

IZMIR KATIP CELEBI UNIVERSITY
GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES

**GROWTH OF ZNO-CH NANOSTRUCTURES ON ITO/GLASS SUBSTRATES
THROUGH ELECTROCHEMICAL ANODIZATION FOR BIOSENSOR
APPLICATIONS**



M.Sc. THESIS

Berkant UZUNBAYIR

Department of Nanoscience & Nanotechnology

JUNE 2019

IZMIR KATIP CELEBI UNIVERSITY
GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES

**GROWTH OF ZNO-CH NANOSTRUCTURES ON ITO/GLASS SUBSTRATES
THROUGH ELECTROCHEMICAL ANODIZATION FOR BIOSENSOR
APPLICATIONS**



M.Sc. THESIS

Berkant UZUNBAYIR

Y160221001

Department of Nanoscience & Nanotechnology

Thesis Advisor: Asst. Prof. Dr. Ahmet AYKAÇ

JUNE 2019

İZMİR KATİP ÇELEBİ ÜNİVERSİTESİ
FEN BİLİMLERİ ENSTİTÜSÜ

**BİYOSENSÖR UYGULAMALARI İÇİN ELEKTROKİMYASAL ANOTLAMA
YÖNTEMİYLE ITO/CAM YÜZEY ÜZERİNDE ZNO-KİTOSAN
NANOYAPILARIN BÜYÜTÜLMESİ**

YÜKSEK LİSANS TEZİ

Berkant UZUNBAYIR

Y160221001

Nanobilim ve Nanoteknoloji Ana Bilim Dalı

Tez Danışmanı: Dr. Öğr. Üyesi Ahmet AYKAÇ

HAZİRAN 2019

Berkant UZUNBAYIR, a M.Sc. student of **IKCU Graduate School Of Natural And Applied Sciences**, successfully defended the thesis entitled “**Growth of ZnO/Chitosan nanostructures on ITO/Glass substrates through electrochemical anodization for biosensor applications**”, which he/she prepared after fulfilling the requirements specified in the associated legislations, before the jury whose signatures are below.

Thesis Advisor :

Asst. Prof. Dr. Ahmet AYKAÇ
İzmir Katip Çelebi University

Jury Members :

Assoc. Prof. Dr. Fethullah GÜNEŞ
İzmir Katip Çelebi University

Assoc. Prof. Dr. Mustafa EROL
Dokuz Eylül University

Date of Submission : 30.05.2019

Date of Defense : 20.06.2019



To my family,

FOREWORD

First and foremost, I would like to thank my advisor, **Asst. Prof. Dr. Ahmet AYKAÇ** for believing in me since beginning and supporting me throughout my Master of Science period. I also thank to **Assoc. Prof. Dr. Mustafa EROL** for advising me on his area of expertise for this MSc. Thesis. I thank to **Assoc. Prof. Dr. Fethullah GÜNEŞ** and **Dr. Tuncay DİKİCİ** for their contributions to the thesis. I thank to **Lecturer Saadet GÜLER** for helping me on this project. Finally yet importantly, I would like to thank my family for always being with me and reminding me that I am capable of doing everything I put on my mind.

This thesis was supported by Izmir Katip Çelebi University, Institute of Applied Sciences, Central Research Laboratories and Department of Materials Science and Engineering Laboratories.

June 2019

Berkant UZUNBAYIR

TABLE OF CONTENTS

	<u>Page</u>
ABBREVIATIONS	v
LIST OF TABLES	vi
LIST OF FIGURES	vii
ABSTRACT	viii
ÖZET	ix
1. NANOTECHNOLOGY	1
1.1 Nanomaterials.....	5
1.1.1 Carbon based nanomaterials	7
1.1.2 Metallic nanomaterials	8
1.1.2.1 Zinc oxide nanoparticles	9
1.2 Fabrication of Nanomaterials	10
1.3 Applications of Nanotechnology.....	11
1.3.1 Sensor applications of nanotechnology.....	12
2. SURFACE COATING TECHNOLOGY	14
2.1 Surface Coating Techniques.....	15
2.1.1 Electrochemical Deposition	16
2.1.2 Electrochemical Anodization.....	18
3. MATERIALS & METHODS	21
3.1 Materials	21
3.2 Methods	21
4. EXPERIMENTAL PROCEDURE	24
5. RESULTS AND CONCLUSION	27
5.1 Conclusion.....	31
REFERENCES	32
CIRRICULUM VITAE	38

ABBREVIATIONS

MWNT	: Multi Walled Carbon Nanotubes
SWNT	: Single Walled Carbon Nanotubes
0D	: Zero-Dimensional
1D	: One-Dimensional
2D	: Two-Dimensional
3D	: Three-Dimensional
DNA	: Deoxyribonucleic Acid
ITO	: Indium tin oxide
CNM	: Carbon nanomaterials
CB	: Carbon black
ND	: Nanodiamonds
GO	: Graphene oxide
MNM	: Metallic nanomaterials
UV	: Ultraviolet
DC	: Direct current
XRD	: X-Ray Diffraction
SEM	: Scanning Electron Microscopy
AFM	: Atomic Force Microscopy

LIST OF TABLES

	<u>Page</u>
Table 2.1: Surface coating techniques	15
Table 3.1: Literature Review	22



LIST OF FIGURES

	<u>Page</u>
Figure 1.1: Nanoscale and its comparison to everyday objects.	1
Figure 1.2: Lycurgus Cup.	2
Figure 1.3: Unique Structure of Graphene [8].	4
Figure 1.4: Different structures and shapes of nanomaterials [28].	6
Figure 1.5: Carbon Based Nanomaterials.	7
Figure 1.6: ZnO nanostructures.	9
Figure 1.7: Top-down and bottom-up approaches for nanomanufacturing.	10
Figure 1.8: Anodization process going through (a) to (d).	11
Figure 2.1: Electroplating unit.	16
Figure 2.2: Anodization bath.	18
Figure 2.3: Coating Thickness in Anodization	19
Figure 2.4: Current density – time curve in anodization process.....	20
Figure 3.1: Desired layered surface structure.	22
Figure 4.1: Ultrasonic bath.....	24
Figure 4.2: Electrochemical deposition setup.	24
Figure 4.3: Electrochemical anodization setup.	25
Figure 5.1: Coatings under different durations.	27
Figure 5.2: Coatings under different voltages.....	27
Figure 5.3: Samples anodized in glycerol.	28
Figure 5.4: Samples anodized in potassium bicarbonate.	28
Figure 5.5: XRD graphics of [A] glass/ITO, [B] glass/ITO/Zn, [C] glass/ITO/ZnO samples;.....	29
Figure 5.6: SEM image of zinc coating on Glass/ITO substrates.	30
Figure 5.7: SEM image of ZnO nanostructures on glass/ITO/Zn substrates.	30
Figure 5.8: SEM image of chitosan coated glass/ITO/ZnO surface	31

**GROWTH OF ZNO-CH NANOSTRUCTURES ON ITO/GLASS
SUBSTRATES THROUGH ELECTROCHEMICAL ANODIZATION FOR
BIOSENSOR APPLICATION**

ABSTRACT

In recent years, the utilization of nanotechnology rapidly developed for the wide range of sciences. Nanomaterials shows unique properties and ZnO nanostructures are the most suitable structures for biosensor applications due to their high surface area and high electrochemical activity. In this project first, we have coated zinc film on to Glass/ITO surface by electrochemical deposition method. Then we have transformed the obtained zinc film to nanostructured ZnO by electrochemical anodization method. At the end, we have tried to modify the ZnO nanostructured surface with chitosan for potential biosensor applications.

BİYOSENSÖR UYGULAMALARI İÇİN ELEKTROKİMYASAL ANOTLAMA YÖNTEMİYLE ITO/CAM YÜZEY ÜZERİNDE ZNO-KİTOSAN NANOYAPILARIN BÜYÜTÜLMESİ

ÖZET

Günümüzde nanoteknoloji, nanomalzemelerin sunduğu eşsiz özellikler sayesinde çok geniş uygulama alanlarına sahiptir. Nanomalzeler arasında çinko oksit (ZnO) nano yapılar, yüksek yüzey alanı ve elektrokimyasal aktiflikleri nedeniyle biyosensör uygulamaları için en uygun yüzeylerdir. Bu projede ilk olarak metalik çinko film, Cam/ITO yüzey üzerine elektrokimyasal kaplama yöntemiyle büyütülür. Ardından metalik film elektrokimyasal anotlama yöntemi ile nano yapılı çinko oksite dönüştürülür. Son olarak, çinko nano yapılı yüzey, biyosensör uygulamaları için kitosanla modifiye edilir.

1. NANOTECHNOLOGY

Nanotechnology, as a word, derived from Greek word “nanos” which means “dwarf or very small” combining with the word “technology”. In definition, nanotechnology means the study of the materials or techniques of very small. In general, nanotechnology is technology, science and engineering applications that concern the nanoscale. Nanoscale refers to range of lengths between 1 to 100 nm (Figure 1.1).

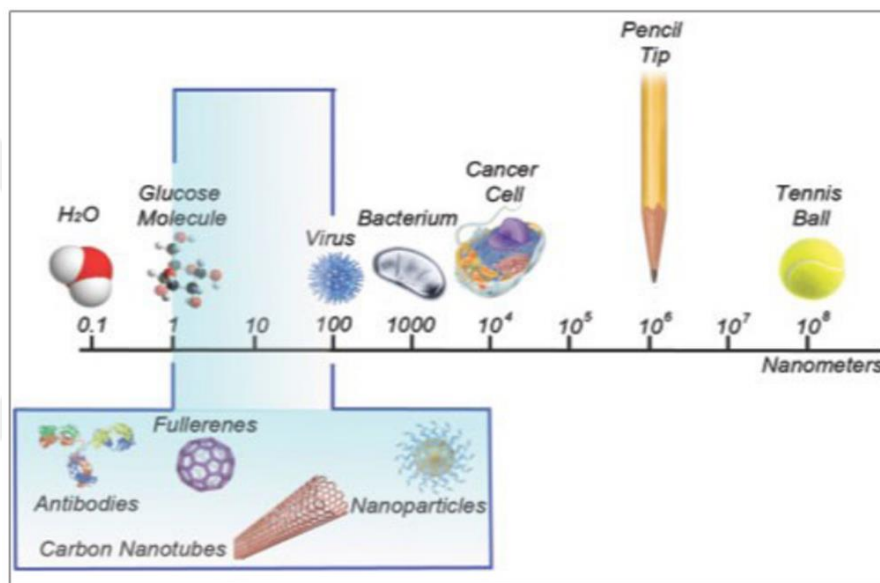


Figure 1.1: Nanoscale and its comparison to everyday objects.

Nanotechnology understands materials in nanoscale; controls and manipulates them in atomic level in order to obtain new materials or features with a new or enhanced functionalities. Over centuries, nature offers exclusive properties of natural beings such as DNA or colors peacock feathers, due to the nanoscale [1].

The overall subject of nanotechnology goes back to ancient times. Archeological findings show that ancient humans used silver nanoparticles in heads of arrows to increase hardness.

In medieval era, metallic nanoparticles were actually used for colorings of cathedral windows. The Lycurgus Cup (4th century) displays color changes depending on whether it is lightened externally or internally due to usage of gold nanoparticles (Figure 1.2). Until the Middle Age, the colloidal gold was only known for supernatural curative powers for diseases, such as heart and venereal problems, dysentery and epilepsy [2]. However, discoveries of these unique structures and applications and using them as novel science and engineering to improve quality of life through nanoscience are new to the world.



Figure 1.2: Lycurgus Cup.

In the modern era, Nobel Prize winning Richard Feynman and chemists like James C. Maxwell, K. Eric Drexler, Richard Smalley, are accredited for generating bigger scientific awareness for nanotechnology. In 1959, Richard Feynman, the professor of Californian Institute of Technology, brings up the concept of nanotechnology for the first time at the session of the American Physical Society with his speech “There is Plenty of Room at the Bottom”. In his speech, Feynman indicated that with controlling and manipulating materials on a small-scale, extraordinary things can be achieved and those leads science and technology to all new area [3].

In 1974, Japanese scientists Norio Taniguchi used the term “nanotechnology” for the first time as a term in a paper on the super thin processing of materials with nanometer accuracy and the creation of nano-sized mechanisms.

Ideas of nanotechnological strategy, which were put forward by Feynman, were developed by E. Drexler in his book “Vehicles of Creation: The Arrival of the Nanotechnology Era” published in 1986 [4].

In the 1980s, scientists were able to investigate materials at never-before-seen atomic level with the invention of scanning tunneling microscope (STM) and then the atomic force microscope (AFM). Between late 1980s to the early 1990s, nanotechnological discoveries and inventions increase by number, which lead an important impact on the future of nanotechnology.

In 1985, Harold W. Kroto, Richard E. Smalley and Robert F. Curl, Jr. made a Nobel Prize winning discovery. They invented the fullerene, a special type of carbon allotrope, which is consist of 60 carbon atoms (C₆₀) arranged as 12 pentagonal and 20 hexagonal faces by single and double bonds to form a hollow sphere — a design that resembles a football, or soccer ball.

Around same years, concepts of carbon nanotubes spoil among the scientist. In 1990, Richard Smalley proposed the concept that if buckyballs get big enough, they become carbon cylinders. Carbon nanotubes come with two varieties. They can either be single-walled carbon nanotubes (SWNT) or multi walled carbon nanotubes (MWNT). As described, an SWNT is just a single cylinder, whereas an MWNT consists of multiple concentric nanotube cylinders.

First, MWNT is discovered in 1991 by Sumio Iijima in REC’s Fundamental Research Laboratory in Japan. Iijima investigated material extracted from solids that grew on the tips of carbon electrodes after being discharged under C₆₀ formation conditions and found that the solids consisted of tiny tubes made up of numerous concentric “graphene” cylinders, each cylinder wall consisting of a sheet of carbon atoms arranged in hexagonal rings. The cylinders usually had closed-off ends and ranged from 2 to 10 micrometers in length and 5 to 40 nanometers in diameter [5].

Then, same method was used to produce SWNT with using cobalt-nickel catalyst. In 1996, a group led by Smalley used laser vaporization of carbon to produce SWNTs in high purity.

Despite the fact that both fullerene and carbon nanotubes are identified as forms of carbon, graphene was discovered later than those were. Studies on graphene goes back to 1859 but it was the year of 2004 when single atomic layer of carbon is discovered and isolated for the first time by Professor Sir Andre Geim and Professor Sir Kostya Novoselov of the University of Manchester [6]. The pair received the Nobel Prize in Physics in 2010 for their groundbreaking discovery.

Graphene is a two-dimensional (2D) crystal made out of carbon atoms arranged on a hexagonal (honeycomb) structure (Figure 1.3). Graphene is the simplest structure of carbon and it is really important for understanding the all unique properties of its and all other allotropes' with sp^2 hybridization [7].

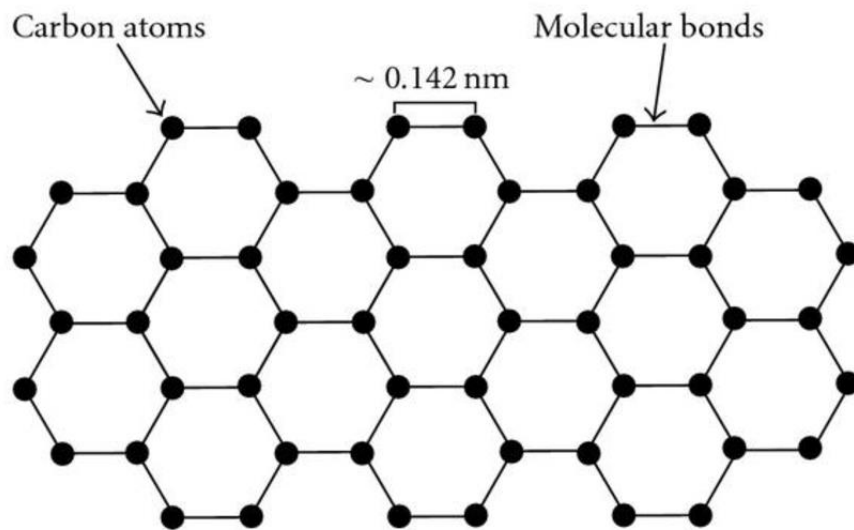


Figure 1.3: Unique Structure of Graphene [8].

In the modern era, all industrialized nations participated in nanotechnology world and nanotechnology activities rapidly increase worldwide.

Nowadays, nanotechnology is a multidisciplinary subject and grows widely based on researches in scientific areas like biology, chemistry and physics, technological areas like engineering and medicine.

1.1 Nanomaterials

Attraction to this new area comes up several new concepts on manufacturing and materials. The rapidly developing field of nanotechnology creates size dependent materials with unique properties and is becoming another source of display nanosized materials. New unique techniques on producing nano-scale products change the way of understanding the materials.

These techniques provided new perspectives about nanomaterial's structures and properties. Nanomaterials can be identified as the substances, which are characterized at least in one of three dimensions by nanometer scale. These nanomaterials have an increased surface area: mass ratio, which greatly enhances their chemical/catalytic reactivity compared to bulk-sized forms of the same substance [9].

The distinctive and often unique properties of nanomaterials offer the promise of broad advances for a wide range of technologies. Nanomaterials have attracted many of researchers in terms of fundamental sciences and technological applications. It is because their physical, chemical, electronic and magnetic properties show impressive difference from their bulk counterparts' [10]. These properties combined make materials more enhanced and increased the potential applications.

Based on the dimension of their structural elements, nanomaterials can be categorized into zero dimensional, one-dimensional, two-dimensional, and three-dimensional nanomaterials [11]. This dimensionality indicates that the number of degrees of freedom in the particle momentum.

Zero dimensional (0D) nanomaterials have all three dimensions are in the range of 1 to 100 nm. Quantum dots, hollow spheres and nanolenses are examples of 0D nanomaterials [12-14]. For one-dimensional nanostructures (1D), the electrons are free to travel in one direction and confined in the other two directions. Those structures such as nanofibers, nanowires, nanotubes, and nanobelts have been synthesized by several research groups [15-18].

In two-dimensional nanostructures (2D), two dimensions larger than 100 nm. The electrons can easily move in that directions and are confined in one direction. Nanocoatings and nanofilms are the most significant examples [19-23]. Three-dimensional nanostructures (3D): usually have three dimensions larger than 100 nm, but components of their structures are at nanoscale. Nanocrystalline or nanoporous materials are useful examples [24-27].

Depending on the degree of confinement, the density of states is remarkably changed for different type of nanostructures. Restriction in one, two, or three dimensions in nanoscale leads nanomaterials to have different structures and shapes (Figure 1.4).

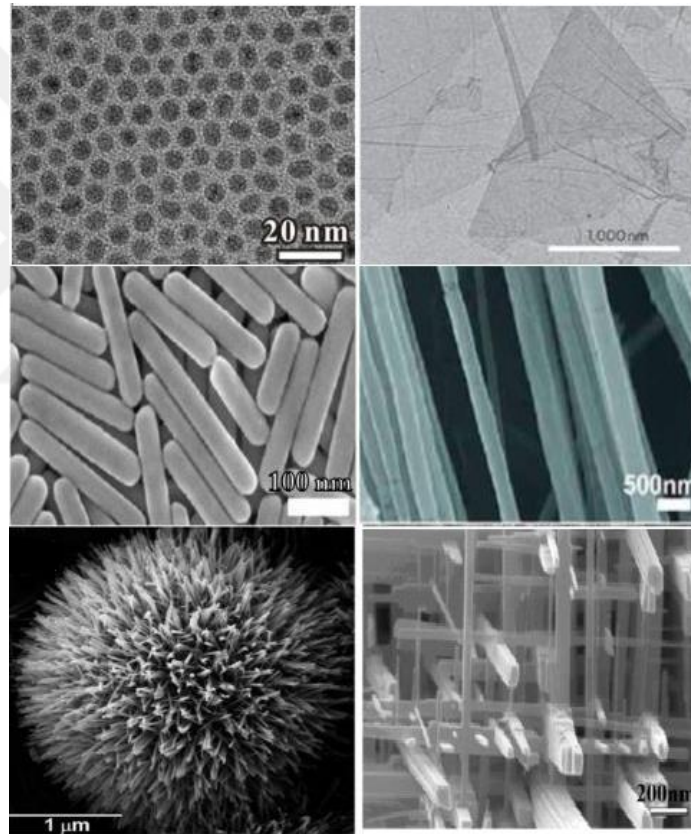


Figure 1.4: Different structures and shapes of nanomaterials [28].

1.1.1 Carbon based nanomaterials

Carbon-based nanomaterials (CNMs) is known form distinct solid-state structured allotropes with diverse structures and properties, such as sp^2 bonded graphite and sp^3 bonded diamond (Figure 1.5). The origination and evolution of carbon nanomaterials (CNMs) were started by discovery of fullerene.

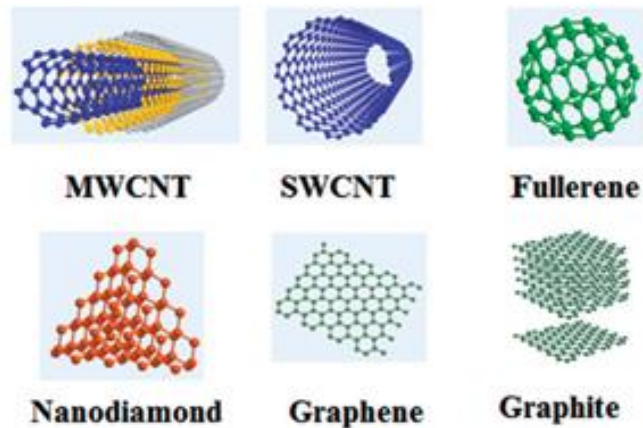


Figure 1.5: Carbon Based Nanomaterials.

Carbon nanotubes (CNTs), fullerenes, carbon black (CB), nanodiamonds (NDs), graphite, graphene, and graphene oxide (GO) are major elements of carbon nanomaterials.

CNMs are major elements in nanotechnology. Generally, carbon nanomaterials' properties are affected by their atomic structures and interfacial interactions with materials in other phases [29]. Functional CNMs exhibit improved chemical, mechanical, optical and physical properties, including low chemical reactivity, good thermal conductivity, chemical stability, super electroconductivity [30], and depends on these exclusiveness, CNMs have attracted so many areas of research since the very beginning of nanotechnology. CNMs show extraordinary potential in environmental sciences, energy industry, biomedical technologies and material sciences [31-34].

1.1.2 Metallic nanomaterials

Metals are type of materials that play fundamental role in materials science and industrial applications. There is direct correlation between structure, size, shape and composition of metallic nanomaterials and their properties and functions. Moreover, with those distinct properties, MNMs have created new pathways and received much popularity in nanotechnology.

Metallic nanoparticles firstly reported in 1857 by Michael Faraday which he investigated the formation of ruby red solutions of colloidal gold in his famous work [35]. He also studied on the optical properties of thin films prepared from colloidal solutions and observed reversible color changes from bluish-purple to green of the films upon mechanical compression. Approximately 100 years later, John Turkevich used electron microscopic investigations to reveal that the ruby-colored colloids made by Faraday's method to produce gold nanoparticles with size of 6 nm approximately [36].

In last two decades, scientists and researchers show great interest for metal nanomaterials such as gold (Au), titanium (Ti), zinc (Zn) and silver (Ag) etc., because of their optical and physicochemical properties in nanoscale [37]. The most important property of metallic nanomaterials is surface to volume ratio. High surface to volume ratio allows MNMs to interact easily with other particles and make MNMs more specific to various functional groups. High surface to volume ratio also makes diffusion faster and is feasible at lower temperatures [38]. Because of these, researchers have increased their attention on the production of novel nano-scale metal oxides, noble metal-doped metal oxides, metal oxide-CNTs nanocomposites, and metal oxide-polymer composites.

Specifically, metal oxide nanostructures are quite attractive for biosensor applications with their intended physical properties (conductivity, luminescence and absorbance) as well as biocompatibility. Using metal oxide nanostructures gives biosensors some unique upgrades like immobilization of enzymes, retaining their bioactivity due to the desirable microenvironment and the direct electron transfer between the enzyme's active sites and the electrode [39].

1.1.2.1 Zinc oxide nanoparticles

ZnO is an important material for the research community due to its novel properties and characteristics. The lack of a center of symmetry in wurtzite, combined with large electromechanical coupling, results in strong piezoelectric and pyroelectric properties and the consequent use of ZnO in mechanical actuators and piezoelectric sensors [40].

ZnO is a semi- conducting material that presents high surface area to volume ratio, chemical stability and electrochemical activities with fast electron interaction. ZnO is also suitable for biomedical application with high biocompatibility, and non-toxic biosafety and biomimetic features. Combining with the easiness of growth, ZnO has shown its novel advantages for the fabrication of electrochemical biosensors. More importantly, with an isoelectric point about 9.5, ZnO nanostructures are highly bioactive and stable surfaces for immobilization of proteins by electrostatic interactions.

In addition, ZnO which is n-type semiconductor with wide band-gap (3.37 eV) and high exciton binding energy (60meV) ensures intense ultraviolet (UV) photoluminescence at room temperature. It makes ZnO suitable for short wavelength, optoelectronic biosensor applications [40-43]. Also, ZnO has a diverse shapes of growth morphologies, such as nanowires, nanocombs, nanocages, nanorings, nanohelices, nanosprings, nanobelts (Figure 1.6).

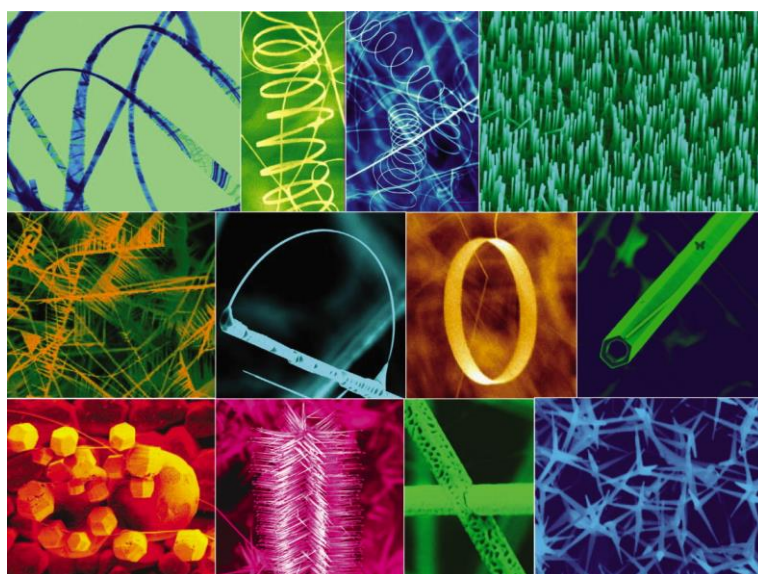


Figure 1.6: ZnO nanostructures.

Numerous biosensors with ZnO have been reported for biomolecules including cholesterol, glucose, urea, phosphate, DNA etc. [43-50].

1.2 Fabrication of Nanomaterials

Nanomaterials are basically “structured” using hard and soft fabrication techniques. These techniques can use “top-down” and “bottom-up” approaches (Figure 1.7). Top-down approach refers to fabrication of bulk materials to get nanomaterials. Opposite of that, bottom-up approach refers to the synthesis of nanomaterials using atoms or molecules. Even though both approaches are very important in modern day nanofabrication, each approach has advantages and disadvantages on their own.

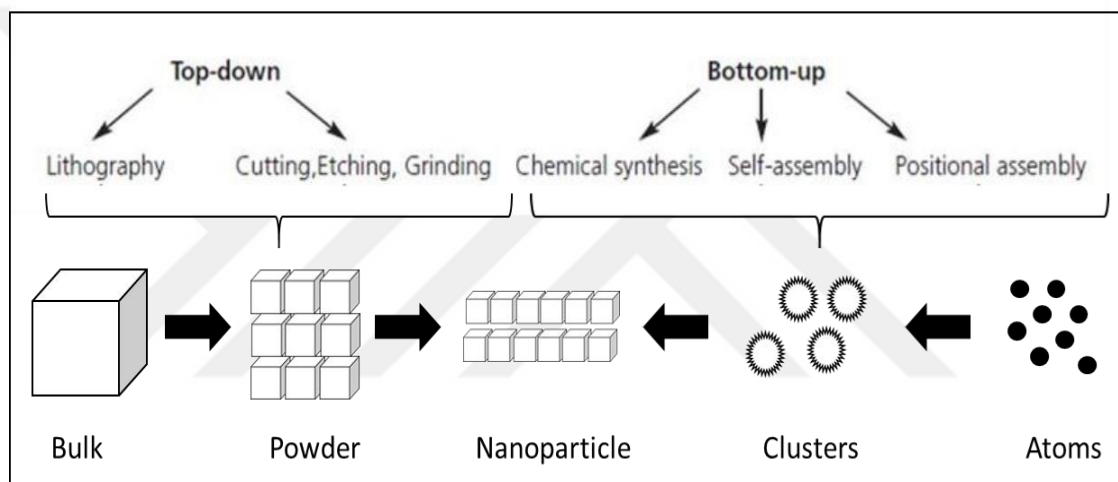


Figure 1.7: Top-down and bottom-up approaches for nanomanufacturing.

With the fact that top-down approaches, like lithography and milling, have well-developed techniques, they have limitations in terms of tool or wavelength of a light. In addition, they can cause imperfection of surface structure and significant crystallographic damage. On the contrary, bottom-up approaches, like chemical synthesis and physical assembly, are able to build smaller structures with desired surface properties and suitable for parallel manufacturing. However, biggest obstacles in front of bottom-up approaches are requirement of compatible molecules and fewer tools to manipulate them. Also, bottom-up techniques generally have much more higher costs than top-down techniques.

Some techniques adopt one approach in definition but use both top-down and bottom-up approaches simultaneously. For instance, in electrochemical anodization, while bulk metal is removing from surface, oxidized metal particles are building up to form nanostructures. (Figure 1.8)

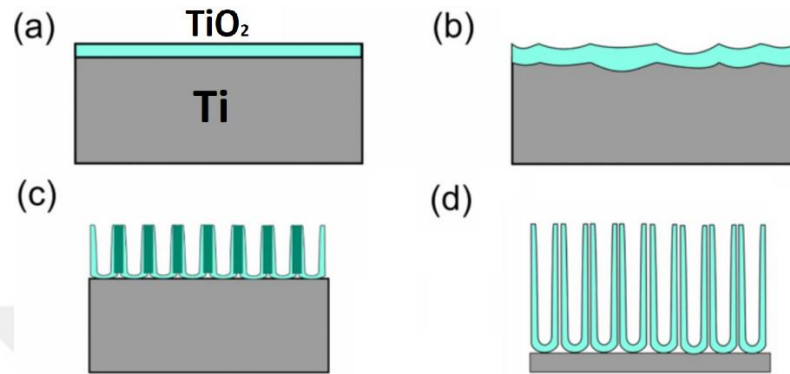


Figure 1.8: Anodization process going through (a) to (d).

1.3 Applications of Nanotechnology

In the recent years, new developments in nanotechnology have eased the way for producing increased number of new materials and new devices of desirable properties [51].

Depends on various size, structure and production methods, nanoparticles are used wide range of areas from health sciences to aerospace engineering, from textile to defense industry. QLED screens, space elevator, targeted drug delivery systems, nanobiosensors, smart clothes, self-cleaning surfaces and non-impact soldier vests are just some examples of commercial usage of nanotechnology.

Nanomaterials have major enhancements on renewable energy. For example, light and stronger nanomaterials can be used in wind turbine's rotor blades. This improves wind energy efficiency. Using nanocoatings in tidal energy equipment prevents the corrosion that affect surfaces in harsh seawater conditions. Nanocomposite materials are used to make more fatigue-resistant drilling machines for geothermal energy [52].

Nanotechnology has many applications on food industry. Polymeric nanocomposites are used in food packaging as a barrier to prevent food from spoiling. Also, nanomaterials used for antimicrobial effect on food [53].

Nanostructures have applications for environmental sciences and wastewater treatment. Photocatalytic effect of metallic nanostructures is used for water purification as a surface coating or dye. Quantum dots used for optical and electrochemical detection of pollution [54].

In textile industry, nanomaterials have wide application areas from smart clothes to antibacterial hospital covers. Hydrophobic surfaces of nanostructures are used in water-repellent clothes. Covers that are used in hospitals show certain degree of sterilizing effect due to antibacterial properties of nanoparticles [55].

1.3.1 Sensor applications of nanotechnology

With reduction in size, novel morphological, structural, electrical, chemical, and optical properties are introduced and these novel properties of nanostructured materials make them as a principally remarkable and innovative choice for biomedical applications [56]. In addition, the surface effects in nanostructures are caused by their low size, surface structure, charge; wettability and high surface-to-volume ratio overcome the challenges for biosensing applications. Also, the researchers have taken an interest in nanomaterials since their dimensions are the same scale as the dimensions of the bio-components, which form a bioselective layer [48].

Ruecha et al. developed a cholesterol biosensor based on graphene/polyvinylpyrrolidone/polyaniline nanocomposite [57]. Another biosensor for detection of cholesterol was developed based on multi walled carbon nanotubes/gold nanoparticles by Cai et al [58]. This cholesterol biosensor has a high sensitivity, wide linear range and low detection limit due to using novel nanocomposite and leads to an alternative way to clinical detection of cholesterol by successfully applied for the detection in human serum. However, these materials does not show satisfactory features in terms of sensitivity and selectivity. They have high costs, and lose their activities because of adsorption and accumulation of intermediates [39; 59].

On the other hand, nanostructured metal oxides have high sensitivity due to the increased surface-to-volume ratio and show exceptional selectivity when coupled with biorecognition molecules [59]. Novel analytical devices based on metal oxide nanomaterials has simple designs and low costs for fabrication point of view. Especially, ZnO nanostructures show high isoelectric point (IEP), excellent biocompatibility, and easy synthetic procedure for nanostructure that enables reliable immobilization of enzymes.

Muahmmmed et al. produced a biosensor for detection of DNA immobilization using ZnO nanorods/APTES structures over SiO₂ thin film [60]. Wang et al. manufactured ZnO nanorods by hydrothermal methods to detect H₂S at low concentration [61]. Rex et al. established a high sensitive detection method for Hg²⁺ ions based on changes in aspect ratio of gold nanorods [62]. Gold nanoparticles also used by Choi et al, in an immunoassay biosensor for detection of PSA [63]. Ahmad et al. growth aspect ratio controlled ZnO nanorods directly on electrodes for detecting glucose [64]. Tereshchenko et al. prepared ZnO nanofilms using atomic layer deposition for optical biosensor to detect *Grapevine virus A-type* proteins [65]. Anusha et al. developed an enzymatic glucose biosensor using ZnO porous nanostructure with platinum and chitosan layers to increase sensing properties [66]. Wei et al. also used ZnO nanostructures in enzymatic glucose biosensor with low detection limit and high sensitivity [39]. Umar et al. produced ultra-sensitive biosensor with using low-grown ZnO nanoparticles for cholesterol monitoring [67].

2. SURFACE COATING TECHNOLOGY

Materials can be found in three phases in nature: solids, liquids and gases. Solids are composed of a bulk material covered by a surface. Surface properties are extremely important for materials. They can determine some important characteristics of materials. For that reason, surface modification plays huge role in materials engineering in order to achieve surfaces with specific properties for specific applications. Surface modifications can be done directly on bulk materials surfaces' or with additional coatings.

Coating is the cover to the surface of a bulk material, generally referred as the substrate. The coatings can be functional, decorative or both. They can cover the substrate completely, or parts of the substrate. Decorative coatings usually applied to change the appearance. Functional coatings can change the surface properties of the materials, such as wettability, corrosion or wear resistance and adhesion. Else, the coatings can add all new properties such as electrical conductivity, selectivity and magnetic response. Functional coatings form an essential part of finished products.

Coatings form a layer of material, called thin film, over the substrate. Thin films range from nanometer to several micrometer in thickness. For that, for applications of thin films, it is a fundamental to produce thin films controllably due to the following reasons:

- Create entirely new products
- Give revolutionary solution to existent problems
- Improve properties of existing products; functional and decorative
- Produce nanostructured coatings with specific design
- Efficient use of source materials

2.1 Surface Coating Techniques

Based on type of applications and type of materials, there are different techniques for surface coating. These techniques can be grouped under four main headings (Table 2.1): Atomic Deposition, Particulate Deposition, Bulk Coatings and Surface Modification.

Table 2.1: Surface coating techniques.

Atomic Deposition	Particulate Deposition	Bulk Coatings	Surface Modification
<ul style="list-style-type: none"> •Electroplating •Electroless Plating •Ion Beam Deposition •Laser Ablation •Molecular Beam Epitaxy •Sputter Deposition •Atomic Layer Deposition •Spray Pyrolysis 	<ul style="list-style-type: none"> •Thermal Spraying •Plasma Spraying •Fusion Coating •Screen Printing •Jet Printing •Electrophoretic •Impact Plating 	<ul style="list-style-type: none"> •Painting •Dip Coating •Electrostatic Spraying •Spin Coating •Cladding •Overlaying •Weld Coating 	<ul style="list-style-type: none"> •Anodization •Chemical-Liquid •Chemical-Vapor •Thermal •Plasma •Leaching •Mechanical •Bulk Sputtering •Ion Implantation

As seen above, there are wide ranges of techniques that each has unique processes. Therefore, it is important to choose suitable technique for each application.

Several criteria are taken into consideration for selection of the techniques;

- Properties of deposition materials
- Limitation caused by the substrates
- Deposition rate
- Adhesion of film to substrate
- Equipment requirement and availability
- Safety considerations
- Process stability
- Manufacturing considerations and cost

Electrochemical methods stand out among all thin film coating techniques with obtaining superior surface properties and ease of transfer to industrial applications [68]. Electrochemical deposition method offers continuous, uniform metallic thin films on conductive surfaces. With electrochemical anodization, which usually applied on metals with passive oxide layer, nanostructured metal oxides can be growth over metal surfaces. Nanostructured surfaces that obtained with electrochemical anodization have increased total surface area.

2.1.1 Electrochemical Deposition

Electrochemical deposition process is a surface coating process for producing a dense, uniform, and adherent coating in presence of electric current. Electrochemical deposition is usually applied to metals or alloys. The coating is usually produced for enhancing specific properties of the surface or decorative or protective purposes.

The core part of the electrochemical deposition process is the electrolytic cell (electroplating unit). (Figure 2.1) In the electrolytic cell, the current is passed from cathode to anode through ion containing electrolyte bath.

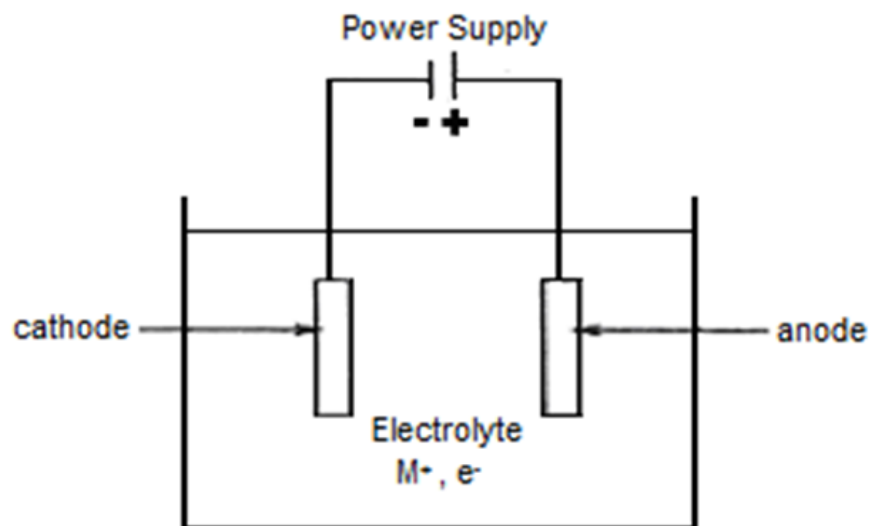


Figure 2.1: Electroplating unit.

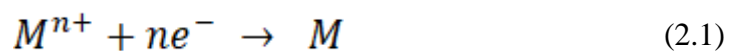
The cathode is the substrate that wanted to be coated. The substrates have to be conductive because it has to be electrically charged to attract ions in electrolyte.

The anode, however, is used for complete electric flow. The anode can be two types. First one is sacrificial anode, which is made of a metal, that wants to be deposited on cathode. It dissolves in the electrolyte during the deposition process to provide metal ions to replace what has been removed from the solution. Second one is permanent anode. The permanent anode has to be inert in the process. It is used only for completing the electrical circuit.

Electrolyte is the electrical conductor that contains negatively and positively charged ions. Electrolyte completes an electric circuit between two electrodes. The current is carried by those ions in the electrolyte. The positively charged ions move toward the cathode and the negatively charged ions move toward the anode.

The metallic ions in the electrolyte are positive charged. When the electrical current is applied, metal ions are attracted by negatively charged cathode. When they reach the cathode, the cathode provides electrons to reduce those positively charged ions to metallic form. This is the main mechanism of deposition of metal film onto the surface of the substrates.

Various reactions take place at the electrodes during electron transfers in deposition process. These electron transfer reactions are called oxidation/reduction reactions. The cathode is attached to the negative side of the electric source. Reduction reactions take place at cathode. In its simplest form, the reduction reaction in aqueous medium follows equation 2.1:



On the contrary, an anode is connected to the positive side of the electric source; therefore, it accepts electrons from the electrolyte. The oxidation reactions take place at the anode. Oxidation reactions follow given equation 2.2:



Results of these equations, electrolyte always contains metal ions and electron during the process.

Thin films thickness is important for applications. Thickness of the deposited layer on the substrate is influenced by several factors [69];

1. Deposition time
2. Current density and waveform
3. Composition and concentration of solution
4. Bath temperature
5. Properties of surface
6. The presence of impurities

With accurate parameters, electrochemical deposition gives perfect thin films with requested thickness and surface properties.

2.1.2 Electrochemical Anodization

Anodization is an electrochemical process that converts the metal surface into an anodic oxide finish. Anodizing means electrochemical oxidation of a metal –the controlled version of a naturally occurring phenomenon. The process takes its name from that the part to be coated becomes the anode in the system. It is different from electroplating, where the coated part the cathode.

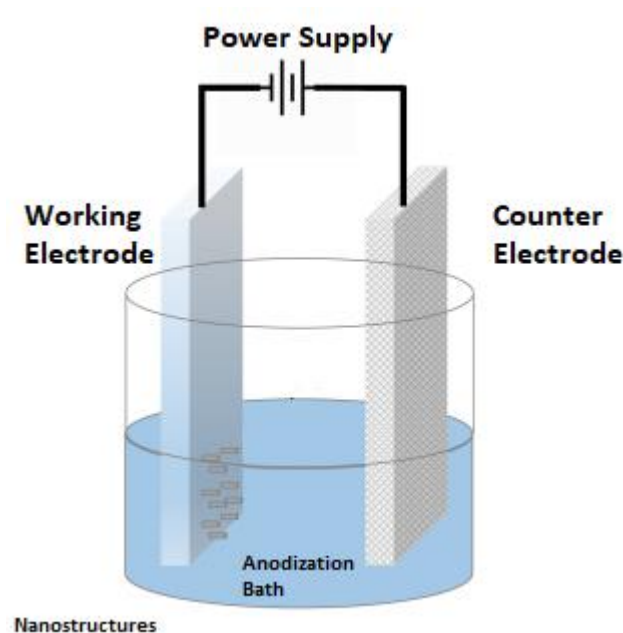


Figure 2.2: Anodization bath.

Anodization process occurs in an acidic electrolyte bath and passing an electric current between two electrodes through the medium (Figure 2.2). The cathode acts as an inert electrode and the metal that wanted to be anodized acts as an anode, hence the origin of the term anodizing. Oxygen ions are released from the electrolyte to combine with the metal atoms at the surface of the part being anodized.

Anodizing is a “conversion coating”, which means the surface of metal converted into metal oxide, and is very different than paints, plating and other common coatings on metal surfaces [70]. While paints and plating place on top of the surface of the bulk metal, anodizing converts the outer layer of metal to coating, so the coating is fully integrated with the metal substrate. The coating penetrates in to the base materials as much as it builds up on the outside. The thickness of structure consist of both penetration and build-up (Figure 2.3).

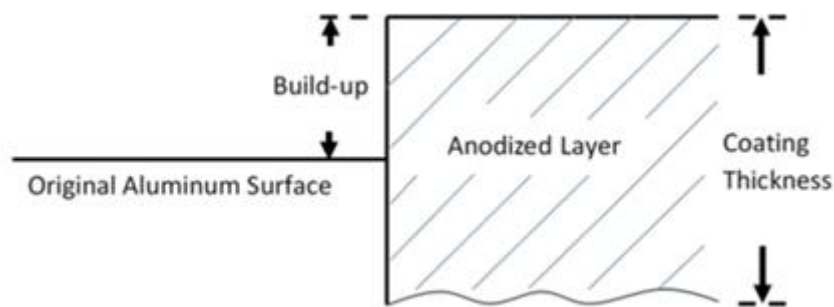


Figure 2.3: Coating Thickness in Anodization

Electrochemical anodization process is affected by different medium and operating conditions. Concentration and composition of the electrolyte and presence of any additives are changing for different applications. Operating conditions such as temperature, voltage, and amperage are effective on nanomaterials structures [71]. Current density, which is the amount of electric current traveling per unit cross-section area, is the leading factor both growth and monitoring of the growth of nanoparticles during electrochemical anodization process. Current density curves can be obtained simultaneously during the anodization process. Even each application has specific curves, generally, all current density curves look like the one is given in figure 2.4.

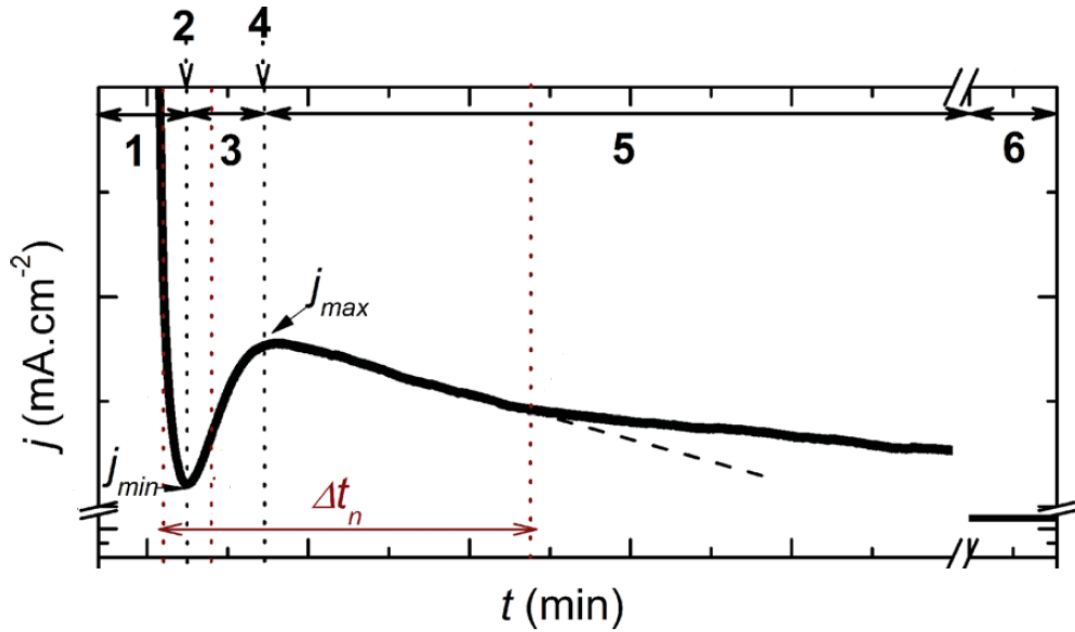


Figure 2.4: Current density – time curve in anodization process.

Beginning of the process, the current density has a high value (1), which encounters rapid drop to j_{min} point (2) depending on rapid formation of barrier oxide layer. Then, current density starts to increase (3) and continues until reaching j_{max} (4). From this point onwards, the anodization steps in to form nanoparticles that proves slow rate decrease of current density (5). At last, the oxidation becomes higher than the dissolution and current density become constant (6). This results limitation of nanoparticle growth [72].

Unique situation of anodizing brings more advantages to the application include:

1. A very thin coating compared to paints and powder coat.
2. Extremely durable, hard, abrasion resistant and long lasting.
3. Excellent corrosion protection.
4. Environmentally friendly finish.
5. Good electrical insulator.
6. Inexpensive.

3. MATERIALS & METHODS

3.1 Materials

All equipment and materials in this project are used with permission of İzmir Katip Çelebi University. DC power supply is used for creating electrical current for deposition and anodization processes. Magnetic stirrer is used for aqueous solutions homogeneity. Multimeter is used to control current throughout electrochemical processes. Oven is used for heat treatment. XRD and SEM are used for characterizations.

All laboratory supplies are used from “Nanomedicine and Biosensor Laboratory” in Central Research Laboratories of İKÇU. ITO coated glass substrates are bought from TEKNOMA in İYTE.

All chemicals that are used in this project are obtained in different ways. Distilled water taken from Central Research Laboratories. Potassium bicarbonate, high-density chitosan and acetic acid are bought from Sigma-Aldrich. Zinc based deposition solution which is used commercially in zinc coating are taken from a factory. Anodization solution is prepared based on KHCO_3 .

3.2 Methods

For this project, several surface coating techniques were used to form proposed hierarchical structure for this project is given in figure 3.1. Electrochemical deposition and electrochemical anodization techniques are used back-to-back firstly, to form zinc layer on Glass/ITO then to grow ZnO nanostructures on zinc layer. This two-step electrochemical method is a novel and simpler way to produce ZnO nanostructures on glass/ITO surfaces. After obtaining ZnO nanostructures, dip coating method is used to seed chitosan over ZnO nanostructures. Chitosan increases immobility of biomolecules on the surfaces [REF]. This modification to the surface makes the ZnO nanostructured electrode more suitable for sensor applications.

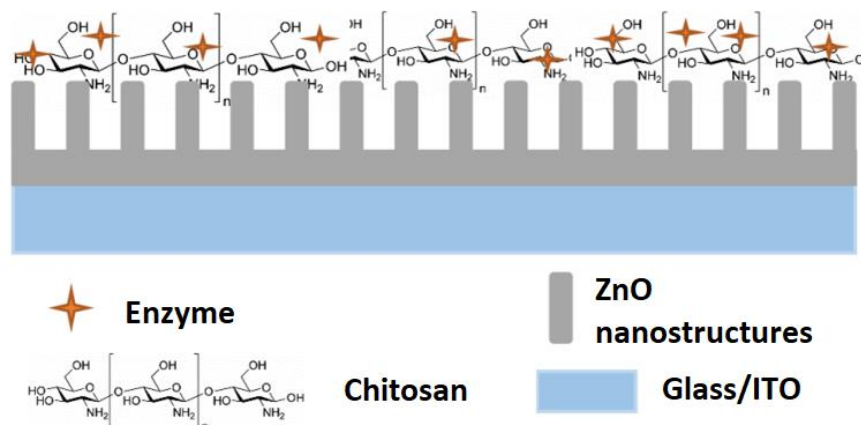


Figure 3.1: Desired layered surface structure.

Literature review of the studies that are similar to this project is given in table 3.1.

Table 3.1: Literature Review.

Electrode Structure	Coating Technique	Sensor for	REF.
Au-ZnO	Hydrothermal	Cholesterol	[39]
ITO/ZnO	Thermal	Glucose	[43]
ZnO-CuO HNC	Electrospinning	Glucose	[49]
ZnO/Pt/Chit	Dip Coating	Glucose	[66]
Ti-ZnO	Dip Coating	Glucose	[73]
Cam/ITO-ZnO-Chit	Spin Coating	Cholesterol	[74]
Au-ZnO	P. Absorbtion	Cholesterol	[75]
ITO/nano-ZnO	Dip Coating	Cholesterol	[76]
GCE-GR-CNT-ZnO	Dip Coating	Glucose	[77]
Si/SiO ₂ /Au/ZnO	Hydrothermal	Glucose	[78]
ZnO-GR	Direct Growth	Glucose	[79]
ITO/ZnO/AuNPs	Spin Coating	Glucose	[80]
ITO/ZnO-CuO	PLD	Cholesterol	[81]
Au/ZnO	RF Sputtering	Cholesterol	[82]
Ag/ZnO	Chemical Sol-Gel	Cholesterol	[83]
Pt-Au@ZnONRs	Hydrothermal	Cholesterol	[84]

As seen from the review, some studies are using same structure as this project. However, current project stands out because of its unique two-steps electrochemical method for growing ZnO nanostructures over Glass/ITO surfaces. Electrochemical deposition and electrochemical anodization methods are used as a new way to produce nanostructures over electrically conductive surfaces. In this project, ITO coated glass is chosen as conductive substrates and zinc oxide is chosen as coating material.

Furthermore, besides biosensors, this two-steps electrochemical process envisioned that with using of conductive, flexible materials as a substrate, antibacterial, self-cleaning textiles and flexible photocatalytic surface applications.



4. EXPERIMENTAL PROCEDURE

ITO coated glass substrates were first annealed at 200°C for 18 hours in order to treat surface roughness. Then, substrates were cut into 2.5 x 2.5 cm pieces. Substrates were cleaned ultrasonically for 10 minutes in acetone, isopropanol and distilled water, respectively (Figure 4.1).



Figure 4.1: Ultrasonic bath.

First, electrodeposition process is applied. Deposition process took place in commercial $ZnCl_2$ aqueous solution (Figure 4.2). Bulk 2.5x10 cm Zn plate was used as cathode. DC power supply was used in order to create voltage.

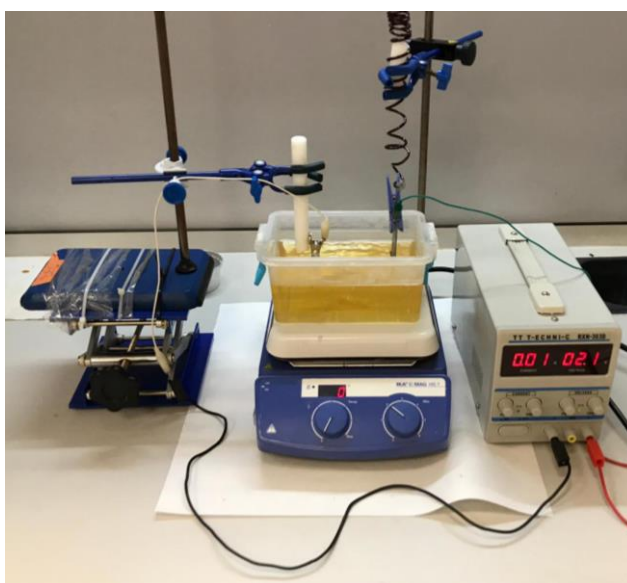


Figure 4.2: Electrochemical deposition setup.

Cleaned substrates were electrochemically deposited in commercial ZnCl_2 aqueous solutions under different deposition durations (2.5 – 5 – 7.5 – 10 min) with constant voltage (0.4V) at ambient temperature to investigate time effect on production of thin Zn layer.

Then, electrochemical deposition process was applied again under different voltage values (0.1 – 0.2 – 0.3 – 0.4 V) with constant time (5 min.) at ambient temperature to investigate voltage effect on production of thin layer.

Coated substrates were compared in terms of film continuity and adhesion. It is important for following processes that thin film must be continuous all over the surface and cannot peel off from glass surface.

After deposition parameters are determined, new sets of substrates are coated for electrochemical anodization process. 5x10 cm platinum mesh plate is used as anode. Same DC power supply was used in order to create voltage.

Electrochemical anodization process also was carried out under different parameters for each substrate. First, anodization took place in glycerol-based solution under various voltages (2 – 4 – 6 – 8 V) with constant 15-minute durations. Then, anodization took place in KHCO_3 based solution under same parameter (Figure 4.3).

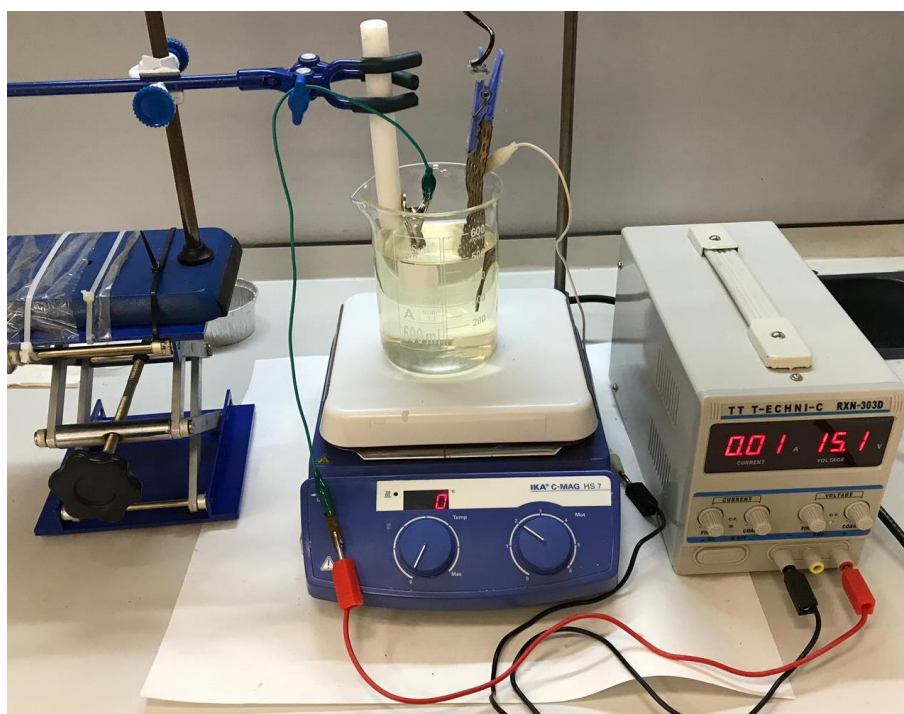


Figure 4.3: Electrochemical anodization setup.

After anodization parameters are set, new sets of samples were prepared for further steps. The samples were covered with chitosan to increase immobilization of enzymes. Dip coating method was used for seeding chitosan on surface. Process took place in chitosan-acetic acid based solution.

The samples were characterized by SEM and XRD to evaluate the structure and the morphology of the Glass/ITO/ZnO nanostructures, respectively.



5. RESULTS AND CONCLUSION

You can see the first deposited samples with different durations in figure 5.1. As you can see, for 2.5 min duration, zinc film is not continuous through the surface. For 5 min, Zinc film is continuous and strongly adhesive on the surface. Over 5 min durations, zinc films peel off from the surface.

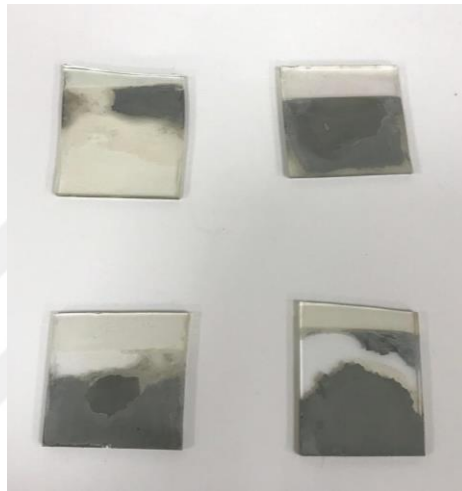


Figure 5.1: Coatings under different durations.

In figure 5.2, you can see photos of deposited substrates under different voltages. For lower voltages, zinc film continuously deposited over the surface. However, when the voltages are higher, zinc layer is peeled off with ITO coatings from the surface.



Figure 5.2: Coatings under different voltages.

In figure 5.3, you can see the surfaces of samples anodized in glycerol-based solution under 2V, 4V, 6V and 8V, respectively. Glycerol based solution did not serve as suitable medium for this anodization process.

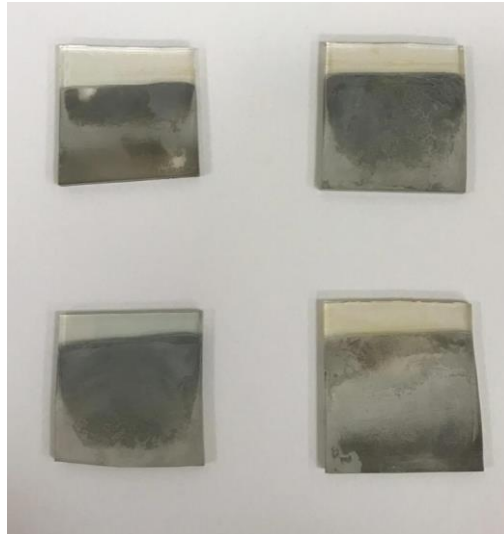


Figure 5.3: Samples anodized in glycerol.

And in figure 5.4, you can see the surfaces of samples anodized in KHCO_3 based solution under same parameter.

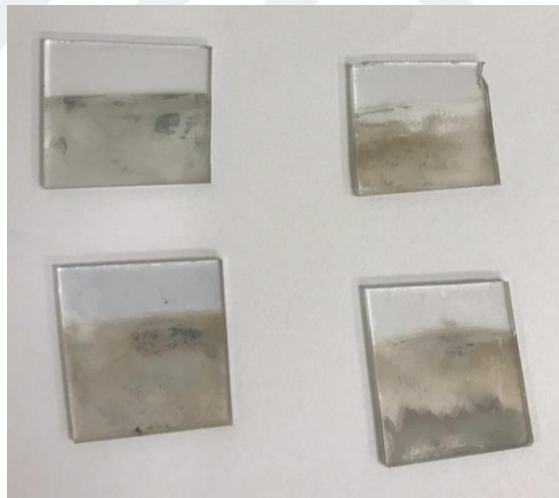


Figure 5.4: Samples anodized in potassium bicarbonate.

As seen in the pictures, anodization process took place successfully in potassium bicarbonate based solution. Oxidation did occur in every samples. But only in samples that were deposited 10 minutes has the surface with ZnO nanostructures. This shows that if the deposition time were shorter than 10 minutes, as coated Zn layer would not be thick enough for growth of ZnO nanostructures.

At this point, we ordered new sets of Glass/ITO substrates. The new substrates have different surface properties and better coatings than previous ones. However, optimization for anodization process was not done again for new substrates. Approximate parameters were selected and applied for all substrates.

New substrates investigated again for deposition time for 2.5, 5, 7.5 and 10 min., respectively. Then electrochemical anodization was performed for all substrates under 2.0V voltage for 15 minutes.

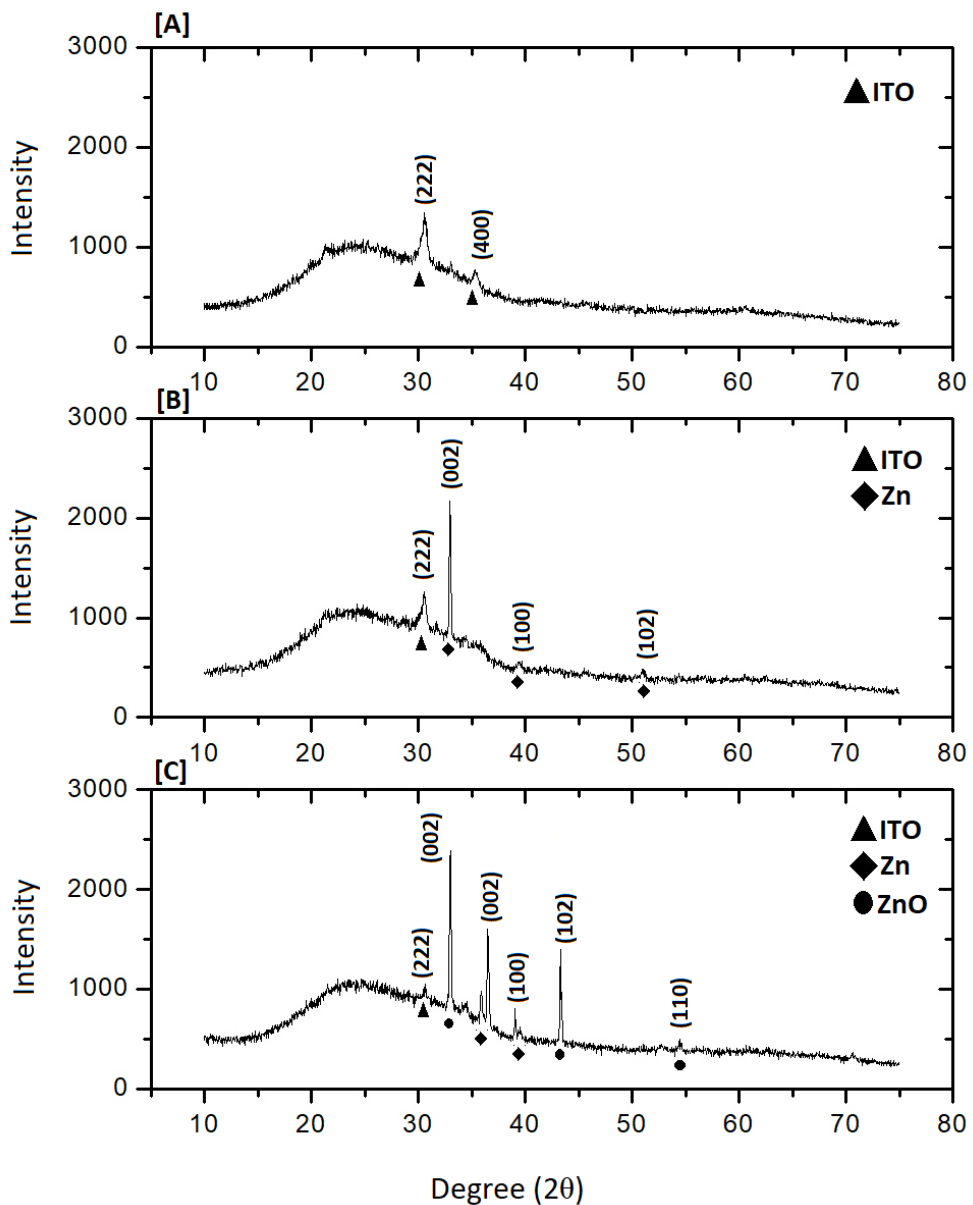


Figure 5.5: XRD graphics of [A] glass/ITO, [B] glass/ITO/Zn, [C] glass/ITO/ZnO samples;

We have studied surface characteristics and morphology of ZnO nanostructures. The XRD results of glass/ITO, glass/ITO/Zn and glass/ITO/ZnO electrodes are shown in figure 5.5 [85].

As seen in the graphics, Zn layer was successfully coated on glass/ITO substrates after electrodeposition process. Likewise, ZnO nanostructures were successfully grown on zinc layer.

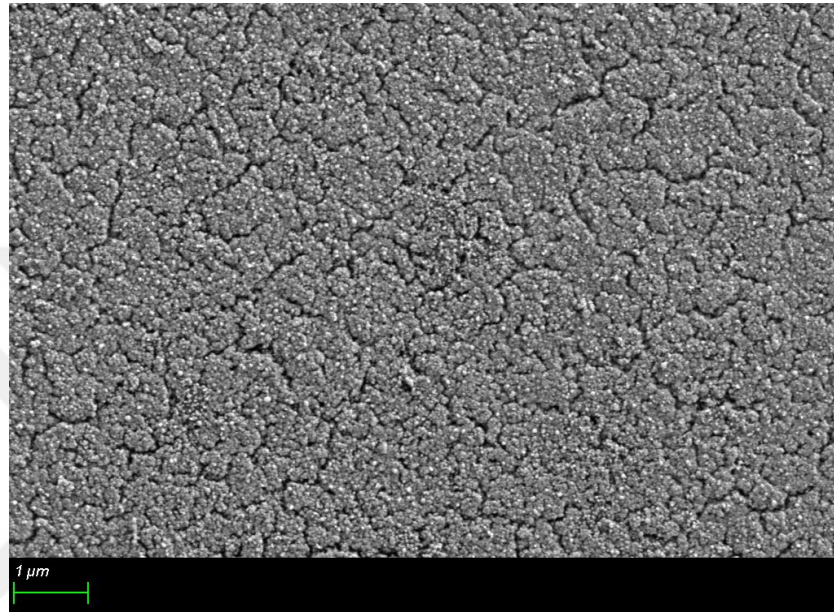


Figure 5.6: SEM image of zinc coating on Glass/ITO substrates.



Figure 5.7: SEM image of ZnO nanostructures on glass/ITO/Zn substrates.

SEM images of the zinc layer and ZnO nanostructures are shown in figure 5.6 and figure 5.7, respectively. As seen in the images, zinc layer was continuous trough the surface and ZnO nanostructures formed as nanoflower like shapes.

After obtaining ZnO nanostructured surfaces, we have attempted to seed chitosan layer over those surfaces. SEM image for one substrate is shown in Figure 5.8. As you can see, sizes of chitosan nanoparticles are around 100 nm, which is too big for ZnO nanostructures underneath. The chitosan coating process has not been attempted again.

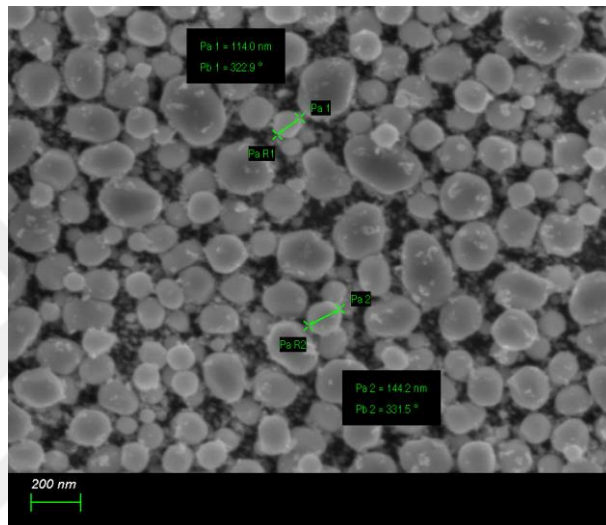


Figure 5.8: SEM image of chitosan coated glass/ITO/ZnO surface

5.1 Conclusion

Proposed 2-steps electrochemical process is faster, cheaper and simpler way to produce ZnO nanostructure. This process can easily applicable to other surface conductive materials like flexible PET/ITO and opens new application areas. Process also can be industrialized with low setup costs.

Deposition time is important on film thickness and thickness of zinc film directly affect growth of ZnO nanostructures. Surfaces covered with ZnO nanostructures can be obtained by using proper parameter. These surfaces are highly active for bonding with other particles. Depends on that, surface modification can be done for various applications. This makes ZnO nanostructures suitable for enzymatic biosensors to detect diseases like cholesterol and diabetics.

REFERENCES

- [1] Malshe, A., Rajurkar, K., Samant, A., Hansen, H. N., Bapat, S., & Jiang, W. (2013). Bio-inspired functional surfaces for advanced applications. *CIRP Annals*, 62(2), 607-628. doi:<https://doi.org/10.1016/j.cirp.2013.05.008>
- [2] Daniel, M.-C., & Astruc, D. (2004). Gold nanoparticles: assembly, supramolecular chemistry, quantum-size-related properties, and applications toward biology, catalysis, and nanotechnology. *Chemical reviews*, 104(1), 293-346.
- [3] Feynman, R. (2018). There's plenty of room at the bottom. In *Feynman and computation* (pp. 63-76): CRC Press.
- [4] Tolochko, N. (2009). History of nanotechnology. *Encyclopedia of Life Support Systems (EOLSS)*.
- [5] Walton, H. W. K. D. R. M. (2019). Fullerene. In *Encyclopædia Britannica*: Encyclopædia Britannica, inc.
- [6] Novoselov, K. S., Geim, A. K., Morozov, S. V., Jiang, D., Zhang, Y., Dubonos, S. V., . . . Firsov, A. A. (2004). Electric field effect in atomically thin carbon films. *science*, 306(5696), 666-669.
- [7] Giannazzo, F., Sonde, S., & Raineri, V. (2011). Electronic properties of graphene probed at the nanoscale. In *Physics and Applications of Graphene-Experiments*: IntechOpen.
- [8] Roberts, M., Clemons, C., Wilber, J., Young, G., Buldum, A., & Quinn, D. (2010). Continuum plate theory and atomistic modeling to find the flexural rigidity of a graphene sheet interacting with a substrate. *Journal of Nanotechnology*, 2010.
- [9] Ema, M., Hougaard, K. S., Kishimoto, A., & Honda, K. (2016). Reproductive and developmental toxicity of carbon-based nanomaterials: a literature review. *Nanotoxicology*, 10(4), 391-412.
- [10] Tiwari, J. N., Tiwari, R. N., & Kim, K. S. (2012). Zero-dimensional, one-dimensional, two-dimensional and three-dimensional nanostructured materials for advanced electrochemical energy devices. *Progress in Materials Science*, 57(4), 724-803.
- [11] Pathakoti, K., Manubolu, M., & Hwang, H.-M. (2017). Nanostructures: Current uses and future applications in food science. *journal of food and drug analysis*, 25(2), 245-253.
- [12] Chen, J., Wu, X., Gong, Y., Wang, P., Li, W., Mo, S., . . . Chen, Y. (2018). General Synthesis of Transition- Metal Oxide Hollow Nanospheres/Nitrogen- Doped Graphene Hybrids by Metal–Amine Complex Chemistry for High- Performance Lithium- Ion Batteries. *Chemistry–A European Journal*, 24(9), 2126-2136.
- [13] Kim, Y. T., Han, J. H., Hong, B. H., & Kwon, Y. U. (2010). Electrochemical synthesis of CdSe quantum- dot arrays on a graphene basal plane using mesoporous silica thin- film templates. *Advanced Materials*, 22(4), 515-518.

- [14] Lee, J. Y., Hong, B. H., Kim, W. Y., Min, S. K., Kim, Y., Jouravlev, M. V., . . . Kaufman, L. J. (2009). Near-field focusing and magnification through self-assembled nanoscale spherical lenses. *Nature*, *460*(7254), 498.
- [15] Brovman, Y. M., Small, J. P., Hu, Y., Fang, Y., Lieber, C. M., & Kim, P. (2016). Electric field effect thermoelectric transport in individual silicon and germanium/silicon nanowires. *Journal of Applied Physics*, *119*(23), 234304.
- [16] Cushing, S. K., Meng, F., Zhang, J., Ding, B., Chen, C. K., Chen, C.-J., . . . Zheng, P. (2017). Effects of defects on photocatalytic activity of hydrogen-treated titanium oxide nanobelts. *ACS Catalysis*, *7*(3), 1742-1748.
- [17] Lin, C., Hu, L., Cheng, C., Sun, K., Guo, X., Shao, Q., . . . Guo, Z. (2018). Nano-TiNb₂O₇/carbon nanotubes composite anode for enhanced lithium-ion storage. *Electrochimica Acta*, *260*, 65-72.
- [18] Zhao, X., Ma, X., & Zheng, P. (2018). The preparation of carboxylic-functional carbon-based nanofibers for the removal of cationic pollutants. *Chemosphere*, *202*, 298-305.
- [19] Dahotre, N. B., & Nayak, S. (2005). Nanocoatings for engine application. *Surface and Coatings Technology*, *194*(1), 58-67.
- [20] Ding, F., Liu, J., Zeng, S., Xia, Y., Wells, K. M., Nieh, M.-P., & Sun, L. (2017). Biomimetic nanocoatings with exceptional mechanical, barrier, and flame-retardant properties from large-scale one-step coassembly. *Science advances*, *3*(7), e1701212.
- [21] Karan, S., Jiang, Z., & Livingston, A. G. (2015). Sub-10 nm polyamide nanofilms with ultrafast solvent transport for molecular separation. *Science*, *348*(6241), 1347-1351.
- [22] Ko, H.-U., Kim, H. C., Kim, J. W., Zhai, L., & Kim, J. (2017). Fabrication Method Study of ZnO Nanocoated Cellulose Film and Its Piezoelectric Property. *Materials*, *10*(6), 611.
- [23] Wang, Z., Chen, X., Gong, Y., Zhang, B., & Li, H. (2017). Superhydrophobic nanocoatings prepared by a novel vacuum cold spray process. *Surface and Coatings Technology*, *325*, 52-57.
- [24] Lei, W., Liu, D., Zhu, P., Chen, X., Hao, J., Wang, Q., . . . Zou, G. (2010). One-step synthesis of AlN branched nanostructures by an improved DC arc discharge plasma method. *CrystEngComm*, *12*(2), 511-516.
- [25] Lu, Q., Wang, H., Eid, K., Allothman, Z. A., Malgras, V., Yamauchi, Y., & Wang, L. (2016). Synthesis of hollow platinum-palladium nanospheres with a dendritic shell as efficient electrocatalysts for methanol oxidation. *Chemistry—An Asian Journal*, *11*(13), 1939-1944.
- [26] Wu, X., Hou, M., & Ge, J. (2015). Metal-organic frameworks and inorganic nanoflowers: a type of emerging inorganic crystal nanocarrier for enzyme immobilization. *Catalysis Science & Technology*, *5*(12), 5077-5085.
- [27] Zhong, D., Cai, B., Wang, X., Yang, Z., Xing, Y., Miao, S., . . . Li, C. (2015). Synthesis of oriented TiO₂ nanocones with fast charge transfer for perovskite solar cells. *Nano Energy*, *11*, 409-418.
- [28] Jeevanandam, J., Barhoum, A., Chan, Y. S., Dufresne, A., & Danquah, M. K. (2018). Review on nanoparticles and nanostructured materials: history, sources, toxicity and regulations. *Beilstein journal of nanotechnology*, *9*(1), 1050-1074.
- [29] Li, Z., Wang, L., Li, Y., Feng, Y., & Feng, W. (2019). Carbon-based functional nanomaterials: Preparation, properties and applications. *Composites Science and Technology*.

- [30] Yee, M. J., Mubarak, N., Abdullah, E., Khalid, M., Walvekar, R., Karri, R., . . . Numan, A. (2019). Carbon nanomaterials based films for strain sensing application—A review. *Nano-Structures & Nano-Objects*, 18, 100312.
- [31] Zhang, X., Hou, L., & Samori, P. (2016). Coupling carbon nanomaterials with photochromic molecules for the generation of optically responsive materials. *Nature communications*, 7, 11118.
- [32] Iannazzo, D., Pistone, A., Salamò, M., Galvagno, S., Romeo, R., Giofrè, S. V., . . . Di Pietro, A. (2017). Graphene quantum dots for cancer targeted drug delivery. *International journal of pharmaceutics*, 518(1-2), 185-192.
- [33] Yi, H., Huang, D., Zeng, G., Lai, C., Qin, L., Cheng, M., . . . Guo, X. (2018). Selective prepared carbon nanomaterials for advanced photocatalytic application in environmental pollutant treatment and hydrogen production. *Applied Catalysis B: Environmental*.
- [34] Dai, L., Chang, D. W., Baek, J. B., & Lu, W. (2012). Carbon nanomaterials for advanced energy conversion and storage. *small*, 8(8), 1130-1166.
- [35] Faraday, M. (1857). LIX. Experimental relations of gold (and other metals) to light.—The bakerian lecture. *The London, Edinburgh, and Dublin Philosophical Magazine and Journal of Science*, 14(96), 512-539.
- [36] Edwards, P. P., & Thomas, J. M. (2007). Gold in a metallic divided state— from faraday to present- day nanoscience. *Angewandte Chemie International Edition*, 46(29), 5480-5486.
- [37] Rao, C., Kulkarni, G., Thomas, P. J., & Edwards, P. P. (2002). Size- dependent chemistry: properties of nanocrystals. *Chemistry—A European Journal*, 8(1), 28-35.
- [38] Kumar, H., Venkatesh, N., Bhowmik, H., & Kuila, A. (2018). Metallic Nanoparticle: A Review. *Biomedical Journal of Scientific & Technical Research*, 4(2), 3765-3775.
- [39] Wei, A., Sun, X. W., Wang, J., Lei, Y., Cai, X., Li, C. M., . . . Huang, W. (2006). Enzymatic glucose biosensor based on ZnO nanorod array grown by hydrothermal decomposition. *Applied Physics Letters*, 89(12), 123902.
- [40] Wang, Z. L. (2004). Zinc oxide nanostructures: growth, properties and applications. *Journal of physics: condensed matter*, 16(25), R829.
- [41] Asif, M. (2009). *Electrochemical Biosensors Based on Functionalized Zinc Oxide Nanorods*. Linköping University Electronic Press,
- [42] Kumar, S. S., Venkateswarlu, P., Rao, V. R., & Rao, G. N. (2013). Synthesis, characterization and optical properties of zinc oxide nanoparticles. *International Nano Letters*, 3(1), 30.
- [43] Liu, X., Hu, Q., Wu, Q., Zhang, W., Fang, Z., & Xie, Q. (2009). Aligned ZnO nanorods: a useful film to fabricate amperometric glucose biosensor. *Colloids and Surfaces B: Biointerfaces*, 74(1), 154-158.
- [44] Ahmad, R., Ahn, M.-S., & Hahn, Y.-B. (2017). ZnO nanorods array based field-effect transistor biosensor for phosphate detection. *Journal of colloid and interface science*, 498, 292-297.
- [45] Arya, S. K., Saha, S., Ramirez-Vick, J. E., Gupta, V., Bhansali, S., & Singh, S. P. (2012). Recent advances in ZnO nanostructures and thin films for biosensor applications. *Analytica chimica acta*, 737, 1-21.
- [46] Foo, K., Hashim, U., Voon, C., Kashif, M., & Ali, M. E. (2016). Au decorated ZnO thin film: application to DNA sensing. *Microsystem Technologies*, 22(4), 903-910.

- [47] Liu, X., Lin, P., Yan, X., Kang, Z., Zhao, Y., Lei, Y., . . . Zhang, Y. (2013). Enzyme-coated single ZnO nanowire FET biosensor for detection of uric acid. *Sensors and Actuators B: Chemical*, 176, 22-27.
- [48] Tereshchenko, A., Bechelany, M., Viter, R., Khranovskyy, V., Smyntyna, V., Starodub, N., & Yakimova, R. (2016). Optical biosensors based on ZnO nanostructures: advantages and perspectives. A review. *Sensors and Actuators B: Chemical*, 229, 664-677.
- [49] Zhou, C., Xu, L., Song, J., Xing, R., Xu, S., Liu, D., & Song, H. (2014). Ultrasensitive non-enzymatic glucose sensor based on three-dimensional network of ZnO-CuO hierarchical nanocomposites by electrospinning. *Scientific reports*, 4, 7382.
- [50] Zong, X., & Zhu, R. (2018). ZnO nanorod-based FET biosensor for continuous glucose monitoring. *Sensors and Actuators B: Chemical*, 255, 2448-2453.
- [51] Yogeswaran, U., & Chen, S.-M. (2008). A review on the electrochemical sensors and biosensors composed of nanowires as sensing material. *Sensors*, 8(1), 290-313.
- [52] Hussein, A. K. (2015). Applications of nanotechnology in renewable energies—A comprehensive overview and understanding. *Renewable and Sustainable Energy Reviews*, 42, 460-476.
- [53] Duncan, T. V. (2011). Applications of nanotechnology in food packaging and food safety: barrier materials, antimicrobials and sensors. *Journal of colloid and interface science*, 363(1), 1-24.
- [54] Qu, X., Alvarez, P. J., & Li, Q. (2013). Applications of nanotechnology in water and wastewater treatment. *Water research*, 47(12), 3931-3946.
- [55] Wong, Y., Yuen, C., Leung, M., Ku, S., & Lam, H. (2006). Selected applications of nanotechnology in textiles. *AUTEX Research Journal*, 6(1), 1-8.
- [56] Bhat, S. S., Qurashi, A., & Khanday, F. A. (2017). ZnO nanostructures based biosensors for cancer and infectious disease applications: perspectives, prospects and promises. *TrAC Trends in Analytical Chemistry*, 86, 1-13.
- [57] Ruecha, N., Rangkupan, R., Rodthongkum, N., & Chailapakul, O. (2014). Novel paper-based cholesterol biosensor using graphene/polyvinylpyrrolidone/polyaniline nanocomposite. *Biosensors and Bioelectronics*, 52, 13-19.
- [58] Cai, X., Gao, X., Wang, L., Wu, Q., & Lin, X. (2013). A layer-by-layer assembled and carbon nanotubes/gold nanoparticles-based bienzyme biosensor for cholesterol detection. *Sensors and Actuators B: Chemical*, 181, 575-583.
- [59] Rahman, M., Ahammad, A., Jin, J.-H., Ahn, S. J., & Lee, J.-J. (2010). A comprehensive review of glucose biosensors based on nanostructured metal-oxides. *Sensors*, 10(5), 4855-4886.
- [60] Mohammed, A. M., Ibraheem, I. J., Obaid, A., & Bououdina, M. (2017). Nanostructured ZnO-based biosensor: DNA immobilization and hybridization. *Sensing and bio-sensing research*, 15, 46-52.
- [61] Wang, C., Chu, X., & Wu, M. (2006). Detection of H₂S down to ppb levels at room temperature using sensors based on ZnO nanorods. *Sensors and Actuators B: Chemical*, 113(1), 320-323.
- [62] Rex, M., Hernandez, F. E., & Campiglia, A. D. (2006). Pushing the limits of mercury sensors with gold nanorods. *Analytical Chemistry*, 78(2), 445-451.

- [63] Choi, J. H., Kim, H. S., Choi, J.-W., Hong, J. W., Kim, Y.-K., & Oh, B.-K. (2013). A novel Au-nanoparticle biosensor for the rapid and simple detection of PSA using a sequence-specific peptide cleavage reaction. *Biosensors and Bioelectronics*, *49*, 415-419.
- [64] Ahmad, R., Tripathy, N., Kim, J. H., & Hahn, Y.-B. (2012). Highly selective wide linear-range detecting glucose biosensors based on aspect-ratio controlled ZnO nanorods directly grown on electrodes. *Sensors and Actuators B: Chemical*, *174*, 195-201.
- [65] Tereshchenko, A., Fedorenko, V., Smyntyna, V., Konup, I., Konup, A., Eriksson, M., . . . Bechelany, M. (2017). ZnO films formed by atomic layer deposition as an optical biosensor platform for the detection of Grapevine virus A-type proteins. *Biosensors and Bioelectronics*, *92*, 763-769.
- [66] Anusha, J., Kim, H.-J., Fleming, A. T., Das, S. J., Yu, K.-H., Kim, B. C., & Raj, C. J. (2014). Simple fabrication of ZnO/Pt/chitosan electrode for enzymatic glucose biosensor. *Sensors and Actuators B: Chemical*, *202*, 827-833.
- [67] Umar, A., Rahman, M., Vaseem, M., & Hahn, Y.-B. (2009). Ultra-sensitive cholesterol biosensor based on low-temperature grown ZnO nanoparticles. *Electrochemistry Communications*, *11*(1), 118-121.
- [68] Dikici, T. (2009). *Çelik malzeme yüzeyine elektrolitik yolla kaplanan Zn-Ni-Co alaşımının mekanik ve yapısal özelliklerinin incelenmesi*. DEÜ Fen Bilimleri Enstitüsü,
- [69] Nur Ubaidah, S., Ying, K. K., & Khuan, N. I. (2011). *Electrodeposition: Principles, Applications and Methods*. Paper presented at the NTC 2011: Nuclear Technical Convention 2011, Malaysia.
- [70] Osborn, J. H. (2014). Understanding and Specifying Anodizing: what. *OMW Corporation*.
- [71] Stevenson Jr, M. F. (2013). Anodizing.
- [72] Apolinario, A., Sousa, C., Ventura, J., Costa, J., Leitao, D., Moreira, J., . . . Araujo, J. (2014). The role of the Ti surface roughness in the self-ordering of TiO₂ nanotubes: a detailed study of the growth mechanism. *Journal of Materials Chemistry A*, *2*(24), 9067-9078.
- [73] Ren, X., Chen, D., Meng, X., Tang, F., Hou, X., Han, D., & Zhang, L. (2009). Zinc oxide nanoparticles/glucose oxidase photoelectrochemical system for the fabrication of biosensor. *Journal of colloid and interface science*, *334*(2), 183-187.
- [74] Khan, R., Kaushik, A., Solanki, P. R., Ansari, A. A., Pandey, M. K., & Malhotra, B. (2008). Zinc oxide nanoparticles-chitosan composite film for cholesterol biosensor. *Analytica chimica acta*, *616*(2), 207-213.
- [75] Umar, A., Rahman, M., Al-Hajry, A., & Hahn, Y.-B. (2009). Highly-sensitive cholesterol biosensor based on well-crystallized flower-shaped ZnO nanostructures. *Talanta*, *78*(1), 284-289.
- [76] Solanki, P. R., Kaushik, A., Ansari, A. A., & Malhotra, B. (2009). Nanostructured zinc oxide platform for cholesterol sensor. *Applied Physics Letters*, *94*(14), 143901.
- [77] Hwa, K.-Y., & Subramani, B. (2014). Synthesis of zinc oxide nanoparticles on graphene-carbon nanotube hybrid for glucose biosensor applications. *Biosensors and Bioelectronics*, *62*, 127-133.

- [78] Marie, M., & Manasreh, O. (2017). Investigation of the influence of the As-grown ZnO nanorods and applied potentials on an electrochemical sensor for in-vitro glucose monitoring. *Chemosensors*, 5(1), 4.
- [79] Zhao, Y., Li, W., Pan, L., Zhai, D., Wang, Y., Li, L., . . . Xu, J.-B. (2016). ZnO-nanorods/graphene heterostructure: a direct electron transfer glucose biosensor. *Scientific reports*, 6, 32327.
- [80] Tian, K., Alex, S., Siegel, G., & Tiwari, A. (2015). Enzymatic glucose sensor based on Au nanoparticle and plant-like ZnO film modified electrode. *Materials Science and Engineering: C*, 46, 548-552. doi:<https://doi.org/10.1016/j.msec.2014.10.064>
- [81] Batra, N., Tomar, M., & Gupta, V. (2015). ZnO–CuO composite matrix based reagentless biosensor for detection of total cholesterol. *Biosensors and Bioelectronics*, 67, 263-271. doi:<https://doi.org/10.1016/j.bios.2014.08.029>
- [82] Singh, S., Arya, S. K., Pandey, P., Malhotra, B., Saha, S., Sreenivas, K., & Gupta, V. (2007). Cholesterol biosensor based on rf sputtered zinc oxide nanoporous thin film. *Applied Physics Letters*, 91(6), 063901.
- [83] Israr, M., Sadaf, J., Asif, M., Nur, O., Willander, M., & Danielsson, B. (2010). Potentiometric cholesterol biosensor based on ZnO nanorods chemically grown on Ag wire. *Thin Solid Films*, 519(3), 1106-1109.
- [84] Wang, C., Tan, X., Chen, S., Yuan, R., Hu, F., Yuan, D., & Xiang, Y. (2012). Highly-sensitive cholesterol biosensor based on platinum–gold hybrid functionalized ZnO nanorods. *Talanta*, 94, 263-270.
- [85] Lupan, O., Chow, L., Chai, G., & Heinrich, H. (2008). Fabrication and characterization of Zn–ZnO core–shell microspheres from nanorods. *Chemical Physics Letters*, 465(4-6), 249-253.

CIRRICULUM VITAE

I, Berkant Uzunbayır, was born in Konak, İzmir in 1992. I got my Bachelor's Degree in Mechanical Engineering from Ege University in 2016. I am currently getting my Master of Science degree in Nanoscience and Nanotechnology at İzmir Katip Çelebi University. I am working as a research assistant in Mechanical Engineering Department at İzmir University of Economics.

Conference Papers:

- “Two-Steps Electrochemical Process for Growth of ZnO Nanostructures on Glass/ITO Substrate” Berkant Uzunbayır, Ahmet Aykaç, Mustafa Erol, Tuncay Dikici, Fethullah Güneş, 2nd International Students Science Congress, May 2018, İKÇÜ
- “Growth of ZnO Nanostructures on Glass/ITO Substrate” Berkant Uzunbayır, Ahmet Aykaç, Mustafa Erol, Tuncay Dikici, Fethullah Güneş, Mustafa Can, Halil İbrahim Çiftçi, 4th International Symposium on Pharmaceutical and Biomedical Sciences, March 2018, Kumamoto University, Japan
- “Polymeric Nanoparticles as Transporting Vehicle for DDS” Berkant Uzunbayır, Büşra Özürgen, Ahmet Aykaç, 1st International Students Science Congress, May 2017, İKÇÜ

Projects:

- “Growth of ZnO-Chit nanostructures on ITO/Glass substrates through electrochemical anodization and their investigation as a biosensor” (MSc. Final Project), İKÇÜ
- “Huntit ve Hidromanyezit Minerali Kullanılarak Yangına Dayanıklı Ahşap Malzemelerin Üretilmesi” (TUBITAK, Research Project), İKÇÜ
- "Heat Exchanger Design for Geothermal Heating" (BE Final Project), Ege University
- Dishwasher Lower Rack Height Adjustment Mechanism (Vestel-Ebiltem "No Bending Projesi"), Ege University