles were controlled by changing the cycle number in electrodeposition process. It was clearly seen in Figure 3.39 that the peak potential of analyte was not changed whereas the maximum peak current was obtained for catechol at 15 consecutive scans deposition procedure of Ni nano particles modified MWCNT-PANI/GCE.

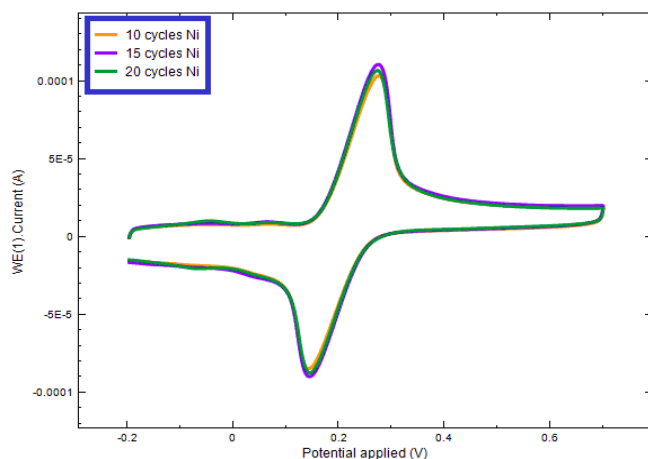


**Figure 3.39** Cyclic voltammogram for catechol at different cycle number of Ni ( $10^{-3}\text{M}$ ) particle deposition.

**Table 3.11** The effect of cycle number of Ni nanoparticles on electrochemical of catechol

| Cycle number of $\text{Ni}^{+2}$ | Peak current ( $\mu\text{A}$ ) | Peak potential (mV) |
|----------------------------------|--------------------------------|---------------------|
| 10 cycles                        | 92.871                         | 276.03              |
| 15 cycles                        | 99.428                         | 273.59              |
| 20 cycles                        | 95.781                         | 273.59              |

As a result, optimum conditions of experimental parameters was summarized at Table 3.12.

**Table 3.12** Optimum conditions of experimental parameters for catechol

| Experimental parameter           | Optimum Conditions |
|----------------------------------|--------------------|
| pH of supporting electrolyte     | pH 7PBS            |
| PANI concentration               | 1 mmol/L           |
| Cycle number of PANI             | 5 cycles           |
| Ni nanoparticles concentration   | 1 mmol/L           |
| Cycle number of Ni nanoparticles | 15 cycles          |

### 3.15.6 Scan rate study at bare GCE and Ni<sub>(15cyc)</sub>-MWCNT-PANI/GCE

In order to confirm the electrode behaviour on the catechol, a series of cyclic voltammograms were recorded at bare GC and Ni<sub>(15cyc)</sub>-MWCNT-PANI/GC electrode by varying potential scan rate. The oxidation peak current increased linearly with the square root of the scan rate (Figure 3.40 and 3.41), suggesting that catechol oxidation reaction at this modified electrode was controlled by diffusion. The oxidation peak potential of catechol shifted positive values with increasing the scan rate, indicating that the electron transfer was quasireversible.

#### 3. 15. 6. 1 Scan rate study at bare GCE

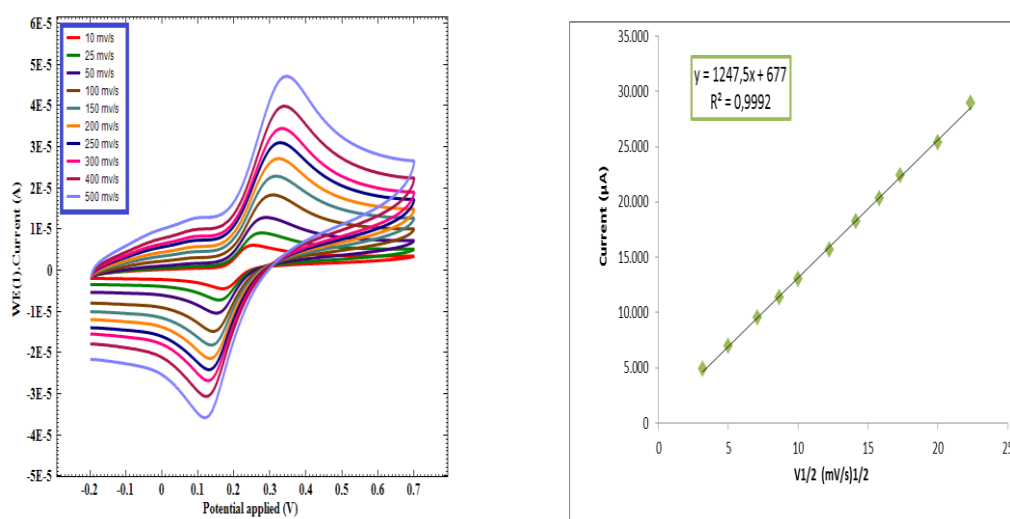


**Figure 3.40** Cyclic voltammogram for catechol of bare GC electrode at different scan rates (10, 25, 50, 75, 100, 150, 200, 250, 300, 400, 500 mV/s ).

### 3. 15. 6. 2 Scan rate study at Ni(15cyc)-MWCNT-PANI/GCE

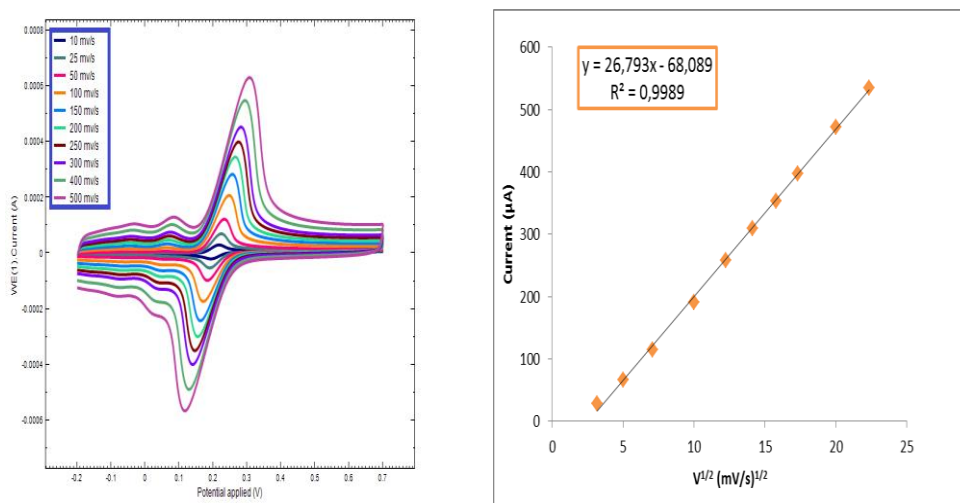


**Figure 3.41** Cyclic voltammogram for catechol of Ni<sub>(15cyc)</sub>-MWCNT-PANI/GC electrode at different scan rates (10, 25, 50, 75, 100, 150, 200, 250, 300, 400, 500 mV/s).

### 3.15.7 Differential pulse voltammetric determination of catechol

Determination of catechol is critical importance in the field of medical applications and food industry. Since differential pulse voltammetry has a much current sensitivity and better separation the analyte peaks than CV, the electroanalytical technique was used for determination of catechol. Limit of detection values were calculated from (S/N:3) and calibration curves. The average value of background current estimated from 10 different voltammograms.

Since differential pulse voltammetry has a much current sensitivity and better separation the analyte peaks than CV, the electroanalytical technique was used for individual and simultaneous determination catechol.

Initial studies with DPV was focused on the electrochemical respons of increasing catechol concentrations at Ni-MWCNT-PANI/GCE in pH 7 PBS. Electrode response was given in Figure 3.42. The catechol oxidation was observed at 203 mV on Ni-MWCNT-PANI/GCE. The electrochemical respons of catechol was increased linearly with the increase of catechol concentration in the range of

$2 \times 10^{-6} \text{ M} - 8 \times 10^{-5} \text{ M}$  at Ni-MWCNT-PANI/GCE .The linear regression equations of Ni-MWCNT-PANI/GCE could be expressed as  $R^2 = 0.9912$ .

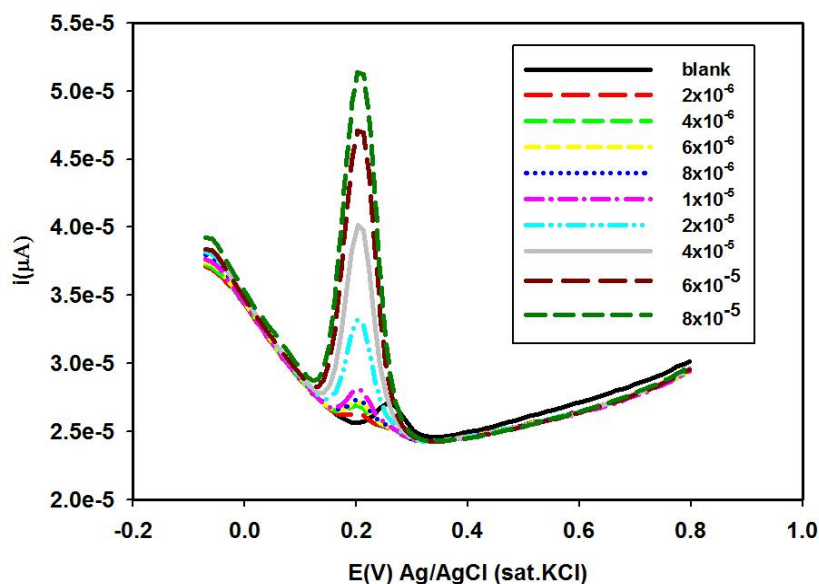


**Figure 3.42** Differential pulse voltammograms at Ni-MWCNT-PANI/GCE for increasing concentrations of catechol in with scan rate 10 mV/s and pulse amplitude 50 mV.(Inset: Corresponding calibration curve of increasing catechol concentrations). catechol concentrations 0 M,  $2 \times 10^{-6} \text{ M}$ ,  $4 \times 10^{-6} \text{ M}$ ,  $6 \times 10^{-6} \text{ M}$ ,  $8 \times 10^{-6} \text{ M}$ ,  $1 \times 10^{-5} \text{ M}$ ,  $2 \times 10^{-5} \text{ M}$ ,  $4 \times 10^{-5} \text{ M}$ ,  $6 \times 10^{-5} \text{ M}$ ,  $8 \times 10^{-5} \text{ M}$ .

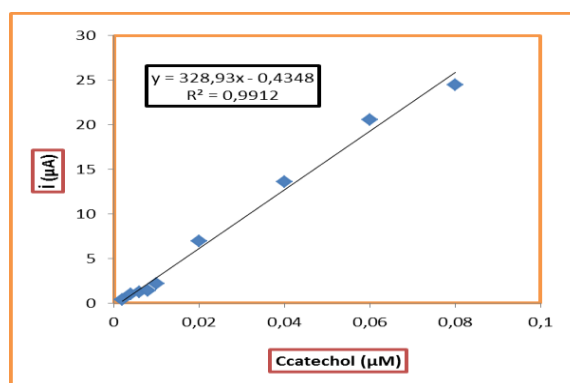


**Figure 3.43** Calibration curve for the determination of catechol using Ni-MWCNT-PANI/GCE.

From the DPV studies results, limit of detection value was calculated as  $1.628 \times 10^{-6}$  M (S/N=3).

Finally, limit of detection (LOD) and linear concentration range of catechol detections at Ni-MWCNT-PANI/GCE was listed in Table 3.13.

**Table 3.13** Limit of detection (LOD) and linear concentration range of Ni-MWCNT-PANI/GCE for catechol in this thesis.

| Analyte      | Catechol                                   |
|--------------|--------------------------------------------|
| Electrode    | Ni-MWCNT-PANI/GCE                          |
| Linear range | $1 \times 10^{-6}$ M- $8 \times 10^{-5}$ M |
| LOD          | $1.628 \times 10^{-6}$ M                   |

\*LOD values calculated from calibration curve.

### 3.15.8 Sample analysis

#### Sample 1

The method was applied to the samples of green tea which could be contain catechol. Figure 3.44 shows the standard addition DP voltammograms obtained for catechol sample. The sample was treated as given in experimental section. As can be seen from the figure, standard addition graph was constructed. 0.0018 mM (198 mg/g) catechol concentration was obtained at Ni-MWCNT-PANI/GCE.

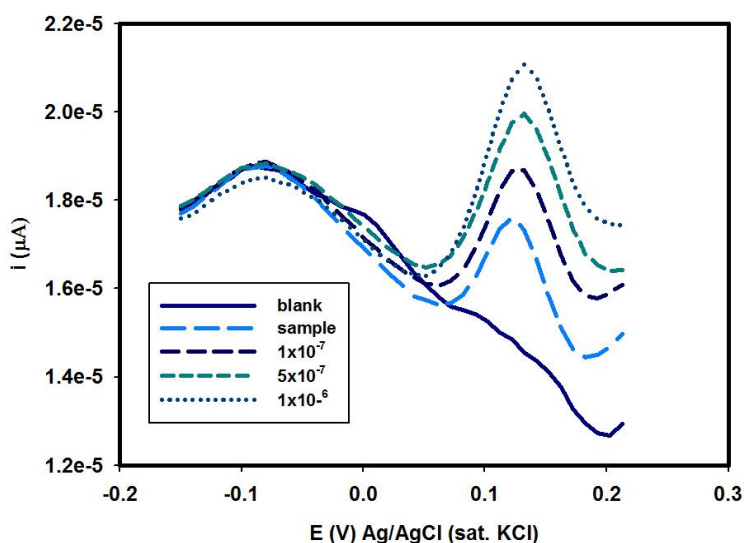


**Figure 3.44** Differential pulse voltammograms at Ni-MWCNT-PANI/GCE, sample in pH 7.0 PBS, 0 M,  $1 \times 10^{-7}$  M,  $5 \times 10^{-7}$  M,  $1 \times 10^{-6}$  M, inset: standart addition curves.

Figure 3.45 shows the standard addition at Ni-MWCNT-PANI/GCE obtained for catechol samples. The calibration curve for catechol samples at Ni-MWCNT-PANI/GCE was found linear  $y = 1885,7x + 3,3656$  ( $R^2 = 0.9984$ ).

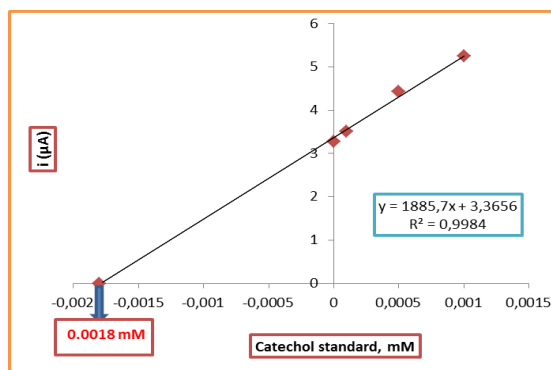


**Figure 3.45** Standard addition graph of green tea with Ni-MWCNT-PANI modified GCE.

## Sample 2

To determine the relevancy of the Ni-MWCNT-PANI/GCE, the electrode was applied to determine catechol concentration in black tea by the standard addition method under the optimized conditions. As can be seen from the figure, standard addition graph was constructed. 0.00469 mM (291 mg/g) catechol concentration was obtained at Ni-MWCNT-PANI/GCE.

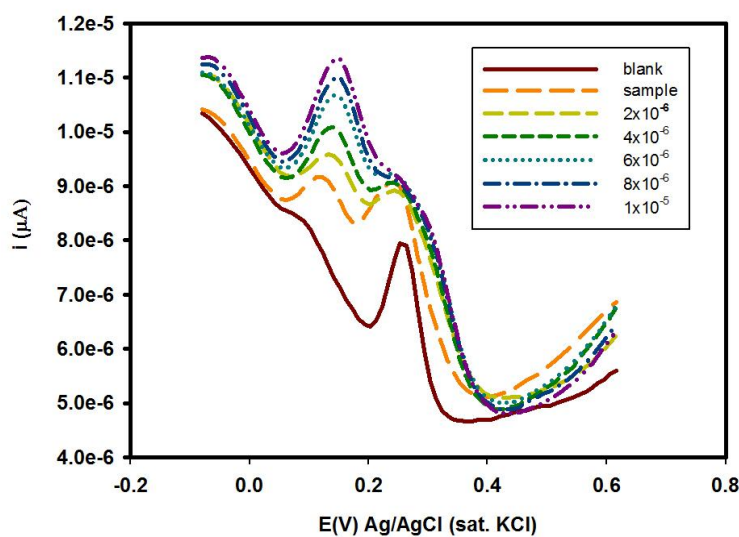


**Figure 3.46** Differential pulse voltammograms at Ni-MWCNT-PANI/GCE, sample in pH 7.0 PBS, 0,  $2 \times 10^{-6}$  M,  $4 \times 10^{-6}$  M,  $6 \times 10^{-6}$  M,  $8 \times 10^{-6}$  M,  $1 \times 10^{-5}$  M, inset: standard addition curves.

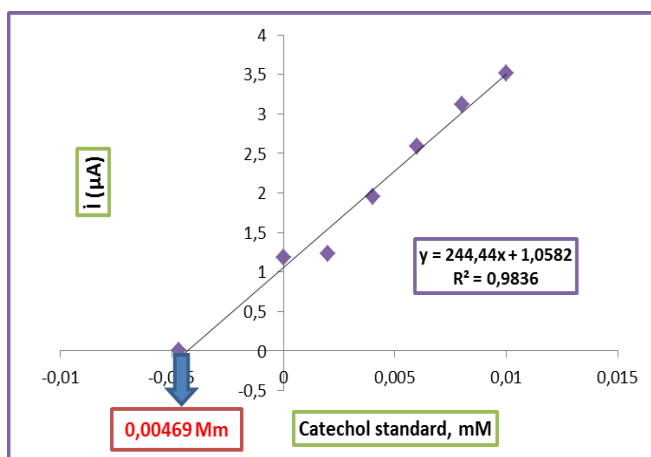


**Figure 3.47** Standard addition graph of black tea with Ni-MWCNT-PANI modified GCE.

Figure 3.47 shows the standard addition at Ni-MWCNT-PANI/GCE obtained for catechol samples. The calibration curve for catechol samples at Ni-MWCNT-PANI/GCE was found linear  $y = 244,44x + 1,0582$  ( $R^2 = 0.9836$ ).

#### 4. GENERAL DISCUSSION AND CONCLUSION

Direct alcohol fuel cells are very promising as a portable power because of their high energy densities ease of available methanol fuel and operation at low temperature. In general, the performance of direct alcohol fuel cells is not excellent because those small alcohols still need higher catalytic activity of electrodes to improve the oxidation kinetics. Therefore, to obtain the best catalysts for small alcohols as fuel, lots of research groups have been focused on this type of researches.

In the first and second section of this thesis, to increase the electrode performance the use of various catalysts was systematically evaluated for direct methanol oxidation. For this aim, graphene oxide, polymer such as aniline, metal nanoparticles such as gold, platinum and copper as the potential catalysts materials were used to modify the bare glassy carbon electrode. The modified GO and PANI covered GCEs were used to direct methanol electrochemistry.

To evaluate the performance of those electrodes, the oxidation peak potential and peak current were compared with those of bare GCE. The electrochemical preparation method for Au, Pt and Cu metal nanoparticles offer high-purity on the electrode surface. Therefore, bimetallic particles containing electrode surfaces have higher catalytic activity towards methanol oxidation. Generally in the fuel cells, a completed oxidation reaction is expecting on the electrode surface. Especially, in the case of methanol, the final oxidation product should be carbon dioxide. But, there was no catalyst to achieve the oxidation reaction in fuel cell technology until today. Therefore, the uncompleted oxidation reaction is still main problem on the electrode surfaces.

However, Pt based electrodes have higher catalytic activity towards small alcohol molecules while reverse peak formation due to the adsorption of carbonaceous species which were decreased the catalytic activity in the present conditions. To overcome this problem on the Pt based electrode surface, the Pt

containing surfaces have been modified with another metal particle such as Au and Cu.

To improve the catalytic activity of Pt based Au-GO/GC and Cu-PANI/GC electrodes were modified with binary metallic form of Pt-Au and Cu-Pt particles modified GO-GCE and higher catalytic activity was obtained for methanol at Pt-Au-GO/GCE and Cu-Pt-PANI/GCE. The supporting electrolyte (NaOH) concentration was also effected positively of the catalytic activity of the Pt-Au and Cu-Pt particles modified GO/GCE and PANI-GCE towards methanol oxidation.

The extraordinary role of nanometaterials in modern analytical chemistry is supported by the electrocatalytic ability of carbon nanotubes and polymer modified electrodes. The modification is enhanced the analytical properties such as the active surface area, high electronic conductivity and the anti-fouling capability of the surface. Furthermore, to improve the unique properties of CNTs and polymers, the modification could be combined with metal nano particles which they can be synthesized and modified chemically or electrochemically. To prepare an effective metal nano particles which are attached on the modified electrodes, an electrochemically deposition procedure is rapid, simple and reproducible.

In third chapter of the thesis, the determination catechol real samples were carried out by cycling and differential pulse voltammetric techniques. Catechol is a model molecule for bisphenol compounds, which usually coexist in plants, tea, fruits, wines, beers, juices, etc. Catechol has been widely studied due to the biological importance such as anti-oxidation, anti-virus and affecting the activities of some enzymes. Therefore, it is important to establish a sensitive, rapid and convenient method for the determination of catechol. Preparation of higher catalytic surface is a key factor for enhancing the performance of the electrodes. For this aim, in this thesis, new electrode materials were prepared using MWCNT modified with Ni metallic nano particles for electrochemical behaviour of catechol. The Ni metallic nano particles modified MWCNT/GCE showed best catalytic activity for catechol. The remarkably enhanced signal of catechol

oxidation the modified electrode can be attributed increasing the synergistic effect of metallic properties and increasing conductivity and effective surface area electrode which can be played important role to accelerate the electron transfer. The presence of Ni as nanoparticles size was also revealed by SEM, EDX and EIS. The prepared Ni-MWCNT/GCE was used for sensitive determination of catechol in real samples.

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