

**Investigation of Electrodeposition Conditions
on the Morphology and Properties of
Zinc Oxide & Iron Oxide Films**

by

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This is to certify that I have examined this copy of a doctoral thesis by

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To my parents, sister and to my just starting family;

I love you all very dearly...

ABSTRACT

Main objective of this study is to explore hydrothermal-electrochemical deposition (HED) as a means of developing semiconductor metal oxide films as photoelectrodes for electricity and hydrogen production with solar energy.

The first part of this dissertation is devoted to preparation of ZnO films of various size and shape as efficient photoelectrodes by manipulating HED parameters and using electrodeposition as a means to coat sensitizers on ZnO with better electrical contact for cells with enhanced performance. It was observed that 1-D ZnO rods are obtained regardless of precursor (and/or KCl) concentration via HED and the adjustment of concentration provides control on the rod diameter. Increasing precursor concentration resulted in enhanced *c*-axis orientation and increase in the rod diameter. Moreover, photoelectrochemical sensitivity is enhanced both with improved *c*-axis orientation and increased rod diameter. A short circuit current density of 2.08 mA/cm² and an open circuit potential of -1.32 V have been achieved for the ZnO100/CdS21 electrode resulting in an overall solar-electrical energy conversion efficiency of 0.93 %.

Since morphological details of a semiconductor electrode such as size, shape, and connectivity of the particles often dictate physical properties, understanding and controlling the morphological aspects of polycrystalline electrodes is critical in producing highly efficient devices. Hence, preparation of ZnO structures in various shapes in synergistic effect of the growth-modifier molecules and HED is also demonstrated. It has been presented that by adjusting [MnCl₂] in deposition bath, diameters of rods can be tuned. HED also provides a single-step synthesis route for hierarchical ZnO architectures by modifying [Cd(CH₃COO)₂/Zn(II)]. HED allows growth of heterogeneous ZnO-Co nanostructures with Co-rich spheres on a zinc rich matrix, where the degree of phase separation and the quantity of the initial Co rich spheres are determined by Co(II) concentration.

Electrochemical deposition is studied as a quicker and cheaper alternative to deposit CdS and Ag₂S coatings on ZnO nanorod arrays. Photoresponse tends to increase with deposition time for CdS coatings due to the increased amount of visible-light sensitive CdS on ZnO film. However, generated photocurrent is reduced by prolonged deposition. A short circuit current density of 1.42 mA/cm² and an open circuit potential of -1.391 V have been achieved for the annealed Mn_doped CdS/ZnO electrode resulting in an overall power conversion efficiency of 0.81 %. Ag₂S/ZnO photoelectrodes exhibit considerably increased and widened light absorption but lower power-conversion efficiency, most probably due to ZnO degradation during deposition step. Furthermore, in an effort to produce buffer layers for solar cells with enhanced photoactivity, photoelectrochemical properties of mixed semiconductor CdS–ZnS films synthesized by electrochemical deposition is explored. The best performing film exhibited a short circuit current density of 1.31 mA/cm² and an open circuit potential of -0.99 V with an overall power conversion efficiency of 0.6 %.

The second part of this thesis is devoted to investigate physical and photoelectrochemical properties of α -Fe₂O₃ films grown by HED and to the synthesis α -Fe₂O₃ particles of varying size and shape via HED in the presence of growth-modifier molecules. It is discovered that HED enables production of crystalline α -Fe₂O₃ phase without thermal annealing as opposed to electrodepositions reported at ambient temperature. Photoelectrochemical studies demonstrated that higher performance can be obtained with the films prepared via HED. Net photocurrent density of 23.6 μ A/cm² is obtained in 0.1 M NaOH under 1 sun conditions at 1.23 V vs NHE with the film prepared from a bath containing 0.05 M FeCl₂ and 0.1 M NaCH₃COOH via hydrothermal-electrodeposition with a photocurrent onset potential of 0.96 V vs NHE. Moreover, α -Fe₂O₃ with different morphologies, including worm-like, spherical, rhombohedral, square planar particles, and platelets, were obtained when HED is used together with growth-modifying species such as CH₃COO⁻, Ce³⁺ and F⁻.

ÖZET

Bu çalışma temel olarak hidrotermal şartlar altında gerçekleştirilen elektrokimyasal sentez yöntemini (HED), güneş enerjisiyle elektrik ve hidrojen üretimi için yarı-iletken metal oksit filmlerin geliştirilmesinde bir araç olarak araştırmayı hedeflemektedir.

Tezin ilk kısmı, çeşitli parçacık boyutu ve şekline sahip ZnO filmlerin HED ile hazırlanmasına ayrılmıştır. Ayrıca elektrokimyasal sentez yöntemini görünür ışığı soğuran parçacıkları ZnO üzerine daha iyi elektrik temas sağlayacak şekilde kaplamak için kullanarak, daha yüksek verimde çalışan güneş pilleri tasarımları oluşturmak hedeflenmektedir. HED ile $\text{Zn}(\text{NO}_3)_2$ (ve de KCl) derişiminden bağımsız olarak tek boyutlu ZnO çubuklar oluşturulduğu gözlenmiştir; $\text{Zn}(\text{NO}_3)_2$ derişimi, elde edilen çubukların çapını kontrol etmektedir. $\text{Zn}(\text{NO}_3)_2$ 'ın başlangıç derişimi arttırıldıkça çubuk çapının arttığı ve *c*-ekseni doğrultusunda büyümenin hızlandığı görülmüştür. Bununla birlikte, *c*-ekseni yönelimi ve çubuk çapı arttıkça foto-elektrokimyasal duyarlılık artmaktadır. $\text{ZnO}/100/\text{CdS}21$ ile $2,08 \text{ mA}/\text{cm}^2$ akım yoğunluğu, $-1,32 \text{ V}$ potansiyel ve toplam % 0,93 güneş-elektrik enerji çevirme verimi elde edilmiştir.

Yarı-iletken elektrotların boyut, şekil ve parçacık bağlantıları gibi morfolojik özellikleri genellikle fiziksel özelliklerini etkilediği için, çok kristalli elektrotların morfolojik özelliklerini anlamak ve kontrol edebilmek son ürünün verimini arttırmada büyük önem taşır. Bu nedenle, HED ve parçacık büyümesini etkileyen moleküllerin sinerjisiyle çeşitli şekilde ZnO yapıların hazırlanması da tartışılmıştır. Başlangıç çözeltisi içerisindeki $[\text{MnCl}_2]$ ayarlanarak, ZnO çubukların çaplarının ayarlanabilir olduğu gösterilmiştir. Başlangıç çözeltisi içerisindeki $[\text{Cd}(\text{CH}_3\text{COO})_2/\text{Zn}(\text{II})]$ oranı ayarlanarak, HED ile tek adımda hiyerarşik ZnO mimariler elde edilmiştir. HED ile ZnO matris üzerinde yoğun olarak kobalt içeren küreler büyütülerek heterojen ZnO-Co nano-parçacıklar oluşturulmuştur. Faz ayrımının derecesinin, çözelti içerisindeki Co(II) miktarı ile kontrol edilebildiği gözlenmiştir.

Elektrokimyasal sentez yöntemi, ZnO filmleri CdS ve Ag_2S ile kaplamak için hızlı ve ucuz bir alternatif olarak çalışılmıştır. CdS ile kaplı filmlerin foto-elektrokimyasal verimleri görünür

ışığı soğuran malzeme arttıkça arttığından, CdS kaplama süresi ile arttığı gözlenmiştir. Kaplama süresi arttırıldıkça bir noktadan sonra elde edilen foto-akım azalmıştır. Mn_CdS/ZnO ile 1,42 mA/cm⁻² akım yoğunluğu, -1,39 V potansiyel ve toplam % 0,81 güneş-elektrik enerji çevirme verimi elde edilmiştir. Ag₂S/ZnO foto-elektrodları çok daha geniş bir aralıkta daha yüksek ışık soğurma kabiliyeti sergilemiştir. Yine de büyük olasılıkla kaplama sırasında ZnO çubukların yapıları bozulduğu için, güneş-elektrik enerji dönüştürme verimleri düşüktür. Bunların yanı sıra daha verimli güneş pilleri geliştirmek adına elektrokimyasal sentez ile üretilmiş CdS-ZnS tampon katmanların foto-elektrokimyasal özellikleri incelenmiştir. En yüksek performans gösteren film ile 1,31 mA/cm² akım yoğunluğu, -0,99 V potansiyel ve toplam %0,6 güneş-elektrik enerji çevirme verimi elde edilmiştir

Tezin ikinci kısmı HED ile hazırlanmış α -Fe₂O₃ filmlerin fiziksel ve foto-elektrokimyasal özelliklerinin incelenmesine ve HED ve parçacık büyümesini etkileyen moleküllerin sinerjisiyle çeşitli büyüklük ve şekillerde α -Fe₂O₃ sentezine ayrılmıştır. Literatürde rapor edilen elektrokimyasal sentezlerden farklı olarak, HED ile ısıtılma işlemi gerek kalmadan kristalin α -Fe₂O₃ fazı elde edilebildiği gözlenmiştir. Foto-elektrokimya testleri, HED ile hazırlanan filmlerin daha yüksek performans verdiğini göstermiştir. 0,05 M FeCl₂ ve 0,1 M NaCH₃COOH içeren çözeltiden, HED ile hazırlanan film 0,1 M NaOH içinde, 1,23 V potansiyelde (vs NHE) 23,6 μ A/cm² akım yoğunluğu üretmiştir ve foto-akım üretimine 0,96 V'da başlamıştır. Bunların yanı sıra, HED çözeltisine değişik miktarlarda CH₃COO⁻, Ce³⁺ ve F⁻ eklenerek; solucan benzeri, küresel, rombohedral, plaka ve en-boy oranı kontrol edilebilen kare prizma şeklinde α -Fe₂O₃ parçacıkları elde edilmiştir.

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NOMENCLATURE

TW	Terawatts
CIGS	Copper indium gallium (di)selenide
DSSCs	Dye-sensitized solar cells
QDSSCs	Quantum dot sensitized solar cells
NREL	National Renewable Energy Laboratory of US Department of Energy
PV	Photovoltaic
PCE	Power conversion efficiency
Poly-Si	Poly-crystalline Silicon cells
Sc-Si	Single-crystal Silicon cells
a-Si	Amorphous silicon
XSCs	Excitonic solar cells
PEC	Photo-electrochemical cell
UV	Ultraviolet
IR	Infrared
AM1.5G	Reference solar spectral irradiance at Air Mass 1.5, global
I-V	Current-voltage
η	Overall solar-to electrical energy conversion efficiency
J_{sc}	Short-circuit photocurrent density
V_{oc}	Open-circuit photovoltage
FF	Fill factor of the cell
P_{in}	Incident light power

P_{max}	Maximum power output of the cell
TCO	Transparent conducting oxide
FTO	Fluorine-doped tin oxide
ITO	Indium-doped tin oxide
CB	Conduction band
VB	Valance band
E_g	Band gap energy
LUMO	Lowest unoccupied molecular orbital
HOMO	Highest occupied molecular orbital
QD	Quantum dots
eV	Electron-volt
e^-	Electron
h^+	Hole
NR	Nanorods
XRD	X-Ray Diffraction
PL	Photoluminescence
NBE	Near-band edge
DLE	deep-level emission
NR	Nanorod
HED	Hydrothermal-electrochemical deposition
CBD	Chemical bath deposition
SILAR	Successive ionic layer adsorption and reaction
HER	Hydrogen-evolution reaction
OER	Oxygen-evolution reaction

E°	Standard Nernst potential
E_F	Fermi energy
E_{redox}	Redox potential
E_C	Conduction band energy
E_V	Valence band energy
MOCVD	Metal organic chemical vapor deposition
ALD	Atomic layer deposition

General Aim, Scope and Overview of the Study

Today, still fossil fuels are being used to meet majority of all the world's energy needs with undesirable consequences. Consuming fossil fuels invites health risks and global warming due to production of CO, CO₂, NO_x, and SO_x which increase green house gas concentration and are responsible for air pollution.¹ In addition to environmental problems, the facts that fuel reserves are not distributed equally throughout the world and they will extinct threaten world peace due to political and military actions taken to own the rights to use oil sources. About 13 terawatts (TW) of energy is currently needed to sustain the life style of 6.5 billion people worldwide.² Taking global population growth and energy consumption rate into consideration and assuming established trends will continue, an energy demand of 30 TW is predicted by 2050 which would result in 900 to 1000 parts per billion CO₂ emission (by volume).² Hence, one of the biggest global problems today's world is up against to is to find economically advantageous, clean, renewable energy sources.

Sustainable, renewable energy source solution is also an eco-friendly and peaceful option that would meet the needs of today without triggering catastrophic changes in Earth's climate since energy will be provided with zero or almost zero emissions of both air pollutants and greenhouse gases. In addition, diversification of energy supplies would lead to increase in economical and political stability by solving local energy and water supply problems. Many more countries will become more independent with increased standard of living since they could supply their own renewable energy instead of having to import fossil fuels which would also increase level of employment. Hence, sustainable development in remote regions would be ensured and migration to urban areas might be decreased with more job opportunities in the rural areas by developing renewable energy projects in remote-rural regions.³

Hence, research on carbon-free, alternative sustainable energy sources, such as solar energy, wind energy, geothermal power, hydro-power, and biomass has become mandatory. Renewable energy sources supply 15-to-20 % of world's total energy demand by 2001.³ The major contribution is in the form of biomass mostly used for cooking and heating especially in developing countries in Africa, Asia and Latin America. Biomass is followed by hydropower which supplies around 20 % of global electricity demand. Solar energy, wind energy, modern bio-energy, geothermal energy, and small hydropower are considered as new renewable energy sources and they currently contribute about two percent. It is predicted that the present figure of ~20 percent might increase to more than 50 percent with the right policies in the second half of 21st century.³

Solar energy, in fact, has many advantages over the other renewable energy sources. Primary and largest clean energy source is the sun. Out of 1.7×10^5 TW solar energy striking earth's surface (10,000 times more than the global demand), global potential that can be used is estimated to be about 600 TW about 40 times of the world's yearly energy demand.⁴ No other renewable energy sources have such a capacity, so they can only serve as auxiliary energy sources in world's future. In addition, solar panels are easy to install with a wide range of scale from single home use to power plants and require very little maintenance with longer life-time of the parts and fewer replacements. The major drawback of solar energy is the still-high cost to manufacture the solar panel (both material and production costs). As a result, electricity is generated at a higher cost compared to fossil fuel and other renewable energy sources. Conversion of this tremendous amount of energy to electrical power with high efficiency is a critical issue before today's scientists and engineers.

Existing solar cells can be grouped under two main classes; solar cells based on semiconductor *p-n* junctions (silicon based, copper indium gallium (di)selenide (CIGS) and CdTe) and excitonic solar cells (organic, hybrid, dye-sensitized (DSSCs) and quantum-dot synthesized (QDSSCs) solar cells). DSSCs are composed of porous thin film wide band-gap semiconductor oxide photoanodes modified by dye molecules. After an initial breakthrough of 7 % efficiency reported by O'Regan and Gratzel in 1991⁵, DSSCs have received considerable attraction. The interest is ever-increasing since DSSCs offer comparable efficiency with easier and cheaper fabrication processes. The key to the breakthrough in 1991 was use of mesoporous TiO₂. Since then, several metal oxides were investigated to serve as the photoanode including ZnO, Fe₂O₃, ZrO₂, Nb₂O₅, Al₂O₃, CeO₂, Bi₂O₃, WO₃, PbO₂, V₂O₅, CuO, CdO,

MnO₂, and SrO.^{6,7} Among these oxides TiO₂, Nb₂O₅, and ZnO have been most popular choices. Although TiO₂ takes the lead, ZnO is the runner up due to the ease of synthesizing highly crystalline ZnO in different structures and its high electron mobility.

Another main challenge in clean, sustainable energy initiative is to store, transfer and distribute large amounts of energy. Hydrogen is one of the promising energy carriers of future due to its high energy content and environmentally friendly combustion. Hydrogen can be obtained by electrolysis of water and upon combustion it returns water again without any harmful byproducts. Solar energy can also be used to produce Hydrogen, future fuel. After the first report of Fujishima and Honda where they showed it was possible to split water by shining light on semiconductor photoanode, the initial studies on photoelectrochemical H₂ production were conducted with TiO₂.⁸ Besides TiO₂ and ZnO (as stated above), α -Fe₂O₃ has become popular in photoelectrochemical studies due to its ideal band gap of 2.0-2.2 eV, abundance, non-toxicity and stability.⁹

The research summarized in this doctoral dissertation includes synthesis of doped and undoped zinc oxide (Part I) for photovoltaic applications and iron oxide (Part II) films for solar hydrogen production via electrochemical deposition. The focus is on combination of electrochemical deposition technique with hydrothermal methods. Effect of this new technique on production and final physical properties of metal oxide films is analyzed in detail.

PART I. PREPARATION OF ZINC OXIDE AND METAL-DOPED ZNO THIN FILMS

by ELECTRODEPOSITION

Chapter 1 Introduction

1.1 Solar Cells

1.1.1 Solar Cells: Brief History

Photovoltaic (PV) devices generate electricity directly from the sun light by taking advantage of the built-in asymmetry created by the contact of two materials of different conduction mechanism that ensures charge separation at the interface. Depending on the underlying technology, PV cells are usually categorized as first-, second-, and third-generation devices. Single- (sc-Si) or poly-crystalline (poly-Si) p–n junction silicon cells are known as the first-generation solar cells which profits from the experience and material availability resulting from the semiconductor industry. They are also known as inorganic solar cells (ISC), on which incident light results in the direct formation of free electron–hole pairs in the bulk of the material and the direct production of charge carriers.¹⁰ They are the most common PV converters that dominate the market (85 % market share)¹¹ with power conversion efficiencies (PCE) up to 20 (poly-Si)-24 % (single-Si) which is close to the theoretical limit¹² (Figure 1.1). These first generation devices suffer from high cost of manufacturing and installation, high material cost, high purity requirements for silicon crystals, high fabrication temperatures and negative environmental impact of the processing technologies.¹¹ Hence, the research is focused on developing PV cells with alternative materials at a lower cost with considerable efficiency rather than enhancement of PCE.

The second generation solar cells are also known as thin film solar cells and include amorphous silicon (a-Si), micro or nano-crystalline silicon or chalcogenide (group VI) semiconductors such as CdTe, CdS, copper indium gallium (di) selenide (CIGS). Compared to production cost of high quality, single crystalline silicon wafers, decreased material cost and suitability of cheaper substrates such as glass offers an economical advantage for thin film solar cells. They are also commercialized with record efficiencies ranging between 12-20 %.¹³ Although the cost is significantly reduced compared to sc-Si (1 dollar/watt), high synthesis and processing temperatures, vacuum processing and lithography requirements still hold thin film

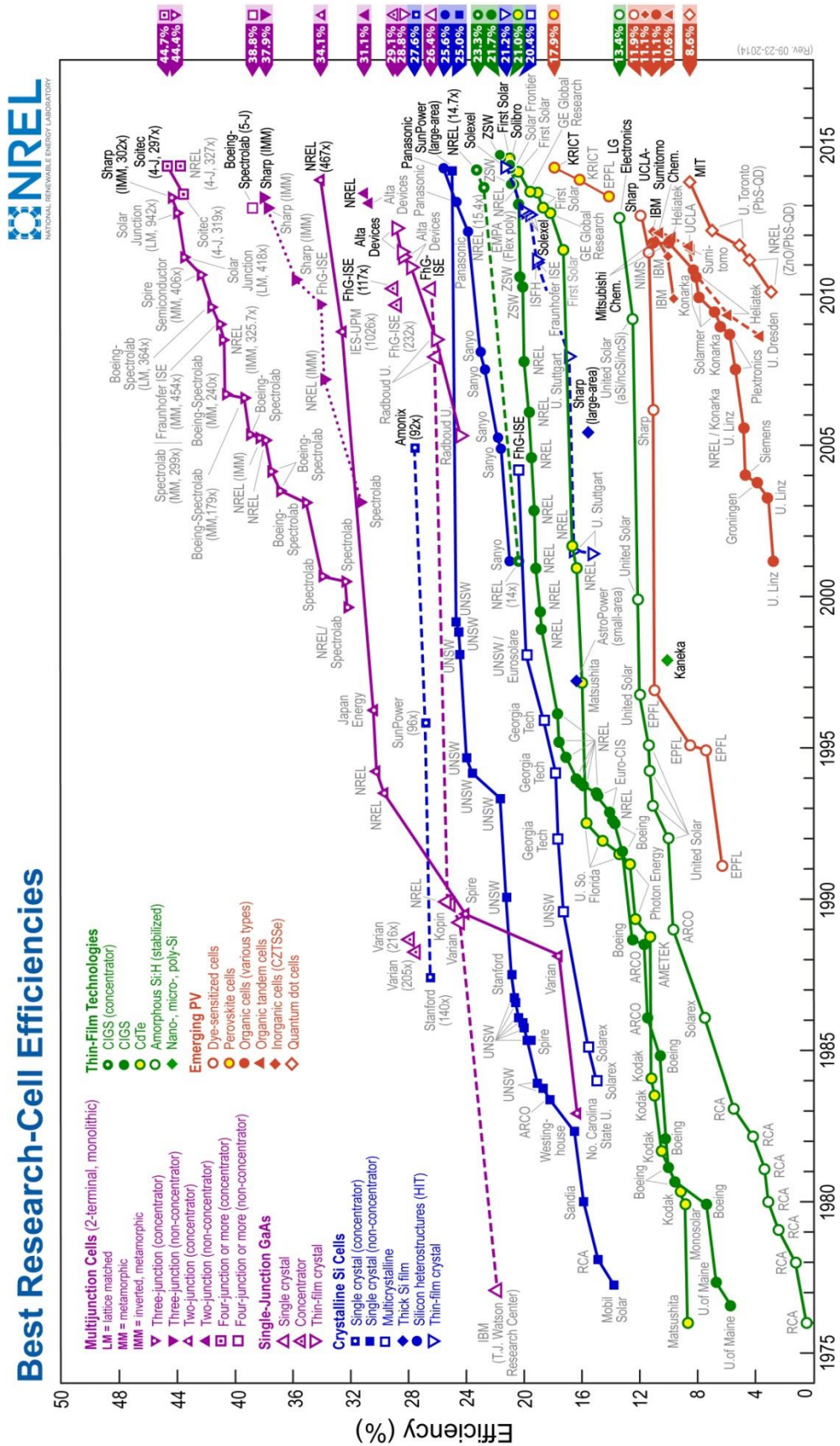


Figure 1.1 Best research cell efficiency records (NREL 2014).

solar cell prices higher than cost of fossil fuels and other renewable energy sources. In addition, despite high efficiencies in the laboratory conditions, commercial-sized cells exhibit one-half to two-thirds of those efficiencies.¹³

PV production cost per square meter with solar cell efficiency and the cost per unit power for the three generations of the technology is shown in Figure 1.2. First-generation silicon wafer technology is characterized by high production costs with average efficiencies of around 20-24 %. Thin film technology decreased the production costs with moderate efficiencies of around 15-20 %. To enhance poor performance of thin film cells, third generation technologies emerged which aim 30-60 % PCEs with low material costs. Both first and second generation solar cells are based on single junction devices. Third generation solar cells have the potential to exceed the theoretical solar conversion efficiency limit that was calculated for Si single junction solar cells by Shockley and Queisser as 31 % under 1 sun illumination and 40.8 % under maximal concentration of sunlight in 1961.¹⁴ Shockley and Queisser limit is based on the assumption that absorption of an individual photon results in the formation of a single electron-hole pair and that all photon energy in excess of the energy gap is lost as heat. The Carnot limit of sun-light-to electricity conversion is 95 %, and the gap between these limits suggests room for research efforts to achieve efficiencies above 31 %. Now the focus is on tandem or stacked multilayers of inorganics based on III-V materials such as GaAs/Ge/GaInP₂ (32 % efficiency), and the excitonic solar cells (XSCs); dye-sensitized solar cells (DSSCs, 11 % efficiency), quantum dot-sensitized solar cells (QDSSCs, 4 % efficiency), and organic solar cells that have the potential to deliver high efficiencies at economically viable costs.^{6,11} The aim is less than 1 dollar/Watt. In XSCs, absorption of photons produces an exciton, a tightly bound electron-hole pair which is dissociated at the materials interface; hence, interfacial processes become extremely important.¹⁰ In DSSCs, a wide band gap metal oxide semiconductor is in contact with a dye; and in QDSSCs, semiconductor nanocrystals with sizes less than their exciton Bohr radius is used to harvest light.

The prototype of this family of devices is DSSC/QDSSC in which conventional solid-solid junction is replaced with solid-liquid junction which forms a photoelectrochemical cell (PEC). DSSCs work without the need of a built-in electrical field, without a strict control of the purity of materials as opposed to the ISCs. DSSC/QDSSC consists of a bulk hetero-junction made by the semiconductor and the light-harvesting dye/material, and an electrochemical junction between the photo-electrode and the redox electrolyte. Record efficiencies up to 12 % for small cells, 1000 h stability at 80°C with 8-9 % efficiency enduring has been reported.⁴

DSSCs also exhibits relatively better performance under diffuse light conditions due to rough surfaces and at high temperatures and offer many options in shape, color, transparency in solar cell designs.⁴

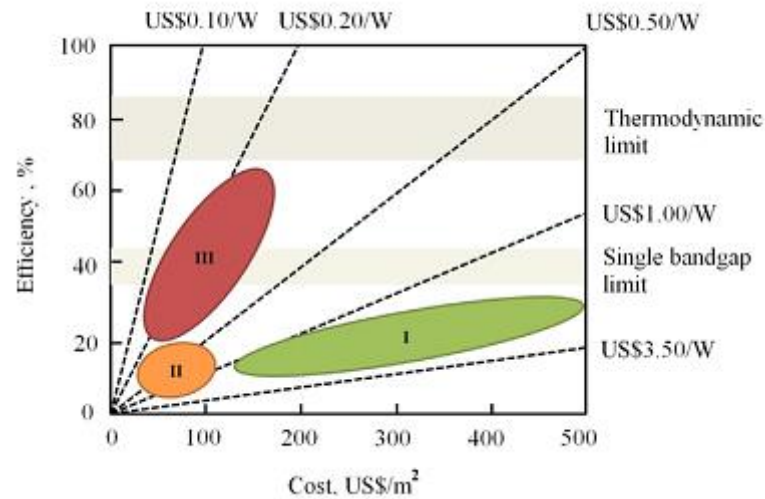


Figure 1.2 Efficiency and cost projection for first (I), second (II), and third generation (III) photovoltaic technology.¹¹

The cost-limiting factor of DSSC is the conducting glass plates that are used to sandwich the dye and the metal oxide; Ti thin films are used in commercial products.⁶ The DSSCs are promising devices as a cost-effective technology for electricity production and have the potential to compete with other power technologies even though the optimum solution will depend on many factors such as the restriction of the application, location, local weather, economics and politics.

1.1.2 Solar Cell Characteristics

The sun emits light in ultraviolet (UV), visible and infrared (IR) regions of electromagnetic radiation. The solar energy distribution peaks in the visible region, as the spectrum follows the black body radiation from a 5760 K source which is surface temperature of the Sun. The irradiance falling on earth's atmosphere varies due to the changes in sun-earth distance over a year (i.e., depends on position of sun) and irradiance falling on to earth's surface is influenced by location, atmospheric conditions including cloud cover, aerosol content, and ozone layer condition, and time of day, earth/sun distance, solar rotation and

atmospheric absorption and scattering. For example, ozone layer filters UV light, and water and CO₂ in air absorb mainly in the infrared region; water absorbs at 900, 1100, 1400, and 1900 nm and CO₂ at 1800 and 2600 nm. Hence, solar spectrum and the incident angle from which light shines on a surface vary. To be able to establish a standard condition that would allow theoretical evaluation of the effects of solar radiation and as a basis for simulator design, standard solar spectrum has been developed.

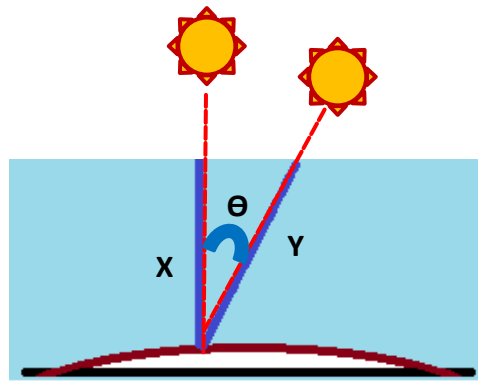


Figure 1.3 The air mass represents the proportion of atmosphere that the light must travel before striking the Earth relative to its direct path length, and is equal to Y/X .

The shortest possible path length which takes through the atmosphere with maximum radiation on earth's surface in a clear sky (i.e., when the sun is directly overhead) is the Air Mass (AM) and defined as $AM = 1/\cos\theta$, where θ is the angle of elevation of the sun (zenith angle). The standard solar spectrum used for efficiency measurements of solar cells is determined to be AM 1.5 G (global), with $\theta = 48.2$ and with a turbidity of 0.27 is by the American Society for Testing and Materials. This spectrum is normalized so that the integrated irradiance (the amount of radiant energy received from the sun per unit area per unit time) is 1000 W/m^2 . The AM 1.5 G solar radiation spectrum as the irradiance of the sun as a function of wavelength is shown in Figure 1.4.

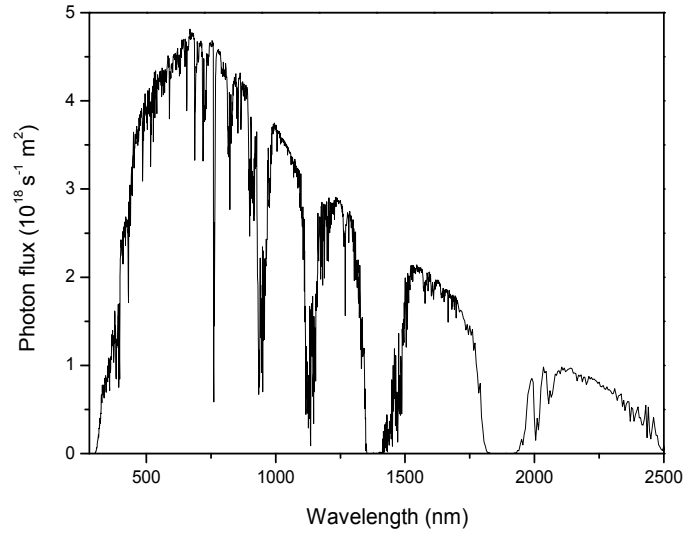


Figure 1.4 Reference solar spectral irradiance at Air Mass 1.5, global.¹⁵

The efficiency is the most common parameter to characterize and compare solar cell performances. The overall solar-to-electrical energy conversion efficiency, η , for a solar cell depends on the short-circuit photocurrent density (J_{sc}), the open-circuit photovoltage (V_{oc}), the fill factor of the cell (FF), and the incident light power (P_{in}). The efficiency of a solar cell is determined as the fraction of incident power which is converted to electricity and is defined as:

$$\eta = \frac{P_{max}}{P_{in}}, \quad P_{max} = J_{sc} \times V_{oc} \times FF \quad (Eqn 1.1).$$

The fill factor determines the ideality of the cell and defined by the ratio of the maximum power (P_{max}) of the solar cell per unit area divided by the product of J_{sc} and V_{oc} , where the maximum power is the product of current and voltage at the maximum power output of the cell;

$$FF = \frac{P_{max}}{J_{sc} \times V_{oc}}, \quad P_{max} = J_{max} \times V_{max} \quad (Eqn 1.2).$$

The maximum power point is located at the “knee” of the current-voltage (I-V) curve and shown in Figure 1.5. FF values range between 0 and less than 1; $FF=1$ implies an outer rectangular area for the I-V curve.

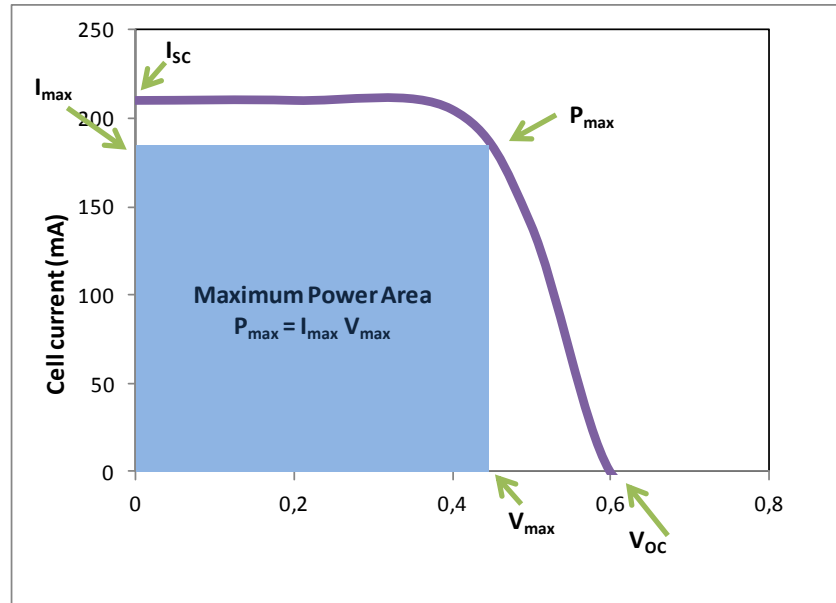


Figure 1.5 Typical IV curve for a PV cell.

1.1.3 Dye Sensitized Solar Cells and Operational Principles

Dye-sensitized solar cells are basically composed of nanostructured wide band gap semiconductor films photosensitized with a dye. In 1991, M. Grätzel and B. O'Regan reported a device made of sensitized nanoporous TiO_2 with a conversion efficiency of 7.1%⁵ which opened an ever-growing research field with many groups working on the improvement of the efficiency and the stability of DSSCs. The pioneering work by the Grätzel group reported a device composed of a layer of titanium dioxide nanoparticles sensitized by a ruthenium-complex dye with the I^-/I_3^- redox couple in an organic solvent, which acts as the redox mediator. Grätzel and O'Regan found a successful combination. The key to the breakthrough in 1991 was use of mesoporous TiO_2 . Mesoporous structure provides a surface area for dye adsorption more than a thousand times larger than a flat electrode of the same geometric area.¹⁶

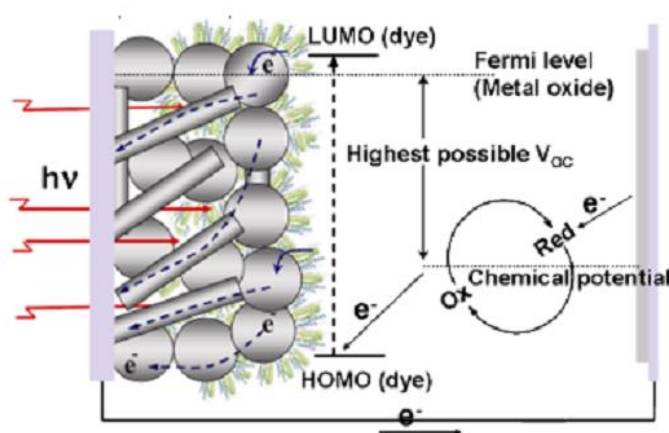


Figure 1.6 Basic DSSC scheme.⁶

Mesoporous layer of semiconductor oxide nanoparticles, which are sintered together to establish a good electric contact on a transparent conducting oxide (TCO) layer forms the backbone of the DSSCs. The film thickness is usually around 10 μm and the nanoparticles are around 25 nm in diameter.⁴ Other components include light harvesting dye, a counter electrode and a redox electrolyte (Figure 1.6). Dye of high extinction coefficient is absorbed on the surface of semiconductor metal oxide and mostly used electrolyte to transfer electrons between the photoanode and counter electrode is I^-/I_3^- couple. The most commonly used substrates are fluorine-doped tin oxide (FTO) or indium-doped tin oxide (ITO) coated glass which allow light to enter in the cell.

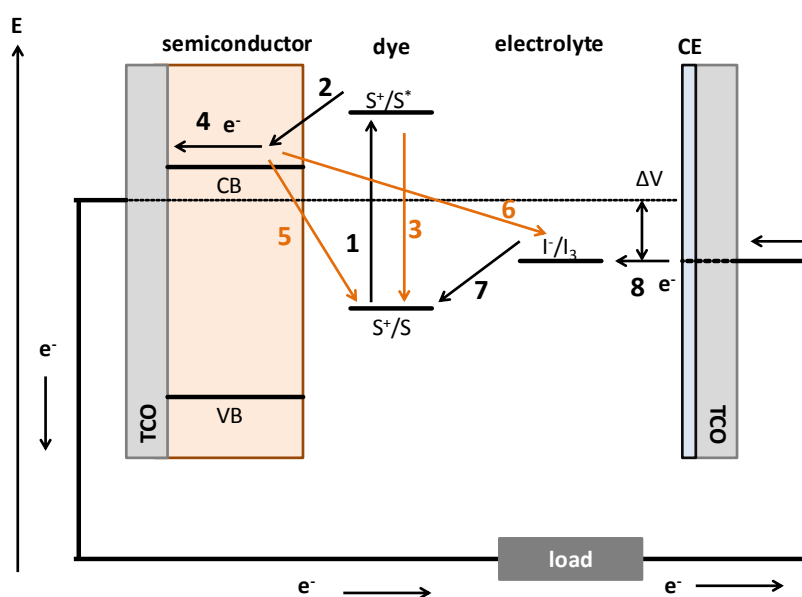


Figure 1.7 Electron transfer processes taking place in the photoconversion by a DSSC. Energy bar is not to scale.

Dye-sensitized solar cells are photoelectrochemical devices where several electron transfer processes take place competitively. Dye-sensitized solar cells are photoregenerative devices where optical absorption and charge-generation are separate functions. A scheme of basic operation principles is given in Figure 1.7. Upon light absorption, the generated photoexcited electron (Reaction 1) leaves the dye in its oxidized state and is injected into the conduction band (CB) of the oxide (Reaction 2). The regeneration of the dye occurs through electron transfer from the electrolyte (Reaction 7). The photogenerated electron travels through the mesoporous oxide film towards the external contact (Reaction 4). The extracted electron can then perform work in the external circuit and return to the counter electrode. Oxidation of I^- during regeneration of the dye, results in formation of I_3^- ions which diffuse a short distance ($<50\text{ }\mu\text{m}$) through the electrolyte to the counter electrode. The counter electrode is usually coated with a thin layer of platinum catalyst, where the regenerative cycle is completed by electron transfer which reduces I_3^- to I^- (Reaction 8).

There are competing loss reactions. Relaxation of the excited dye (Reaction 3) might take place even before electron injection depending on the excited state lifetime. The fate of the injected electrons also depend on the rate of the competing process; recombination with either oxidized dyes (Reaction 5) or acceptors in the electrolyte (Reaction 6) can take place. The back-electron-transfer reaction from the conduction band to the oxidized sensitizer occurs on a microsecond to millisecond time scale depending on electron concentration in the semiconductor and thus the light intensity.⁴ The major loss stems from the recombination of the injected electrons with the oxidized redox mediator. In principle, electron transfer to the acceptors in the electrolyte can occur either at the metal oxide/electrolyte interface or at areas of the anode that are exposed to the electrolyte. Hence, in an effort to prevent loss with this pathway, a compact blocking layer of oxide deposited on the anode is used by several groups.^{4,6,17}

The timescale of the different processes is the key point for obtaining high energy conversion efficiency. Light intensity, light absorption, injection efficiency, and regeneration of oxidized dye determine the value of J_{sc} . Both the Fermi level of the semiconductor and the level of dark current influence V_{oc} . The maximum value of the open circuit photovoltage is determined by the difference between Fermi level of the semiconductor and the redox potential of the electrolyte.

All the components of a DSSC are tunable. The work in this thesis is based on alternative materials to this standard configuration with the basic operation principles described. The characteristic of each standard component as well as process are described in the following sections.

1.1.4 Material Requirements of Dye Sensitized Solar Cells

1.1.4.1 Metal Oxide Electrode

The semiconductor oxide is the physical support of the sensitizer molecules and the electron conductor in a dye-sensitized solar cell. Electron injection to the CB of the metal oxide (Reaction 2) is three orders of magnitude faster than radiative recombination (Reaction 3) and electron back transfer (Reaction 6) is two orders of magnitude faster than interfacial charge recombination (Reaction 5).⁶ Hence, it is assumed that effect of radiative recombination and interfacial electron transfer to overall solar-to-power conversion efficiency, η , is negligible. Among the rest of the processes reaction 1, 4 and 7 are controlled by the dye, photoelectrode and the electrolyte, respectively. Reactions 2 and 6 are processes at the dye-photoelectrode and photoelectrode–electrolyte interfaces, respectively. Hence it can be concluded that the metal oxide plays a central role on the determination of final energy conversion efficiency of the DSSC since it participates in more processes than the electrolyte or the dye do and it forms a major part of the study to investigate synthesis of photoelectrodes with enhanced properties.

The exciton generated at the dye is separated into free carriers at the dye–photoelectrode interface. For this charge separation to be energetically favored, the conduction band of the metal oxide must be at lower energies than the lowest unoccupied molecular orbital (LUMO) of the dye. Many metal oxide systems have been tested, such as TiO_2 , ZnO , SnO_2 , Nb_2O_5 , Fe_2O_3 , ZrO_2 , Al_2O_3 , CeO_2 , SrTiO_3 and Zn_2SnO_4 .⁴ TiO_2 , ZnO and Nb_2O_5 are the best candidates in view in terms of their electronic band structure. When the electronic configuration and recombination probability are taken into consideration, TiO_2 and ZnO are the best choice as photoelectrodes among 3d transition metal oxides.⁶ Titanium dioxide is a very versatile, non-toxic, cheap and chemically stable material that is widely used in DSSCs so far with highest efficiency record. Hexagonal ZnO has been the second choice and studied widely as a replacement for the TiO_2 electrodes since it exhibits superior transport properties.⁶ Single-crystalline ZnO presents much higher electron mobility than anatase TiO_2 , which should

favor electron conduction. In addition, lower trap density and longer carrier lifetime is reported for ZnO. In addition, the ease to synthesize highly crystalline ZnO with different morphologies, such as nanoparticles, nanowires, nanorods, nanotubes, tetrapods, nanoflowers, nanosheets, and branched nanostructure adds another charm as a photoelectrode material. The synthesis ZnO materials of various shape and sizes and the investigation of the effect of different morphological features on physical and photoelectrochemical properties are explored in this thesis. Detailed information on ZnO properties and growth techniques will be discussed in the following sections.

1.1.4.2 Light Harvesting: Dyes and Quantum Dot Sensitization

The semiconductor oxides used in DSSCs are wide band gap materials, which do not absorb in the visible region. The function of harvesting the solar light is carried out by the sensitizer molecules attached to metal oxide surface. The absorption spectrum of the optimum dye for high efficiency DSSCs should cover the whole visible region and even part of the near-infrared (ideally, a threshold of 950 nm should be harvested to increase the efficiency above 15 %). In addition, strong attachment of the dye to the semiconductor oxide is important so the dye should possess suitable anchoring groups.

The lifetime of the excited state of the dye is crucial to the overall performance. The key rate requirement at this step is that injection must be at least 100 times faster than the relaxation of the dye from its excited state which is even several orders of magnitude for standard cells with ruthenium-complex dyes.¹⁶ In addition, the excited state level of the photosensitizer should be higher in energy than the CB edge of n-type semiconductor for efficient electron transfer process. The oxidized state level of the photosensitizer must be more positive than the redox potential of electrolyte for favorable regeneration of the dye. The regeneration of the dye by the electron donor, usually I^- , is in the microsecond time domain. The lifetime of the oxidized dye must be 100 times faster if the regeneration time is 1 μ s, for a turnover number above 10, which is required for a DSSC lifetime of 20 years in outdoor conditions.⁴ This task is best fulfilled again by ruthenium- complexes.

Ruthenium dyes are not suitable for ZnO due to its low stability in acidic conditions. The electron injection efficiency decreases because of the generated Zn/dye aggregates.⁶ Furthermore, despite of the extensive efforts to enhance the efficiency of DSSCs, 12% is the

record efficiency after the first breakthrough.¹¹ Therefore, inorganic semiconductor nanocrystals and size quantized semiconductors, quantum dots (QDs) are proposed to serve as dye replacements for next-generation sensitizers. By controlling the size of the QDs, the band gap can be tuned which allows utilization of energy from visible to IR regions of solar spectrum. In addition to size tunability, properties like multiple exciton generation, high molar extinction coefficients, sufficient photostability make QDs attractive candidates for sensitization in XSCs. Multiple-exciton generation is reported to contribute to the higher power conversion efficiency of QDSSCs than that of DSSCs.¹¹

The QDs employed in QDSSCs as sensitizers include PbS¹⁸, Ag₂S¹⁹, CdS²⁰, CdSe²¹, CdS/CdSe²², CdS/CdSe/PbS²³, CdTe-CdTeS_{1-x}²⁴, ZnS and CuInS₂¹¹. CdS and CdSe QDs have been considered as adequate materials as stable materials in QDSSCs.¹¹

CdS and Ag₂S semiconductors are chosen as sensitizers in the work described in this dissertation. The charge injection from narrow band gap of CdS (2.4 eV) into wide-band-gap ZnO (3.3 eV) leads to efficient and longer charge separation by decreasing the recombination probability of electron-hole pairs (Figure 1.8).²⁵ The band gap of Ag₂S ($E_g \sim 1.1$ eV¹⁹) suggests that wider absorbance range in the solar spectrum making Ag₂S a promising sensitizer for high efficiency systems.

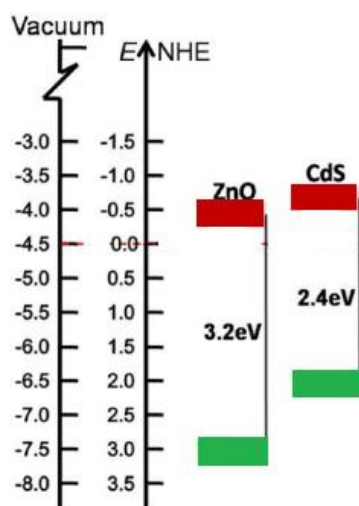


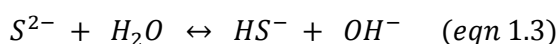
Figure 1.8 Band gap positions of ZnO-CdS.²⁶

1.1.4.3 Electrolyte

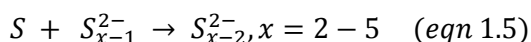
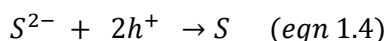
The electrolyte is a key component in a dye solar cell, which plays different roles in the functioning of the device. First criterion for selection of the electrolyte is that the oxidized state level of the photosensitizer must be more positive than the redox potential of electrolyte for favorable regeneration of the dye. Although successful results were obtained with various redox coupler such as $\text{SCN}^-/(\text{SCN})_3$, $\text{SeCN}^-/(\text{SeCN})_3$ and organic systems based on TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy) and TDP (N,N'-di-m-tolyl-N,N'-diphenylbenzidine); the most frequently used and the most successful electrolyte up to now in a DSSC is composed of the redox couple the I^-/I_3^- in an organic solvent. The inverse of the rate of electron back transfer (reaction 6) can be referred to as the electron lifetime. The success of the I^-/I_3^- couple is explained by the long electron lifetime (1-20 ms under one sun light intensity) compared with other redox systems used in DSSC.⁴

The photovoltage and hence ultimately the efficiency of the cell depends to a great extent on the redox couple, which sets the electrochemical potential at the counter electrode. Thus, one of the techniques to enhance overall solar-power conversion efficiency, η , is to increase the photovoltage by replacing the conventionally used I^-/I_3^- redox couple with a system having a more positive redox potential. The emergence of QDSSCs also lead scientists to search for different hole transport medium since, most QDs suffer from photodegradation in the presence of I^-/I_3^- redox couple.²⁷ The sulfide/polysulfide redox couple has shown to be effective in scavenging the photogenerated holes and hence regenerating the semiconductor became a popular choice in chalcogenide sensitized solar cells.²⁸

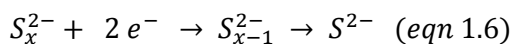
In aqueous sulfide solutions, predominant species is the HS^- according to the equilibrium;



The pH of a 0.1 M Na_2S solution is around 13 which suggests, almost complete shift of the equilibrium (1.3) to the right. Although HS^- is the predominant species, dissolved sulfide will be referred as S^{2-} throughout the text. Upon photon absorption, electron-hole (e^- - h^+) pairs are created in the QDs as they progress from the lower to the excited state. Photoexcited electrons are injected into metal oxide as described above which results in the oxidation of the photosensitizer. QDs are regenerated through electron donation from S^{2-} , which in turn is oxidized;



The redox couple is regenerated at the counter electrode, completing the circuit;



The initial concentration of the sulfide electrolyte is shown to significantly affect the performance of QDSSCs.^{22,29} High concentration of Na₂S alters the kinetics of the polysulfide oxidation reactions shown in Eqn 1.4 and 1.5 are faster at the photoelectrode/ electrolyte interface which results in faster hole recovery. However, at Na₂S concentrations higher than 0.2 M, efficiency of the cell decreases again due to photocorrosion. The enhancement in the efficiency is explained by the increase of V_{oc} due to the negative change of the redox potential of the sulfur–polysulfide electrolyte with increasing the initial sulfur concentration.

1.1.4.4 Counter Electrode

Counter electrode is the place where photo-regenerative cycle is completed by electron transfer to the electrolyte coming from the external circuit. The counter electrode for common DSSCs with iodide/triiodide electrolytes is composed of a thin catalytic layer of platinum on a conducting glass substrate. However, platinum is not a convenient choice as a counter electrode in QDSSCs with CdS- and CdSe-based photoanodes because it inhibits the charge transfer to polysulfide species due to sulfur adsorption on the catalytic surface.^{22,30} Therefore, metal sulfides such as CoS, NiS, PbS and CuS have become promising candidates as electrocatalysts for polysulfide redox reactions in photoelectrochemical cells (PECs).^{22,27,31} CdSe QD-sensitized photoelectrode exhibited total light to electric power conversion efficiencies of 0.8 % and 3.0 % with Pt and PbS counter electrode, respectively.²⁷ Efficiency as high as 3.4% was obtained with CdS/CdSe QDSSC incorporating a CoS counter electrode.²²

1.2 Material of Interest : Zinc Oxide (ZnO)

In the last few decades ZnO regained its popularity among scientists, especially in the materials research and device fabrication technologies. Wide band gap (3.37 eV)¹ of ZnO together with its large exciton binding energy (60 meV)³³ makes it a very promising material in a wide range of application areas from sensors³⁴ to optoelectronic devices such as lasers^{35,36}, optical switches³⁷, light emitting diodes³⁸, phototransistors³⁹ and solar cells⁴⁰. Especially when size scale decreases down to nano-regime, ZnO particles attain exotic properties including high surface to volume ratio, nontoxicity, biocompatibility, chemical and photochemical stability, optical transparency, electrochemical activity, and high electron communication features^{33,41}. Its unique ability to form a variety of nanostructures such as nanowires, nanoribbons, nanobelts, nanocombs, nanospheres, nanofibers, nano-tetrapods has become one of the main advantages. Especially, ZnO in the form of nanorods (NRs) and nanorod arrays vertically arranged with respect to the substrate attracts special attention due to their potential to enhance performance of various technologically important devices, particularly solar cells. These excellent properties together with the ease of production make ZnO nanostructures a very appealing choice in the environmental and bio-industries. ZnO has much simpler crystal-growth technology, resulting in a potentially lower cost for ZnO-based devices which makes ZnO also economically appealing. In this section, basic physical properties and growth of ZnO is described.

1.2.1 Structure

ZnO is a group II-VI semiconductor that can exist in Wurtzite, zinc blende, and rocksalt structure as shown in Figure 1.9. At ambient conditions, the thermodynamically stable phase is Wurtzite. The zinc-blende ZnO structure can be stabilized only by growth on cubic substrates, and the rocksalt structure may be obtained at relatively high pressures.³³

The Wurtzite structure has a hexagonal unit cell with two lattice parameters, a and c , in the ratio of $c/a=8/3= 1.633$ and belongs to the space group of C_{6v}^4 or $P6_3mc$ (Figure 1.10). The structure is composed of two interpenetrating hexagonal-close-packed sublattices of Zn^{2+} and O^{2-} with the zinc ion surrounded by oxygen ions in the tetrahedral vacancies and vice versa. This tetrahedral coordination gives rise to a polar symmetry along the hexagonal axis, which is responsible for a number of the physical and chemical properties of ZnO, including piezoelectricity, spontaneous polarization, and surface dependent photocatalytic activity.^{42,43}

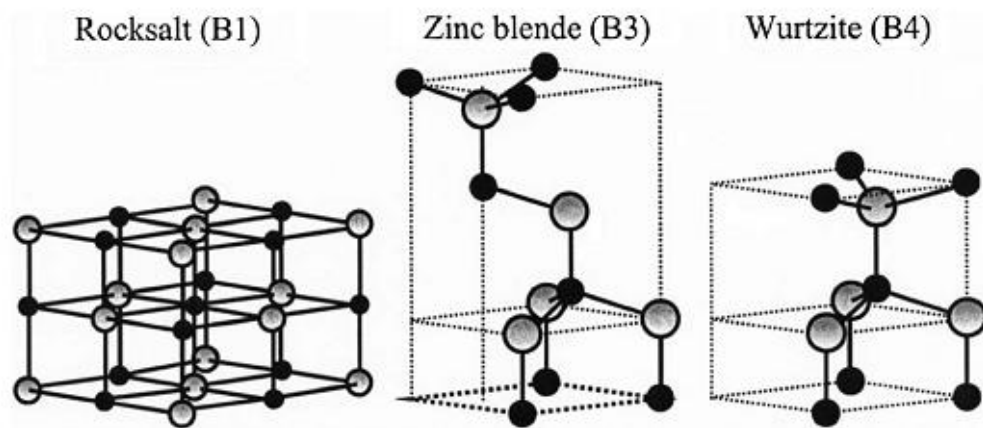


Figure 1.9 Crystal structures of ZnO shown in stick and ball configuration.³³

Oriented growth and growth of various shaped is possible due to the lack of inversion symmetry and the polarity of the c -axis which results in the Zn^{+2} terminated and O^{2-} terminated planes displaying vastly different properties. In Wurtzite ZnO, the polar plane (0001) and associated direction $\langle 0001 \rangle$ are the most commonly used surface and direction for growth. Non-polar side surfaces exhibit lower energy than the $\{0001\}$ facets.⁴⁴

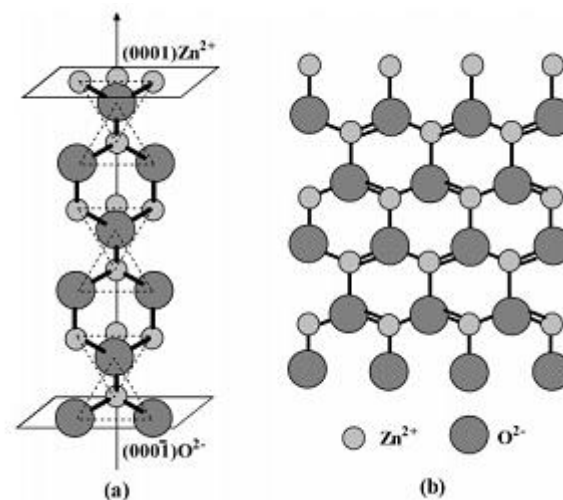


Figure 1.10 Hexagonal Wurtzite structure of ZnO a) $\langle 0001 \rangle$ direction b) $\{10\bar{1}0\}$ face.⁴⁵

Difference in the surface activities of various growth facets under given conditions is an important parameter to determine the growth habit of crystals. Macroscopically, a crystal

has different kinetic parameters for different crystal plane and, after an initial period of nucleation and incubation, a crystallite will commonly develop into a 3D object with well-defined, low index crystallographic faces. The growth of ZnO can be controlled with modifier molecules due to the difference in the surface energies of the crystallographic planes which results in selective adsorption of molecules to particular crystal faces. Hence, selectively certain faces are blocked to the access of incoming Zn-containing solution species. For example, adsorption to the (0001) face is expected to hinder growth in the [0001] direction while allowing growth in the (10 $\bar{1}$ 0) directions to continue, thereby producing larger areas of the (0001) face and a crystal with a low aspect ratio.⁴⁶

Xu *et al.* reported electrodeposition of ZnO in the form of platelets, hexagonal tapers, hexagonal rods and Rhombohedral rods by changing the compositions of various capping agents.⁴⁵ X-Ray diffraction (XRD) patterns of electrodeposited hexagonal Wurtzite ZnO of different morphologies are shown in Figure 1.11. According to the {JCPDS 01-076-0704} the peaks at scattering angles (2θ) of 31.36, 34.02, 35.85, 47.16, 56.25, 62.53, 67.63, and 68.79 correspond to the reflection from (100), (002), (101), (102), (110), (103), (200), and (112) crystal planes, respectively with (101) reflection exhibiting maximum intensity. The texture effect of the anisotropic morphology and orientation can be deduced from the relative intensities of the diffraction peaks. For highly aligned nanorod arrays (Figure 1.11d), (002) diffraction peak shows a significantly high intensity indicating that the ZnO crystallites are oriented perfectly with their *c*-axis being perpendicular to the substrate. The intensity of (100) diffraction peak is enhanced at the expense of the (002) peak for hexagonal platelet sheets (Figure 1.11b). When the particles are taper-shaped, the XRD pattern (Figure 1.11c) presents a preferential (001) orientation.

Wurtzite crystal structure of ZnO belongs to space group $^4C_{6v}$ as stated above for which Raman active zone-center optical modes with symmetries $A_1+2B_1+E_1+2E_2$ are predicted by group theory.⁴⁷ Out of these modes, A_1 and E_1 phonons are polar modes, which split into transverse-optical (TO), and longitudinal-optical (LO) phonon modes at different energies and all are both Raman and IR active modes. The nonpolar $E_2(\text{low})$ and $E_2(\text{high})$ are attributed to the vibration of zinc sublattice and oxygen motion, respectively.^{48,49} The B_1 mode on the other hand, is silent. Raman spectrum ZnO exhibit strong bands at 98 and 438 cm^{-1} which are attributed to the non-polar $E_2(\text{low})$ and $E_2(\text{high})$ vibration modes, respectively corresponding to the Wurtzite phase.^{47,50,51} $E_2(\text{high})$ mode dominates the spectrum for nanowalls, nanowires, nanosheets and the single crystal.^{51,52} A weak peak appears around 332-334 cm^{-1} that arises

from the (E_2-E_1) combination. A broad and weak E1 (TO) mode at about 410 cm^{-1} , E1 (LO) mode at $\sim 581\text{ cm}^{-1}$, A1 (TO) and A1 (LO) phonon modes at $\sim 382\text{ cm}^{-1}$ and $\sim 574\text{ cm}^{-1}$, respectively are observed for single crystal and nanowall structures.⁵¹ E1 (TO) mode is ascribed to the contribution of the polarization due to mixed oriented crystallites and absence of E1 (TO) mode is observed for c-axis-oriented ZnO nanorods.^{47,53}

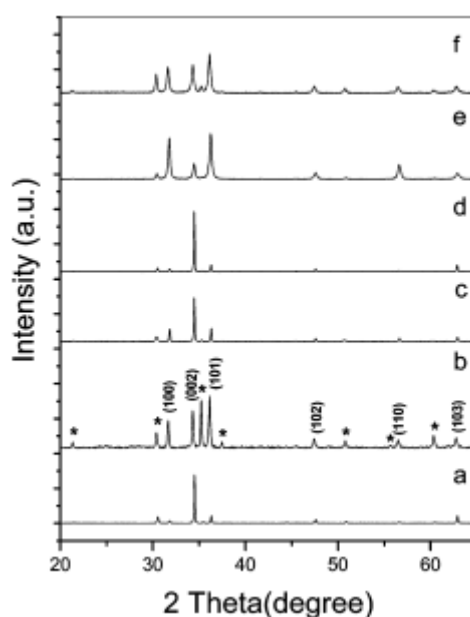


Figure 1.11 XRD patterns of the ZnO nanostructures with different morphologies a) hexagonal particles b) hexagonal platelets c) hexagonal tapers d) hexagonal rod arrays e) woven nanoneedles and f) Rhombohedral rods. An asterisk indicates the ITO substrate.⁴⁵

1.2.2 Optical Characteristics

As stated above ZnO has a large band gap of 3.2-3.4 eV. The large band gap energy of 3.4 eV corresponds to a wavelength of around 365 nm which is the absorption onset of bulk ZnO. The optical properties of ZnO are strongly influenced by crystal quality and presence of defects as well as dopants that can alter the fundamental band gap. It is possible to shift the absorbance of ZnO to visible region in an effort to increase overall device performance in DSSCs. It was shown that the band gap of the ZnO nanocrystals can be tuned in the range of 2.9-3.8 eV by the use of Cd, Mg, Mn, and Fe ions as dopants.⁵⁴ ZnO thin films that show strong absorption bands between 540 and 680 nm was obtained with Co ion doping.⁵⁵ The visible absorption resulted in exhibiting photocurrents four times the photocurrent of pure ZnO from visible-band illumination for moderated concentration of Co.

The photoluminescence (PL) spectrum of ZnO at room temperature usually shows a near band-edge UV emission peak centered at 3.26 eV (380 nm) and at least one broad band in the visible region. UV emission is the near-band edge (NBE) emission which corresponds to the radiative transition of the excited electrons from conduction band to the valance band. The peak position of NBE emission can vary due to the presence of ZnO doping^{56,57} or/and quantum confinement effect (blue-shift), and particle shape (rod-plate).⁵⁸ Visible emission, or also known as deep-level emission (DLE), on the other hand is attributed to the defect sites which might trap the photogenerated electron and/or hole. The defect band might be located in green (centered around 2.4 eV), yellow (about 2.2 eV) and red or orange (around 2.07 eV) part of the spectrum.⁵⁹ Although the origins of these defect-related visible emissions are still highly controversial, mostly they are attributed to the singlet defect states such as zinc vacancy V_{Zn} , oxygen vacancy V_O , interstitial zinc Zn_i , interstitial oxygen O_i , and antisite oxygen O_Z .⁴⁵⁻⁶⁰ It was also reported that yellow emissions stem from the presence of OH groups while red and green emissions involve defect complexes.⁵⁹

The above description implies that the UV emission peak is expected to be a dominant signal in the PL spectrum of ZnO particles of good crystallinity, free of structural defects. Hence, the ratio of relative intensity of NBE emission to visible DLE band is used to evaluate the crystal quality of different ZnO samples.^{61,45,62,63} Regardless of the origins of the defects, the ratio of UV to visible emissions can be improved by decreasing the defect density. The defect emission can be significantly reduced by annealing ZnO samples although the defect emission shape, position and intensity are strongly dependent on the annealing atmosphere and temperature.^{59,64}

1.2.3 ZnO as a Photoelectrode

As stated in the previous sections ZnO is the runner up to replace TiO_2 as photoanode material in XSCs. The first application of ZnO in DSSCs was reported by Gerisher *et al.* in 1969 where a single crystal oxide was used as the electrode.⁶⁵ In 1980, 2.5 % efficiency at 562 nm using sintered porous disks of ZnO was reported by Matsumura *et al.*¹⁰ Recently, ZnO nanostructured electrodes made of colloidal nanoparticles with 6.58 % efficiency and ZnO nanostructures with high surface area such as nanoflower (1.9 %), nanosheets (3.9 %), hierarchically structured (3.5 %), or its application together with other oxides as mesoporous SnO_2 -ZnO (6.34 %), core-shell ZnO- TiO (9.8 %) or more recently doped-ZnO nanoparticles are

reported with highest efficiency being 7.2% with single crystal.¹⁰ Besides nanoparticles and structures described above, various one-dimensional nanostructures of ZnO including nanowires, nanotubes, nanorods, as well as electrospun ZnO nanofibers has been explored to be used in DSSCs.⁶ Using 1D-vertically-aligned nanostructures instead of nanoparticle electrodes has emerged as a possible way to obtain faster electron transport since the electron diffusion coefficient of one-dimensional ZnO nanowires is found to be several hundred times larger than that is reported for TiO₂ and ZnO nanoparticles.⁶ ZnO nanowires and structures that combine nanowires and nanoparticles to ensure high surface area for dye loading that were grown on FTO by chemical vapor deposition and hydrothermal method have been reported for the first time by Baxter *et al.*¹⁷ Solar cells made from branched nanowires showed overall efficiencies of 0.5% whereas solar cells made from appropriate hybrid morphologies combine the high surface area of nanoparticles with the improved carrier transport of nanowires exhibited overall efficiencies of 1.1%. The effect of the nanorod (NR) dimensions; length and diameter are directly effective to the device performance due to direct relation to the surface area available for dye. Baxter *et al.* obtained short circuit current density of 1.3 mA/cm⁻², and overall power conversion efficiency of 0.3% with 8 μm long nanowires.⁶⁶ It was reported that photocurrent density and efficiency increase with increasing nanowire length and electron transport is not limited by the nanowire dimensions for aspect ratios less than 70. A very recent study reported a double light- scattering-layer boron-doped ZnO (BZO) composed of well-dispersed sub-micrometer-sized BZO sphere arrays as the over-layer and a nonporous BZO nanoparticles as the under-layer for the DSSC photoanode which resulted in 7.2 % efficiency with N3 dye.⁶⁷

Recently, the dye sensitizer is replaced by semiconductor quantum dots (QDs) or extremely thin absorber film (in ETA cells) as described in the previous sections. Among various particles CdS is a popular choice. Some examples include ZnO nanorods sensitized with CdS QDs that displayed short circuit current density and open circuit voltage of 680 μA/cm⁻² and 520 mV, respectively, in ferro(i)cyanide electrolyte under 10 mW/cm⁻² of illumination²⁰ and CdS/ZnO nanotube arrays that exhibited photocurrent as high as 10.64 mA/cm⁻².⁶⁸

Vanalakkar *et al.* studied effect of nanorod length on the device performance prepared with CdS/ZnO NR array photoanode.⁶⁹ The length of ZnO nanorod arrays was shown to be an effective parameter to improve the photoelectrochemical performance of CdS nanoparticles sensitized ZnO solar cells like DSSCs. Power conversion efficiency of 1.2 % was obtained with 2.5 μm long NRs which decreased when the length of nanorods reached 4.5 μm. CdS-

sensitized ZnO nanorod arrays grown twice to increase the nanorod length displayed photo-induced current density as high as 23.7 mA/cm^2 .⁷⁰

Despite of very promising features, the QD semiconductor-sensitized solar cells (QDSSCs) reveal rather low power conversion efficiency and the main limiting factor is probably recombination of the charge carriers due to slow electron transfer from semiconductor to the electron acceptor (ZnO or TiO_2). Moreover, low QD loading and the weak electronic connection between QDs and the metal oxide decrease cell efficiency. In addition, specific band gap of single QD-sensitized solar cells restrict the absorption range and limits the achievable efficiency. To improve the performance of the QDs solar cells, another strategy is to broaden the absorption region by co-sensitization of the nanorods by two semiconductors of different size or type, for example with CdS/CdSe sensitization efficiencies up to 3.4 % were reported where CdS interlayer between ZnO nanorods and CdSe QDs passivates the ZnO surface and suppresses the charge carrier recombination.^{71,22}

1.2.4 Growth and Synthesis of ZnO

Several methodologies including solution based approaches^{41,72}, chemical vapor deposition (CVD)⁷³, physical vapor deposition (PVD), atomic layer deposition (ALD),⁷⁴ metal organic chemical vapor deposition (MOCVD)⁷⁵, pulsed laser deposition⁷⁶ and molecular beam epitaxy⁷⁷ were employed to grow ZnO crystals with very rich variety of structures like nanorods, nanobelts, branched nanorods, nanowires, hierarchical nanostructures, nanocombs, nansprings, nanospirals, nanorings, core-shell nanostructures, nanocages, nanoflowers. Most common methods include vapor based (CVD, PVD, ALD, MOCVD and etc.) , solution based (hydrothermal and electrodeposition) techniques. The emphasis will be on 1D ZnO since the main focus in this dissertation is the production of ZnO nanorods.

The most common method to synthesize ZnO nanostructures utilizes a vapor transport process. In such a process, Zn and oxygen or oxygen mixture vapor produced by evaporation, chemical reduction or gaseous reaction transferred and condensed onto the surface of a solid substrate, forming ZnO nanostructures. Generally, the vapor phase synthesis process is carried out at high temperatures from 500°C to 1500°C and some forms require introduction of metal catalysts which results in possible incorporation of catalytic impurities into ZnO structure.⁷⁴ Seed layers or metal catalysts are important requirements for highly aligned 1D ZnO growth. The morphology of fabricated nanostructures is dependent on presence and thickness of seed

layer, position of the substrate relative to the source, the source material, quantity, and system geometry which affect the local vapor pressure of the reactants at the substrate and consequently the morphology.⁷⁴

Solution phase synthesis has many advantages when compared to vapor phase synthesis, such as low cost, low temperature, scalability, and ease of handling. Generally, solution phase reactions occur at relatively low temperatures (<200°C) compared to vapor phase synthesis methods. Thus, solution synthesis methods allow for a greater choice of substrates including inorganic and organic substrates. Solution-based deposition methods can be classified as hydrothermal (water used as a solvent), solvothermal (other solvents), and electrodeposition (electric field assisted synthesis). The majority of ZnO nanostructures grown by solution-based methods are grown by a hydrothermal method which has become the most attractive synthesis technique for obtaining well-aligned nanostructures of ZnO.

In general, the hydrothermal technique is based on a two-step method involving the coating of a substrate with ZnO nanoparticles that will act as nucleation sites (seed layer) followed by growth in aqueous solution with an alkaline reagent (such as NaOH or hexamethylenetetramine) and zinc ion precursor. The synthesis conditions, like zinc ion concentration in solution, growth time, and growth temperature determine the final nanorod dimension and quality as well as the seed layer and the substrate. One of the key parameters for synthesizing 1D nanomaterials in solution is to control the supersaturation of reactants. It is generally believed that high supersaturation levels favor nucleation whereas low supersaturation levels favor crystal growth. Low super saturation levels of reactants has to be maintained during the growth process to favor 1D ZnO growth.⁷⁸

Electrochemical synthesis is also a simpler and cheaper alternative to produce semiconductor nanostructures as compared to the vapor based techniques. It is an efficient and environmental-friendly method where thin films on various substrates of any shape and size can be produced at relatively lower temperatures from aqueous media. Furthermore, by controlling deposition parameters like pH, solvent type, additive concentration, temperature, applied potential, precursor concentration; growth rate, growth direction, film thickness, composition and morphology of the films can be modified^{79–81} which are important factors for manipulation of morphology of the product, thereby optimization of material properties. The deposition potential and current provide additional control over the nucleation and growth as compared to hydrothermal processes. The material's growth rate in electrochemical synthesis

can be set by deposition current independently from the concentration of the reactants as it is in solution based synthesis.⁸² Therefore, electro- deposition can create various combinations of growth rate and mass-transport rate which provides more systematic control over mass-transport-limited growth. Moreover, application of a seed layer might be omitted. Hence, electrochemical synthesis is used to prepare ZnO based and Fe₂O₃ materials of various size and shape. Electrodeposition of ZnO is reviewed in the next section.

1.2.5 Electrodeposition of ZnO

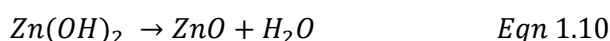
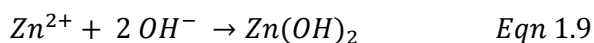
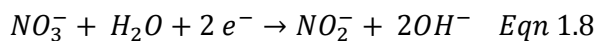
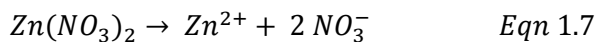
Electrodeposition of ZnO was first introduced in 1996 independently with two different groups. Izaki *et al.*⁸³ used reduction of nitrate ions and dissolved oxygen was used by Peulon *et al.*⁸⁴ for hydroxide production which precipitates as Zn(OH)₂ which is then dehydrated to ZnO. Since then, these methods have been studied further extensively to exploit reaction mechanisms and effects of reaction parameters such as synthesis temperature, electrical potential, precursor concentration and additives on the physical and chemical properties of the final products.

In electrochemical deposition of ZnO, OH⁻ can be provided by electroreduction of the different precursors, such as molecular oxygen (O₂)⁸⁵, hydrogen peroxide (H₂O₂)⁸⁶ or nitrate ions (NO₃⁻)⁸⁷. It is reported that deposition of ZnO from H₂O₂ solution leads to formation of porous films but vertically orientated nanorods cannot be obtained.⁵⁶ Moreover, electrochemical synthesis under hydrothermal conditions which require a closed, pressurized system was employed in the studies presented. Therefore, nitrate reduction pathway is chosen over molecular oxygen and will be discussed in detail.

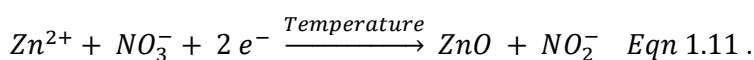
Nitrate pathway also seems to be more advantageous since the Zn(NO₃)₂ precursor is a single source for both Zn²⁺ and OH⁻ ions. In addition, it has been reported that reduction of aqueous nitrate ions is catalyzed by Zr(IV) and La(III) ions which are adsorbed on the electrode surface.⁵⁶ Yoshida *et al* similarly suggested that Zn ion has the catalytic role in the reduction of nitrate deduced from enhanced electron transfer kinetics in the presence of Zn²⁺ ions.⁸⁸

Electroreduction of nitrate ions in the growth solution (coming from the dissolution of Zn(NO₃) precursor (eqn 1.7)) gives rise to formation of OH⁻ ions (eqn 1.8).⁸⁸ Hence, pH of the solution increases in the close proximity of the working electrode surface and hydroxide ions in turn, cause precipitation of zinc hydroxide (eqn 1.9; hydroxylation) at the cathode. Zn(OH)₂

is the major soluble species in the pH range from 9 to 11.2 at the temperature of 25°C and from pH 7.8 to 10.5 at 75°C.⁵⁶ Hence, zinc hydroxide is subsequently dehydrated to generate ZnO (eqn 1.10; dehydration) at elevated temperatures.



The reaction might be written as follows since Zn plays the role of both the catalyst and the reagent;



Transparent Wurtzite ZnO grown preferentially along the *c*-axis with a 2-step electrodeposition from 0.1M $\text{Zn}(\text{NO}_3)_2$ at 335 K was reported by Izaki.⁸³ Izaki first performed electrodeposition of a seed layer at -1.2 V which is followed by electrodeposition at -0.7 V. A high concentration of Zn^{2+} ions under the presented conditions resulted in rapid consumption of electroreduced OH^- and ZnO is deposited forming a smooth film. Yoshida *et al.* demonstrated that the electrodeposition of ZnO from nitrate bath is a kinetically very slow process with low rate constant for NO_3^- reduction (5.98×10^{-10}) which is the rated determining step.⁸⁸ Otani *et al.* studied deposition mechanism and the effect of temperature on deposition by the electrochemical quartz crystal microbalance (EQCM) technique.⁸⁷ The change in deposition mechanism with temperature is found to be closely related to the increased thermodynamic stability of ZnO at high temperature. Based on EQCM analysis, it was suggested that the precursor of ZnO is slowly transformed to ZnO at low temperature (313 K), but the formation of ZnO is extremely rapid at high temperature (343 K), i.e., ZnO directly deposits at high temperature. Similar to Lincot⁸⁹, they observed preferential *c*-axis orientation gets stronger with increasing temperature. According to the proposed mechanism (Figure 1.12), at high temperature, ZnO deposits directly on the substrate. At low temperature, a finite amount of precursor with specific morphology dependent on temperature is deposited and the initial nucleation and nuclear growth of ZnO occurs at the interface between the precursor of ZnO and the substrate.

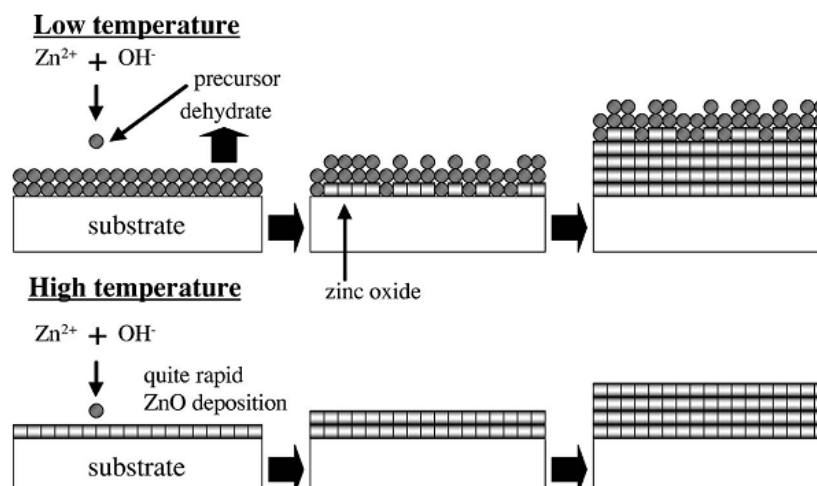


Figure 1.12 Electrodeposition mechanism of ZnO film.⁸⁷

The concentration of the $Zn(NO_3)_2$ precursor is also an important parameter that controls the growth orientation. C-axis orientation is observed in coatings obtained from low $Zn(NO_3)_2$ concentration and (10l) orientation is observed at high $Zn(NO_3)_2$ concentrations (Figure 1.13).⁹⁰ When the deposition was carried out at moderate temperature with low $Zn(NO_3)_2$ concentration (60°C, 0.04 M), the coatings obtained show the thermodynamically stable c-axis orientation.⁹⁰ This behavior is discussed to stem from the competition between hydroxylation (eqn 1.9) and dehydroxylation (eqn 1.10) reactions. The hydroxyl ion production is slow at low nitrate concentrations and the rate of hydroxylation is slower than the rate of dehydroxylation. Orientation along 10l direction is observed when the deposition is carried out from concentrated $Zn(NO_3)_2$ solution (0.1 M). The rate of hydroxyl ion production is higher than that of dehydroxylation at high nitrate concentration. Hence, there is a competition between growth along thermodynamically stable (002) direction and other directions. Growth also takes place along the less thermodynamically stable 10l (l=1, 2, 3) faces. Due to the competition between different 10l planes present at different angles to the c-axis for the addition of atoms, the hexagonal columns grow with their long axes titled at different angles to the normal to the substrate.

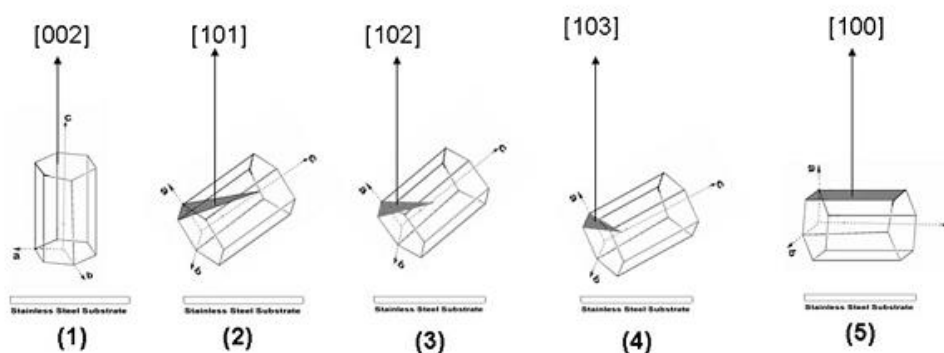


Figure 1.13 A schematic of a hexagonal columnar crystal of ZnO with its long axis tilted at different angles with respect to the surface of the substrate⁹⁰

Not only growth orientation but also morphology of the ZnO crystals can be modified by controlling precursor concentration.^{61,91,92} Different structures ranging from nanowalls to nanopillars by decreasing the concentration of $\text{Zn}(\text{NO}_3)_2$ 100-fold were presented by Pradhan and Leung; with formation of one-dimensional (1D) nanospikes and nanopillars (with 50-500 nm diameter) below 0.01 M and of two-dimensional (2D) nanowalls and nanodisks (with 50-100 nm wall/disk thickness) above 0.05 M.⁷⁹ $\text{Zn}(\text{NO}_3)_2$ concentration also influences the average diameter and surface coverage of the film; both are increased with increasing concentration.⁵⁶ The influence of deposition current density on the nanorod diameter and length, at constant concentration of $\text{Zn}(\text{NO}_3)_2$ (0.005 M) is also investigated and it is reported that the increase of the current density from -0.9 to -2 mA/cm^2 , (thereby the increase of concentration of generated OH^- at the electrode) resulted in the increase of both dimensions of the obtained nanorods so that the aspect ratio of nanorods also increased from about 4.6 to 8.4.⁵⁶

Electrodeposition of ZnO nanorods vertically arranged on non-seeded substrate was also successfully performed from the solution of 0.005 M $\text{Zn}(\text{NO}_3)_2$ by potentiostatic deposition at the potentials from the range between -0.6 V and -1.1 V and it was demonstrated that the size of nanorods was also very sensitive to deposition potential.⁵⁶

As explained before due to the presence of polar planes and planes with varying surface activity by using organic or inorganic additives, such as ethylenediamine (EDA), hexamethylenetetramine (HMT) or Cl^- , it is possible to obtain ZnO films in the form of

hexagonal particles, hexagonal plates, hexagonal rods, flower-like rod bundles and hexagonal nanowire arrays.^{45,89}

Higher bath temperatures were reported to be promising also to obtain ZnO nanorods with high degree of crystallinity^{89,93} with low concentration of structural defects which is required to design materials with excellent optical properties. The reported temperatures for electrochemical deposition of ZnO range between 60-90°C below 100°C which is the limit for aqueous reactions. Recently, Park *et al.* has been demonstrated a combination of hydrothermal-electrochemical methods to grow ZnO nanorods with better optical properties at even higher temperatures of 120-180°C.⁹⁴ However, in this study ZnO seed layer prepared by atomic layer deposition (ALD) was used to grow ZnO nanorods. Using a seed layer is both economically and energetically inefficient. Furthermore, although high temperature enhancement on the optical quality has been studied, the effects of the high bath temperature and high pressure on the photoelectrochemical properties of the ZnO films have not been investigated so far. In this study, effect of hydrothermal-electrochemical deposition on the morphology and crystal growth of ZnO film is reported.

1.3 Present Study and Objectives

ZnO is a promising semiconductor metal oxide in DSSCs and photoelectrochemical cells (PECs) due to the ease of synthesizing highly crystalline ZnO in different morphologies and its high electron mobility. Especially, dense and vertically aligned ZnO structures such as nanowires and nanorods have been studied for light-harvesting applications since they are efficient in both charge collection and transport.²⁰ Unfortunately, efficiencies of DSSCs utilizing ZnO (below 3%) is still lower than DSSCs prepared with mesoporous TiO₂ (up to 12%).⁵⁶ Recently, dye sensitizers are being replaced by semiconductor materials such as CdS, CdSe, PbS and Ag₂S to overcome the low efficiencies due to slow electron injection from dye to ZnO caused by dissolution of ZnO in acidic dye solutions.^{56,95,96,23,19} However, recent trends have shown that the overall conversion efficiency of QDSSCs is lower than that of DSSCs due to charge recombination at the electrolyte–electrode interfaces.

Main objective of the study introduced in PART 1, is to explore the newly introduced hydrothermal-electrochemical deposition (HED) as a means of developing ZnO films of various morphology for efficient photoelectrochemical applications and investigate the ability of

electrodeposition to form a fine electrical contact between the semiconductor sensitizer and ZnO to enhance overall efficiency of XSCs as well as search for efficient window layers.

Chapter 2 is devoted to investigate the effects of the high bath temperature and high pressure on the photoelectrochemical properties of the ZnO films. In addition, Although it has been shown that DSSC efficiency depends on different parameters like type of dye, type of electrolyte and especially the electrode morphology, it was observed that solar cell efficiency is related to the diameter of the nanorods rather than length with no systematic study.¹⁰ It will be shown that HED provides control on the rod diameter, hence effect of diameter and the aspect ratio on the overall power conversion efficiency is explored.

Morphological details of a semiconductor electrode such as size, shape, and connectivity of the particles have a significant impact on the interfacial energetics, kinetics, and charge-transport properties.⁸² Therefore, understanding and controlling the morphological aspects of polycrystalline electrodes is critical in producing highly efficient devices. Chapters 3-5 focus on preparation of ZnO structures in various shapes in synergistic effect of the growth-modifier molecules and electrodeposition under hydrothermal conditions is demonstrated. In chapter 3, possibility of controlling rod diameter by adjusting $[\text{MnCl}_2]$ is described. In chapter 4, *synthesis of hierarchical ZnO architectures at a single step with HED is reported. The key role of $\text{Cd}(\text{CH}_3\text{COO})_2$ ratio in the deposition bath and $[\text{Cd}(\text{CH}_3\text{COO})_2]/[\text{Zn}(\text{II})]$ to obtain hierarchical ZnO architectures is discussed in detail.* In chapter 5, growth of heterogeneous ZnO-Co nanostructures via HED directly on conducting glass is presented and the effect of cobalt ion amount on the morphology and physical properties of ZnO films is discussed.

QD sensitizers can be synthesized by two fundamentally different techniques; in situ fabrication and attachment of pre-synthesized colloidal QDs (ex situ fabrication). Ex situ fabrication enables precise control over the size and shape. However, low QD loading and the subsequent weak electronic connection between QDs and semiconductor introduce defects in cell performance and subsequently reduce cell efficiency.¹¹ The problem can be overcome by chemical bath deposition (CBD) and successive ionic layer adsorption and reaction (SILAR) to some degree. Recently, it has been shown that electrodeposited CdSe and CdS coatings can effectively sensitize ZnO.^{40,68} It has been demonstrated that a fine electric contact between a dense and compact electrodeposited CdS layer and ZnO is advantageous for fast charge-transport.⁶⁸ Hence, chapter 6 is focused on preparation of QD sensitizers by electrodeposition.

The effect of electrodeposition parameters such as potential, current and time on photoelectrochemical properties of CdS/ZnO NRs and Ag₂S/ZnO NRs is discussed.

Lastly, in chapter 7, in an effort to produce buffer layers for solar cells with enhanced photoactivity, photoelectrochemical properties of mixed semiconductor CdS–ZnS films synthesized by electrochemical deposition is explored.

Chapter 2 Photoelectrochemical Properties of ZnO Films Deposited by Electrochemical Deposition under Hydrothermal Conditions

2.1 Introduction

Electrodeposition of ZnO was first introduced in 1996. Izaki *et al.*⁸³ used reduction of nitrate ions and dissolved oxygen was used by Peulon *et al.*⁸⁴ to drive the reaction. Since then, these methods have been studied further to exploit reaction mechanisms and effects of reaction parameters such as synthesis temperature, electrical potential, precursor concentration and additives on the physical and chemical properties of the final products. For example, it has been shown that morphology of the ZnO crystals can be modified by controlling precursor concentration.^{61,91,92} Different structures ranging from nanowalls to nanopillars by decreasing the concentration of $\text{Zn}(\text{NO}_3)_2$ 100-fold were presented by Pradhan and Leung.⁷⁹ Furthermore, the morphology of the crystals was also displayed to be dependent on the synthesis temperature.⁸⁰ Higher bath temperatures were also reported to be promising to obtain ZnO nanorods with high degree of crystallinity^{89,93} with low concentration of structural defects which is required to design materials with excellent optical properties. The reported temperatures for electrochemical deposition of ZnO range between 60-90°C below 100°C which is the limit for aqueous reactions. Recently, Park *et al.* has been demonstrated a combination of hydrothermal-electrochemical methods to grow ZnO nanorods with better optical properties at even higher temperatures of 120-180°C.⁹⁴ However, in this study ZnO seed layer prepared by atomic layer deposition (ALD) was used to grow ZnO nanorods. Using a seed layer is both economically and energetically inefficient. Furthermore, although high temperature enhancement on the optical quality has been studied, the effects of the high bath temperature and high pressure on the photoelectrochemical properties of the ZnO films have not been investigated so far. In this chapter, investigation of effect of hydrothermal-electrochemical deposition on the morphology and crystal growth of ZnO films is reported.

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Moreover, effect of rod diameter on photoelectrochemical properties of ZnO films is also discussed.

2.2 Experimental

2.2.1 Materials

All the chemicals used were of analytical grade or of the highest purity commercially available. Zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) and methanol were purchased from Sigma-Aldrich. Cadmium acetate hexahydrate ($\text{Cd}(\text{CH}_3\text{COO})_2 \cdot 6\text{H}_2\text{O}$), manganese chloride tetrahydrate ($\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$) and sodium sulfide nonahydrate ($\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$) were obtained from Merck. Sodium thiosulfate pentahydrate ($\text{Na}_2(\text{S}_2\text{O}_3) \cdot 5\text{H}_2\text{O}$) was purchased from Horasan Chemicals (Turkey). Indium Tin Oxide (ITO) ($\Omega < 5.0 \times 10^{-4} \text{ ohm.cm}$ ($R_s < 100 \text{ ohm/sq}$)) was purchased from Teknoma Ltd. Izmir, Turkey. Double distilled, high purity water was used from Milli-Q water (Millipore) system.

2.2.2 Synthesis and Characterization

A conventional 3 electrode cell system in a hydrothermal glass reactor was used for electrochemical deposition. The reference electrode was Ag/AgCl saturated with KCl (S/N P11092) whereas Pt wire served as counter electrode. ITO coated glass substrate of $1 \times 1 \text{ cm}^2$ area was used as the working electrode. The substrate was cleaned ultrasonically by acetone, ethanol, and distilled water. The growth temperature was 130°C . The potentiometric deposition was performed at -1.1 V for 30 minutes from $\text{Zn}(\text{NO}_3)_2$ bath on a VSP potentiostat/galvanostat (Biologic-Science Instruments). $\text{Zn}(\text{NO}_3)_2$ concentration was varied between 0.001 M and 0.1 M .

After deposition the oxide films were subjected to post-annealing at 450°C for an hour. CdS deposition was carried out by successive ion layer adsorption method (SILAR). The annealed ZnO films were dipped into $0.1 \text{ M Cd}(\text{CH}_3\text{COOH})_2$ - 0.01 M MnCl_2 and $0.1 \text{ M Na}_2\text{S}$ solutions, respectively for 10 minutes each. The films were rinsed with water for 30 seconds in between to remove any excess precursor solution. The as-obtained samples were denoted for ZnOm/CdSn , where m represents molarity of precursor $\text{Zn}(\text{NO}_3)_2$ solution (mM) and n represents the repetitions of (Mn_Cd)S deposition. The current-voltage (I-V)

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characteristics of the electrodes were measured under amplitude modulated-light illumination with a 300 W Xenon arc lamp (Oriel, Stratford, CT) with the 3 electrode cell system in an aqueous solution of 0.1 M Na_2S , 0.1M $\text{Na}_2(\text{S}_2\text{O}_3)$ and 1% methanol. AM 1.5 air filter was used to mimic solar radiation.

The crystal structure and crystallinity of the samples were analyzed by X-Ray diffraction (XRD) analysis using Bruker/D8 Advance with $\text{Cu K}\alpha$ radiation. The surface morphology of the films was examined with ZEIS EVO or with ZEISS Ultraplus Field Emission Scanning Electron Microscope (FE-SEM). The film composition was studied by X-Ray photoelectron spectroscopy (XPS, Thermo K-Alpha). The binding energies were calibrated by taking C1s binding energy (285 eV) as reference. Photoluminescence spectra of the films were recorded by Horiba Jobin Yvon–Fluoromax 3 spectrofluorometer between 375-700 nm at 355 nm excitation wavelength. Diffuse reflectance spectra of the investigated samples were performed using a Shimadzu UV–vis–NIR 3600 spectrophotometer using integrating sphere attachments.

2.3 Results and Discussion

2.3.1 Morphology

Seedless electrochemical deposition of ZnO films was carried out on an ITO electrode at constant potential (-1.1 V vs Ag/AgCl electrode) at 130°C in a closed glass reactor where pressure autonomously increases to 2.0-2.5 bar at this temperature. Electron microscopy was used to investigate the effect of Zn^{2+} concentration on the morphology of the films. The seedless electrochemical growth of ZnO structures under hydrothermal conditions resulted in rods with different sizes depending on concentration of Zn^{2+} in the solution as seen in Figure 2.1. The hexagonal feature of ZnO rods is more pronounced for higher Zn^{2+} concentrations and ZnO rod sizes are regular. Surface coverage increases with the concentration of Zn^{2+} in the deposition solution. Figure 2.1a shows SEM image of ZnO film deposited from 0.001 M Zn^{2+} aqueous solution. This low concentration gives 100-200 nm thick rods covering the surface homogenously. As seen in the image rods are not perfectly aligned but have tendency to grow normal to the surface. Increasing Zn^{2+} concentration by 10-fold increases the average diameter of rods as seen in Figure 2.1b. Further increase in Zn^{2+} concentration brings about increase in the diameter of rods further and the rods seem to be aligned normal to the surface of the substrate better with increasing concentration as seen in Figure 2.1c (0.05 M Zn^{2+}) and 1d (0.1

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M Zn²⁺). Alignment of ZnO rods normal to the surface was reported to be dependent on the presence of a seed layer.⁹⁷ However, vertically aligned ZnO nanowires were also produced by seedless electrodeposition by V.A. Antohe *et al.*⁹⁸ They reported flat substrate surface plays an important role on the vertical alignment. At low concentrations, deposition produces very thin rods distinctively separated from each other. Higher concentrations, on the other hand, result in rods penetrating into each other as they grow. Distribution of the thickness of ZnO rods seems to be homogenous, which could be related with the fast nucleation of ZnO growth centers.⁸⁵ Thick rods have generally flat tips. ZnO rods deposited from 0.05 M Zn²⁺ solution is distinguishable from other films with distinctively hexagonal structure and etched ends. Etching of the tips is generally observed at higher pH values due to selective dissolution of meta-stable (001) polar plane of ZnO by forming a soluble hydroxide complex and it also depends on the rod diameter. X. Gan *et al.* showed that ZnO nanorods with diameters less than 100 nm could not be etched but a critical diameter of 250-300 nm is required.⁹⁹

The only work related with the electrochemical deposition under hydrothermal conditions was carried out by Park *et al.*⁹⁴ The deposition, however, was carried out on a pre-deposited ZnO layer by DC-sputtering technique. Electrochemical deposition of ZnO in atmospheric condition at moderate temperatures results in morphologies depending on the concentration of Zn²⁺ in the deposition solution.^{45,79} According to reports on the electrochemical growth of ZnO structures, a very low concentration of Zn²⁺ in the solution (<0.01 M) gives nanorods or needles and higher concentrations generally produce morphologies different than rods.^{61,79,80} In contrast to these reports, the seedless electrochemical growth under hydrothermal conditions resulted in crystal growth in (002) direction regardless of the concentration of Zn²⁺ in the solution. The concentration, on the other hand, determined the diameter of the crystals as seen in the SEM images (Figure 2.1).

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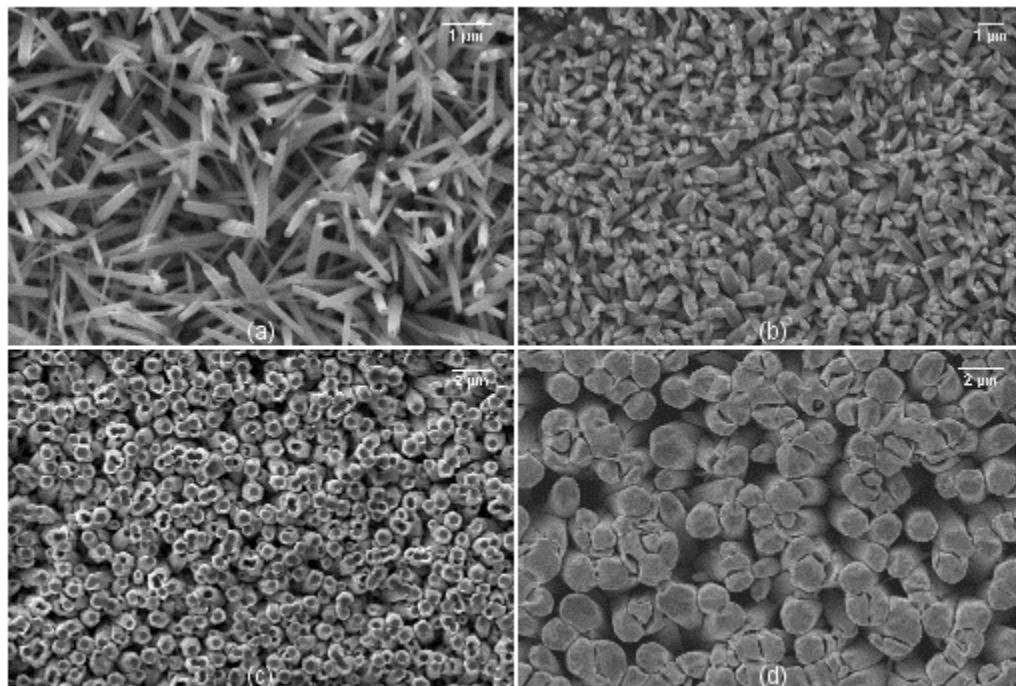


Figure 2.1 SEM images of pristine ZnO films electrodeposited at 130°C, ~2 bar from baths containing a) 0.001 M $\text{Zn}(\text{NO}_3)_2$ b) 0.01 M $\text{Zn}(\text{NO}_3)_2$ c) 0.05 M $\text{Zn}(\text{NO}_3)_2$ d) 0.1 M $\text{Zn}(\text{NO}_3)_2$ for 30 min.

2.3.2 Crystal Structure

The crystal structures of the films were investigated with XRD. Films deposited from solutions with Zn^{2+} concentrations below 10 mM produced very weak diffraction patterns as seen in Figure 2.2, although weak, a peak indexed to (002) crystal direction was dominant in all patterns. Diffraction peaks of ITO {JCPDS card No. 89-4597} was also observed for all films. Films deposited from a solution with Zn^{2+} concentration higher than 50 mM gave highly oriented and crystalline films (Figure 2.2). All figures indicate that the seedless electrochemical growth of ZnO films resulted in orientation of crystal growth preferred in (002) direction with high crystallinity. All patterns include also diffraction peaks for (101) and (102) orientations. This is in accordance with the inclined rods seen in SEM images. Although there is a strong orientation in c-crystal direction for all films as seen in SEM images, X-rays would diffract from (101) and (102) planes for inclined rods in Bragg-Brentano conditions.

Electrochemical Deposition under Hydrothermal Conditions

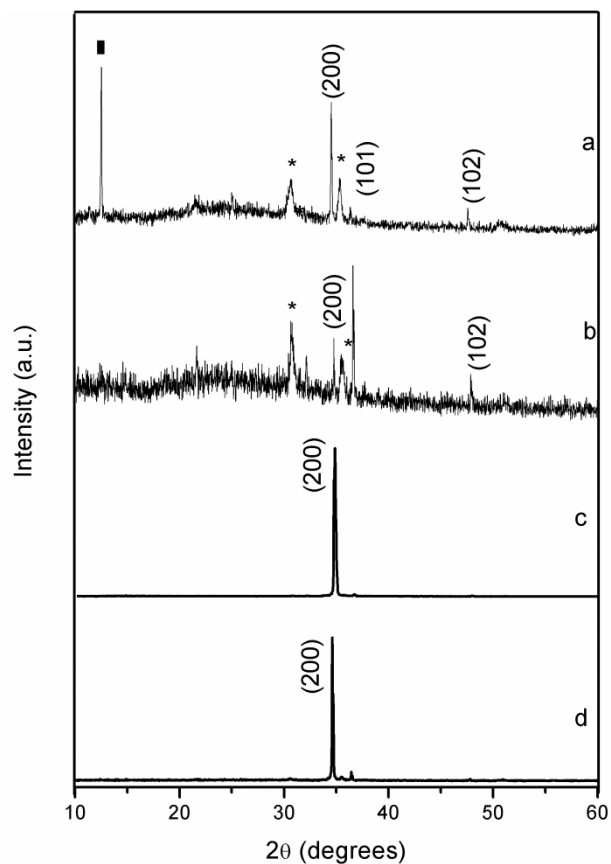


Figure 2.2 XRD profiles of pristine ZnO films electrodeposited at 130°C, ~2 bar from baths containing a) 0.001 M $\text{Zn}(\text{NO}_3)_2$ b) 0.01 M $\text{Zn}(\text{NO}_3)_2$ c) 0.05 M $\text{Zn}(\text{NO}_3)_2$ d) 0.1 M $\text{Zn}(\text{NO}_3)_2$ for 30 min. The following symbols represent reflections associated with ■ zinc hydroxide nitrate hydrate (JCPDS card no.27-1491) and * ITO.

2.3.3 Crystal Growth

In order to find out the possible crystal growth mechanism under hydrothermal conditions, ZnO films grown from 0.1 M Zn^{2+} concentration at different times at 130°C were investigated. As it is seen in Figure 2.3a, the structure is mainly zinc hydroxide nitrate hydrate {JCPDS No. 00-027-1491} at 5 min deposition time. The zinc hydroxide layer is acting as a seed and ZnO films grown on this layer as time passes. At 5 min, some sheet like morphologies were observed together with the formation of hexagonal filled or empty structures, which are ZnO crystals grown on zinc hydroxide layer (Figure 2.4a). Extended synthesis time resulted in disappearance of Zinc hydroxide nitrate hydrate phase and the formation of ZnO rods on these structures as evident both from XRD data (Figure 2.3) and SEM images (Figure 2.4). According

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to the standard card {JCPDS card No. 36-1451}, (101) reflection is the most intense peak and the intensity ratio of (002) reflection to (101) ($I_{(002)}/I_{(101)}$) is 0.44. $I_{(002)}/I_{(101)}$ ratio is calculated to be 2.27 for the film prepared in 20 minutes and 15.5 after 30 minutes supporting highly enhanced oriented growth of the ZnO rods along *c*-axis.

In hydrothermal-electrochemical synthesis we observed preferential growth along (0001) plane perpendicular to the substrate even at high electrolyte concentrations. This concentration independent morphology is unique. It is observed that 2-D ZnO structures are obtained from highly concentrated $\text{Zn}(\text{NO}_3)_2$ baths (100 mM, 50 mM), whereas 1D rod-like architectures are induced at lower electrolyte concentrations (1mM).^{45,79} This behavior can be explained by the increased rate of dehydration reaction under hydrothermal conditions. Formation of ZnO in this study is as a result of the reduction of nitrate ions as discussed in Chapter 1.2.5. Electroreduction of nitrate ions in the growth solution (dissolution of $\text{Zn}(\text{NO}_3)_2$ precursor (eqn 1.7) gives rise to formation of OH^- ions (eqn 1.8).⁸⁸ Hence, pH of the solution increases in the close proximity of the working electrode surface and hydroxide ions in turn, cause precipitation of zinc hydroxide (eqn 1.9; hydroxylation) at the cathode. Zinc hydroxide is subsequently dehydrated to generate ZnO (eqn 1.10; dehydration).

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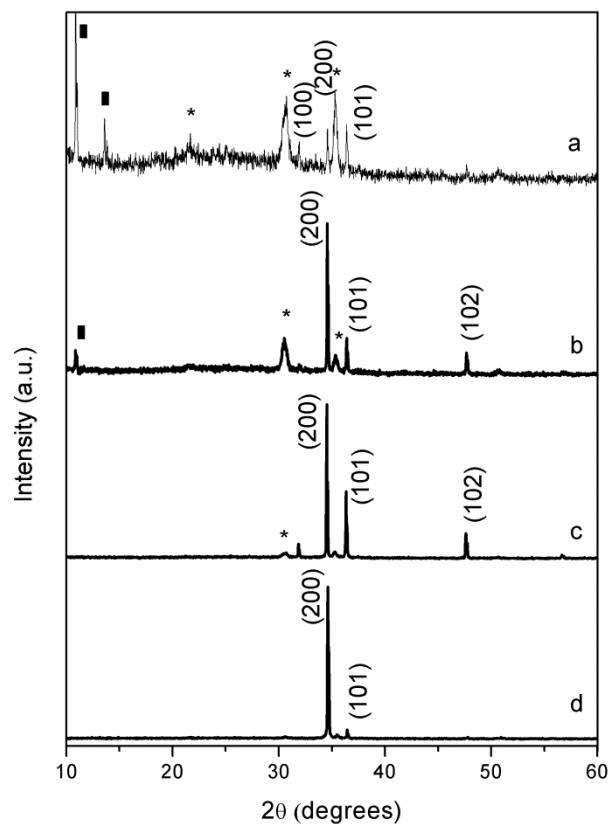


Figure 2.3 XRD profiles of pristine ZnO films electrodeposited at 130°C, ~2 bar from baths containing 0.1 M $\text{Zn}(\text{NO}_3)_2$ a) for 5 min. b) for 10 min. c) for 20 min. d) for 30 min. The following symbols represent reflections associated with ■ zinc hydroxide nitrate hydrate (JCPDS card no.27-1491) and * ITO.

According to this electrodeposition reaction scheme explained in Chapter 1, zinc hydroxide layer grows first on the surface of ITO substrate and ZnO structures form from the top hydroxide layer. XPS analysis reveals the hydroxide layer on top of the film as seen in the O1s spectrum in Figure 2.5. The peak around 532.5 eV on O1s spectrum is attributed to the chemisorbed and dissociated oxygen species or OH^- on the surface.¹⁰⁰ In accordance with the XRD data, we may conclude that the component at 532.5 eV corresponds the OH^- species. Etching the surface with Ar^+ beam for 300 second decreases the intensity of this peak and leaves the peak corresponding to O^{2-} in ZnO on the spectrum. OH^- component still exists as a weak shoulder peak. 300 sec etching removes approximately 20 nm so we may conclude that the thickness of $\text{Zn}(\text{OH})_2$ layer is close to this value.

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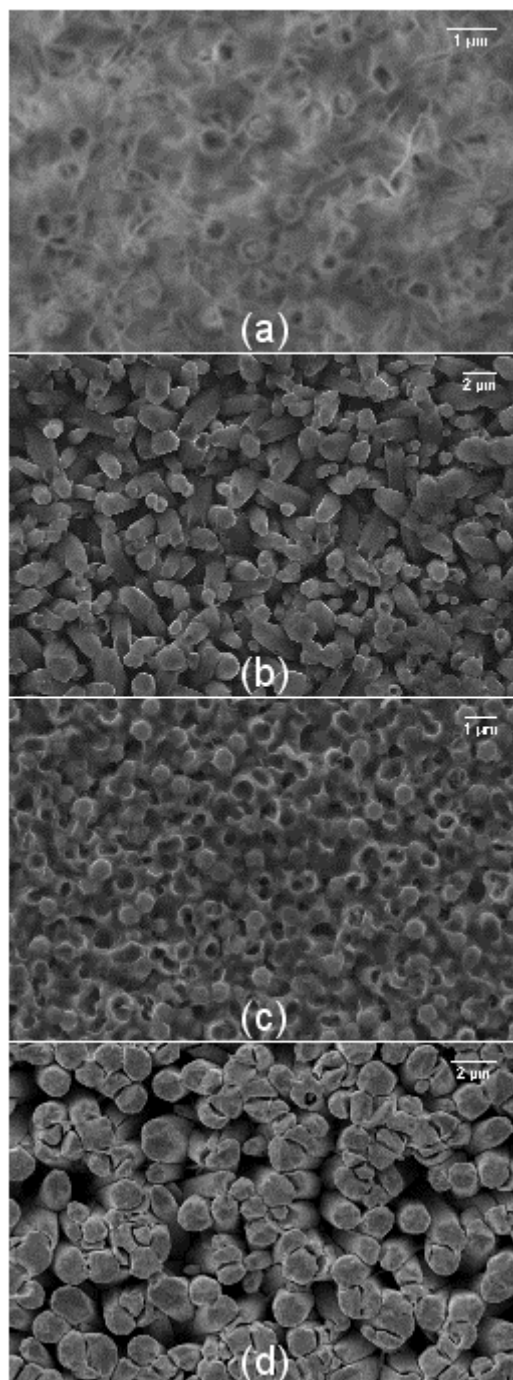


Figure 2.4 SEM images of pristine ZnO films electrodeposited at 130°C, ~2 bar from baths containing 0.1 M $\text{Zn}(\text{NO}_3)_2$ a) for 5 min. b) for 10 min. c) for 20 min. d) for 30 min.

The dehydration reaction, conversion of the initially formed zinc hydroxide to zinc oxide (eqn 1.10), is shown to be increasing with deposition temperature noticeably by *Goux et al.* in solutions including dissolved oxygen.⁸⁹ Similarly, transformation of the precursor to ZnO

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was reported to be slow at low temperature (25°C) by Matsuoka and his group but ZnO forms extremely rapidly at higher temperatures (70°C).⁸⁷ Formation of ZnO was discussed to be more favorable than Zn(OH)₂ formation at higher temperature since free energy changes of Eqn.1.4 decreases with increasing temperature. Hence, we propose rate of the dehydration reaction at high temperature (130°C) is even faster and this increased dehydration rate gives rise to the formation of zinc oxide seeds which grow and coalesce at later stages and result in formation of 1D structures independent of the concentration.

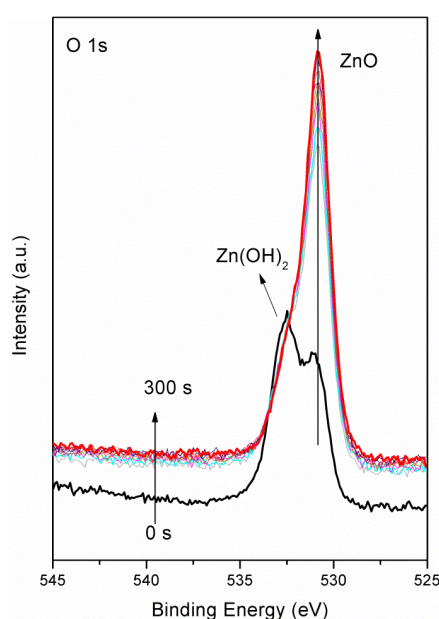


Figure 2.5 O1s XPS spectra of ZnO film electrodeposited at 130°C, ~2 bar for 30 minutes from bath containing 0.1 M Zn(NO₃)₂ as a function of Ar⁺ etching time.

2.3.4 Preparation and Photoelectrochemical Characterization of Mn(1%)-CdS Sensitized ZnO Photoelectrodes

ZnO nanorod arrays prepared by hydrothermal-electrodeposition from 0.01 M Zn(NO₃)₂ baths were tested for photoelectrochemical activity. Due to its large band-gap ZnO shows poor photoresponse in the visible region. In order to increase the visible response, ZnO nanorods were sensitized with Mn(1%)-CdS by successive ion layer adsorption method (SILAR). The amount of deposited Mn-CdS was varied by changing the number *n* of repetitions of SILAR procedure from 12 to 21. The light-absorption properties of the annealed ZnO

Electrochemical Deposition under Hydrothermal Conditions

nanorods and ZnO films sensitized with Mn_CdS were investigated using UV/visible light absorption spectroscopy (Figure 2.6).

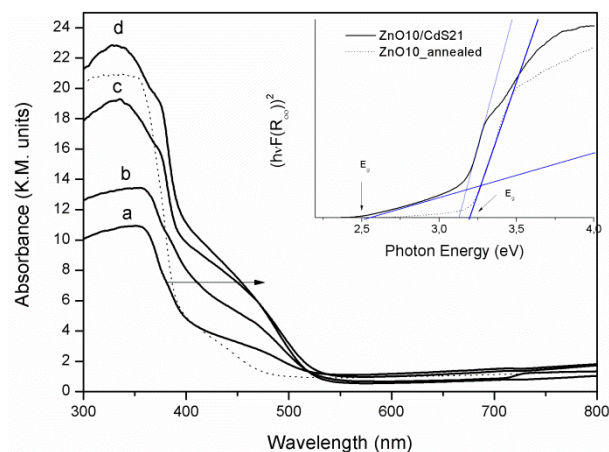


Figure 2.6 UV/visible light absorption spectra of annealed ZnO film (dotted line), a) ZnO10/CdS12, b) ZnO10/CdS15, c) ZnO10/CdS18 d) ZnO10/CdS21.

The absorption spectrum of annealed ZnO has an absorption edge shorter than 400 nm. The low absorbance between 400–450 nm might be due to the defects introduced during annealing as discussed above. Calculations using first-principles density-functional theory has shown vacancies take part in visible absorbance of ZnO nanowires.¹⁰¹ Optical band gaps, E_g of ZnO arrays were calculated using Tauc method. Modified Kubelka Munk function which is correlated with extinction coefficient was used to plot $(F(R_{\infty})h\nu)^2$ vs $h\nu$ and E_g value was obtained by extrapolating the slope to $x = 0$.¹⁰² E_g of ZnO nanorods prepared from 10 mM $\text{Zn}(\text{NO}_3)_2$ bath were calculated (inset of Figure 2.6) to be 3.19 eV. The absorption onset is shifted to around 540 nm when surface is coated with Mn_CdS. The band gap of Mn_CdS particles were estimated by assuming absorbance in the higher wavelength region is due to Mn_CdS. E_g is calculated to be 2.49 eV for the film ZnO/CdS12 after 12 cycles of Mn_CdS deposition and decreases to a final value of 2.5 eV after 21 cycles, which are slightly higher than the reported value of 2.4 eV for bulk CdS.¹⁰³ In addition, visible light absorption of the films gradually increase with increasing number of Mn_CdS deposition cycles on ZnO which can be ascribed to increased Mn_CdS deposition. Visible absorption increase seems to level off after 18 cycles of Mn_CdS deposition.

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Table 2.1 Photovoltaic parameters of the Mn_CdS sensitized ZnO Films.

Samples	J_{sc} (mA/cm ²)	V_{oc} (V)	FF (%)	η (%)
ZnO10/CdS12	0.55	-1.09	40	0.24
ZnO10/CdS18	1.48	-1.19	37	0.67
ZnO10/CdS21	1.48	-1.16	42	0.73

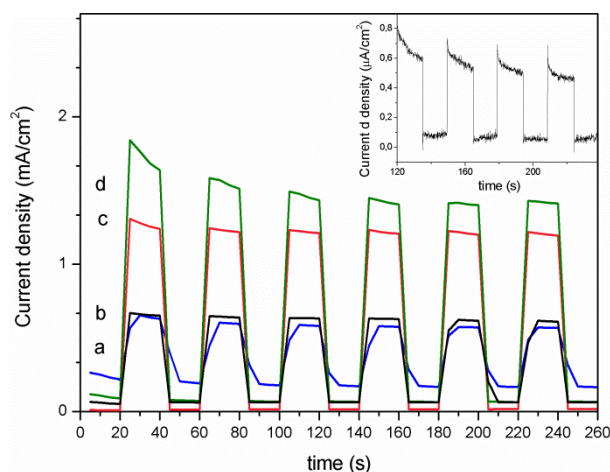


Figure 2.7 The photocurrent responses of the annealed ZnO film (inset), a) ZnO10/CdS12, b) ZnO10/CdS15, c) ZnO10/CdS18, d) ZnO10/CdS21 in Na₂S/Na₂S₂O₃ mixture at 0V under amplitude modulated illumination at 100 mW/cm² (AM 1.5 air filter).

Figure 2.7 shows the photoresponse of the films in an aqueous mixture of 0.1 M Na₂S and 0.1 M Na₂S₂O₃ solution at 0 V bias potential under amplitude modulated illumination under 1 sun conditions (100 mW/cm², AM 1.5 air filter). The low photocurrent response of annealed ZnO film (0.54 µA/cm²) is due to the poor visible light response of ZnO (inset Figure 2.7). The Mn_CdS coated ZnO films show an increased photo-sensitivity ~100-1000 magnitude higher than annealed ZnO nanorods, which can be attributed to the visible-light sensitivity of CdS and enhancement in the photogenerated hole-electron separation efficiency. Enhanced photo sensitivity continues to increase gradually with increasing Mn_CdS amount deposited. The net photocurrent densities of the films are 0.41, 0.57, and 1.21 mA/cm², respectively for ZnO/CdS12, ZnO/CdS15, ZnO/CdS18. The best performance is observed with ZnO/CdS21; 1.39 mA/cm². In agreement with optical absorption measurement photo response increase levels

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off after 18 cycles of Mn(1%)-CdS deposition. The photocurrent–voltage (J–V) curves of the films measured under identical conditions are shown in Figure 2.8. The photovoltaic measurement results are also summarized in Table 2.1. As revealed also by photoresponse measurements, the short circuit current density, J_{sc} of the annealed ZnO films gradually increase with the increase of the Mn-CdS deposition amount, while the open-circuit voltage (V_{oc} , V vs. Ag/AgCl) is ~ -1 V for all of the films. Highest efficiency is obtained with ZnO/CdS21 ($\eta = 0.73\%$ under 1 sun conditions) due to higher fill factor of the J–V curve ($FF=42\%$). The efficiency is, however, still limited because of relatively low photocurrent. The small J_{sc} could arise from a number of sources, including recombination losses within CdS, recombination of electrons in ZnO with the oxidized redox species through uncoated regions in the CdS, trapping of photoexcited electrons at the ZnO/CdS interface, and inefficient hole transfer to the electrolyte.

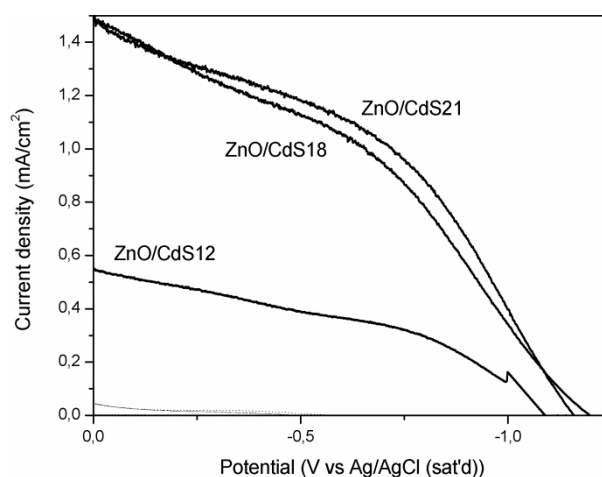


Figure 2.8 Photocurrent–voltage (J–V) curves of the Mn-CdS sensitized ZnO films in $\text{Na}_2\text{S}/\text{Na}_2\text{S}_2\text{O}_3$ mixture.

To further evaluate the effect of precursor concentration, rod diameter (and alignment) on the photoelectrochemical performance, ZnO nanorod arrays prepared from baths containing varying amount of precursor were sensitized with Mn(1%)-CdS by 21 cycles of successive ion layer adsorption method (SILAR). Figure 2.9 shows the photoresponse of the films in an aqueous mixture of 0.1 M Na_2S and 0.1 M $\text{Na}_2\text{S}_2\text{O}_3$ solution at 0 V bias potential under amplitude modulated illumination under 1 sun conditions ($100 \text{ mW}/\text{cm}^2$, AM 1.5 air filter). Photoresponse is increased from 0.30 to $2.08 \text{ mA}/\text{cm}^2$, as precursor concentration in

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the deposition bath increased 100-fold, hence diameters of the rods are increased from about 100-200 nm to around $\sim 1 \mu\text{m}$. Net photocurrent densities obtained are 0.30, 1.39, 1.92 and 2.08 mA/cm^2 for ZnO1/CdS21, ZnO10/CdS21, ZnO50/CdS21, ZnO100/CdS21, respectively. The current density–voltage (J–V) characteristics of the films are displayed in Figure 2.10 and key performance parameters are summarized in Table 2.2.

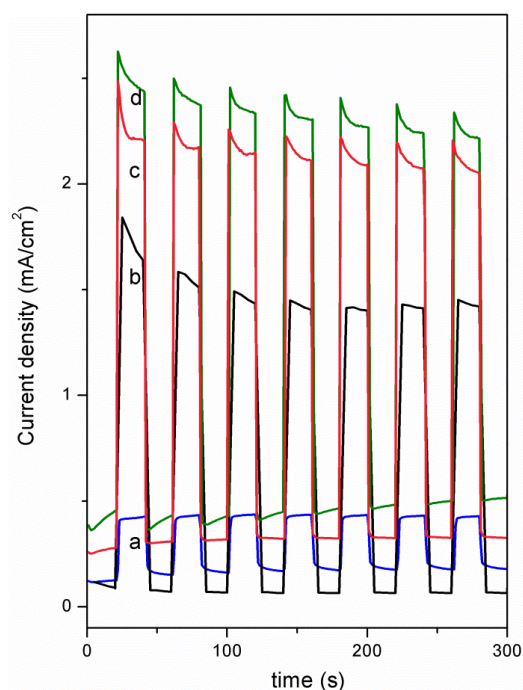


Figure 2.9 The photocurrent responses of a) ZnO1/CdS21, b) ZnO10/CdS21, c) ZnO50/CdS21, d) ZnO100/CdS21 in $\text{Na}_2\text{S}/\text{Na}_2\text{S}_2\text{O}_3$ mixture at 0V under amplitude modulated illumination at 100 mW/cm^2 (AM 1.5 air filter).

As revealed also by photoresponse measurements, the short circuit current density, J_{sc} of the annealed ZnOm/CdS21 films gradually increase with the increasing rod diameter and enhanced vertical alignment, while the open-circuit voltage (V_{oc} , V vs. Ag/AgCl) is around $\sim -1\text{V}$ for all of the films. Highest efficiency is obtained with ZnO100/CdS21 ($\eta = 0.93\%$ under 1 sun conditions). It would be expected that due to their higher specific surface area thinner ZnO rods, would provide more space both for sensitizer loading and photoelectrochemical reactions, thereby enhance photoinduced current density.

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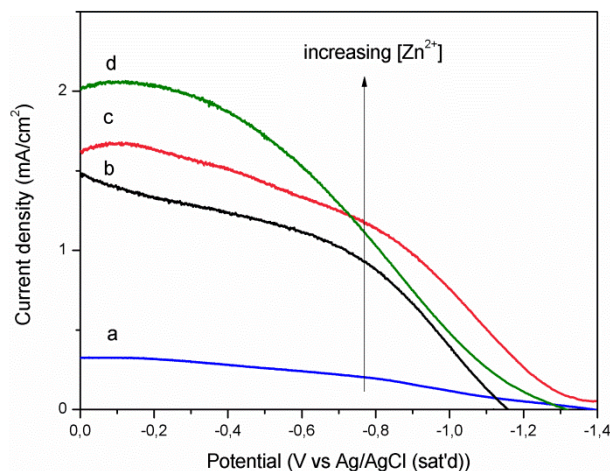


Figure 2.6 Photocurrent–voltage (J–V) curves of a) ZnO1/CdS21, b) ZnO10/CdS21, c) ZnO50/CdS21, d) ZnO100/CdS21 in $\text{Na}_2\text{S}/\text{Na}_2\text{S}_2\text{O}_3$.

When light absorbance profiles of the ZnOm/CdS21 films are analyzed (Figure 2.11), ZnO1/CdS21 evidently shows highest optical absorption intensity in the visible region which implies higher Mn_CdS loading for ZnO1/CdS21 than the rest of the films as predicted.

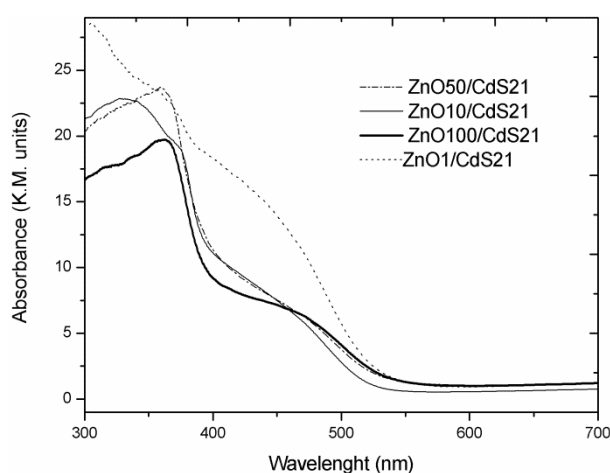


Figure 2.7 UV/visible light absorption spectra Mn_CdS sensitized ZnO Films as a function of precursor concentration in the deposition solution.

However, ZnO1/CdS21 film exhibits lowest photoelectrochemical efficiency. ZnO film deposited from 1 mM Zn^{2+} aqueous solution is composed of 100-200 nm thick rods which are

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not perfectly aligned (Figure 2.1) as compared to the ZnO rods prepared from more concentrated precursor solutions. It is known that more ordered rod structures could provide the photoinjected electrons with direct electrical pathway to the photoanode and thereby lead to fast carrier transport along the *c*-axis.¹⁰⁴ Superior charge transport, in turn decreases recombination rate of the photogenerated hole and electron. Hence, highly aligned rod structures show better PEC performances. Electrodeposition from more concentrated baths [$\text{Zn}(\text{NO}_3)_2$] > 0.05 M) under hydrothermal conditions give rise to very tight and highly enhanced oriented growth of the ZnO rods along *c*-axis. In addition, a complete upper surface coverage of Mn_CdS on ZnO rods for ZnO50/CdS21 and ZnO100/CdS21 is observed (Figure 2.12). On the other hand, ZnO1/CdS21 and ZnO10/CdS21 are partially covered with Mn_CdS particles and Mn_CdS particles seem to be deposited on all surfaces of ZnO1/CdS21 (Figure 2.12). Hence, enhancement of photoresponse for ZnO50/CdS21 and ZnO100/CdS21 can be attributable at least, in part, to tight surface coverage of Mn_CdS which might be better for shielding photoelectrons from recombination with oxidized species in electrolyte at ZnO/electrolyte interface.^{70,105}

Table 2.2 Photovoltaic parameters of the Mn_CdS sensitized ZnO films: effect of precursor concentration in the deposition solution.

Samples	J_{sc} (mA/cm ²)	V_{oc} (V)	FF (%)	η (%)
ZnO1/CdS21	0.32	-1.39	35	0.16
ZnO10/CdS21	1.48	-1.16	42	0.73
ZnO50/CdS21	1.63	-1.40	40	0.92
ZnO100/CdS21	2.01	-1.32	35	0.93

Our experiments show rod diameter and alignment are effective parameters to improve photocurrent generation. Current highest power conversion efficiency of 0.93 % with micrometer thick ZnO rods can be further enhanced by optimizing rod length, polysulfide electrolyte concentration and proper choice of counter electrode. Overall, combined hydrothermal-electrochemical deposition is a promising technique for fabricating efficient, cheap solar conversion devices, since it offers the possibility of producing thick ZnO rods effectively from highly concentrated precursor solutions.

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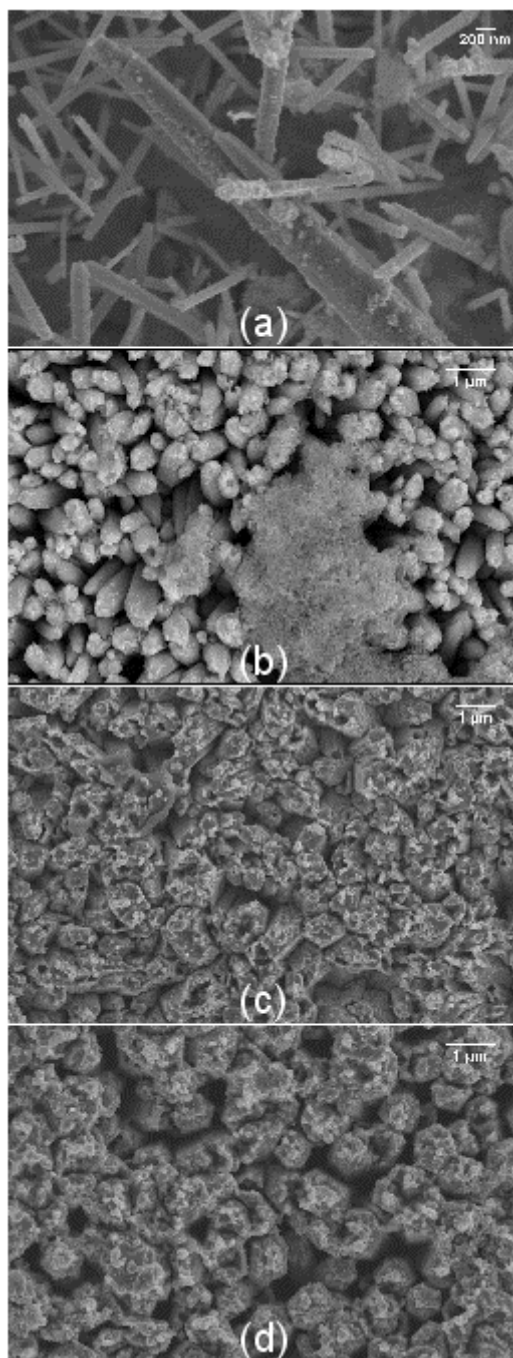


Figure 2.8 FE-SEM images of a) ZnO1/CdS₂₁, b) ZnO10/CdS₂₁, c) ZnO50/CdS₂₁, d) ZnO100/CdS₂₁.

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2.4 Conclusions

Seedless electrochemical growth of ZnO under hydrothermal conditions was successfully performed to yield vertically aligned ZnO nanorods to the substrate surface with well-defined hexagonal caps. Highly enhanced texturation along c-axis even at high electrolyte concentrations was observed. Formation of 1D structure independent of the concentration is attributed to faster dehydration reaction at elevated temperature and high pressure. In addition, diameter of these 1D rods can be tuned by precursor concentration in the deposition solution. High crystal quality ZnO rods were grown as indicated by high intensity ratio of UV emission to visible emission. Highly enhanced photo-electrochemical performance has been demonstrated by sensitization with Mn_CdS particles by SILAR process over pristine ZnO nanorods. A short circuit current density of 1.48 mA/cm^2 and an open circuit potential of -1.16 V have been achieved for the ZnO10/CdS21 electrode resulting in an overall power conversion efficiency of 0.73 %. Photoelectrochemical sensitivity is further enhanced when highly c-axis oriented ZnO rods with diameters $\sim 1 \mu\text{m}$ are sensitized with Mn_CdS particles. A net short circuit current density of 2.08 mA/cm^2 and an open circuit potential of -1.32 V have been achieved for the ZnO10/CdS21 electrode resulting in an overall power conversion efficiency of 0.93 %.

Chapter 3 Electrochemical Deposition of Mn:ZnO Films Under Hydrothermal Conditions

3.1 Introduction

It is possible to modify electrical and optical properties of ZnO to broaden possible applications through impurity incorporation. To tune these properties which are very sensitive to the shape of the particles and the preparation method, considerable attention has been paid to metal doping; a few examples are Mn^{2+} , Cu^{2+} , Cd^{2+} , Co^{2+} , Ni^{2+} , Mg^{2+} and Fe^{2+} .^{106,12-107} Among these materials, Mn-doped ZnO crystals receive growing attention; modifying optical properties of ZnO through engineering the band gap with Mn doing is also of interest to many groups.^{14,108,109}

Several methodologies were employed to obtain Mn-doped ZnO particles including spray pyrolysis¹⁰⁹, chemical vapor deposition¹¹⁰, magnetron sputtering¹¹¹, sol-gel process¹¹², pulsed laser deposition¹⁰⁸ and electrodeposition¹¹³. The first few techniques require high temperatures. Moreover, vapor-based techniques involve introduction of catalysts that might affect the physical properties of the product. Electrochemical synthesis, on the other hand, has emerged as a simpler alternative to produce semiconductor nanostructures. It is a cost effective method where large area thin films on various substrates of arbitrary shapes can be produced at lower temperatures while control over growth rate, film thickness and morphology are maintained. However, there are no reports on synthesis of Mn-doped ZnO by a combination of hydrothermal techniques and electrochemistry which allows electrodeposition at higher temperatures than it is possible with air-open systems. In this chapter, we report seedless electrochemical growth of Mn-doped ZnO films with this combined hydrothermal-electrochemical method for the first time and the effect of manganese ion amount on the morphology and physical properties of ZnO films were characterized.

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3.2 Experimental

3.2.1 Materials

All the chemicals used were of analytical grade or of the highest purity commercially available. Manganese chloride tetrahydrate ($\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$) were obtained from Merck and zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) was purchased from Sigma-Aldrich. Dimethyl sulfoxide (DMSO) was supplied from Alfa Aesar. Indium Tin Oxide (ITO) ($\Omega < 5.0 \times 10^{-4} \text{ ohm.cm}$ ($R_s < 100 \text{ ohm/sq}$)) was purchased from Teknoma Ltd. Izmir, Turkey. Double distilled, high purity water was used from Milli-Q water (Millipore) system.

3.2.2 Synthesis and Characterization

Doped ZnO layers were grown on ITO-coated glass electrode ($1 \times 1 \text{ cm}^2$ area) in DMSO, water and 1:1 DMSO/water mixture. MnCl_2 was used as dopant metal source and baths with fixed $\text{Zn}(\text{NO}_3)_2$ concentration (50 mM) and different $[\text{Mn}^{2+}]$ to $[\text{Zn}^{2+}]$ ratios were prepared. Electrodepositions were carried out with a conventional 3 electrode cell system in a hydrothermal glass reactor (Büchiglasuster, picoclave) at constant potential. The reference electrode was Ag/AgCl saturated with KCl (Corr Instruments, S/N P11092) whereas Pt wire served as counter electrode. The substrate was cleaned ultrasonically by ethanol, acetone and distilled water prior to depositions. The growth temperature was 130°C . The potentiometric deposition was performed at -1.1 V vs Ag/AgCl reference electrode with a potentiostat/galvanostat (VSP, Biologic-Science Instruments).

The crystal structure and crystallinity of the samples were analyzed by X-ray diffraction (XRD) analysis using Bruker/D8 Advance with Cu $K\alpha$ radiation. The surface morphology of the films was examined with ZEISS Ultraplus Field Emission Scanning Electron Microscope (FE-SEM). The film composition was studied by X-Ray photoelectron spectroscopy (XPS, Thermo K-Alpha). The binding energies were calibrated by taking C1s binding energy (285 eV) as reference. The Mn content relative to Zn was calculated by integrating the area under the Zn $2p_{3/2}$ and Mn $2p_{3/2}$ curves.

3.3 Results and Discussion

3.3.1 Morphology

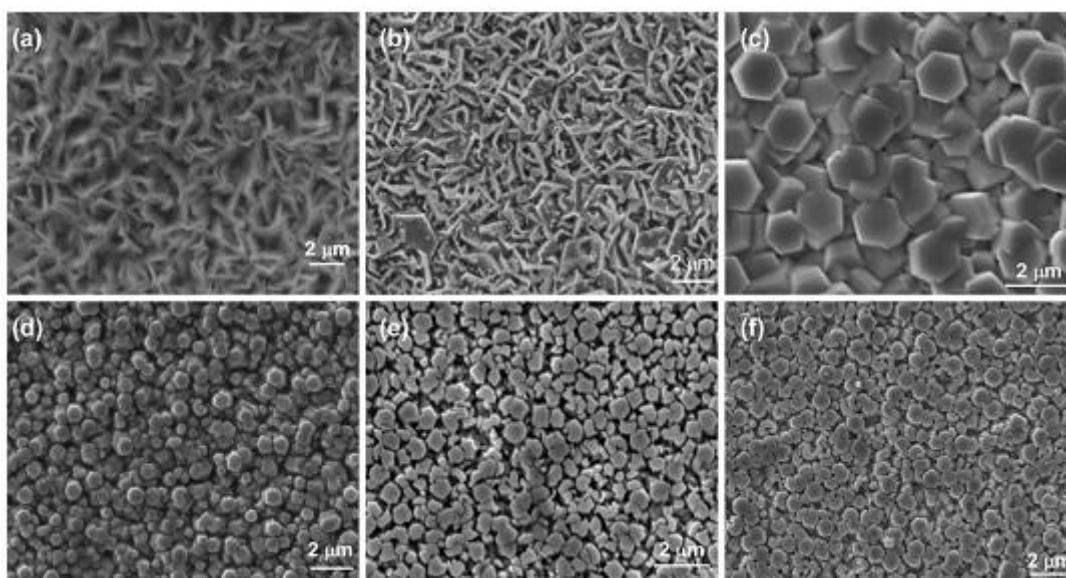


Figure 3.1 FE-SEM images of films prepared from baths with different feed ratios. a) only $\text{Zn}(\text{NO}_3)_2$ b) $[\text{Mn}(\text{II})]/[\text{Zn}(\text{II})]=0.2$ c) $[\text{Mn}(\text{II})]/[\text{Zn}(\text{II})]=0.4$ d) $[\text{Mn}(\text{II})]/[\text{Zn}(\text{II})]=0.6$ e) $[\text{Mn}(\text{II})]/[\text{Zn}(\text{II})]=0.8$ f) $[\text{Mn}(\text{II})]/[\text{Zn}(\text{II})]=1$.

We have investigated the affect of Mn^{2+} on the morphology of ZnO films with an electron microscope. Figure 3.1a shows SEM image of the ZnO film prepared from 50mM $\text{Zn}(\text{NO}_3)_2$ in DMSO: H_2O mixture. For this undoped ZnO film, formation of thick platelets with edges on the order of about 1-2 μm was observed. Rest of the Figure 3.1 displays as-prepared (Mn)-doped ZnO films deposited from baths with different Mn(II):Zn(II) feed ratios. Addition of Mn(II) into the electrodeposition bath also gave rise to platelets that were grown into each other with smaller sized edges which were ranging between 1.3 and 1.5 μm . When Mn(II) concentration was increased, fairly uniform, well-aligned hexagonal rods strongly oriented towards the c axis were observed. Crystals smaller in the (0001) faces were grown along $\langle 0001 \rangle$ direction with hexagonal caps. Further addition of Mn(II) into the mixture induced further reduction in the width-to-length ratio of the particles without triggering any change in the morphological characteristics of the crystals. Diameters of the hexagonal rods decreased gradually from about 1.7-1.4 μm to 0.7 μm with increasing Mn(II) concentration. On the other

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hand, increase in Mn(II) concentration does not affect the thickness of the films as seen in Figure 3.2.

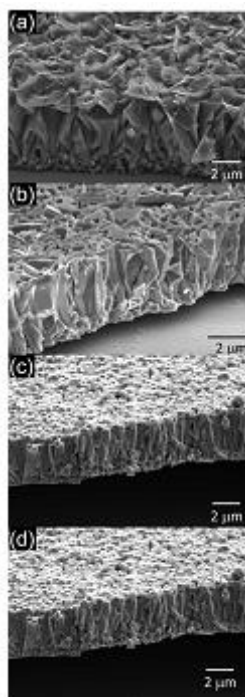


Figure 3.2 Cross-sectional FE-SEM images of the films prepared with different feed ratios. a) Only $\text{Zn}(\text{NO}_3)_2$, b) $[\text{Mn}(\text{II})]/[\text{Zn}(\text{II})]=0.2$ c) $[\text{Mn}(\text{II})]/[\text{Zn}(\text{II})]=0.6$ d) $[\text{Mn}(\text{II})]/[\text{Zn}(\text{II})]=1$.

3.3.2 Crystal Structure

The structure of the transition metal doped ZnO films were characterized by X-ray diffraction. For the sample prepared in the absence of Mn^{2+} , XRD pattern revealed typical three peaks which can be indexed to (100), (002) and (101) reflections of hexagonal Wurtzite ZnO structure {JCDPDS No. 0361451} without any other phase being detected (Figure 3.3), although (002) peak is highly intensified. The strong (002) peak observed in all of the samples indicated highly crystalline, well aligned doped ZnO particles that were preferentially grown vertically to the substrate in line with SEM images. The intensity ratio of (002) reflection to (100) reflection was 14 for the film prepared in the absence of Mn^{2+} . For all other Mn-doped ZnO films the same ratio was around 100. Regardless of the concentration of Mn(II) ions, no shift in the position of (002) peak hence in the lattice parameters was observed. It can be attributed either to similar radii of the two cations⁵⁴ (where Mn^{2+} ionic radius is 0.66 Å and

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those of Zn^{2+} ionic radius is $0.60\text{\AA}^{107}$) or to low doping level of manganese ions. It is already established for Cd-doped ZnO films that doping levels lower than 9 % does not induce a change in the lattice parameters.¹¹⁴

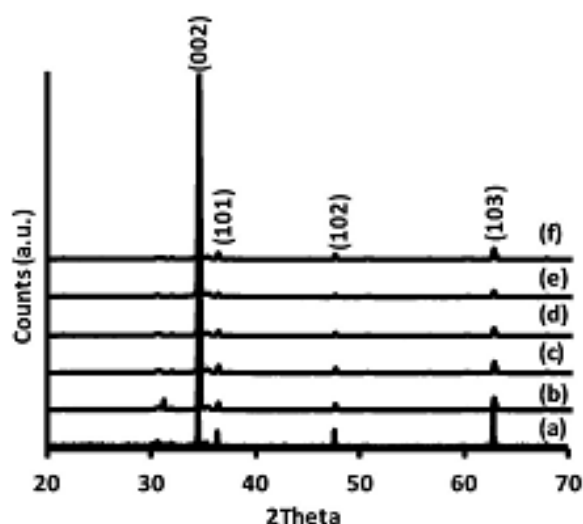


Figure 3.3 XRD patterns of films prepared from baths with different feed ratios. a) only $\text{Zn}(\text{NO}_3)_2$ b) $[\text{Mn}(\text{II})]/[\text{Zn}(\text{II})]=0.2$ c) $[\text{Mn}(\text{II})]/[\text{Zn}(\text{II})]=0.4$ d) $[\text{Mn}(\text{II})]/[\text{Zn}(\text{II})]=0.6$ e) $[\text{Mn}(\text{II})]/[\text{Zn}(\text{II})]=0.8$ f) $[\text{Mn}(\text{II})]/[\text{Zn}(\text{II})]=1$.

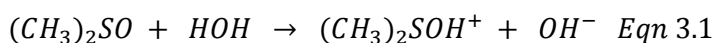
3.3.3 Crystal Growth

Surfactants or capping agents are commonly used to modify the morphology of the particles through passivation of one or more faces selectively at the expense of the others in the colloid science. We believe capping ability of $\text{Mn}(\text{II})$ ions together with the high temperature are the key actors in the formation of the obtained structures. Electrodeposition from nitrate precursors is driven by the reduction of nitrate as discussed in Chapter.1.2.5.⁸⁸

Tetrahedrally coordinated O^{2-} and Zn^{2+} ions stacked alternatively along the c axis make up the Wurtzite crystal structure.¹¹⁵ Due to this arrangement of atoms, ZnO possesses a negatively charged, basal $\text{O}-(0001)$ polar plane and a positively charged $\text{Zn}-(0001)$ plane. In addition, ZnO crystal growth rate was shown to be five times faster on the $\{0001\}$ planes than it is on the $\{1010\}$ and $\{0110\}$ planes⁸⁵ which would yield particles with a relatively high aspect ratio. Despite of this preferential growth direction it is possible to obtain 2-D ZnO structures in

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the presence of KCl from highly concentrated $\text{Zn}(\text{NO}_3)_2$ baths (100mM, 50mM).^{45,79} It is suggested that selective adsorption of Cl^- ions on the polar (0001) plane is responsible for the redirected growth on the nonpolar (1010) plane. However, Pradhan and Leung observed an opposite behavior with dilute $\text{Zn}(\text{NO}_3)_2$ solutions.⁷⁹ They explained the contradictory behavior at low $\text{Zn}(\text{NO}_3)_2$ electrolyte concentrations with hydroxylation kinetics. It is suggested that slower hydroxylation reaction (formation of $\text{Zn}(\text{OH})_2$) at low electrolyte concentrations provides time for desorption of Cl^- ions from the polar surface. Since the hydroxylation reaction is slower, as soon as zinc hydroxide is formed, it is converted to zinc oxide leading to the formation of 1-D materials. In hydrothermal-electrochemical synthesis we observed preferential growth along (0001) plane perpendicular to the substrate even at high electrolyte concentrations with or without KCl (100 mM Zn, 100 mM KCl). We believe this concentration independent morphology can be explained by the combined effect of desorption of Cl^- at low concentrations and the increased rate of dehydration reaction at even higher temperature and pressure. The dehydration reaction, conversion of the initially formed zinc hydroxide to zinc oxide, is already shown to be increasing with deposition temperature noticeably.⁸⁹ Development of zinc oxide seed crystals might be even faster at 130°C. Since Cl^- ions does not alter the morphology of the crystals, Mn(II) ions are responsible for the transformation from coalesced hexagonal platelets to formation of thinner rods. Being a polar basic aprotic solvent DMSO also is a major component in controlling the growth of ZnO structures obtained by electrodeposition.¹¹⁶⁻¹¹⁷ In these studies, DMSO was shown to be also inducing anisotropic growth. A mass of DMSO is most likely absorbed on to the polar plane, hence restrains the growth along (0001) plane. Hence, ZnO particles obtained in the absence of Mn(II) ions in DMSO- H_2O mixture are in the form of platelets. DMSO also behaves as a reactant by increasing the OH^- ion concentration according to the following equation¹¹⁸:



Higher OH^- concentration also accelerates the hydroxylation reaction (eqn 1.9) as well as nucleation rate. However, Mn(II) addition stimulates formation of hexagonal rods. It is very important to note that although the mixture contains high amount of DMSO, the final product is the film composed of rods. Presence of Mn^{2+} in the mixture together with the reasons given above results in the formation of rod structures. It is most likely that the Mn(II) species in the deposition solution are adsorbed onto the nonpolar surfaces of ZnO parallel to the *c* axis and

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hence preventing the growth in the lateral direction. Below 20 mM Mn(II) ions are not sufficient to induce thinner rod formation (Figure 3.1b). As Mn(II) concentration increases above 20 mM, lateral growth is far more restricted hence diameter of hexagonal rods decreases as it is observed for Cr³⁺-doped ZnO particles before.¹¹⁹ Similar observation was also reported by Lincot *et al.*^{120,121} In their manuscripts related with ZnO deposition in the presence of lanthanide ions, they have reported that increase in the lanthanide concentration and formation of hydroxide layer resulted in lower rod density. Formation of Mn related species in between the rods during the deposition might be responsible for thinner rods in our films. We have not, however, found any evidence of hydroxide layer beneath the ZnO layers when we analyze the films with electron microscope and Energy Dispersive X-ray Fluorescence (EDX). On the other hand, SEM and EDX investigations revealed the presence of Mn containing precipitates on small areas, particularly at the edges, on some films (data not shown) and this could be the evidence for the growth of thinner ZnO rods on the surface as a result of the absorption of Mn-species on lateral surface of ZnO structures.

3.3.4 XPS

The composition of the Mn-doped ZnO films and the chemical bonding states of the metals were examined by studying the Zn 2p and Mn 2p core level XPS spectra. The peak positions were same for all of the films. Figure 3.4a displays Zn 2p XPS spectrum of the film prepared with lowest [Mn(II)]/[Zn(II)] feed ratio. There appear two peaks centered around 1022.45 and 1045.38 which corresponds to Zn 2p_{3/2} and 2p_{1/2} respectively matching the binding energy of Zn²⁺ in ZnO. The Zn 2p binding energies are very similar for all of the films. The position of the Zn 2p_{3/2} peak does not vary with etching time indicating good chemical stability of Zn through the film. Mn 2p core level XPS spectrum of the same film is shown in Figure 3.4b. It can be seen that there are three peaks appearing at 641.62, 652.91 and 655.46 eV which are obtained similarly for all other samples.

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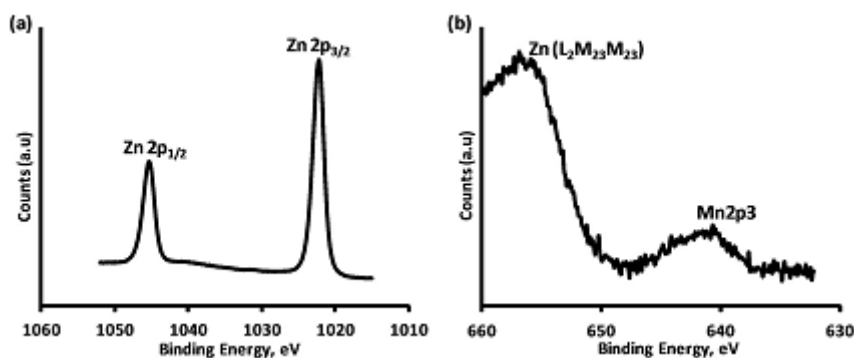


Figure 3.4 The XPS spectra of Mn-ZnO film prepared by $[\text{Mn(II)}]/[\text{Zn(II)}]$ ratio of 0.2 a) Zn 2p scan b) Mn 2p scan.

The peak centered at 641.62 is at higher binding energy than Mn^{2+} ($2p_{3/2}$) (~ 641 eV) found in Mn-doped ZnO samples earlier and at lower binding energy than the value which is commonly observed for Mn^{3+} ($2p_{3/2}$) (~ 642 eV) in literature.^{110,112,122,111,123} Nesbitt and Banerjee proposed 640.8 ± 0.3 eV as the binding energy of Mn^{2+} ($2p_{3/2}$) after a detailed study and literature search on XPS spectra of Mn(2p).¹²⁴ Plus, they determined that the position of the Mn^{3+} ($2p_{3/2}$) peak of oxides range between 641.7 and 641.9 eV. An earlier study on the transition metal oxide spectra assigns 641.7 eV to the $2p_{3/2}$ peak to manganese 3+ oxidation state both in Mn_2O_3 and mixed metal oxide Mn_3O_4 .¹²⁵ In addition, the 11.29 eV spin orbit splitting between the Mn $2p_{3/2}$ and Mn $2p_{1/2}$ is in agreement with previous reports on XPS spectrum of Mn_3O_4 .^{126,127} Hence, the peaks at 641.62 and 652.91 eV can be attributed to $2p_{3/2}$ and $2p_{1/2}$ orbitals in the mixed valence oxide. Metallic manganese formation was not observed (637.7 eV).¹⁰⁹ According to the XPS results, the real manganese content in the films is around 3% regardless of the Mn(II) concentration in the deposition solution (Table 3.1).

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Table 3.1 The Mn content in the films obtained by different feed ratios. (determined by XPS)

Mn(II):Zn(II)	Mn %	Zn%	Mn(II):Zn(II)
In the deposition bath	In the film	In the film	In the film
0.2	3.3	96.7	0.03
0.4	3.26	96.74	0.033
0.6	2.88	97.12	0.029
0.8	3.83	96.17	0.039
1	3.64	96.34	0.037

3.4 Conclusions

Hydrothermal-electrodeposition at 130°C was successfully employed to produce Mn-doped ZnO films. Hexagonal Wurtzite ZnO structure growing towards (002) direction was obtained with no impurity phases. The lattice parameters are not altered on addition of Mn. Mn-doping affected the crystal growth enhancing formation of particles with high aspect ratio. As concentration of Mn(II) in the deposition bath increased, coalesced platelets were transformed into hexagonal particles of smaller diameter. XPS results display that Mn is present both in divalent and trivalent state in ZnO lattice.

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Chapter 4 Synthesis and Characterization of Hierarchical ZnO Structures by A Single-Step Electrodeposition under Hydrothermal Conditions

4.1 Introduction

Interest in ZnO has been dramatically increased in the last decade due to its high exciton binding energy (60meV) and wide band-gap (3.3eV) that is tunable through doping with rare earth elements, metal ions or *chalcogens* such as sulfur.⁷⁴ This tunability permits ZnO to possess a wide range of adjustable physical properties like conductivity, room temperature ferromagnetism, high transparency, chemical sensing, conductivity which make it possible to fabricate electronic, optoelectronic, electrochemical, and electro-mechanical nanodevices.¹²⁸ Furthermore, the morphology of ZnO particles can also be modified by adjusting growth conditions. Controllable morphology adds another charm to ZnO since effectiveness and efficiency of the fabricated product depends on the shape and size of the constituent particles. Especially, 1D ZnO nanostructures such as nanorods, nanowires, nanoribbons and nanotubes have become very attractive for optoelectronic device applications due to their high accessible area and efficient diffusion path of charge carriers.⁷⁴ In comparison to 1D nanostructures, hybrid morphologies of nanosheets and nanowires or branched structures which form hierarchical architectures are becoming more desirable for sustainable energy applications like dye-sensitized solar cells (DSSCs) and solar powered water splitters. These hierarchical assemblies combine characteristic aspects of nanometer and micrometer sized building blocks, provide higher surface area (allows higher dye loading in DSSCs) and reduced charge recombination which allows enhanced light absorption and faster charge separation, hence increase the overall efficiency of the device.^{129,130,131}

Several methodologies have been reported to obtain hierarchical ZnO nanostructures including vapor transport and condensation technique¹³², sequential hydrothermal processes^{131,133} and electrodeposition^{129,130,134,135}. Vapor-based techniques require high vacuum and high

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temperatures and they might involve introduction of catalysts which might affect the physical properties of the product. On the other hand, multi-step procedures are employed to produce hierarchical ZnO nanostructures via solvothermal processes or electrodeposition. Xu *et al.* reported electrochemical deposition of ZnO nanoneedles on surfaces of ZnO nanosheets, nanorods, and nanoneedles grown a priori by electrodeposition in the presence of different additives.¹³⁴ Similarly, both C. Yao *et al.*¹²⁹ and Wang's group¹³⁵ demonstrated formation of hierarchical ZnO structures by electrodeposition of ZnO nanorods using previously electrodeposited ZnO microsheets as the working electrode. Correspondingly, hydrothermal methods involve a series of nucleation and growth sequences¹³³ and also might require introduction of surfactants¹³¹. Xu *et al.* also constructed hierarchical ZnO structures by combining a low-temperature electrodeposition process and subsequent aqueous chemical growth.¹³⁰ However, there are no reports on synthesis of hierarchical ZnO structures with a single electrodeposition step, to the best of our knowledge. In this chapter, synthesis of hierarchical ZnO architectures with a facile, single-pot process which combines benefits of hydrothermal conditions and electrochemistry at a single step is reported. The key role of $\text{Cd}(\text{CH}_3\text{COO})_2$ ratio in the deposition bath and $[\text{Cd}(\text{CH}_3\text{COO})_2/\text{Zn}(\text{II})]$ to obtain hierarchical ZnO architectures is discussed in detail.

4.2 Experimental

4.2.1 Materials

All the chemicals used were of analytical grade or of the highest purity commercially available. Cadmium acetate hexahydrate ($\text{Cd}(\text{CH}_3\text{COO})_2 \cdot 6\text{H}_2\text{O}$) was obtained from Merck and zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) was purchased from Sigma-Aldrich. Indium Tin Oxide (ITO) ($\Omega < 5.0 \times 10^{-4} \text{ ohm.cm}$ ($R_s < 100 \text{ ohm/sq}$)) was purchased from Teknoma Ltd. Izmir, Turkey. Double distilled, high purity water was used from Milli-Q water (Millipore) system.

4.2.2 Synthesis and Characterization

Cd-doped ZnO layers were grown on ITO (Indium tin oxide) coated glass electrode ($1 \times 1 \text{ cm}^2$ area) by cathodic electrodeposition in an aqueous solution of $\text{Cd}(\text{CH}_3\text{COO})_2$ and $\text{Zn}(\text{NO}_3)_2$ mixture in different proportions. The $\text{Zn}(\text{II})$ concentration was fixed to 50 mM and

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[Cd(II)]/[Zn(II)] ratio was varied between 0.2 and 1. A conventional 3-electrode cell system in a hydrothermal glass reactor (Büchiglasuster, modified picoclave) was used for the electrochemical deposition. The volume of the reactor was 100 ml. The reference electrode was Ag/AgCl saturated with KCl (Corr Instruments, S/N P11092) whereas Pt wire served as counter electrode. The substrate was cleaned ultrasonically by ethanol, acetone and distilled water prior to depositions. Electrodepositions were carried out at constant potential of -1.1V at 130°C for 30 minutes on a potentiostat/galvanostat (Biologic-Science Instruments, VSP model).

The crystal structure and crystallinity of the samples were analyzed by X-ray diffraction (XRD) method using Bruker/D8 Advance with DaVinci with Cu K α radiation. The surface morphology of the films was examined with ZEISS Ultra Plus Field Emission Scanning Electron Microscope (FE-SEM). The film composition was studied by X-Ray Photoelectron Spectroscopy (Thermo K-Alpha, XPS). Binding energy of C1s (285 eV) peak served as a reference to calibrate the binding energies. The area under the Cd 2p and Zn 2p curves was integrated after performing a Gaussian-Lorentzian fitting to calculate the relative Cd content in the films. Both the top surface of the films and inner layers were measured after 540 s of etching with Ar⁺. Raman scattering experiments were carried out using a Renishaw Raman Microscope system at room temperature. 532 nm laser was used for excitation.

4.3 Results and Discussion

4.3.1 Morphology

Cd(CH₃COO)₂ concentration was varied to provide [Cd(II)]/[Zn(II)] ratio between 0.2 and 1 to investigate the effect of introducing Cd²⁺ and CH₃COO⁻ to the aqueous electrodeposition bath of ZnO films. Figure 4.1 and 4.2 show typical FE-SEM images of the as-prepared films on ITO substrates prepared by 30 minutes deposition at 130°C, -1.1V vs Ag/AgCl. When there is no Cd(CH₃COO)₂ in the precursor solution, vertically aligned ZnO rod arrays with hexagonal facets were obtained (data not shown). As soon as Cd(CH₃COO)₂ was included in the deposition solution hierarchical structures with different symmetries were observed. When [Cd(II)]/[Zn(II)] ratio was 0.2, besides the array of vertically aligned ZnO rods, larger assemblies on this nanorod array were observed (Figure 4a-c). Larger structures were formed by arrangement of 4 extensions joined together at their base perpendicular to each

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other. Each extension is composed of rods fused together on their lateral side. In between these extensions, secondary rods with hexagonal tips have grown at various angles (Figure 4a). The length of each assembly was varied between 15-20 μm . Structures that are even $\sim 42 \mu\text{m}$ long were detected (Figure 4b). Secondary nanorods were $\sim 700 \text{ nm}$ long with $\sim 300 \text{ nm}$ diameters. Figure 4c shows some variations in the structure of larger assemblies. There exists a single $5 \mu\text{m}$ long extruded hexagon-channel with multiple nanorod arrays on all the 6 sides of the hexagon. The upper surface of the nanorods seemed to be eroded. In current synthesis conditions, the surface of the rods might be eroded as explained in further paragraphs. These surface eroded rods are assembled to each other to form microchannels. In addition to these micro-channels, star-flower like structures were also present (Figure 4.1c). Each bunch was composed of closely packed rods with diameters of $\sim 400 \text{ nm}$ and $1 \mu\text{m}$ long. These flower-like ZnO architectures seemed to root both on the nanorod matrix and at the vertex of the hierarchical structures.

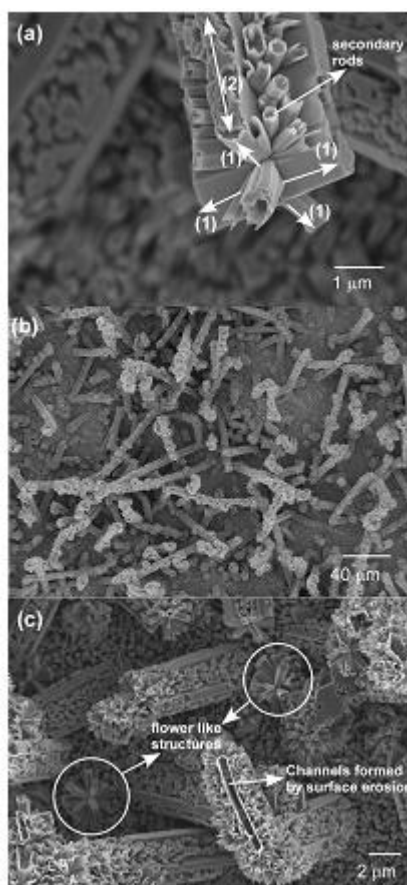


Figure 4.1 FE-SEM images of the Cd₂ZnO film prepared from a bath with a feed ratio $[\text{Cd(II)}]/[\text{Zn(II)}] = 0.2$. at a) 30K magnification, b) 1.5K magnification, c) 10K magnification.

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Morphologies of the doped ZnO products varied with changing $\text{Cd}(\text{CH}_3\text{COO})_2$ concentration. Hierarchical, micrometer long, joined micro-channels could only be obtained with $[\text{Cd}(\text{II})]/[\text{Zn}(\text{II})]=0.2$. When $[\text{Cd}(\text{II})]/[\text{Zn}(\text{II})]$ ratio was 0.4, main morphology was structured by hexagonally faceted ZnO nanorod arrays with diameters ranging from 700 nm to 900 nm (Figure 4.2a). On the surface of this nanorod matrix, 1D and 2D ZnO crosses were observed. 1D hierarchical ZnO assemblies were composed of two micrometer long rods with matching diameters that were fused together in a head-to-head configuration forming dumbbell-like twinned ZnO structures. 2D ZnO structures were shaped by micrometers-long intersecting ZnO rods with 6-fold and 2 different 4-fold symmetries. When $[\text{Cd}(\text{II})]/[\text{Zn}(\text{II})]$ ratio was 0.6, entire film was composed of densely packed 1D ZnO assemblies at random orientations and 2D ZnO crosses were also spotted (Figure 4.2b). Morphology of the ZnO film prepared with a feed ratio of $[\text{Cd}(\text{II})]/[\text{Zn}(\text{II})]=0.8$ (Figure 4c) is very similar to that of the film obtained when $[\text{Cd}(\text{II})]/[\text{Zn}(\text{II})]=0.4$. As $\text{Cd}(\text{CH}_3\text{COO})_2$ concentration was increased further to achieve a feed ratio of $[\text{Cd}(\text{II})]/[\text{Zn}(\text{II})] = 1$, star flower-like structures that are made up of ZnO nanorods on a matrix of randomly oriented ZnO nanorods were detected (Figure 4.2d).

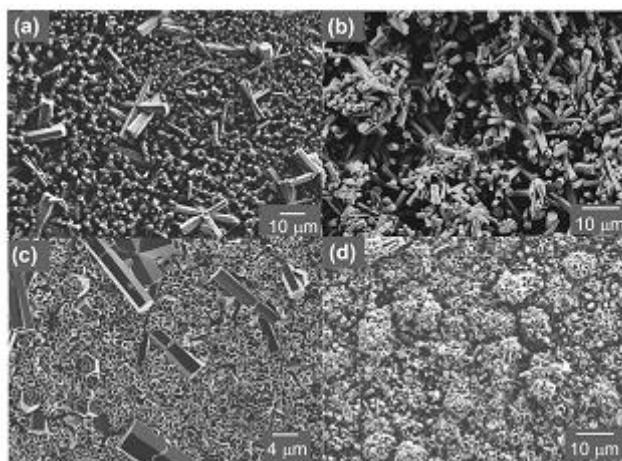


Figure 4.2 FE-SEM images of the films prepared with different feed ratios. a) $[\text{Cd}(\text{II})]/[\text{Zn}(\text{II})]=0.4$, b) $[\text{Cd}(\text{II})]/[\text{Zn}(\text{II})]=0.6$, c) $[\text{Mn}(\text{II})]/[\text{Zn}(\text{II})]=0.8$, d) $[\text{Cd}(\text{II})]/[\text{Zn}(\text{II})]=1$.

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4.3.2 Crystal Structure

The crystal structures of the deposited films were examined by X-Ray diffraction and the patterns are presented in Figure 4.3. The anisotropic morphology and orientation can be deduced from relative intensities of the diffraction peaks. For all of the films, hexagonal ZnO crystal structure was obtained with typical intense peaks that can be indexed to (100), (002) and (101) reflections along with weaker (102) and (110) reflections (JCPDS card, No. 36-1451). Although appearance of strong (100) and (101) reflections implies lateral growth is enhanced for Cd_doped ZnO films, preferential growth direction varies with Cd(II) concentration. No reflections that belong to secondary phases such as CdO or Cd (metal) due to introduction of Cd(II) ions to the solution could be detected in the XRD diagrams. When Cd(II) is introduced to the deposition solution with lowest $[Cd(II)]/[Zn(II)]$ ratio (0.2), (002) reflection is distinguished with highest intensity. The stronger (002) peak points out growth along perpendicular direction to the film surface which is well consistent with FE-SEM image displaying vertically aligned ZnO nanorod matrix (Figure 4.1a). However, higher Cd(II) amounts stimulates a change in the preferred orientation of growth from (002) to (100) direction until $[Cd(II)]/[Zn(II)]$ ratio is 1 as reflected from relative intensities. For these films, intensity of the (100) reflection is highly enhanced at the expense of (002) and (101) peaks which suggests preferential a -axis growth. Most of the ZnO rods have grown with their c -axes parallel to the substrate surface as revealed by XRD diagrams which are in line with FE-SEM pictures (Figure 4.2). When Cd(II) and Zn(II) amount is equal in the deposition solution, no preferential growth axis is present indicating random orientation. For this film, it can be seen that intensity of (002) and (101) reflections are increased to match that of (100) peak. Furthermore, Cd(II) concentration does not induce a significant shift in the position of main Bragg reflections which might suggest a limitation in the amount of Cd(II) that can be incorporated. M. Tortosa *et al.* established that doping levels lower than 9 % does not induce a change in the c -axis lattice parameters of Cd-doped ZnO.¹³⁶ XPS analysis (details discussed below) displayed that Cd(II) amount incorporated into the films is around 1 % regardless of the Cd(II) concentration in the deposition solution.

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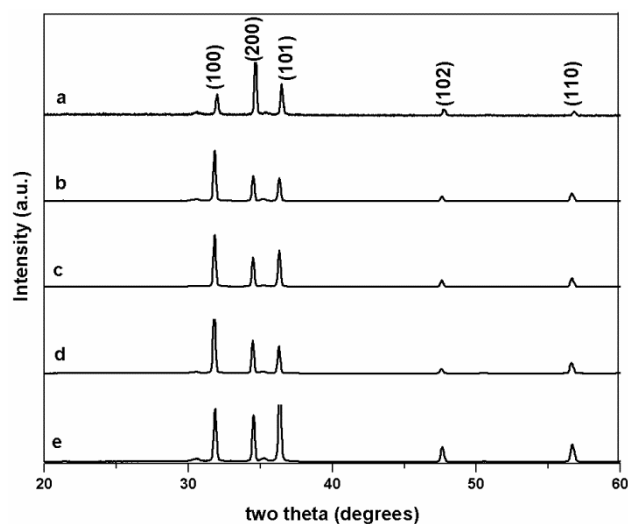


Figure 4.3 XRD patterns of films prepared from baths with different feed ratios. a) $[\text{Cd(II)}]/[\text{Zn(II)}] = 0.2$, b) $[\text{Cd(II)}]/[\text{Zn(II)}] = 0.4$, c) $[\text{Cd(II)}]/[\text{Zn(II)}] = 0.6$, d) $[\text{Cd(II)}]/[\text{Zn(II)}] = 0.8$, e) $[\text{Cd(II)}]/[\text{Zn(II)}] = 1$.

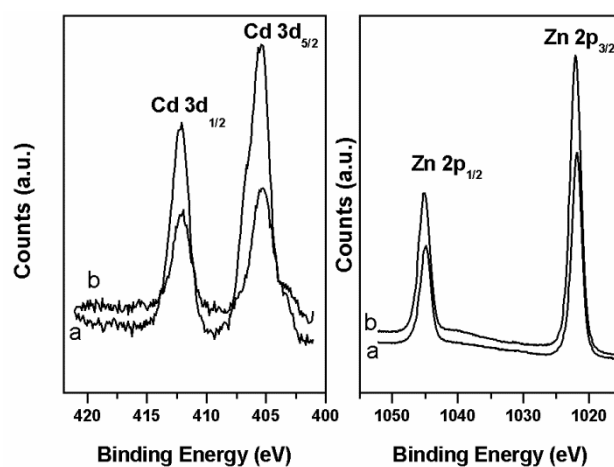


Figure 4.4 The XPS spectra of Cd_ZnO film prepared by $[\text{Cd(II)}]/[\text{Zn(II)}]$ ratio of 0.2; Cd 3d scan(left) and Zn 2p scan (right). Line a: Surface, Line b: After etching for 720 seconds.

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4.3.3 XPS

The composition of the Cd-doped ZnO films and the chemical bonding states of the metals were examined by studying the Zn 2p and Cd 3d core level XPS spectra. The peak positions were same for all of the films. Figure 4.4 displays Zn 2p XPS (right) spectrum of the film prepared with lowest $[\text{Cd(II)}]/[\text{Zn(II)}]$ feed ratio as a representative and Cd 3d core level XPS spectrum of the same film (left). As can be seen in Figure 4.4 no traces indicating presence of metallic Zn or metallic cadmium were encountered. Instead, both metals were found to be existing in oxidized states. Zn 2p XPS spectrum of the film prepared with lowest $[\text{Cd(II)}]/[\text{Zn(II)}]$ feed ratio displays two peaks centered around 1022.45 and 1045.38 eV which corresponds to Zn 2p_{3/2} and Zn 2p_{1/2} respectively matching the binding energy of Zn²⁺ in ZnO.¹³⁷ The Zn 2p binding energies are very similar for all of the films. Etching the film to obtain chemical information from deeper regions did not induce any change in the position of these peaks which indicates good chemical stability of Zn through the films. Cd 3d core level XPS spectra of Cd-ZnO films from the surface of the films reveal two peaks at about 405 eV (Cd 3d_{5/2}) and 412 eV (Cd 3d_{3/2}) which are separated by binding energy of 7 eV which is consistent with what was reported for Cd-ZnO^{53, 138}, CdO^{139, 140} and Cd(OH)₂^{141, 142}. The Cd 3d binding energies were also very similar for all of the films both on the surface and even after surface etching of 720 seconds binding energies were not shifted. Only, intensity of the peaks decreased to 50-80 % of the initial values. Figure 4.5 displays surface O 1s XPS spectra of the Cd_doped films as well as the spectra after etching. On the surface of all of the films, peaks appear at 531 eV and 532 eV. After surface etching, intensity of the higher binding energy peaks were highly reduced and the lower energy peaks were shifted to lower energies to around 530 to 531 eV and dominated the spectra. The peak at higher energy is usually attributed to adsorbed oxygen and/or OH moieties on the surface of ZnO¹⁰⁰ and also reported for Cd(OH)₂¹⁴³. The peak localized at lower energy is usually attributed to O²⁻ ions in the Wurtzite crystal structure of hexagonal ZnO lattice⁷⁹ and also assigned to the oxygen in Cd(OH)₂¹⁴² and to adsorbed oxygen on CdO surface¹⁴¹. In addition, oxygen binding energy that is coordinated to Cd (CdO), is usually reported to appear around 529 eV.^{141,143} Since neither XRD nor Raman spectroscopy analysis (discussed below) showed any evidence of CdO and/or Cd(OH)₂ formation, the peaks on the surface can be ascribed to Zn-OH and the peaks in the deeper levels to Zn-O-Zn.

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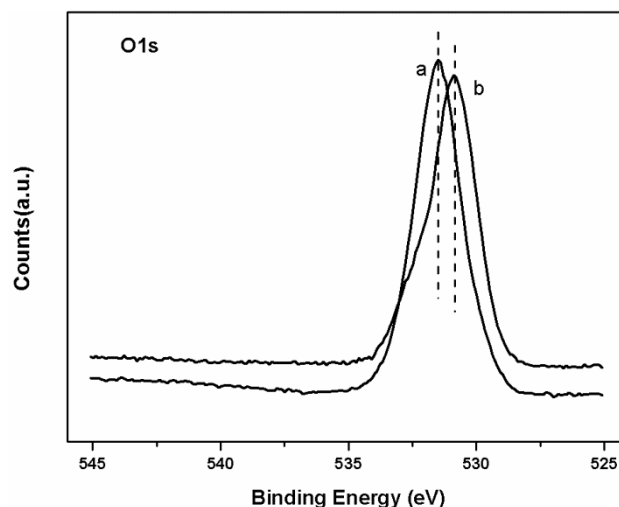


Figure 4.5 The XPS spectrum (O 1s scan) of Cd_ZnO film prepared by [Cd(II)]/[Zn(II)] ratio of 0.2. Line a: Surface, Line b: After etching for 720 seconds.

4.3.4 Raman

The presence of secondary phases and the effect of doping on the structure of ZnO films were further investigated by Raman spectroscopy. Raman spectra obtained at room temperature for undoped ZnO films and as-prepared Cd-doped ZnO films deposited from baths with different [Cd(II)]:[Zn(II)] feed ratios in the range of 150 and 1000 cm^{-1} are displayed in Figure 4.6. The Raman bands of the undoped ZnO film are located at 333, 377 and 437 cm^{-1} . The low intensity peak at 331 cm^{-1} and the peaks observed at 377 and 437 cm^{-1} for undoped ZnO can be indexed to second order scattering, $A_1(\text{TO})$, and $E_2(\text{high})$, respectively; where $E_2(\text{high})$ mode dominates and indicates Wurtzite ZnO crystal structure.^{144,145,48} The broad feature around 479 cm^{-1} was observed for ZnO nanorods in literature and attributed to surface optical phonons.^{47,146} When Cd(II) was introduced into the electrodeposition solution, Raman spectrum of the films deposited displayed an additional broad band between 500 and 600 cm^{-1} centered around 579 cm^{-1} . Earlier, similar behavior was reported for Mn_doped ZnO⁵⁰, N_doped ZnO¹⁴⁷ and referred as anomalous since it was not present in pure ZnO Raman spectrum. Dem'yanets *et al.* discussed that this band is due to the resonance of an overtone of the Raman forbidden mode B_1 with electronic transitions of the Mn^{2+} ion for Mn_doped ZnO.⁵⁰ The appearance of the silent mode was also explained by the breakdown of crystal symmetry induced by defects and impurities by Manjón *et al.*¹⁴⁸ Since the silent mode is observed only

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for the doped films, it can be concluded that the structural defects introduced by Cd(II) doping are responsible for symmetry breakdown rather than the synthesis process.

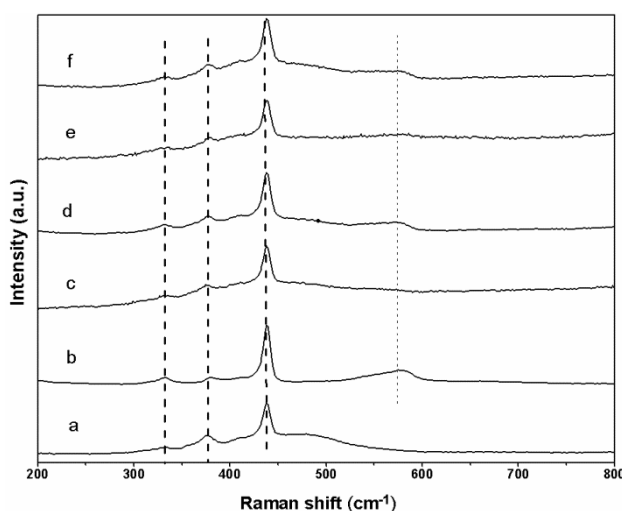


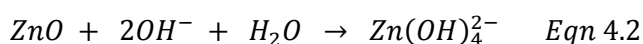
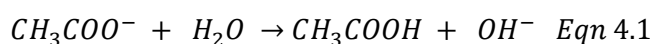
Figure 4.6 Micro-Raman spectra of the Cd_doped ZnO films. a) 50mM $\text{Zn}(\text{NO}_3)_2$, b) $[\text{Cd}(\text{II})]/[\text{Zn}(\text{II})]=0.2$, c) $[\text{Cd}(\text{II})]/[\text{Zn}(\text{II})]=0.4$, d) $[\text{Cd}(\text{II})]/[\text{Zn}(\text{II})]=0.6$, e) $[\text{Cd}(\text{II})]/[\text{Zn}(\text{II})]=0.8$, f) $[\text{Cd}(\text{II})]/[\text{Zn}(\text{II})]=1$.

4.3.5 Crystal Growth

The aforementioned results clearly reveal that ZnO crystal growth habit drastically changes in the presence of $\text{Cd}(\text{CH}_3\text{COO})_2$. To determine whether Cd^{2+} or CH_3COO^- ions are responsible for the induced morphology, additional depositions under identical conditions with either adding $\text{Cd}(\text{NO}_3)_2$ ($[\text{Cd}(\text{II})]/[\text{Zn}(\text{II})] = 0.2$) or NaCH_3COO ($[\text{CH}_3\text{COO}^-]/[\text{Zn}(\text{II})]=0.4$) on $\text{Zn}(\text{NO}_3)_2$ solution were performed. Hexagonal nanorods have formed in the presence of $\text{Cd}(\text{NO}_3)_2$ (Figure 4.7a). The upper surface of the nanorods seemed to be eroded. However, in the presence of NaCH_3COO , besides hexagonal nanorods, also star-flower shaped ZnO architectures composed of rods have grown (Figure 4.7b). Surface erosion is observed also for this film which results in residues that look like protruding ‘nano-tips’ on the top surface of nanorods. These nano-tips just like the ones on the nanorods of the hierarchical structures ($[\text{Cd}(\text{II})]/[\text{Zn}(\text{II})]=0.2$) (Figure 4.1) point out both selective growth direction along the c-axis and selective etching on Zn-rich, polar (0001) face. It is well-established that due to the crystal

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anisotropy of Wurtzite structure, ZnO possesses a negatively charged, basal O-(000 $\bar{1}$) polar plane and a top tetrahedron corner-exposed, positively charged Zn-(0001) plane with lateral faces (parallel to the c-axis) consisting of a nonpolar{10 $\bar{1}$ 0}face. Taking the crystal structure and the form of element of the coordination polyhedron exposes at different interfaces, W.J. Li *et al.* determined the following relationship between growth rate through various facets of ZnO; $V_{<0001>} > V_{<01\bar{1}1>} > V_{<01\bar{1}0>} > V_{<01\bar{1}1>} > V_{<000\bar{1}>}$.¹⁴⁹ Hence, (002) is the preferential growth direction. In addition, the “low-symmetry” nonpolar faces, with 3-fold coordinated atoms are the most stable ones, whereas the polar ones are metastable. The structural surface metastability of the polar surface results in different dissolution velocities on different facets. The etching rate of the meta stable Zn-rich polar face (0001) is much faster than that of the side planes which allows selective dissolution of rod core on (0001) face at high pH values.^{99, 43} Electrodeposition of ZnO from nitrate baths follows the mechanism explained in Chapter 1.2.5 (eqn 1.7-10) Reduction of nitrate ions increases OH $^-$ concentration (eqn 1.8) which causes precipitation of zinc hydroxide (eqn 1.9) which acts as primary seeds for further growth. Zn(OH) $_2$ is later dehydrated to produce ZnO (eqn 1.10) and by adsorption of additional growth units ZnO crystals continue to grow. Reduction of nitrate ions in the close proximity of the electrode surface results in an increase of the local pH on the surface of the films. Surface of the rods is dissolved at high pH and residues (protruding nanotips) remain on the surface of rods. Acetate ion, on the other hand, increases bulk OH $^-$ concentration and contributes to the etching of of the rods from the top surface according to the following equations:



However, the micrometer long micro-channels were not spotted in either of the films. These facts reveal that acetate ion has the key role in the formation of hierarchical structures yet it shares the main act with Cd $^{2+}$ ions.

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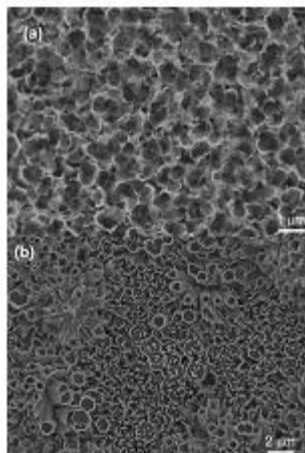


Figure 4.7 FE-SEM images of the a) Cd_ZnO film prepared in the presence of $\text{Cd}(\text{NO}_3)_2$, b) ZnO film prepared in the presence of NaCH_3COO .

To better understand formation of hierarchical structures in the presence of $\text{Cd}(\text{II})$, the particle growth was analyzed through time-dependent deposition experiments with $[\text{Cd}(\text{II})]/[\text{Zn}(\text{II})] = 0.2$. Formation of the hierarchical structures on a ZnO nanorod matrix was observed even in the first minute of the deposition (Figure 4.8a). Twinned-nanorods were arranged together very tightly to form irregular shapes of lengths ranging from a few micrometers to $10\text{ }\mu\text{m}$. After 10 minutes, densely packed twinned-nanorods grew laterally and fused together to form sheets on the surfaces (Figure 4.8b). In between these sheets, there were many more secondary nanorods that have grown from the junction point of the twinned structure. These structures continue to grow and form micrometer-long structures in 30 minutes. However, as concentration of $\text{Cd}(\text{CH}_3\text{COO})_2$ was increased 1D twinned-rods, 2D-ZnO crosses and star flower-like ZnO structures were obtained. Formation of the hierarchical structures together with ZnO nanorod matrix even in the first minute of the deposition suggests morphology is also controlled by nucleation and growth in aqueous solution in the presence of $\text{Cd}(\text{CH}_3\text{COO})_2$. When $[\text{Cd}(\text{II})]/[\text{Zn}(\text{II})]$ ratio is 0.2, free Zn^{2+} ions that are not precipitated as $\text{Zn}(\text{OH})_2$ (eqn 1.9) probably forms zinc acetate colloids under hydrothermal conditions. Since acetate concentration is the limiting factor number of nuclei initially formed is low. These initial nuclei come together to form twinned crystals. Wang *et al.* reported formation of twinned ZnO crystals in the presence of H_2O , weak base, KOH or NaOH under hydrothermal conditions.¹⁵⁰ They discussed K^+ and Na^+ ions act as a ‘bonding bridge’ between the growth units to give rise to formation of dumbbell like twinned crystals under

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hydrothermal conditions.¹⁵⁰ It is also shown that positively charged $\text{Cd}(\text{NH}_3)_6^+$ ions bound on the negatively polarized (000^-1) planes act as bonding bridge to join two (000^-1) planes, hence cause the twining of ZnO crystal.¹⁵¹ It is possible that also in our experiments, positively charged Cd^{2+} that are adsorbed on negatively charged, basal O-(0001) polar plane serve as the bonding bridge. Then these structures continue to grow along the c -axis and are fused together and form long extensions since there are still excess zinc ions in the solution. When $[\text{Cd(II)}]/[\text{Zn(II)}]$ ratio is increased, acetate concentration increases as well and even outnumbers total $[\text{Zn(II)}]$ at a ratio of $[\text{Cd(II)}]/[\text{Zn(II)}]=0.6$. Hence, more and more nuclei form initially. In addition, higher acetate concentration will lead into higher pH value (eqn 4.1), which will also result in supersaturation. Under supersaturated conditions, the nucleation rate will be higher as a result of lowered nucleation activation energy.⁴³ In those supersaturated solutions, nuclei tend to aggregate to give rise to 2D-crosses or flower-like architectures formed from thin rods without being able to grow into hierarchical structures.

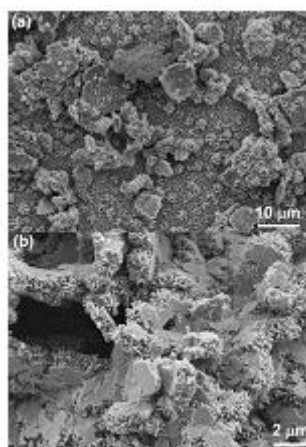


Figure 4.8 FE-SEM images of the film prepared with a feed ratio of $[\text{Cd(II)}]/[\text{Zn(II)}]=0.2$ in a) 1 minute, b) 10 minutes.

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4.4 Conclusions

In summary, we report a single-step hydrothermal-electrochemical deposition route to produce hierarchical ZnO architectures on ITO substrate. It required introduction of $\text{Cd}(\text{CH}_3\text{COO})_2$ into deposition bath to build such complicated structures. Both Cd^{2+} and CH_3COO^- ions play crucial roles to induce formation of hierarchical ZnO structures. Cd^{2+} ions act as bridges that combine growth units and consequently dumbbell like twinned ZnO crystals forms. In addition, acetate concentration controls the amount of initial nuclei which grow into 1D twinned structures, 2D ZnO crosses, star flower-like structures or micrometer-long micro-channels depending on $[\text{Cd}(\text{CH}_3\text{COO})_2]/[\text{Zn}(\text{II})]$ ratio. Although $\text{Cd}(\text{CH}_3\text{COO})_2$ is necessary to obtain the desired morphology, it does not induce formation of secondary phases such as CdO or Cd (metal) according to XRD diagrams and XPS and Raman spectra

Chapter 5 Hydrothermal-Electrochemical Growth of Heterogeneous ZnO-Co Films

5.1 Introduction

Zinc oxide (ZnO) has attracted considerable attention in the scientific world especially in the materials research and device fabrication technologies due to its unique optical and electrical properties as discussed above.

Another exciting feature of ZnO is that electrical and optical properties can be modified to broaden possible applications. One of the methods to manipulate such properties is to introduce impurity atoms, or dopants. To tune these properties which are very sensitive to the shape of the particles and the preparation method, considerable attention has been paid to metal doping; a few examples are Mn^{2+} , Cu^{2+} , Cd^{2+} , Ni^{2+} , Mg^{2+} and Fe^{2+} and substantial amount of Co^{2+} -doped ZnO.^{107,152–156} In addition, to be able to have strict control on the materials properties, one should be able to control the shape and structure of the particles, which depends on the preparation method. Besides affecting magnetic properties, Co-doping of ZnO crystals was also shown to alter the electronic properties. Photoluminescence (PL) spectroscopy is also a common method to evaluate the quality and crystallinity of ZnO films through comparison of the intensities of room temperature UV and visible emissions of the particles.⁶³ UV emission is the near-band edge (NBE) emission whereas, visible emission is attributed to the defect sites which might trap the photogenerated electron and/or hole. Increasing cobalt amount in zinc oxide is reported to both increase¹⁴⁴ and quench¹⁵⁷ visible emissions of ZnO. Consequently, understanding the influence of cobalt dopant on the optical properties of ZnO is still an unanswered question.

Some of the methods that were reported to obtain Co-doped ZnO particles include spray pyrolysis¹⁵⁸, chemical vapor deposition¹⁵⁹, magnetron sputtering¹⁶⁰, solution based approaches^{145,161,162}, pulsed laser deposition¹⁶³ and electrodeposition¹⁶⁴. Electrochemical synthesis has emerged as a simple, cheap and efficient technique. Large area-thin films on various substrates of arbitrary shapes can be produced at relatively lower temperatures with

this method. Furthermore, control over growth rate, film thickness and morphology is possible. Electrochemical deposition of ZnO has been widely studied and it has been shown that morphology of ZnO particles highly depends on precursor concentration⁶¹ and growth temperature⁸⁰. 1-D structures are preferred at low $\text{Zn}(\text{NO}_3)_2$ concentrations (below 10 mM), whereas 2-D assemblies favored above 50 mM precursor concentration at 70°C, in the presence of KCl.⁷⁹ Park *et al.* used a combination of electrochemical deposition and hydrothermal technique where elevated temperature (120-180 °C) was used to grow ZnO on a seed layer.⁹⁴ In Chapter 3, formation of 1-D structures even at high electrolyte concentrations with or without KCl (100 mM Zn(II), 100 mM KCl) with hydrothermal-electrochemical deposition at 130°C was shown. In addition, possibility of controlling rod diameter by adjusting $[\text{MnCl}_2]$ was discussed.¹³⁷ In Chapter 4, we have shown that besides precursor concentration, identity of the additive metal cation and counter ion in the deposition solution are important to produce various ZnO morphologies.¹⁶⁵ In this chapter, growth of heterogeneous ZnO-Co nanostructures via combination of electrochemical deposition with the benefits of the hydrothermal conditions directly on conducting glass is reported. The effect of cobalt ion amount on the morphology and physical properties of ZnO films is discussed in detail.

5.2 Experimental

5.2.1 Materials

All the chemicals used were of analytical grade. Cobalt nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) was obtained from Merck and zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) was purchased from Sigma-Aldrich. Dimethyl sulfoxide (DMSO, $\text{C}_2\text{H}_6\text{OS}$) was supplied from Alfa Aesar. Indium Tin Oxide (ITO) ($\Omega < 5.0 \times 10^{-4}$ ohm cm ($R_s < 100$ ohm/sq)) was purchased from Teknoma Ltd. Izmir, Turkey. Double distilled, high purity water was used from Milli-Q water (Millipore) system.

Table 5.1 Details of the reaction parameters.

[Co(II)]/[Zn(II)]	[Co(II)] (mM)	[Zn(II)] (mM)	[NO ₃ ⁻] (mM)	Charge (C)
0.2	20	50	120	16.58
0.4	30	50	140	18.90
0.6	40	50	160	19.45
0.8	50	50	180	18.25
1	60	50	200	22.89

5.2.1 Synthesis and Characterization

ZnO-Co layers were grown on ITO (Indium tin oxide) coated glass electrode (1×1 cm² area) in 50 ml of 1:1 (v:v) DMSO:H₂O mixture. A conventional 3-electrode cell system in a hydrothermal glass reactor (Büchiglasuster, modified picoclave) was used for electrochemical deposition. The volume of the reactor was 100 ml. The reference electrode was Ag/AgCl saturated with KCl (Corr Instruments, S/N P11092) whereas Pt wire served as the counter electrode. The distance between the electrodes is approximately 2 cm. The substrate was cleaned ultrasonically by ethanol, acetone and distilled water prior to depositions. The thin films were cathodically electrodeposited from baths containing Zn(NO₃)₂ and Co(NO₃)₂. The Zn(II) concentration was fixed to 50 mM and [Co(II)]/[Zn(II)] ratio was varied between 0.2 and 1. Details of the synthesis parameters are provided in Table 5.1. The pH of the solutions varied between 5 and 7. Electrodepositions were carried out at constant potential of -1.1 V vs Ag/AgCl at 130 °C for 30 minutes (unless stated otherwise) on a potentiostat/galvanostat (Biologic-Science Instruments, VSP model) which resulted in approximately tens of micrometers thick films (Figure 5.1).

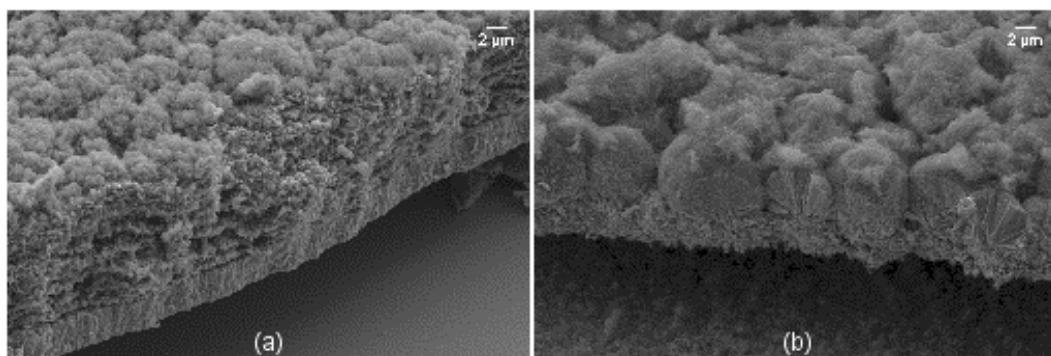


Figure 5.1 SEM micrographs displaying side view of ZnO-Co film prepared with a feed ratio of [Co(II)]/[Zn(II)]=0.4 a) after 10 minutes of deposition b) after 15 minutes of deposition.

The crystal structure and crystallinity of the samples were analyzed by X-Ray diffraction (XRD) using Bruker/D8 Advance with Cu K α radiation. The surface morphologies of the films were examined with ZEISS Ultra Plus Field Emission scanning electron microscope (FE-SEM). Zn-Co surface distribution was profiled by Bruker Energy Dispersive Spectrometer (EDX) attached to ZEISS Ultra Plus Field Emission Scanning Electron Microscope (FE-SEM). The film composition was studied by X-ray photoelectron spectroscopy (Thermo K-Alpha, XPS). C1s (285 eV) binding energy served as a reference to calibrate the binding energies. Depth-profile analysis was performed by etching the surface with Ar⁺. Raman scattering experiments were carried out using a Renishaw Raman Microscope system at room temperature. 532 nm laser was used for excitation.

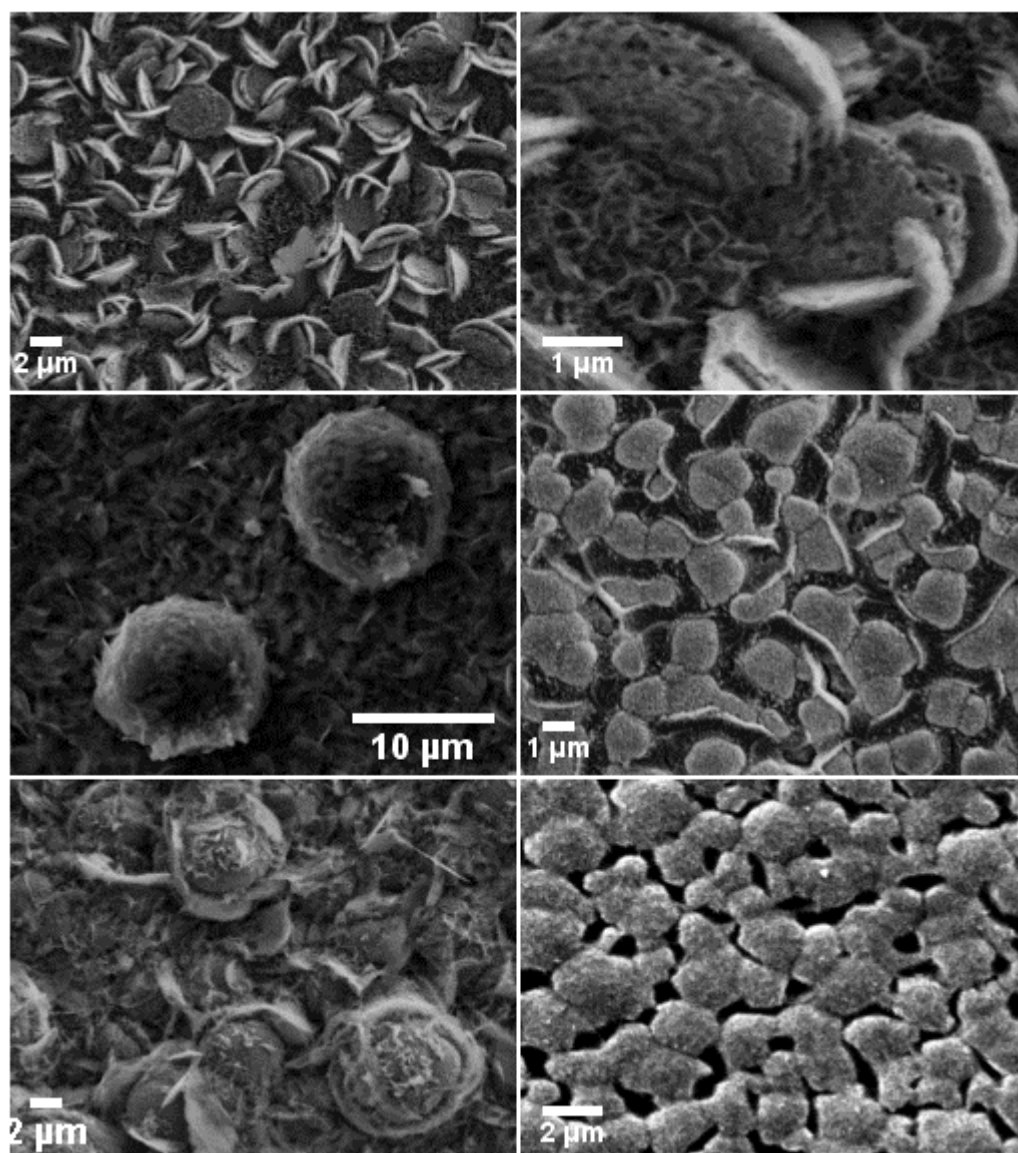


Figure 5.2 SEM micrographs of ZnO-Co films a) $[\text{Co(II)}]:[\text{Zn(II)}]=0.2$, low magnification. b) $[\text{Co(II)}]:[\text{Zn(II)}]=0.2$, high magnification. c) $[\text{Co(II)}]:[\text{Zn(II)}]=0.4$. d) $[\text{Co(II)}]:[\text{Zn(II)}]=0.6$. e) $[\text{Co(II)}]:[\text{Zn(II)}]=0.8$. f) $[\text{Co(II)}]:[\text{Zn(II)}]=1$.

5.3 Results and Discussion

5.3.1 Morphology and Structure

Electron microscopy was used to investigate the effect of cobalt doping on the morphology of the films. Thin platelets that display intermittent growth with about 1-2 μm sized edges were observed for pure ZnO film prepared from 50 mM $\text{Zn}(\text{NO}_3)_2$ deposition solution in 1:1 DMSO: H_2O mixture in Chapter 3 (Figure 3.1) SEM images of the as-prepared heterogeneous ZnO-Co films with increasing Co(II) amount in the electrodeposition bath

constitute Figure 5.2. Addition of small amount of Co(II) into the deposition solution ($[\text{Co(II)}]:[\text{Zn(II)}]=0.2$) did not alter the morphology significantly, but resulted in an increase in the ZnO platelet size. Platelets that were grown perpendicular to the surface of the film with diameters of about 2-4 μm can be seen at a first glance on the low magnification image (Figure 5.2a). High magnification image shows that there exists a network of porous, sponge-like structures among these plates (Figure 5.2b). EDX analysis of the film revealed that cobalt-rich porous network grew in between the ZnO platelets (Figure 5.3).

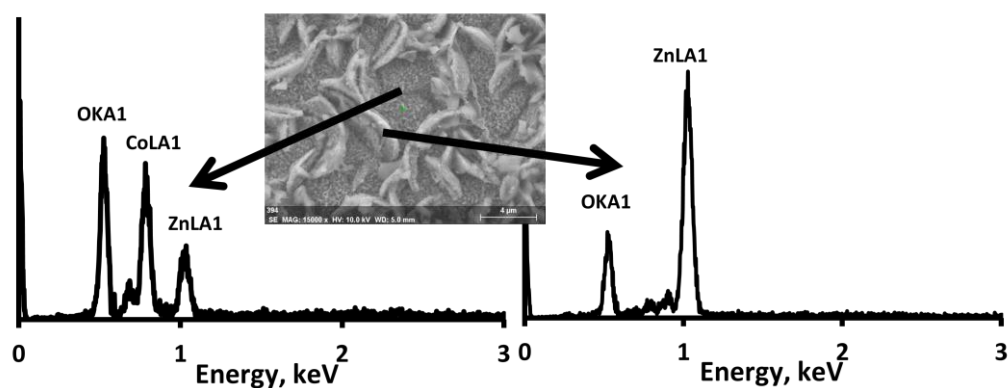


Figure 5.3 SEM image and EDX spectra of the film prepared with a feed ratio of $[\text{Co(II)}]/[\text{Zn(II)}]=0.2$.

As the concentration of Co(II) was increased further, spheres with diameters of about 6-to-8 μm were observed on an interconnected-network of platelets (Figure 5.2c). EDX results indicated that cobalt-rich spheres that were composed of aggregated plate-like particles were formed on a matrix of ZnO-Co platelets (Figure 5.4). When $[\text{Co(II)}]/[\text{Zn(II)}]$ ratio was 0.6, a clear phase separation was observed, where cobalt-rich islands develop on the ZnO-Co matrix (Figure 5.2d). Further Co(II) addition into the deposition bath, resulted in an increased concentration of cobalt-rich spheres covered with numerous zinc-rich platelets (Figure 5.2e) and the porous network on the phase-separated matrix (Figure 5.2f) as seen in SEM figures and EDX analysis (Figure 5.4-5.5).

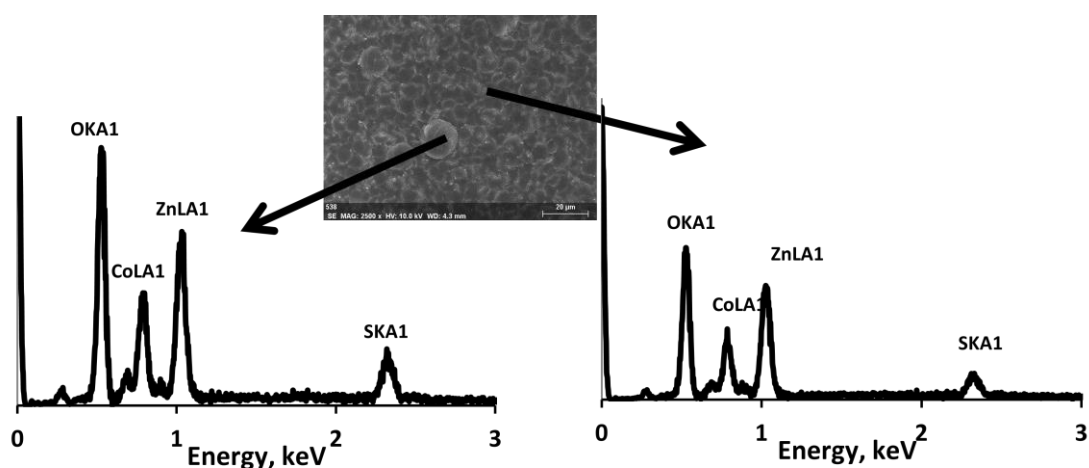


Figure 5.4 SEM image and EDX spectra of the film prepared with a feed ratio of $[\text{Co(II)}]/[\text{Zn(II)}]=0.4$.

The structure and phase of the ZnO-Co films were determined by X-ray diffraction (Figure 5.6). When $[\text{Co(II)}]/[\text{Zn(II)}]$ ratio was smallest, three major peaks that can be indexed to hexagonal Wurtzite ZnO {JCDPDS No.0361451} were present at $2\theta = 31.7^\circ$, 34.4° and 36.2° corresponding to (100), (200), and (101) reflections, respectively. Relative higher intensity of (100) and (101) reflections to (200) peak is consistent with the observed plate morphology of the films. Similar patterns were reported for disk and wall shaped ZnO structures.⁷⁹ Furthermore, three more reflections arising at $2\theta = 41.67^\circ$, 44.5° and 47.46° were detected which showed the existence of metallic cobalt formation in the form of hexagonal closed-pack (hcp) or face-centered cubic (fcc) crystal structure or a mixture of both.^{166,167} As the concentration of Co(II) in the electrodeposition bath was increased, a strongly preferential growth along the perpendicular direction to the substrate surface was observed for the rest of the films as pointed out by the highly intense (002) peak. The strong (002) peak indicates highly crystalline, well aligned doped ZnO particles which suggests cobalt(II) doping does not alter the crystallinity of the ZnO films.

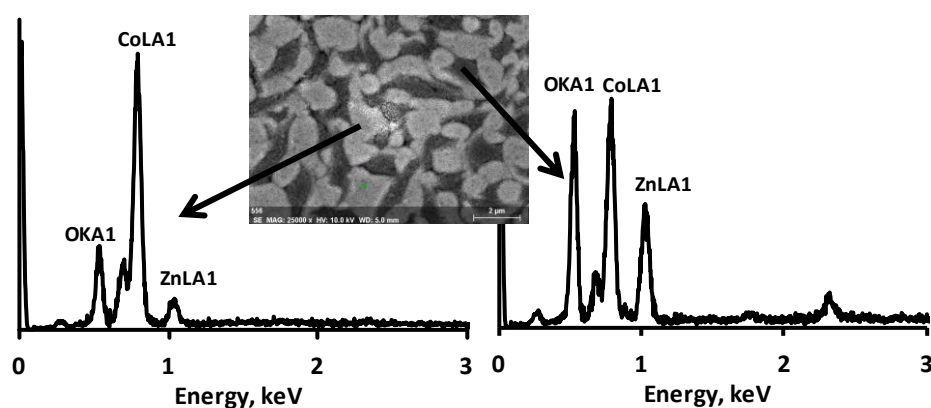


Figure 5.5 SEM image and EDX spectra of the film prepared with a feed ratio of $[\text{Co(II)}]/[\text{Zn(II)}]=0.6$.

Furthermore, cobalt(II) addition into the deposition solution did not induce shift in the position of (002) reflection regardless of Co(II) concentration. This behavior was reported before by M. Tortosa *et al.* for $\text{Zn}_{1-x}\text{Co}_x\text{O}$ films electrodeposited from DMSO solution.¹¹³ They suggested that, similar to Cd-doped ZnO films, potential changes in the unit cell volume and cell parameters due to metal doping only affects the direction perpendicular to the *c*-axis but not the *c*-axis parameter. It might be also due to low doping levels since it was already established for Cd-doped ZnO films that doping levels lower than 9 % does not induce a change in the lattice parameters.¹³⁶ In addition, similar radii of the two cations ($0.58 \text{ \AA}$ for Co^{2+} and $0.6 \text{ \AA}$ for Zn^{2+})⁴⁸ might also account for the lack of peak shift. Crystal sizes calculated by Debye-Scherrer equation using (002) peak does not display significant change with cobalt(II) amount in solution (3-4 nm) but they are all larger than the calculated crystal size of undoped ZnO (2.5 nm) which is also supported by SEM images.

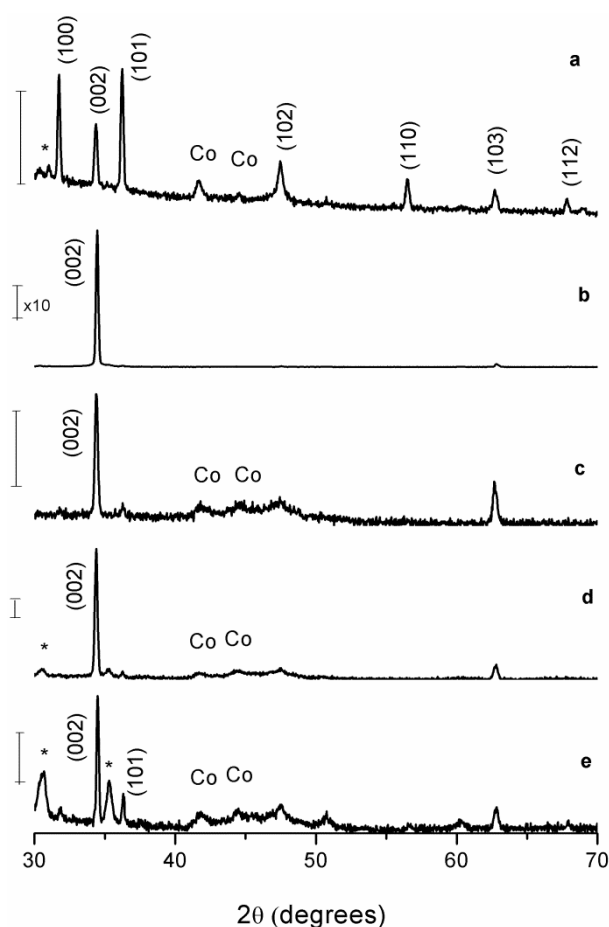
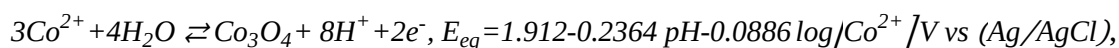
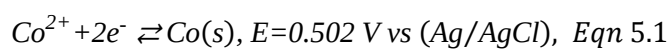


Figure 5.6 XRD patterns of films prepared from baths with different feed ratios; a) $[\text{Co(II)}]:[\text{Zn(II)}]=0.2$, b) $[\text{Co(II)}]:[\text{Zn(II)}]=0.4$, c) $[\text{Co(II)}]:[\text{Zn(II)}]=0.6$, d) $[\text{Co(II)}]:[\text{Zn(II)}]=0.8$, e) $[\text{Co(II)}]:[\text{Zn(II)}]=1$ (The * symbol represents reflections associated with substrate ITO. The scale bars represent 2000 counts unless stated otherwise.)

5.3.2 XPS

X-ray photoelectron spectroscopy was used to study both the nature of chemical bonding states of the metals and the composition of the films. Figure 5.7 displays surface Co 2p XPS spectra of the ZnO-Co films as well as the spectra after etching. For the film with lowest $[\text{Co(II)}]/[\text{Zn(II)}]$ feed ratio, after surface etching, the Co 2p_{3/2} and Co 2p_{1/2} peaks were located at 780.7 eV and 796.5 eV, respectively and separated by 15.8 eV. Two strong satellite bands at approximately 6 eV higher binding energies accompanied the main peaks. These features imply presence of oxidized cobalt in the form of Co^{2+} in a tetrahedral crystal field surrounded by oxygens.^{154,168} Strong satellite peaks are attributed to the charge-transfer structure characteristics of 3d transition metal (TM) monoxides. On the other hand, the surface of the film was characterized by two main peaks separated by 14.9 eV, which appeared at 781.7 eV

and 796.6 eV. The main peak at 781.7 eV was sharper and the satellites were wider and of lower intensity than those of the peaks exposed after surface etching. These aspects of the lines suggest presence of cobalt oxide as Co_3O_4 where Co^{2+} and Co^{3+} located at tetrahedral and octahedral sites, respectively or mixed oxide with a valence state of +3 for cobalt in an octahedral geometry on the surface of the film.^{154,169} Even though XRD analysis indicated the presence of metallic cobalt for the film with lowest $[\text{Co(II)}]/[\text{Zn(II)}]$ ratio, no peaks associated with cobalt metal was detected on the XPS spectra. Metallic cobalt might be located deeper than the detection depth of the XPS measurement. The ligand field splitting energy of octahedral geometry is lower than the tetrahedral one. Hence, the color of appearance is shifted to lower energies. The films appear dark-brown to black which is consistent with what is reported for Co_3O_4 before.¹⁷⁰ When the cobalt(II) amount in the electrodeposition solution was increased further to deliver $[\text{Co(II)}]/[\text{Zn(II)}]$ feed ratio of 0.4, main Co $2p_{1/2}$ peak on the surface was shifted to 795.8 eV and Co $2p_{3/2}$ peak was shifted to 779.9 eV. Main peaks appeared with two satellites now at binding energies of 786.4 and 789.9 eV, all again consistent with Co_3O_4 on the surface.¹⁷¹ After surface etching of 540 seconds, a similar transformation from Co_3O_4 to CoO was observed. The main Co $2p_{1/2}$ and Co $2p_{3/2}$ peaks have shifted to 0.4-0.6 eV higher binding energies. The satellite peak at 789.9 eV disappeared and the satellite intensity for both Co $2p_{1/2}$ and Co $2p_{3/2}$ have increased to be higher than 50% of the main peaks as expected to be observed in CoO spectrum.^{154,171} The film prepared with a $[\text{Co(II)}]/[\text{Zn(II)}]$ feed ratio of 0.8 displayed a very similar XPS spectra as the film prepared by the lowest cobalt(II) amount. When the $[\text{Co(II)}]/[\text{Zn(II)}]$ feed ratio is 0.6 and 1, cobalt region of the XPS spectra showed a distinct feature. The surfaces of the films demonstrated Co_3O_4 like character as the other films. However, after etching the surface for 540 seconds, two additional peaks located at 778.4 and 793.5 eV appeared which corresponds to the Co $2p_{1/2}$ and Co $2p_{3/2}$ peaks of metallic cobalt, respectively.^{172,173} Following half cell reactions can account for reduction and oxidation of Co^{2+} ions¹⁷⁴:



Eqn 5.2

The pH range in which ZnO is thermodynamically stable was calculated to be above 6.10 at 298 K and above 5.28 at 333 K by Otani and coworkers.⁸⁷ E_{eq} for reaction 1b is 0.622, 0.150, 0.587 and 0.150 V(Ag/AgCl), respectively for conditions $[\text{Co}^{2+}] = 0.05 \text{ M}$ At pH =5,

$[\text{Co}^{2+}] = 0.05 \text{ M}$ At $\text{pH} = 7$, $[\text{Co}^{2+}] = 0.02 \text{ M}$ At $\text{pH} = 5$ and $[\text{Co}^{2+}] = 0.02 \text{ M}$ And $\text{pH} = 7$. Hence, formation of metallic cobalt and mixed cobalt oxide is thermodynamically possible under applied potential of -1.1 V (Ag/AgCl).

Figure 5.8 shows the XPS spectra of the O1s region (bottom) and Zn 2p region (top) from the surface of the film prepared with lowest cobalt(II) amount and after surface etching. The spectra are asymmetric and the deconvoluted peaks exhibit intensity changes with etching time. On the surface of the film, the peaks appear at 531.4 eV and 529.8 eV. The peak localized at lower energy is usually attributed to O^{2-} ions in the Wurtzite crystal structure of hexagonal ZnO lattice.⁵⁹ The peak at higher energy on the other hand, usually reported to result from the presence of loosely bound oxygen on the surface, such as OH^- species or O^{2-} ions oxygen deficient regions.¹⁰⁰ The intensity of this defect related peak at higher energy after etching suggests oxygen vacancies/hydroxides to be mostly on the surface. In addition, the signal from the peak due to Zn-O bond is amplified in the inner layers. The spectrum of the Zn 2p region displays two peaks centered at 1021.4 and 1045.3 eV which could be assigned to Zn $2p_{3/2}$ and $2p_{1/2}$ of Zn^{2+} in ZnO, respectively (Figure 5.8). These lines are not shifted after etching process, which implies good chemical stability of Zn throughout the film. Similar trend is observed for all of the ZnO-Co films for O1s and Zn 2p region of the XPS spectra (data not shown).

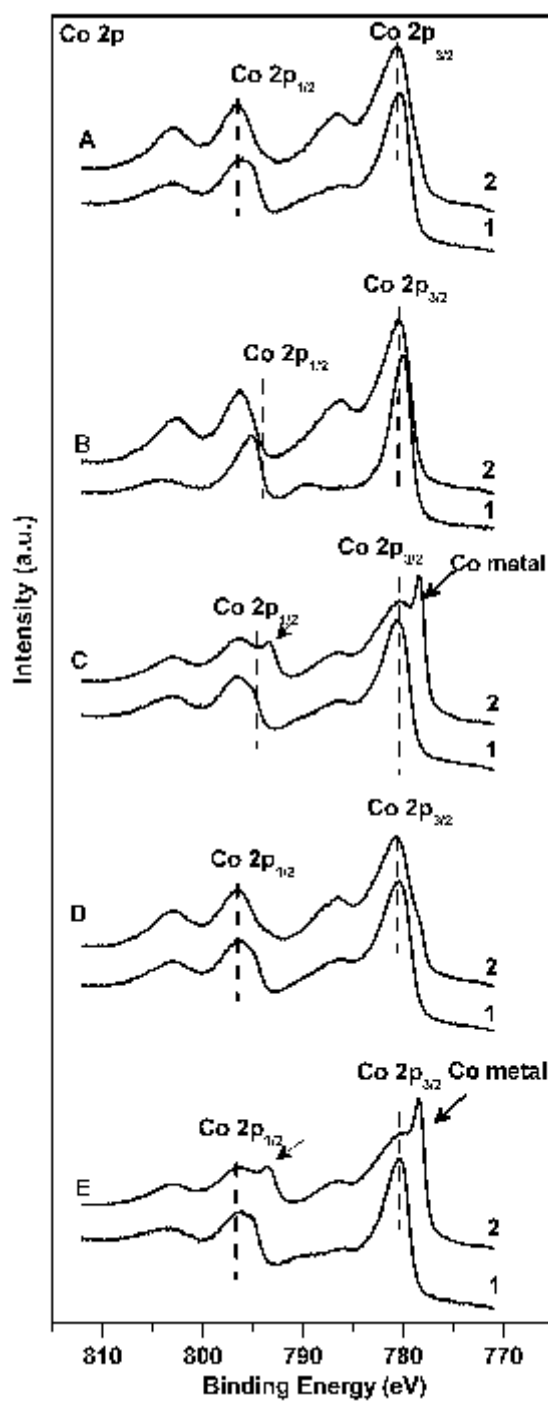


Figure 5.7 Co 2p XPS spectra of the ZnO-Co films prepared with a feed ratio of a) [Co(II)]:[Zn(II)]=0.2, b) [Co(II)]:[Zn(II)]=0.4, c) [Co(II)]:[Zn(II)]=0.6, d) [Co(II)]:[Zn(II)]=0.8, e) [Co(II)]:[Zn(II)]=1. (Line 1 shows XPS spectrum from surface and Line 2 displays the XPS spectrum after 540 seconds of etching.)

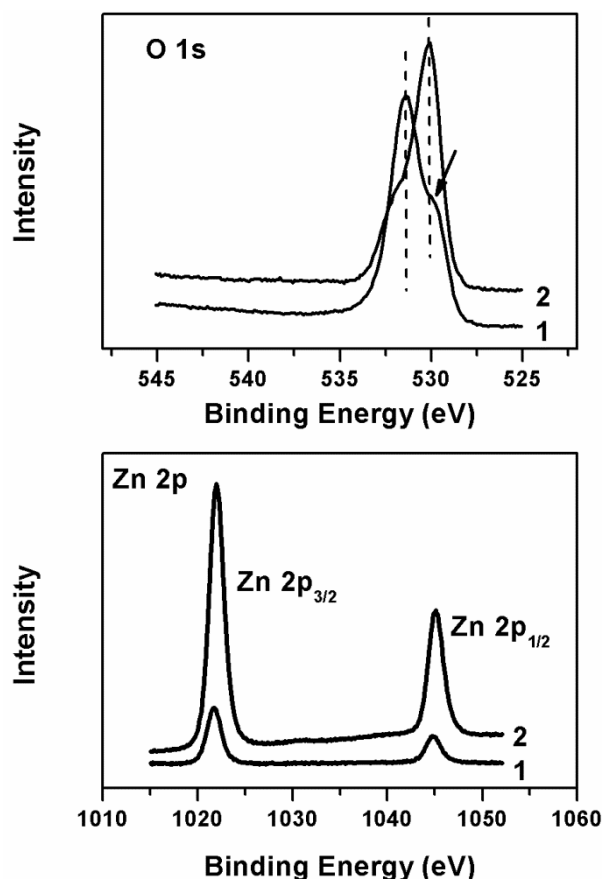


Figure 5.8 Zn 2p (top) and O 1s (bottom) XPS spectra of the film prepared with a feed ratio of $[\text{Co(II)}]:[\text{Zn(II)}]=0.2$. (Line 1 shows XPS spectrum from surface and Line 2 displays the XPS spectrum after 540 seconds of etching.)

5.3.3 Raman

Raman spectroscopy has been used to understand consequences of impurity doping on host lattice characteristics, modification of lattice vibrational modes as well as to investigate secondary phase formation that might not be detectable by conventional characterization methods like XRD due to detection limit of the measurement.^{49,144,158} Substitution of the dopant atoms would introduce additional vibrational modes. Wurtzite crystal structure of ZnO belongs to space group $^4C_{6v}$ for which Raman active zone-center optical modes with symmetries $A_1+2B_1+E_1+2E_2$ are predicted by group theory. Out of these modes, A_1 and E_1 phonons are polar modes, which split into transverse-optical (TO), and longitudinal-optical (LO) phonon modes at different energies and all are both Raman and IR active modes. The nonpolar $E_2(\text{low})$ and $E_2(\text{high})$ are attributed to the vibration of zinc sublattice and oxygen motion, respectively.^{48,49} The B_1 mode on the other hand, is silent.

Raman spectra obtained at room temperature for pure ZnO films and as-prepared ZnO-Co films deposited from baths with different [Co(II)]:[Zn(II)] feed ratios in the range of 150 and 1000 cm^{-1} are displayed in Figure 5.9. The broad, low intensity peak at 331 cm^{-1} and the peaks observed at 378 and 436 cm^{-1} for undoped ZnO can be indexed to second order scattering, $A_1(\text{TO})$, and $E_2(\text{high})$, respectively; where $E_2(\text{high})$ mode dominates and indicates highly crystalline Wurtzite ZnO.^{48,144,145} The frequency of 331 cm^{-1} mode matches with the difference of $E_2(\text{high}) - E_2(\text{low})$ modes. Cusco *et al.* analyzed this second-order mode by temperature dependent Raman studies and assigned the symmetry of this mode to be composed of predominantly A_1 , with a smaller E_2 component and an even smaller E_1 component.¹⁷⁵ The comparatively weak Raman band at 484 cm^{-1} is assigned as surface optical phonon modes of highly *c-axis* oriented ZnO nanorods in literature which is observed when the size of the crystals is much smaller than the wavelength of the incident light.^{47,146} The absence of $E_1(\text{TO})$ mode at 410 cm^{-1} further supports preferential growth through *c-axis*⁴⁷ in line with XRD data.

When Co(II) was introduced into the electrodeposition solution, Raman spectrum of the film deposited displayed additional bands together with alterations in ZnO frequencies. The high intensity $E_2(\text{high})$ mode of ZnO was redshifted to 427 cm^{-1} as well as two-phonon-difference mode (from 333 cm^{-1} to 321 cm^{-1}). The $E_2(\text{high})$ mode of ZnO films has found to be predominantly due to oxygen atom motions through isotopic mass dependence measurements of the E_2 phonons.¹⁷⁶ The asymmetric line shape and frequency of this mode is shown to be sensitive to oxygen mass fluctuations. Hence, blueshift in the frequency of the $E_2(\text{high})$ mode might stem from the oxygen vacancies which would create oxygen mass loss depending on the abundance.⁴⁹ Furthermore, the blueshift and broadening of this mode also suggests structural defect formation and lattice distortions due to cobalt doping.⁴⁸ In addition, compared to undoped ZnO Raman spectra rather broad and low-intensity bands appeared at 197, 464, 522 and 662 cm^{-1} . The peaks at 197 and 522 cm^{-1} were blueshifted to 185 and 510 cm^{-1} and the peak at 662 cm^{-1} narrowed down to be centered at 669 cm^{-1} as introduced Co(II) amount was increased. The peaks at 185, 464, 510 and 669 cm^{-1} can be assigned to $F_{2g}(1)$, E_g , $F_{2g}(2)$ and A_{1g} phonon modes of Co_3O_4 , respectively.⁴⁸ Co_3O_4 belongs to $Fd3m$ space group for which $\Gamma=A_{1g}+E_g+F_{1g}+3F_{2g}+2A_{2u}+2E_u+4F_{1u}+2F_{2u}$ modes are predicted by group theory. Out of these vibrations A_{1g} , E_g , $3F_{2g}$ are Raman active, $4F_{1u}$ is Infrared active and F_{1g} , A_{2u} , E_u , F_{2u} are silent. The peak for A_{1g} mode strengthened and was redshifted in frequency as Co(II) amount increased. This change might be due to increased octahedral/ Co^{3+} (CoO_6) subunit concentration, since A_{1g} mode is stimulated by octahedral oxygen motion.^{48,177} The $F_{2g}(1)$

mode, on the other hand, is ascribed to be excited by tetrahedral sites (CoO_4).¹⁷⁷ The appearance of Co_3O_4 -like modes as early as $[\text{Co(II)}]:[\text{Zn(II)}]$ feed ratio of 0.2 implies that second-spinel phase is forming as soon as cobalt(II) is introduced into the system as also confirmed by XPS analysis. When the $[\text{Co(II)}]:[\text{Zn(II)}]$ feed ratio was 0.6 and higher, Co_3O_4 overwhelmed the Wurtzite structure and the $\text{E}_2(\text{high})$ and $\text{A}_1(\text{TO})$ modes were diminished significantly.

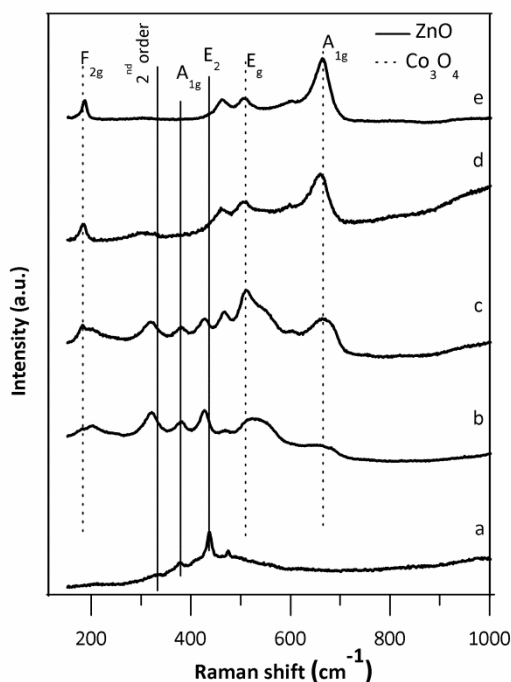


Figure 5.9 Micro-Raman spectra of the ZnO-Co films a) 50mM $\text{Zn}(\text{NO}_3)_2$, b) $[\text{Co(II)}]:[\text{Zn(II)}]=0.2$, c) $[\text{Co(II)}]:[\text{Zn(II)}]=0.4$, d) $[\text{Co(II)}]:[\text{Zn(II)}]=0.6$, e) $[\text{Co(II)}]:[\text{Zn(II)}]=1$.

5.3.4 Crystallization

Deposition of cobalt rich-cobalt oxide spheres on ZnO-Co matrix might be explained by the electrochemical reactions as follows, in accordance with XRD data. As described in Chapter 1.2.5, electroreduction of the nitrate ions in the growth solution results in formation of hydroxide ions, which increases the pH (eqn 1.8). The hydroxide ions in turn react with Zn^{2+} ions to cause precipitation of zinc hydroxide (eqn 1.9; hydroxylation) at the cathode which is subsequently dehydrated to generate ZnO (eqn 1.10; dehydration).

Wurtzite ZnO structure is composed of O^{2-} terminated and Zn^{2+} terminated layers stacked on top of each other along the *c*-axis.³³ This arrangement of the atoms let ZnO possess high energy polar planes such as $\pm (0001)$ which are the primary growth surfaces and six

symmetric, nonpolar {1010} planes parallel to the *c*-axis. Hence, incoming precursors tend to add on the polar surfaces of a newly formed ZnO seed leading to a faster growth along $\pm$ [0001] direction actually which is shown to be five times faster than the growth on the {1010} and {0110} planes.⁸⁵ This anisotropic growth behavior gives rise to particles growing with relatively high aspect ratios. However, it is possible to modify the morphology of the particles by preventing the growth on particular surfaces using selectivity of the surfaces to surfactants and capping agents. The morphology of the polar inorganic crystals can also be controlled by taking advantage of their sensitivity to reaction solvents.¹⁷⁸ Solvent polarity and saturated vapor pressure play an important role on the growth habits through crystal-solvent interfacial interactions.¹⁷⁹ Preferred growth direction is hindered in the case of strongly polar solvents/molecules since they interact with the polar surfaces and hinder the direct growth on nonpolar planes. Being a polar, basic, aprotic solvent DMSO is also responsible for the anisotropic growth of ZnO structures^{116,180} A mass of DMSO is most likely absorbed on to the polar basal plane of ZnO inhibiting adsorption of additional growth units on (0001) plane. As a result, growth proceeds along six symmetric nonpolar planes and ZnO platelets were obtained in the absence of Co(II) ions in DMSO-H₂O mixture.¹³⁷ Besides morphological control, DMSO undergoes hydrolysis in aqueous solutions and also contributes to increasing the OH⁻ ion concentration according to the equation 3.1.¹⁸¹ Higher OH⁻ concentration in turn, accelerates the hydroxylation reaction (eqn 1.9) further, hence the nucleation rate increases. Enhanced nucleation rate would result in formation of amplified number of primary nuclei adjacent to each other, which might account for the intermittent particle growth. In addition, it is known that DMSO undergoes decomposition to yield sulfur at elevated temperatures.¹⁸² Since the reactions were carried out at 130 °C and at the corresponding vapor pressure, DMSO decomposition was expected. Production of sulfur was confirmed by XPS analysis which implies the presence of sulfur as sulfide incorporated in the films (Figure 5.10).

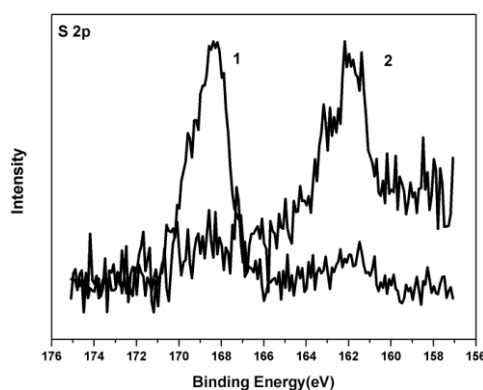


Figure 5.10 S 2p region from the XPS spectrum of the ZnO-Co film prepared with a feed ratio of $[\text{Co(II)}]/[\text{Zn(II)}]=0.4$. Line 1: Surface, Line 2: After etching for 480 seconds.

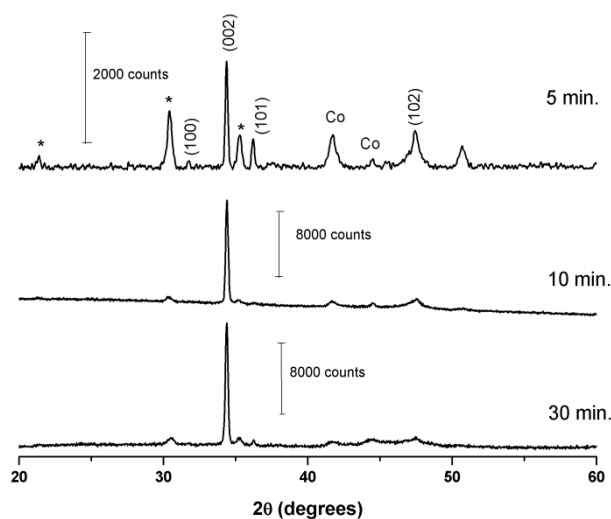


Figure 5.11 XRD diagrams of the ZnO-Co film prepared with a feed ratio of $[\text{Co(II)}]:[\text{Zn(II)}]=0.8$ using different deposition times.

Addition of Co(II) into the deposition solution significantly affected the crystal growth and hence morphology of the obtained products. To better understand formation of spheres and the observed phase separation as explained in the previous sections (Figure 5.2), the particle growth was analyzed through controlled experiments with different deposition times at selected $[\text{Co(II)}]/[\text{Zn(II)}]$ ratios. Analysis of XRD and XPS data of the films prepared with varying deposition times revealed some growth habits. First of all, metallic cobalt formation was detected to occur early in the reaction. In the XRD diagram of the film with $[\text{Co(II)}]:[\text{Zn(II)}]=0.8$ (Figure 5.11), metallic cobalt reflections at $2\theta = 41.6^\circ$, 44.5° , and 47.5° were present even after first 5 minutes of the deposition. Early metallic cobalt formation was also verified by analysis of XPS spectra (5.12). Peaks that correspond to binding energy of

cobalt metal appeared also for the films with $[\text{Co(II)}]:[\text{Zn(II)}]=0.6$ and $[\text{Co(II)}]:[\text{Zn(II)}]=0.4$ with shorter reaction times after 480 seconds of etching (Figure 5.12). Presence of cobalt metal only on the underneath of the film explains why it could not be detected in the XPS spectra of the thicker films (30 min.) as discussed above.

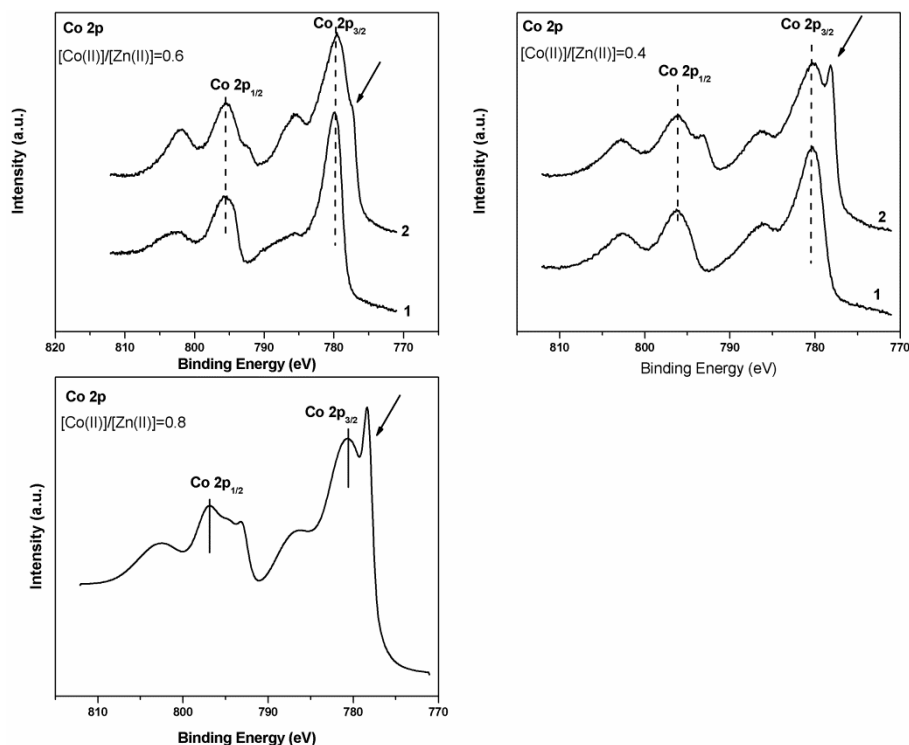


Figure 5.12 Co 2p region from the XPS spectra of the ZnO-Co film prepared with a feed ratio of $[\text{Co(II)}]:[\text{Zn(II)}]=0.4$ by deposition for 10 min and $[\text{Co(II)}]:[\text{Zn(II)}]=0.6, 0.8$ by electrodeposition for 5 minutes. Line 1: Surface, Line 2: After etching for 480 seconds. XPS spectrum only after etching for 480 seconds is given for $[\text{Co(II)}]:[\text{Zn(II)}]=0.8$.

In addition, hydroxide-to-oxide transformation consistent with the deposition mechanism was observed during film growth as hydroxide peak (531.4 eV) intensity relative to the oxide peak (530.1 eV) in XPS spectra (Figure 5.13) of the film with $[\text{Co(II)}]:[\text{Zn(II)}]=0.8$ was decreased with deposition time. Lastly, highly preferential ZnO growth along *c*-axis was observed. After first 5 minutes of deposition, three major hexagonal Wurtzite ZnO reflections ((100), (200), and (101)) were present in the XRD diagram of the film with $[\text{Co(II)}]:[\text{Zn(II)}]=0.8$ (Figure 5.11). Intensity of (002) reflection was progressively enhanced at the expense of

(100) and (101) peaks in time and became the major diffraction line after 30 minutes indicating preferential growth vertical to the substrate surface.

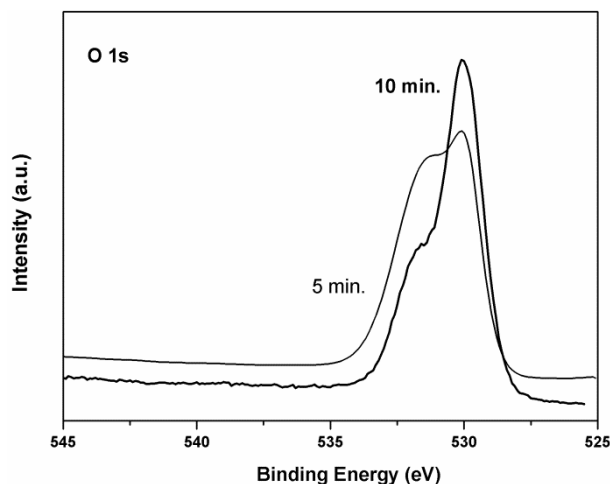


Figure 5.13 O1s region from the XPS spectra of the ZnO-Co film prepared with a feed ratio of $[\text{Co(II)}]/[\text{Zn(II)}]=0.8$ using different deposition times (after etching for 480 seconds).

In light of the above analysis, for the films prepared with $[\text{Co(II)}]:[\text{Zn(II)}]$ ratios of 0.4 and higher, it can be concluded that cobalt rich phase (mainly oxide according to the XPS data (Figure 5.12), and Zn(OH)_2 rich matrix form in the first 10 minutes of the reaction. As the reaction proceeds and OH^- is produced, Zn(OH)_2 continues to grow both on the initial Zn(OH)_2 nuclei and in between the cobalt rich islands so that Zn(OH)_2 has grown beneath cobalt rich oxide spheres which is then converted to ZnO later with time. When $[\text{Co(II)}]:[\text{Zn(II)}]$ ratio is raised to and above 0.6, number of the initial cobalt-rich spheres is amplified (Figure 5.2d and 5.14). This increase suggests that cobalt-rich phase grows faster than zinc-rich phase. EDX data clearly shows that spheres are composed mainly of cobalt and zinc hydroxide phase grows under these spheres even after first 5 minutes of the deposition (Figure 5.14). O1s XPS data for this film confirms that the topmost layer is composed of zinc hydroxides as expected. Removing upper layers with Ar^+ etching reveals the ZnO layer beneath which is in accordance with the crystallization mechanism shown in equations 4-5. In the end, a hierarchical assembly is constructed where ZnO rods are the core building blocks that carry cobalt rich oxide plates, which form the roots of the cobalt rich-cobalt oxide spheres after 30 minutes of deposition (Figure 5.15). The spheres arrange together to form micro-islands which are inter-connected by ZnO network (Figure 5.2d).

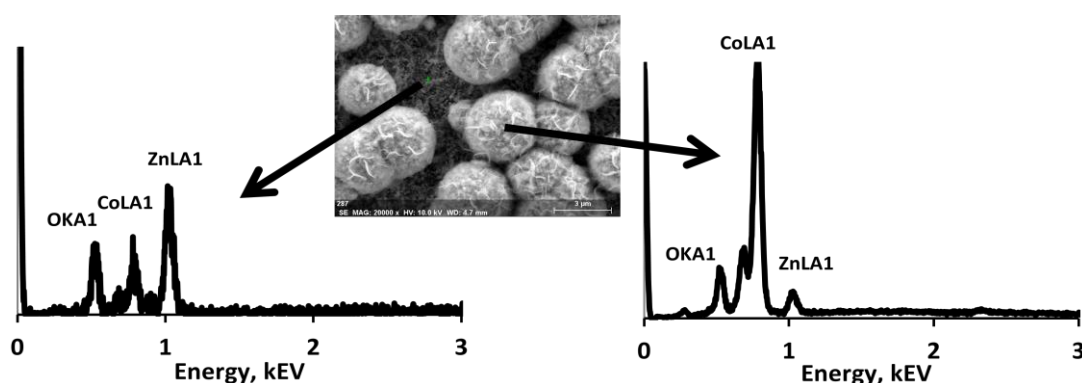


Figure 5.14 SEM image and EDX profile of the film prepared with a feed ratio of $[\text{Co(II)}]/[\text{Zn(II)}]=0.6$ by deposition for 5 minutes.

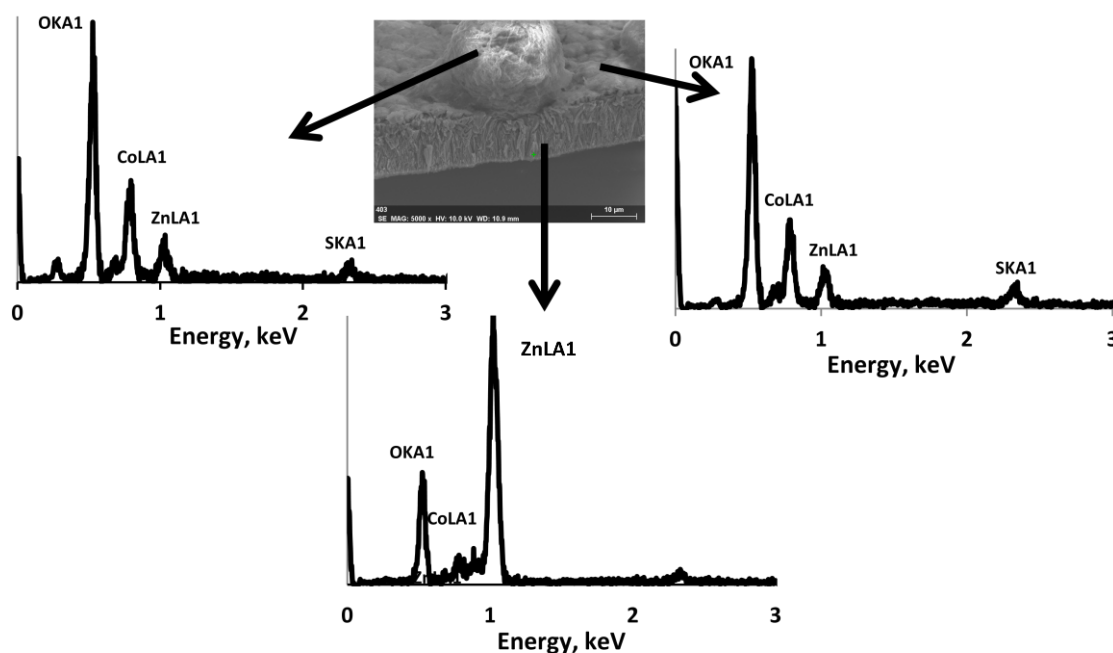


Figure 5.15 SEM micrograph displaying a side view and EDX profile of ZnO-Co film prepared with a feed ratio of $[\text{Co(II)}]/[\text{Zn(II)}]=0.6$ after 30 minutes of deposition.

Hence, examination of the initial and later stages of the reaction suggests growth of the particles occurs through Ostwald Ripening (OR) mechanism, which has been widely proposed for the growth of spherical particles and ZnO structures. In addition, the fact that numerous platelets form the spheres, reveals oriented attachment mechanism (OA).^{178,183–186} The initial Zn(OH)_2 and cobalt rich nuclei (poorly crystallized particles characterized by low

intensity diffraction peaks) are unstable due to large surface area exposed and to minimize the interfacial energy they tend to aggregate so that spheres form out of platelets. Then, irregularities due to oriented aggregation is removed to produce round and smooth particles through OR mechanism.¹⁸³ At this stage, Zn(OH)_2 and cobalt rich grains grow further locally at the expense of smaller nuclei (in the perpendicular direction to the film surface depicted by highly intense (002) reflection) and tend to fuse by decreasing the gap between as can be seen in SEM images after 30 minutes of deposition, especially when Co(II) amount is higher.

Total charge passed through the systems during depositions was calculated from current-time curves and are summarized in Table 5.1. Total charge passed and hence current increase with increasing Co(II) amount in the deposition solutions. It is also noticeable that this increase in total charge is correlated with increase in nitrate amount. Hence, it can be concluded that this parameter monitors the reduction of nitrate ions (eqn 1.8) and the increase corresponds to an increase of the rate of this reaction with increasing Co(II) concentration.

In a previous study regarding synthesis of mesoporous ZnO microspheres with a hydrothermal process it was documented that higher temperatures (80 °C) induce more ZnO microsphere formation by aggregation of plate-like structures¹⁸⁵. Hydrothermal treatment improves OR process by facilitating growth of larger particles via dissolution of smaller particles and suggested to be a flourishing environment to obtain special structures. Hence, electrodeposition in a hydrothermal environment at a higher temperature (130°C) than conventional systems might have prompt OR as growth mechanism.

It was observed for all samples that Co rich spheres were grown on a zinc hydroxide layer in the first stages of deposition. Amount of Co, however played a crucial role in determination of the final morphology. As $[\text{Co(II)}]$ was increased, phase separation was observed; the degree of which was positively correlated with Co concentration (Figure 5.2). When Co concentration was increased further, both sizes and the amount of the Co rich spheres raised and some were fused together. Moreover, zinc oxide platelets continued to grow under and around Co rich phase so that Co rich spheres were covered with zinc oxide platelets.

5.4 Conclusions

In summary, we report seedless hydrothermal-electrochemical growth of heterogeneous ZnO-Co nanostructures in DMSO:H₂O mixture. Introduction of Co brought about a unique structure. Phase separation was observed together with formation of Co-rich spheres on a zinc rich matrix. Amount of Co determined the degree of phase separation and the quantity of the initial Co rich spheres. XRD and XPS analysis indicated the presence of cobalt metal as well as a mixture of cobalt(II) and cobalt(III) oxides in cobalt rich microzones.

Chapter 6 Growth of CdS and Ag₂S on ZnO towards All Electrodeposited Solar Cells

6.1 Introduction

Dye-sensitized solar cells (DSSCs) have received considerable attraction as an environmentally friendly and economic solution to green energy quest, since the initial breakthrough of 7 % efficiency reported by O'Regan and Gratzel.⁴ The interest is ever-increasing since DSSCs offer comparable efficiency with easier and cheaper fabrication processes. The key to the breakthrough in 1991 was use of mesoporous TiO₂. Since then, several metal oxides were investigated to serve as the photoanode including ZnO, Fe₂O₃, ZrO₂, Nb₂O₅, Al₂O₃, CeO₂, Bi₂O₃, WO₃, PbO₂, V₂O₅, CuO, CdO, MnO₂, and SrO.^{6,7} Among these oxides TiO₂, Nb₂O₅, and ZnO have been most popular choices. Although TiO₂ takes the lead, ZnO is the runner up in DSSCs and photoelectrochemical cells (PECs) due to the ease of synthesizing highly crystalline ZnO in different morphologies and its high electron mobility.

Electrodeposition is shown to be a convenient and fast method for the preparation of ZnO thin films.⁵⁶ Electrodeposition is also one of the eco-friendly and cheaper choices in solar cell technologies. It is a low temperature, atmospheric process that allows control over growth rate, particle morphology and film thickness by adjusting several parameters like precursor concentration, applied potential, current and temperature. In addition, various conductive substrates can be used with arbitrary shapes. Since deposition occurs at positions where substrate conductivity is highest, it is also one of the most selective techniques. Especially, dense and vertically aligned ZnO structures such as nanowires and nanorods have been studied for light-harvesting applications since they are efficient in both charge collection and transport.²⁰ Unfortunately, efficiencies of DSSCs utilizing ZnO (below 3 %) is still lower than DSSCs prepared with mesoporous TiO₂ (up to 12 %).⁵⁶ Recently, dye sensitizers are being replaced by semiconductor materials such as CdS, CdSe, PbS and Ag₂S to overcome the low efficiencies due to slow electron injection from dye to ZnO caused by dissolution of ZnO in acidic dye solutions.^{56,95,96,23,19}

Among these semiconductors, CdS has been continuously attracting interest since improved charge separation in the CdS-ZnO coupled semiconductor systems was demonstrated²⁵ due to matching band edge positions. In such architectures the conduction band of ZnO acts as a collector of the photogenerated electrons transferred from CdS while the holes accumulate at CdS. Hence, CdS with narrow band gap ($E_g = 2.2$ eV) acts as a visible-light sensitizer for wide band gap ZnO ($E_g=3.3$ eV).¹⁸⁷

Ag₂S is an important photoelectric material for optoelectronics and photocatalysis. Its narrow bulk band gap of 1.0 eV which is close to the optimal band gap of 1.1 to 1.4 eV for photovoltaic devices²⁹ suggests Ag₂S can function also as a promising solar absorber. Due to its non-toxicity, Ag₂S has been considered as an environmentally-friendly choice compared to toxic Cd-Pb based solar cells. Recently, Ag₂S-ZnO system is reported to exhibit a considerably higher short-circuit current density (J_{sc}) and a strongly enhanced light-harvesting efficiency than its CdS-based counterpart.¹⁸⁸

Mostly used approaches to synthesize CdS and Ag₂S are chemical bath deposition (CBD) and successive ionic layer adsorption and reaction (SILAR) method.^{20,187,189–192} Aside from CBD and SILAR, pre-synthesized quantum dots (QDs) were also used as sensitizers, since attachment of colloidal QDs would provide precise control over size and shape which might be advantageous to control the length of charge transport pathway.^{11,31} However, due to low surface coverage utilization colloidal QDs resulted in lower power conversion efficiencies than their directly grown counterparts.³¹ Recently, it has been shown that electrodeposited CdSe and CdS coatings can effectively sensitize ZnO.^{40,68} It has been demonstrated that a fine electric contact between a dense and compact electrodeposited CdS layer and ZnO is advantageous for fast charge-transport.⁶⁸

In this chapter, facile electrochemical synthesis of CdS and Ag₂S on ZnO nanorod arrays is reported. The effect of electrodeposition parameters such as potential, current and time on photoelectrochemical properties of the final structures have been investigated.

6.2 Experimental

6.2.1 Materials

All the chemicals used were of analytical grade or of the highest purity commercially available. Zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) was purchased from Sigma-Aldrich. Cadmium acetate hexahydrate ($\text{Cd}(\text{CH}_3\text{COO})_2 \cdot 6\text{H}_2\text{O}$), silver nitrate ($\text{Ag}(\text{NO}_3)$), manganese chloride tetrahydrate ($\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$), sodium sulfide nonahydrate ($\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$) and elemental sulphur were obtained from Merck. Sodium thiosulfate pentahydrate ($\text{Na}_2(\text{S}_2\text{O}_3) \cdot 5\text{H}_2\text{O}$) was purchased from Horasan Chemicals (Turkey). Dimethyl sulfoxide (DMSO, $\text{C}_2\text{H}_6\text{OS}$) was supplied from Alfa Aesar. Indium Tin Oxide (ITO) ($\Omega < 5.0 \times 10^{-4}$ ohm.cm ($R_s < 100$ ohm/sq)) was purchased from Teknoma Ltd. Izmir, Turkey. Double distilled, high purity water was used from Milli-Q water (Millipore) system.

6.2.2 Synthesis and Characterization

ZnO layers were grown on ITO (Indium tin oxide) coated glass electrode ($1 \times 1 \text{ cm}^2$ area) by cathodic electrodeposition in aqueous solution of 0.01 M $\text{Zn}(\text{NO}_3)_2$. A conventional 3-electrode cell system was used for the electrochemical deposition. The reference electrode was Ag/AgCl saturated with KCl (Corr Instruments, S/N P11092) whereas Pt wire served as counter electrode. The substrate was cleaned ultrasonically by ethanol, acetone and distilled water prior to depositions. Electrodepositions were carried out at constant potential of -1.1V (vs Ag/AgCl) at 90°C for 30 minutes on a potentiostat/galvanostat (Biologic-Science Instruments, VSP model).

After deposition the oxide films were subjected to post-annealing at 450°C for an hour. Electrodeposition technique to deposit CdS /Ag₂S on ZnO films were also employed.^{40,68,193–195} CdS was galvanostatically deposited onto from a dimethyl sulphoxide (DMSO) solution containing 50 mM each of $\text{Cd}(\text{CH}_3\text{COOH})_2$ and elemental sulphur, at 90-100°C and a current density of 2 mA/cm^2 .^{195,194} Potentiostatic electrodeposition from the same bath at 100°C, -1V was also performed. Ag₂S was deposited from DMSO solution containing 50 mM $\text{Ag}(\text{NO}_3)$ and 190 mM elemental sulphur, at 100°C, at -0.8V, stated otherwise.^{196, 197}

The current-voltage (I-V) characteristics of the as-grown and annealed films were measured under illumination with a 300 W Xenon arc lamp (Oriel, Stratford, CT) with the 3

electrode cell system in an aqueous solution of 0.1 M Na₂S, 0.1M Na₂(S₂O₃) and 1% methanol. AM 1.5 air filter was used to mimic solar radiation.

The crystal structure and crystallinity of the samples were analyzed by X- diffraction (XRD) analysis using Bruker/D8 Advance with Cu K α radiation. The surface morphology of the films was examined with ZEIS EVO or with ZEISS Ultraplus Field Emission Scanning Electron Microscope (FE-SEM). Diffuse reflectance spectra of the investigated samples were performed using a Shimadzu UV–vis–NIR 3600 spectrophotometer using integrating sphere attachments. Raman scattering experiments were carried out using a Renishaw Raman Microscope system at room temperature. 532 nm laser was used for excitation.

6.3 Results and Discussion

6.3.1 CdS/ZnO Films

6.3.1.1 Morphology and Structure

Electrochemical-growth of CdS directly on ZnO films both by galvanostatic and potentiostatic deposition from DMSO bath in the presence of elemental sulphur and Cd²⁺ was investigated. CdS can exist in either a stable hexagonal phase or a meta-stable cubic phase, and identity of the substrate is crucial factor that determines the final phase of deposited CdS.¹⁸⁷ XRD pattern of CdS grown by galvanostatic deposition at 2.5 mA/cm² for 25 minutes on ZnO film (CdS(G)) is shown in Figure 6.1. It can be seen that hexagonal Wurtzite ZnO {JCDPDS No. 0361451} and hexagonal CdS phase {JCDPDS No. 800006} coexists. The diffraction peaks at 24.8, 26.4 and 28.3 coincide well with the (100), (002) and (101) diffraction lines of hexagonal CdS. CdS peaks are broadened compared to ZnO reflections which suggest smaller crystal size for CdS particles. Potentiostatic deposition was carried out at -1 V for 10 minutes (CdS(P)). XRD pattern of CdS(P)/ZnO displays hexagonal Wurtzite ZnO peaks with enhanced (002) reflection (JCDPDS No. 0361451) and a very broad peak at around 26.2° degrees. It is possible that the broadness of the peak shadows (100) and (101) reflections of hexagonal CdS which might indicate selective crystal alignment¹⁹⁸ or very small crystal size¹⁹⁹. A.McDonald *et al.*, has observed electrodeposition of cubic CdS grown along the <111> planes on Pt substrate.¹⁹⁵ Hence, this diffraction peak can be also attributed to strongest reflection of cubic CdS at 2 θ =26.47° {JCDPDS No. 800019}, however no other peaks related to cubic CdS phase could be observed.

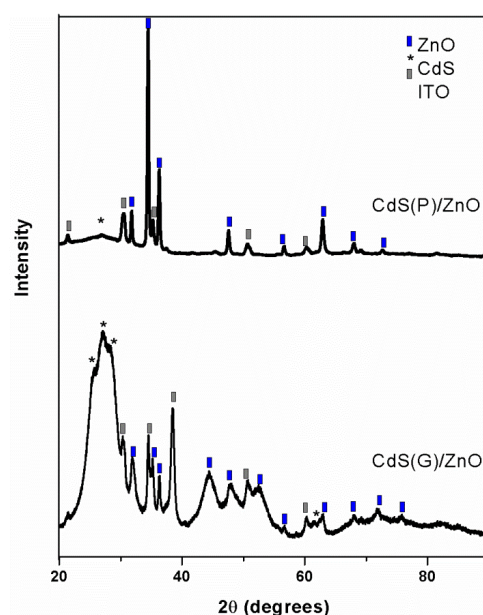


Figure 6.1 XRD patterns of a) CdS (G, 25min)/ZnO and cb) CdS (P, 10min)/ZnO films.

To further evaluate the identities of CdS phases Raman spectroscopy was used (Figure 6.2). The Raman spectrum of CdS(P)/ZnO exhibits bands at 306, 331, 438, $\sim 595\text{--}600\text{ cm}^{-1}$. The very weak shoulder at 331, and an intense peak at 438 cm^{-1} can be indexed to second order scattering and nonpolar $E_2(\text{high})$ modes of Wurtzite ZnO crystal structure respectively.^{144,145,48} The peaks at ~ 306 and $595\text{--}600\text{ cm}^{-1}$ can be attributed to the first-order longitudinal-optical (1LO) phonons and second-order longitudinal-optical (2LO) phonons of hexagonal CdS, respectively.^{187,200} For cubic CdS phase only TO phonon at 243 cm^{-1} would be present.^{201,202} The absence of 243 cm^{-1} peak further supports hexagonal CdS also for CdS(P)/ZnO. Raman spectrum of CdS(G)/ZnO is dominated by hexagonal CdS peaks. Absence of ZnO peaks can be explained by formation of thicker CdS layer with full surface coverage (as shown below) with longer galvanostatic deposition (25 min vs 10 min). Formation of hexagonal CdS for both galvanostatic and potentiostatic electrodeposition might be substrate effect.

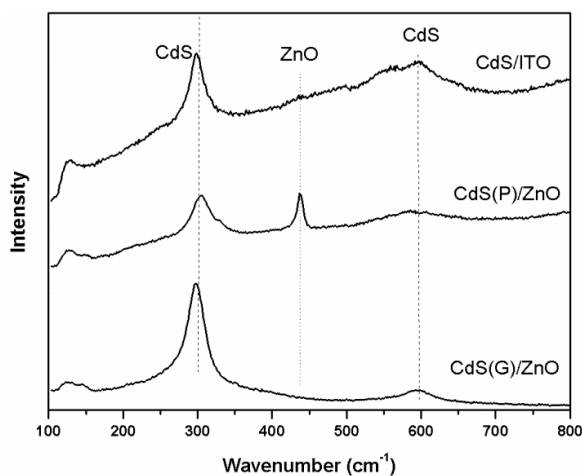


Figure 6.2 Raman spectra of CdS (G, 25min)/ZnO and CdS (P, 10min)/ZnO films.

Figure 6.3 compares the surface morphologies of pristine ZnO, CdS (G)/ZnO and CdS (P)/ZnO films. A very dense array of nanorods with hexagonal caps (diameters around 200-250 nm) are observed for pristine ZnO film. When CdS was deposited galvanostatically for 25 min on ZnO, surface of the nanorods observed to be completely covered with CdS layer. Cracking of the film is consistent with previous reports of A.McDonald and L.M. Peter *et al.*^{195,203} In our case, cracking of the film can also be attributed to loss of solvent which can be incorporated during deposition due to strong interaction of Cd²⁺ with DMSO.¹⁹⁵ When CdS was deposited potentiostatically for 10 minutes, irregular particles with various sizes formed on the surface of the nanorods with inhomogeneous surface coverage.

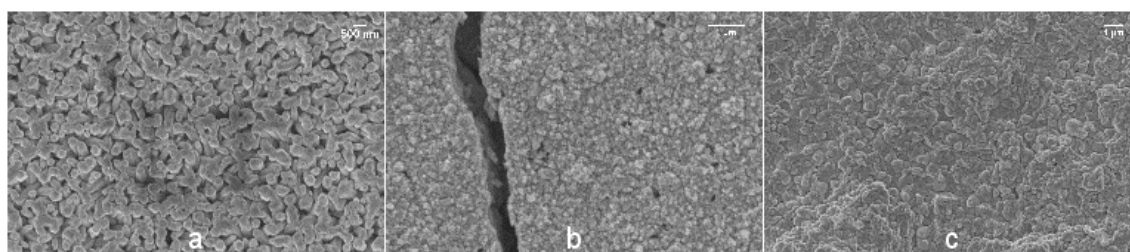


Figure 6.3 SEM images of pristine a) ZnO, b) CdS (G, 25min)/ZnO and c) CdS (P, 10min)/ZnO films.

6.3.1.2 Optical and Photoelectrochemical Properties

The absorption spectra of the prepared samples are presented in Figure 6.4. The absorption spectrum of annealed ZnO nanorods has an absorption edge shorter than 400 nm. The low absorbance between 400-450 nm might be due to the defects introduced during annealing. Calculations using first-principles density-functional theory has shown vacancies take part in visible absorbance of ZnO nanowires.¹⁰¹ CdS(G) deposition for 5 minutes shifts the absorption edge to around 520 nm. CdS (G, 5min)/ZnO film shows stronger and lower absorbance in the visible and UV regions, respectively. Weaker band edge absorption might suggest deformation of ZnO structure during CdS(G) deposition.¹⁸⁷ Increased visible absorption and absorption edge shift continue to increase with CdS(G) deposition time. CdS (G, 5min)/ZnO films displays a different behavior; stronger UV absorption than annealed ZnO film and lower visible absorption than CdS (G, 15min)/ZnO film. CdS(P) deposition for 10 minutes shifts the absorption edge to around 500 nm and it has the highest absorbance between 400-500 nm.

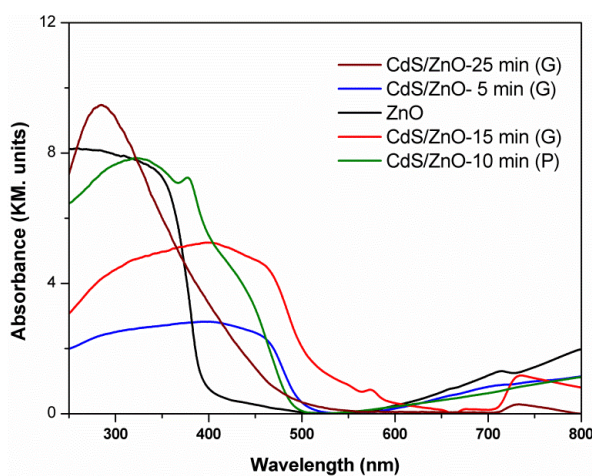


Figure 6.4 UV/visible light absorption spectra of ZnO and CdS/ZnO films.

Photoelectrochemical properties of the prepared films were studied in a three-electrode setup in 0.1M Na₂S, 0.1M Na₂S₂O₃ solution. Figure 6.5 shows the photoresponse of the films in an aqueous mixture of 0.1 M Na₂S and 0.1 M Na₂S₂O₃ solution at 0 V bias potential under amplitude modulated illumination under 1 sun conditions (100 mW/cm², AM 1.5 air filter). The photocurrent response of annealed ZnO is 0.015 mA/cm². ZnO film shows higher photoresponse than usually observed which might stem from the absorbance of the film

between 400-500 nm (Figure 6.4). The CdS (G, 5min) coated ZnO film shows an increased photo-sensitivity 0.20 mA/cm^2 , which is due to the higher visible-light sensitivity of CdS (G, 5min)/ZnO film. In agreement with optical absorption measurement photo response increases with CdS amount but levels off after 15 minutes of deposition and decrease after 25 minutes. The photocurrent density of the films are 0.15 , 0.20 , and 0.15 mA/cm^2 , respectively for CdS (G, 5min)/ZnO, CdS (G, 15min)/ZnO and CdS (G, 25min)/ZnO films. A similar trend is also observed for CdS(P)/ZnO films. The photocurrent density of the films are 0.34 , 0.44 , and 0.38 mA/cm^2 , respectively for CdS (P, 3min)/ZnO, CdS (P, 5min)/ZnO and CdS (P, 10min)/ZnO films. The best performance is observed for the CdS (P, 5min)/ZnO sample with photocurrent density of 0.44 mA/cm^2 , hence potentiostatic electrodeposition was used for the rest of the study.

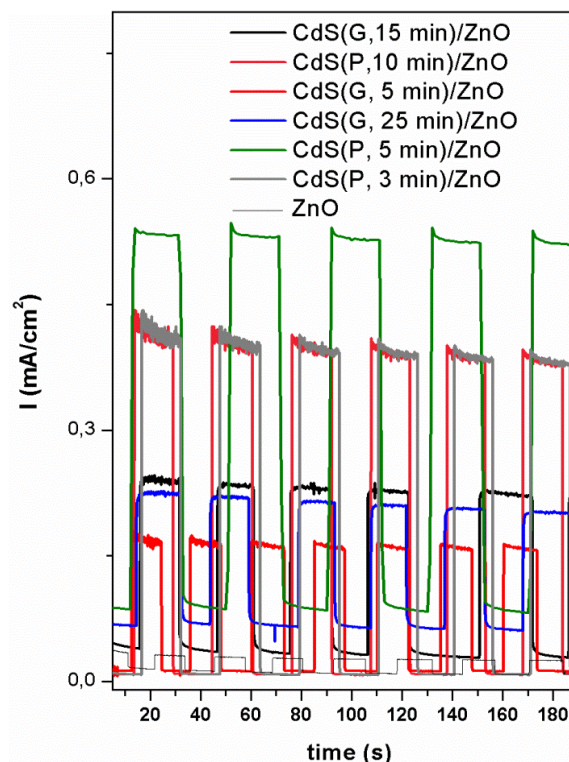


Figure 6.5 Photoresponse of the ZnO and CdS/ZnO films at 0 V (vs. Ag/AgCl) bias potential under amplitude modulated illumination at 100 mW/cm^2 (AM 1.5 air filter) in $0.1\text{M Na}_2\text{S}$, $0.1\text{M Na}_2\text{S}_2\text{O}_3$ solution.

The small photocurrent density of the films might arise from interfacial recombination losses. In order to increase the photoresponse ZnO layers were coated with electrodeposited Mn-doped CdS. It has been shown that electron accumulation within the film is enhanced by

Mn-doping by Santra and Kamat.²⁰⁴ Depositions were carried out from DMSO baths containing 0.0375 M Mn²⁺, 0.05 M Cd²⁺ and 0.19 M sulphur at -1.0 V, 100°C. Figure 6.6 shows the photoresponse of the films in an aqueous mixture of 0.1 M Na₂S and 0.1 M Na₂S₂O₃ solution at 0 V bias potential under amplitude modulated illumination under 1 sun conditions (100 mW/cm², AM 1.5 air filter). Photocurrent densities obtained are 0.15, 0.55, and 0.64 mA/cm² for 3, 5 and 10 minutes of Mn_CdS deposition on ZnO, respectively. Mn_CdS(10 min)/ZnO exhibited significant increase (~60%) in the photocurrent as compared to the corresponding semiconductor film without dopant.

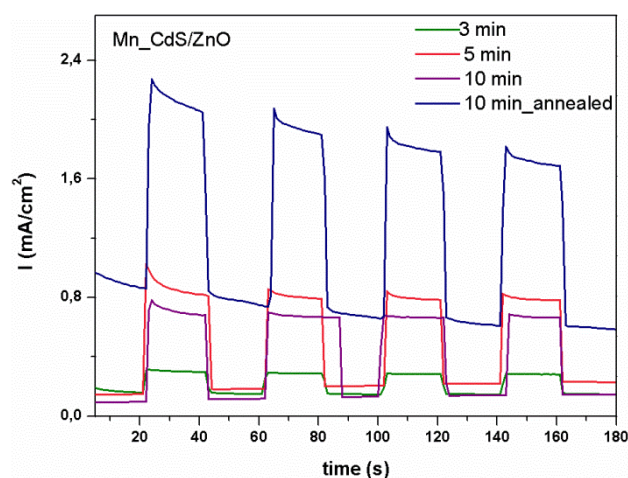


Figure 6.6 The photocurrent responses Mn-CdS/ZnO films in Na₂S/Na₂S₂O₃ mixture at 0V under amplitude modulated illumination at 100 mW/cm² (AM 1.5 air filter).

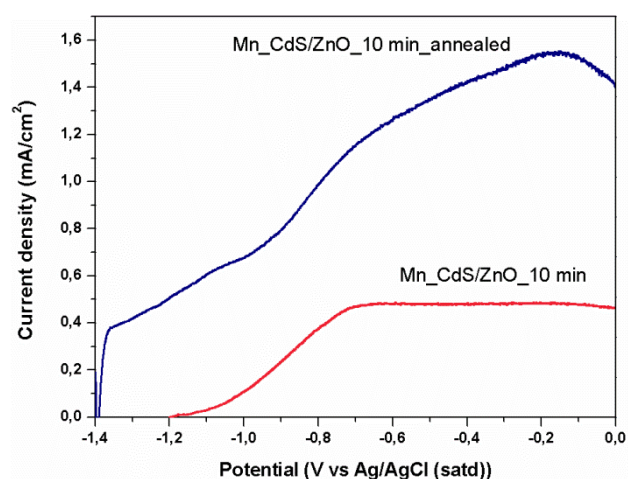


Figure 6.7 Photocurrent–voltage (J–V) curves of pristine and annealed Mn_CdS(10 min)/ZnO.

The photocurrent density of Mn_CdS(10 min)/ZnO is further enhanced by annealing at 450°C for 30 min. to 1.45 mA/cm². The current density–voltage (*J*–*V*) characteristics of the pristine and annealed Mn_CdS(10 min)/ZnO are displayed in Figure 6.7. The short circuit current density, J_{sc} of the annealed film is higher by a factor of 3. The open-circuit voltage (V_{oc} , V vs. Ag/AgCl) is also slightly higher for the annealed film. The overall efficiency for annealed Mn_CdS(10 min)/ZnO is 0.81 % under 1 sun conditions due to higher J_{sc} and V_{oc} . Fill factor of the *J*-*V* curve, however significantly decreased from 63 % to 41 % after annealing. Higher J_{sc} and efficiency imply that annealing process might have reduced recombination losses by improving the crystallinity of CdS phase and the contacts in various interfaces. The facts that relative intensity of CdS peaks in the XRD diagram (Figure 6.8) increase after annealing and (100), (002) and (101) reflections of hexagonal CdS becomes clearly identifiable suggests enhanced crystallinity upon annealing. Light absorption of the annealed Mn_CdS(10 min)/ZnO red shifts by about 20 nm with an obviously increasing intensity, ascribed to the size enlarging of CdS particles (Figure 6.9).

The efficiency is, however, still limited because of relatively low photocurrent. The small J_{sc} could arise from a number of sources, including recombination losses within CdS, trapping of photoexcited electrons at the ZnO/CdS interface, and inefficient hole transfer to the electrolyte.

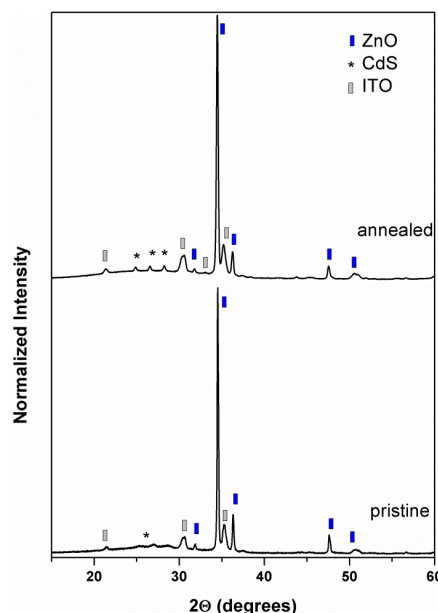


Figure 6.8 XRD diagrams of pristine and annealed Mn_CdS(10 min)/ZnO.

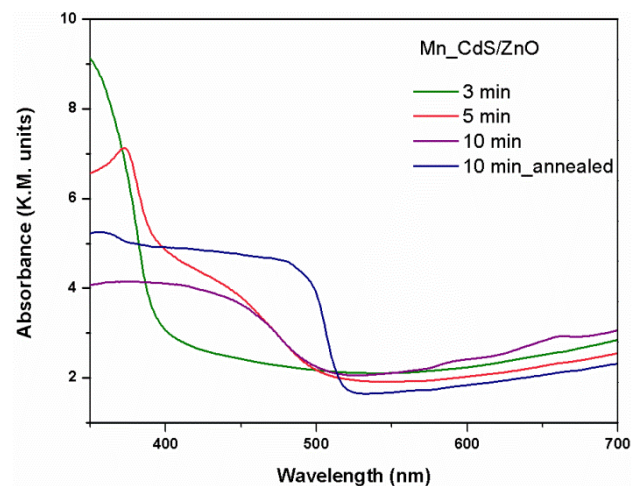


Figure 6.9 UV/visible light absorption spectra Mn_CdS/ ZnO films as a function deposition time.

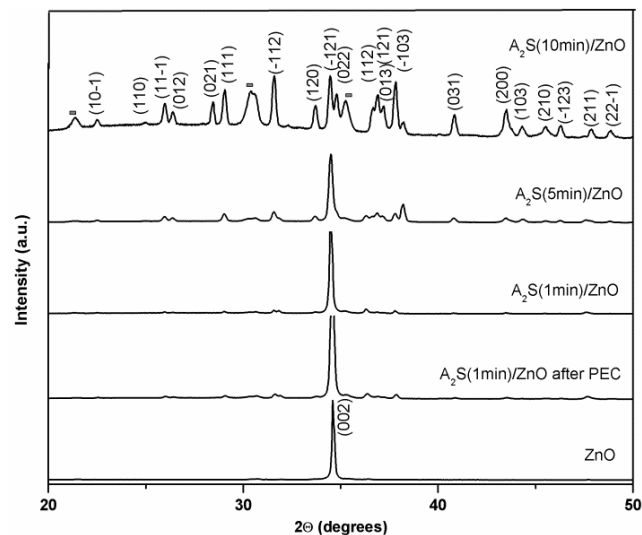


Figure 6.10 XRD diagrams Ag₂S/ZnO films.

6.3.2 Ag₂S/ZnO Films

6.3.2.1 Morphology and Structure

Electrochemical-growth of Ag₂S directly on ZnO nanorod arrays by potentiostatic deposition from DMSO bath in the presence of elemental sulphur and Ag⁺ at -0.8V, 100°C was investigated. The crystalline structures of the pristine ZnO nanorods and Ag₂S/ZnO films are characterized by XRD, and the results are shown in Figure 6.10. XRD pattern of pristine ZnO film revealed typical three peaks which can be indexed to (100), (002) and (101) reflections of hexagonal Wurtzite ZnO structure (JCDPDS No. 0361451) with a highly intensified (002) peak.

The strong (002) peak indicated highly crystalline, well aligned ZnO nanorods that were preferentially grown vertically to the substrate in line with SEM image (Figure 6.3). The (10-1), (11-1), (012), (111), (-112), (120), (121), (-103), and (031) peaks that corresponds to diffraction peaks of monoclinic β -Ag₂S {Acanthite, JCPDS: 14-0072} start to emerge after 1 minute of Ag₂S electrodeposition. The (002) reflection of ZnO coincides with (-121) reflection of Acanthite, hence it is not very clear from XRD diagram of Ag₂S(1min)/ZnO film whether ZnO is being etched during deposition. Crystallization of Acanthite phase is enhanced with deposition time, and degradation of ZnO rods is evident in the XRD diagrams after 10 minutes. Figure 6.11 shows FE-SEM images of Ag₂S/ZnO films. It can be seen in Figure 11a that etching of ZnO rods starts even after 1 minute of electrodeposition and becomes very severe in time. After 10 minutes of deposition, no rod-like structure is observed throughout the film.

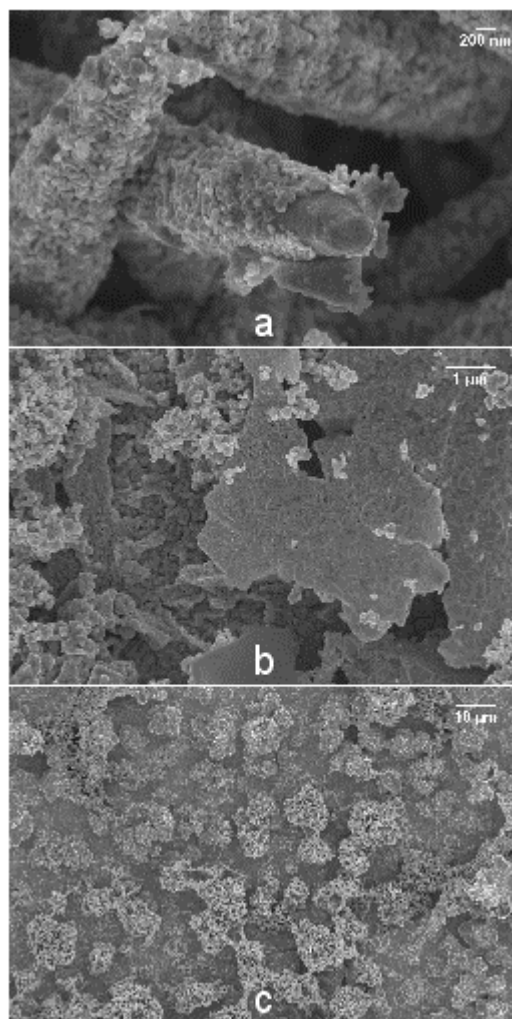


Figure 6.11 FE-SEM images of Ag₂S/ZnO films, a) Ag₂S(1min)/ZnO b) Ag₂S(5min)/ZnO c) Ag₂S(10min)/ZnO.

6.3.2.2 Optical and Photoelectrochemical Properties

The light-absorption properties of the Ag₂S/ZnO films were investigated using UV/visible light absorption spectroscopy (Figure 6.12). In comparison with the annealed ZnO nanorods (Figure 6.4), significant enhancement in both visible and NIR light absorption is observed after Ag₂S electrodeposition. Visible light absorption of the films decreases as deposition time is prolonged from 1 minute to 5 minutes then slightly increases after 10 minutes. On the other hand, the absorption intensity in the NIR region gradually increases with increasing deposition time. Moreover, the absorption edges of the Ag₂S particles are slightly red-shifted with increasing deposition time. Band-gap energies (BG) of Ag₂S(5min)/ZnO and Ag₂S(10min)/ZnO are estimated by applying equation to 1.00 and 0.96 which are close to reported values of 1.1 for bulk Ag₂S.²⁰⁵ Due to low band gap of Ag₂S, Ag₂S/ZnO films are expected to harvest a more extended range of light than CdS/ZnO films during photoelectrochemical measurements.

$$BG(eV) = 1240/\lambda (nm) \quad \text{Eqn 6.1}$$

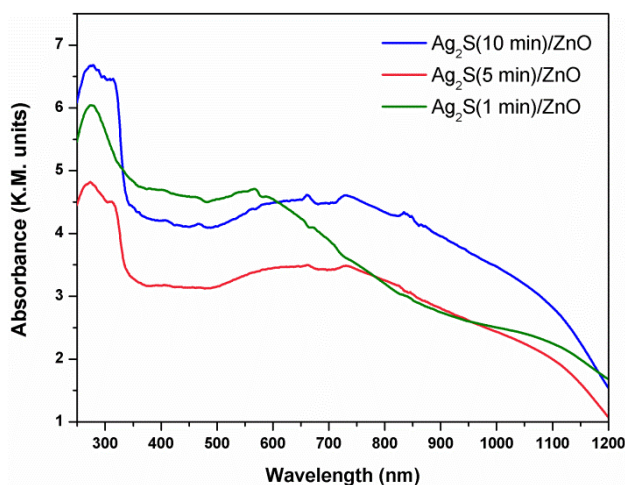


Figure 6.12 UV/visible light absorption spectra of pristine Ag₂S/ZnO films.

Figure 6.13 shows the photoresponse of the pristine films in an aqueous mixture of 0.1 M Na₂S and 0.1 M Na₂S₂O₃ solution at 0 V bias potential under amplitude modulated illumination under 1 sun conditions (100 mW/cm², AM 1.5 air filter). Ag₂S(1min)/ZnO exhibits a significantly better performance (~8 times higher) than Ag₂S(5min)/ZnO. However, photoresponse of Ag₂S(1min)/ZnO is not stable and decays from 1.72 to 0.76 mA/cm² in 5 minutes. The current density–voltage (J–V) characteristics of the film are displayed in Figure

6.14. A short circuit current density of 0.61 mA/cm^{-2} and an open circuit potential of -0.717 V have been achieved for the Ag₂S(1min)/ZnO electrode resulting in an overall power conversion efficiency of 0.2%. Photocurrent density even decayed more until J–V measurement is conducted. The initial photocurrent density of Ag₂S(1min)/ZnO is also higher than that of Mn_CdS(10min)/ZnO film, most probably due to the superior light absorption properties of Ag₂S. When XRD diagram of the film is analyzed after PEC measurements (Figure 6.10), no sign of oxidation could be detected. Hence, photocurrent decay can be ascribed to ZnO degradation that starts even after 1 min. of deposition (Figure 6.11). Since ZnO is primarily responsible for charge-transport process, its degradation would result in a loose structure and long charge transmission paths.²⁰⁶ The decrease in photocurrent density with increasing deposition time can be explained by disruption of ZnO rod structure after 5 minutes of Ag₂S electrodeposition, according to XRD diagrams and FE-SEM images (Fig.6.10-11). It has been reported that transportation of photo-generated charge carriers in pure Ag₂S is relatively difficult even though photoactivated charge carriers can be produced.²⁰⁶

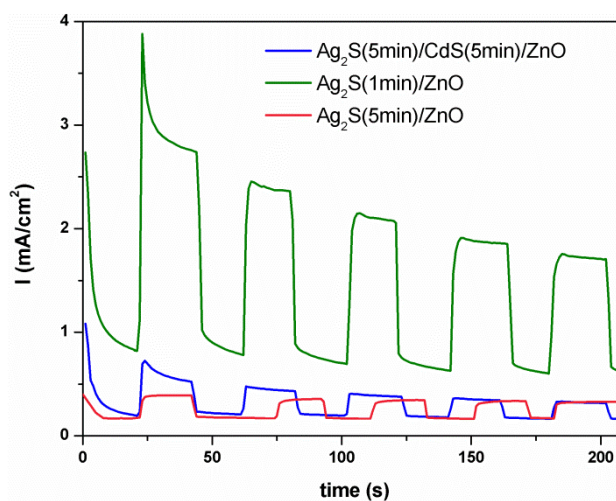


Figure 6.13 The photocurrent responses of the pristine Ag₂S/ZnO films in Na₂S/Na₂S₂O₃ mixture at 0V under amplitude modulated illumination at 100 mW/cm^2 (AM 1.5 air filter).

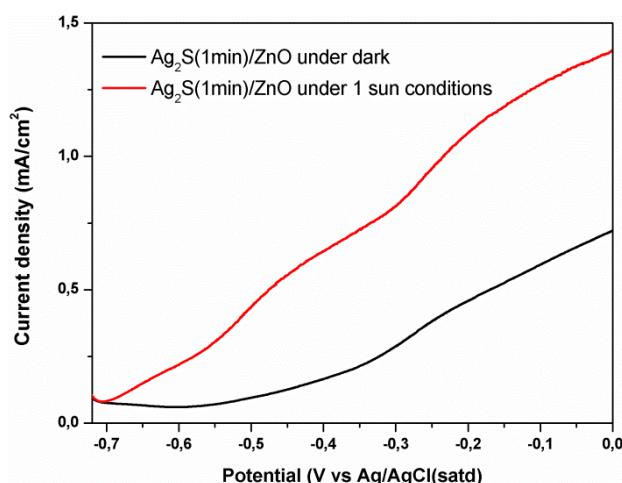


Figure 6.14 Photocurrent–voltage (J–V) curves of the pristine Ag₂S(1min)/ZnO in Na₂S/Na₂S₂O₃ mixture.

6.4 Conclusions

CdS and Ag₂S coatings are deposited on ZnO nanorod arrays via electrochemical deposition. Hexagonal CdS is grown on ZnO NRs both by galvanostatic and potentiostatic deposition. The best photoelectrochemical performance is observed for CdS deposited at -1V for 5 min. which yielded photocurrent density of 0.44 mA/cm² under 1 sun conditions. PEC activity is enhanced with Mn_doped CdS electrodeposition. Mn_CdS electrodeposition for 5 min. results in significant increase (~45 %) in the photocurrent as compared to the corresponding semiconductor film without dopant; however highest photocurrent density, 0.64 mA/cm², is obtained after 10 minutes of Mn_CdS deposition. The performance is further improved through thermal annealing most probably due to reduced recombination losses which stem from improved crystallinity of CdS phase and the contacts in various interfaces. β-Ag₂S crystallizes by potentiostatic deposition from DMSO bath in the presence of elemental sulphur and Ag⁺ which also accompany ZnO degradation. Still the Ag₂S/ZnO film displays 1.72 mA/cm² photocurrent density but photoresponse decays 0.76 mA/cm² in 5 minutes. Although the overall efficiency is relatively low, Ag₂S/ZnO films prepared by electrodeposition provide promising photoelectrochemical activity which can be enhanced by preventing ZnO NR disruption by forming a barrier layer of high conductivity.

Chapter 7 Photoelectrochemical Properties of Electrodeposited CdZnS Films

7.1 Introduction

II–VI semiconducting compounds are important group of materials because of their wide use in the fabrication of solar cells and other optoelectronic devices. The optical band gap and high absorption coefficients of cadmium chalcogenides make them useful in various electronic and optoelectronic devices. $\text{Cd}_x\text{Zn}_{1-x}\text{S}$ (CdZnS) has been attracting interest as a promising material as buffer layers in copper indium gallium (di)selenide (CIGS) and CdTe heterojunction solar cells.^{207–209} In solar cell architectures, where CdS films have been demonstrated to be effective, the replacement of CdS with the higher band gap CdZnS has shown to enhance short-circuit current density and to reduce window absorption losses.^{210,211}

CdZnS thin films have been prepared by several methodologies, which include thermal evaporation²¹², spray pyrolysis²¹³, screen printing²¹⁴, chemical bath deposition^{209,210,215,216}, and organic chemical vapor deposition²⁰⁸. However, most of these techniques require high temperatures. Furthermore, vapor-based techniques involve introduction of catalysts that might affect the physical properties of the product. Among various techniques, electrochemical deposition is a relatively simpler, economical and viable alternative for semiconductor thin film production. Electrodeposition offers the advantage over techniques in terms of controlled deposition; control over growth rate, film thickness and morphology can be maintained by adjusting parameters like temperature, applied potential, precursor concentration. Electrodeposition is suitable for large area deposition and can be carried out using substrates with different sizes and shapes. Electrodeposition of CdZnS has been reported in a few studies.^{217–219} However, reports assessing photocatalytic and photoelectrochemical properties of CdZnS by itself are rare. In this study, we explore photoelectrochemical properties of mixed semiconductor CdS–ZnS films synthesized by electrochemical deposition. Our efforts are guided to produce buffer layers for solar cells with enhanced photoactivity. It is demonstrated that films with superior photoelectrochemical properties can be produced via

electrodeposition with short circuit current density as high as 1.31 mA/cm^2 and an overall power conversion efficiency of $\sim 0.6 \%$.

7.2 Experimental

7.2.1 Materials

All the chemicals used were of analytical grade or of the highest purity commercially available. Cadmium acetate hexahydrate ($\text{Cd}(\text{CH}_3\text{COO})_2 \cdot 6\text{H}_2\text{O}$), Lanthanum nitrate hexahydrate ($\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$) and thioacetamide ($\text{C}_2\text{H}_5\text{NS}$) (TAA) were obtained from Merck. Zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) was purchased from Sigma-Aldrich. Indium Tin Oxide (ITO) ($\Omega < 5.0 \times 10^{-4} \text{ ohm.cm}$ ($R_s < 100 \text{ ohm/sq}$)) was purchased from Teknoma Ltd. Izmir, Turkey. Double distilled, high purity water was used from Milli-Q water (Millipore) system.

7.2.2 Synthesis and Characterization

CdZnS layers were grown on ITO-coated glass electrode ($1 \times 1 \text{ cm}^2$ area) in aqueous mixtures containing $\text{Cd}(\text{CH}_3\text{COO})_2$, $\text{Zn}(\text{NO}_3)_2$, thioacetamide and $\text{La}(\text{NO}_3)_3$ in varying proportions. Deposition solutions with fixed $\text{Cd}(\text{NO}_3)_2$ (50 mM) and TAA (10mM) concentrations and different $[\text{Cd}^{2+}]$ to $[\text{Zn}^{2+}]$ ratios were prepared. Details of bath composition are given in Table 7.1. Electrodepositions were carried out with a conventional 3-electrode cell system. The reference electrode was Ag/AgCl saturated with KCl whereas graphite rod served as counter electrode. The potentiometric deposition was performed at -1.0 V (vs Ag/AgCl) on a VSP potentiostat/galvanostat (Biologic-Science Instruments) at 70°C .

The crystal structure and crystallinity of the samples were analyzed by X- diffraction (XRD) analysis using Bruker/D8 Advance with Cu K α radiation. The surface morphology of the films was examined with ZEISS Ultraplus Field Emission Scanning Electron Microscope (FE-SEM). Diffuse reflectance spectra of the investigated samples were performed using a Shimadzu UV-vis-NIR 3600 spectrophotometer using integrating sphere attachments. The current-voltage (I-V) characteristics of the a electrodes were measured under amplitude modulated-light illumination with a 300 W Xenon arc lamp (Oriol, Stratford, CT) with the 3 electrode cell system in an aqueous solution of 0.1 M Na_2S , 0.1M $\text{Na}_2(\text{S}_2\text{O}_3)$ and 1% methanol. AM 1.5 air filter was used to mimic solar radiation.

7.3 Results and Discussion

Seedless electrochemical deposition of CdZnS films was carried out on ITO electrodes at constant potential (-1.0 V vs Ag/AgCl electrode) at 70°C . $[\text{Cd}^{2+}]/[\text{TAA}]$ ratio was kept constant in all cases and $[\text{Cd}^{2+}]/[\text{Zn}^{2+}]$ ratio was varied between 1 and 10 to investigate its effects on morphology, structure, optical and photoelectrochemical properties of the films. Furthermore, La^{3+} ion was included in additional experiments otherwise under identical conditions so that $[\text{Ln}^{2+}]/[\text{Cd}^{2+}]$ ratio was 0.02 (Details of bath composition are given in Table 7.1). Lanthanide ions were shown to suppress electrodeposition of metal oxides by Matsumoto *et al.*, although the mechanism and extent of restraint depends on the identity of the oxide.^{220,221} In addition, presence of La^{3+} ion in the electrolyte was shown to affect the morphology of layered ZnO and zinc hydroxide nanosheets.²²² Hence, effect of La^{3+} structure, optical and photoelectrochemical properties of the films were also evaluated.

Figure 7.1 shows FE-SEM images of CdZnS films. The as-grown CdZnS films consist of worm-like chains that are composed of aggregated, nano-sized particles and some large particles are embedded along.

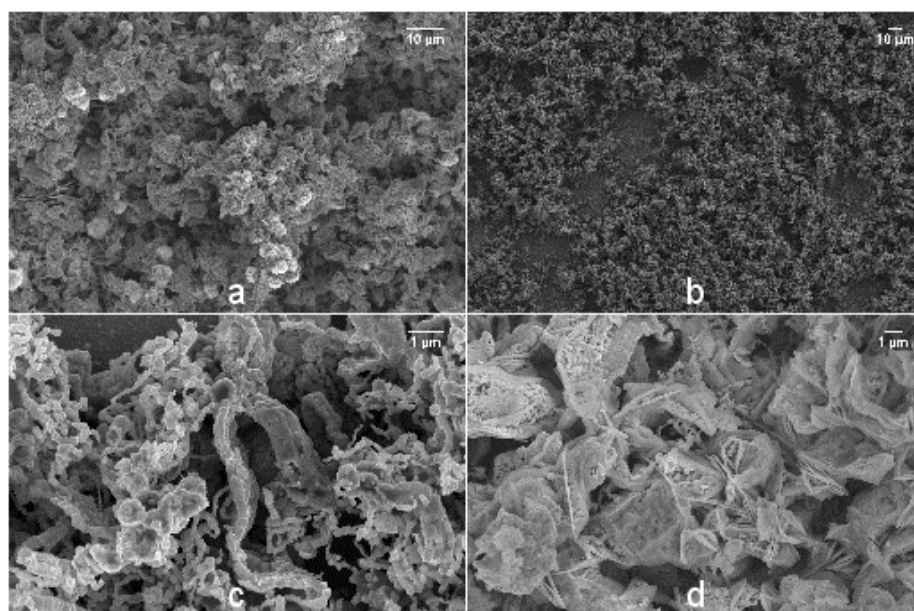


Figure 7.1 FE-SEM images of pristine CdZnS films; a) CdZnS1, b) CdZnS2, c) CdZnS3 d) CdZnS4.

The crystal structure and crystalline quality of CdZnS films were characterized by X-ray diffraction (Figure 7.2). The XRD diagrams of CdZnS1, CdZnS2 and CdZnS3 exhibit three major peaks that can be attributed to (002), (100), and (101) reflections of hexagonal, elemental Cd. High intensity of the major peaks together with the presence of higher order reflections ((012), (013), (110), (004), (112), (200), (201), (014), and (202) respectively) indicates high crystallinity. In addition to hexagonal Cd metal, relatively weak reflections are observed for CdZnS2 and CdZnS3 that are consistent with the hexagonal 'Wurtzite-type' structure of CdZnS.^{212,213} The major peaks can be indexed to the scattering from (100), (002), (101), (111), (102), (110), (103) and (201) planes of CdZnS with the reported JCPDS card data JCPDS-49-1302 and/or JCPDS-24-1137.

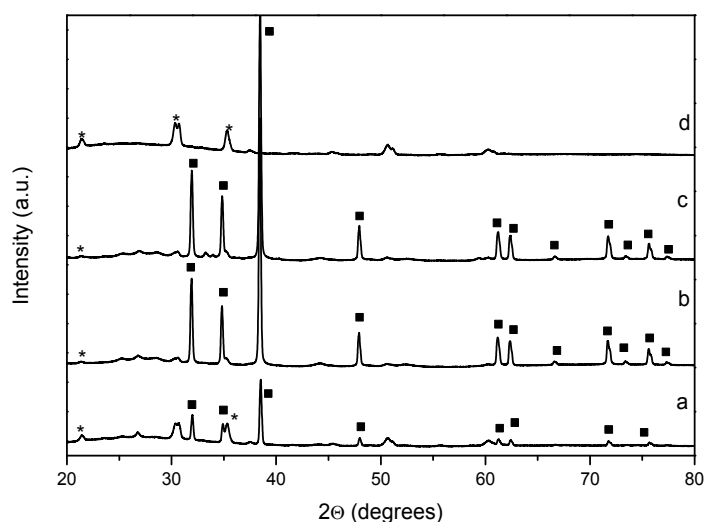


Figure 7.2 XRD profiles of pristine CdZnS films; a) CdZnS1, b) CdZnS2, c) CdZnS3 d) CdZnS4. The following symbols represent reflections associated with ■ Cd and * ITO.

We have evaluated the optical and photo-electrochemical performances of the as-prepared films. The light-absorption properties of pristine CdZnS films were investigated using UV/visible light absorption spectroscopy (Figure 7.3). As it can be seen, absorption onset is ~510-520 nm for all of the films. The optical absorbance spectra of CdZnS1 and CdZnS4 exhibit two broad absorption bands centered at around 323-328 nm and 390-420 nm. These bands can be assigned to first excitonic absorption peaks of ZnS and CdS quantum dots, respectively²²³ which suggests size confinement. On the other hand, no clearly resolved

absorbance peaks can be observed in the spectra of the films prepared with low $[\text{Cd}^{2+}]/[\text{Zn}^{2+}]$ ratio (CdZnS2 and CdZnS3) which might be attributed to homogenous formation of CdZnS phase and/or to differences in optical properties of the materials due to different quantum confinement regimes.²²³

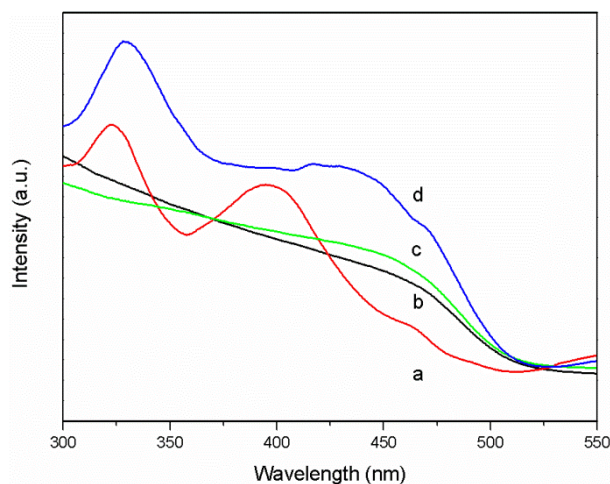


Figure 7.3 UV/visible light absorption spectra of pristine CdZnS films; a) CdZnS1, b) CdZnS2, c) CdZnS3 d) CdZnS4.

Due to their absorbance both in UV and the visible portion of light, the CdZnS films were eligible for photoelectrochemical testing under 1 sun conditions. Figure 7.4 shows the photoresponse of the films in an aqueous mixture of 0.1 M Na_2S and 0.1 M $\text{Na}_2\text{S}_2\text{O}_3$ solution at 0 V, non-biased potential, with repeating ON–OFF irradiation cycles (100 mW/cm^2 , AM 1.5 air filter). A fast photocurrent production for each switch-ON event is observed for all of the films. The anodic nature of the photocurrent produced suggests n-type behavior for all of the films and the responses are fairly stable with negligible photocorrosion. The net photocurrent densities of the films are 0.57, 0.86 and 0.28 mA/cm^2 , respectively for CdZnS1, CdZnS3, and CdZnS4. The best performance is observed with CdZnS2; 1.29 mA/cm^2 which was prepared with lower $[\text{Cd}^{2+}]/[\text{Zn}^{2+}]$ ratio in the presence of La^{3+} ion. Despite the fact that CdZnS4 exhibits highest light absorption, its photoresponse is poor compared to the other films. Hence, higher photocurrent densities can be attributed to alloying with Cd metal and high degree of crystallinity of both phases since CdZnS4 shows no evidence for presence of Cd and with the lowest X-ray diffraction intensities. In addition, it is also observed that films prepared with

higher Zn(II) content in the deposition bath displays higher photocurrent densities. Higher Zn content can be correlated with enhanced electron-injection ability²²⁴ and hence became advantageous for the photoelectrodes despite of their lower light absorption.

Reports assessing photoelectrochemical properties of only CdZnS layers are relatively rare. $\text{Zn}_x\text{Cd}_{1-x}\text{S}$ -graphene quantum dots grown hydrothermally were shown to produce $\sim 10 \mu\text{A}/\text{cm}^2$ photocurrent at 0.2 V in phosphate buffer under illumination with a 500 W-Xe lamp.²²⁴ For $\text{Cd}_x\text{Zn}_{1-x}\text{S}$ films synthesized by screen printing method less than $2 \times 10^{-5} \text{ A}/\text{cm}^2$ photoresponse was obtained in 0.1M Na_2SO_3 under illumination with $60 \text{ mW}/\text{cm}^2$ white light.²¹⁴ Superior photoelectrochemical properties of CdZnS1-3 samples show that they are very promising candidates as window/buffer materials.

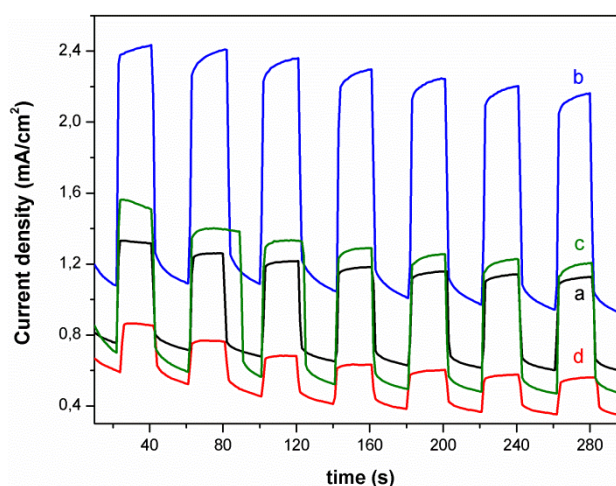


Figure 7.4 The photocurrent responses of pristine CdZnS films; a) CdZnS1, b) CdZnS2, c) CdZnS3 d) CdZnS4 in $\text{Na}_2\text{S}/\text{Na}_2\text{S}_2\text{O}_3$ mixture at 0V under amplitude modulated illumination at $100 \text{ mW}/\text{cm}^2$ (AM 1.5 air filter).

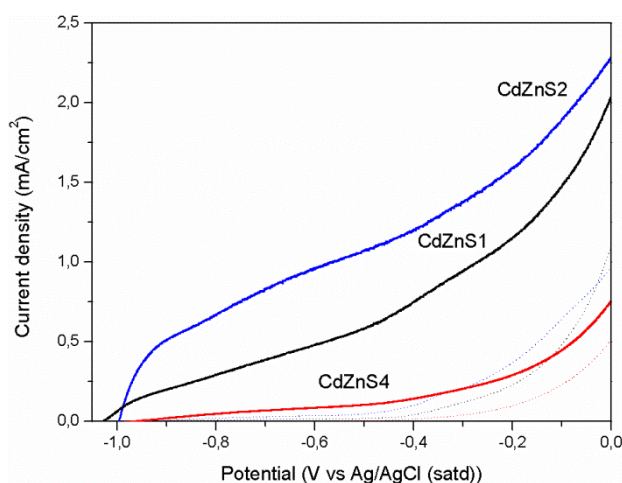


Figure 7.5 Photocurrent–voltage (J – V) curves of pristine CdZnS films in $\text{Na}_2\text{S}/\text{Na}_2\text{S}_2\text{O}_3$ mixture. (Solid lines; under illumination at $100 \text{ mW}/\text{cm}^2$, dotted lines; under dark conditions).

The current density–voltage (J – V) characteristics of the films are displayed in Figure 7.5 and key performance parameters are summarized in Table 7.1. The measurements were conducted in an aqueous mixture of $0.1 \text{ M Na}_2\text{S}$ and $0.1 \text{ M Na}_2\text{S}_2\text{O}_3$ solution under dark and 1 sun conditions and the sweep rate was kept at $10 \text{ mV}/\text{s}$. As revealed also by photoresponse measurements, the short circuit current density, J_{sc} of the films increase with the increased Zn content, while the open-circuit voltage (V_{oc} , V vs. Ag/AgCl) is $\sim -1 \text{ V}$ for all of the films. Highest efficiency is obtained with CdZnS2 ($\eta = 0.56 \%$ under 1 sun conditions) due to higher fill factor of the J – V curve ($FF = 43 \%$) along with high J_{sc} . These results indicate that CdZnS2 photoelectrode exhibits the best photoelectrochemical properties, and it is the most appropriate window material for photoelectrochemical cells.

Table 7.1 Photovoltaic parameters of the CdZnS films.

Films	$[\text{Cd}^{2+}]/[\text{Zn}^{2+}]$	$[\text{La}^{3+}] \text{ (mM)}$	$J_{sc} \text{ (mA}/\text{cm}^2)$	$V_{oc} \text{ (V)}$	$FF \text{ (%)}$	$\eta \text{ (%)}$
CdZnS1	10	—	0.94	-1.12	27	0.29
CdZnS2	1	—	1.31	-0.99	43	0.56
CdZnS3	1	1	—	—	—	—
CdZnS4	10	1	0.24	-1.09	22	0.06

7.4 Conclusions

Mixed semiconductor CdS–ZnS films are synthesized by electrochemical deposition and their photoelectrochemical properties are investigated. Photoresponse tends to increase with increasing Zn(II) amount. As-prepared films display significantly enhanced photocurrent compared to the literature. The best performing film exhibited a short circuit current density of 1.31 mA/cm^2 and an open circuit potential of -0.99 V with an overall power conversion efficiency of $\sim 0.6 \%$. These promising current-voltage characteristics suggest possibility of efficient solar cell construction by electrodeposited CdZnS buffer layers.

PART II. PREPARATION OF HEMATITE THIN FILMS by ELECTRODEPOSITION

Chapter 8 Introduction

8.1 Hydrogen and Photoelectrochemical Splitting of Water

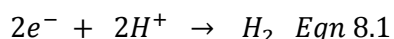
Growing energy demand, depletion of fossil fuels, environmental and political concerns resulted in search for new, sustainable energy sources. Primary and largest clean energy source is the sun; however, direct use of solar energy by solar thermal power or photovoltaic solar cells is still limited, and only 0.04% of the total energy is generated by PVs. Yet, solar cell market is one of today's fastest growing markets by 35-40 % growth per year.²²⁵ Ever-growing research on solar energy and large-scale use face an energy storage problem. Hydrogen is one of the most promising future energy carriers due to its high energy content and environmentally friendly combustion. Hydrogen can be obtained by electrolysis of water and upon combustion it returns water again without any harmful byproducts. Conversion of solar energy into hydrogen would provide long-term storage of the world's most abundant source of energy. Hence, it is one of the main research areas; the development of clean and sustainable methods for hydrogen production from renewable energy sources. Solar energy can also be used to produce Hydrogen, the future fuel. The basic energy conversion scheme in the photon-driven water-splitting method is the transformation of light energy into chemical energy. Photoelectrolysis can be accomplished using PV cells connected directly to electrolyzers which would exhibit an average overall conversion efficiency of 8 %.²²⁵ A more attractive strategy is to design photo-electrochemical cells (PECs) where photo-generated electrons and electron-holes are directly used to reduce and oxidize water, respectively at the semiconductor surface. Hence, the functions of solar cell and electrolyzer are now combined in a single device, which avoids significant fabrication and systems cost.

The efficiency of PEC depends mostly on the semiconductor properties. Water splitting cells require semiconductor materials with suitable band gap positions for the redox reactions that are able to support rapid charge transfer at a semiconductor/liquid interface, that exhibit long-term stability, resistance to photocorrosion, and that can efficiently harvest a large

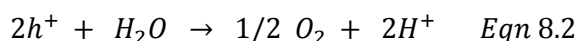
portion of the solar spectrum. After the first report of Fujishima and Honda in 1972 where they showed it was possible to split water by shining light on semiconductor photoanode, the initial studies on photoelectrochemical H_2 production were conducted with TiO_2 .⁸ Besides TiO_2 , ZnO , $SrTiO_3$, $NaTaO_3$, WO_3 and various titanates, niobates and tantalates have been also tested.²²⁶ Among tested materials, $\alpha-Fe_2O_3$ (hematite) has become popular in photoelectrochemical studies due to its ideal band gap of 2.0-2.2 eV, abundance, non-toxicity and stability.⁹ The research summarized in this part of the dissertation is focused on developing hematite nanostructures of various morphologies by hydrothermal-electrodeposition technique. Subsequent sections describe the greater details of basic principle involved in the photoelectrochemical splitting of water for generation of hydrogen

8.1.1 Operational Principles of Photoelectrochemical Cells (PECs)

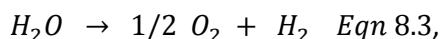
Water splitting PEC cells can be regarded as the second type, photosynthetic cells that operate on a similar principle with PECs explained in Chapter 1, except that there are two redox systems: one reacts with the holes at the surface of the semiconductor electrode and the second reacts with the electrons entering the counter-electrode. The principle of operation for water splitting PEC with an n-type semiconductor is presented in the energy diagram of Figure 8.1. When the film is illuminated with photons that have an energy that is equal to or larger than the band gap, electrons are excited from the valence band into the conduction band. The electrons travel to the back contact and are transported to the counter electrode where they reduce water to form hydrogen gas, hydrogen-evolution reaction (HER);



The holes in the valence band migrate to the surface, where they oxidize water to form oxygen gas, oxygen evolution reaction (OER);



The overall reaction is;



with the free energy change of 237.2 kJ/mol under standard conditions, which, according to the Nernst equation, corresponds to potential ΔE° of 1.23 V per electron transferred. The overall solar-to-hydrogen conversion efficiency of the device can be calculated using eqn 8.4

(assuming no corrosion reaction at the photoelectrodes and a Faradaic efficiency of unity for both reactions);

$$\eta_{STH} = \frac{j(1.23 V - V_{appl})}{P_{in}} \quad \text{Eqn 8.4 ,}$$

where V_{appl} is the applied voltage measured between the oxygen-evolving photoanode and the hydrogen-evolving photocathode, j is the externally measured current density, and P_{in} is the power density of the illumination. By measuring the photocurrent (j) at 0 V (under short-circuit conditions) a true solar-to-hydrogen (STH) production efficiency, where the only inputs are sunlight and water, can be calculated.

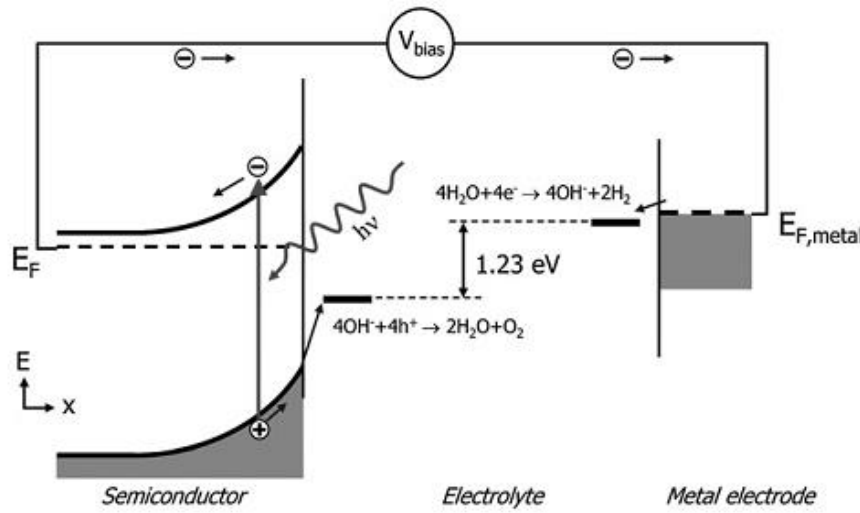


Figure 8.1 Energy diagram of a PEC cell for the photo-electrolysis of water.²²⁵

The recombination of electron-hole pairs is prevented by an electric field close to the surface of the semiconductor.²²⁵ When a semiconductor is in contact with an electrolyte, electric current initially flows across the junction until electronic equilibrium between the Fermi energy of the electrons in the solid (E_F) and the redox potential of the electrolyte (E_{redox}) is established. The transfer of electric charge produces a region on each side of the junction where the charge distribution differs from the bulk material, and this is known as the space-charge layer and result in band bending on the semiconductor side depending on the position of Fermi level. For a typical n-type semiconductor photoanode in equilibrium with a redox species in solution (e.g., O_2/H_2O), the electrode will have an excess positive charge, arising from the ionized dopant atoms in the semiconductor, and the solution will have an excess

negative charge. The electric field that is developed in equilibrium with a redox couple results in band bending that directs photogenerated holes to move into the solution.

8.1.2 Material Requirements of PEC Cells

Selection of materials as photoelectrodes in water splitting PEC cells to split water requires satisfying several specific semiconducting and electrochemical properties. The material must have suitable band gap, strong visible light absorption, and suitable band-edge positions to enable oxidation/reduction of water, low overpotentials for the reduction/oxidation reactions as well as electrical properties such as doping and resistivity that allow efficient collection of charge carriers. Moreover, the material needs to be stable under water oxidation conditions and resistive against photocorrosion. These aspects will be described in detail in the following sections.

6.4.1.2 8.1.2.1 Band gap and Position of Band Edges in Semiconductors

The minimum band gap required is determined by the energy required to split water (1.23 eV) plus the thermodynamic losses (0.4 eV) and the overpotentials that are required at various points in the system to ensure sufficiently fast reaction kinetics (0.3–0.4 eV).²²⁵ Hence, the minimum band gap value is 1.9 eV, which implies an absorption onset of 650 nm. The maximum value of the band gap is determined by the solar irradiance spectrum given in Chapter 1(Figure 1.4). Below 400 nm the intensity of sunlight drops rapidly, which sets 3.1 eV as an upper limit. Hence, the optimum value of the band gap should be between 1.9 and 3.1 eV, which corresponds to the visible region. For a PEC cell involving single photoelectrode, a maximum efficiency of 16.8% is calculated for a hypothetically ideal material with a band gap of 2.03 eV.²²⁵

In addition to the band gap, the positions of the conduction band and valence band edges of the semiconductor are crucial parameters for effective functioning of PECs since spontaneity of the water splitting depends on the relative position of the band edges of the semiconductor and redox potential of the water. Higher conversion efficiency is obtained for a spontaneous reaction without externally applied potential.

A semiconductor ($E_g \geq 2$ eV) with conduction band (E_c) above $E_{red}(H_2/H^+)$, and valence band (E_v) below $E_{ox}(OH^-/O_2)$ is required for spontaneous water splitting. Under these conditions charge transfer between the semiconductor and the electrolyte is energetically

favorable. The band-edge positions of various semiconductors, along with the reduction and oxidation potentials of water are shown in Figure 8.2. It is apparent from the figure that most non-oxide semiconductors are able to reduce, but not oxidize water, whereas most oxide semiconductors are able to oxidize, but not reduce water. Wide band-gap materials (over 3 eV) have a conduction band edge above $E_{red}(H_2/H^+)$. Only $SrTiO_3$ ($E_g \sim 3.2$ eV) has been shown to exhibit spontaneous water splitting, however, the efficiency was less than 1% due to the large band gap.²²⁵ In most cases, oxide semiconductors (due to the stability factor, Section 8.1.2.2) with a suitable band-gap around 2~eV is used in the presence of an externally applied voltage to assist the reduction reaction.

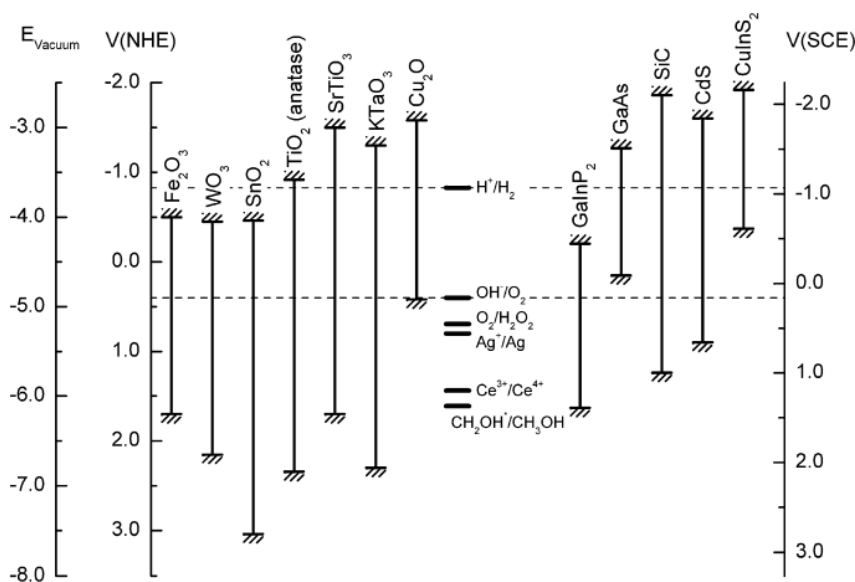


Figure 8.2 Energy band positions for various semiconductors at pH 14. (the band positions are extrapolated using -59 mV per pH unit, if no experimental data were available for pH 14.)²²⁵

6.4.1.3 Stability of the Electrodes

Stability against photocorrosion is another requirement for photoelectrodes. Semiconductor photoelectrodes should exhibit excellent oxidative/reductive stability in contact with aqueous electrolyte solutions. For thermodynamic stability, a semiconductor's reductive and oxidative decomposition potentials must be more negative than the semiconductor's conduction band-edge for water reduction or more positive than the semiconductor valence band-edge potential for water oxidation.²²⁶ Most non-oxide

semiconductors, such as Si, GaAs, GaP, CdS either dissolve or form a thin oxide film which prevents electron transfer across the semiconductor/electrolyte interface. Almost all metal oxide photo-anodes are thermodynamically unstable, which means that the photogenerated holes are able to oxidize the semiconductor.²²⁵ Photocorrosion can be avoided, if the kinetics of charge transfer (OER kinetics) across the interface is faster than the anodic decomposition reaction.

6.4.1.4 Metal Oxides Suitable for PEC Splitting of Water and Hematite Photoanode

In the past few decades, metal oxide semiconductor photoelectrodes proved themselves efficient for solar water splitting. After the pioneering work of Fujishima and Honda in 1972, showing the possibility of splitting water by shining light on semiconductor TiO₂ photoanode, several other metal oxides such as SrTiO₃, KTaO₃, BaTiO₃, WO₃, ZnO, Cu₂O, α -Fe₂O₃ were also brought to attention.^{227,226} But so far, no material has been found to exhibit efficient splitting of water fulfilling all the requirements listed in the previous sections.

TiO₂, the most extensively studied material, possess excellent chemical stability but only absorb a small fraction of solar light due to its large band gap ($E_g = 3.2$ eV).²²⁵ Efforts are focused on the improvement of the PEC properties of TiO₂ photoelectrodes by controlling the morphology and through doping.²²⁶ Similar to TiO₂, SrTiO₃, KTaO₃, and BaTiO₃ suffer from low solar conversion performances due to their large band gaps.²²⁸ Tungsten oxide, WO₃, ($E_g = 2.7$ eV) can utilize a portion of the visible spectrum to generate electron-hole pairs, and its valence band edge is located at approximately 3 eV versus NHE, providing enough overpotential to evolve oxygen.²²⁹ WO₃ is also thermodynamically stable against anodic photocorrosion in a PEC because its anodic decomposition potential is located 1.1 V more positive than the O₂ evolution potential. However, it does not possess a conduction band capable of spontaneous photogeneration of H₂. Mesoporous WO₃ photoanodes are shown to exhibit the highest incident photon-to-electron conversion efficiency (IPCE) 80% at 400–410 nm, which is the maximum among the visible-light-responsive semiconductor photoelectrodes; however, the theoretical solar-to-hydrogen conversion efficiency of WO₃ photoelectrode is only 4.8%.²²⁸ Compared with TiO₂, ZnO exhibits similar band gap and band edge positions. Although, ZnO has a direct band gap and higher electron mobility than TiO₂, ZnO photoelectrodes usually exhibit less efficient PEC performances than TiO₂.²²⁸

Hematite ($\alpha\text{-Fe}_2\text{O}_3$) with a band gap of ~ 2.05 eV, corresponding to an absorption onset wavelength of ~ 605 nm, is an attractive candidate for the photoelectrolysis of water due to abundance, good photoelectrochemical stability and chemical inertness. $\alpha\text{-Fe}_2\text{O}_3$ photoelectrode has been a hot topic for several decades, since it exhibits 12.9 % of the theoretical solar-to-hydrogen conversion efficiency.²²⁸ Additionally, it is easily doped, can be synthesized with many technologies in various morphologies, and on a broad range of substrates. However, PEC performance of hematite photoelectrodes has been much below its theoretical maximum of 12.9 %. This is attributed to rapid electron-hole recombination resulting in short diffusion lengths of charge carriers, as well as a rapid falloff in the absorption cross-section of the material for wavelengths approaching the band gap value. In addition, the conduction band edge is too positive to reduce water to hydrogen directly which is overcome by applying an external bias.

Several approaches have been used to improve PEC performance of hematite electrodes; mostly doping (to improve the conductivity of hematite) and structural enhancement (to increase the surface area and reduce the distance photogenerated charge carriers have to travel for charge collection).²³⁰ Of the many dopants introduced into hematite, tetravalent dopants like Ti(IV), Si(IV), or Sn(IV) are promising for enhancing the photoelectrochemical response. Doping hematite with between roughly 1 and 10 % Ti(IV), Si(IV), or Sn(IV) can substantially increase photocurrents by enhancing conductivity through introducing additional majority carriers.²³¹ Gratzel *et al.* have reported that silicon doping of hematite promotes both its electrical conductivity and the development of dendritic nanostructures.²³² These researchers have thus far attained a short-circuit current density of 2.3 mA/cm^2 at 1.23 V vs RHE under AM 1.5G sunlight.

Hematite nanostructures with different dimensionality and levels of complexity have been investigated for PEC applications. To address poor hole transport high-aspect-ratio nanowire electrodes is proposed. By ensuring that the wires have a radius which is less than the hole diffusion length of hematite (2–4 nm or 20 nm), hole transport limitations can be avoided.²²⁵ The large specific surface area provided by the nanowire electrode addresses the intrinsically slow water oxidation kinetics by valence band holes. Sn-doped nanocorals as well as nanowires are reported to exhibit photocurrent densities of 1.3 mA/cm^2 under AM 1.5 illumination.²³³

8.1 Material of Interest : Hematite (α -Fe₂O₃)

There is a strong motivation to prepare ferric oxide nanoparticles of various sizes due to their novel properties and potential applications in medicine, catalysts, magnetic recording media, pigments, anticorrosive agents, gas sensors and electrochemical capacitors.²³⁴ Ferric oxide (α -Fe₂O₃, hematite) has become a very desirable material also to construct photoelectrochemical cells due its band gap ($E_g \sim 2.2$ eV) which allows utilization of a considerable portion of solar energy and stability in harsh chemical environments.²³³ Non-toxicity, low cost and relative abundance of hematite on earth also add on its charm. Despite these exiting features hematite suffers from poor conductivity, short photogenerated carrier life-time and a short hole diffusion length.²³¹ It has been demonstrated that poor charge-transport properties can be improved with nanostructured morphology which provides higher surface area.²³⁵ Hence, hematite particles of various size and morphology has been prepared in the present study. Subsequent sections describe physical properties of hematite.

8.2.1 Structure

Iron is found with an average estimate of 2 to 3% in sedimentary rocks rising to 8.5% in basalt and gabbro, making it the fourth most abundant element in the earth's crust.²³³ Because iron is readily oxidized in air to the ferrous (+2) and ferric (+3) states, iron oxide is ubiquitous. Many well-defined crystalline forms of iron oxide, hydroxide and oxyhydroxide exist in nature. Hematite is the most thermodynamically stable form of iron oxide under ambient conditions and it is also the most common form of crystalline iron oxide.

Hematite is isostructural with corundum with Fe(III) cations in a slightly distorted octahedral environment. The unit cell is hexagonal with $a=0.5034$ nm and $c= 1.3752$ nm and there are six formula units per unit cel.²³⁶ Hematite can also be indexed to Rhombohedral system with a Rhombohedral unit cell ($a_{rh}=0.5427$ nm and $\alpha=55.3^\circ$) and two formula units per unit cell. Hematite's structure based on the packing of the anions (O²⁻) which are arranged in a hexagonal closed-packed lattice along the [001] direction. The cations (Fe³⁺) occupy the two-thirds of the octahedral interstices (regularly, with two filled followed by one vacant) in the (001) basal planes, and the tetrahedral sites remain unoccupied (Figure 8.3). The arrangement of cations can also be thought of producing pairs of FeO₆ octahedral that share edges with three neighboring octahedra in the same plane and one face with an octahedron in an adjacent plane in the [001] direction. Face sharing occurs along the c-axis.

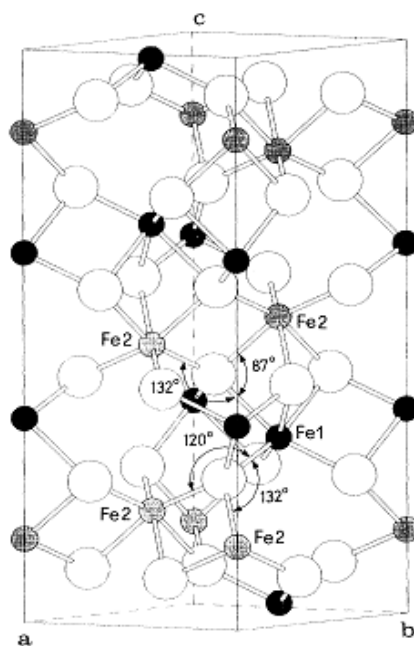


Figure 8.3 View of the crystal structure (ball and stick model) of $\alpha\text{-Fe}_2\text{O}_3$, with outline of the hexagonal unit cell. Black and open circles denote Fe and O, respectively.²³⁷

Typical XRD pattern of electrodeposited, Rhombohedrally centered hexagonal structure of $\alpha\text{-Fe}_2\text{O}_3$ together with JCPDS pattern is given in Figure 8.4. According to the {JCPDS card No. 86-0550} the peaks at scattering angles (2θ) of 24.2°, 33.3°, 35.8°, 39.5°, 41.1°, 43.9°, and 49.6°, correspond to the reflection from (012), (104), (110), (006), (113), (202), (024), and (116) crystal planes, respectively with (104) reflection exhibiting maximum intensity.

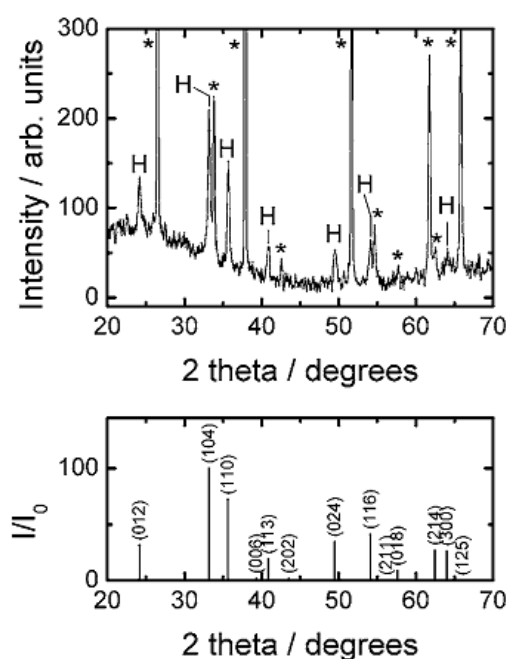


Figure 8.4 XRD pattern of an electrodeposited $\alpha\text{-Fe}_2\text{O}_3$ thin film Hematite JCPDS pattern is also shown for comparison. (*indicates the peaks originated from SnO_2 , the others are related to the hematite phase, H.)²³⁸

The common growth habit of hematite crystal is to form platy and rounded rhombohedra.²³⁶ The plates can be round, hexagonal or of irregular shape. The plane with lowest surface energy is (001) and the surface energies for various low index faces calculated to be similar.²³⁶ Like ZnO, the stability of the facets can be altered by preferential adsorption of ionic species or by slight alterations of growth conditions. Iron oxide with shapes such as spheres, cubes, ellipsoids, and rods are obtained by the forced hydrolysis of ferric salt.²³⁹ Distinctive iron oxides such as ellipsoidal, rod-like and tube-like, quasicubic, hollow spheric, Rhombohedral, cantaloupe-like, and ring-like hematite have been synthesized in the presence of several different surfactant molecules.²³⁹

Hematite belongs to the D_{3d}^6 space group and seven transitions are expected in the Raman spectrum^{240,241,242}. Two A_{1g} modes at 225 and 498 cm^{-1} and five E_g modes at 247, 293, 299, 412 and 613 cm^{-1} are expected. Hematite is an antiferromagnetic material and the collective spin movement can be excited in what is called a magnon. The intense feature observed in many reported spectra at 1320 cm^{-1} is assigned to a two-magnon scattering which arises from the interaction of two magnons created on antiparallel close spin sites.²⁴⁰ In

several published spectra a mode appears around 660 cm^{-1} which is either assigned to magnetite/wüstite (FeO) impurity or considered as characteristics of hematite and assigned to a disorder phase.^{243,244,232} It has been reported that large inclusions of magnetite ($\geq 30\%$) are required (due to its weak Raman spectrum) in order for a 660 cm^{-1} magnetite peak to appear and be detected in the hematite spectrum.²⁴⁴ Such significant amounts of magnetite should be identifiable by other characterization techniques such as X-ray diffraction that can be used to differentiate between disorder or impurity 660 cm^{-1} peak. The mode is also suggested to be related to surface and grain boundary disorder which is used to explain why the peak is not always observed in hematite spectra.²⁴⁴

8.2.2 Optical Properties

Hematite's strong absorption of yellow to ultraviolet photons in the visible region and transmission of orange to infrared photons gives it a characteristic red color. Types of electronic transitions that are responsible for the UV-Vis spectra include ligand field (d-d) transitions and ligand (oxygen)-metal charge transfer excitations. The ligand field transitions involve excitations from the ground state ${}^6A_1$ to the excited ligand field states which are normally spin forbidden. However, in iron oxide compounds, the intensity of these transitions are higher than expected due to the magnetic coupling of the next nearest neighbor Fe^{3+} in the crystal structure.²³⁶ The charge transfer transitions ($\text{O}_2 \rightarrow \text{Fe}^{3+}$) are mainly responsible for the visible absorption; they are located near UV with absorption edge at 570 nm .²³⁶

8.2.3 Growth and Synthesis of Hematite

Several methodologies were employed to grow hematite nano-crystals including high-temperature based techniques such as pulsed layer deposition, catalyst-assisted chemical vapor deposition and thermal oxidation.²² Techniques which required lower temperatures like solution based approaches; chemical precipitation, sol-gel, forced hydrolysis and hydrothermal synthesis were also applied.²³⁴

Gas deposition synthesis including physical vapor evaporation, chemical vapor deposition, atomic layer deposition, and reactive sputtering used to prepare $\alpha\text{-Fe}_2\text{O}_3$, with different morphologies such as nanowires, nanorod arrays, nano-dendritic structures and thin films.²⁴⁵ An important advance is the fabrication of perpendicularly oriented dendritic silicon-

doped hematite nanostructures using atmospheric pressure chemical vapor deposition (APCVD) by Cesar *et al.*²⁴⁶ The as-prepared dendritic α -Fe₂O₃ nanostructures exhibit large surface area, and good contact between α -Fe₂O₃ and the growth substrate, which is critical for charge carrier transfer. Atomic layer deposition (ALD) has also attracted attention as a means of fabricating hematite, with or without intentional doping.^{228,247} The most compelling features of ALD methods are that they provide close to angstrom-level control over thickness, and they deposit material reproducibly and uniformly. ALD is especially useful for preparing smooth and ultra-thin films of precise, predetermined thickness, either on flat platforms or on high-area platforms.²³¹ Although high quality nanostructured hematite films have been prepared by vapor phase deposition methods, there are certain drawbacks such as high temperature, high cost, highly toxic materials required for some of the techniques and some vapor based methods require introduction of catalysts.

The solution-based method is a facile and scalable method to fabricate nanostructures. α -Fe₂O₃ with different morphologies such as nanoparticles, nanowires, nanotubes, hollow spheres, and nanoflowers has been fabricated via solution-based methods such as hydrothermal, solvothermal and sol-gel routes.²⁴⁵ Zhu *et al.* used co-precipitation followed with hydrothermal treatment to obtain hierarchical mesoporous α -Fe₂O₃ nanoarchitectures with a pod-like shape which exhibit an improved performance for Li-ion storage with good rate performance.²⁴⁸ Single-crystalline α -Fe₂O₃ submicron cubes have been prepared via a simple hydrothermal process.²⁴⁹ α -Fe₂O₃ particles with morphologies from rod-like to Rhombohedral were prepared by hydrothermal method using four different surfactants, sodium dodecylsulfonate (SDS), sodium dodecylbenzene sulphonate (DBS), cetyltrimethyl ammonium bromide (CTAB) and hexadecylpyridinium chloride (HPC).²⁵⁰

Thermal oxidation of iron metal is another approach to obtain α -Fe₂O₃ particles. By controlling the oxidation parameters, different morphologies of hematite have been synthesized, including nanoparticles, nano-wires, and nanoflakes.²⁴⁵ High surface area, nanostructured hematite thin films are fabricated by thermal oxidation in air of DC sputter deposited iron films at temperatures as low as 255°C with net photocurrent density of 0.18 mA/cm² in 1 M NaOH at 1.23 V vs. RHE under simulated AM1.5 sunlight.²³⁰

A low-cost, versatile and easily up-scalable technique for preparing hematite photoanodes is electrodeposition. Electrochemical synthesis is a simpler and cheaper alternative to produce semiconductor nanostructures. It is an efficient and environmental-

friendly method where thin films on various substrates of any shape and size can be produced at relatively lower temperatures from aqueous media. Furthermore, by controlling deposition parameters like temperature, applied potential, precursor concentration; growth rate, film thickness, composition and morphology of the films can be modified^{79–81} which are important factors for optimization of hole diffusion length or recombination rate in hematite structures²³³. Details will be discussed in the following section.

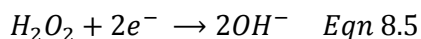
8.2.4 Electrodeposition of Hematite

In spite of its advantages, electrochemical synthesis of hematite requires strict control over applied potential and pH since Pourbaix diagram of Fe-water system shows possibility to obtain several different iron oxide phases.²⁵¹ It has been reported that well-faceted polyhedral magnetite (Fe_3O_4) crystallites, goethite ($\alpha\text{-FeOOH}$) layers composed of Rhombohedral columns and lath-like Lepidocrocite ($\gamma\text{-FeOOH}$) crystals can be obtained by increasing the potential from -0.4 V to 1.0 V vs Ag(AgCl) from aqueous solutions containing $\text{FeSO}_4(\text{NH}_4)_2\text{SO}_4\cdot 6\text{H}_2\text{O}$ and CH_3COOK (pH=6) at 90°C.⁸¹ In addition, nano-crystalline hematite $\alpha\text{-Fe}_2\text{O}_3$ film with nano-petal morphology was prepared using pulse reverse electrodeposition including cathodic and anodic pulses.²⁵² Either cathodic or anodic electrodepositions of $\alpha\text{-Fe}_2\text{O}_3$ from aqueous solutions involve deposition of an iron oxyhydroxide phase followed by heat treatment to produce hematite phase.^{238,253–255}

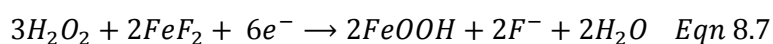
In 1998, Zotti *et al.* reported electrodeposition of amorphous Fe_2O_3 films of nanometer size by reduction of $\text{Fe}(\text{ClO}_4)_3$, or $\text{Fe}(\text{ClO}_4)_2$, in oxygenated acetonitrile.²⁵⁶ The amorphous film is converted to crystalline $\alpha\text{-Fe}_2\text{O}_3$ after heating at 500°C. They discussed oxidation of electrodeposited metal by dissolved oxygen is responsible for the amorphous oxide formation. In 2003, Kulkarni *et al.*, demonstrated potentiostatic electrodeposition of iron oxide at room temperature from a ferrous sulfate bath complexed with citric acid in an alkaline medium.²⁵⁷ However, $\epsilon\text{-Fe}_2\text{O}_3$ a rare orthorhombic polymorph of hematite is obtained. A potential cycling procedure in an aqueous solution of $\text{Fe}(\text{III}) + \text{KF} + \text{H}_2\text{O}_2$ at room temperature is introduced by Schrebler *et al.* in 2006 and become one of the mostly preferred electrodeposition technique to prepare hematite films.²³⁸ Electrodeposition route introduced by Schrebler *et al.* is based on electrochemical generation of OH^- ions by reduction of H_2O_2 in a solution containing Fe^{3+} ions. The resulting pH increase in the close proximity of the working electrode causes iron(III) oxyhydroxide precipitation. Produced FeOOH is then converted to

hematite phase and generally oval, round, globular particles are produced.^{143,238,258–260} Since then, α -Fe₂O₃ films doped with Mo or Cr as²⁵⁹, zirconium²⁶⁰, Cd¹⁴³, Al²⁶¹, and Ti²⁶² are prepared by using directly Schrebler method or with slight modifications and tested for Photoelectrochemical activity.

The involved reactions are,²⁶³



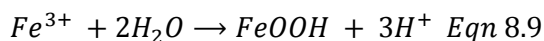
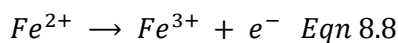
With a global reaction,



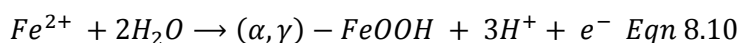
Fluoride anion is used as a complexing agent to move the reduction of Fe(III) toward more negative potentials which would allow the reduction of hydrogen peroxide first, thereby resulting in OH⁻ formation. Researchers preferred potential cycling over potentiostatic reduction of H₂O₂ to avoid the formation of iron(II) oxo-hydroxo species. Preparation of amorphous iron oxide from 0.1M hydrated ammonium iron(II) sulfate ((NH₄)₂Fe(SO₄)₂·6H₂O) solution via potentiostatic cathodic deposition is also performed.²⁶⁴ The cathodic bias resulted in the generation of hydroxide ions from the electroreduction of water that subsequently promoted the precipitation of Fe(OH)₂ and thus Fe(OH)₃, onto the FTO substrate. The deposited Fe(OH)₃ is converted to Fe₂O₃ after dehydration.

The anodic deposition of FeOOH films from ferrous sulfate solutions was introduced by Cohen and Leibenguth in 1972.²⁵³ Examination of the deposition kinetics suggested that the rate of deposition was increased by increases in pH and ferrous ion concentration. They also discussed that the film is deposited mainly by the diffusion and oxidation of a complex hydroxy ferrous ion with some contribution from a sulfate containing ion. Spray and Choi modified the neutral deposition bath reported by Cohen and Leibenguth via replacing ammonium sulfate/ammonium or boric acid/sodium borate with NH₄Cl, and compared the photoelectrochemical properties of the products with that of the films obtained by anodic electrodeposition from acidic bath.²⁶⁵ The electrodeposited FeOOH films were then converted to hematite phase by annealing. The anodic deposition condition results in oxidation of Fe²⁺ ions to Fe³⁺ ions (eqn 8.8), which is followed by precipitation of Fe³⁺ ions as amorphous ferric

oxyhydroxide due to the limited solubility of Fe^{3+} ions in the plating solution ($[\text{Fe}^{3+}] \approx 1 \times 10^{-7}$ at pH 4.1) (eqn 8.9)^{265,81};



The global reaction is;



Shape-controlled preparation of α -FeOOH films through an anodic electrodeposition route is also reported with CH_3COO^- , NH_4F , and pyridine as capping agent.²⁶⁶ After heat treatment hematite particles of various morphologies were obtained including platelets, Rhombohedral rods, square rods, six-fold snowflakes, and hexagonal particles. The shape evolution of the electrodeposited α -FeOOH could be attributed to the capping effect of the additives, in which the preferential adsorption of additives would lower the surface energy of the bound plane and hinder the crystal growth perpendicular to this plane, resulting in a change in the final morphology. α -FeOOH samples are transferred into the α - Fe_2O_3 nanostructures with the same morphologies through thermal annealing.

8.3 Present Study and Objectives

Among various metal oxides ferric oxide nanoparticles of various sizes are of particular interest due to their novel properties and potential applications in medicine, catalysts, magnetic recording media, pigments, anticorrosive agents, gas sensors and electrochemical capacitors.²³⁴ Essentially, ferric oxide (α - Fe_2O_3) has become a very desirable material also to construct photoelectrochemical cells due its band gap ($E_g \approx 2.2\text{eV}$) which allows utilization of a considerable portion of solar energy and stability in harsh chemical environments.²³³ Non-toxicity, low cost and relative abundance of hematite on earth also add on its charm. It is noted that the morphology and size of α - Fe_2O_3 have a great impact on its chemical and physical properties. With the hopes to improve device performance, much effort has been made to produce various α - Fe_2O_3 materials with desired structure and morphology. Different morphologies, such as pseudocubic, cubic, disk, wire, belt, tube and rod, have been reported with solvent-assisted methods²⁴⁹ and it has been shown that hydrothermal approach also

offers some advantages such as control over particle size and shape, homogeneity of the products and well-crystallized particles.²⁵⁰

Electrochemical synthesis is a simpler and cheaper alternative to produce semiconductor nanostructures. It is an efficient and environmental-friendly method where thin films on various substrates of any shape and size can be produced at relatively lower temperatures from aqueous media. Furthermore, by controlling deposition parameters like temperature, applied potential, precursor concentration; growth rate, film thickness, composition and morphology of the films can be modified^{79–81} which are important factors for optimization of hole diffusion length or recombination rate in hematite structures²³³. Although it is known that, temperature is a crucial parameter that affects the crystallinity and morphology of the products, reported temperatures to obtain hematite films via electrodeposition vary between room temperature to 75°C.

Main objective of the study introduced in PART 2 is to explore the newly introduced hydrothermal-electrochemical deposition (HED) as a means of developing $\alpha\text{-Fe}_2\text{O}_3$ films of various shape and size. Chapter 9 is devoted to investigate the effects of electrodeposition at high temperature and pressure on the physical photoelectrochemical properties of the hematite films. Since understanding and controlling the morphological aspects of polycrystalline electrodes is critical in producing highly efficient devices, Chapter 10 is focused on preparation of iron oxide structures in various shapes in synergistic effect of the growth-modifier molecules and electrodeposition under hydrothermal conditions.

Chapter 9 Hydrothermal Electrochemical Deposition of α -Fe₂O₃ Films and Investigation on the Physical and Photoelectrochemical Properties

9.1 Introduction

Several methodologies were employed to grow hematite nano-crystals including high-temperature based techniques such as pulsed layer deposition, catalyst-assisted chemical vapor deposition and thermal oxidation.⁵ Techniques which required lower temperatures like solution based approaches; chemical precipitation, sol-gel, forced hydrolysis and hydrothermal synthesis were also applied.²³⁴ Electrochemical synthesis is a simpler and cheaper alternative to produce semiconductor nanostructures. It is an efficient and environmental-friendly method where thin films on various substrates of any shape and size can be produced at relatively lower temperatures from aqueous media. Furthermore, by controlling deposition parameters like temperature, applied potential, precursor concentration; growth rate, film thickness, composition and morphology of the films can be modified^{79–81} which are important factors for optimization of hole diffusion length or recombination rate in hematite structures²³³. In spite of its advantages, electrochemical synthesis requires strict control over applied potential and pH since Pourbaix diagram of Fe-water system shows possibility to obtain several different iron oxide phases.²⁵¹ It has been reported that magnetite (Fe₃O₄), goethite (α -FeOOH) and Lepidocrocite (γ -FeOOH) can be obtained by increasing the potential from -0.4 V to 1.0 V vs Ag(AgCl) from aqueous solutions containing FeSO₄(NH₄)₂SO₄·6H₂O and CH₃COOK (pH=6) at 90°C.⁸¹ Either cathodic or anodic electrodepositions of α -Fe₂O₃ from aqueous solutions involve deposition of an iron oxyhydroxide phase followed by heat treatment to produce hematite phase.^{238,253–255}

Hydrothermal approach also offers some advantages such as control over particle size and shape, homogeneity of the products and well-crystallized particles.²⁵⁰ However, similar to electrodeposition, most cases of hydrothermal hematite synthesis involve formation of β -

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FeOOH precursor which is further dehydrated into α -Fe₂O₃ through calcinations or annealing.²³⁴ Jia and Gao reported direct synthesis of single-crystalline α -Fe₂O₃ submicron-cubes via hydrothermal method at 180°C in the presence of surfactant with relatively long reaction times (16-36h).²⁴⁹ Hence, in this study we combined benefits of hydrothermal synthesis with electrochemical deposition to obtain α -Fe₂O₃ films directly. It is demonstrated that synthesis of crystalline hematite nanostructures via single-step is possible with hydrothermal-electrochemical deposition (HED), owing to the high growth rate facilitated by high temperature.

9.2 Experimental

9.2.1 Materials

Iron(II) chloride hexahydrate (FeCl₂·6H₂O, 99 % purity) and Iron(III) chloride hexahydrate (FeCl₃·6H₂O, 99 % purity) were purchased from Sigma-Aldrich. Sodium acetate (NaCH₃COO, NaAc) was obtained from Merck. Indium Tin Oxide (ITO) ($\Omega < 5.0 \times 10^{-4}$ ohm.cm ($R_s < 100$ ohm/sq)) was purchased from Teknoma Ltd. Izmir, Turkey. Double distilled, high purity water was used from Milli-Q water (Millipore) system.

9.2.2 Synthesis and Characterization

The depositions were performed in a hydrothermal glass reactor (100 ml, Büchiglasuster, picoclave) at constant potential at 130°C. The reference electrode was Ag/AgCl saturated with KCl (Corr Instruments, S/N P11092) whereas Pt wire served as counter electrode. Both acidic and neutral plating solutions were used for the anodic depositions at 1.2 V (vs Ag/AgCl(satd)).²⁶⁵ Acidic plating solution contained 0.02M FeCl₂ (pH~ 3.8) and neutral plating solution consisted of 0.02M FeCl₂ and 0.08M NaCH₃COO (pH~6.2-6.8). The films were annealed at 520°C for 30 minutes. Reaction parameters are summarized in Table 9.1. The crystal structure and crystallinity of the thin films were analyzed by X-ray diffraction (XRD) analysis. ZEISS Ultraplus Field Emission Scanning Electron Microscope (FE-SEM) was used to study the surface morphology of the samples.

Raman scattering experiments were carried out using a Renishaw Raman Microscope system at room temperature. Before conducting any measurements, the instrument was

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calibrated using an internal Si sample, which was measured at a Raman shift of 520cm^{-1} . A 633 nm laser beam was focused on the samples. Phase transformations from FeO to Fe₃O₄, from Fe₃O₄ directly to α -Fe₂O₃ (martitization)²⁴⁰ and from Fe₃O₄ first to γ -Fe₂O₃ then to α -Fe₂O₃²⁶⁷ are reported for iron oxide films during Raman scattering at high laser powers. Hence sacrificial films were first excited at different laser powers to determine a threshold power so that no phase transformations take place and high enough power for reasonable signal-to-noise ratio. At 0.12 mW signal intensity was very low and a laser power of 1.2 mW was determined to be a safe limit with no change in the observed spectra and high intensity signals. Spectra were taken over a range from wavenumbers 200 cm^{-1} to 1500 cm^{-1} . The acquisition time was 10 s to 30 s.

Diffuse reflectance spectra of the investigated samples were performed using a Shimadzu UV–vis–NIR 3600 spectrophotometer using integrating sphere attachments. The current-voltage (I-V) characteristics of the electrodes were measured under amplitude modulated-light illumination with a 300 W Xenon arc lamp (Oriel, Stratford, CT) with the 3 electrode cell system in an aqueous solution of 0.1 M NaOH. AM 1.5 air filter was used to mimic solar radiation.

Table 9.1 Reaction variables for hydrothermal-electrochemical deposition at 130°C, 1.2 V vs Ag/AgCl(satd).

Film	[Fe ²⁺]	[NaAc]	Deposition Time
H1	0.02M	–	8 min.
H2	0.02M	0.08M	8 min.
H3	0.05M	–	8 min.
H4	0.05M	0.1M	8 min.

9.3 Results and Discussion

9.3.1 Morphology and Structure

We have investigated the effect of electrodeposition under hydrothermal conditions on the structure and phase of iron oxide films. The hematite thin films deposited using the hydrothermal-electrochemical deposition range in color from brown to deep red. It was observed that the films tend to adhere on FTO surface more strongly than ITO-coated glass. Hence, FTO was chosen as the substrate for the rest of the study. Increasing substrate concentration and high pH enhances adherence of iron oxide on the substrates. Figure 9.1 shows FE-SEM images of pristine and annealed films deposited at 130°C and ~2 bar. FE-SEM study showed that the pristine film prepared from an aqueous bath containing 0.02M FeCl₂ (pH=3.8) with anodic electrodeposition, H1, is composed of monodisperse almost-spherical particles of around 300-400 nm which preserved their size and morphology after annealing (Figure 9.1a-b). With increasing the concentration of Fe²⁺ from 0.02 to 0.05 M, H3, the spherical shape develops into more like polyhedra and a high polydispersity in size is observed (Figure 9.1e). Particle size tends to increase upon annealing (Figure 9.1f).

The anodic deposition of FeOOH films from neutral aqueous bath (pH 6.6-8.0) was reported before by Cohen and Leibenguth²⁵³ and Spray and Choi²⁶⁵. The electrodeposited FeOOH films were then converted to hematite phase by annealing. Cohen and Leibenguth used ammonium sulfate/ammonium or boric acid/sodium borate to stabilize Fe²⁺ ions in neutral solution.²⁵³ NH₄Cl was preferred as complexing agent for Fe²⁺ by Spray and Choi. NaCH₃COO was chosen for stabilization of Fe²⁺ ions in this study (pH ~6.4-6.8) and electrodeposition was carried out otherwise identical conditions. Nano-iron oxide particles prepared from neutral deposition bath, H2, exhibit higher polydispersity than its counterpart which prepared from acidic deposition bath and distortion from spherical morphology (Figure 9.1c). Nanoparticles with diameters of 50-100 nm are observed to form large, spherical aggregates on the order of micrometers. Size and morphology are preserved after annealing (Figure 9.1d). When Fe²⁺ concentration was increased from 0.02 to 0.05 M (and corresponding [NaCH₃COOH]), H4, spherical nanoparticles with diameters ~50 nm and well-faceted polyhedra with a broad range of particle sizes form together (Figure 9.1g). After annealing, increase in average diameter of spherical nanoparticles to around 100 nm and formation of micrometer sized aggregates are observed (Figure 9.1h). In addition, polyhedral particles seem to have disappeared.

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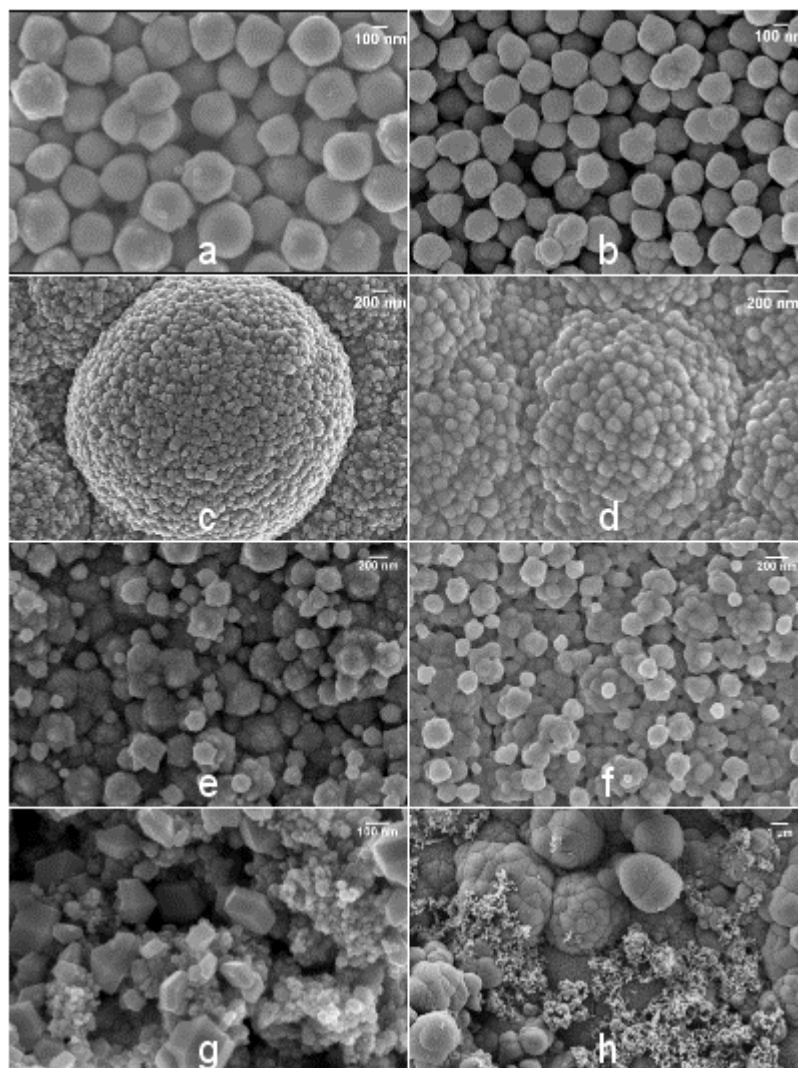


Figure 9.1 FE-SEM of the films a) H1 as-deposited b) H1annealed c) H2 as-deposited d) H2 annealed e) H3 as-deposited f) H3 annealed g) H4 as-deposited h) H4 annealed.

The anodic deposition condition used in this study results in oxidation of Fe²⁺ ions to Fe³⁺ ions (eqn 8.8), which is followed by precipitation of Fe³⁺ ions as amorphous ferric oxyhydroxide due to the limited solubility of Fe³⁺ ions in the plating solution ([Fe³⁺] $\approx$ 1×10^{-7} at pH 4.1) (eqn 8.9) as discussed in Chapter 8.^{265,81} Hence, it is expected that as-deposited films contain amorphous ferric oxyhydroxide which is converted to crystalline α -Fe₂O₃ upon annealing as reported before.^{265,253} To identify the structure and phases of the obtained films, XRD was employed (Figure 9.2). XRD patterns of the as-synthesized films revealed peaks with highest intensities at $2\theta = 24^\circ$, 33° , and 35° which can be indexed to (012), (104) and (110) reflections of crystalline, Rhombohedral α -Fe₂O₃, hematite structure {JCPDS card No. 86-0550} even before the

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annealing step without any other phase being detected (Figure 9.2). The patterns exhibit an intensity distribution corresponding to the standard polycrystalline hematite structure, where the crystallites are randomly oriented. Moreover, crystallinity of the films improves with no accompanying compositional changes after annealing (Figure 9.2).

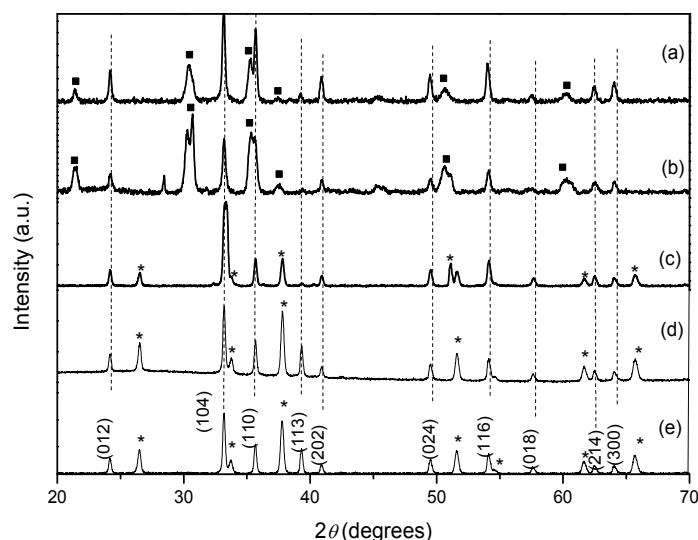


Figure 9.2 XRD profiles of the hematite films electrodeposited at 130°C, ~2 bar. The following symbols represent reflections associated with ■ ITO (JCDPDS card No. 89-4597) and * SnO₂ (JCDPDS card No. 41-1445).

To further evaluate purity of hematite phase, Raman spectroscopy was used. Hematite belongs to the D_{3d}^6 space group and seven transitions are expected in the Raman spectrum^{240,241,242}. Two A_{1g} modes at 225 and 498 cm⁻¹ and five E_g modes at 247, 293, 299, 412 and 613 cm⁻¹ are expected. Raman spectrum of the as-synthesized films at 130 °C exhibit major peaks at 226, 247, 296, 411, and 615 cm⁻¹ with 226 and 296 cm⁻¹ being strongest all correspond well to α -Fe₂O₃ peaks (Figure 9.3). In addition to these peaks, modes around ~660 cm⁻¹ and ~1320 cm⁻¹ were present in all hematite Raman spectra obtained in the whole study. The 660 cm⁻¹ mode is present in several published hematite spectra and it is either assigned to magnetite/wüstite (FeO) impurity or considered as characteristics of hematite and assigned to a disorder phase.^{243,244,232} There is no evidence of any other iron oxide phase in the XRD diagrams of (Figure 9.2). Lack of evidence for presence of impurity phase suggests 660 cm⁻¹

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peak is related to hematite phase which has been ascribed to disorder in the crystal lattice and the breaking of symmetry upon crystallization.²⁴³ The mode around 1320 cm⁻¹ has been suggested to be an overtone of the peak at 660 cm⁻¹.²⁴³ It was also ascribed to a two-magnon scattering including magnon-magnon interactions of antiferromagnetic hematite.²⁴⁰ There are also additional peaks around 820 and 1050–1100 cm⁻¹. They are reported to exist in the xx polarized hematite spectra.²⁴¹ Hence, Raman spectroscopy data (Figure 9.3) together with XRD (Figure 9.2) demonstrates hematite phase forms directly with hydrothermal-electrochemical deposition at 130°C. This behavior is contradictory to expected amorphous ferric oxyhydroxide (γ -FeOOH, as stated above)^{265,253} or goethite²⁶⁶ formation with anodic electrodeposition under ambient conditions and moderate temperatures. An example Raman spectrum for one of the annealed films is also provided in Figure 9.3.

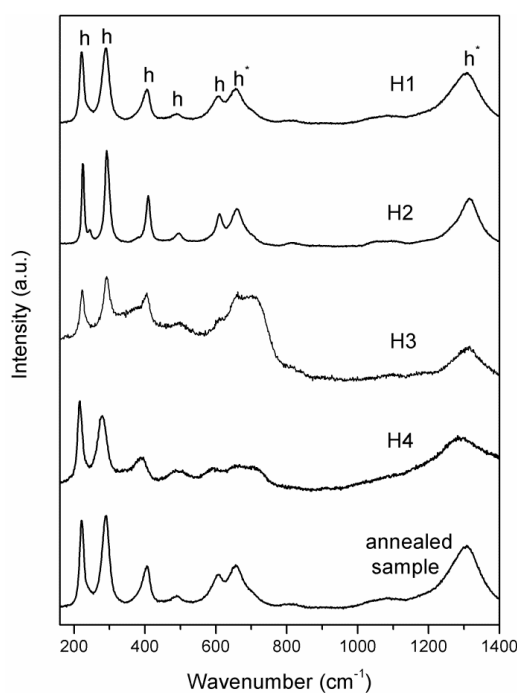
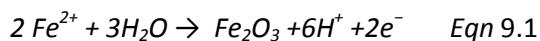


Figure 9.3 Raman spectra of the hematite films electrodeposited at 130°C, ~2 bar.

Cohen and coworkers carried out the anodic deposition from ferrous sulfate solutions in neutral medium (pH varying between 6.6 and 8) and studied reaction kinetics.²⁵³ They have shown that the deposition rate increases both with pH and [Fe²⁺]. Leibenguth and Cohen

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discussed that deposition proceeds through diffusion and oxidation of ferrous hydroxyl complex and the formation of FeOOH instead of Fe₂O₃ depends on how fast ions are transferred to the anode. They proposed FeOOH forms rather than Fe₂O₃ owing to the fact that OH⁻ ions migrate easier than Fe⁺² ions because of their smaller positive charge. The fact that α -Fe₂O₃ phase is obtained directly from both acidic and neutral HED suggests temperature effect rather than OH⁻ ion concentration has a major role. Figure 9.4 shows charge vs. time plot for depositions with varying parameters such as temperature, pH and initial [Fe²⁺]. (Electrodeposition at 75°C was also carried out under identical conditions otherwise. Physical properties of the films deposited at 75°C can be found in Chapter 10.) It can be seen that deposition rate increases with concentration (H1 ([Fe²⁺]=0.02 M) and H3 ([Fe²⁺]=0.05M) at pH 3.8); H2 ([Fe²⁺]=0.02 M) H4 ([Fe²⁺]=0.05 M) at pH ~6.4) and pH (when H1 is compared with H2 and H3 is compared with H4) in accordance with what is reported by Leibenguth and Cohen. Moreover, the deposition rate increases much more effectively when temperature is increased from 75°C to 130°C while all other parameters are kept constant (Figure 9.4). Growth of hematite can be explained by the reaction



with the following equilibrium potential at 25°C calculated by using tabulated thermodynamic values for chemical species and Nerst equation;

$$E = 0.728 - 0.177\text{pH} - 0.0592\log[\text{Fe}^{2+}] \quad \text{Eqn 9.2}$$

which results in thermodynamic potentials of -0.734 V for [Fe²⁺]=0.02 M and -0.75 V for [Fe²⁺]=0.05 M at 130°C, pH=6.4, and -0.112 V for [Fe²⁺]=0.02 M and -0.128 V for [Fe²⁺]=0.05 M at 130°C, pH=3.8. Taking the fact that a high overpotential is applied during deposition also into consideration, formation of hematite phase directly at high temperature might be explained by higher reaction kinetics.

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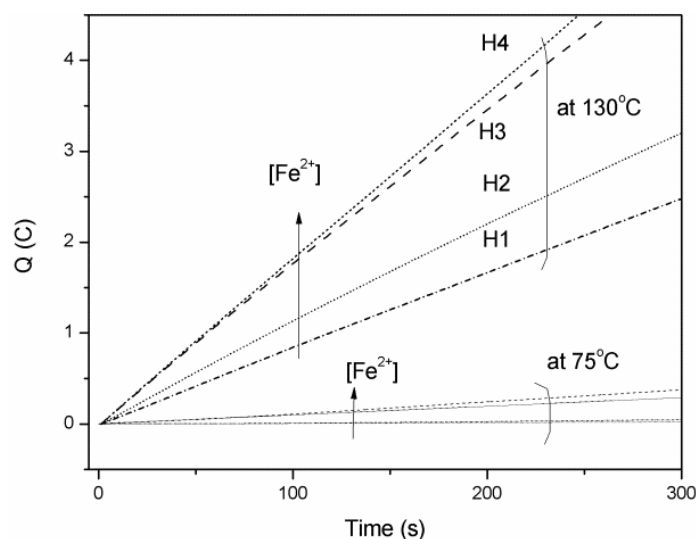


Figure 9.4 Effect of initial $[\text{Fe}^{2+}]$, pH and temperature on electrodeposition rate.

9.3.2 Optical and Photoelectrochemical Properties

Hematite nanoparticles are useful for various applications such as the anode of photoelectrochemical cells for water splitting, detection electrode for gas sensors, the positive electrode for Li-ion batteries and photodegradation of dyes may be promising. We have evaluated the optical and photo-electrochemical performances of the films after postannealing at 520°C except H1, since H1 did not adhere onto the substrate very effectively. The optical absorbance spectra of the films (Figure 9.5) exhibit two broad absorption bands centered at around 345 nm and 514 nm. These bands are slightly blue shifted from the reported absorption bands of hematite which are normally observed at around 400 and 530 nm.^{260,143,268} The degree of change of the peak positions is reported to depend on the shape and size of the particles.²⁴⁸ Hence, the shift can be attributed to size quantization of the hematite nano-particles. The band at lower wavelength can be attributed to ${}^6\text{A}_1 \rightarrow {}^4\text{E}$ and ${}^6\text{A}_1 \rightarrow {}^4\text{E}$, ligand field transitions of Fe^{3+} .^{260,248} The low energy band is ascribed to ${}^6\text{A}_1 \rightarrow {}^4\text{T}_2$ ligand field transition of Fe^{3+} .^{143,248} In addition, two charge- transfer transitions accompany these processes; a direct transition corresponding to the ligand-metal transfer ($\text{O}_2 \rightarrow \text{Fe}^{3+}$) at higher energy and an indirect transition at higher wavelength from the metal-metal transfer.^{248,269}

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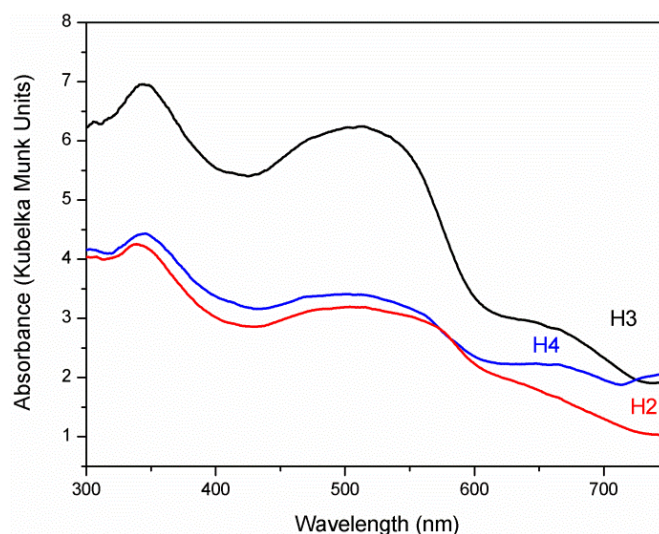


Figure 9.5 UV/visible light absorption spectra of hematite films electrodeposited at 130°C, ~2 bar.

PEC performances of annealed α -Fe₂O₃ electrodes were measured under amplitude modulated 1 sun illumination at 1.1 V vs NHE in 1 M NaOH (Figure 9.6) at a lower than theoretical water oxidation potential (eqn. 9.3, $E^0_{(O_2/H_2O)} = 1.23$ V vs NHE at pH 13.5). The anodic nature of the photocurrent produced suggests n-type behavior for all of the films and the responses are quite stable with no sign of photocorrosion. The net photocurrent densities of the films are 11.3, 11.4, and 23.6 $\mu\text{A}/\text{cm}^2$, respectively for H2, H3 and H4. The photoresponse of film prepared from a highly concentrated, neutral bath (H4) is almost twice of the responses of the other films. In addition the photocurrent switching (ON/OFF) response of H4 is faster than both H2 and H3. Even though, H2 consists of smaller sized particles (Figure 1), which provide higher surface area and thereby beneficial to decrease recombination losses²⁷⁰, H4 generates higher photocurrent than H2.

Investigation on the Physical and Photoelectrochemical Properties

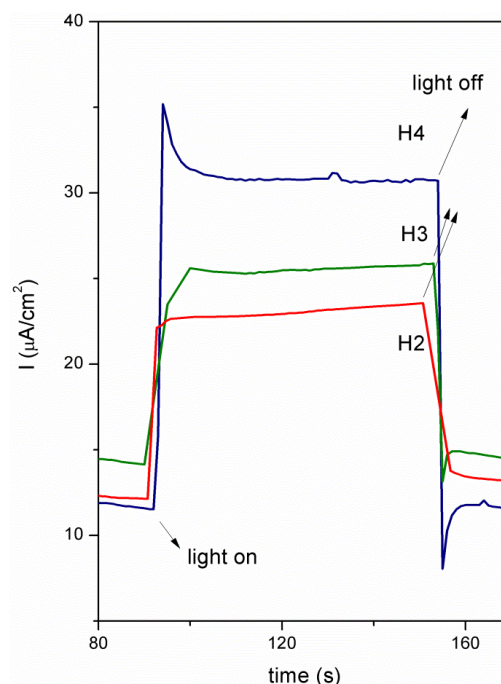


Figure 9.6 The photocurrent responses of the hematite films at 1.1 V vs. NHE under amplitude modulated illumination at 100 mW/cm² (AM 1.5 air filter).

The difference in photoresponses of H2 and H4 can be attributable at least, in part, to higher Fe₂O₃ loading on H4. As discussed above, deposition rate increases with increasing [Fe²⁺]. Hence, higher amount of hematite should be deposited from more concentrated deposition bath at a given time which would result in increased number of generated electron-hole pairs that can contribute to photocurrent generation for H4. On the other hand, similar deposition rate for H3 and H4 (Figure 9.4) suggests similar Fe₂O₃ loading for these films. In addition, as can be seen in Figure 9.5, H3 displays higher photon absorption. Therefore, H3 was expected to generate higher photocurrent. However, H3 is composed of 300-400 nm sized polyhedral whereas spherical nanoparticles of around 100 nm are observed for H4. Smaller particle size, hence higher surface area of H4 allows more holes to reach the hematite/electrolyte interface which reduces recombination losses²⁷⁰ and results in higher photocurrent generation.

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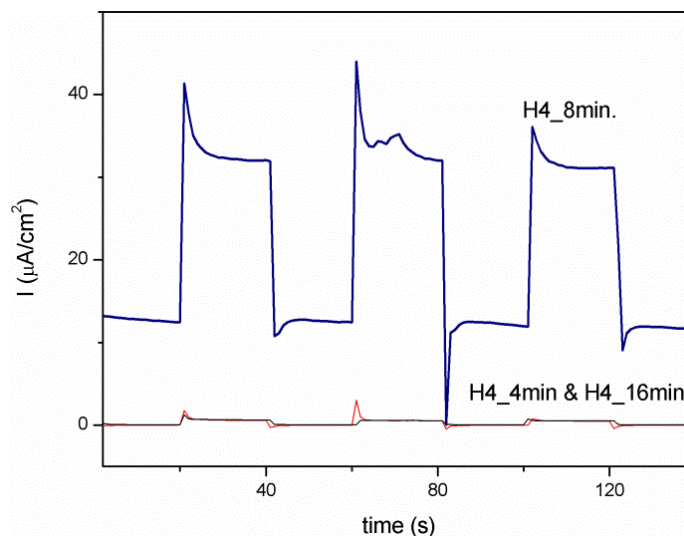


Figure 9.7 The photocurrent responses of hematite films at 1.1 V vs. NHE under amplitude modulated illumination at 100 mW/cm² (AM 1.5 air filter).

As an effort to optimize obtained photoresponse, films were prepared from neutral, concentrated (0.05M Fe²⁺) deposition bath with different deposition times (H4_4min, H4_16min). PEC performances were measured under identical conditions. Photocurrent density increased ~40-fold as the deposition time increased from 4 min. (0.66 μ A/cm²) to 8 min. (23.6 μ A/cm²) (Figure 9.7). Analyzing FE-SEM images implies that surface morphologies of the films are very similar with nanometer-sized spherical particles and micrometer-sized aggregates (Figure 9.1 and 9.8). The thickness of the samples was measured by taking cross sectional SEM images. Films deposited for 4 and 8 min. resulted in films with average thickness of 1.2 and 1.33 μ m. (Cross-sectional SEM images of H4_4min and H4_8min is shown in Figure 9.9.) The increase in the photoresponse from 4 to 8 min. can be attributed to increase in the number of electron-hole pairs due to the presence of additional photoactive oxide in the thicker film. After 16 min. of deposition, photocurrent density generated decreased to around 0.7 μ A/cm² similar to H4_4min. When the thickness of the hematite film reaches beyond 2.6 μ m, the distance that holes would travel to reach the Fe₂O₃/electrolyte interface is increased which results in higher recombination probability.²⁶¹ Increased hole-diffusion length together with a reduced photon penetration for a thicker film¹⁴³ might account for decrease in produced photocurrent with H4_16min.

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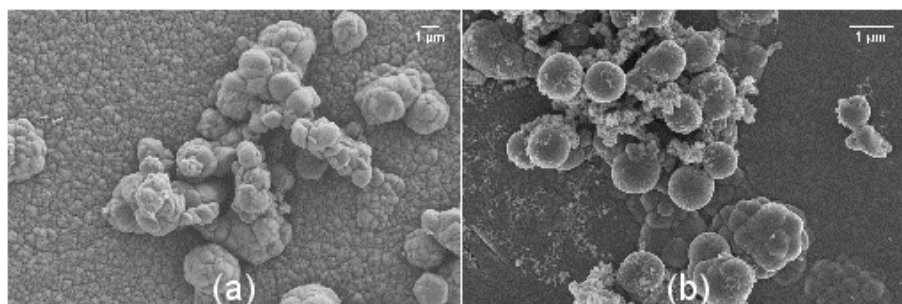


Figure 9.8 FE-SEM images of the films a) H4_4min. b) H4_16min.

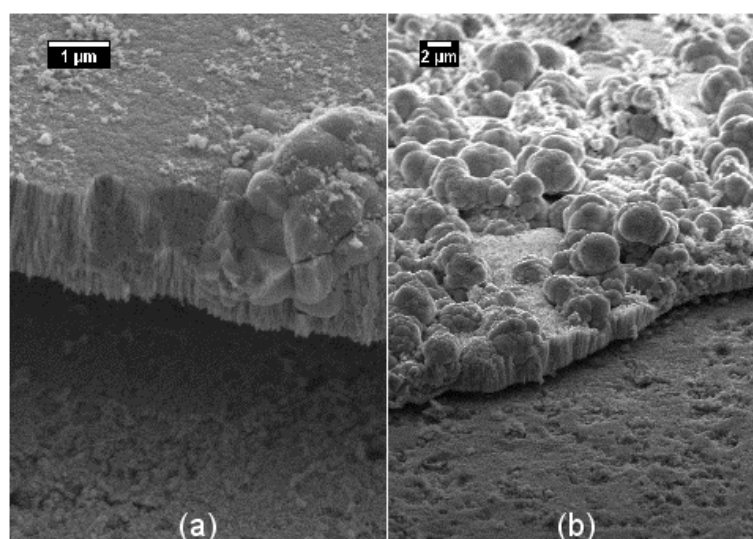


Figure 9.9 Cross-sectional FE-SEM images of the films a) H4_4min (tilt angle: 45°). b) H4_8min (tilt angle: 60°).

The photocurrent–voltage (J–V) pattern of H4 measured under identical conditions is shown in (Figure 9.10). The onset potential for H4 is calculated by extrapolating the linear portion of the J–V curve to zero current from where current densities range from 15 to 60 $\mu\text{A}/\text{cm}^2$. The photocurrent onset potential calculated to be 0.96 V vs RHE. After onset, photocurrent shows two separated potential regions.¹⁴³ In the first region photocurrent increases to reach 26.5 $\mu\text{A}/\text{cm}^2$ at 1.23 V vs NHE and 72.75 $\mu\text{A}/\text{cm}^2$ at 1.6 V vs NHE. This region corresponds to where four-electron water oxidation reaction takes place (eqn 9.3). From 1.6 V to 1.8 V (where photocurrent density reaches 102 $\mu\text{A}/\text{cm}^2$) is the second region where also two-electron water oxidation (eqn 9.4) takes place.

Investigation on the Physical and Photoelectrochemical Properties

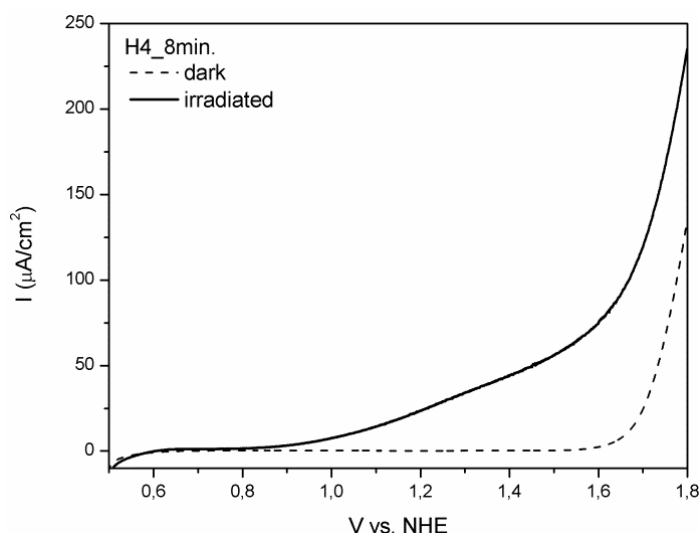
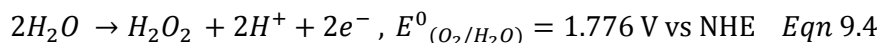
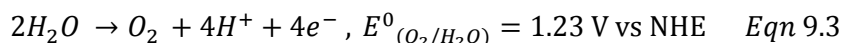


Figure 9.10 Photocurrent–voltage (J–V) curves of H4_8min under dark and illumination with at 100 mW/cm² (AM 1.5 air filter).

Preparation of doped hematite films to enhance the PEC performances by presented hydrothermal-electrochemical deposition technique and surface modifications to reduce surface recombination probability is under study.

9.4 Conclusions

Hydrothermal-electrodeposition was successfully employed to produce α -Fe₂O₃ and the effect of electrodeposition temperature on the structure and phase of iron oxide films was studied. Hydrothermal-electrodeposition was successfully employed to produce α -Fe₂O₃ and the effect of electrodeposition temperature on the structure and phase of iron oxide films was studied. The as-synthesized films deposited at 75°C either from acidic or neutral solution were X-ray amorphous. Raman analysis showed that γ -FeOOH forms under these conditions which is converted to α -Fe₂O₃ after annealing at 520°C. On the other hand, α -Fe₂O₃ phase is produced

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directly at a single step when electrodepositions were carried out at 130°C (hydrothermal) under otherwise similar conditions most probably due to higher reaction kinetics at high temperature. Net photocurrent density of the 23.6 $\mu\text{A}/\text{cm}^2$ in 0.1M NaOH under 1 sun conditions at 1.23 V vs NHE with the film prepared from a bath containing 0.05M FeCl₂ and 0.1M NaCH₃COOH via hydrothermal-electrodeposition. The photocurrent onset potential calculated to be 0.96 V vs NHE.

in the Presence of Ce³⁺ and/or F⁻ Ions

Chapter 10 Hydrothermal Electrochemical Deposition of α -Fe₂O₃ Films in the Presence of Ce³⁺ and/or F⁻ Ions

10.1 Introduction

There is a great interest in obtaining advanced materials with altered morphologies, since often shape and size are as crucial as crystal structure in determining the performance.^{69,239,271} Particularly, controlling the shape-guiding process during electrodeposition attracts interest since uniform and distinct morphologies in large scales with remarkable reliability and ease can be produced by a cheap and eco-friendly process. Furthermore, various semiconductor metal oxides and metallic crystals can be deposited directly on a conducting substrate which can be integrated into opto-electrical devices easily.^{45,58,90,272,273}

Electrodeposition offers a high degree of freedom in manipulating and monitoring the crystal growth processes via deposition potential, current, temperature, precursor concentration and additives. Either cathodic or anodic electrodepositions of α -Fe₂O₃ from aqueous solutions involve deposition of an iron oxyhydroxide phase followed by heat treatment to produce hematite phase.^{238,253–255} Mostly, cathodic electrodeposition route introduced by Schrebler *et al.* which is based on electro chemical generation of OH⁻ ions by reduction of H₂O₂ in a solution containing Fe³⁺ ions, is used to electrochemically produce hematite films.²³⁸ The resulting pH increase in the close proximity of the working electrode causes iron oxyhydroxide precipitation. Produced FeOOH is then converted to hematite phase and generally oval, round, globular particles are produced.^{143,238,258–260}

It has been reported that well-faceted polyhedral magnetite (Fe₃O₄) crystallites, goethite (α -FeOOH) layers composed of Rhombohedral columns and lath-like Lepidocrocite (γ -FeOOH) crystals can be obtained by increasing the potential from -0.4 V to 1.0 V vs Ag(AgCl) from aqueous solutions containing FeSO₄(NH₄)₂SO₄·6H₂O and CH₃COOK (pH=6) at 90°C.⁸¹ In addition, nano-crystalline hematite (α -Fe₂O₃) film with nano-petal morphology was prepared

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using pulse reverse electrodeposition including cathodic and anodic pulses.²⁵² Shape-controlled preparation of α -FeOOH films is reported through an anodic electrodeposition route is also reported with CH₃COO⁻, NH₄F, and pyridine as capping agent.²⁶⁶ After heat treatment hematite particles of various morphologies were obtained including platelets, Rhombohedral rods, square rods, six-fold snowflakes, and hexagonal particles.

It is known that the oxidation rate, concentration of the reagents, pH, temperature and other additives (anions or cations) present in the system, are the essential factors in determining the phase and shape of the Fe-oxide/hydroxide during the oxidation of aqueous ferrous systems.²³⁴ Therefore understanding the effect of these factors on the phase and shape control is required. During the present investigations, the influence of the Ce³⁺, CH₃COO⁻ and F⁻ ions on crystal structure, particle shape and size of the end product during iron oxide/hydroxide electrodeposition has been examined. In addition, the effect of temperature during electrochemical deposition on morphology of the products is also studied via a combined hydrothermal-electrochemical deposition (HED) approach.

10.2 Experimental

10.2.1 Materials

Iron(II) chloride hexahydrate (FeCl₂·6H₂O, 99% purity) and Iron(III) chloride hexahydrate (FeCl₃·6H₂O, 99% purity) were purchased from Sigma-Aldrich. Sodium acetate (NaCH₃COO, NaAc) was obtained from Merck. Indium Tin Oxide (ITO) ($\Omega < 5.0 \times 10^{-4}$ ohm.cm ($R_s < 100$ ohm/sq)) was purchased from Teknoma Ltd. Izmir, Turkey. Double distilled, high purity water was used from Milli-Q water (Millipore) system.

10.2.2 Synthesis and Characterization

Potentiostatic electrodepositions were carried out 75°C with a conventional 3-electrode cell system where ITO (Indium tin oxide) coated glass was the working electrode, Ag/AgCl saturated with KCl was reference electrode and Pt was the counter electrode. The depositions at higher temperature (130°C) were performed in a hydrothermal glass reactor (Büchiglasuster, picoclave) at constant potential. The reference electrode was Ag/AgCl saturated with KCl (Corr Instruments, S/N P11092) whereas Pt wire served as counter

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electrode. Both acidic and neutral plating solutions were used for the anodic depositions at 1.2V (vs Ag/AgCl(satd)).²⁶⁵ Acidic plating solution contained 0.02M FeCl₂ (pH=3.8) and neutral plating solution consisted of 0.02M FeCl₂ and 0.08M NaCH₃COO or 0.08M NaF (pH=6.2-6.8) with different amount of cerium salt. The films were annealed at 520°C for 30 minutes to obtain the desired crystallinity. Reaction parameters are summarized in Table 10.1. The crystal structure and crystallinity of the thin films were analyzed by X-ray diffraction (XRD) analysis. ZEISS Ultraplus Field Emission Scanning Electron Microscope (FE-SEM) was used to study the surface morphology of the samples. Film composition was examined by X-ray photoelectron spectroscopy (XPS).

Raman scattering experiments were carried out using a Renishaw Raman Microscope system at room temperature. Before conducting any measurements, the instrument was calibrated using an internal Si sample, which was measured at a Raman shift of 520cm⁻¹. A 633 nm laser beam was focused on the samples. Phase transformations from FeO to Fe₃O₄, from Fe₃O₄ directly to α -Fe₂O₃ (martitization)²⁴⁰ and from Fe₃O₄ first to γ -Fe₂O₃ then to α -Fe₂O₃²⁶⁷ are reported for iron oxide films during Raman scattering at high laser powers. Hence sacrificial films were first excited at different laser powers to determine a threshold power so that no phase transformations take place and high enough power for reasonable signal-to noise ratio. At 0.12 mW signal intensity was very low and a laser power of 1.2 mW was determined to be a safe limit with no change in the observed spectra and high intensity signals. Spectra were taken over a range from wavenumbers 200 cm⁻¹ to 1500 cm⁻¹. The acquisition time was 10 s to 30 s. X-ray fluorescence measurements were carried out with a Bruker S8 Tiger XRF spectrometer under Helium atmosphere. (A 4 kW, Rh anode X-ray tube was used to generate X-rays.) The solutions were measured in liquid sample cups and Prolene (4 μ m) film was used as the sample support window material. For the calculation of Ce amounts, a calibration curve was created from known concentrations of Ce solutions.

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Table 10.1 Reaction variables for hydrothermal-electrochemical deposition at 1.2 V vs Ag/AgCl(satd) for 8 min.

Film	[Fe ²⁺]	[NaAc]	[Ce ³⁺]	[NaF]	Deposition Temperature
H1	0.02 M	–	–	–	75°C
H2	0.02 M	–	0.002 M	–	75°C
H3	0.02 M	–	–	–	130°C
H4	0.02 M	–	0.002 M	–	130°C
H5	0.02 M	–	0.01M	–	130°C
H6	0.02 M	0.08 M	–	–	75°C
H7	0.02 M	0.08 M	0.002 M	–	75°C
H8	0.02 M	0.08 M	–	–	130°C
H9	0.02 M	0.08 M	0.002 M	–	130°C
H10	0.02 M	–	–	0.08 M	130°C
H11	0.02 M	–	0.002 M	0.08 M	130°C
H12	0.02 M	–	0.01M	0.08 M	130°C

10.3 Results and Discussion

10.3.1 Electrodeposition in the Presence of Ce³⁺ Ions from Acidic Bath

We have investigated the effect of Ce³⁺ and F⁻ ions on the morphology of hematite films. Ce(NO₃)₂ was introduced into the electrodeposition bath so that [Ce³⁺]/[Fe²⁺] ratio was 0.1 or 0.5. Depositions were carried out either under ambient conditions at 75°C or under hydrothermal conditions at 130°C and ~2 bar. When anodic electrodeposition was conducted at 75°C, addition of Ce³⁺ ions into the electrolyte did not affect morphology of the film (Figure 10.1a-d). Similar to the film prepared from an aqueous bath containing 0.02M FeCl₂ (pH=3.8), H1 (as reported by Spray and Choi²⁶⁵), FE-SEM study showed that the pristine film prepared from an aqueous bath containing Ce³⁺ ions, H2, were also composed of particles with no particular shapes. Upon annealing they were transformed into oval-round particles with diameters ranging between 10-50 nm (Figure 1a-d). Electrodeposition at higher temperature

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and pressure from an aqueous bath containing 0.02M FeCl₂, H3, resulted in formation of monodisperse, almost-spherical polyhedra of around 300-400 nm which preserved their size and morphology after annealing (Figure 10.1e-f) as explained in the previous chapter. Electrodeposition at 130°C with 10% Ce³⁺ ions resulted in formation of polyhedral particles, H4, similarly (Figure 10.1g). However, the film was very polydisperse; growth of smaller polyhedra on the faces of the larger crystals can be observed. Upon annealing at 520°C, polyhedral particle shape was transformed into Rhombohedral nanosized particles (Figure 10.1h). When Ce³⁺ amount was increased to 50% of Fe²⁺ ions, H5, size of the polyhedra formed decreased significantly from μ m to nm range and only some of the particles were transformed into rhombohedra after annealing (Figure 10.1i-j).

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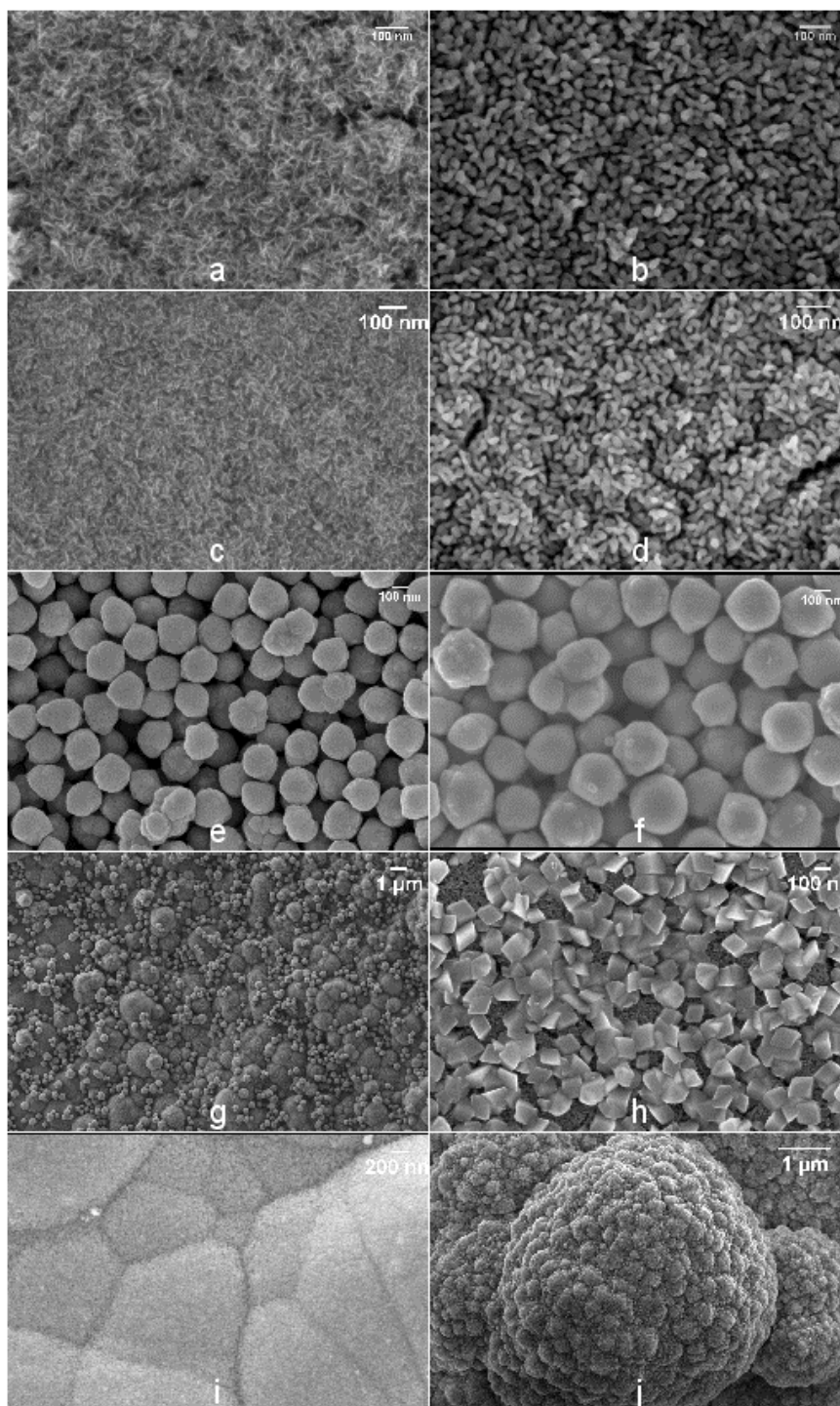


Figure 10.1 FE-SEM of hematite films obtained with electrodeposition at 1.2V (vs Ag/AgCl) from solutions containing 0.02 M Fe²⁺ a) H1, at 75°C, as-deposited b) at 75°C, annealed c) H2, at 75°C, 10 % Ce³⁺, as-deposited d) at 75°C, 10 % Ce³⁺ annealed e) H3, at 130°C, as-deposited f) at 130°C, annealed g) H4, at 130°C, 10 % Ce³⁺, as-deposited h) at 130°C, 10 % Ce³⁺, annealed. i) H5, at 130°C, 50 % Ce³⁺, as-deposited j) at 130°C, 50 % Ce³⁺, annealed.

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The anodic deposition condition used in this study results in oxidation of Fe²⁺ ions to Fe³⁺ ions (eqn 8.8), which is followed by precipitation of Fe³⁺ ions as amorphous ferric oxyhydroxide due to the limited solubility of Fe³⁺ ions in the plating solution ($[\text{Fe}^{3+}] \approx 1 \times 10^{-7}$ at pH 4.1) (eqn 8.9)^{265,81} as discussed in the previous chapter. Hence, as-deposited films should contain amorphous ferric oxyhydroxide which would be converted to crystalline α -Fe₂O₃ upon annealing. To identify the structure and phases of the obtained films, XRD and Raman spectroscopy was employed. As expected H1 and H2, were amorphous with only substrate peaks present (data not shown) but converted to crystalline form upon annealing at 520°C (Figure 10.2). XRD patterns revealed very weak peaks at 24°, 33°, and 35° which can be indexed to (012), (104) and (110) reflections of Rhombohedral α -Fe₂O₃, hematite structure {JCPDS card No. 86-0550} for the annealed films, with no other phase being detected. On the other hand, the as-synthesized films deposited at 130°C, H3 and H4, showed crystalline structure that can be indexed to pure Rhombohedral hematite even before the annealing step (Figure 10.2). The presence of higher-order reflections imply higher crystallinity for the pristine films deposited under hydrothermal conditions. No phase related to ceria could be observed.

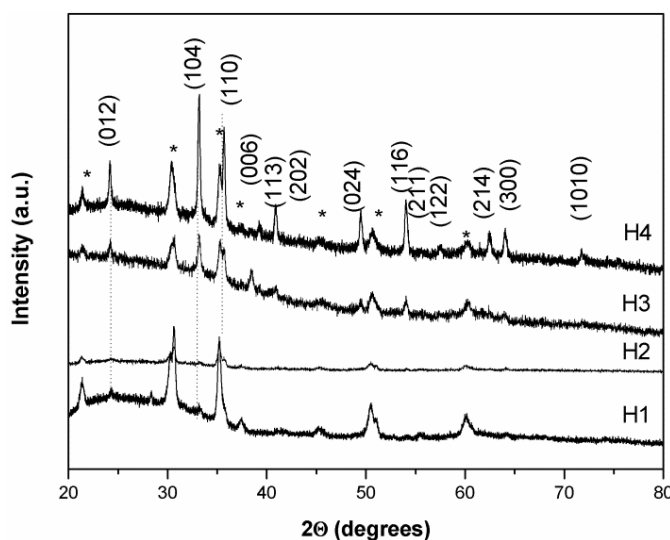


Figure 10.2 XRD diagrams of hematite films obtained with electrodeposition at 1.2 V (vs Ag/AgCl) from acidic solution (annealed H1 and H2, pristine H3 and H4).

To further evaluate phase purity of hematite, Raman spectroscopy was used. Raman spectrum of the annealed film deposited at 75°C from only Fe²⁺ containing solution, H1, and

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the as-synthesized film at 130 °C, H3, exhibit major peaks at 226, 247, 296, 411, and 615 cm⁻¹ all correspond to well known α -Fe₂O₃ modes at 225, 247, 293, 299, 412, 613 and 498 cm⁻¹ (Figure 10.3a).²⁴⁰ In addition to these peaks, modes around ~660 cm⁻¹ and ~1320 cm⁻¹ were present in all hematite Raman spectra obtained in the whole study. The 660 cm⁻¹ mode is present in several published hematite spectra and it is either assigned to magnetite (Fe₃O₄)/wüstite (FeO) impurity or considered as characteristics of hematite and assigned to a disorder phase.^{243,244} There is no evidence of any other iron oxide phase in the XRD diagrams (Figure 10.2). In addition, no trace of iron in (+2) state could be found in XPS analysis (discussed below). Lack of evidence for presence of impurity phase suggests 660 cm⁻¹ peak is related to hematite phase which has been ascribed to disorder in the crystal lattice and the breaking of symmetry upon crystallization.²⁴³ The mode around 1320 cm⁻¹ has been suggested to be an overtone of the peak at 660 cm⁻¹.²⁴³ It was also ascribed to a two-magnon scattering including magnon-magnon interactions.²⁴⁰ There are also additional peaks around 820 and 1050–1100 cm⁻¹. They are reported to exist in the xx polarized spectra.²⁴¹ Chemical bonding state of iron in the films was analyzed by XPS spectroscopy and Fe 2p spectrum is shown in Figure 10.3b. The peaks at 724.3 eV and 710.4 eV can be attributed to binding energies of Fe 2p_{3/2} and Fe 2p_{1/2} of Fe³⁺.²⁷⁴ The peak obtained at 719 eV corresponds to satellite peak of Fe 2p_{3/2}. There exists another peak at 730 eV which can be ascribed to be a satellite peak of Fe 2p_{1/2}.²⁷⁴

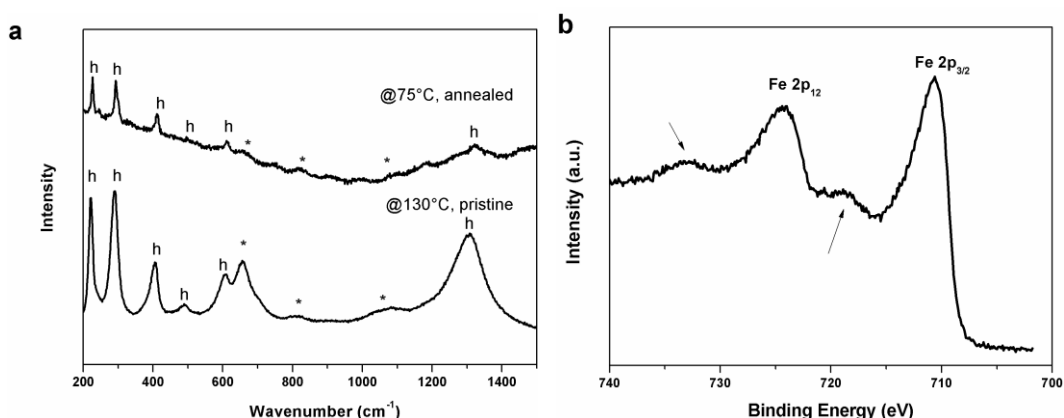


Figure 10.3 a) Raman spectra of hematite films obtained with electrodeposition at 1.2 V (vs Ag/AgCl), at 75°C, H1, and 130°C, H3, from solutions containing 0.02 M Fe²⁺. b) Fe 2p spectrum.

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Raman spectroscopy data of H2, H4 and H5 similarly indicates hematite phase for as-deposited film at 130°C and annealed sample synthesized at 75°C (Figure 10.4). Raman spectra of the films were analyzed to evaluate presence of secondary ceria phase. Cerium dioxide fluorite phase has a single allowed triply degenerate Raman active mode of F_{2g} symmetry which represents the symmetrical stretching vibration of CeO₈ vibrational unit.¹⁷⁴ In addition to F_{2g} mode, CeO₂ also exhibit weak bands at 258, 595, and 1179 cm⁻¹, due to second-order transverse acoustic (2TA) mode, defect-induced (D) mode, and second-order longitudinal optical (2LO) mode, respectively.²⁷⁵ Absence of strongest F_{2g} peak at 462 cm⁻¹ in Raman spectra of the films suggests there is no CeO₂ phase in any of the films. Absence of Ce³⁺ signal in either EDX or XPS spectra suggests Ce³⁺ ion is also excluded from hematite crystal lattice. XRF analysis confirmed that the entire Ce³⁺ signal is still retained in electrolyte solution after deposition.

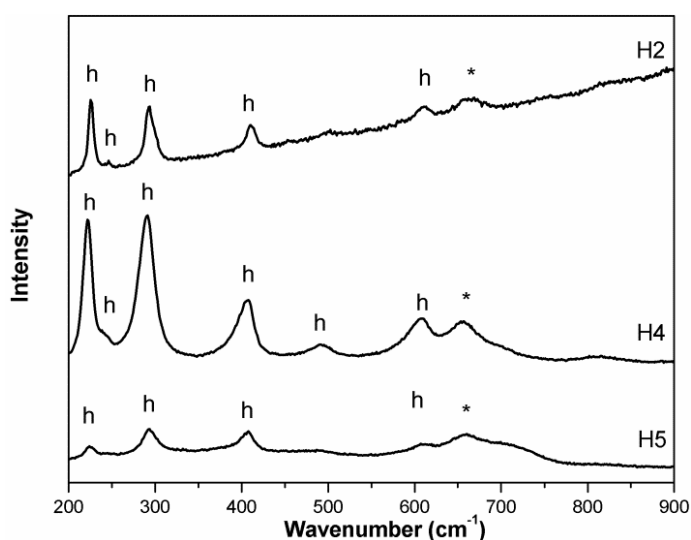


Figure 10.4 Raman spectra of hematite films obtained with electrodeposition at 1.2 V (vs Ag/AgCl) from solutions containing 0.02 M Fe²⁺ a) H2, at 75°C, 10 % Ce³⁺, annealed b) H3, at 130°C, 10 % Ce³⁺, as-deposited c) H4, at 130°C, 50 % Ce³⁺, as-deposited.

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10.3.2 Electrodeposition in the Presence of Ce³⁺ Ions from Neutral Bath

Anodic deposition of FeOOH films which were converted to hematite phase by annealing, from a neutral aqueous medium (pH 6.6-8.0) was reported before by Cohen and Leibenguth²⁵³ and Spray and Choi²⁶⁵. To stabilize Fe²⁺ ions in neutral solution ammonium sulfate/ammonium or boric acid/sodium borate was used as complexing agents by Cohen and Leibenguth.²⁵³ Spray and Choi used NH₄Cl for the same purpose. We added NaCH₃COO into the deposition solution for stabilization of Fe²⁺ ions as discussed in the previous chapter (pH ~6.4-6.8) and carried out electrodeposition similarly at 75 and 130°C. Particles with no particular shapes were observed for the as-synthesized films prepared at low temperature (Figure 10.5a). The annealed film was composed of 10-20 nm worm-like particles (Figure 10.5b). The film prepared from neutral solution at high temperature was composed of aggregated polyhedra just after the synthesis (Figure 10.5c). The aggregates came together to form larger spheres after annealing (Figure 10.5d). We have investigated the effect of Ce³⁺ ions on the morphology of hematite films electrodeposited from neutral bath. Ce(NO₃)₂ amount in the solution was adjusted so that [Ce³⁺]/[Fe²⁺] was 0.1. When Ce³⁺ ions were present in the deposition solution, platelets formed with both low and high temperature electrodeposition (Figure 10.5e-h). The platelets were elongated in the c-direction, with each individual plate grown almost normal to the substrate surface. The particles grown by hydrothermal-electrochemical deposition were larger, ~50 nm thick and ~200 nm wide in the pristine films. Particle shape did not change but particle size increased after annealing (Figure 10.5).

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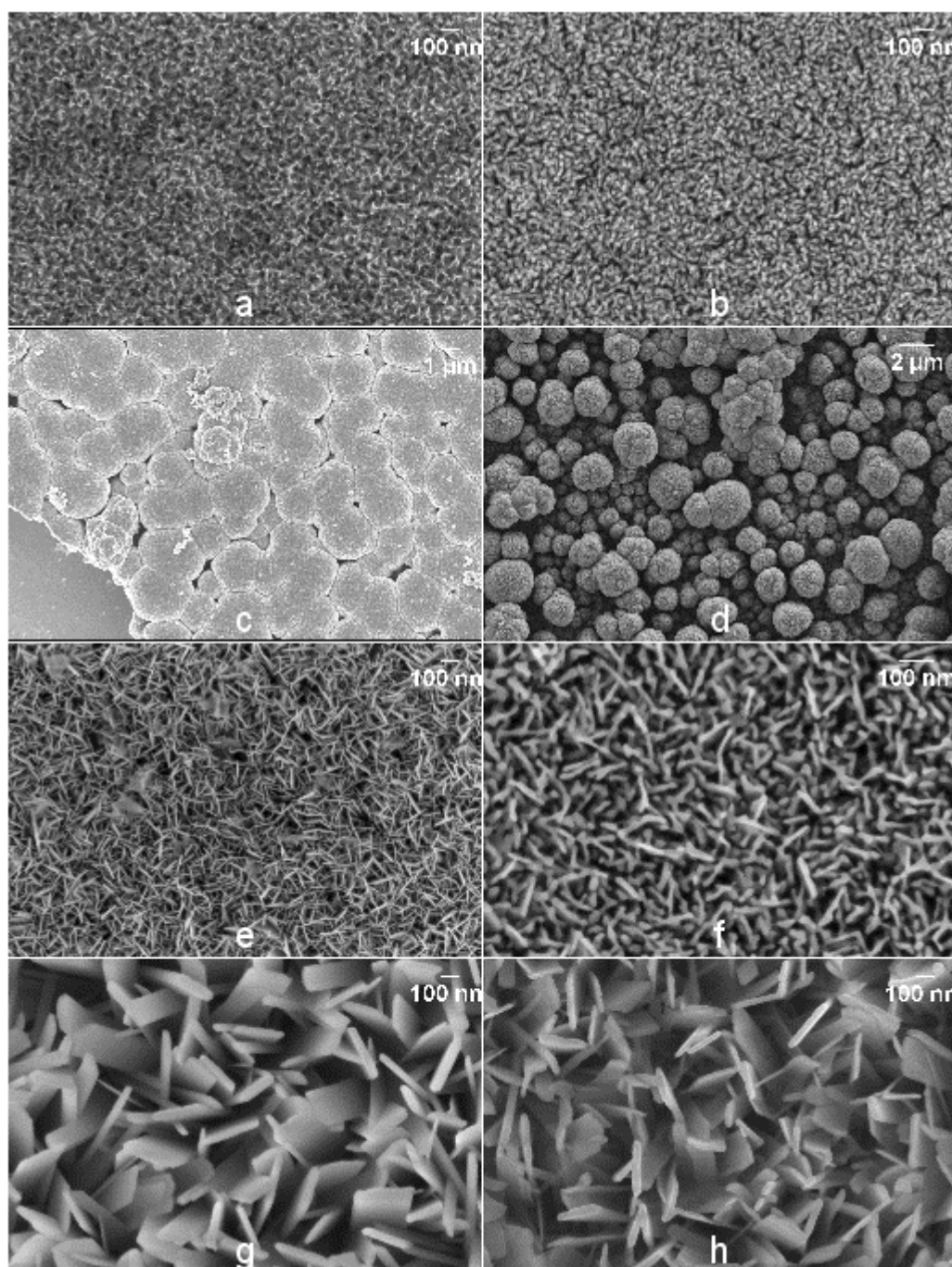


Figure 10.5 FE-SEM of hematite films obtained with electrodeposition at 1.2V (vs Ag/AgCl), at 75°C from solutions containing 0.02 M Fe²⁺ and 0.08 M NaCH₃COO a) H6, at 75°C, as-deposited b) at 75°C, annealed c) H8, at 130°C, as-deposited d) at 130°C, annealed e) H7, at 75°C, 10 % Ce³⁺, as-deposited f) at 75°C, 10 % Ce³⁺ annealed g) H9, at 130°C, 10 % Ce³⁺, as-deposited h) at 130°C, 10 % Ce³⁺, annealed.

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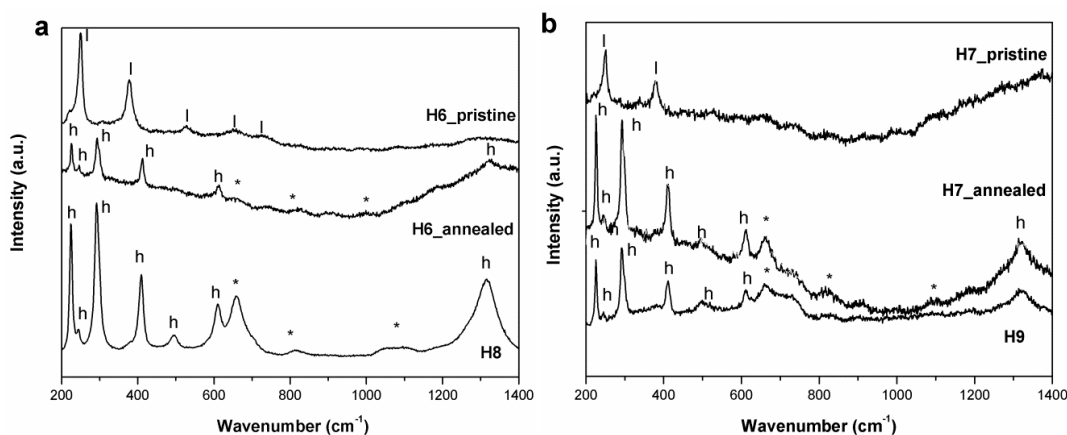


Figure 10.6 a) Raman spectra of hematite films obtained with electrodeposition at 1.2 V (vs Ag/AgCl) from solutions containing 0.02 M Fe²⁺ and 0.08 M NaCH₃COO. b) Raman spectra of hematite films obtained with electrodeposition at 1.2 V (vs Ag/AgCl) from solutions containing 0.02 M Fe²⁺ and 0.08 M NaCH₃COO and 0.002 M Ce³⁺.

Raman spectrum of the as-synthesized film deposited at 75°C from only Fe²⁺ containing solution, H6, exhibits major peaks at 251, 377 cm⁻¹ and some weak features at 528, 652, 733 and 1292 cm⁻¹ which can be ascribed to orthorhombic Lepidocrocite (γ -FeOOH) structure (Figure 10.6a)^{265,240} which is consistent with literature. It has been demonstrated that under anodic potentials from 200 to 1000 mV vs Ag/AgCl, γ -FeOOH is the only single phase deposited from electrolyte containing FeSO₄(NH₄)₂SO₄·6H₂O and CH₃COOK at 90°C.⁸¹ After annealing, Lepidocrocite phase is converted to hematite (Figure 10.6a). Raman spectroscopy data similarly to the films prepared in acidic conditions suggests hematite phase is directly formed by hydrothermal-electrodeposition as discussed in the previous chapter (Figure 10.6a, H8) and Lepidocrocite forms at low temperature from neutral deposition baths. Addition of Ce³⁺ ions into the deposition solution did not induce formation of different iron oxide/hydroxide phases (Figure 10.6b). Hence, it can be concluded that obtained crystal structure on contrary to morphology depends on the temperature under present circumstances and Ce³⁺ is a significant factor in determining the morphology of the products. Raman spectroscopy data also verifies hematite phase for the as-synthesized film deposited at 130°C, H9, and annealed film deposited at 75°C, H8, in the presence of Ce³⁺ from neutral bath and there is no evidence of Cerium-related phase in the films. Similarly to the acidic deposition EDX, XPS and XRF studies showed that Ce³⁺ ion is excluded from hematite crystal lattice, although it directed the growth

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process. Hence, hematite platelets can be produced with hydrothermal-electrochemical deposition in the presence of Ce³⁺ ions.

Lepidocrocite, γ -FeOOH, is a layered compound with an orthorhombic unit cell. The mineral is built by corrugated sheets of double-chained Fe(O,OH)₆ octahedra that are stacked perpendicular to [010] direction and held together by hydrogen bonds (Figure 10.7).²³⁶ It is assumed that hydrogen atoms occupy the centers of inversion and are located at the same distances from two oxygen atoms of the adjacent layers, thus forming continuous O–H–O–H–O chains with symmetric hydrogen bonds.²³⁴ The basic morphologies of Lepidocrocite are lath-like or tabular.

Without Ce³⁺ ions present in the deposition solution, round, worm-like particles at 75°C and spheres of aggregated polyhedral at 130°C were obtained. In the presence of Ce³⁺ ions, on the other hand, lath-like platelets elongated significantly perpendicular to the substrate were formed. Spray and Choi produced round, oval Lepidocrocite particles with anodic electrodeposition from FeCl₂ solution and plate-like particles from neutral deposition solution.²⁶⁵ They discussed this anisotropic columnar structure occurs when the growth process is more favored than the nucleation process. In addition, Sudakar *et al.* observed formation of lath/lamellar shaped particles in the presence of Pt⁴⁺, Pd²⁺, or Rh³⁺ cations whereas aggregates of small particles precipitated without these cationic additives due to preferential adsorption on (0k0) planes of Lepidocrocite.²⁷⁶ Hence, it can be concluded that Ce³⁺ additive in the initial deposition solution act as growth regulating agent by being adsorbed on specific crystallographic planes in the neutral electrodeposition solution.

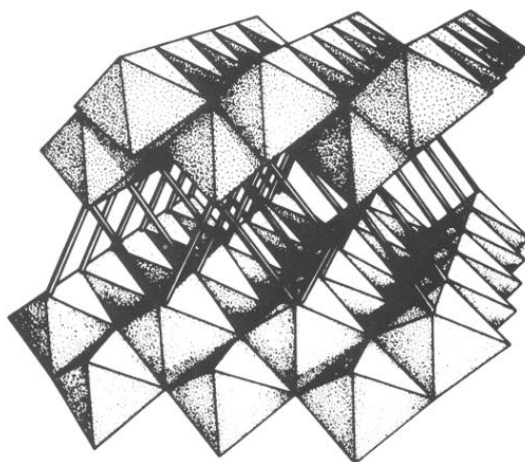


Figure 10.7 The crystal structure of Akaganeite shown viewed down the b-axis. Large spheres represent chlorides, small terminal spheres represent hydrogens.²⁷⁷

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10.3.3 Electrodeposition in the Presence of Ce³⁺ and/or F⁻ Ions

For stabilization of Fe²⁺ ions at pH ~6.0-6.4, F⁻ ions were also used and electrodepositions carried out at 130°C. The film prepared with 0.02 M FeCl₂ and 0.08 M NaF, H10, consists of spheres composed of square planar particles with edges around 1 μ m (Figure 10.8a). Particles seemed to be aggregated and a porous structure was observed after annealing (Figure 10.8b). When Ce³⁺ ions were introduced into the deposition solution so that [Ce³⁺]/[Fe²⁺] was 0.1, H11, square planar particles with slightly smaller sizes (edges around 800 nm) were obtained (Figure 10.8c). Square plate structure was more apparent for the film prepared with [Ce³⁺]/[Fe²⁺] ratio of 0.5, H12, and square caps had smaller edges (~400 nm) (Figure 10.8e). In addition, it can be observed from FE-SEM images that the aspect ratio of the particles tends to increase with increasing Ce³⁺ in the deposition solution. Particles seemed to be aggregated and a porous structure was observed for all of the films after annealing (Figure 10.8b-d-f).

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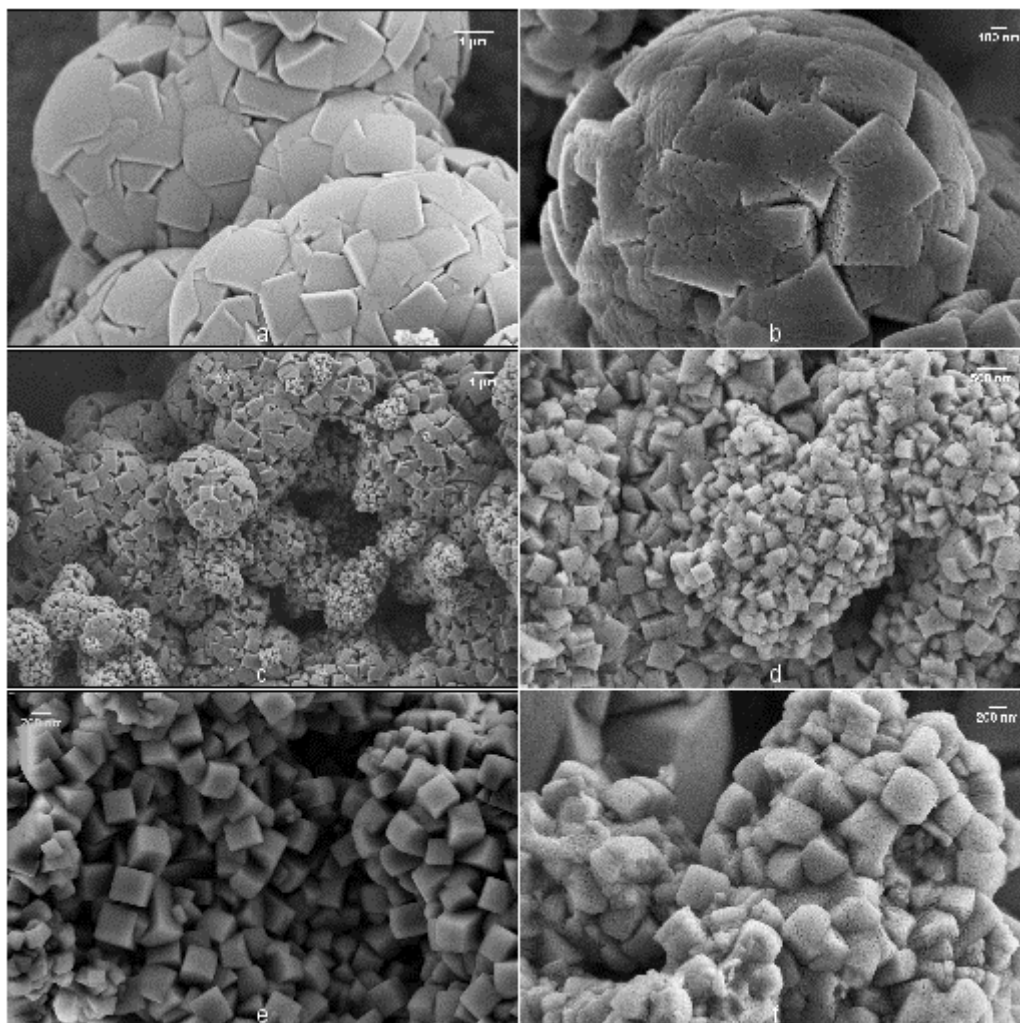


Figure 10.8 FE-SEM of hematite films obtained with electrodeposition at 1.2 V (vs Ag/AgCl) from solutions containing 0.02 M Fe²⁺ and 0.8 M NaF at 130°C a) H10, only Fe²⁺, as-deposited b) H10, annealed c) H11, 10 % Ce³⁺ as-deposited, d) H11, annealed e) H12, 50 % Ce³⁺, as-deposited f) H12, annealed.

Raman spectra of the as-prepared films in the presence of NaF exhibit strong bands at around 307, 400-409, and weaker bands around 548-550, 620 and 730 cm⁻¹ (Figure 10.9a). These bands can be attributed to Akaganeite (β -FeOOH) structure with reported band positions at 310, 385, 535, 615, and 725 cm⁻¹.²⁴² Upon annealing at 520°C Akaganeite structure is transformed to hematite for all of the films (Figure 10.9b). Absence of 462 cm⁻¹ peak in Raman spectra suggests there is no CeO₂ phase in any of the films. Similarly to the acidic deposition EDX, XPS and XRF studies showed that Ce³⁺ ion is excluded from Akaganeite and hematite crystal lattices.

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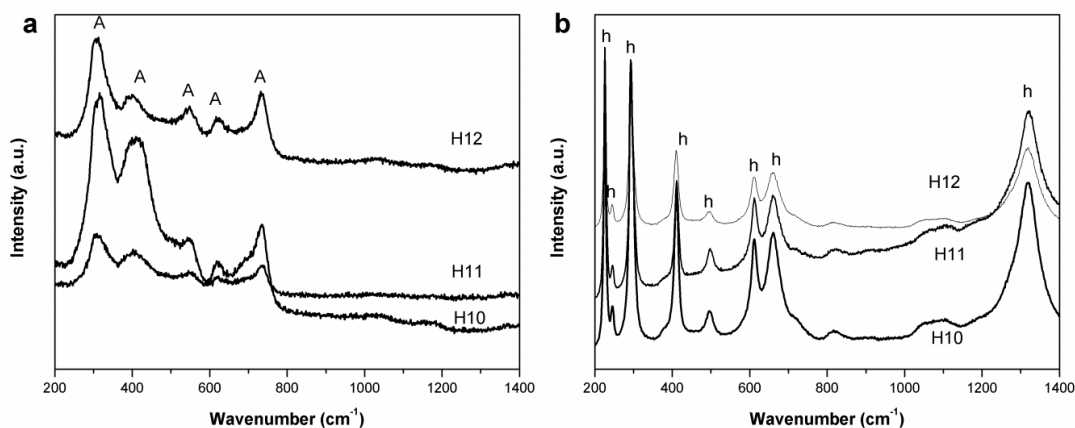


Figure 10.9 Raman spectra of hematite films obtained with electrodeposition at 1.2 V (vs Ag/AgCl) from solutions containing 0.02 M Fe²⁺ and 0.8 M NaF at 130°C a) as-deposited films b) annealed films.

It was reported before that the shape and size of the iron oxyhydroxides and oxides depended on the anion(s) of the Fe(III) salts used for the synthesis.²⁷⁸ K.Hu *et al.*, have investigated effect of ions on the morphology of iron oxyhydroxides and demonstrated formation of platelets, Rhombohedral rods, square rods, six-fold snowflakes, and hexagonal particles with different capping agents.²⁶⁶ They obtained platelets in the presence of CH₃COO⁻ and Rhombohedral rods were formed when NH₄F was added into the deposition solution. The synthesis of β -FeOOH nanorods was also shown to be highly influenced by the presence of salt ions (e.g., NO₃⁻, SO₄²⁻, F⁻, Cl⁻, and Br⁻); depending on the nature of their interaction with Fe³⁺ ions they can influence greatly the morphology, size, porosity, and crystalline structure of β -FeOOH particles.²⁷⁹

Akaganeite has a tetragonal unit cell where all the anions are arranged in a *body-centered* cubic array and Fe³⁺ ions are placed in the octahedral sites.²³⁶ Double chains of edge-sharing octahedra run parallel to the four-fold symmetrical *b*-axis while sharing a corner with other double chains. This arrangement let the structure possess a 3-D tunnel per unit cell which also runs parallel to the *b*-axis delineated by {110} planes. X. Jiang's group has reported that FeCl₃ favors tetragonal phase of Akaganeite, whereas the Fe(NO₃)₃ and Fe₂(SO₄)₃ salt leads to the formation of nitrate and an amorphous mixture of goethite and schwertmannite, respectively.²⁷⁹ They discuss some of the Cl⁻ ions are incorporated into the lattice of Akaganeite tunnel structure (Figure 10.10) and help to stabilize the tunnel structure along the

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c-axis favoring nanorod formation. However, larger ions destabilize Akaganeite structure and favor formation of goethite. They also compared ability of F⁻ and Cl⁻ to stabilize Akaganeite tunnel. They discussed that due to its high electronegativity, F⁻ can form strong interactions with Fe³⁺ ions. However F⁻ ion would lead to a deformed Akaganeite structure due to its smaller size. Hence, changing stabilizing anion from CH₃COO⁻ to F⁻ resulted in formation of square planar particles of β -FeOOH rather than Lepidocrocite platelets which were transformed into hematite particles upon annealing. Porous, square planar hematite particles were obtained after transformation. It has been demonstrated that potential microporosity of Akaganeite due to the tunnel structure develops into slit shaped micropores which coalesce into mesopores and phase transformation take place as temperature is increased.²³⁶

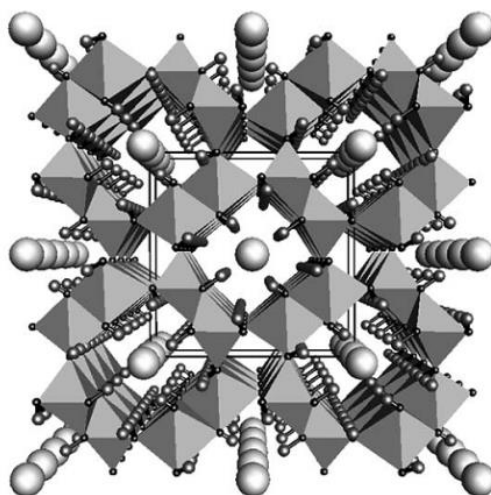


Figure 10.10 Crystal structure of Akaganeite shown viewed down the b-axis. Large spheres represent chlorides, small terminal spheres represent hydrogens.²⁸⁰

It has been discussed that side planes of Akaganeite rod (i.e.; $(100) \equiv (-100) \equiv (010) \equiv (0-10)$; $(110) \equiv (-110) \equiv (1-10) \equiv (-1-10)$ and the parallel planes in the growth direction $(001) \equiv (00-1)$ are equivalent in surface energy due to their mirror symmetry in the tetragonal lattice (Figure 10.11).²⁷⁹ However, anisotropic growth still takes place since diffusion constants of anions vary according to the crystal plane they interact. It has been shown with molecular dynamics simulation that the β -FeOOH (100) and (110) surfaces have a minimal interaction with the anions whereas F⁻ is highly adsorbed on the (001) surface.²⁷⁹ Hence the growth along the [001] direction is faster to form a nanorod. The aspect ratio of the nanorods can be

in the Presence of Ce³⁺ and/or F⁻ Ions

controlled by [Fe³⁺]. It has been demonstrated that length of the rods decrease with decreasing concentration and even spherical particles can be obtained with dilute solutions.²⁷⁹ In this study, Fe²⁺ concentration is under critical value which might be responsible for square planar particles (Figure 10.7). As [Ce(NO₃)₃] in the deposition solution is increased, size of the squares decrease whereas thickness of the particles increase which suggests growth in lateral direction is repressed. Since It has been shown that NO₃⁻ ions does not interact strongly with any of the Akaganeite planes²⁷⁹, Ce³⁺ ions are responsible for the morphology change. It is most likely that the Ce³⁺ ions in the deposition solution are adsorbed onto the side surfaces of β -FeOOH parallel to the c-axis and hence preventing the growth in the lateral direction.

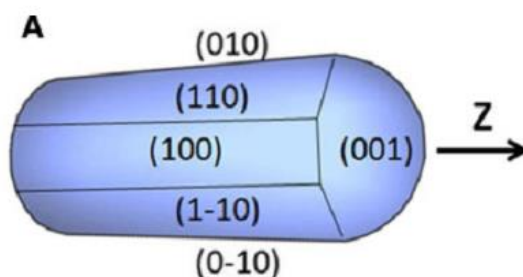


Figure 10.11 Schematic diagram illustrating the crystal faces of Akaganeite.²⁸⁰

10.4 Conclusions

Hydrothermal-electrodeposition was successfully employed to produce α -Fe₂O₃ and the effect of electrodeposition temperature on the structure and phase of iron oxide films was explored. X-ray amorphous iron oxyhydroxide phase forms when the films are deposited at 75°C which is converted to α -Fe₂O₃ after annealing at 520°C. On the other hand, α -Fe₂O₃ phase is produced directly when electrodepositions are carried out at 130°C under hydrothermal conditions regardless of Ce³⁺ and/or CH₃COO⁻ presence.

The study also discusses the influence of Ce³⁺, CH₃COO⁻ and F⁻ ions under presented conditions. Different morphologies including, worm-like, spherical, rhombohedra, platelets and square planar particles with varying aspect ratio were obtained. When Ce³⁺ ions present in the acidic deposition solution, worm-like particles and polyhedra are obtained at 75°C and 130°C, respectively. Anodic deposition of FeOOH/hematite films from ~neutral aqueous

in the Presence of Ce³⁺ and/or F⁻ Ions

medium (pH 6.6-6.8) by adding NaCH₃COO into the deposition solution for stabilization of Fe²⁺ ions is also performed. Lepidocrocite phase is favored with electrodeposition from this solution under ambient conditions. Worm-like, round-oval Lepidocrocite, γ -FeOOH, particles at 75°C and Rhombohedral hematite particles at 130°C are prepared. Electrodepositions from neutral solutions containing Ce³⁺ ions resulted in platelets both for low and high temperature synthesis. Here, Ce³⁺ ions act as shape-dictating additive due to preferential adsorption on (0k0) planes of Lepidocrocite and result in anisotropic columnar structures. Addition of F⁻ into the deposition solution induces Akaganeite, β -FeOOH, formation composed of bundles of square planar particles even under hydrothermal-electrochemical deposition. When Ce³⁺ ions are introduced into the deposition solution, they act as growth-regulating agent via specific absorption rather than inducing formation of a different phase. The aspect ratio of the particles tends to increase with increasing Ce³⁺ concentration in the deposition solution due to restriction of lateral growth.

Chapter 11 Conclusions & Outlook

This thesis work is devoted to electrodeposition of two technologically important semiconductor metal oxides; zinc oxide (Part I) for photovoltaic applications and α -iron oxide (Part II) films for solar hydrogen production. The focus is on combination of electrochemical deposition technique with hydrothermal methods. Basically, effect of this new technique on production and final physical properties of metal oxide films is analyzed in detail.

The first part of this dissertation discusses preparation of ZnO films of various size and shape for efficient photoelectrochemical applications by manipulating of hydrothermal-electrochemical deposition parameter and using electrodeposition as a means to coat sensitizers on ZnO with better electrical contact. In line with literature, HED resulted in vertically aligned ZnO nanorods to the substrate surface with well-defined hexagonal caps. Moreover, growth of ZnO NRs with enhanced *c*-axis texturation without a seed layer, directly on the conducting glass with HED has been demonstrated. Regardless of precursor concentration, formation of 1-D structures is observed via HED. Precursor concentration, on the other hand controlled diameter of the rods. It has been presented that photoelectrochemical sensitivity increases with increased amount of Mn_CdS particles on ZnO NRs and increasing rod diameter with a certain amount of sensitizer. A short circuit current density of 2.08 mA/cm^2 and an open circuit potential of -1.32 V have been achieved for the ZnO100/CdS21 electrode resulting in an overall power conversion efficiency of 0.93 %. Although the optimum rod diameter for improved PEC activity is found, there is still room for optimization of the sensitizer particles by modifying SILAR parameters, for example a lower band gap with a particularly long absorption tail that extends far into the red is possible¹⁰³ and amount of Mn dopant has to be adjusted for better activity²⁰⁴. After optimization process, a cell will be constructed for further testing.

Additives play a significant role as growth modifiers by selective adsorption on various surfaces of ZnO. However, effect of additives is significantly influenced by high temperature

electrodeposition with each cation and anion behaving differently. The rod diameter can also be controlled by adjusting Mn(II) ions concentration in the deposition bath. Mn(II) ions act as growth-modifier molecules and manipulate the crystal growth enhancing formation of particles with high aspect ratio. As concentration of Mn(II) in the deposition bath increased, coalesced ZnO platelets were transformed into hexagonal particles of smaller diameter. Moreover, HED allows formation of hierarchical ZnO structures at single step synthesis by introducing $\text{Cd}(\text{CH}_3\text{COO})_2$ into deposition bath. ZnO structures such as 1D twinned structures, 2D ZnO crosses, star flower-like structures or micrometer-long micro-channels can be obtained by adjusting $[\text{Cd}(\text{CH}_3\text{COO})_2]/[\text{Zn}(\text{II})]$ ratio in the deposition solution. When Co(II) ions are introduced into the deposition solution, phase separation is observed together with formation of Co-rich spheres on a zinc rich matrix, thereby forming heterogeneous ZnO-Co nanostructures. The degree of phase separation and the quantity of the initial Co rich spheres is determined by Co(II) concentration in the deposition bath. Effect of morphology of ZnO particles on photoelectrochemical properties can be testing by coating the films with suitable sensitizers.

In recent years, metal sulfide sensitizers have been utilized to fabricate quantum dot-sensitized solar cells (QDSSCs). Although, QD semiconductors have a high potential to become new-generation energy devices, they still suffer from low QD loading, weak electronic contact and recombination losses. Hence, electrodeposition is studied to form a fine electric contact between a dense and compact chalcogenide semiconductor sensitizer and ZnO which would be advantageous for fast charge-transport. For CdS due to the increased amount of visible-light sensitive CdS on ZnO film, photoresponse tends to increase with deposition time. However, photocurrent produced is reduced by prolonged deposition. A short circuit current density of 1.42 mA/cm^2 and an open circuit potential of -1.391 V have been achieved for the annealed Mn_doped CdS/ZnO electrode resulting in an overall power conversion efficiency of 0.81 %. $\text{Ag}_2\text{S}/\text{ZnO}$ photoelectrodes exhibit considerably enhanced and widened light absorption but lower power-conversion efficiency in spite of initial high photocurrent, most probably due to degradation of ZnO during electrodeposition. $\text{Ag}_2\text{S}/\text{ZnO}$ films prepared by electrodeposition have a great potential to be highly efficient photoelectrodes once disruption of ZnO NRs during synthesis can be prevented, which is currently studied.

Lastly, in this part electrodeposition of CdZnS buffer layers for solar cells with enhanced photoactivity is discussed. Photoresponse tends to increase with increasing Zn(II)

amount. Reported photocurrent values for CdZnS films are in the order of μA . As-prepared films displayed significantly enhanced photocurrent according to the literature. The best performing film exhibited a short circuit current density of 1.31 mA/cm^2 and an open circuit potential of -0.99 V with an overall power conversion efficiency of 0.6% . These promising current-voltage characteristics suggest possibility of efficient solar cell construction by depositing CdZnS on ZnO nanorods which is currently under process.

One of the major hurdles in attaining high fill factor, FF, and thereby high power conversion efficiency in XSCs is the poor charge transfer rate at the counter electrode. The search for a higher FF is still an open question. It is believed that higher FFs will be obtained with more functional counter electrodes. Especially for semiconductor sensitized solar cells, metal sulfides such as CoS, NiS, PbS and CuS are becoming promising candidates as electrocatalysts for polysulfide redox reactions in photoelectrochemical cells (PECs). Electrodeposition of CoS as counter electrode with enhanced performance are reported.^{281,282} Metal sulfide counter electrodes with different morphologies and physical properties can be obtained and investigated for improved electrocatalyst activity by modifying deposition parameters or using hydrothermal-electrochemical deposition, which is a continuum to the study described here.

The second part of this dissertation describes the effects of electrodeposition at high temperature and pressure on the physical and photoelectrochemical properties of the iron oxide films and routes to obtain iron oxide structures in various shapes. Among reported deposition techniques, anodic electrodeposition is preferred since it does not require H_2O_2 which is safer for a closed system at high temperature and pressure. In line with the literature, potentiostatic electrodeposition at ambient temperatures such as 75°C results in formation of amorphous iron oxide particles which can be converted to hematite ($\alpha\text{-Fe}_2\text{O}_3$) upon thermal treatment. Combining electrochemistry with advantages of hydrothermal synthesis allows growth of crystalline $\alpha\text{-Fe}_2\text{O}_3$ phase directly at a single step on the conducting glass. It is demonstrated that regardless of pH, growth time and additives (Ce^{3+} , CH_3COO^-) hematite crystals are obtained with anodic HED most probably due to increased reaction kinetics at high temperature (with the exception of F⁻ which strongly favors Akaganeite phase). Thickness of the films can be adjusted with growth time and pH is found to be effective on both reaction kinetics and the final particle size. Higher pH and higher precursor concentration favor increased deposition rate in line with the observations of Cohen and Leibenguth and smaller

particle size. Moreover, α -Fe₂O₃ with different morphologies including, worm-like, spherical, rhombohedra, platelets and square planar particles with varying aspect ratio were obtained when HED is used together with growth-modifying species.

Iron oxyhydroxide particles with no particular shapes which are transformed into oval-round particles with diameters ranging between 10-50 nm after annealing were obtained by electrodeposition at 75°C from an aqueous bath containing 0.02 M FeCl₂ whereas high temperature electrodeposition resulted in formation of monodisperse, almost-spherical hematite polyhedra of around 300-400 nm. When Ce³⁺ ions present in the acidic deposition solution, worm-like iron oxyhydroxide particles and hematite polyhedra are obtained at 75 and 130°C, respectively. Worm-like, round-oval Lepidocrocite, γ -FeOOH, particles at 75°C and Rhombohedral hematite particles at 130°C are prepared by electrodeposition from baths containing CH₃COO⁻. Electrodepositions from baths containing both CH₃COO⁻ and Ce³⁺ ions resulted in platelets both for low (Lepidocrocite phase) and high (hematite phase) temperature synthesis. Here, Ce³⁺ ions act as shape-dictating additive due to preferential adsorption on (0k0) planes of Lepidocrocite and result in anisotropic columnar structures. Addition of F⁻ into the deposition solution induces Akaganeite, β -FeOOH, crystallization composed of bundles of square planar particles even under hydrothermal-electrochemical deposition. When Ce³⁺ ions are introduced into the deposition solution, they act as growth-regulating agent via specific absorption rather than inducing formation of a different phase. The aspect ratio of the particles tends to increase with increasing Ce³⁺ concentration in the deposition solution due to restriction of lateral growth.

Photoelectrochemical studies demonstrated that higher performance can be obtained with the films prepared via HED. Net photocurrent density of the 23.6 μ A/cm² is obtained in 0.1 M NaOH under 1 sun conditions at 1.23 V vs NHE with the film prepared from a bath containing 0.05 M FeCl₂ and 0.1 M NaCH₃COOH via hydrothermal-electrodeposition with a photocurrent onset potential of 0.96 V vs NHE. Although there are a few reports presented photocurrents in the mA regime for hematite films, the values obtained are comparable to most of the literature values. Hence, it can be concluded that HED is a tool that can provide strong control over crystalline phase, shape and size of iron oxide particles and is a technique that produced crystalline hematite films with promising photoelectrochemical properties.

Significant effort has been devoted towards the development of doped hematite films, and Si doping is proved to be an effective strategy for increasing the efficiency.²³³ Recently

electrochemical synthesis of $\text{Zn}_{1-x}\text{Fe}_x\text{O}$ ternary thin films²⁸³ and Zn-doped $\alpha\text{-Fe}_2\text{O}_3$ nanotube arrays²⁸⁴ were reported. The nanotube-array architecture is demonstrated to facilitate the charge collection and the light absorption and resulted in positive photocurrent onset potential of 1.3 V vs RHE and a cathodic photocurrent of $40.4 \mu\text{A}/\text{cm}^2$ at 0.5 V vs RHE. These reports encouraged us to study hydrothermal-electrodeposition of FeZnO structures which exhibit photocurrent around $50\text{--}60 \mu\text{A}/\text{cm}^2$ in 0.1M NaOH under 1 sun conditions at 1.1 V vs NHE according to the preliminary research conducted. This mini-study showed that promising photoelectrochemical properties of hematite films prepared via HED can be enhanced by impurity doping which will be investigated further. Another effective strategy to improve PEC characteristics is to carry out surface treatments to catalyze oxygen evolution reaction which is accomplished by passivating surface-localized electron trap states; for example, via adsorption of Co(II) ions²³¹, cobalt–phosphate²⁸⁵ or deposition of redox-inactive materials such as alumina by ALD²⁴⁷, ZnO by spin coating²⁴⁷ on hematite. This strategy can be used to enhance PEC characteristics of our films further in future.

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