DOKUZ EYLÜL UNIVERSITY

GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES

INVESTIGATION OF STRUCTURAL PROPERTIES OF COATINGS WITH DOPED NANOPARTICLES

by

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İZMİR

INVESTIGATION OF STRUCTURAL PROPERTIES OF COATINGS WITH DOPED NANOPARTICLES

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M.Sc THESIS EXAMINATION RESULT FORM

We have read the thesis entitled **"INVESTIGATION OF STRUCTURAL PROPERTIES OF COATINGS WITH DOPED NANOPARTICLES"** completed by **DOĞACAN DAĞDELEN** under supervision of **ASSIST. PROF. DR. IŞIL BİRLİK** and we certify that in our opinion it if fully adequate, in scope and in quality, as a thesis for the degree of Master of Science.

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Doğacan DAĞDELEN

INVESTIGATION OF STRUCTURAL PROPERTIES OF COATINGS WITH DOPED NANOPARTICLES

ABSTRACT

Main purpose of this thesis is to synthesize doped nanoparticles with sol-gel method in order to use them for deposition of Ni based nanocomposite coatings by electrodeposition technique and to investigate its effect on structural properties of the nanocomposite coatings.

At first, undoped, Mn doped and Mn-N codoped titanium dioxide nanoparticles were synthesized by sol-gel method. Titanium tetraisopropoxide were used as the precursor. Structural analysis and particle size measurements of the nanoparticles were conducted by using X-Ray Diffraction (XRD) and particle size analyzer, respectively.

Subsequently, Ni and Ni based nanocomposite coatings were fabricated on steel substrate by electrodeposition method. XRD and Scanning Electron Microscope (SEM) analysis were done to investigate crystalline structure and surface morphology, respectively. Electrochemical measurements of Ni and Ni based nanocomposite coatings were performed using a Gamry potentiostat/galvanostat system controlled by Gamry Framework Software. It was observed that nanocomposite coatings with doped nanoparticles has shown enhanced surface properties, compared to the undoped nanoparticle coatings.

Keywords: Nanoparticles, sol-gel technique, doping, nickel coating, nanocomposites, electrodeposition

KATKILI NANOPARTİKÜL İÇEREN KAPLAMALARIN YAPISAL ÖZELLİKLERİNİN İNCELENMESİ

ÖZ

Yapılan tez çalışmasının ana amacı katkılı nanoparçacıkları sol-jel yöntemi ile sentezleyerek, bu nanopartiküllerin Ni esaslı elektroçöktürme yöntemi ile üretilen nanokompozitler üzerindeki yapısal etkisini incelemektir.

İlk olarak, katkısız, Mn katkılı ve Mn-N eş katkılı titanyum dioksit nanopartikülleri, titanyum tetra izopropoksit başlangıç kimyasalı olmak üzere sol-jel yöntemi ile sentezlenmiştir. Nanopartiküllerin yapısal karakterizasyonu ve partikül boyutu analizi, sırasıyla X ışını diffraktometresi (XRD) ve partikül boyut analiz cihazı kullanılarak incelenmiştir.

Daha sonra, Ni esaslı nanokompozit kaplamalar elektroçöktürme yöntemi ile çelik altlık üzerinde üretilmiştir. Yapılan kaplamaların kristal yapıları ve yüzey morfolojisi sırasıyla XRD cihazı ve taramalı elektron misroskobu (SEM) cihazında incelenmiştir. Yapılan Ni bazlı kaplamaların elektrokimyasal analizi Gamry Framework programında Gamry potentiostat/galvanostat sistemi ile ölçülmüştür. Elde edilen sonuçlar doğrultusunda, katkılı nanopartikül ile yapılan Ni esaslı elektroçöktürme yöntemi ile yapılan kaplamaların, katkısız nanopartiküller ile yapılan kaplamalara göre daha iyi yapısal özellik gösterdiği görülmüştür.

Anahtar kelimeler: Nanopartiküller, sol-jel yöntemi, katkı, nikel kaplama, nanokompozitler, elektroçöktürme

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CHAPTER ONE
INTRODUCTION

The term ‘nano’ can be used as defining one divided by 100 million of a meter. Many of the modern society might mistakenly believe that ‘nano’ size is just the extension of micrometer, as micrometer is extension of a meter. However, as the analysis methods have advanced by the end of 20th century, scientists started to see that these claims are basically wrong. They found out that the nano sized matter properties were different, compared to the higher scale materials. When the matter dimension decrease below 100 nm, extraordinary changes in properties starts to ocur. These new unique properties have been exploited for commerical applications that benefits the society (Winkelmann & Bhushan, 2016).

There are various ways to synthesize nanoparticles such as spray pyrolysis, physical vapor deposition, chemical vapor deposition sol-gel synthesis and hydrothermal technique (Hingant & Albe, 2010). Among these methods, sol-gel synthesis consists of simple hydrolysis and condensation reactions of metal alkoxide precursors in a solution to form a gel from colloidal suspension which consists of dispersed 1-100 nm collodial particles. This structure eventually forms a three dimensional rigid network, which ends up as xerogels, aerogels, micro/nanoparticles, fibers and thin films (Styskalik, Skoda, Barnes & Pinkas, 2017). Sol-gel process can happen in moderate conditions, especially considering how costly it can be to synthesize nano-sized product. Furthermore, easy conditions makes it possible to obtain nanomaterials with various sizes, shapes and formats. Theese variety choices of sol-gel synthesis made it possible for materials synthesized by sol-gel method to develop, even after few decades (Kumar, Gaurav, Malik, Tewary & Singh, 2007).

For the past two decades, doping of nanoparticles has been attracted many scientists. Basically, by doping method, another element is introduced into the crystal structure of the nanoparticle. The change in the crystal structure can mean many things such as surface area charge, porosity, homogenity, electroconductivity and particle size (Pelaez et al., 2012).

Nanocomposites can be produced by many methods such as thermal, plasma spraying, physical and chemical vapor deposition. Compared to these methods, electrodeposition stands out as it offers several advantages. Mild conditions, easily controllable synthesis, low energy requirements, cost-effectiveness, high production rate and low waste output are properties that made electrodeposition widely researched and used (Ahmad & Mohamed, 2014).

Nickel is considered as engineering material because of its high hardness, high brightness and corrosion resistances (Rostami, Fahami, Tabrizi, Kahrizsangi & Saatchi, 2013; Rusu, Ispas, Bund & Gheorghies, 2012).

Currently, nanocomposite coatings are being researched and improved focusing on higher microhardness, corrosion resistance and wear resistance. The electrodeposited nickel matrix is considered to have high density, minimum porosity, high wear and corrosion resistance. This made Ni matrix coatings widely used in chemical, mechanical and electrionic industries. Currently, widely used incorporated nano size materials are SiC, ZrO_2, Al_2O_3, TiO_2, La_2O_3 and CeO_2 for nickel matrix nanocomposites. Incorporated inert particles are very important factor for enhancing corrosion and wear resistance of the Ni matrix (Aruna, Grips & Rajam, 2009).

The purpose of this study is to synthesize Ni matrix nanocomposite coatings with doped nanoparticles on steel substrates by using electrodeposition technique and to investigate the effect of doped nanoparticles on structural and electrochemical properties of nanocomposite coatings.

The structure of this thesis consists of five different chapters which are summarized below:

Chapter 2 is a literature review of nanoscience, nanomaterial production, sol-gel process and doping mechanism. Sol-gel technique was reviewed in detail as this work is connected to sol-gel synthesis.

Chapter 3 is literature review of nanocomposites, Ni coating and diffrent types of Ni coating baths, Ni matrix nanocomposite production techniques and electrodeposition. Electrodeposition technique was reviewed in detail.

Chapter 4 consists of experimental work conducted, starting with preparation of undoped and doped nanoparticles, preparation of steel substrates, synthesis of Ni and Ni matrix nanocomposite coatings, characterization techinques and electrochemical measurements.

Chapter 5 is where results and their discussions are presented. Particle size of synthesized nanoparticles, XRD, SEM, electrochemical measurements of Ni and Ni matrix nanocomposite coating results were discussed.

Chapter 6 reviews the main conclusions of the study.

CHAPTER TWO
THEORITICAL BACKGROUND

2.1 Nano, Nanotechnology and Nanoengineering

The worldwide interest in nanotechnology cannot simply defined as exploiting 'starting from the smallest scale'. Scientists had two major motivations that played crucial role in advancement of nanotechnology. These two can be categorized as 'something has not been done before' and 'conquering nature'. As science advanced in analysis methods, scientists found out that the nano sized matter properties were different compared to the larger scale materials. When the matter size drops below 100 nm, extraordinary changes in properties starts to occur. These new unique properties have been exploited for commerical applications that benefits the society (Winkelmann et al., 2016; Ramsden, 2016).

In 1958, nano, together with other terms such as giga, tera, and pico was recognized as a newly formed international system of units. For the first time, the term 'nanotechnology' were used by Norio Taniguchi in Tokyo, 1974. Starting at 2000, US government recognized the importance of nanotechnology and intiated the National Nanotechnology Initiative (NNI). Over the past decades, scientists and engineers have been synthesizing and improving nanoscale materials (Boholm, 2016).

Nanotechnology covers the nanofacturing and the use of physical, synthetic and natural frameworks at scales extending from individual atoms to submicron measurements. Therefore, it spans across chemistry, physics, material science, enginering and manifacturing. As scientists exploit nanotechnogy for commercial use, the most successful results have still been limited with cementitious materials, as currently, they have been converted into marketable products (Winkelmann & Bhushan, 2016).

'Nanoengineering', sometimes called as nanomodification, is a term that is commonly used in nanotechlonology world. Nanoscience, as explained before, deals

with measurement of nano scale structures. Nanoengineering on the other hand, encompasses the techniques of manipulation of the nano sized structure to develop a product with new properties, such as superior mechanical properties and durability. Properties such as self-sensing, self-cleaning, self-control of cracks of the nanomaterials, low electrical resistivity are common examples for the current usage of the nanoengineering (Sanchez & Sobolev, 2010).

In current science, the research efforts has resulted in the production of nano-sized materials such as nanoparticles, nanowires, nanorods, nanosheets. With their assemblies, materials with internal structures such as mesorphous products, metal-organic framworks mainly with polymers were used in numerous industries. Successfully developed nano concepts includes catalysts, energy conversion, sensors and biomedical applications. Nanotechlonogy is therefore called as multidisciplinary science as it is still extending with new unique products. It is expected to have impact on all industries in the near future (Hingant & Albe, 2010).

2.2 Synthesis of nano sized materials

Nanostructure synthesis and their fabrication can be categorized as two main routes, which are top-down and bottom-up methods. Top-down approach can be explained as breaking up a solid substance such as attrition and grinding. Grain refining process increases the surface energy or the particles, it results in aggreation. Most commonly used method is milling. Theese milling methods can be defined as hammer, roller, jet, shock shearing and ball milling (Horikoshi & Serpone, 2013).

The main problems of top-down method is the imperfection of the surface structure. Processes such as grinding or etching can cause significant crystal structure damage, as etching could also introduce additional defects. These imperfections would have significant effect on physical and chemical properties of nanoparticles, considering the fact that surface over volume ratio in nanomaterials is very large. For example, the defects would have effect on the reduction of conductivity, which would result in

excessive heat production that would impose challange to device design and fabrication (Naschie, 2006).

Bottom-up refers to creating something from the bottom scale, atom-by-atom or molecule-by-molecule. Bottom-up synthesis is quite important for fabrication of nanostructures and nanomaterials. As scientists deal with 'one millionth' of a meter, there is not much choice in materials for top-down approach. Compared to the top-down approach, a nanomaterial synthesized with bottom-up method would have less defects and more homogenious chemical composition. Since bottom-up method reduces the Gibbs free energy, the synthesized nanometarials can be considered thermodynamically balanced, which makes them more stable compared to materails synthesized with top-down method (Horikoshi et al., 2013). Various preparation techniques for nanomaterials classified according to their dimensions are summarized in Figure 2.1.

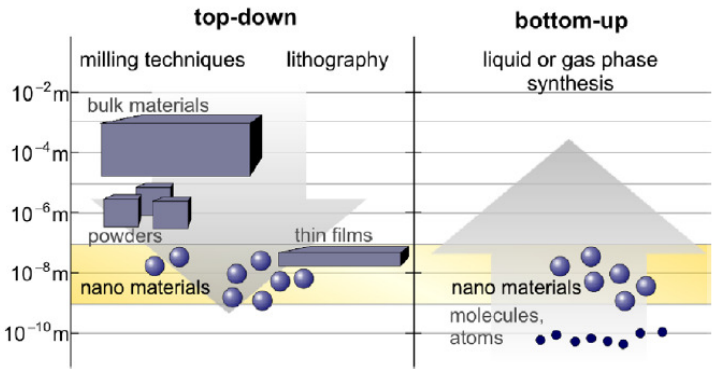


Figure 2.1 Synthesis of nano size materials with two main methods (Schmitz-Antoniak, 2015)

2.2.1 Molecular Self Assembly

Molecular self-assembly (MSA) is one of the surface nanofabrication process where molecules can assemble themselves without the help of outside interactions. Therefore, the process is spontaneous. MSA is a promising approach in order to control the intermolecular forces between the molecular systems. Any diffrence between theese values could result unique nanomaterials. Hovewer, the nature complexity of

nanoscience and molecular assembly is not easy to control; therefore, MSA is still in experimental approach state.

Extensive research has been done past three decades have been devoted to design and fabrication of nanomaterials through peptide self-assembly, as arguably the most common and successful MSA synthesis method. Drug release, gene delivery, membrane protein stabilisation to tissue engineering can be done with thanks to its biocompatiblity (Horikoshi et al., 2013).

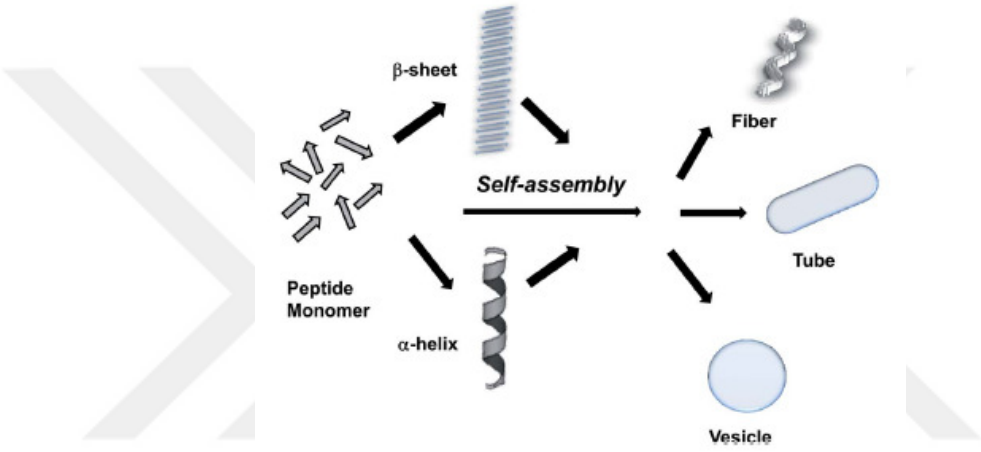


Figure 2.2 Self-assembly of peptides into different types of nanostructures (Panda & Chauhan, 2014)

2.2.2 Spray Pyrolysis

Spray pyrolysis is a techique where nanomaterials are obtained in vapor phase at moderate high temperatures. Firstly, the precursor is dissolved in a solution in order to spray in a vector gas as droplet-wise. Since the substrate is heated, the solvent evaporates or decomposes into gaseous products. This technique is mainly used for depositing TiO_2 and ZnO compact layers on the surface of transparent state conductive material substrate (Lévy-Clément, 2006).

Spray pyrolysis method is one of the physical methods that has been widely used thanks to its cost-effectiveness, easy particle size control, simple processing and high production rate which makes it easier to mass manifacture. The evaporation of droplets mechanic can lead unifrom and high quality coatings on substrate, even on substrates

with complex geometries. These advantages of spray pyrolysis have been exploited in order to synthesize transparent layer on a glass, uniform layer for gas sensing applications, solar cell applications and anodes for lithium-ion batteries (Tok, Boey & Zhao, 2004).

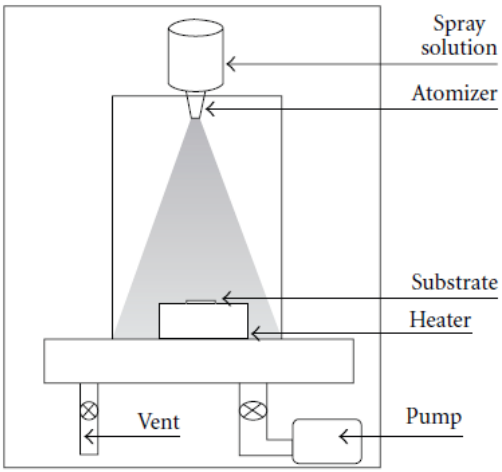


Figure 2.3 Basic illustration of spray pyrolysis method (Bari, Khadayate, B.Patil, Bari, Jain, A.Patil & Kale, 2012)

2.2.3 Inert Gas Condensation

Inert gas condensation (IGC) method is mainly used for metal nanoparticle synthesis. In order to obtain nanoparticles from this method, precursor materials are evaporated in high vacuum under very high pressure. This room is filled with argon or helium gas. In evaporated state, metal atoms lose their kinetic energy by colluding with the gas, therefore condensing into small particles, which ending up forming nanocrystals.

IGC was the first technique developed in order to synthesize metals and alloys in nanocrystalline state. The synthesized particle properties can be affected by gas pressure, particles growth type and vapor pressure. The major advantage of IGC over other methods is easily controllable particle size by controlling gas flow. Hovewer, with this method, synthesized metallic and ceramic materials were only limited to laboratory scale. One other disadvantage is that it is hard to mass manifacture because

the method is slow. The synthesized materials can be around 1g/day, while metal oxides are around 20g/day (Rane, Kanny, Abitha & Thomas, 2018).

2.2.4 Hydrothermal Technique

Hydrothermal technique have been used by scientists from different disciplines for the past decade. This technique consists of chemical reactions of substances in a closed space heated solution, which is above ambient temperature and pressure in order to synthesize nanomaterials (Rane et al., 2018). Hydrothermal techinque is a method for the prepration of solids, porous crystals, superionic conductors, chemical sensor oxides and magnetic materials. It can be also used as baseline for synthesis of dense materials, including nano materials such as nanoparticles, gels and thin films. The synthesized crystal structure depends on the hot water pressure. The growth of the crystal is maintained and performed in appratus called autoclave, which consists of steel pressure vessel (Tatarchuk, Peter, Al-Najar, Vijaya & Bououdina, 2018).

Most materials can made soluable thanks to the autoclave heating and pressure which can be modified. This process also makes easy control of the particle size, shape distribuion and crystallinity of the synthesized product. With this method, materials which may not be obtained via solid-state reaction may be prepared by this method. Hovewer, the main strength of this method can also become disadvantage because solution is preprared in the autoclave, so the process can be called ‘blackbox’, which is impossible to obverve (Rane et al., 2018).

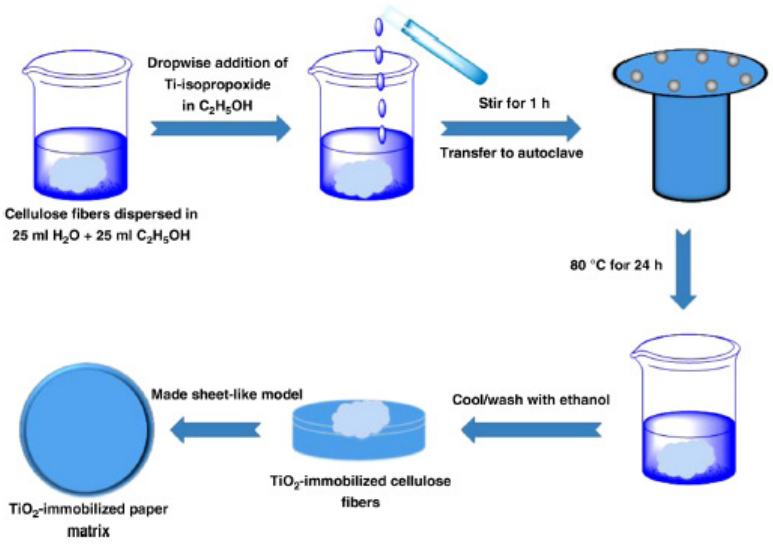


Figure 2.4 Schematic diagram of hydrothermal technique synthesis of TiO_2 (Tatarchuk et al., 2018)

2.2.5 Chemical vapor deposition (CVD)

Chemical vapor deposition is a technique has been widely used thanks to its process versatility for mass producing of powders, coating and fibers. CVD techinque makes it possible to synthesize most metals, mainly nonmetallic elements (such as carbon and silicon) and numerous compounds including carbides, nitrides and oxides. Currently, this process is used mainly for the manifacture of semiconductors and other electronic components, coatings, wear- resistant parts, optical and corrosion applications.

CVD can be defined as obtaining solid structure with chemical reactions on a heated surface in the vapor phase. The structure is obtained via deposition of atoms of molecules that can be called vapor-transfer process. CVD has several important advantages over bottom-up synthesis methods. Thick coatings can be obtained the since the process deposition rate is high as the high quality coating can be competitive for cost-effective synthesis. CVD equipments does not require high vacuum and can adapt various processes to synthesize nanomaterials with unique properties. Three dimensional configurations can be archieved with CVD process, unlike PVD process which make configurement harder. The requirement of at least 600°C and above is one of the weaknesses of CVD method. Chemical productions preprared by vapor pressure is hazardous and neutralizing it may be a costly operation (Pierson, 1999).

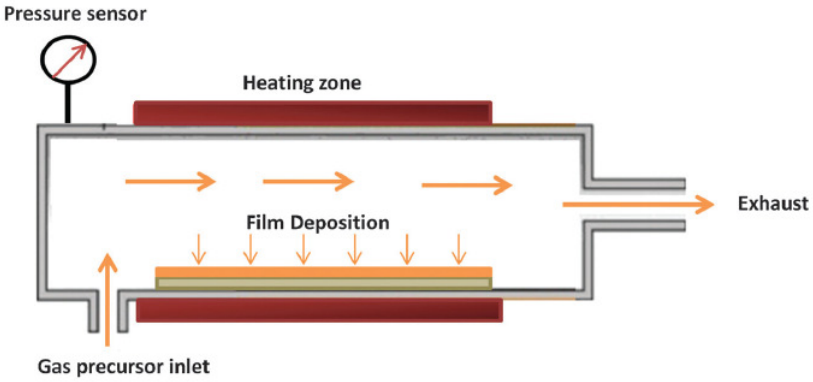


Figure 2.4 Schematic diagram of a chemical vapor deposition system (Zhang, Sando & Nagarajan, 2016)

2.2.6 Physical Vapor Deposition (PVD)

Physical vapor deposition process is atomistic deposition process which uses vapor through a vaccuum in order to obtain solid structure on the substrate. The solid or liquid precursor material is vaporized, forming atoms or molecules for depositon. With PVD, deposited films with few or thousands of nanometer thickess can be archieved. Moreover, multilayer coatings, graded composition deposits, very thick deposits can also be obtained.

Elements, alloys as well as compound films can be obtained though PVD process. In deposition process, ambient gas enviroment (e.g. titanium nitride, TiN) and depositing material are used. They react with each other in order to from a compound or a desired material with co-depositing another material. PVD uses relatively low temperature compared to the CVD (250-450°C) and deposition occurs with condensation instead of chemical reaction. Also, the material introducted the substrate is in solid form, instead of a gaseous form (Mattox, 2010).

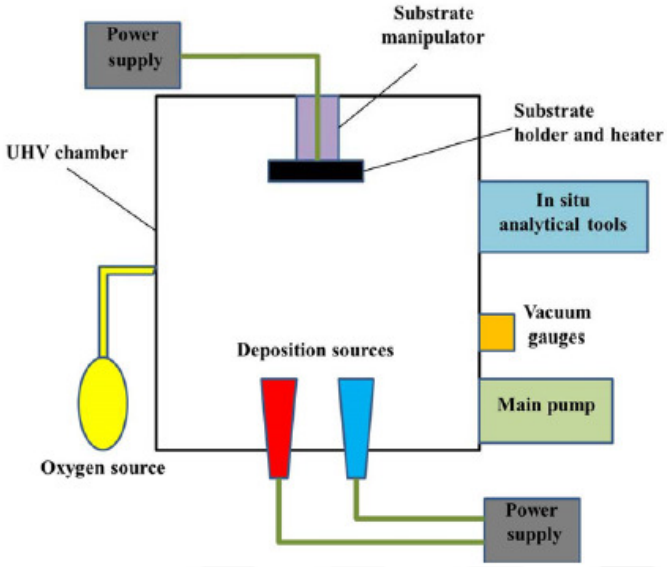


Figure 2.5 Schematic diagram of a basic physical vapor deposition system (Y. Wang, Chen, B. Wang & Zheng, 2014)

2.2.7 Sol-Gel Method

Sol-gel method is based on synthesizing solid materials starting from small molecules. In this process, the sol (or solution) slowly becomes a gel-like diphasic system containing both solid and liquid phase. The mophology of the particles depends on the polymer network structure of the sol. With this method, uniform ceramic powders can be synthesized. Sol-gel synthesis starts with creating a solution from precursors. Afterwards, hydrolysis and condensation reactions occur in order to obtain a transparent sol system. This system is aged to form three-dimensional structure. The structure enters various processes such as drying, calcining and sintering, which ends up forming nanostructures (Kumar et al., 2015).

The chemistry of sol-gel is based on hydrolysis and condensation of metal alkoxide precursors, which ends up as xerogels, aerogels, micro/nanoparticles, fibers and thin films (Styskalik, Skoda, Barnes & Pinkas, 2017). In this synthesis, inorganic metal salts (nitrate, sulfate) or alkoxides are used as starting materials. In order to make a transparent solution, solvents such as water and ethanol have been mainly used in this process Since metal salts can dissolve easily in theese solvents, its been used more

than alkoxides. Some of the alkoxides of Si, Ti, Al and Zr have been widely used for commercial purposes thanks to their cost-effectiveness (Niederberger & Pinna, 2009).

Historically, the usage of sol-gel method has mentioned in mid 18th century when French chemist, J.J. Ebelmen reported his work on uranium oxide by heating the hydroxide, afterwards agings and heating the material. This process took a year for him in order to prevent cracking on the structure, therefore this paper did not have much attention. Hovewer, in mid 19th century, R.Roy and his colleagues focused on synthesizing new ceramic oxides using this method, making sol-gel silicate powders quite popular in the market. Around three decades later, H. Schmidt and G.L. Wilkes started to synthesize both organic and inorganic materials by sol-gel process. They published numerous research articles about this method. Until this point, sol-gel technology attracted lots of scientists in the field of ceramics, polymer chemistry, organic-inorganic chemistry and physics (Wang & Bierwagen, 2007).

Sol-gel process can occur in mild conditions, which makes it commonly used method, especially considering the fact that how costly it can be to synthesize nano-sized product with other methods. Furthermore, easy conditions makes it possible to obtain nanomaterials with various sizes, shapes and formats (e.g. films, fibers, monosized particles). Theese sol-gel properties led to synthesis of new materials for chemical sensors, membranes, fibers and electrochemical devices. Obtaining homogeneous structure is another reason what makes sol-gel method desirable than other synthesis methods (Rane et al., 2018). The solution medium of sol-gel makes it possible to create multicomponent materials with varying properties. Currently sol-gel synthesis is used in various industries such as ceramics, nuclear fields and electronics. Better homonegity and purity, low temperature synthesis and cost-effective precursors made sol-gel widely studied, compared to the other bottom-up synthesis methods. Good mixing for multi-component systems makes it possible to fabricate nanomaterials with varying properties, which is possible with this method (Kumar, Gaurav, Malik, Tewary & Singh, 2007).

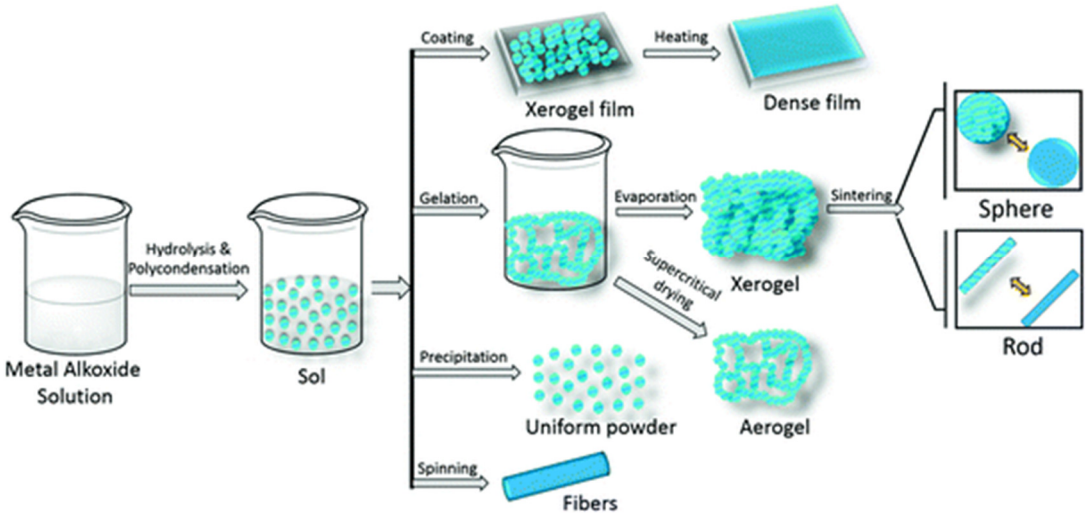


Figure 2.6 Sol-gel synthesis and its products (Ullattil & Periyat 2017)

Generally, the sol-gel process occurs in four stages: (a) The hydrolysis of the precursor, (b) condensation and polymerization of the precursor solution, forming chains to particles (c) growth stage of the particles, (d) formation of network in polymer structure, forming a gel (Wang et al., 2007).

Inorganic or organic sols and gels can be obtained by diffrent methods. They are mainly synthesized from chemical precursors dissolved in a liquid medium. The chemical reactants which contains cation element atom in the final inorganic sol and gel is called chemical precursor. As long as the precursor is miscible, any kind of precursor can be used. Two main groups that can be used for a precursor, which are metallic salts and alkoxides. Metallic salts formula is M_nX_n where M is the metal, X is an anionic group, such as aluminum chloride ($AlCl_3$). For alkoxides, their fomula is $M(OR)_n$ where M is cation and ROH is alcohol groups. For example, titanium tetra isopropoxide ($C_{12}H_{28}O_4Ti$) is commonly used as alkoxide to synthesize TiO_2 nanoparticles (Pierre, 2013).

The molecular structure of polar non-aqueous solvent potential can be determined by dipole moment and relative dielectric constant. Higher dipole moment would mean stronger bond between atoms which would make it difficult to obtain transparent solution in sol-gel synthesis. On the other hand, solvents with high dielectric constant values have good ionizing properties therefore they can dissolve in other polar solute.

If the dielectric constant is low, the ioinizing property of the solvent will be lower. Considering theese values, water, methanol and ethanol have been commonly used thanks to their high dielectric constant and relatively low dipole moment values (Pierre, 2013).

Table 2.1 List of commonly used solvents with their dielectric properties

Solvent	**Dielectric constant (ε_r)**	**Dipole moment (μ)**
Acetone (C_3H_6O)	20.7	3.00
Benzene (C_6H_6)	2.3	0.00
Water (H_2O)	78.5	1.85
Methanol (CH_3OH)	32.6	1.70
Ethanol (C_2H_5OH)	24.3	1.71
Formamide (CH_3ON)	110.0	3.39
Chloroform ($CHCl_3$)	4.8	1.11

When it comes to hydrolysis and condensation process, alkoxides and metal salts have similiar chemisty. Hydrolysis can be defined as the deprotonation of a solved metal precurspor. It consists in the loss of a proton by solvent molecules that surrounds the metal M in the liquid medium. For example; in alkoxide hydrolysis, alkoxy groups (OR) are replaced by either hydroxo ligands (OH) or oxo ligands (O). This hydrolysis reaction can be affected by the nature of the solvent, the nature of the alkyl group, temperature and solvent to alkoxide molar ratio (Pierre, 2013). Formation of hydroxo ligand example with water solvent is given chemical reaction below;

$$M(OR)_z + H_2O \rightarrow M(OH)(OR)_{z-1} + ROH \quad (2.1)$$

By principle, hydrolysis consists in a nucleophilic substitution, in this case, a water molecule attacks the alkoxide. In most cases, leaving group of the reaction is either an alcohol or water molecule. The hydrolysis of titanium alkoxide in water solvent are given below;

$$Ti(OR)_z + H_2O \rightarrow Ti(OH)(OR)_{z-1} + ROH \quad (2.2)$$

After the first deprotonation, the deprotonation of the newly obtained chemical will continue as solvent anions keep attacking the cations of the precursor. These repeating processes are called condensation reaction. In the continuous condensation of the alkoxide precursor, an ‘‘ol’’ bridge forms, which turns into ‘oxo’ bridge afterwards. Once this “ol” bridge has been build with hydrolysis process, its corresponding hydrogen nets only to transfer either to a terminal alkoxy ligand or to a hydroxo ligand to form the “oxo” one (Pierre,2013).

The condensation process is there the first tri-dimensional network is formed, then eventually forms a solid structure. This process can be accelerated by heat as rate of both reactions increases together since the kinetics of hydrolysis and condensation will change. This makes hydrolysis-condensation process of the sol-gel as the most complex part of the process. Obtaining linear polymers or dense colloidal partices, particle sizes, crystal structures all depend on kinetics and pH values of the solution (Pierre, 2013). The tridimensional network obtained by condensation process from titanium tetra isopropoxide precursor in alcohol solvent is given in Figure 2.7.

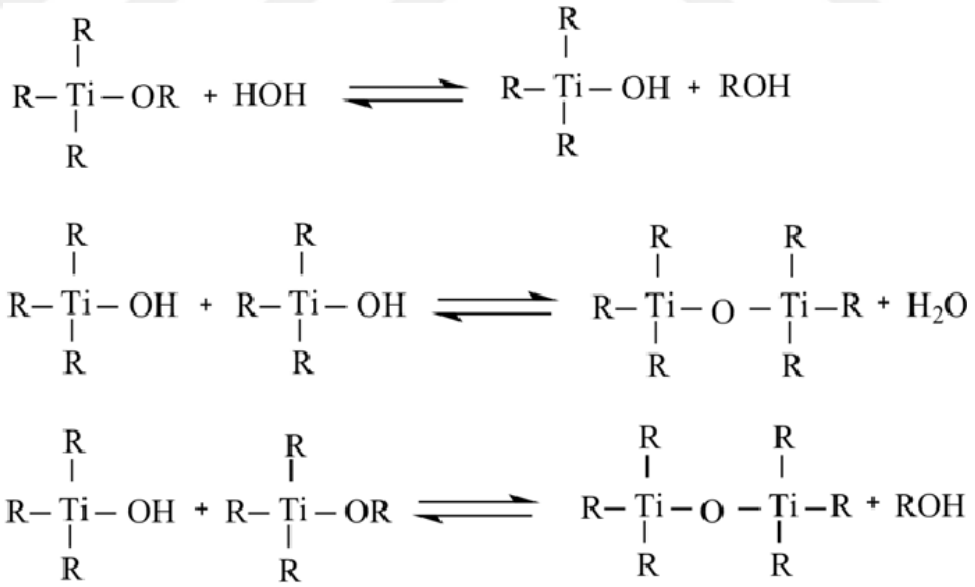


Figure 2.7 The hydrolysis and condensation reactions of titanium isopropoxide ($Ti(OR)_4$) with sol-gel method (Gutierrez, Tercjak, Garcia, Peponi & Mondragon, 2008)

The most commonly used nanoparticles obtained via sol-gel method, such as TiO_2, SiO_2, CrO_2 can be obtained according to these reactions:

$$M(OR)_z + zH_2O \rightarrow M(OH)_z + zROH \quad (2.3)$$

$$M(OH)_z \rightarrow MO_{z/2} + (z/2)H_2O \quad (2.4)$$

After the condensation process, tridimensional network becomes a structure that is called ‘sol’. The solid particles are formed after the nucleon and growth processes. Nucleation is due to statistical thermodynamic fluctuations. The nucleation processes are enhanced by aging the sol, heating and the addition of chemical ligands. Aging makes it possible for bigger fluctuations to occur. Heating is used to accelerate all chemical reactions, which helps to prevent obtaining unwanted structures (Sugimoto, Zhou & Muramatsu, 2002).

Colloidal particles obtained after condensation process are bound to collide with each other. There are two types of phenomena on how this will happen. The two particles can either remain associated, where aggregation occurs and a precitipate forms. On the other hand, particles can also remain independent, therefore they are dispersed in the liquid. This part is crucial part of the sol-gel process as controlling powder transformations starts from here. Aggreation of colloidal particles is the first step of obtaining sol. The dispersion of the particles must be stable for a sufficient time. The dispersion of the particles also relies on interaction forces between the particles. These interactions can be described as Van der Waals interactions, electrostatic interactions and steric interactions. After this process, the sol transforms into a gel, which is called ‘gelation’ process of the sol (Sugimoto et al., 2002).

In the gelation process, a link is established between the sol particles to obtain tri-dimensional solid network. This solid structure remains completely impregnated with the sol, or solution. When polymerization reactions reaches the critical value, gelation starts to occur. This state is called ‘gel point’ of the sol. At this point, the viscous liquid turns into a material with elastic properties. The gel point can be measured as when viscosity value reaches near infinity, it means that it is close to its gel point (Pierre, 2013).

After this point, formed wet gel keeps transforming if its stored for a long time. This evaluation is called ‘aging’ process. Two main types of transformations occur in this process. After hydrolysis-polymerization reactions, it’s not guaranteed that the gel structure will be composed of most stable chemicals. Silica gel, one of the most used gel in the industry, is a good example of this transformation process. If the pH is low, the polymeric species in the gel network are not very soluable, therefore the network can be considered frozen. However, at high pH, colloidal silica gel slowly transforms into coarser structures. Therefore, both pores and the gel network comes closer. The specific area of a gel decreases as the aging time incrases, therefore it’s very important to determine the ideal aging time of the sol-gel process in order to obtain nanostructure with desired properties (Sugimoto et al., 2002).

In order to obtain nanoparticles, solvent and resuidal chemicals has to be removed. Drying is used to remove the solvent, and calcination is used to evaporate the chemicals. In drying process, the solvent is removed without any kind of change to the crystal structure of the solid state of the network. The structure of the dry gels are usually amorphous, according to the XRD results. Once the gel is dried, the dried structure is heated in temperatures quite different than drying temperature values. In most cases, the first notable change involves a chemical evaluation. The crystallographic structure of the solid network and pore texture starts to change. In order to obtain thermodynamically stable phase for these changes to happen, the calcination process is done between 100 - 1000°C, which is termed as intermediate temperature range. This calcination temperature value can be modified in order to obtain the desired crystallographic structure (Macwan, Dave & Chaturvedi, 2010). For example, TiO_2 nanoparticles synthesized with sol-gel method can be obtained in three different crystallographic forms, as shown in Figure 2.8.

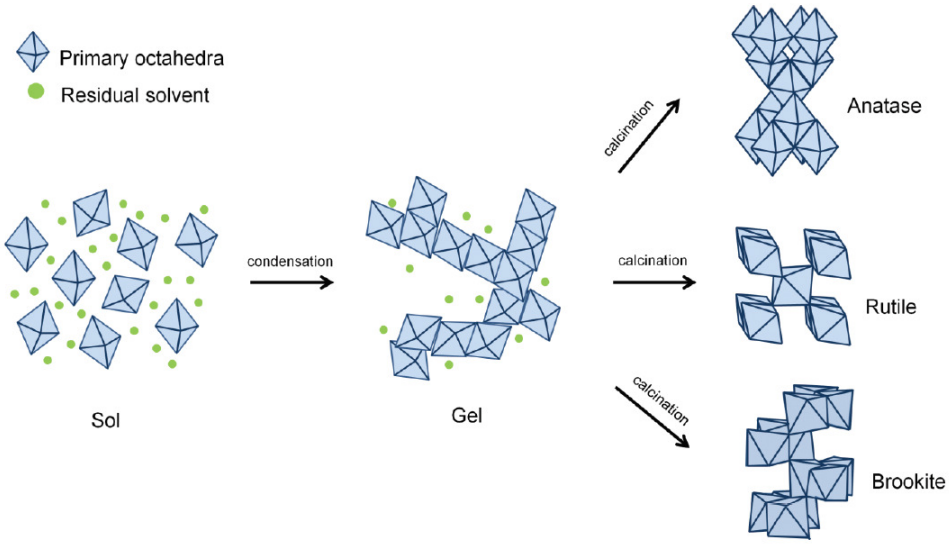


Figure 2.8 The changes within TiO_2 crystal structure with condensation and calcination process (Yahaya, Azam, Teridi, Singh & Mohamad, 2017)

According to Sugimoto et al. report, they have managed to synthesize uniform TiO_2. In their work, they used solvent as water, titanium isopropoxide as presurcor and triethanol amine to control synthesized particle size. In order to control the pH of the solution, sodium hydroxide have been used. After two step aging, they finally synthesized TiO_2 nanoparticles (Sugimoto et al., 2002). On the other hand, Su et al. synthesized TiO_2 using titanium butoxide as precursor, isopropyl alcohol as solvent and acetyacetone as catalyst. Nitric acid were used to control pH of the solution (Su, Lin, Lin & You, 2006). One interesting report made by Abbad et al. focuses on parameters of ZnO synthesis with sol-gel method. After using zinc acetate, oxalic acid and ethanol as starting materials, they still kept stirring the solution, even after gel was already formed. After trying out various pH and calcination parameters, they stated that pH = 2 value and 400 ^oC calcination temperature is ideal for synthesize small ZnO nanoparticles (Abbad, Kadhum, Mohammad, Takriff & Sopian, 2012).

2.3 Enhancement of nanoparticles synthesized by sol-gel method

Recently, many scientists have been interested in developing physical and chemical properties of metallic nanoparticles, expecting to obtain new light on the quantum confined nanosystems (Lue, 2000). Currently, nanoparticles can be synthesized from

materials which can be synthesized from numerous methods with different particle properties. Particle shape, size, chemical and physical properties may differ with synthesis methods and precursor elements (Kango, Celli, Njuguna, Habibi & Kumar, 2013).

In the case of synthesized metal oxide nanoparticles by sol-gel method, the solvent or the precursor acts as oxygen source. Since synthesis routes depend on the chemistry of oxygen-carbon bonds, this opens up the possiblity of adjusting structural, compositional and morphological characteristics of synthesized nanoparticles. The sol-gel process is a great choice for adjusting nanoparticle properties as sol-gel synthesis is cost-effective and the synthesis process is easy to control. A few nanometer or shape diffrence may greatly change the property of the nanoparticle (Bilecka & Niederberger, 2010; Oskam, 2006).

Nanoparticles with unique optical, magnetic, electonic and mechanical properties can be used in different application fields, such as waste water treatment, textile paints, drug delivery, magnetic resonance, tissue engineering and cancer treatment (Kango et al., 2013).

The main focus on current field of nanoparticle synthesis is without a doubt, size and shape control. In the next few decades, this focus might change considering how industry will evolve, as socio-economic aspects will also change in the future (Bilecka et al., 2010). Small nanoparticle sizes are responsible for the diffrent properties. When the material is below 100nm in size, the surface size of atoms inceases, which increases the reactivity of the nanoparticle. As the surface atoms increase, the materials will become more reactive yet less stable. Therefore, modifications of nanoparticles plays important role to overcome this problem. Physical modifications are done with surfactants or macromolecules which are adsorbed on the metal oxide nanoparticle surface. Surfactants can affect particle-particle interactions to prevent agglomeration of the nanoparticles (Mallakpour & Madani, 2015).

The study of the organic reaction pathway of the sol-gel synthesis provided various information on the chemical mechanisms of the formation of the nanoparticles. The common ground of these study results show that in nanocrystal form, organic species are complex. The common path of current nanoparticle improvement studies are;

- Developing the surface modification technique. Tailoring the surface properties is the crucial part of building blocks of atom strategy for synthesis of nanoparticles.
- Development of new synthesis routes with chemical modification. This process can be done by adding a new material, new function or new catalyst to the synthesis.
- Searching for new application fields to take advantage of variable possiblities of nanoparticles to adapt to industry (Mallakpour et al., 2015).

Noshin Mir and Masoud Salavati-Niasari synthesized TiO_2 nanoparticles by using tripodal tetraamine as complexing agent to improve TiO_2 nanoparticle properties. In their study, they added tripodal tetramine after titanium dioxide dissolved and before solid sol particles were formed. Its been shown that 3D structure and symmetry of the complexing agent played crucial role in morphology of the structure, such as hindering the aggleromation of the nanoparticles, therefore obtaining smaller particles with new properties (Mir & Salavati-Niasari, 2013). In another study, Sara L. Isley and R. Lee Penn focused on pH and aging effect on synthesized nanoparticles via sol-gel method. Nitric acid were used to control pH value of the solution and hydrothermal aging were conducted to prevent aggleromation and coarsening. They reported that synthesized nanoparticles at 0.5 pH value titania solution had better particle size and surface charge, compared to the 3.5 pH value titania solution (Isley & Penn, 2008).

2.3.1 Doping and codoping method

For the past two decades, doping method has been attracted many scientists. Basically with doping method, another element is introduced to the crystal structure of the nanoparticle which might cause a displacement or strain. The change in the crystal

structure can mean many things on the nanoparticle properties such as surface area charge, porosity, homogenigty, electroconductivity and particle size (Pelaez et al., 2012).

The effects of electrical conductivity of nanomaterials are complex, since they are based on distinct mechanism where quantum effects take place. By doping another atom to the crystal structure of the nanoparticle, in order words the impurity atom, causes defects such as vacancies and grain boundries that locally distrupts the electric potential of the lattice, therefore causes electron scattering which is temperature independent. The change in electrical properties are influenced by electrons scattered at the surface, which is a function of electron free path and particle size (Karthik, Pandian & Jaya, 2010). In order to introduce the impurity atom to the structure, the dopant atom should have comparable size to nanomaterial. The impurity could negatively affect the electrical and optical properties of the nanomaterial, therefore making doping process a delicate treatment (Jagalade et al., 2008).

The sol-gel technique has been widely regarded as one of the versatile methods for prepration of doped nanoparticles, such as TiO_2. Since sol-gel process is based on solution, it makes it easier to control and allows flexibility. The relatively slow process of sol-gel permits tailoring certain desired characteristics of the nanoparticle (Hamanadian, Reisi-Vanani & Majedi, 2010). The illustration of the four-stage of doped particles in sol-gel synthesis is shown in the Figure 2.9.

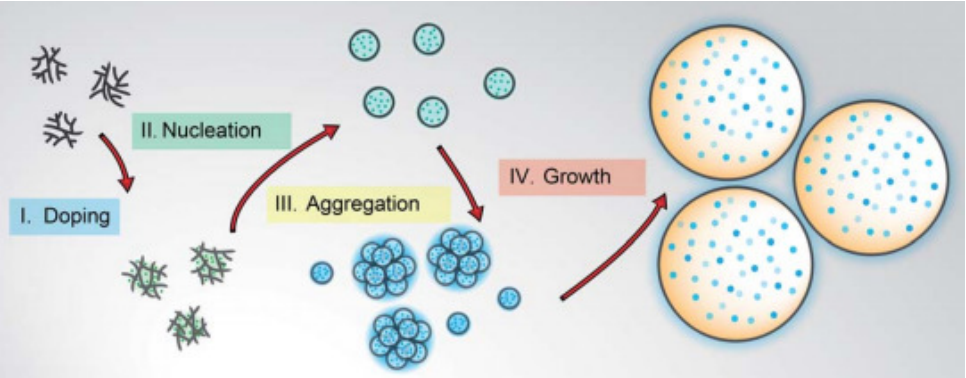


Figure 2.9 The stages of sol-gel doping mechanism (Wu, Li, Xu & Wu, 2014)

Recent reports suggest that the photocatalytic activity and ferromagnetic properties of commonly used metal oxides such as TiO_2 and ZnO have been enhanced with doping method. Hamadanian et al. doped cobalt and copper at %2 wt on TiO_2 structure using sol-gel method. They reported that by adding impurity to the nanostructure, they have managed to prevent the recombination of atoms when the material is affected by UV light. This ended up improving the photocatalytic activity of TiO_2 (Hamadanian, Karimzadeh, Jabbari & Villagran, 2016).

In another study, Lee et al. reported that doping cobalt (Co) on ZnO films synthesized with sol-gel method improves its ferromagnetic property. Despite the fact that Co contcentration was relatively high (%25), it has been reported that there we no changes in crystal structure of ZnO while lattice constants have been changed. Therefore they report that ferromagnetism of cobalt doped ZnO was still intact, even in high temperatures (350K) (Lee, Jeong, Cho & Park, 2002). In other report made by Dinkar V. Aware and Shridhar S. Jadhav, %5 Zn were doped to the TiO_2 structure. There were no changes to the crystal structure to TiO_2. They report that since Zn^{2+} has lower ionic radius than Ti^{4+}, the Zn atoms easily incorporated to the crystal structure and reduced the crystal size of TiO_2, therefore increasing the surface area of the nanomaterial. This ended up improving the photocatalytic activity, shifting light absorbsion to higher wavelengths (Aware & Jadhav, 2016).

More recently, simultanious doping method of two atoms have been attracted many researchers. The main objective of codoping is to further improve optical and structural

efficiency, compared to the single doped nanoparticles (Chen, Jiang, Geng, Wang & Yang, 2007). For example, the addition of transition metals on TiO_2 crystal structure will end up in creation of new energy level between valance band and conduction band, however, it can still negatively affect the quantum efficiency. On the other hand, doping anionic atoms to the structure might end up creating charge unbalance. Therefore, in order to overcome these problems, codoping method has been developed (Pelaez et al., 2012).

Codoping can be defined as incorporation of acceptor and donor dopants on nanoparticle structure. For example, in ZnO codoping process, a transition metal, such as zinc, can substitute Zn atoms as n-type, and a nonmetal such as N can replace O atoms to p-type dopant to act as donor and acceptor, respectively. Substitution of these atoms would from new bonds, resulting in diffrent orbital energies in the doped ZnO nanoparticle. Therefore, acceptor to donor ratio becomes an important factor to determine the properties of the new doped structure (Yamamoto, 2002; Gai, Li, Xia & Wei, 2009).

Silvearv et al. reported codoping manganese and aluminum to ZnO synthesis with sol-gel method. On their work, focused on ferromagnetism of the new ZnO nanoparticles. They state that, since doping creates defects, such as Zn or O vacancies, the (Mn, Al) doped ZnO structure can induce ferromagnetism (Silvearv, Rosa, Lebegue & Ahuja, 2012). On the other hand, Thota et al. tried to reduce the bandgap of TiO_2 in order to improve the photocatalytic efficiency. They codoped phosphorus (P) and manganese (Mn) to ZnO nanoparticles. They stated that Mn addition succesfully trapped electrons in order to prevent electron/hole recombination, while P doping caused visible light response (Thota, Tirukkovalluri & Bojja, 2014). In the similiar synthesis report, given by Xu et al. codoped aluminum (Al) and potassium (K). According to their XRD results, the crystal structure is not affected while crystal size has been reduced with Al doping. They also stated that creating defects in the ZnO enhanced the photocatalytic efficiency (Xu, Shi, Zhang, Wang, Zhu & Li, 2013).

CHAPTER THREE
NICKEL AND NICKEL MATRIX NANOCOMPOSITE COATINGS

3.1 Nickel Coating

Surface modification with coatings have been widely used and considered one of the most reliable method to improve surface properties of materials. If the material is coated, the metal substrate can be protected from the enviroment. The nanostructure coatings have been widely researched by scientists because of its technologically attractive properties and fine microstructure. In general, these nanocomposites can be used in aircraft, space, automative, chemical industries and construction. Having a light-weight, high performance and useful mechanic, electronic properties of the coating is desired in industrial applications (Davim, 2015).

Nickel is considered as an engineering material because of its high hardness, high brightness and high corrosion resistance in normal atmosphere, natural freshwaters and alkaline media. Nickel is mainly used for electrodepositing the materials (Rostami et al.; Rusu et al., 2012). Since nickel has face-centered cubic crystalline structure below its melting point, it is considered as ducile and tough. Electrodeposition of Ni is still the most widely used method for plating process, mainly used for engineering applications (Rusu et al., 2012).

Bottger has developed the first practical use for nickel plating, using nickel and ammounium sulfates in 1843, even though there were other works similiar to it in earlier years. The solution developed by Bottger remained in use for 70 years, and he is considered to be originator of the nickel plating. Dr. Isaac Adams, Jr., a doctor educated in Harvard University, was one of the main scientists to commercialize the nickel plating in United States. In his work, he used nickel ammonium sulfate solution. Even though his solution was similiar to Bottger's, his works on the quality of the coatings made his work inventive in the science world. He worked on pH of the solution as excessive amounts of ammonia would tend to lower cathode efficiency.

The publicity that Adams generated made nickel plating became known worldwide in 1886 (Rusu et al., 2012).

Nickel coatings are mainly used for corrosion resistance. Another importance of nickel coating is cost-effectiveness as a thin nickel coating only requires a small amnout of anode while the anode may be used to repair an expensive component which would have been thrown away. A damaged material, worn or overused machine, heated, small dents on the surface can be restored by building up these areas with nickel to restore them to their original property. Therefore, nickel coating is not only used for corrosion protection, but for also greater abrasion resistance. This ended up in nickel electroforming quite popular method in world market. It has been researched past two decades and it appearly it will likely to grow (Dennis & Such, 1993).

3.2 Nickel electroplating Baths

The surface-finishing versatility of nickel electroplating made it quite important commerically in the industrial world. Currently, roughly 100.000 metric tons of metal and salts consumed for electroplating for many diffrent applications. These applications of nickel plating are mainly done for three purposes: decorative, functional and electroforming.

Nickel eletroplating is one of the most commonly used deposition process. This method use soluable metal anodes; in order to make a flow between two electrodes in a conductive aqueous solution of nickel salts. The flow of current causes the anode to dissolve then nickel ions cover the cathode. Most electroplating processes are done with soluable nickel anode materials. The ions gained from nicked anode replaces the discarged atoms from the cathode in the plating solution. The quantity of solution material, temperature and pH of the solution makes a big diffrence in coating properties of the material (Di Bari, 2010).

Currently, the electrodeposition process is dominated by Watts solutions. The solution is challanged by other solutions time to time, but the only notable solution is

nickel sulfamate solution. These solutions are mainly used for functional plating and electroforming (Rose & Whittington, 2014).

3.2.1 Watts Bath

In 1910, Canning introduced a bath as a mixture of nickel sulphate, sodium chlorite and boric acid. He also stated that the bath must be slighly acidic. This bath is quite similiar to Watts bath, which originated at in 1916 by Professor O.P. Watts of University of Wiscousin. This bath is used even now, with a little modification for application of various industries. The main composition of the bath is shown in Table 3.1 (Dennis et al., 1993).

Table 3.1 Chemicals and concentration range of basic Watts Bath composition (Dennis et al., 1993)

Chemical	**Concentration range, g/lt**
Nickel chloride, $NiCl_2 \cdot 6H_2O$	100 - 300
Nickel sulphate, $NiSO_4 \cdot 6H_2O$	0 - 200
Boric acid, H_3BO_3	20 - 55

Watts bath makes high-speed electrodeposition possible. Nickel electrodeposition from Watts bath is the most used bath and has been used for many applications in order to modify properties of the materials such as hardness, wear resistance and corrosion resistance. Electrodeposited Ni coating properties depends on the surface properties of the deposit sample. The coating properties are mainly affected by current density, pH, cathode material, deposition time and the bath temperature (Di Bari, 2010). The basic schematic of Watts bath is shown in Figure 3.1.

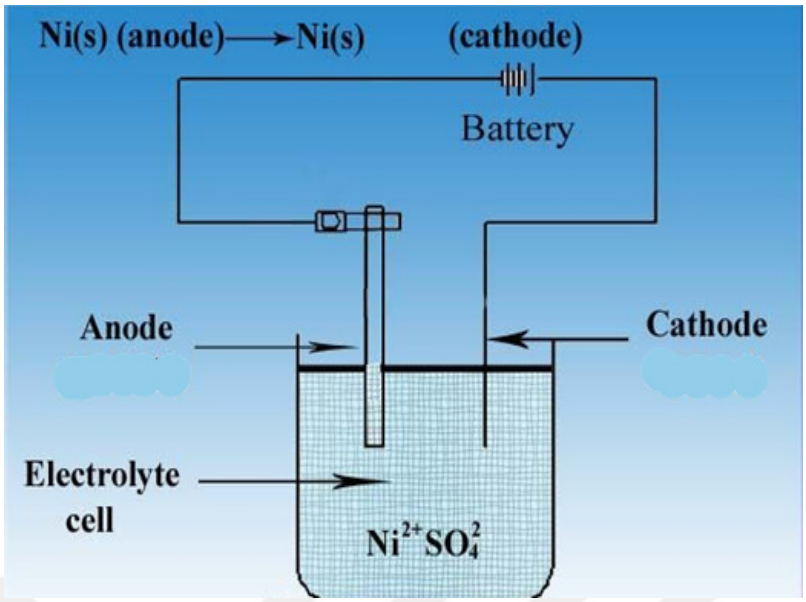


Figure 3.1 Basic electroplating process with Watts bath solution (Ferreira, 2007)

3.2.2 Nickel Sulphamate Bath

Nickel sulfamate bath is mainly used for deposition of various material type coatings or electroforming. In this bath, additional chemical agents are not required as coatings will have low stress regardless. Even though nickel sulfamate bath is costly compared to the Watts Bath, the high deposition rate and desposit properties still make nickel sulfamate bath desirable bath choice (Rose et al., 2014). Typical composition of Nickel sulfamate bath is shown in Table 3.2.

Table 3.2 Basic composition of nickel sulfamate bath (Rose et al., 2014)

Chemical	**Concentration range g/lt**
Nickel Sulphamate, $[Ni(NH_2SO_3)_2 \cdot 4H_20)]$	300-450
Nickel Chloride, $NiCl_2 \cdot 6H_2O$	0-30
Boric Acid, H_3BO_3	30
Temperature	40-60°C
pH	3.5 - 4.5
Cathode Current Density	2 – 15 A dm^{-2}

The nickel sulphamate has higher solubility compared to the nickel sulphate, which makes one of the advantages of nickel sulphamate bath. Therefore, it is possible to use higher nickel concentrations and use higher current densities for nickel coatings for diffrent surface modifications (Rose et al., 2014).

3.2.3 Other electroplating baths

Other solutions that have been used but not worldwide recognized or made wide industrial approach are fluoborate, all chrorite, all sulfate and sulfate-chlorite solutions.

The fluoborate soltions can be used in wide range of nickel concentrations, temperature and density, which also makes the solution easier to control. The fluoborate anion is corrosive, therefore any other material that enter the solution are chemically attacked. The coating process is similiar to Watts bath. The main adventage of fluoborate bath is the fact that it can be performed in high current densities (Di Bari, 2010).

The all chloride solutions have their advantage at their availability to operate at high cathode current density. Since the chloride concentration is higher compared to the other solutions, it has better conductivity and reduced tendecy to form nodular growth on the edge of the coating. Therefore, despositions from this solution is smoother, harder and stronger from Watts solutions. However, in this solution, substrate variety is limited and the process is harder to control and modify (Di Bari, 2010).

All sulfate bath has been used in situations where auxiliary anodes are insoluable. Especially when coating steel pipes and fittings, auxiliary anodes are nessecary. In this process, oxygen is evolved at insoluable anodes, therefore bath pH and nickel concentration rapidly changes. In order to control the bath properties, nickel carbonate is added to the bath. Insoluable anodes in this bath may be lead, carbon, graphite or platinum (Di Bari, 2010).

In order to overcome the disadvantages in all chloride solution, nickel chloride and nickel sulfate are used in roughtly same amount. This solution has high conductivity and it can be operated in high current densities. The stress of deposits are between Watts solution and all-chloride solution. Other properties can be also considered midway between Watts and all-chloride (Di Bari, 2010).

3.3 Nanocomposites

A nanocomposite is considered as a material compromised by at least two immiscible phases, seperated by interface region. One of the dimensions has to be at least nanoscale and the other, which is major portion of structure, is defined as matrix. Nanocomposite coatings definitons can be based on two methods which are nanostructred fillers or matrix, where filler nanostructures are dispersed (Tri, Nguyen, Carriere & Xuan, 2018).

Nanocomposite coating has wide range of applications, such as mechanics and automobiles, paper mills, textiles, food industries, microelectronics and magnoelectronics. The nanocomposites are mainly used as bulk and thin film forms. The reason nanocomposites have this wide range of application is because the synthesized nanocomposite structure acquires synergistic properties of its matrix and the guest material (Ahmad & Mohamed, 2014).

When evaluating the performance of the coating, one should always remember that there is no ‘best’ coating. The perfomance of the coating depends on many factors. For example, a coating is best suited for automobiles may seem ineffective in aircraft industry. There is also the factor a perfect coating in one machine may fail in another. Because of that, extensive testing is required to obtain the most suitable coating for a specific material. The behaviour of nanocomposite coatings are quite dependent on its bulk of the grain where disclocations play an important role. Even 10 nanometer diffrence in the nanocomposite might create a new nanocomposite with unique morphological properties (Davim, 2012).

According to the nature of matrices, nanocomposites can be classified into three main categories which are called metal-matrix, ceramic-matrix and polymer-matrix nanocomposites. Diffrent types of metal, ceramic and polymer matrix composites are shown in the Table 3.3.

Table 3.3 Various types of nanocomposites (Camargo, Satayanarayana & Wypych, 2009)

Material	**Examples**
Metal	Fe-Cr/Al_2O_3 - Ni/Al_2O_3 - Fe/MgO - Mg/CNT(carbon nanotube)
Ceramic	Al_2O_3/SiO_2 - SiO_2/Ni - Al_2O_3/TiO_2
Polymer	Thermoplastic/thermoset - polyester/TiO_2 - polymer /CNT

CVD and spray pyrolysis is considered as chemical synthesis methods for nanocomposites. Carbon nanotubes (CNT) are used for these methods. For example, alumina matrix structure can be obtained by anodizing the growth of carbon nanotubes into porous walls. Afterwards, CNT grows into hexagonal array, extending to the substrate of the matrix surface (Camargo et al., 2009).

Liquid Infiltration is another popular method for metal based nanocomposite synthesis such as Pb/Cu, Nb/Cu and Pb/Fe nanocomposites. At first, particles are mixed in order to obtain matrix metal material. Afterwards, heat treatment is done to melt the matrix, which matrix turns into liquid state in order to eliminate internal porosity (Yoon, Lee, Oh & Kim, 2001).

High ball milling can be considered a physical method especially if homogenious and uniform distribution is desired. Another mechanical method can be classified as ‘melt mixing’ as carbon nanotubes are mixed with the structure before polymer forms, afterwards extrusion and compression moulding processes in order to melt-mix (Camargo et al., 2009).

3.3.1 Ceramic Matrix Nanocomposites

In order to overcome intristic brittleness and mechanical problems of ceramics, ceramic matrix nanocomposites (CMCs) have been developed. Since ceramics have high stiffness and strength, ceramic nanocomposite synthesis have been widely researched. In addition, high-temperature stability, corrosion resistance and electrical insulation of the ceramic materials makes CMCs very attractive for variety of applications. Compared to the metallic alloys, ceramic have also particular revelance under harsh conditions. The first usage of CMCs were reported in 1960s, and is still currently being developed. For example, SiC fiber reinforced glass-ceramic composites can reach very high stiffness rate, while being mechanically stable (Cho, Boccaccini & Shaffer, 2009).

3.3.2 Polymer Matrix Nanocomposites

While ceramic and metals have been chosen as they have high stiffness and high thermal stability, they also have critical problem such as high dielectic potential. Hovewer, this problem does not have much influence on polymers because of its easy processing and mechanical flexibility, while also being cost-effective. Mechanical flexibility, tunable properties, and low dielectric constant makes polymer matrix nanocomposites (PMCs) widely used as a support for electronic circuits and electromechanical devices (Dang, Yuan, Zha, Zhou, Li & Hu, 2012).

3.3.3 Metal Matrix Nanocomposites

Metal matrix composites (MMCs) are widely used for various engineering applications for enhancement of the material compared to monolithic metals or alloys. For example, one can obtain MMCs by incorporating nanoparticles to the metal matrix. Silicon carbide, aluminum oxide, titanium dioxide, boron nitride nanoparticles are great examples of incorporation materials that have been used to enhance coating properties such as corrosion resistance and microhardness, depending on the characteristic of the nanoparticles (Shahri, Allahkaram & Zarebidaki, 2013).

The process of incorporation of the nanoparticles during electrodeposition method, which is used in order to synthesize MMCs, can be described in these steps:

- The particles transfer to the metal surface from the bulk of the solution
- Electrode surface adsorbes the nanoparticles
- Particles settling in the growing metal matrix (Gomes, Pereira, Fernandez & Pereiro, 2014).

3.3.4 Ni Matrix Nanocomposite Coatings

For the few past decades, scientists have worked on Nickel coatings because of its excellent properties such as corrosion-wear resistance and hardness There are various ways to synthesize Ni nanocomposite coatings such as thermal, plasma spraying, physical-chemical vapor deposition. Compared to these methods hovewer, electrodeposition stands out as it offers several advantages. Precise control, low energy requirements, uniform deposition, cost-effectiveness, versatility, high production rate and reduction of waste are properties that made electrodeposition widely researched and used (Ahmad et al., 2014).

Another notable Ni matrix nanocomposite synthesis method is process through sol-gel. Structures like SiO_2/Ni and Al_2O_3/Ni nanocomposites can be obtained thanks to metal-oxygen polymer bonds that occur after hydrolysis and condensation in organic media solvent. After gel structure forms, the gel is dried in order to obtain solid material, afterward termal treatment if needed (Camargo et al., 2009).

The electrodeposion prepared by nickel matrix is considred to have high density, minimum porosity, high wear and corrosion resistance. This made Ni matrix coatings commenly used in chemical, mechanical and electrionic industries. Currently, nanocomposite coatings are being researched and improved focusing on better microhardness, corrosion resistance and wear resistance. Therefore, a lot of metal articles focuses on this method and its nature. Currently, widely used incorporated nano size materials are SiC, ZrO_2, Al_2O_3, TiO_2, La_2O_3 and CeO_2 for nickel matrix

nanocomposites. Incorporated inert particles are very important factor for enhancing corrosion and wear resistance of the Ni matrix (Aruna et al., 2009).

In order to synthesize Ni based nanocomposites with electrodeposition, metallic, non-metallic compound or polymer particles are plated to a layer under electic field. The particles are incorporated on a conventional plating electrolyte in order to capture them as a metal film. In addition, synthesized film properties depends on the particle properties such as size, shape and charge, while also depending on the nature of the plating conditions of the bath, like current density, temperature, time and pH (Ahmad et al., 2014). In order to incorporate particles successfully, mechanical dispersion electroplating is also needed. This method is basically means suspending the particles in electrolyte while using mechanical mixing or ultrasonification (Xia, Wu, Wang, Jia & Wang, 2007).

Xia et al. synthesized Ni-TiN nanocomposite coatings on steel substrate while focusing on mechanical dispersion properties on the coating process. TiN nanoparticles were used in pH = 4-5 Watts bath while using 2-5 $A.dm^{-2}$ curent density Their results show that ultrasonicifaction greatly enhances the nanoparticle coating properties, having dense and homogeniously dispersed structure (Xia, Wu, Wang, Jia & Wang, 2009). Similiar work reported by Zheng & An synthesized Zn-Ni-Al_2O_3 nanocomposite, using Ni-Zn alloy as substrate while using Watts bath for electrodeposition. They state that incorporated Al_2O_3 nanoparticles were 100nm size. The bath conditions were pH = 5, while using 4 $A.dm^{-2}$ current density. They report that nano-alumina content enhanced the corrosion resistance property, as dispersion was also homogenious thanks to ultrasonic vibration they applied while coating (Zheng & An, 2007). Wang et al. used TiO_2 as nanoparticles to incorporate to synthesize Ni-P-TiO_2 nanocomposites. In their work, the bath temrerature was relatively high, having 70 ^oC temperature while the pH of the bath is around 3.5. They reported that using TiO_2 nanoparticles greatly enhanced the microhardness and wear resistance. Hovewer, they also stated that using higher concentration of TiO_2 causes agglomeration of particles, therefore resulting in reduction of mechanical properties of the coating (Wang et al., 2014).

3.4 Electrodeposition Method

Electroplating can be defined as one specific type of electrolysis. In electrolysis, when dielectric current passes through an electrolyte, chemical reactions take place between the circuit and the solution. Understanding the principles of electrodeposition is crucial for development of electroplating technology (Lou & Huang, 2006).

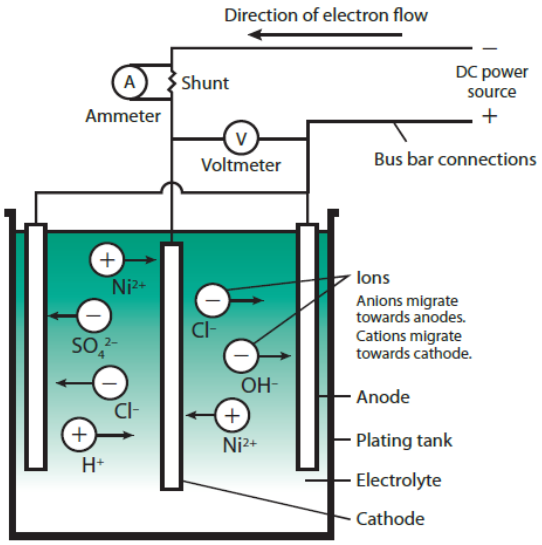


Figure 3.2 Basic schematic of electrodeposition (Rose et al., 2014)

Cathode is connected to the negative pole of the electric source, meaning that it will supply electrons to the electrolyte. The anode is connected to the positive pole, it will accept electrons from the electrolyte. Initially, with the efect of the current, the metal ions from the electrolyte is reduced. At the cathode, electrons are supplied to cations, which will migrate to anode (Lou et al., 2006). The reaction in aquaeous medium follows this equation:

$$M^{n+} + ne^- \rightarrow M \qquad (3.1)$$

While at the anode, electrons are supplied to the anions with the effect of the current, migrating to the anode.

$$M \rightarrow M^{n+} + ne^- \qquad (3.2)$$

In the case of nickel deposition, positively charged Ni^{2+} ions react with two electrons ($2e^-$) and are converted to metallic nickel Ni^0 at the matrix surface. The amnout of nickel deposited is dependent on current time and can be calculated from this equation below;

$$m = 1.095 \text{ x } aIt \tag{3.3}$$

where m is the amnout of N^0 deposited at the cathode in grams, I is the current in tank in amperes, t is the time the current flows in hours and a is the current efficiency ratio. 1.095 comes from the atomic weight of nickel (M= 58.69 g/mole) divided to number of electrons (n) and Faraday constant (F) that is equal to 26.799 A-h (M/nF).

When electroplating, anode efficiency for nickel dissolution is practically at %100, while cathode efficiency is between 90-97 percent. Hovewer, if the pH of the concentration is too high, hydroxyl ions may be discharged to the nickel solution, disturbing the properties of the electrolyte. Additionally, because anode and cathode efficiencies are not equal, nickel ion concentration and pH of the nickel solution will gradually increase, therefore requiring optimization or new path prepration after electrodeposition process (Di Bari, 2010). Therefore, pH is very important factor in electrodeposition process. The hydrogen ion concentration play important role in bath performance, as bright plating range, cathode efficiency, effect of impurities, stress, throwing power and physical properties depend on it. In many baths, additives are used in order to control the pH value of the bath, such as boric acid in the Watts bath solutions, hovewer, as explained before, the pH value still changes gradually while electroplating occurs. In order to counter this issue, dilute sulphuric or hydrochloric acid is used to keep the pH stable. On the other hand, pH of the bath can also be increased by adding nickel carbonate or sodium hydroxide to the solution (Rose et al., 2014).

Eq. 3.3 demonstrates that the current density is important factor in electroplating. In addition to deposition rate, it is important to keep current in the constant rate in order to obtain uniform appereance and avoid accidental burning. In order to avoid

these problems, higher surface area is suggested for cathode. Therefore it is important to evaluate current density to obtain plating with desired thickness and homogenity (Rose et al., 2014).

If the bath temperature increases, it might affect the coating on the substrate because of the rate of nucleation and growth of the grains, brightness range, throwing power, hardness and internal stress. Many research work has been done to find optimum temperature for the nickel coating process. It was concluded that 45 ºC is the optimized temperature of the nickel coating (Ahmad et al., 2014).

Recently, many studies supported the idea of Ni coatings in the prescence of nanoparticles such as Al_2O_3, TiO_2, SiC or lubricating particles in order to improve mechanical and tribological properties of surfaces. Therefore, many researchers studied the incorporation of nanoparticles to the substrate structure in Ni-based nanocomposited synthesized by electrodeposition (Fahami, Tabziri, Rostami & Kahrizsangi, 2013).

Nowadays, nanoparticle coatings are considered valuable asset for improving surface sciences and applications. There might be imperfections such as voids between the particle matrixes, however, increasing the nanoparticle concentraiton in the bath results in stonger and more resistant coating (Rostami et al., 2013).

Electrodeposition with nanoparticles can be expressed in two steps. First, nanoparticles are weakly adsorbed to the surface of the cathode with Van der Waals force effect. Afterwards, particles are adsorbed to the surface, affected by Coulomb forces, thanks to the applied electric field in the electrodeposition process (Ahmad et al., 2014). Simple co-deposition with electrodeposition is given in Figure 3.3.

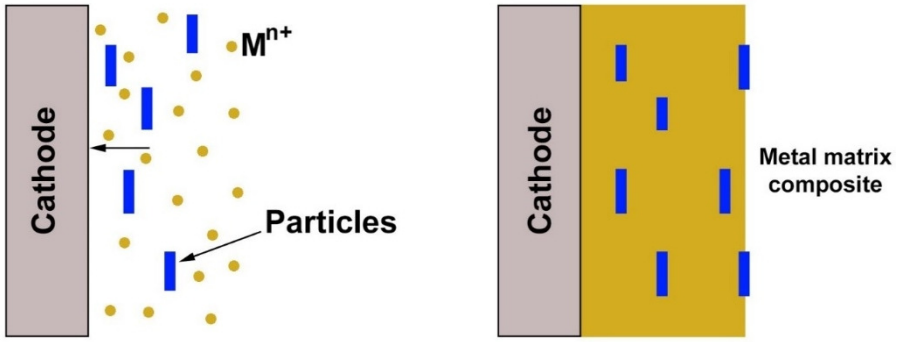


Figure 3.3 Electro co-deposition process with nanoparticles (Thurber, Mohamed & Golden, 2016)

Electrode/particle interaction is highly dependant on particle properties such as type, size, surface charge and concentration. If the particle is smaller, Van der Waals and electrostatic forces will be greater in the matrix. Hovewer, smaller particle size makes it diffult to co-deposit the particles because of particle aggloremation. The deposition of particles also relies on the current density of the bath. It is reported by many papers stating that until the thresold value of current density, nanoparticle incorporation is enhanced. At lower current densities, particle incorporation rate on the metal is faster than growing coating metal. On the other hand, situation is reverse in higher current densities, resulting in lower nanoparticle content in the composite (Ahmad et al., 2014).

CHAPTER FOUR
EXPERIMENTAL STUDIES

This experimental work covers the preparation of titanium dioxide (TiO_2), doped TiO_2, and codoped TiO_2 nanoparticles by sol-gel method. These synthesized nanoparticles were used to deposite Ni matrix nanocomposite coatings by electrodeposition method using diffrent current density values and nanoparticle concentrations.

4. 1 Synthesis of Nanoparticles

4.1.1 Production of TiO_2 nanoparticles

Titanium (IV) isopropoxide and deionized water have been used as starting materials for sol-gel synthesis of TiO_2 nanoparticles. The solution was prepared with titanium (IV) isopropoxide dissolving in deionized water with them molar ratio of 1:220. This solution was stirred until the precursor dissolved. After mechanically strirring the solution for 30 minutes, polyethylene glycol (PEG) was used as capping agent which prevents particles from agglomeration. PEG is a perfect capping agent for this synthesis because it can dissolve various solvents such as deionized water, alcohol and benzene. PEG reduces the tendecy of particles to aggreate by stericstabilization (Shameli et al., 2012). Citric acid ($C_6H_8O_7$) solution was added dropwise to the solution until the pH value got to 3.06, as pH of the solution has important role in the final particle size produced by sol-gel method (Ibrahim & Sreekantan, 2011). The solution is left to drying for 43 hours in 100ºC in order to evaporate the solvent. Finally, the driel gel calcined in a furnace at 550 ºC for 2 hours. The flow chart of this synthesis is illustrated in Figure 4.1.

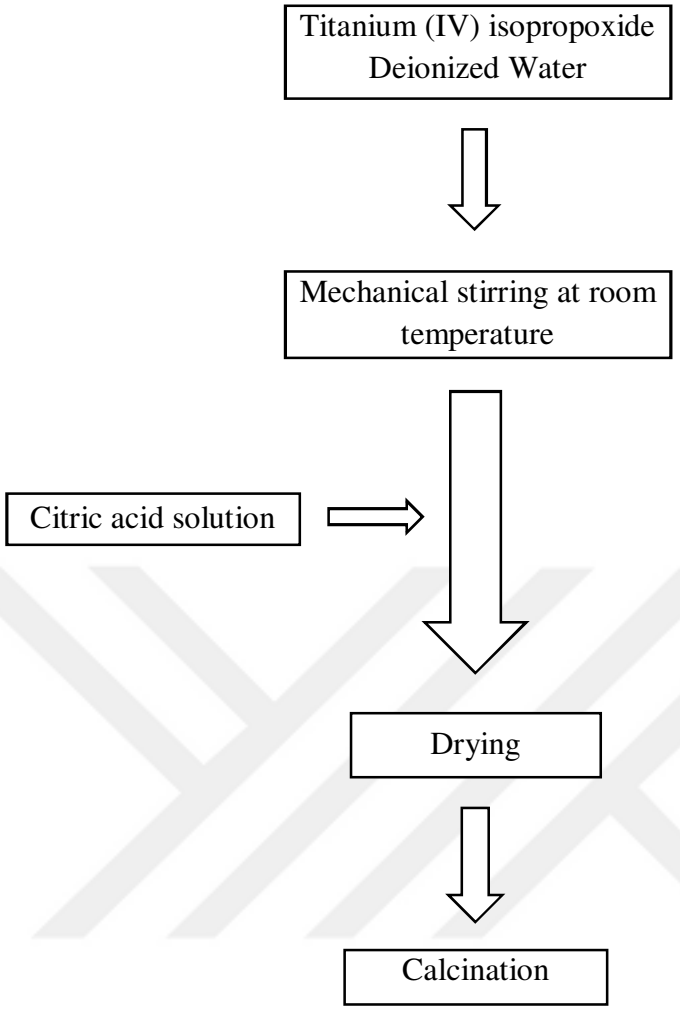


Figure 4.1 Schematic illustration of TiO_2 synthesis by sol-gel method

4.1.2 Production of Mn-doped and Mn-N codoped TiO_2 nanoparticles

In order to synthesize Mn doped TiO_2 nanoparticles, titanium (IV) isopropoxide was dissolved in deionized water solvent with molar ratio of 1:220, which is titania solution. At the same time, manganese (II) chloride tetrahyrate ($MnCl_2 \cdot 4H_2O$) solution was prepared with 100 mL deionized water in order to create 0.25 mol% manganese/titania solution. The manganese solution was added to titania solution dropwise, forming solution A. After stirring process, PEG was added to the solution after the precursor dissolved. Citric acid were added to modify the pH of the solution, similiar to the undoped TiO_2 synthesis of this work. Finally the solution was dried for 43 hours at 100 ºC, then calcined at 550 ºC for 2 hours.

On the other hand, codoping Mn and N into TiO_2 process has been conducted with titanium (IV) isopropoxide, manganese (II) chloride tetrahydrate and urea (CH_4N_2O) have been used as titania, manganese and nitrogen precursors for this synthesis, respectively. Solution A was prepared by adding manganese solution (%0.25 wt.) dropwise to the titania solution. Solution B was prepared similiarly to solution A, as dissolved nitrogen precursor (%0.5 wt.) used this time. The nitrogen precursor was added dropwise to the titania solution, forming solution B. It is important to note that, in order to manganese and nitrogen to substitute O and Ti atoms in TiO_2 cystal stucture succesfully, the doping process has to be done before condensation process starts, because that is the process where the first tri-dimensional network of gel structure forms (Akpan & Hameed, 2010). After stirring this solution, PEG was added in order to control aggleromation of the particles and citric acid solution was used to modify the pH of the solution. The solution was left for aging. After aging process, it was dried for 43 hours at 100 ºC, then calcined at 550 ºC for 2 hours. This process is explained in the Figure 4.2.

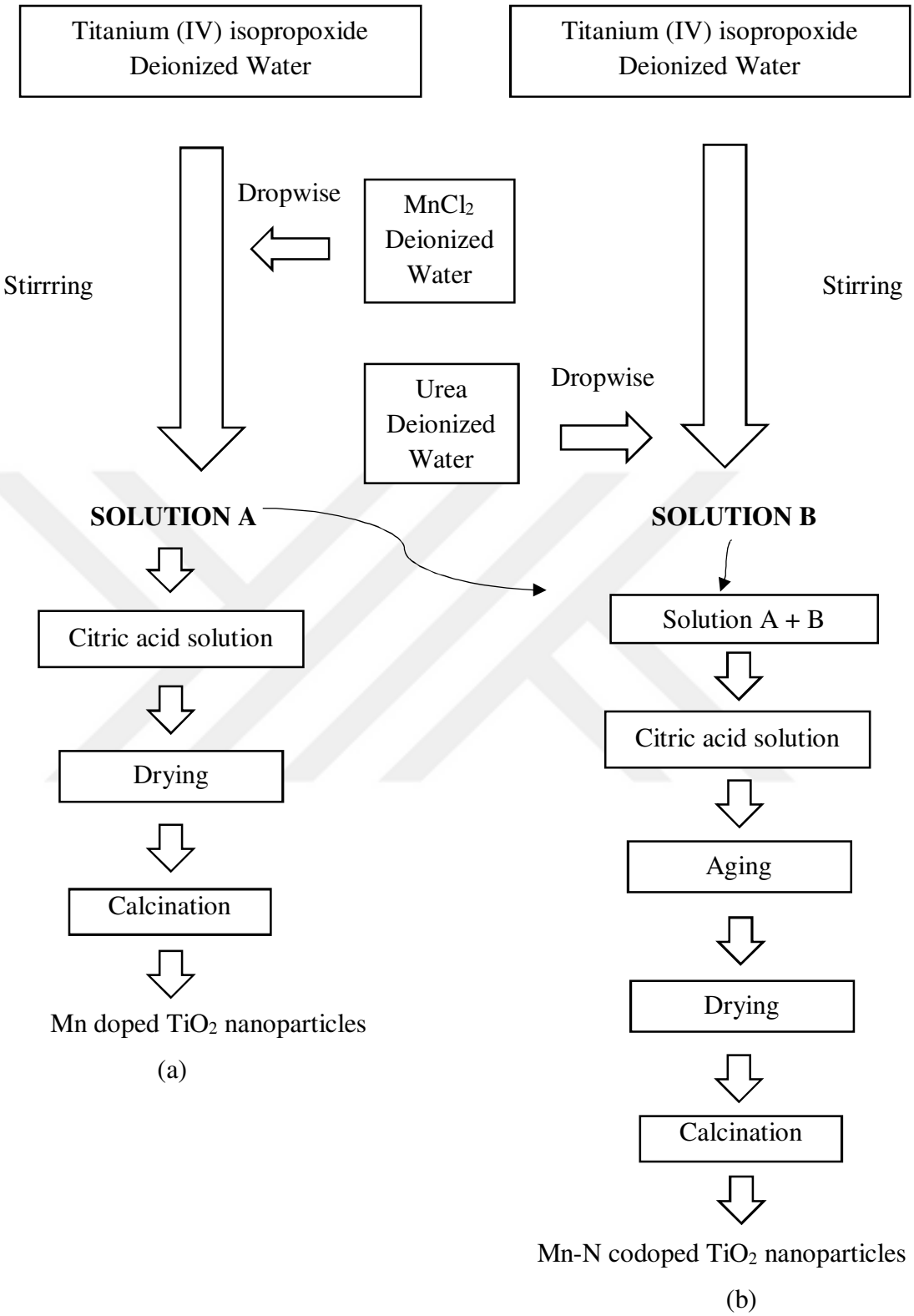


Figure 4.2 Schematic illustration of doped (a) and codoped (b) TiO_2 nanoparticle synthesis by sol-gel method

4.2 Prepration of the substrate

Stainless steel with dimensions of 100mm×25mm were used as substrate material. The surface of steel substrates were mechanically polished using SiC paper with 400, 800 and 1200 grit. Before etching the substrates, they were treated in a solution with ethanol, acetone and deionized water in ultrasonic bath for 10 minutes. Afterwards, substrates were pre-treated for 20 seconds in etching solution, which is given in Table 4.1. After etching process, the substrates were washed with distilled water.

Table 4.1 Etching solution

Chemical	**Amount (vol %)**
Nitric acid (HNO_3)	2.5
Hydrochloric acid (HCl)	1.5
Hydrofluric acid (HF)	1
Deionized water	95

4.3 Production of Nickel and Nickel matrix nanocomposite coatings with electrodeposition method

Ni and Ni matrix nanocomposite coatings were produced with electrodeposition method using Watts type solution. Nickel sulfate, nickel chloride and boric acid were used in Watts bath composition. Nickel sulfate is used as Ni source and nickel chloride is used in order to keep anode active. Boric acid were used to modify the pH of the solution. Sodium dodecly sulfate (SDS) is used as additive in order to modify the surface structure (Rose et al., 2014). TiO_2, Mn doped TiO_2 and Mn-N codoped TiO_2 particles, ranging between 50 – 80 nm in particle size have been added to the Watts bath in order to obtain Ni matrix nanocomposite coatings. Before electrodeposition process started, the Watts bath was stirred for 24 hours in order to avoid precipitation of the nanoparticles. The stirring also continued during the electrodeposition process.

304 stainless steel is used as cathode for Ni matrix nanocomposite coating with electrodeposition method. CHROMA 62050P-100-100 is used as power supply and

KUDOS SK7210LHC is used as ultrasonic/mechanical stirrer for coating. The Watts bath composition and operating conditons are given in Table 4.1 and 4.2, respectively. The nanocomposite are named according to their current density and nanoparticle concentration and abbreviations are given in Table 4.3. The experimental setup is illustrated in the figure below.

Table 4.2 Watts bath electrodeposition composition and parameters

Substrate	Stainless steel
Surface modification	Acidic surface treatment
Particle size of undoped/doped/codoped TiO_2 nanoparticles (nm)	50 – 80
Concentration of undoped/doped/codoped TiO_2 nanoparticles (g/L)	1 - 3
Time (min)	15
Current Density (A dm^{-2})	2 - 4 - 6
Temperature (°C)	45

Figure 4.3 Experimental setup (Personal archive, 2019)

Table 4.3 Abbreviation of substrates and their coating properties

Abbreviation	Nanoparticle type (g/L)	Current density ($A.dm^{-2}$)
C-2	-	2
C-4		4
C-6		6
CT1-2	1 g/L TiO_2	2
CT1-4		4
CT1-6		6
CT3-2	3 g/L TiO_2	2
CT3-4		4
CT3-6		6
CTM1-2	1 g/L Mn doped TiO_2	2
CTM1-4		4
CTM1-6		6
CTM3-2	3 g/L Mn doped TiO_2	2
CTM3-4		4
CTM3-6		6
CTMN1-2	1 g/L Mn-N codoped TiO_2	2
CTMN1-4		4
CTMN1-6		6
CTMN3-2	3 g/L Mn-N codoped TiO_2	2
CTMN3-4		4
CTMN3-6		6

4.4 Characterization of the Nanoparticles and Ni matrix Nanocomposite Coatings

4.4.1 X-ray Diffraction (XRD)

X-ray diffraction is commonly used technique for studying the crystal structure and atomic spacing of a material. Basically, the crystal structure is exposed to the monochromatic X-ray and this incident results are investigated. Cathode ray tube is

used to generate X-rays, afterwards, it is filtered to create monochromatic radiation directed to the sample. This interaction between sample and X-ray diffraction can be explained by Bragg's law:

$$n\lambda = 2d\sin\theta \tag{4.1}$$

where n is integer, λ is wavelength of the monochromatic X-rays illuminated on the sample, d is the interplanar spacing generating the diffraction and θ is the diffraction angle. This law is used for investigating lattice spacing and electromagnetic radiation angle which are detected, processed and counted. If the sample is scanned through a range of 2θ angle all possible X-ray diffraction date should be obtained, therefore completely analyzing the crystal structure and lattice (Bunaciu, Udriştioiu & Enein, 2015).

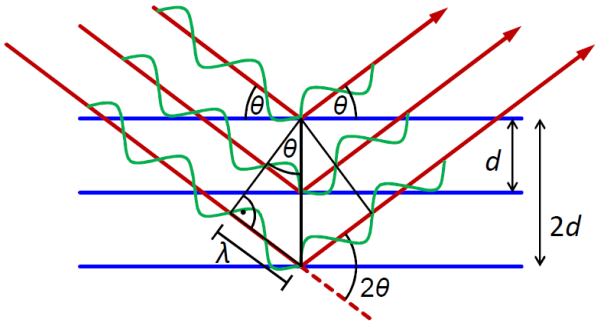


Figure 4.4 The diffraction of light according to Bragg's law (Bunaciu et al., 2015)

X-ray diffractometers consists of X-ray tube, which is the illumination source, a sample holder for the sample and X-ray detector to analyze diffracted X-rays. In order to procude electrons from the cathode, filament is heated, aftewards by applying the voltage, electrons bombard the sample. When electrons have sufficient energy to affect the electrons of the material and dislodge them, characteristic X-ray spectra is obtained (Bunaciu et al., 2015).

Unkown crystalline materials such as minerals and inorganic compound crystal structure can be indentified with this analysis. This information is quite important for geology, enviromental science, material science, engineering and biology.

Furthermore, X-ray diffraction is also used when a grains, clays etc. can't be determined optically, but possible with XRD (Robinson, 2012).

XRD is considered high-tech and nondestructive technique for analyzing various materials such as polymers, catalysts, minerals, solar cells and semiconductors. Therefore XRD can be used in microelectronics, power generators, aerospace and many more. Understanding the defects of the particular crystal is quite important to determine a materials stress, its texture, size and degree of crystalinity (Robinson, 2012).

In this study sol-gel synthesized undoped, doped, codoped nanoparticles and electrodeposited coatings were analyzed using X-Ray Diffraction (XRD, Rigaku, D/Max-2200/PC). The grazing incident angle was 1° at 40 kV and 30 mA using Cu Kα radiation with a scanning speed of 4° 2θ/min, from diffraction angle of 3° to 90°.

4.4.2 Particle Size Analysis

The population of particles in a powder can be desribed as 'particle size distribution' (PSD), which affects the properties of the material and dispersions in a lots of ways. For example, electric conductivity, chemical reactivity, optical efficiency of the material and many more can be affected by sizes of the particles which makes up the structure (Allen, 1990).

In the matter of single sphere, their size can be described as one figure, which is its diameter. For other regular shapes it is usually necessary to specify more than one dimension; a cuboid is defined by length, width and height. For the vast majority of materials, particles are rarely spherical. For such irregular particles, the "size" of the particle depends on the measurement methods. Therefore, it is important to decide which technique to use to analyze the size of the particle, which can differ with the purpose of the analysis. Mainly, instead of the generic size value, the size value of some property of the partciles which are size-dependent should be preffered when making the analysis (Allen, 1990).

Currently, the most commonly method to measure particle sizes of materials that ranges between few nanometers up to one micron, is dynamic light scattering method. Typical applications of this method are emulsions, micelles, polymers, nanoparticles and colloids. The sample is illuminated by a laser beam and fluctuations of the scattered laser are detected at a known scattering angle. The particles, scatter the light, thefore giving information about their motion (Horiba, 2017).

In this study, Malvern Zeta Sizer Nano ZS90 device is used to determine particle size of TiO_2, Mn doped TiO_2 and Mn-N codoped TiO_2 particles with laser diffraction principle.

4.4.3 Scanning Electron Microscopy (SEM)

Scanning electron microscope (SEM) is widely used in order to obtain microstructure morphology and chemical composition information. The principle of SEM relies on basic principles of light optics. The experiments of electrons under magnetic field started around 1890s which can be described as the first version of SEM. Until this decade, SEM has been developed by using diffrent light source and high quality energy beam.

In SEM, electrons produced passed through a combination of lenses and apertures to produce a focused beam of electrons which hits the surface of the sample. The electrons in the beam interact with the sample, producing various signals that can be used to obtain information about the surface topography and composition. Electrons are generated with a heated filament and accelerated to an anode. However, in SEM there is a column under high vacuum ($<10^{-5}$ Torr). Electrons are accelerated toward the anode under potential differences generally of 1-30 kV. The electrons can be focused to a narrow beam (5 nm to 1 µm) that is capable of producing a response on a small area of the sample. These responsive electrons are later analyzed by detector, giving information about surface structure and chemical composition (Zhou, Apkarian, Wang & Joy, 2006).

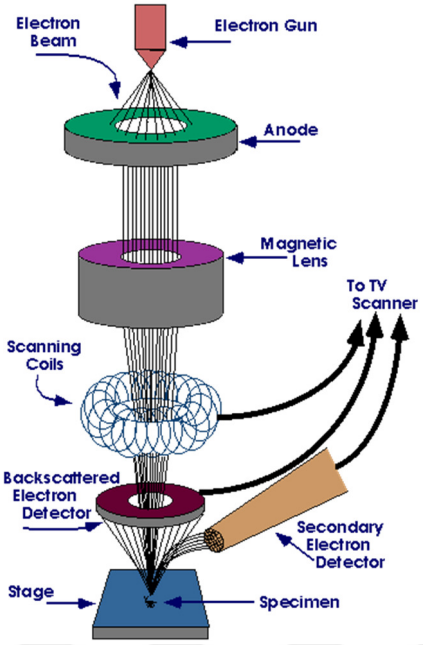


Figure 4.5 Basic schematic of SEM analysis (Joshi & Bhattacharyya, 2008)

SEM is widely used compared to the other similiar analysis methods because of its easy specimen prepration and the specimen surface can easily observed. If the material is stable, all that is required is preparation of the surface and affixing to a mounting stub. However, since electrons are highly absorbed by matter, including air, this means that the specimen chamber of the microscope must have a high vacuum during viewing. SEM is the requirement that nonconducting surfaces must be metallized. Primary beam electrons will, upon surface bombardment, build up a static charge if not conducted to ground. For nonconducting materials, the metal coating serves this function (Joshi et al., 2008).

In this study, the surface morphology and elemental composition of the coatings was examined by using JEOL-JSM 6060 Scanning Electron Microscopy with an Energy Dispersive X-ray spectroscopy (IXRF System EDS) system attachment.

4.4.4 Electrochemical method

Electochemical method is widely used in order to determine the corossion resistance properties of the material. In this study, the corrosion measurements of Ni

and Ni based nanocomposite coatings were performed using a Gamry potentiostat/galvanostat system controlled by Gamry Framework Software. In order to obtain electrochemical information, Echam Analyst Software was used. The corrosion measurements were conducted in ParaCell Kit for Flat Specimens Gamry Cell, using 3.5 (%wt) NaCl solution at 25 °C. AgCl electrode was used as referance electrode in order to determine the electrochemical properties of the coating. Electrochemical properties were analyzed to measure corrosion performence of Ni based nanocomposite coatings by potentiodynamic measurements. Open circuit potential (OCP) was measure in NaCl solution for 30 minutes. Tafel measurements were carried out between -0.25 V and + 0.25 V at 0.25 mV/s scaning rate. Potentiodynamic measurements were conducted between -0.3 V and 0.8 V at 1 mV/s scanning rate.

CHAPTER FIVE
RESULTS AND DISCUSSION

5.1 Characterization of sol-gel synthesized nanoparticles

Titania is widely used and investigated material for various reasons. Its chemical structure stability, biocompatiliblity, non-toxicity, cost effectiveness, physical, optical and electrical properties can be described as these reasons. Among these properties, its photocatalytic properties have been exploited in various enviromental applications to remove unwanted organics from water and air. This leads to production of pigments, fillers, catalyst supports and photocatalysts.

It has been previously mentioned that the final properties of the material depends on size, morphology and crystal state of the TiO_2, therefore obtaining nano-sized TiO_2 nanoparticles with excellent crystalliny is desirable for nano-sized products. The most common and effective way is to synthesize TiO_2 nanoparticles with sol-gel method, carrying out hydrolysis and condensation process on titanium alkoxides in aqueous media (Macwan, Dave & Chaturvedi, 2011).

XRD analysis results of undoped TiO_2 nanoparticles are shown in Figure 5.1. The nanoparticles show only anatase phase of TiO_2 (JCPDS card No. 21-1272) diffraction peaks on the XRD patterns. The XRD pattern is characterized by (101), (103), (004), (112), (200), (105), (211), (204), (116), (220) and (215) diffraction peaks of anatase phase at 25.28°, 37.03°, 37.80°, 38.60°, 48.08°, 53.8°, 55.1°, 62.74°, 68.8°, 70.3° and 75.08°, respectively.

According to the literature reseach, it has been widely regarded as having anatase structure reduces the particle size and improved cystalinity, therefore enhancing photocatalytic properties, which affects electron-hole recombination of the surface (Papadimitriou, Stefanopoulos, Romanias, Paganiannakopoulos, Sambani & Tudose, 2011; Thota et al., 2014).

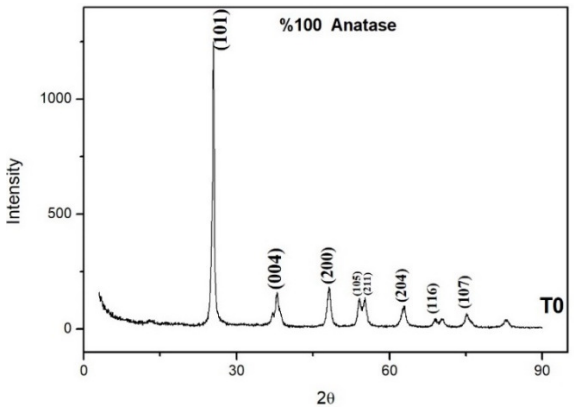


Figure 5.1 X-ray θ-2θ scans of undoped TiO_2 nanoparticles

In order to analyze the particle size of the nanoparticles, a solution was prepared with 20 ml butanone and 20 mg TiO_2 for Zeta-sizer device. Figure 5.2 shows the particle size distribution and particle size value.

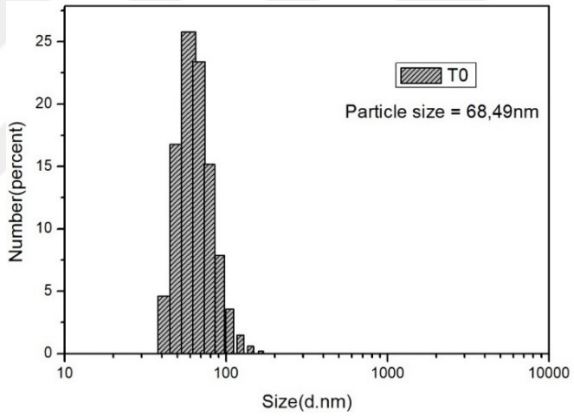


Figure 5.2 Distribution chart and particle size value of T0 nanoparticles

Doping method is one of the many paths to enhance various properties of TiO_2 nanoparticles such as particle size and crystallinity. These materials can be nonmetal, metal and noble metals. Mn doped TiO_2 nanoparticles were prepared by adding $MnCl_2$ solution to the sol-gel synthesis. For Mn-N codoped TiO_2 nanoparticle synthesis, urea solution was included to the solution with $MnCl_2$ solution.

XRD analysis results of Mn doped and Mn-N codoped TiO_2 nanoparticles are shown in Figure 5.3. The nanoparticles show only anatase phase of TiO_2 (JCPDS card No. 21-1272) diffraction peaks on the XRD patterns, similiar to the undoped TiO_2. The XRD pattern is characterized by (101), (103), (004), (112), (200), (105), (211), (204), (116), (220) and (215) diffraction peaks of anatase phase at 25.28°, 37.03°, 37.80°, 38.60°, 48.08°, 53.8°, 55.1°, 62.74°, 68.8°, 70.3°and 75.08°, respectively.

XRD results show that doping Mn and N to the TiO_2 crystal structure did not change the crystal structure of TiO_2. The main absorbstion peak has slightly changed and peak broadening has been observed. The broadening of the main peak is a result of the changes occurred in the crystal structure with Mn and N addition. Mn, a transition metal which has less charge than Ti would affect the concentration of oxygen vacancies in TiO_2 matrix. This results in bond rupturing and ionic rearrangement, which changes the crystal structure of TiO_2 (Larios, Gordillo, Mendoza, Rojas, Mantilla & Gomez, 2016).

Similiarly, nitrogen has similar ionic radius to oxygen, which makes it easier to use as a dopant while not greatly changing the TiO_2 crystal structure. Furthermore, reduction of particle size were observed with Mn-N codoped nanoparticles. This occurrence can be explained with two reasons. The impurity N atom inhibiting the particle growth because of its charge difference with oxygen, while also internal structural incoherence can occur within the crystal structure due to dopant induced distorsions (Cheng, Yu, Xing & Wan, 2012; Jagadale, Takale, Sonaware, Joshi, Patil & Kale et al., 2008).

Similar work has been done by Nurhasanah et al. with their experiment on doping process on CeO_2, as they doped Zn in order to enhance its optical capabilities. Their XRD peak results state that since dopant materials has different ionic charge and radius, this results in lattire strain which ends up XRD main peak broadening. They mentioned that low doping content does not affect the XRD diffraction peaks (Nurhasanah, Sutanto & Futikhaningtyas, 2014). In a different work, Ebrahimifard et. al. synthesized Al-Ga codoped ZnO and investigated its optoelectronic properties.

Their XRD results state that, impurity dopant atoms with different properties such as ionic charge and radius resulted in a change in crystal lattice, which resulted in broadening in the meain peak. This broadening resulted in crystal size reduction which enhanced the optoelectrical properties of codoped ZnO (Ebrahimifard, Golobostanfard & Abdizadeh, 2013).

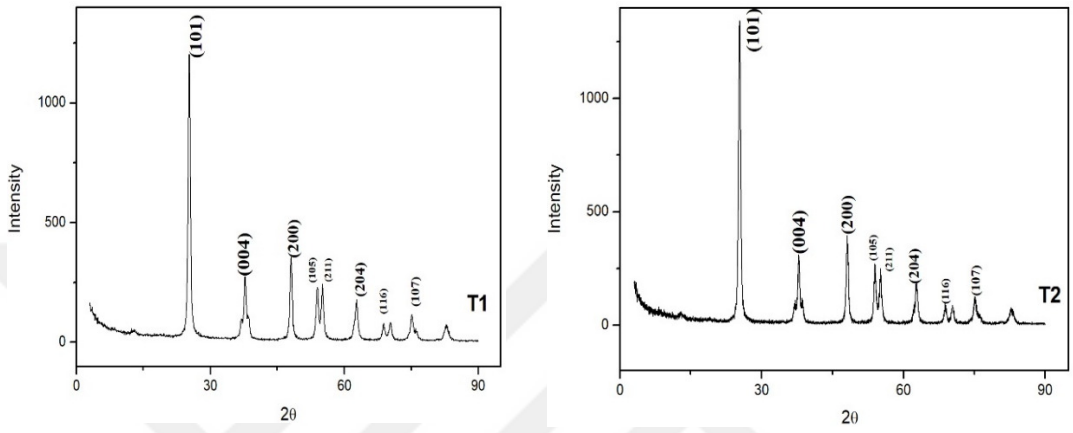


Figure 5.3 X-ray θ-2θ scans of (a) Mn doped, (b) Mn-N codoped TiO_2 nanoparticles

Similiar to undoped TiO_2 particle size analysis, 20 ml butanone and 20 mg Mn doped/ Mn-N codoped TiO_2 nanoparticle solution was prepared for Zeta-sizer device. Particle size distribution of these nanoparticle are shown is Figure 5.4. Synthesized nanoparticle sizes were between 50-80nm.

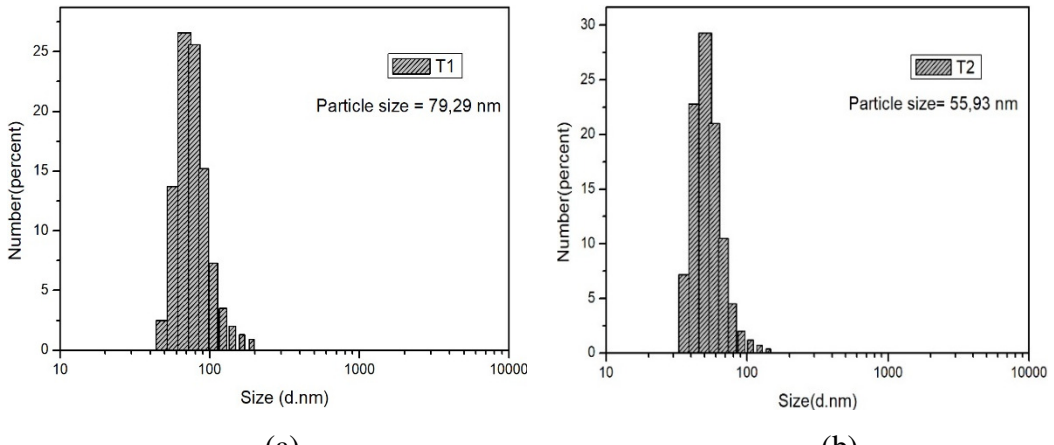


Figure 5.4 Distribution chart and particle size value of (a) Mn doped, (b) Mn-N codoped nanoparticles

5.2 Characterization of Electrodeposited Nickel and Nickel Matrix Nanocomposite Coatings

Ni coatings were prepared with diffrent current densities and their X-ray diffraction patterns for 2, 4, 6 A.dm^{-2} current density electrodeposition are shown in Fig. 5.5. The XRD peaks shows typical 2θ characteristic peaks of nickel at 44.48°, 51.83° and 76.35°, which corresponds to (111), (200) and (220) crystalographic plane, respectivevly (Nickel XRD JCPDS Ref. No. 70-1849). It can be seen that as current density changes, the Ni peak at XRD graph intensity also changes. Ni atom incorporation from anode to stainless steel increases at higher density values, resulting in more incorporated Ni atoms on the surface (Ahmad et al., 2014). Nickel matrix coatings are named with C, Ni matrix nanocomposite coatings with TiO_2 nanoparticles are named with CT, Ni matrix nanocomposite coatings with Mn doped TiO_2 nanoparticles are named with CTM and finally, Ni matrix nanocomposite coatings with Mn-N codoped TiO_2 nanoparticles are named with CTM abbreviations.

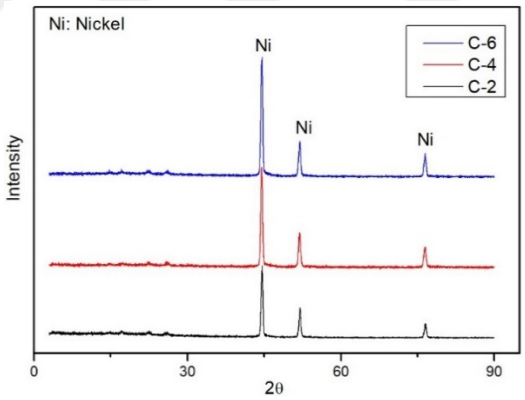
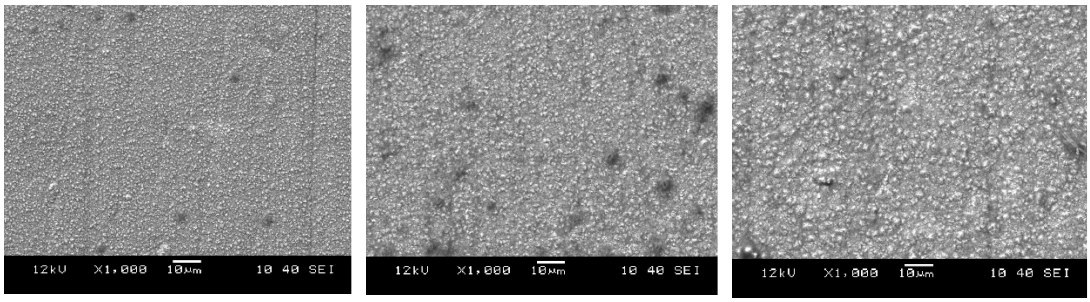


Figure 5.5 X-ray θ-2θ scans of Ni coatings at 2, 4 and 6 A dm^{-2}

The surface morphologies of nickel composite coatings electrodeposited at 2, 4, 6 A.dm^{-2} current densities analyzed by SEM are shown in Figure 5.6. The results show that surface morphology depends on current densities as higher current density coatings results in dense surface, resulting in more Ni atoms on the surface of stainless steel (Rostami et al., 2013).

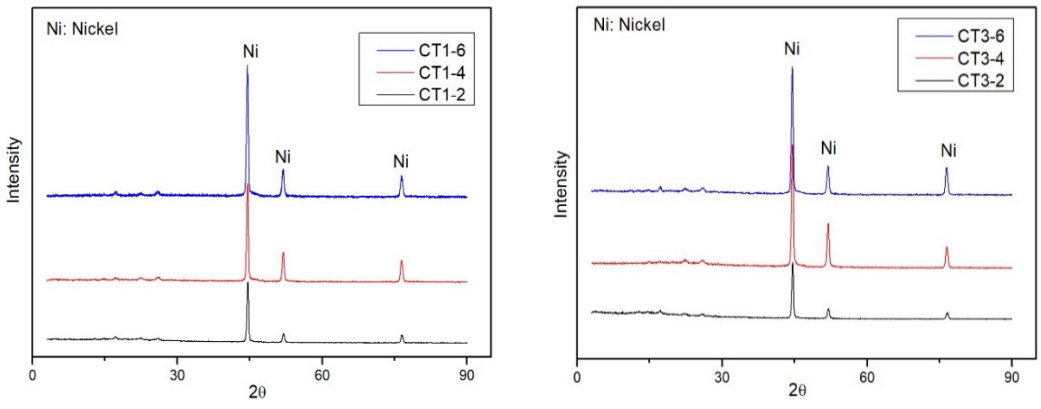


(a) (b) (c)

Figure 5.6 Surface morphologies of nickel coatings electrodeposited at (a) 2, (b) 4 and (c) 6 A.dm^{-2} current densities

5.2.1 Characterization of Electrodeposited Ni/TiO$_2$ Nanocomposite Coatings

Ni-TiO$_2$ nanocomposite coatings were conducted with 2, 4 and 6 A.dm^{-2} current density and nanoparticle concentrations of 1 and 3g/l TiO$_2$. The X-ray diffraction patterns of these coatings are shown in Figure 5.7. Similiar to the Ni coatings, the 2θ characteristic peaks of nickel at 44.48°, 51.83° and 76.35° corresponding to (111), (200) and (220) planes of the crystal lattice, respectively. Even though there is TiO$_2$ in the structure, the respective titania peaks were not observed because of its very low concentration compared to the nickel concentration.

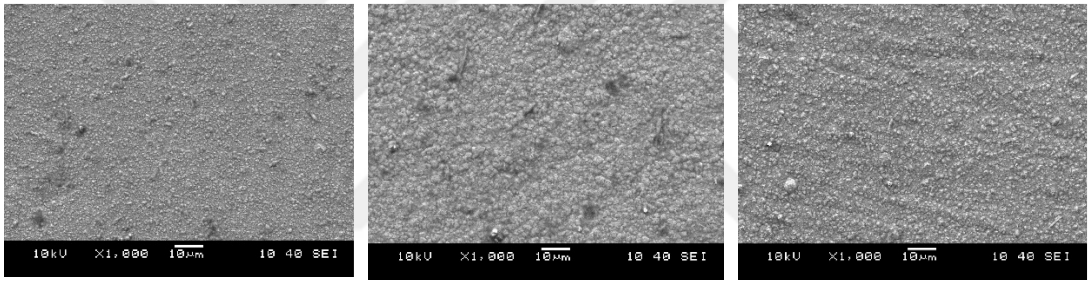


(a) (b)

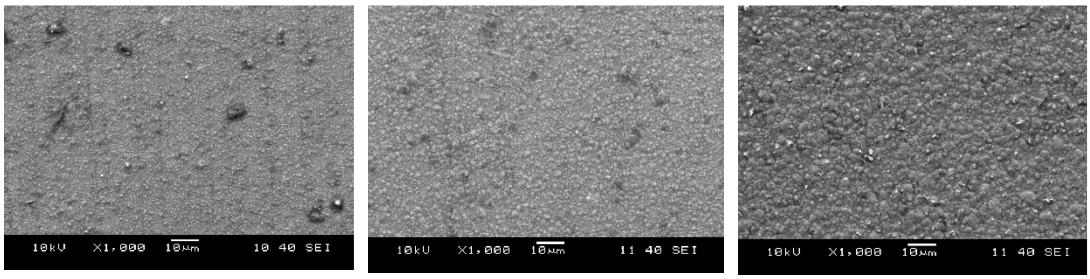
Figure 5.7 X-ray θ-2θ scans of Ni-TiO$_2$ nanocomposite coatings with TiO$_2$ nanoparticles (a) 1g/l, (b) 3g/l concentration electrodeposited at 2, 4, 6 A.dm^{-2} current densities

Surface morphology analysis of Ni-TiO$_2$ nanocomposite coatings are shown in Figure 5.8. Similar to Ni coatings, increasing current density results in dense surface

compared to the lower current densities. Furthermore, SEM micrographs of higher nanoparticle concentration have smoother surfaces. Higher current density values positively affects the coatings properties because the structure becomes homogenious. This result also coincides with report by Huang et al. They used ZrO_2 nanoparticles co-electroposition in Watts bath as they report different nanoparticle concentration results. Their work shows that higher concentration shown higher grain sizes, which they report that the reason for that is introducing particles decreases the rate of nucleation on the surface (Huang, Zhang, Hou & Deng, 2013). Similar work by Sen et al. reports the research of different CeO_2 nanoparticle concentrations for coating purposes, even going to high 50g/L concentration rate value, using Watts bath. They report that higher concentrations results in aggleromation of atoms becomes significant problem, resulting in a rough surface (Sen, S. Das & K. Das, 2012).



(a)



(b)

Figure 5.8. Surface morphologies of Ni-TiO_2 nanocomposite coatings with (a) 1 g/l TiO_2 (b) 3 g/l TiO_2 nanoparticles electrodeposited at 2, 4 and 6 A dm^{-2} current densities

5.2.2 Characterization of Electrodeposited Ni/Mn TiO_2 and Ni/Mn-N TiO_2 Nanocomposite Coatings

Ni/Mn and Ni/Mn-N TiO_2 nanocomposite coatings were conducted with 2, 4 and 6 $A.dm^{-2}$ current density and nanoparticle nanoparticle concentrations of 1 and 3g/l TiO_2. The XRD patterns are shown in Figure 5.9. The graphs are similiar to Ni and Ni-TiO_2 XRD graphs, considering there is no other peak than Ni and its intensity increases with current density. The 2θ characteristic peaks of nickel at 44.48°, 51.83° and 76.35° corresponding to (111), (200) and (220) planes of the crystal lattice, respectively.

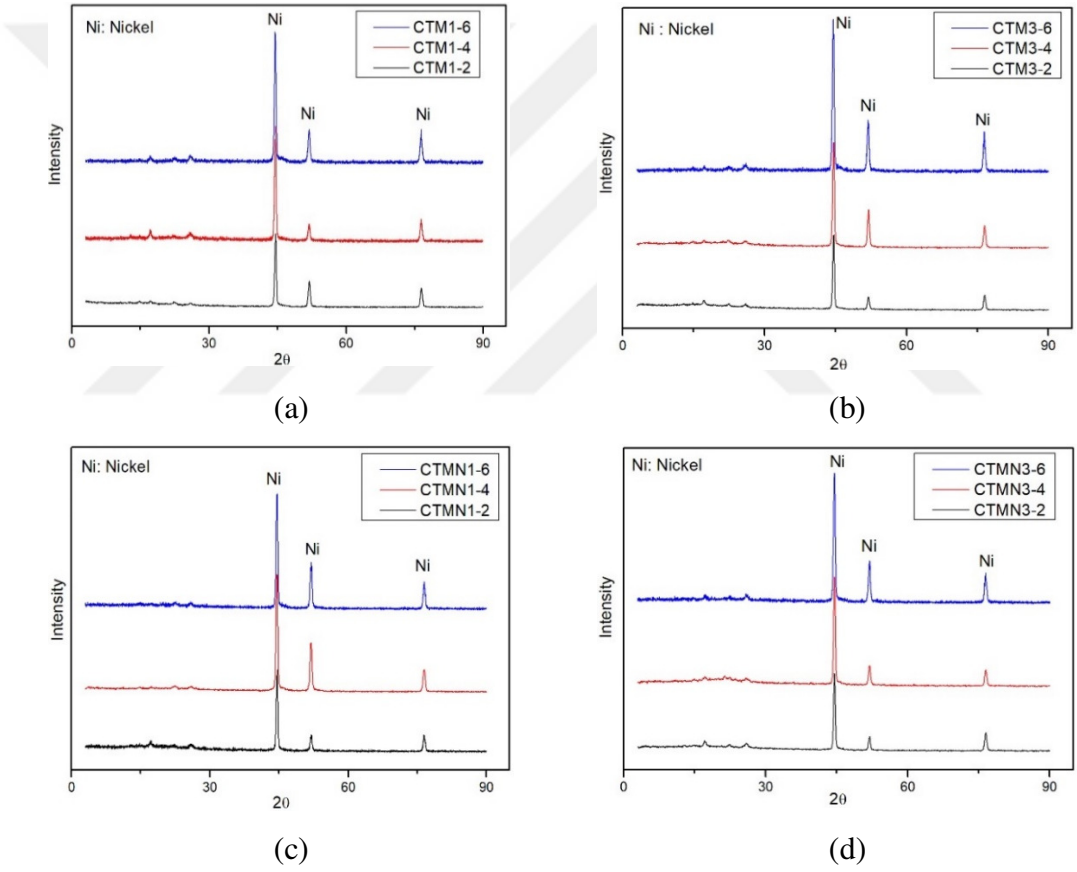


Figure 5.9 X-ray θ-2θ scans of Ni/Mn TiO_2 nanocomposite coatings with TiO_2 nanoparticles (a) 1g/l, (b) 3g/l concentration and Ni/Mn-N TiO_2 with (c) 1g/l, (d) 3g/l concentration electrodeposited at 2, 4, 6 $A.dm^{-2}$ current densities

SEM micrographs of Ni/Mn TiO_2 and Ni/Mn-N TiO_2 nanocomposite coatings are shown in Figure 5.10 and 5.11. Similar to the undoped TiO_2 nanoparticle surface density changes as current density increases. Increasing nanoparticle concentration

also shows more TiO_2 particles on the surface. The surface becomes homogenious and dense in 4 and 6 A.dm^{-2} current densities, compared to the lower current density coating values. Li and Fu et al. reported using chromium doped TiO_2 nanoparticles for nanocomposite deposited on stainless steel. They report that using chromium doped TiO_2 resulted in with a surface with less cracks, therefore they had more smooth and homogenious structure. They report that %1 chromium doped TiO_2 nanoparticle incorporated surface were most smooth and uniform (Li & Fu, 2012). A different study has been done by using two different nanoparticles (Al_2O_3 and SiC) on Ni matrix nanocomposites, reported by Deghani et al. They also report that introducing nanoparticles results in less homogenious structure, especially in low concentration values (Deghahi, Amini & Alizadeh, 2016).

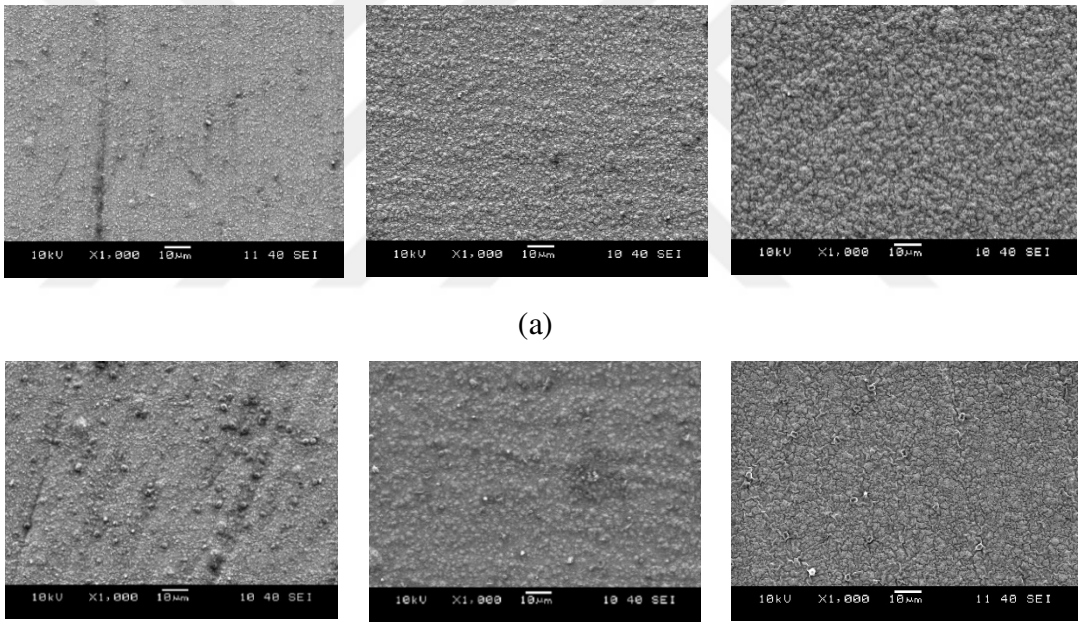
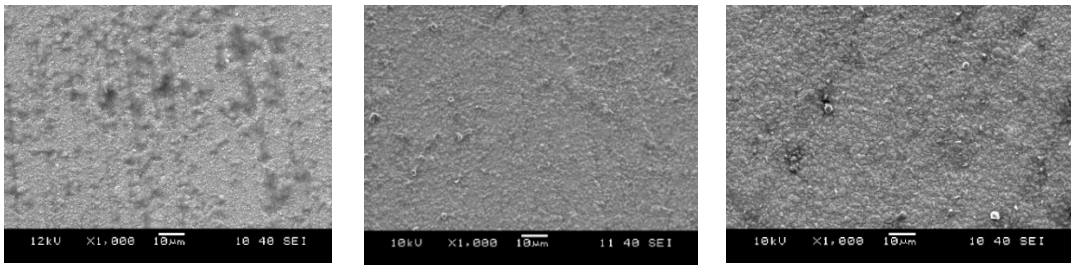
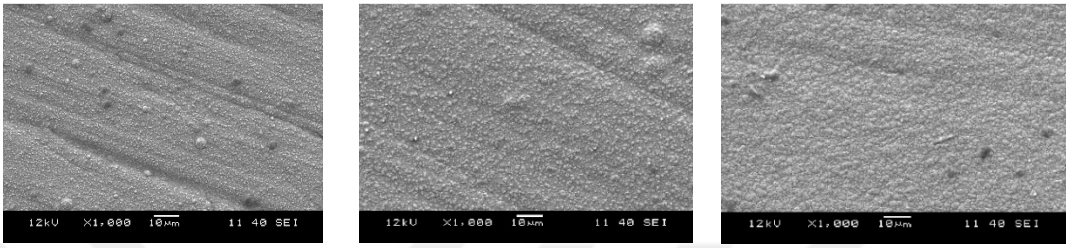


Figure 5.10 Surface morphologies of Ni/Mn TiO_2 nanocomposite coatings with (a) 1 g/l Mn doped TiO_2 (b) 3 g/l Mn doped TiO_2 nanoparticles electrodeposited at 2, 4 and 6 A dm^{-2} current densities



(a)



(b)

Figure 5.11 Surface morphologies of Ni/Mn N TiO_2 nanocomposite coatings with (a) 1 g/l Mn-N codoped TiO_2 (b) 3 g/l Mn-N codoped TiO_2 nanoparticles electrodeposited at 2, 4 and 6 A dm^{-2} current densities

In order to analyze the distribution of the TiO_2 nanoparticles in the coating surface, elemental mapping was conducted with EDS attached to SEM. The mapping images of CTM3-6 coating were given to analyze both TiO_2 and dopant material distribution. The images presented in Figure 5.12 show that the TiO_2 nanoparticles in the structure were uniformly distributed.

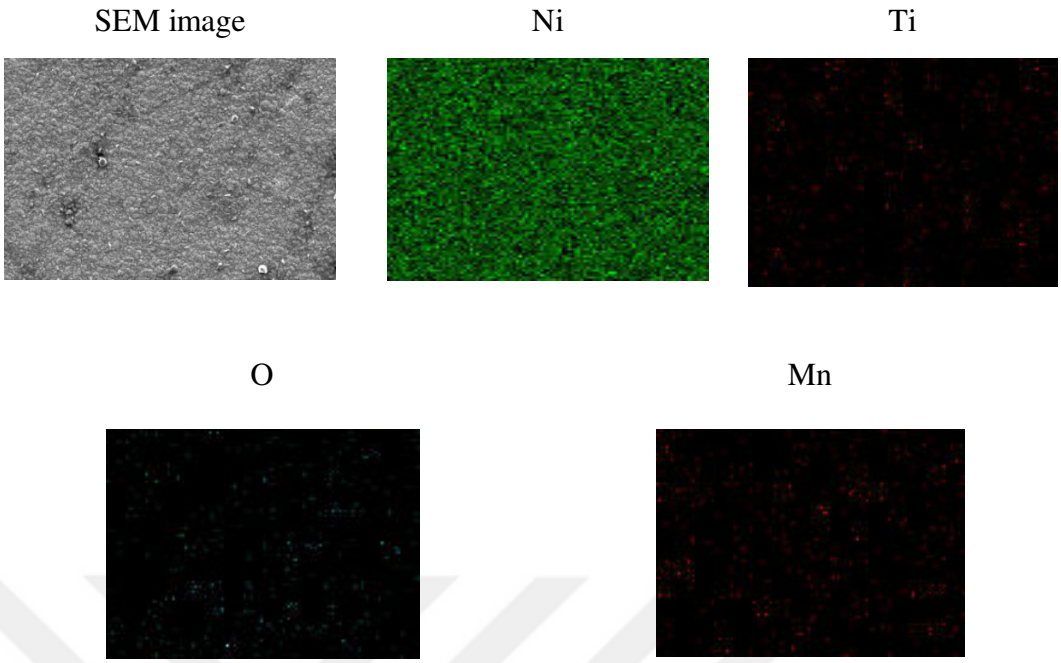


Figure 5.12 Mapping image of Ni/Mn TiO_2 nanocomposite coatings at 6 $A.dm^{-2}$ current density with 3g/L TiO_2 nanoparticle concentration

5.3 Corrosion Analysis of Electrodeposited Nickel and Nickel Matrix Nanocomposite Coatings

One of the most widely researched of coating process is their corrosive resistance. Having excellent coating on a valuable material in unfavorable enviroment is important for a material and its effectiveness. While engineers are trying to find cost-effective process for required protection, scientists mainly focus on obtaining highest corrosion protection of the materials. This cycle results in constant improvement of corrosion protection techlonogy. Among theese methods, the versatility and constant improvement of electodeposition technique stands out in producing novel materials for science and engineering applications (Dennis & Such, 1993).

Nickel coatings are mainly used for corrosion resistance. Another importance of nickel coating is cost-effectiveness as a thin nickel coating only requires a small amnout of anode while the anode may be used to repair an expensive component which would have been thrown away. Nowadays, nanoparticle coatings are considered valuable asset for improving surface sciences and applications. There might be

imperfections such as voids between the particle matrix. However, increasing the nanoparticle concentration in the bath results in stonger and more resistant coating (Rostami et al., 2013). Therefore, Ni matrix nanocomposite with varying TiO_2 nanoparticles were analyzed throughout this study.

Potentiodynamic polarization curves of Ni and Ni matrix nanocomposite coatings with varying TiO_2 nanoparticles and concentration at different current densities of 2, 4 and 6 $A.dm^{-2}$ in a 3.5 wt. % NaCl solution are shown in Figure.5.13 and 5.14. Corrosion potential (E_{corr}), corrosion current density (i_{corr}), β_a and β_c are obtained from the intersection of cathodic and anodic Tafel curve tangents. The corrosion rate is expressed in mm $year^{-1}$ and calculated with Gamry Framework Software. These values are listed in Table 5.1-5.3. Open circuit potentials were stabilized before calculating potendiodynamic polarization values.

Compared to the Ni (-222.4 mV) coatings, Ni/TiO_2, Ni/Mn TiO_2 and Ni/Mn-N TiO_2 coating corrosion potential values shifted to more positive potential (-155 mV). There are few factors on why this change happened. Adding more cationic nanoparticles compared to the Ni to the surface results in more noble potential values. Therefore it is expected that having higher current densities and nanoparticle concentration would result in high noble surface, considering that Ti atom concentration increases. In coating process, the TiO_2 particles are adsorbed to the Ni ions, acquire positive surface charge. Afterwards they are potentially adsorbed on the electrode surface. Another reason is that the process also results in TiO_2 nanoparticles acting as inert barriers and prevent defect corrosion as the surface structure becomes homogenious. The results also agree with this explanation as bath concentration of 3g/l TiO_2 coatings have positive potential compared to the 1g/l TiO_2 bath concentration coatings. The coatings with 6$A.dm^{-2}$ current density have positive potential compared to the 4 $A.dm^{-2}$ and 2 $A.dm^{-2}$ coatings (Özkan, Hapçı, Orhan & Kazmanlı, 2013; Baghery, Farzam, Mousavi & Hosseini, 2010).

Table 5.1 and 5.2 shows that coatings with doped, codoped nanoparticles had positive potential and lower corrosion rate values, compared to the Ni or Ni/TiO_2

coatings. This can be explained by doped atom and the difference it makes in the TiO_2 crystal structure. When impurity atom is introduced to the TiO_2 structure as substitute, it causes structural change in the crystal structure, which plays a role in locally disrupting the electric potential of the lattice. The structure becomes better inert barrier to corrosive attacks (Karthik et al, 2010). According to SEM micrographs, the doped and codoped TiO_2 show better surface properties as it shows more smooth and homogenious surface, which results in better corrosive resistance.

Shao et al. reported a similar work using TiO_2 for Ni based nanocomposite. They report that introducing nanoparticles reduced the holes and cracks of the surface and titanium worked as a cathode, as opposed to Ni, resulting in inhibition of corrosion (Shao, Nabb, Renevier, Sherrington, Fu & Luo, 2012). Li et al. has doped cerium to the TiO_2 structure and researched its optical and corrosive properties of the nickel coating in %3 NaCl solution. They report that cerium doped TiO_2 shown better performance than undoped TiO_2 nanoparticle nanocomposites. They also said further increasing the cerium concentration in TiO_2 might cause defects and cracks therefore negatively affecting corrosion resistance property of the coating (Li, Wang, Chen, Zhou, Wang & Fu, 2012). On the other hand, Li & Fu et al. doped transition metal chromium for its ability to induce local corrosion process, which derives from cracks in sol-gel synthesized in TiO_2 coatings. They report that using chromium reduced the cracks in the coating therefore reduced the grain size and nanoparticles homogeniously distributed (Li et al., 2013). Kumar et al. reported using %1 Mn doped TiO_2 nanoparticles for their nanocomposite coatings.They report that using doped TiO_2 nanoparticles resulted in compact and uniform surface, compared to the undoped TiO_2 nanoparticle nanocomposites (Kumar, Venkastesha, Pavithra & Shetty, 2015).

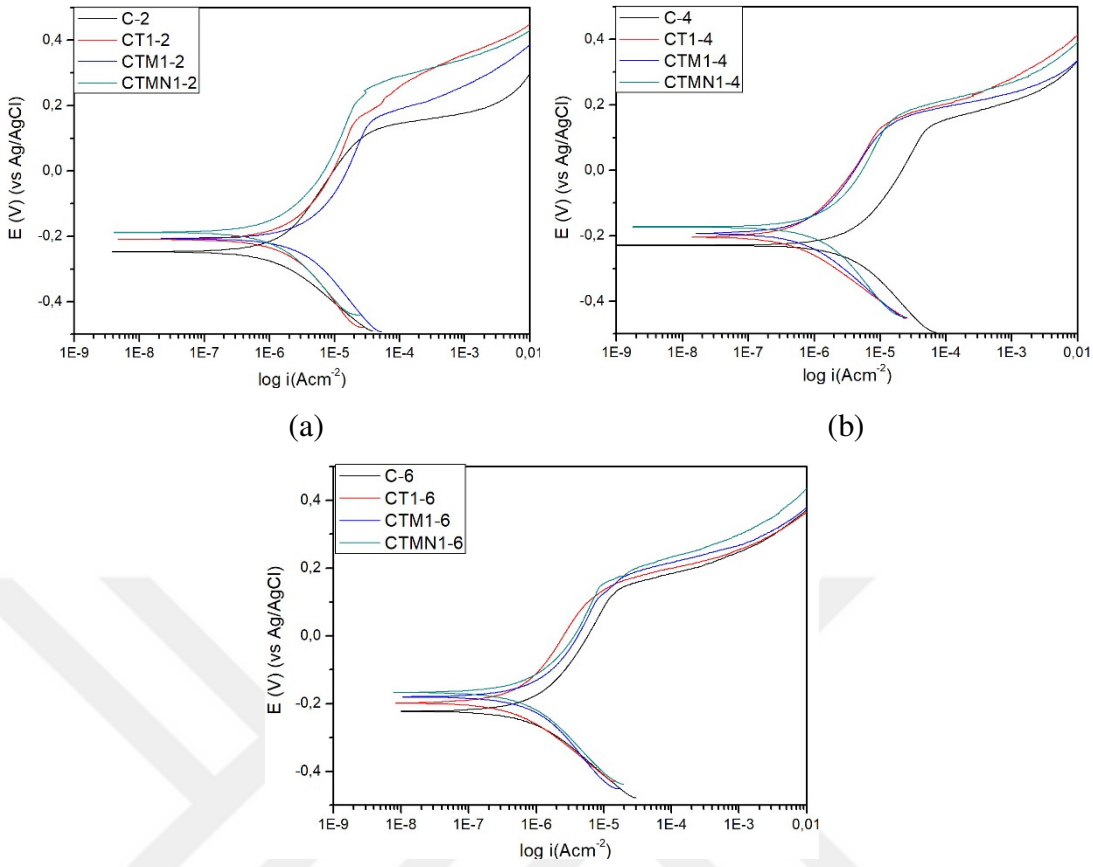


Figure 5.13 Comperative potentiodynamic diagrams of Ni, Ni/TiO_2, Ni/Mn TiO_2 and Ni/Mn-N TiO_2 nanocomposite coatings with 1g/l concentration electrodeposited at (a) 3, (b) 5 and (c) 7 A dm^{-2} current densities

Table 5.1 Corrosion characteristics of C, CT, CTM, CTMN nanocomposite coatings with 1g/l concentration

Coating	**E_{corr} (mV)**	**i_{corr} (nA)**	**β_a(V/decade)**	**β_c(V/decade)**	**C_{corr}(mpy)**
C-2	-247.2	2620	0.2513	0.2943	598.7 $x10^{-3}$
C-4	-229.1	1360	0.3148	0.2977	309.7 $x10^{-3}$
C-6	-222.4	1230	0.1716	0.1938	282.0 $x10^{-3}$
CT1-2	-209.0	1150	0.1143	0.1112	262.6 $x10^{-3}$
CT1-4	-203.8	755	0.1380	0.1378	173.7 $x10^{-3}$
CT1-6	-198.2	699	0.093	0.1268	165.6 $x10^{-3}$
CTM1-2	-206.4	995	0.1287	0.1326	227.4 $x10^{-3}$
CTM1-4	-192.4	688	0.1181	0.1072	157.3 $x10^{-3}$
CTM1-6	-179.9	424	0.1265	0.1240	96.78 $x10^{-3}$
CTMN1-2	-187.5	577	0.1534	0.1627	131.9 $x10^{-3}$
CTMN1-4	-173.0	308	0.1739	0.1310	70.31 $x10^{-3}$
CTMN1-6	-166.9	213	0.1159	0.1100	48.77 $x10^{-3}$

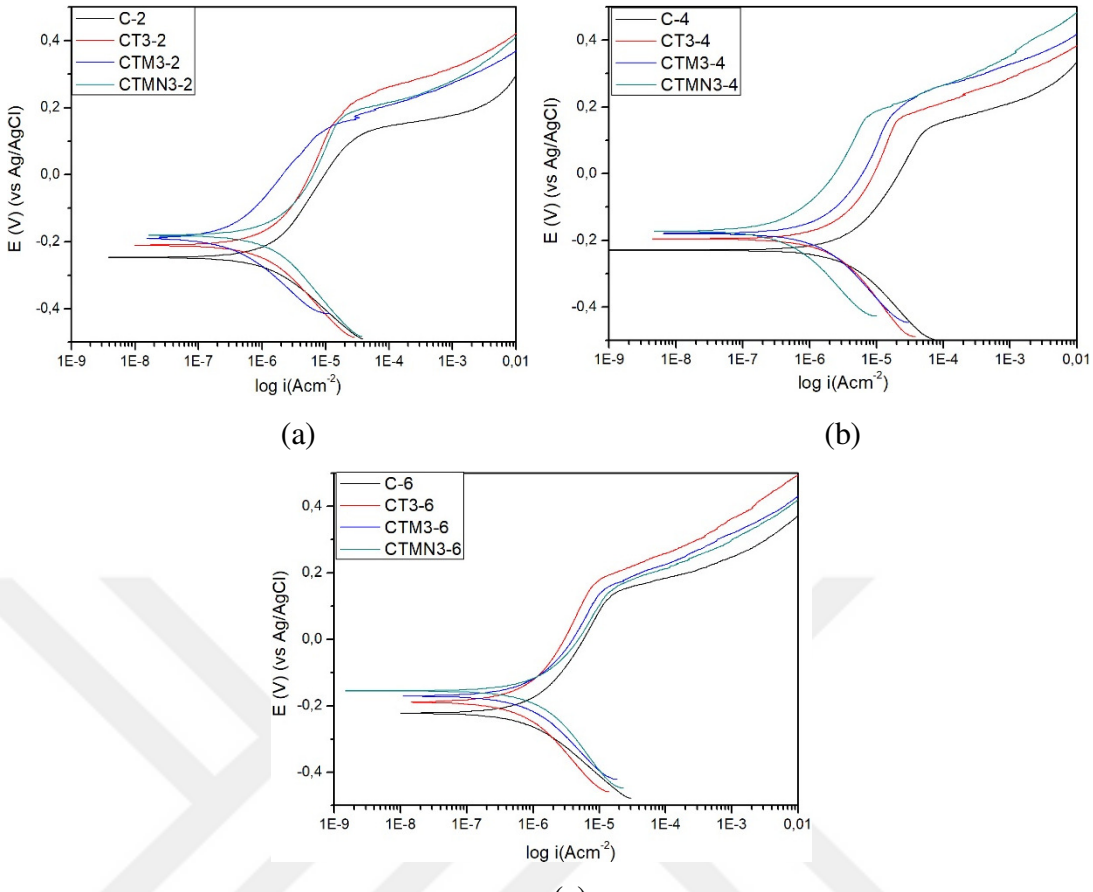


Figure 5.14 Comperative potentiodynamic diagrams of Ni, Ni/TiO_2, Ni/Mn TiO_2 and Ni/Mn-N TiO_2 nanocomposite coatings with 3g/l concentration electrodeposited at (a) 3, (b) 5 and (c) 7 $A.dm^{-2}$ current densities

Table 5.2 Corrosion characteristics of C, CT, CTM, CTMN nanocomposite coatings with 3g/l concentration

Coating	**E_{corr} (mV)**	**i_{corr} (nA)**	**β_a(V/decade)**	**β_c(V/decade)**	**C_{corr}(mpy)**
C-2	-247.2	2620	0.2513	0.2943	598.7 $x10^{-3}$
C-4	-229.1	1360	0.3148	0.2977	309.7 $x10^{-3}$
C-6	-222.4	1230	0.1716	0.1938	282.0 $x10^{-3}$
CT3-2	-211	1210	0.1537	0.1546	277.0 $x10^{-3}$
CT3-4	-195.5	716	0.1084	0.1362	163.6 $x10^{-3}$
CT3-6	-188.5	592	0.1794	0.1524	135.2 $x10^{-3}$
CTM3-2	-190.1	616	0.1169	0.1277	140.7 $x10^{-3}$
CTM3-4	-179.4	357	0.1471	0.1502	81.53 $x10^{-3}$
CTM3-6	-171.5	176	0.1228	0.1191	40.23 $x10^{-3}$
CTMN3-2	-180.8	503	0.0818	0.1006	119.6 $x10^{-3}$
CTMN3-4	-172.8	253	0.0765	0.0499	57.81 $x10^{-3}$
CTMN3-6	-155	157	0.1091	0.1090	35.76 $x10^{-3}$

CHAPTER SIX
CONCLUSION

This thesis focused on synthesizing undoped, doped and codoped TiO_2 nanoparticles and their effect on corrosive resistance effect on nanocomposite coatings. Nanocomposite coatings were prepared on steel substrate using electrodeposition technique. Effects of different nanoparticle addition types and their diffrent content have been investigated.

Zeta sizer device has been used to measure nanoparticle particle size values. Crystalline structure of nanoparticle additions and coatings were analyzed using X-ray Diffraction (XRD). Surface morphology of the coatings were determined with Scanning Electron Microscopy (SEM). The corrosion resistance properties of the coatings were investigated electrochemically by potentiodynamic polarization technique in NaCl solution.

The experimental work results can be summarized with these interperations:

- According to the XRD results, undoped, doped and codoped TiO_2 nanoparticles are composed of only anatase state. Adding additional elements while synthesizing TiO_2 nanoparticles did not affect the crystal state of the synthesized TiO_2.

- Synthesized nanoparticles were succesfully synthesized in nanoscale. Overall the particle size were between 50 nm - 80 nm, while codoped nanoparticles had smallest particle size compared to the other TiO_2 nanoparticle types.

- It can be observed from XRD results of nickel coatings, the nickel coatings were successfully formed on steel substrate.

- SEM and mapping results show that the TiO_2 nanoparticles were successfully imbedded on steel substrate while being uniformly distributed. Higher current

density and increasing nanoparticle concentration resulted in dense and smooth surface.

- Corrosion test results show that doped and codoped TiO_2 nanoparticle addition on Ni matrix nanocomposite has shown better corrosion resistance perfomance on the substrate, compared to the undoped TiO_2 nanoparticles. Mn-N codoped TiO_2 nanoparticles in Ni matrix nanocomposite coatings have affirmative effect on corrosion resistance of coatings.

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