UNIVERSITI PUTRA MALAYSIA

ELECTROCHEMICAL SYNTHESIS AND PROPERTIES OF CADMIUM SELENIDE SENSITISED TITANIA NANOTUBES FOR PHOTOELECTROCHEMICAL CELLS

ASMAA KADIM AYAL

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By

ASMAA KADIM AYAL

Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in Fulfillment of the Requirements for the Degree of Doctor of Philosophy

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Chairman : Professor Zulkarnain Zainal, PhD
Faculty : Science

Solar energy is an alternative sustainable energy resource that can be harvested using photoelectrochemical cell comprised of inorganic sensitized nanostructured oxide semiconductor electrode. In this work, the electrochemical synthesis, characteristics and photoelectrochemical performance of cadmium selenide (CdSe) sensitized titanium dioxide nanotube arrays (TiO_2 NTAs) were studied. TiO_2 NTAs thin film electrodes were prepared by the anodisation method of titanium foil in a two electrode cell containing NH_4F solution. Parameters affecting the morphology, structure and geometry of TiO_2 NTAs were investigated in three different electrolytic media namely the acidic aqueous solution (NH_4F/H_2O), mixture of aqueous/organic solution ($NH_4F/H_2O/EG$) and an organic solution (NH_4F/EG). The characteristics of TiO_2 NTAs were examined using X-ray diffractometry (XRD), energy dispersive X-ray analysis (EDX), field emission scanning electron microscopy (FESEM), Transmission Electron Microscopy (TEM) and High Resolution Transmission Electron Microscopy (HRTEM) and UV-visible diffuse reflectance spectroscopy (UV-DRS). Meanwhile, the photoelectrochemical responses of TiO_2 NTAs were investigated using linear sweep photovoltammetry (LSPV).

Three electrochemical deposition methods were used to deposit CdSe onto TiO_2 NTAs by applying the potentiostatic deposition, cyclic voltammetric deposition and pulse electrodeposition methods. CdSe was electrodeposited onto TiO_2 NTAs from an electrolyte containing $CdCl_2$ and SeO_2 with Na_2SO_4 as the supporting electrolyte. Cyclic voltammetry was used to select the probable range of the potential for deposition which was found to be from -0.65 V to -1.00 V. Potentiostatic electrodeposition techniques has been carried out at the different potential of deposition, time of deposition, concentration of SeO_2, concentration of $CdCl_2$, pH and temperature of annealing. For pulse electrodeposition, the effect of varying deposition potential, deposition time, duty cycle, concentration of SeO_2, concentration of $CdCl_2$, pH, and temperature of annealing were studied. The effect of different potential range, scan rate, number of cycles, pH and temperature of annealing were investigated for cyclic voltammeric deposition. X-ray diffraction (XRD) patterns showed that the deposited CdSe onto TiO_2 NTAs were polycrystalline with hexagonal structure. The photoelectrochemical (PEC) properties of the synthesised films were evaluated using linear sweep photovoltammetry (LSPV) by illuminating the samples intermittently with a halogen lamp (120 V, 300 W) while immersing in 0.01 M Na_2S electrolyte. Photocurrent was observed due to the reaction involving generated minority carriers (holes) on the electrode surface. Therefore, the deposited CdSe is an n-type semiconductor in this work. The XRD and PEC results suggested that the suitable electrolyte bath composition for CdSe deposition was 20 mM $CdCl_2$, 5 mM SeO_2, and 20 mM Na_2SO_4. Uniform potentiostatic deposition of CdSe onto TiO_2 NTAs was obtained at the potential of -0.7 V with the deposition time of 30 minutes at pH 3.0 under the annealing condition of 250 °C in N_2 atmosphere for 60 minutes. Meanwhile, pulse electrodeposition involved pulse potential of -0.85 V at 20 minutes of T_{on} with 50% duty cycle under the annealing condition of 350 °C in N_2 atmosphere for 60 minutes. Besides, cyclic voltammetric deposition was conducted at the potential range of -0.60 V to -1.00 V with the scan rate of 5 mV/s for 6 cycles at pH 3.0 under the annealing condition of 250 °C in N_2 atmosphere for 60 minutes. It was found that the optical properties of CdSe/TiO_2 nanotubes films have direct optical band gap energy values (Eg) in the range of 1.7 eV to 1.84 eV. The morphological property of the prepared samples was examined by field emission scanning electron microscopy (FESEM). The crystallite sizes of CdSe determined from XRD were in between 10.80 for potentiostatic technique, 15.50 nm for pulse electrodeposition and 7.00 nm for cyclic voltammetric deposition. The ratio of Cd:Se was 1:1 as shown in EDXenergy dispersive X-ray analysis. The photoefficiency was evaluated in 0.01 M Na_2S under halogen illumination. The CdSe/TiO_2 nanotubes film deposited using pulse deposition displayed the best photoefficiency (1.96%) compared to potentiostatic and cyclic voltammetric techniques.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk Ijazah Doktor Falasafah

SINTESIS ELEKTROKIMIA DAN PENCIRIAN NANOTIUB TITANIA YANG DIPEKAKAN DENGAN KADMIUM SELENIDA UNTUK SEL FOTOELEKTROKIMIA

Oleh

ASMAA KADIM AYAL

April 2017

Pengerusi : Profesor Zulkarnain Zainal, PhD
Fakulti : Sains

Tenaga solar adalah sumber tenaga lestari alternatif yang boleh dituai menggunakan sel photoelektrokimia terdiri daripada semkonduktor oksida terpeka tak organic. Dalam karya ini, sintesis elektrokimia, ciri-ciri dan prestasi fotoelektrokimia titanium dioksida bertiub nano (TiO_2 NTAs) terpeka kadmium selenide (CdSe) telah di kaji. Elektrod filem nipis TiO_2 NTAs disediakan dengan kaedah penganodan plat titanium tulen dalam sel piawai 2-elektod mengandungi larutan NH_4F. Parameter yang memepengaruhi morfologi, struktur dan geometri NTAs telah dikaji dalam tiga media elektrolisis yang berbeza iaitu larutan akua berasid (NH_4F/H_2O), campuran larutan akua-organik ($NH_4F/EG/H_2O$) dan larutan organik neutral (NH_4F/EG). Ciri TiO_2 NTAs telah dianalisis menggunakan pembelauan sinar-X (XRD), analisis penyerakan tenaga sinar-X (EDX), mikroskopi pengimbasan electron pancaran medan (FESEM), mikroskopi pancaran electron (TEM) dan spektoskopi ultra lembayung Nampak-pantulan resapab (UV_DRS). Sementara itu, gerakbalas fotoelektrokimia TiO_2 NTAs dianalisis dengan menggunakan ujian fotovoltammetri pengimbas linear (LSVP).

Tiga kaedah pengendapan elektrokimia telah digunakan untuk mengendap CdSe di atas TiO_2 NTAs iaitu dengan menggunakan kaedah potensiostat, kaedah pengendapan voltammetri siklik dan kaedah elektropengendapan denyut. CdSe telah dimendapkan di atas TiO_2 NTAs daripada elektrolit yang mengandungi $CdCl_2$ dan SeO_2 bersama Na_2SO_4 sebagai elektrolit penyokong. Kaedah voltammetri siklik digunakan untuk memilih kemungkinan julat untuk keupayaan pengendapan dan julat keupayaan yang diperolehi adalah daripada -0.65 V kepada -1.00 V. Teknik elektropengendapan potensiostat telah dijalankan pada keupayaan pengendapan yang berbeza, masa pengendapan, kepekatan SeO_2, kepekatan $CdCl_2$, pH dan suhu penyepuhlindapan. Untuk kaedah elektropengendapan denyut, kesan perbezaan keupayaan pengendapan, masa pengendapan, kitaran kerja, kepekatan SeO_2, kepekatan $CdCl_2$, pH dan suhu penyepuhlindapan telah dikaji. Kesan perbezaan julat keupayaan, kadar imbas, jumlah kitaran, pH dan suhu penyepuhlindapan telah dikaji untuk kaedah pengendapan voltametri berkitar. Corak pembelauan sinar-X (XRD menunjukkan bahawa mendapan CdSe di atas TiO_2 NTAs adalah berpolihablur dengan struktur heksagon. Sifat fotoelektrokimia (PEC) filem yang telah disintesis telah dinilai dengan menggunakan ujian fotovoltammetri pengimbas linear (LSVP) dengan memancarkan lampu halogen (120V, 300W) ke atas sampel sambal menenggelamkan sampel ke dalam elektrolit 0.01 M Na_2S. Fotoarus telah diperhatikan kerana tindakbals melibatkan lubang yang janaan pembawa minoriti. Oleh yang demikian, mendapan CdSe di dalam kajian ini adalah semikonduktor jenis n. Keputusan XRD dan PEC telah mencadangkan komposisi rendaman elektrolit yang sesuai untuk CdSe adalah pada 20 mM $CdCl_2$, 5 mM SeO_2, dan 20 mM Na_2SO_4. Pengenapan potensiostat yang seragam oleh CdSe di atas TiO_2 NTAs telah diperolehi pada keupayaan 0.7 V dengan masa pengendapan selama 30 minit pada pH 3.0 di bawah suhu penyepuhlindapan 250 °C di dalam keadaan N_2 selama 60 minit. Sementara itu, elektropengendapan denyut mencatatkan keupayaan denyut -0.85 V di T_{on} pada masa 20 minit dengan 50% kitaran kerja di bawah suhu penyepuhlindapan 350 °C di dalam keadaan bernitrogen selama 60 minit. Selain itu, voltammetry siklik pula telah dilakukan pada julat keupayaan dari 0.60 V sehingga 1.00 V dengan kadar imbas 5 mV/s sebanyak 6 kitaran pada pH 3.0 di bawah suhu penyepuhlindapan 250 ^{o}C dalam keadaan bernitrogen selama 60 minit. Didapati jalur ruang optik filem nanotiub CdSe/TiO_2 adalah jalur ruang terus dengan nilai diantara julat 1.7 eV hingga 1.84 eV. Morfologi sampel yang telah disediakan telah diuji dengan menggunakan mikroskopi pengimbasan electron pancaran medan (FESEM). Saiz hablur CdSe yang ditentukan daripada XRD adalah di antara 10.80 nm untuk kaedah potensiostat, 15.50 nm untuk kaedah elektropengendapan denyut dan 7.00 nm untuk kaedah pengendapan voltammetri siklik. Nisbah Cd-Se adalah 1:1 seperti yang ditunjukkan daripada analisis penyerakan tenaga sinar-X. Fotokecekapan telah diuji di dalam 0.01 M Na_2S di bawah sinaran halogen. Filem nanotiub CdSe/TiO_2 dimendapkan menggunakan pengendapan denyut memaparkan fotokecekapan (1.96%) yang paling terbaik berbanding teknik potensiostat dan voltammetry siklik.

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I certify that a Thesis Examination Committee has met on 20 April 2017 to conduct the final examination of Asmaa Kadim Ayal on her thesis entitled "Electrochemical Synthesis and Properties of Cadmium Selenide Sensitised Titania Nanotubes for Photoelectrochemical Cells" in accordance with the Universities and University Colleges Act 1971 and the Constitution of the Universiti Putra Malaysia [P.U.(A) 106] 15 March 1998. The Committee recommends that the student be awarded the Doctor of Philosophy.

Members of the Thesis Examination Committee were as follows:

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Professor
Institute of Advance Technology
Universiti Putra Malaysia
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Nor Azah binti Yusof, PhD
Professor
Faculty of Science
Universiti Putra Malaysia
(Internal Examiner)

Tan Yen Ping, PhD
Senior Lecturer
Faculty of Science
Universiti Putra Malaysia
(Internal Examiner)

Jih-Jen Wu, PhD
Professor
National Cheng Kung University
Taiwan
(External Examiner)

NOR AINI AB. SHUKOR, PhD
Professor and Deputy Dean
School of Graduate Studies
Universiti Putra Malaysia

Date: 2 June 2017

This thesis was submitted to the Senate of the Universiti Putra Malaysia and has been accepted as fulfillment of the requirement for the degree of Doctor of Philosophy. The members of the Supervisory Committee were as follows:

Zulkarnain Zainal, PhD
Professor
Faculty of Science
Universiti Putra Malaysia
(Chairman)

Zainal Abidin Talib, PhD
Professor
Faculty of Science
Universiti Putra Malaysia
(Member)

Janet Lim Honge Ngee, PhD
Associate Professor
Faculty of Science
Universiti Putra Malaysia
(Member)

Lim Ying Chin, PhD
Senior Lecturer
Faculty of Applied Sciences
Universiti Teknologi MARA
(Member)

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School of Graduate Studies
Universiti Putra Malaysia

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PROF. DR. ZULKARNAIN ZAINAL
Department of Chemistry
Faculty of Science
Universiti Putra Malaysia
43400 UPM Serdang
Selangor Darul Ehsan

Signature: ____________________
Name of Chairman of Supervisory Committee: Professor Dr. Zulkarnain Zainal

PROF. DR. ZAINAL ABIDIN TALIB
Dean
Faculty of Science
Universiti Putra Malaysia
43400 UPM Serdang
Selangor, Malaysia

Signature: ____________________
Name of Member of Supervisory Committee: Professor Dr. Zainal Abidin Talib

ASSOC. PROF DR JANET LIM HONG NGEE
SENIOR LECTURER
DEPARTMENT OF CHEMISTRY
FACULTY OF SCIENCE
UNIVERSITI PUTRA MALAYSIA
43400 SERDANG, SELANGOR DARUL EHSAN

Signature: ____________________
Name of Member of Supervisory Committee: Associate Professor Dr. Janet Lim Honge Ngee

DR. LIM YING CHIN
Senior Lecturer
Faculty of Applied Sciences
Universiti Teknologi MARA
40450 Shah Alam, Selangor, Malaysia

Signature: ____________________
Name of Member of Supervisory Committee: Dr. Lim Ying Chin

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

eV	Electron Volt
VB	Valence Band
CB	Conduction Band
E_g	Band Gap Energy
E_f	Fermi Energy Level
PEC	Photoelectrochemical
NTAs	Nanotubes Arrays
CBD	Chemical Bath Deposition
SILAR	Successive Ionic Layer Adsorption and Reaction
CV	Cyclic Voltammetric Deposition
DC	Direct Current
NH_4F/H_2O	0.5 wt.% aqueous NH_4F solution
NH_4F/ 50 %H_2O/EG	Mixture of 0.5 wt.% NH_4F, ethylene glycol and 50 vol.% H_2O solution
NH_4F/ 95%EG	Mixture of 0.5 wt.% NH_4F, 95 vol.% ethylene glycol and 5 vol.% H_2O
NH_4F/ EG	Mixture of 0.5 wt.% NH_4F, 100 vol.% ethylene glycol
Vol.%	Volume Percentage
Wt.%	Weight Percentage
h*v*	Photon Energy
JCPDS	Joint Committee Powder Diffraction Standard
UV-DRS	Ultraviolet–Visible Diffuse Reflectance Spectrophotometer
XRD	X-ray Diffraction
FESEM	Field Emission Scanning Electron Microscopy

TEM	Transmission Electron Microscopy
HRTEM	Transmission Electron and High Resolution Microscopy
EDX	Energy Dispersive Analysis of X-rays
LSPV	Linear Sweep Photovoltametry

CHAPTER 1

INTRODUCTION

1.1 Background of study

Solar energy is considered to be the best solution for the global energy crisis because of some its unique and important properties that include environment friendliness, cleanliness, abundance and sustainability. There are a number of methodologies using which the sunlight can be transformed into usable energy. The silicon-based solar cells have been extensively used for the process of photovoltaic conversion. However, the material expenses for these solar cells and the consumption of energy for producing the high purity wafers are usually high. So far TiO_2 is considered to be one of the most studied PEC materials and it is believed to have the maximum potential (Burda *et al*., 2003; Linsebigler *et al*., 1995). TiO_2 is compatible with various sensitizer systems and electrolytes that are utilised to increase solar conversion efficiency (Bak *et al*., 2002; Linsebigler *et al*., 1995) and it offers a great deal of stability during photocorrosion. A combination of different parameters that can be optimised to improve efficiency determines the performance of TiO_2 PEC materials. The following are the factors that influence the performance of PEC cells and the perpetual adoption of TiO_2 as the prime PEC material:

a) Uniform films and viable nanostructures
b) Porosity and adequate surface area
c) Absorption in the visible region of solar spectrum
d) Lessen charge carrier recombination and increased charge carrier production

From doped materials to unique nanostructures, a number of variants of TiO_2 have been analysed to optimise these four factors and in turn improve the PEC performance. Due to the high number of grain boundaries of TiO_2 nanoparticles which can encourage recombination. Therefore, TiO_2 nanoparticles used in solar cells undergo to difficulties with electron transport. Also, porous TiO_2 is low in mobility largely because of the random movement of charge carrying electrolytes, charge trapping at defects, and the tapering of the electric field as a result of the polarizable TiO_2 nanoparticles (Hendry *et al*., 2006; Kopidakis *et al.*, 2000).

1D structure like nanotubes (Lim *et al.*, 2012) and nanowires (Chen *et al.*, 2007) are deemed to offer solution to these mobility issues. 1D structure holds a greater advantage over 0D nanoparticles in regard to charge carrier dynamics for materials used as photoanodes. The exceptional light absorption features of TiO_2 can be attributed to the antenna-like structure of vertically oriented TiO_2 nanostructures (Bang and Kamat, 2010; Fitzmorris *et al*, 2012; Hoang *et al*, 2012; Hurum *et al.*, 2003; Kopidakis et al., 2000; Villa *et al.*, 2010). Because of fewer interfacial grain boundaries, nanowires, nanotubes, and nanorods will demonstrate slower charge recombination. Despite these benefits, their use is limited on the industrial scale as they exhibit numerous problems related to adherence to different surfaces and uniformity.

The TiO_2 absorption to UV wavelengths is limited due to the band gaps of anatase and rutile which are 3.2 and 3.0 eV, respectively (Chen Mao, 2007; Coronado *et al*., 2013; Hurum *et al*., 2003). Since visible light accounts for ~45% of solar output and UV light accounts for ~3% (Wheeler *et al*., 2013), the final objective of researchers is to transform TiO_2 so that it can absorb visible light and utilise this feature in the solar output. To improve visible light absorption, and in turn the PEC effectiveness of TiO_2, two potential paths, namely sensitisation and doping, have been adopted and followed.

Sensitisation is usually accomplished with charge introducing molecules such as small band gap semiconductors (Baker and Kamat, 2009; Chen *et al*., 2011; Hensel *et al*., 2010; Kongkanand *et al*., 2008), or dyes (Grätzel, 2004; Law *et al*., 2005; Macák *et al*., 2005; Zhu *et al*., 2007) which absorb visible light and enable the charge transfer of photoexcited electrons into the TiO_2 conduction band. Hence, the necessity for TiO_2 to absorb visible light becomes irrelevant. Doping TiO_2 in order to modify the band structure is another potential technique to improve the visible light absorption ability of TiO_2. The alteration of the crystal structure of TiO_2 using deposition techniques or chemical treatment comprises lattice substitution of oxygen with C, N, F, P or S (Asahi *et al*., 2001; Hensel *et al*., 2010; Hoang *et al*., 2012; Park *et al*., 2006). Additionally, since TiO_2 has the capability to combine with molecules, it can be coupled with sensitising agents such as small band gap semiconductors or dyes that are responsive to visible light. As a result of this molecular binding, the electron injection properties of the sensitising agents improve the photocurrent of TiO_2 production. Hence, to improve the photoresponse of pure TiO_2 in the visible spectrum, the approach of sensitisation mediated by charge injection offers the most practicable route. The latest endeavours to raise the visible absorption in TiO_2 have encompassed photosensitisation through the usage of metal, dyes, and semiconductor nanoparticles (Fitzmorris *et al*., 2012; Hensel *et al*., 2010; Hu *et al*., 2010; Kongkanand *et al*., 2008; Osterloh, 2013) or heterostructures involving other items (Kudo and Miseki, 2009; Osterloh, 2013). Sensitizers have been favourably deployed in PEC materials and solar cells. If a semiconductor (for example, a metal chalcogenide or a sensitizer) is to offer sensitisation to TiO_2, the semiconductor's conduction band edge has to be a bit higher compared to that of the metal oxide. This facilitates electron injection (Kongkanand *et al*., 2008). Metal chalcogenides, including CdSe, have a more negative conduction band which facilitates alignment of band edges and transfer of electrons with greater efficacy.

Many methodologies have been deployed to deposit metal chalcogenides like CdS and CdSe. These include chemical bath deposition (Hensel *et al*., 2010; Liu *et al*., 2010; Wang *et al*., 2012), sputtering (Fitzmorris *et al*., 2012; Larsen *et al*., 2012), direct attachment through modification with a linker (Tvrdy and Kamat, 2009), SILAR (Lana-Villarreal *et al*., 2010), and electrochemical deposition (Bang and Kamat, 2010; Robel *et al.,* 2006). CdS (Kudo and Miseki, 2009; Lana-Villarreal *et* *al*., 2010; Larsen *et al*., 2012; Liu *et al*., 2010; Wang *et al*., 2012) and CdSe (Leschkies *et al*., 2007) have been favourably used in TiO_2 sensitisation.

Recently, binary and multinary-metal chalcogenide-based semiconductor films have been drawing more and more attention in the field of innovative solar technology because of their greater efficacy, adaptability and handiness. Moreover, thin film solar cells are beneficial with regards to their cost of processing and the minimum material that they consume. Thus, this technology can be definitely elevated to a large manufacturing scale. In recent times, groundwork and analysis of the physical properties of thin films have turned into a remarkable research as the various techniques bring out the different properties of films so that they can be used in electronic devices and solar cells, etc. Several researchers have laid emphasis on physical procedures to formulate CdSe; this encompassed an intricate and high-cost setup.

This work has deployed electrochemical deposition methods as they provide adaptable parameter control, easy setup and a single-step deposition to acquire films of good quality. Even though, previous study had shown that CdSe deposited by cyclic voltammetric technique onto TiO_2 particluate films on ITO glass, the efficiency obtained was low eventhough the band gap energy of the hybrid film was 1.7 eV (Liu and Kamat, 1993). Furthermore, Lv et al. (2014) have studied the influence of electrolyte concentration and deposition time on potentiostaitc deposition CdSe on TiO_2 NTAs for photocatalytic degradation. The variation of the preparation conditions on the structural and optical properties of films have been studied by many researchers. Nevertheless, there is a need to study the structural and optical properties of thin films prepared by electrochemical deposition and with different stoichiometric conditions in order to obtain uniform and homogeneous CdSe/TiO_2 NTAs thin films.

In this study, we have conducted a methodical and thorough scrutiny on the effect of parameters utilised in the electrochemical technique on CdSe's photoelectrochemical properties onto TiO_2 NTAs.

1.2 Problem statements

The earth is facing difficult global environmental degradation and energy resources because of continuing use of conventional fossil fuels which lead to the greenhouse effect. In order to solve this energy resource and environmental problems, photoelectrochemical cell has been at the centre of attention. In order to improve the photoresponse of semiconductor materials under sunlight, different synthesis methods have been adopted to obtain these materials in the nanoscale range**.** Therefore, it is important to innovate methods to produce nanostructured multicomponent materials to improve light absorption capability as well as facilitate interfacial reactions and carrier injection and flow which may lead to higher measured photoconversion efficiency. Some of the current methods used involve air-sensitive or toxic chemicals which require intensive controlled conditions and long preparation time. Even though these methods are capable of producing high quality materials, they are too expensive for large scale production and utilisation.

Moreover, in some cases the materials produced has poor dispersion, non-uniform, amorphous, and contaminated with impurities. Therefore, emphasis should be on methods which are environmentally-friendly, energy efficient and low-cost. The electrochemical technique can control some of these disadvantages and improve the composition of multi-component particles and heterostructures. In this work, a full electrochemical approaches are adopted in the preparation of nanostructured CdSe/TiO_2. The effect the three type's electrodeposition methods to deposit CdSe onto TiO_2 NTAs to improve electronic properties, specifically on the PEC characteristics, has been performed here for the first time, to the best of our knowledge, there was a gap of knowledge in the area. It is not clearly understood how the type of electrodeposition may effect of the deposition CdSe onto TiO_2 NTAs and their photoelectrochemical properties.

1.3 Objectives of study

The objectives of this work are summarized as follows:

1. To prepare nanotubes thin film of TiO_2 by electrochemical anodization of Ti in the mixture of an aqueous solution of NH_4F and ethylene glycol.
2. To enhance photocurrent response of TiO_2 nanotubes by deposition of CdSe nanoparticles via potentiostatic, pulsed, and cyclic voltammetric deposition.
3. To optimize the deposition parameters for electrodeposition of CdSe onto the TiO_2 nanotubes.
4. To determine the surface morphology, elemental composition and crystal structure of the CdSe on TiO_2 nanotubes.
5. To evaluate the optical properties, the photoelectrochemical properties, and the photoconversion efficiency of CdSe on TiO_2 nanotubes.

1.4 Scope of study

This work dealt with the understanding of the relationships between the synthesis conditions, surface sensitisation processes and the photoresponse performance of cadmium selenide on titania nanotubes in photoelectrochemical cells. In particular, this work thoroughly examined the effect of parameters utilized in the electrochemical technique on photoelectrochemical properties of CdSe/TiO_2 NTAs resulted from their interesting physico-chemical properties and their potential for further extensive researches. A composite material, CdSe nanoparticle/TiO_2 nanotube arrays (CdSe/TiO_2 NTAs) were assembled through the insertion of CdSe nanoparticles onto the anodized TiO_2 nanotube arrays via electrochemical deposition. Electrochemical techniques are capable of producing high purity uniformly distributed nanoparticles. In order to understand how to tune the properties of nanoparticles, it is necessary to have an understanding of the nucleation and growth processes that affect the morphology, particle size, uniform distributions and other properties of the CdSe nanoparticles onto TiO_2 NTAs. The experimental condition such as potential, deposition time, concentration of precursors, pH of electrolyte, duty cycles, cycle's number, scan rate, and annealing temperature affect the quality of nanoparticles on TiO_2 NTAs. In the first step of this work, the self-organized TiO_2 NTAs were fabricated by anodisation due to the capability of this method to produce the product with high spatial orientation, excellent charge transfer structure, and large internal surface area which are crucial properties influencing the absorption and propagation of light. The anodisation process was optimised using different electrolyte composition and voltage. The subsequent stage was surface modification of TiO_2 NTAs by depositing CdSe using electrochemical techniques to enhance photoelectrochemical response. The effect of parameters utilized in the electrochemical deposition were investigated in order to search for the optimum condition to deposit CdSe onto TiO_2 NTAs. The work was concluded by analyzing the photoelectrochemical response of CdSe/ TiO_2 NTAs in photoelectrochemical cell.

BIBLIOGRAPHY

Adachi, M., Murata, Y., Okada, I., & Yoshikawa, S. (2003). Formation of titania nanotubes and applications for dye-sensitized solar cells. *Journal of the Electrochemical Society*, *150*(8), G488-G493.

Ai, G., Sun, W., Gao, X., Zhang, Y., & Peng, L. M. (2011). Hybrid CdSe/TiO_2 nanowire photoelectrodes: fabrication and photoelectric performance. *Journal of Materials Chemistry*, *21*(24), 8749-8755.

Albu, S. P., Ghicov, A., Aldabergenova, S., Drechsel, P., LeClere, D., Thompson, G. E., & Schmuki, P. (2008). Formation of Double‐Walled TiO_2 Nanotubes and Robust Anatase Membranes. *Advanced Materials*, *20*(21), 4135-4139.

Aruchamy, A., Aravamudan, G., & Rao, G. S. (1982). Semiconductor based photoelectrochemical cells for solar energy conversion—an overview. *Bulletin of Materials Science*, *4*(5), 483-526.

Asahi, R. Y. O. J. I., Morikawa, T. A. K. E. S. H. I., Ohwaki, T., Aoki, K., & Taga, Y. (2001). Visible-light photocatalysis in nitrogen-doped titanium oxides. *Science*, *293*(5528), 269-271.

Azpiroz, J. M., Ugalde, J. M., Etgar, L., Infante, I., & De Angelis, F. (2015). The effect of TiO_2 surface on the electron injection efficiency in PbS quantum dot solar cells: a first-principles study. *Physical Chemistry Chemical Physics*, 17(8), 6076-6086.

Bak, T., Nowotny, J., Rekas, M., & Sorrell, C. C. (2002). Photo-electrochemical hydrogen generation from water using solar energy. Materials-related aspects. *International journal of hydrogen energy*, *27*(10), 991-1022.

Baker, D. R., & Kamat, P. V. (2009). Disassembly, reassembly, and photoelectrochemistry of etched TiO_2 nanotubes. *The Journal of Physical Chemistry C*, *113*(41), 17967-17972.

Baker, D. R., & Kamat, P. V. (2009). Photosensitization of TiO_2 nanostructures with CdS quantum dots: particulate versus tubular support architectures. *Advanced Functional Materials*, *19*(5), 805-811

Bandyopadhyay, S. (2012). *Physics of nanostructured solid state devices*. Springer Science & Business Media.

Bang, J. H., & Kamat, P. V. (2010). Solar cells by design: photoelectrochemistry of TiO_2 nanorod arrays decorated with CdSe. *Advanced Functional Materials*, *20*(12), 1970-1976.

Bard, A. J. (1979). Photoelectrochemistry & heterogeneous photo-catalysis at semiconductors. *Journal of Photochemistry*, *10*(1), 59-75.

Benamar, E., Rami, M., Fahoume, M., Chraibi, F., & Ennaoui, A. (1998, January). Electrodeposited cadmium selenide films for solar cells. In *Annales de Chimie Science des Matériaux*, *23*(1-2), 369-372.

Berger, S., Hahn, R., Roy, P., & Schmuki, P. (2010). Self-organized TiO_2 nanotubes: Factors affecting their morphology and properties. *physica status solidi (b)*, *247*(10), 2424-2435.

Bessegato, G. G., Guaraldo, T. T., & Zanoni, M. V. B. (2014). Enhancement of photoelectrocatalysis efficiency by using nanostructured electrodes. *Modern Electrochemical Methods in Nano, Surface and Corrosion Science*, 271-319.

Burda, C., Lou, Y., Chen, X., Samia, A. C., Stout, J., & Gole, J. L. (2003). Enhanced nitrogen doping in TiO_2 nanoparticles. *Nano letters*, *3*(8), 1049-1051.

Chen, C., Xie, Y., Ali, G., Yoo, S. H., & Cho, S. O. (2011). Improved conversion efficiency of Ag2S quantum dot-sensitized solar cells based on TiO_2 nanotubes with a ZnO recombination barrier layer. *Nanoscale research letters*, *6*(1), 1-9.

Chen, L. Y., Yang, Z., Chen, C. Y., Ho, T. Y., Liu, P. W., & Chang, H. T. (2011). Cascade quantum dots sensitized TiO_2 nanorod arrays for solar cell applications. *Nanoscale*, *3*(12), 4940-4942.

Chen, X., & Mao, S. S. (2006). Synthesis of titanium dioxide (TiO_2) nanomaterials. *Journal of nanoscience and nanotechnology*, *6*(4), 906-925.

Chen, X., & Mao, S. S. (2007). Titanium dioxide nanomaterials: synthesis, properties, modifications, and applications. *Chemical reviews*, *107*(7), 2891-2959.

Chi, C. F., Liau, S. Y., & Lee, Y. L. (2009). The heat annealing effect on the performance of CdS/CdSe-sensitized TiO_2 photoelectrodes in photochemical hydrogen generation. *Nanotechnology*, *21*(2), 1-6.

Chopra, K. L., Paulson, P. D., & Dutta, V. (2004). Thin-film solar cells: an overview. *Progress in Photovoltaics: Research and Applications*, *12*(2-3), 69-92.

Clement, C. L., Arvamuthan, S., & Santhanam, K. S. V. (1988). Stabilization of the polycarbazole protected n-InSe photoanode for photoelectrochemical solar cells. *Journal of electroanalytical chemistry and interfacial electrochemistry. 248*(1), 233-237.

Coronado, J. M., Fresno, F., Hernández-Alonso, M. D., & Portela, R. (Eds.). (2013). *Design of advanced photocatalytic materials for energy and evvironmental.* London: Springer.

Costa, L. L., & Prado, A. G. (2009). TiO_2 nanotubes as recyclable catalyst for efficient photocatalytic degradation of indigo carmine dye. *Journal of Photochemistry and Photobiology A: Chemistry*, *201*(1), 45-49.

Grimes, C. A., & Mor, G. K. (2009). *TiO_2 nanotube arrays: synthesis, properties, and applications*. Springer Science & Business Media.

Danek, M., Jensen, K. F., Murray, C. B., & Bawendi, M. G. (1994). Preparation of II–VI quantum dot composites by electrospray organometallic chemical vapor deposition. *Journal of Crystal Growth*, *145*(1-4), 714-720.

Diebold, U. (2003). Structure & properties of TiO_2 surfaces: a brief review. *Applied Physics A: Materials Science & Processing*, *76*(5), 681-687.

Diguna, L. J., Shen, Q., Kobayashi, J., & Toyoda, T. (2007). High efficiency of CdSe quantum-dot-sensitized TiO_2 inverse opal solar cells. *Applied Physics Letters*, *91*(023116), 1-6.

Ebrahimiasl, S., Yunus, W. M. Z. W., Kassim, A., & Zainal, Z. (2011). Synthesis of nanocrystalline SnOx (x = 1-2) thin film using a chemical bath deposition method with improved deposition time, temperature and pH. *Sensors*, *11*(10), 9207–9216.

Elahifard, M. R., Rahimnejad, S., Haghighi, S., & Gholami, M. R. (2007). Apatite-coated Ag/AgBr/TiO_2 visible-light photocatalyst for destruction of bacteria. *Journal of the American Chemical Society*, *129*(31), 9552–9553.

Fernandes, J. A., Migowski, P., Fabrim, Z., Feil, A. F., Rosa, G., Khan, S., & Dupont, J. (2014). TiO_2 nanotubes sensitized with CdSe via RF magnetron sputtering for photoelectrochemical applications under visible light irradiation. *Physical Chemistry Chemical Physics*, *16*(19), 9148-9153.

Fitzmorris, B. C., Larsen, G. K., Wheeler, D. A., Zhao, Y., & Zhang, J. Z. (2012). Ultrafast charge transfer dynamics in polycrystalline CdSe/TiO_2 nanorods prepared by oblique angle codeposition. *The Journal of Physical Chemistry C*, *116*(8), 5033-5041.

Fox, M. A., & Dulay, M. T. (1993). Heterogeneous photocatalysis. *Chemical Reviews*, *93*(1), 341-357.

Fratoni, S. S., & Perone, S. P. (1976). Studies in Photoelectrochemistry III. Theory for Induced Charging Currents in Potentiostatic Chronoamperometry Involving Competing Chemical Reactions. *Journal of the Electrochemical Society*, *123*(11), 1672-1676.

Fujishima, A. (1972). Electrochemical photolysis of water at a semiconductor electrode. *Nature*, *238*, 37-38.

Gan, J., Zhai, T., Lu, X., Xie, S., Mao, Y., & Tong, Y. (2012). Facile preparation and photoelectrochemical properties of CdSe/TiO_2 NTAs. *Materials Research Bulletin*, *47*(3), 580–585.

Ghicov, A., & Schmuki, P. (2009). Self-ordering electrochemistry: a review on growth and functionality of TiO_2 nanotubes and other self-aligned MO(x) structures. *Chemical Communications (Cambridge, England)*, *2009*, 2791–2808.

Girija, K., Thirumalairajan, S., Mohan, S. M., & Chandrasekaran, J. (2009). Structural, morphological and optical studies of CdSe thin films from ammonia bath. *Chalcogenide Letters*, *6*(8), 351–357. *Science*

Gong, J., Lai, Y., & Lin, C. (2010). Electrochemically multi-anodized TiO_2 nanotube arrays for enhancing hydrogen generation by photoelectrocatalytic water splitting. *Electrochimica Acta*, *55*(16), 4776–4782.

Gong, J., Pu, W., Yang, C., & Zhang, J. (2012). A simple electrochemical oxidation method to prepare highly ordered Cr-doped titania nanotube arrays with promoted photoelectrochemical property. *Electrochimica Acta*, *68*, 178–183.

Gratzel, M. (2001). Photoelectrochemical cells. *Nature (London, U. K.)*, *414*(6861), 338–344.

Grätzel, M. (2004). Conversion of sunlight to electric power by nanocrystalline dye-sensitized solar cells. *Journal of Photochemistry and Photobiology A: Chemistry*, *164*(1), 3-14.

Green, M. A. (2007). Thin-film solar cells: review of materials, technologies and commercial status. *Journal of Materials Science:Materials in Electronics*, *18*(1), 15-19.

Grimes, C. a. (2007). Synthesis and application of highly ordered arrays of TiO_2 nanotubes. *Journal of Materials Chemistry*, *17*(15), 1451-1457.

Hashimoto, K., Irie, H., & Fujishima, A. (2005). A Historical Overview and Future Prospects. *Japanese Journal of Applied Physics*, *44*(12), 8269–8285.

Hendry, E., Koeberg, M., O'Regan, B., & Bonn, M. (2006). Local field effects on electron transport in nanostructured TiO_2 revealed by terahertz spectroscopy. *Nano Letters*, *6*(4), 755–759.

Hensel, J., Wang, G., Li, Y., & Zhang, J. Z. (2010). Synergistic effect of CdSe quantum dot sensitization and nitrogen doping of TiO_2 nanostructures for photoelectrochemical solar hydrogen generation. *Nano Letters*, *10*(2), 478–483.

Hoang, S., Berglund, S. P., Hahn, N. T., Bard, A. J., & Mullins, C. B. (2012). Enhancing visible light photo-oxidation of water with TiO_2 nanowire arrays via cotreatment with H_2 and NH3: synergistic effects between Ti^{3+} and N. *Journal of the American Chemical Society*, *134*(8), 3659–3662.

Holeman, B. R. (1974). Semiconductor radiation detectors. *Microelectronics Reliability*, *13*(5), 425-432.

Hossain, M. F., Biswas, S., Zhang, Z. H., & Takahashi, T. (2011). Bubble-like CdSe nanoclusters sensitized TiO_2 nanotube arrays for improvement in solar cell. *Journal of Photochemistry and Photobiology A: Chemistry*, *217*(1), 68–75.

Hu, X., Li, G., & Yu, J. C. (2010). Design, fabrication, and modification of nanostructured semiconductor materials for environmental and energy applications. *Langmuir*, *26*(5), 3031–3039.

Huang, M. H., Wu, Y., Feick, H., Tran, N., Weber, E., & Yang, P. (2001). Catalytic growth of zinc oxide nanowires by vapor transport. *Advanced Materials*, *13*(2), 113–116.

Hui, Z., Xie, Q., Shuo, C., Hongtao, Y., & Ning, M. (2009). Mulberry-like CdSe nanoclusters anchored on TiO_2 nanotube arrays:A Novel architecture with remarkable photoelectrochemical performance. *Chemistry of Materials*, *21*(7), 3090–3095.

Hurum, D. C., Agrios, a G., Gray, K. a, Rajh, T., & Thurnauer, M. C. (2003). Explaining the enhanced photocatalytic activity of Degussa P25 mixed-phase TiO_2 using EPR. *Journal of Physical Chemistry B*, *107*(19), 4545–4549.

HyukáIm, S., & HyeokáPark, J. (2010). CdS or CdSe decorated TiO_2 nanotube arrays from spray pyrolysis deposition: use in photoelectrochemical cells. *Chemical Communications*, *46*(14), 2385-2387.

Iijima, S. (1991). Helical microtubules of graphitic carbon. *Nature*, *354*(6348), 56–58.

Ikram, A., Sahai, S., Rai, S., Dass, S., Shrivastav, R., & Satsangi, V. R. (2014). Synergistic effect of CdSe quantum dots on photoelectrochemical response of electrodeposited α-Fe_2O_3 films. *Journal of Power Sources*, 267, 664–672.

Indira, K., Mudali, U. K., Nishimura, T., & Rajendran, N. (2015). A Review on TiO_2 Nanotubes: Influence of Anodization Parameters, Formation Mechanism, Properties, Corrosion Behavior, and Biomedical Applications. *Journal of Bio- and Tribo-Corrosion*, *1*(4), 1-28.

Kale, R. B., & Lokhande, C. D. (2004). Room temperature deposition of ZnSe thin films by successive ionic layer adsorption and reaction (SILAR) method. *Materials Research Bulletin*, *39*(12), 1829–1839.

Kalmus, G. (1988). Optical & Structural Properties of Polycrystalline CdSe Deposited on Titanium Substrates. *Applied Physics A*, *46(*1961), 107–112.

Karthik, S., Gopal, K. M., Haripriya, E. P., Sorachon, Y., Maggie, P., Oomman, K. V., & Craig, A. G. (2007). Highly-ordered TiO_2 nanotube arrays up to 220nm in length: use in water photoelectrolysis and dye-sensitized solar cells. *Nanotechnology*, *18*(6), 65707.

Kasuga, T., Hiramatsu, M., Hoson, A., Sekino, T., & Niihara, K. (1998). Formation of Titanium Oxide Nanotube. *Langmuir*, *14*(12), 3160–3163.

Kim, M. J., Cho, S. K., Koo, H. C., Lim, T., Park, K. J., & Kim, J. J. (2010). pulse electrodeposition for improving electrical properties of Cu thin film. *Journal of the Electrochemical Society*, *157*(11), D564-D569.

Kongkanand, A., Tvrdy, K., Takechi, K., Kuno, M., & Kamat, P. V. (2008). Quantum dot solar cells. Tuning photoresponse through size and shape control of CdSe-TiO_2 architecture. *Journal of the American Chemical Society*, *130*(12), 4007-4015.

Kopidakis, N., Schiff, E. A., Park, N. G., Van de Lagemaat, J., & Frank, A. J. (2000). Ambipolar diffusion of photocarriers in electrolyte-filled, nanoporous TiO_2. *The Journal of Physical Chemistry B*, *104*(16), 3930-3936.

Kosanovic, T., Karoussos, D., & Bouroushian, M. (2010). CdSe electrodeposition on anodic, barrier or porous Ti oxides. A sensitization effect. *Journal of Solid State Electrochemistry*, *14*(2), 241–248.

Kudo, A., & Miseki, Y. (2009). Heterogeneous photocatalyst materials for water splitting. *Chemical Society Reviews*, *38*(1), 253–278.

Lana-Villarreal, T., Shen, Q., Toyoda, T., Go, R., Guijarro, N., Go mez, R., & Gomez, R. (2010). Sensitization of Titanium Dioxide Photoanodes with Cadmium Selenide Quantum Dots Prepared by SILAR: Photoelectrochemical and Carrier Dynamics Studies. *The Journal of Physical Chemistry C*, *114*(3), 21928–21937.

Larsen, G. K., Fitzmorris, B. C., Longo, C., Zhang, J. Z., & Zhao, Y. (2012). Nanostructured homogenous CdSe–TiO_2 composite visible light photoanodes fabricated by oblique angle codeposition. *Journal of Materials Chemistry*, *22*(28), 14205-14218.

Law, M., Greene, L. E., Johnson, J. C., Saykally, R., & Yang, P. D. (2005). Nanowire dye-sensitized solar cells. *Nature Materials*, *4*(6), 455–459.

Lee, W. H., Lai, C. W., & Hamid, S. B. A. (2015). One-Step Formation of WO_3-Loaded TiO_2 Nanotubes Composite Film for High Photocatalytic Performance. *Materials*, *8*(5), 2139-2153.

Leschkies, K. S., Divakar, R., Basu, J., Enache-Pommer, E., Boercker, J. E., Carter, C. B., & Aydil, E. S. (2007). Photosensitization of ZnO nanowires with CdSe quantum dots for photovoltaic devices. *Nano Lett*, *7*(6), 1793–1798.

Li, G., Wu, L., Li, F., Xu, P., Zhang, D., & Li, H. (2013). Photoelectrocatalytic degradation of organic pollutants via a CdS quantum dots enhanced TiO_2 nanotube array electrode under visible light irradiation. *Nanoscale*, *5*(5), 2118-2125.

Li, M., Zhang, S., Peng, Y., Lv, L., & Pan, B. (2015). Enhanced visible light responsive photocatalytic activity of TiO_2 -based nanocrystallites: impact of doping sequence. *RSC Advances.*, *5*(10), 7363–7369.

Li, Y., Wei, L., Zhang, R., Chen, Y., & Jiao, J. (2012). Annealing Effect on Photovoltaic Performance of CdSe Quantum-Dots-Sensitized TiO_2 Nanorod Solar Cells. *Journal of Nanomaterials*, *2012*, 1–6.

Li, Y., & Zhang, J. Z. (2010). Hydrogen generation from photoelectrochemical water splitting based on nanomaterials. *Laser and Photonics Reviews*, *4*(4), 517–528.

Liang, H. C., and Li, X. Z. (2009). Effects of structure of anodic TiO_2 nanotube arrays on photocatalytic activity for the degradation of 2,3-dichlorophenol in aqueous solution. *Journal of Hazardous Materials*, 162(2), 1415-1422.

Liao, W., Zhang, Y., Zhang, M., Murugananthan, M., & Yoshihara, S. (2013). Photoelectrocatalytic degradation of microcystin-LR using Ag/AgCl/TiO_2 nanotube arrays electrode under visible light irradiation. *Chemical Engineering Journal*, *231*(2013), 455–463.

Lifshitz, E., Dag, I., Litvin, I., Hodes, G., Gorer, S., Reisfeld, R., & Minti, H. (1998). Optical properties of CdSe nanoparticle films prepared by chemical deposition and sol–gel methods. *Chemical Physics Letters*, *288*(2), 188-196.

Lim, Y.-C., Zainal, Z., Tan, W.-T., & Hussein, M. Z. (2012). Anodization Parameters Influencing the Growth of Titania Nanotubes and Their Photoelectrochemical Response. *International Journal of Photoenergy*, *2012*, 1–9.

Lim, Y. C., Zainal, Z., Hussein, M. Z., & Tan, W. T. (2012). Effect of Water Content on Structural and Photoelectrochemical Properties of Titania Nanotube Synthesized in Fluoride Ethylene Glycol Electrolyte. *Advanced Materials Research*, *501*, 204–208.

Lim, Y. C., Zainal, Z., Hussein, M. Z., & Tan, W. T. (2013). Morphology and Dimensions Controlled of Titania Nanotubes in Mixed Organic-Inorganic Electrolyte. *Advanced Materials Research*, *686*, 13–17.

Lim, Y. C., Zainal, Z., Hussein, M. Z., & Tan, W. T. (2016). Investigation on optical and photoelectrochemical properties of self-assembled titania nanotube arrays prepared by anodization. *Malaysian Journal of Analytical Sciences*, *20*(1), 121-130.

Linsebigler, A. L., Linsebigler, A. L., Yates Jr, J. T., Lu, G., Lu, G., & Yates, J. T. (1995). Photocatalysis on TiO_2 Surfaces: Principles, Mechanisms, and Selected Results. *Chemical Reviews*, *95*(3), 735–758.

Liu, D., & Kamat, P. V. (1993). Photoelectrochemical behavior of thin cadmium selenide and coupled titania/cadmium selenide semiconductor films. *The Journal of Physical Chemistry*, *97*(41), 10769–10773.

Liu, D., & Kamat, P. V. (1993). Electrochemical Rectification in Cdse+TiO_2 Coupled Semiconductor-Films. *Journal of Electroanalytical Chemistry*, *347*(1–2), 451–456.

Liu, L., Hensel, J., Fitzmorris, R. C., Li, Y., & Zhang, J. Z. (2010). Preparation and photoelectrochemical properties of CdSe/TiO_2 hybrid mesoporous structures. *Journal of Physical Chemistry Letters*, *1*(1), 155–160.

Liu, Y., Zhao, L., Li, M., & Guo, L. (2014). TiO_2/CdSe core–shell nanofiber film for photoelectrochemical hydrogen generation. *Nanoscale*, *6*(13), 7397-7404.

Lou, H. H., and Huang, Y. (1978). Electroplating. *Encyclopedia of Chemical Processing*, *1*, 839–848.

Luo, J., Ma, L., He, T., Ng, C. F., Wang, S., Sun, H., & Fan, H. J. (2012). TiO_2/(CdS, CdSe, CdSeS) nanorod heterostructures and photoelectrochemical properties. *The Journal of Physical Chemistry C*, *116*(22), 11956-11963.

Lv, J., Su, L., Wang, H., Liu, L., Xu, G., Wang, D., & Wu, Y. (2014). Enhanced visible light photocatalytic activity of TiO_2 nanotube arrays modified with CdSe nanoparticles by electrodeposition method. *Surface and Coatings Technology*, *242*, 20–28.

Macák, J. M., Tsuchiya, H., Ghicov, A., & Schmuki, P. (2005). Dye-sensitized anodic TiO_2 nanotubes. *Electrochemistry Communications*, *7*(11), 1133–1137.

Macak, J. M., Tsuchiya, H., Ghicov, A., Yasuda, K., Hahn, R., Bauer, S., & Schmuki, P. (2007). TiO_2 nanotubes: Self-organized electrochemical formation, properties and applications. *Current Opinion in Solid State and Materials Science*, *11*(1), 3–18.

Manna, L., Scher, E. C., & Alivisatos, A. P. (2000). Synthesis of soluble and processable rod-, arrow-, teardrop-, and tetrapod-shaped CdSe nanocrystals. *Journal of the American Chemical Society*, *122*(51), 12700-12706.

Mario Pagliaro, Giovanni Palmisano, & R. C. (2014). *Flexible Solar Cells*. *Igarss 2014*(1), 32-34.

Masuda, H., & Fukuda, K. (1995). Ordered metal nanohole arrays made by a two-step replication of honeycomb structures of anodic alumina. *Science*, *268*(5216), 1466-1468.

Materials, E., & Division, S. (2008). Electrical properties of sintered CdS x Se 1-x films. *Chalcogenide Letters 5*(9), 181–186.

Mills, A., & Le Hunte, S. (1997). An overview of semiconductor photocatalysis. *Journal of Photochemistry and Photobiology A: Chemistry*, *108*(1), 1–35.

Mishra, K. (2001). Electrodeposition & Characterization of SnS Thin Films. *Journal of The Electrochemical Society*, *70*(7), 255–268.

Mo, S. D., & Ching, W. Y. (1995). Electronic and optical properties of three phases of titanium dioxide: Rutile, anatase, and brookite. *Physical Review B*, *51*(19), 13023-13032.

Moellmann, J., Ehrlich, S., Tonner, R., & Grimme, S. (2012). A DFT-D study of structural and energetic properties of TiO_2 modifications. *Journal of physics: Condensed Matter*, *24*(42), 1-8.

Mor, G. K., Carvalho, M. A., Varghese, O. K., Pishko, M. V., & Grimes, C. A. (2004). A room-temperature TiO_2-nanotube hydrogen sensor able to self-clean photoactively from environmental contamination. *Journal of Materials Research*, *19*(2), 628–634.

Mor, G. K., Varghese, O. K., Paulose, M., Mukherjee, N., & Grimes, C. a. (2003). Fabrication of tapered, conical-shaped titania nanotubes. *Journal of Materials Research*, *18*(11), 2588–2593.

Mor, G. K., Varghese, O. K., Paulose, M., Shankar, K., & Grimes, C. a. (2006). A review on highly ordered, vertically oriented TiO_2 nanotube arrays: Fabrication, material properties, and solar energy applications. *Solar Energy Materials and Solar Cells*, *90*(14), 2011–2075.

Morrison, V. S. R. (1980). Electrochemistry at Semiconductor and Oxidized Metal Electrodes. New York .: Plenum Press, New York 1980.

Murakoshi, K., Kano, G., Wada, Y., Yanagida, S., Miyazaki, H., Matsumoto, M., & Murasawa, S. (1995). Importance of binding states between photosensitizing molecules and the TiO_2 surface for efficiency in a dye-sensitized solar cell. *Journal of Electroanalytical Chemistry*, *396*(1–2), 27–34.

Murali, K. R., & Venkatachalam, K. (2008). Electrical properties of sintered CdSxSe1-x films. *Chalcogenide Letters*, *5*(9), 181-186.

Muthukumarasamy, N., Jayakumar, S., Kannan, M. D., & Balasundaraprabhu, R. (2009). Structural phase change and optical band gap bowing in hot wall deposited CdSexTe1-x thin films. *Solar Energy*, *83*(4), 522–526.

Naji, I. S. (2014). Carrier transport mechanism of CdSe x S 1-x / Si heterojuction. *International Journal of Innovative Research in Science, Engineering and Technology*, *3*(1), 8503–8509.

Nakata, K., & Fujishima, A. (2012). TiO_2 photocatalysis: Design and applications. *Journal of Photochemistry and Photobiology C: Photochemistry Reviews*, *13*(3), 169–189.

Narayanan, R., Kwon, T. Y., & Kim, K. H. (2009). Anodic TiO_2 from stirred Na_2SO_4/NaF electrolytes: Effect of applied voltage and stirring. *Materials Letters*, *63*(23), 2003–2006.

Negishi, N., Takeuchi, K., & Ibusuki, T. (1997). The surface structure of titanium dioxide thin film photocatalyst. *Applied Surface Science*, *121*(122), 417–420.

Ni, M., Leung, M. K. H., Leung, D. Y. C., & Sumathy, K. (2007). A review and recent developments in photocatalytic water-splitting using TiO_2 for hydrogen production. *Renewable and Sustainable Energy Reviews*, *11*(3), 401–425.

Nielsch, B. K., Müller, F., & Li, A. (2000). Uniform Nickel Deposition into Ordered Alumina Pores by Pulsed Electrodeposition. *Advanced Materials*, *8*, 582–586.

Oomen, R. (2008). Characteristics of pulsed plated CdS. *Chalcogenide Letters*, *5*(8), 165–170.

Osterloh, F. E. (2013). Inorganic nanostructures for photoelectrochemical and photocatalytic water splitting. *Chemical Society Reviews*, *42*(6), 2294–320.

Park, J. H., Kim, S., & Bard, A. J. (2006). Novel carbon-doped TiO_2 nanotube arrays with high aspect ratios for efficient solar water splitting. *Nano Letters*, *6*(1), 24–28.

Pathinettam Padiyan, D., & Henry Raja, D. (2012). Synthesis of various generations titania nanotube arrays by electrochemical anodization for H_2 production. *Energy Procedia*, *22*, 88–100.

Pawar, S. M., Moholkar, A. V., & Bhosale, C. H. (2007). Influence of pH on electrochemically deposited CdSe thin films. *Materials Letters*, *61*(4–5), 1034–1038.

Peter,L., & Peter, L. (1990). Dynamic aspects of semiconductor photoelectrochemistr .*Chemical Reviews*, *90*(5), 753–769.

Pfaff, G., & Reynders, P. (1999). Angle-Dependent Optical Effects Deriving from Submicron Structures of Films and Pigments. *Chemical Reviews*, *99*(7), 1963–1981.

Pop, L. C., Sygellou, L., Dracopoulos, V., Andrikopoulos, K. S., Sfaelou, S., & Lianos, P. (2015). One-step electrodeposition of CdSe on nanoparticulate titania films and their use as sensitized photoanodes for photoelectrochemical hydrogen production. *Catalysis Today*, *252*, 157–161.

Rajesh, S. (2013). Thickness Dependent Microstructure, Optical and Photo Conducting Properties of Zno Thin Films Prepared By Spin Coating Process. *Journal of Oelectronic Devices*, *17*, 1417–1422.

Rajeshwar, K. (2007). Fundamentals of Semiconductors Electrochemistry and Photoelectrochemistry. *Encyclopedia of Electrochemistry*:

Robel, I., Subramanian, V., Kuno, M., & Kamat, P. V. (2006). Quantum Dot Solar Cells. Harvesting Light Energy with CdSe Nanocrystals Molecularly Linked to Mesoscopic TiO_2 Films. *Journal of the American Chemical Society*, *128*(7), 2385–2393.

Roy, P., Berger, S., & Schmuki, P. (2011). TiO_2 nanotubes: Synthesis and applications. *Angewandte Chemie - International Edition*, *50*(13), 2904–2939.

Roy, P., Kim, D., Lee, K., Spiecker, E., & Schmuki, P. (2010). TiO_2 nanotubes and their application in dye-sensitized solar cells. *Nanoscale*, *2*(1), 45–59.

Ruan, C., Paulose, M., Varghese, O. K., Mor, G. K., & Grimes, C. A. (2005). Fabrication of highly ordered TiO2 nanotube arrays using an organic electrolyte. *The Journal of Physical Chemistry. B*, *109*(33), 15754–15759.

Samsudin, N. A., Zainal, Z., Lim, H., & Chang, S. (2016). Titania Nanotubes Synthesised via the Electrochemical Anodisation Method : Synthesis and Supercapacitor Applications. *Pertanika Journal of Scholarly Research Reviews*, *2*, 107–128.

Schoch, K. F. (1998). The CRC Handbook of Solid State Electrochemistry (Book Review). *IEEE Electrical Insulation Magazine*, *14*(1), 49-49.

Schlesinger, T. E., Rajeshwar, K., & De Tacconi, N. R. (2010). *Electrodeposition of semiconductors* (p. 383À411). Springer: New York.

Seo, D., & Hoffmann, R. (1999). Direct and indirect band gap types in one-dimensional conjugated or stacked organic materials. *Theoretical Chemistry Accounts,* 102, 23–32.

Shankar, K., Basham, J. I., Allam, N. K., Varghese, O. K., Mor, G. K., Feng, X., & Grimes, C. A. (2009). Recent Advances in the Use of TiO_2 Nanotube and Nanowire Arrays for Oxidative photoelectrochemistry. *The Journal of Physical Chemistry C*, *113*(16), 6327–6359.

Shao, Z., Zhu, W., Li, Z., Yang, Q., & Wang, G. (2012). One-step fabrication of CdS nanoparticle-sensitized TiO_2 nanotube arrays via electrodeposition. *Journal of Physical Chemistry C*, *116*, 2438–2442.

Sharma, R. K., Singh, G., & Rastogi, A. C. (2004). Pulsed electrodeposition of CdTe thin films: Effect of pulse parameters over structure, stoichiometry and optical absorption. *Solar Energy Materials and Solar Cells*, *82*(1–2), 201–215.

Shen, C. M., Zhang, X. G., & Li, H. L. (2001). Effect of pH on the electrochemical deposition of cadmium selenide nanocrystal films. *Materials Science and Engineering: B*, *84*(3), 265-270.

Shen, C. M., Zhang, X. G., & Li, H. L. (2005). Influence of different deposition potentials on morphology and structure of CdSe films. *Applied Surface Science*, *240*(1), 34-41.

Shen, Q., Yamada, A., Tamura, S., & Toyoda, T. (2010). CdSe quantum dot-sensitized solar cell employing TiO_2 nanotube working-electrode and Cu_2S counter-electrode. *Applied Physics Letters*, *97*(12), 123107.

Shreekanthan, K. N., Rajendra, B. V., Kasturi, V. B., & Shivakumar, G. K. (2003). Growth and characterization of semiconducting cadmium selenide thin films. *Crystal Research and Technology*, *38*(1), 30–33.

Sun, Y., Wang, G., & Yan, K. (2011). TiO_2 nanotubes for hydrogen generation by photocatalytic water splitting in a two-compartment photoelectrochemical cell. *International Journal of Hydrogen Energy*, *36*(24), 15502–15508.

Swaminathan, V., Subramanian, V., & Murali, K. R. (2000). Characteristics of CdSe films electrodeposited with microprocessor based pulse plating unit. *Thin Solid Films*, 359(1), 113–117.

Syed Basheer Ahamed, M. G., Balu, A. R., Nagarethinam, V. S., Thayumanavan, A., Murali, K. R., Sanjeeviraja, C., & Jayachandran, M. (2010). Structural, optical, and electrical properties of electron beam evaporated CdSe thin films. *Crystal Research and Technology*, *45*(4), 387–392.

Taveira, L. V., Macák, J. M., Tsuchiya, H., Dick, L. F. P., & Schmuki, P. (2005). Initiation and Growth of Self-Organized TiO_2 Nanotubes Anodically Formed in $NH_4F/(NH_4)_2SO_4$ Electrolytes. *Journal of The Electrochemical Society*, *152*(10), B405-B410.

Tiwari, J. N., Tiwari, R. N., & Kim, K. S. (2012). Zero-dimensional, one-dimensional, two-dimensional and three-dimensional nanostructured materials for advanced electrochemical energy devices. *Progress in Materials Science*, *57*(4), 724–803.

Tsunetomo, K., Kawabuchi, A., Kitayama, H., Osaka, Y., & Nasu, H. (1990).Quantum size effect and HRTEM observation of CdSe microcrystallites doped into SiO_2-Glass films prepared by Rf-Sputtering. *Japanese Journal of Applied Physics*, *29*(11R), 2481-2486.

Tvrdy, K., & Kamat, P. V. (2009). Substrate driven photochemistry of CdSe quantum dot films: charge injection and irreversible transformations on oxide surfaces. *The Journal of Physical Chemistry A*, *113*(16), 3765-3772.

Van de Krol, R., & Grätzel, M. (2012). *Photoelectrochemical hydrogen production* (Vol. 90). New York: Springer

Van Noort, R. (1987). Titanium: The implant material of today. *Journal of Materials Science*, *22*(11), 3801–3811.

Vega, V., Cerdeira, M. A., Prida, V. M., Alberts, D., Bordel, N., Pereiro, R., & Vázquez, M. (2008). Electrolyte influence on the anodic synthesis of TiO_2 nanotube arrays. *Journal of Non-Crystalline Solids*, *354*(47), 5233-5235.

Velumani, S., Narayandass, S. K., Mangalaraj, D., Sebastian, P. J., & Mathew, X. (2004). Dielectric and conduction studies on hot-wall deposited CdSe films. *Solar Energy Materials and Solar Cells*, *81*(3), 323–338.

VijayaDurga, C., Srividya, A., Ajitha, A., & Umamaheswara, R. V. (2014). An overview on cyclic voltammetry and its application in pharmaceutical analysis. *International Journal of Chemical and Pharmaceutical Sciences 2014*, *5*(2), 13–19.

Villa, R. D., Trovó, A. G., & Nogueira, R. F. P. (2010). Soil remediation using a coupled process: soil washing with surfactant followed by photo-Fenton oxidation. *Journal of Hazardous Materials*, *174*(1), 770–775.

Walter, M. G., Warren, E. L., McKone, J. R., Boettcher, S. W., Mi, Q., Santori, E. A., & Lewis, N. S. (2010). Solar Water Splitting Cells. *Chemical Reviews (Washington, DC, United States)*, *110*(11), 6446–6473.

Wang, H., Wang, G., Ling, Y., Lepert, M., Wang, C., Zhang, J. Z., & Li, Y. (2012). Photoelectrochemical study of oxygen deficient TiO_2 nanowire arrays with CdS quantum dot sensitization. *Nanoscale*, *4*(5), 1463–1466.

Wang, P., Li, D., Chen, J., Zhang, X., Xian, J., Yang, X., & Shao, Y. (2014). A novel and green method to synthesize CdSe quantum dots-modified TiO_2 and its enhanced visible light photocatalytic activity. *Applied Catalysis B: Environmental*, 160(1), 217–226.

Wang, P., Zhang, Y., Su, L., Gao, W., Zhang, B., Chu, H., & Yu, W. W. (2015). Photoelectrochemical Properties of CdS / CdSe Sensitized TiO_2 Nanocable Arrays. *Electrochimica Acta*, *165*, 110–115.

Wang, W., Li, F., Zhang, D., Leung, D. Y. C., & Li, G. (2016). Applied Surface Science Photoelectrocatalytic hydrogen generation and simultaneous degradation of organic pollutant via CdSe / TiO_2 nanotube arrays. *Applied Surface Science*, *362*, 490–497.

Wei, D., & Amaratunga, G. (2007). Photoelectrochemical cell and its applications in optoelectronics. *International Journal of Electrochemical Science. Sci*, *2*(12), 897-912.

Wheeler, D. A., Ling, Y., Dillon, R. J., Fitzmorris, R. C., Dudzik, C. G., Zavodivker, L., & Zhang, J. Z. (2013). Probing the nature of bandgap states in hydrogen-treated TiO_2 nanowires. *Journal of Physical Chemistry C*, *117*(50), 26821–26830.

Williams, G., Seger, B., & Kamat, P. V. (2008). TiO_2-Graphene Nanocomposites. UV-Assisted Photocatalytic Reduction of Graphene Oxide. *ACS Nano*, *2*(7), 1487–1491.

Xiao, F.-X., Miao, J., Wang, H.-Y., Yang, H., Chen, J., & Liu, B. (2014). Electrochemical construction of hierarchically ordered CdSe-sensitized TiO_2 nanotube arrays: towards versatile photoelectrochemical water splitting and photoredox applications. *Nanoscale*, *6*, 6727–6737.

Xie, R. C., & Shang, J. K. (2007). Morphological control in solvothermal synthesis of titanium oxide. *Journal of Materials Science*, *42*(16), 6583-6589.

Xu, D., Shi, X., Guo, G., Gui, L., & Tang, Y. (2000). Electrochemical Preparation of CdSe Nanowire Arrays. *The Journal of Physical Chemistry B*, *104*, 5061–5063.

Xu, Z., & Yu, J. (2010). A novel solid-state electrochemiluminescence sensor based on $Ru(bpy)_3^{2+}$ immobilization on TiO_2 nanotube arrays and its application for detection of amines in water. *Nanotechnology*, *21*(24), 245501.

Xue, J., Shen, Q., Liang, W., Liu, X., & Yang, F. (2013). Photosensitization of TiO_2 nanotube arrays with CdSe nanoparticles and their photoelectrochemical performance under visible light. *Electrochimica Acta*, *97*, 10–16.

Xue, J., Shen, Q., Yang, F., Liang, W., & Liu, X. (2014). Investigation on the influence of pH on structure and photoelectrochemical properties of CdSe electrolytically deposited into TiO_2 nanotube arrays. *Journal of Alloys and Compounds*, *607*, 163–168.

Yan, J., & Zhou, F. (2011). TiO_2 nanotubes: Structure optimization for solar cells. *Journal of Materials Chemistry*, *21*(26), 9406-9418.

Yang, D. J., Kim, H. G., Cho, S. J., & Choi, W. Y. (2008). Thickness-conversion ratio from titanium to TiO_2 nanotube fabricated by anodization method. *Materials Letters*, *62*(4), 775–779.

Yang, F., Liang, W., & Xue, J. B. (2013). Preparation of CdSe-TiO_2 Nanotube Array Films and their Photoelectric Properties under Visible Light. In *Materials Science Forum*, *743*, 932-936.

Yang, H., Fan, W., Vaneski, A., Susha, A. S., Teoh, W. Y., & Rogach, A. L. (2012). Heterojunction engineering of CdTe and CdSe quantum dots on TiO_2 nanotube arrays: Intricate effects of size-dependency and interfacial contact on photoconversion efficiencies. *Advanced Functional Materials*, *22*(13), 2821–2829.

Yin, H., Liu, H., & Shen, W. Z. (2009). The large diameter and fast growth of self-organized TiO_2 nanotube arrays achieved via electrochemical anodization. *Nanotechnology*, *21*(3), 035601.

Ying, C. L., Zulkarnain, Z., Hussein, M. Z., & Tan, W. T. (2011). Effect of Electrolyte Composition in Electrochemical Synthesis of Self-Organized TiO_2 Nanotubes. *Advanced Materials Research*, *364*, 298–302.

Yoshikawa, K., Kawasaki, H., Yoshida, W., Irie, T., Konishi, K., Nakano, K., & Yamamoto, K. (2017). Silicon heterojunction solar cell with interdigitated back contacts for a photoconversion efficiency over 26%. *Nature Energy*, *2*, 1-8.

You-Wen, Y., Tian-Ying, L., Wen-Bin, Z., Dong-Ming, M., & Dong, C. (2013). Fabrication and Characterization of Single-Crystalline $AgSbTe_2$ Nanowire Arrays. *Chinese Physics Letters*, *30*(10), 12394-12398.

Yu, J., Fan, J., & Lv, K. (2010). Anatase TiO_2 nanosheets with exposed (001) facets: improved photoelectric conversion efficiency in dye-sensitized solar cells. *Nanoscale*, 2(10), 2144–2149.

Yu, W., Yuan, S., Li, Y., Zhang, Q., & Wang, H. (2011). Preparation of TiO_2 Nanoparticle/Nanotube Composites via a Vapor Hydrolysis Method and Their Photocatalytic Activities. *ISRN Nanotechnology*, *201*, 1–7.

Zainal, Z., Hussein, M. Z., Kassim, A., & Ghazali, A. (1997). Electrodeposited SnS thin films from aqueous solution. *Journal of Materials Science Letters*, *16*(17), 1446-1449.

Zayat, M., Garcia-Parejo, P., & Levy, D. (2007). Preventing UV-light damage of light sensitive materials using a highly protective UV-absorbing coating. *Chemical Society Reviews*, *36*(8), 1270–1281.

Zhuang, H. F., Lin, C. J., Lai, Y. K., Sun, L., & Li, J. (2007). Some critical structure factors of titanium oxide nanotube array in its photocatalytic activity. *Environmental Science & Technology*, *41*(13), 4735-4740.

Zhang, M., Bando, Y., & Wada, K. (2001). Sol-gel template preparation of TiO_2 nanotubes and nanorods. *Journal of Materials Science Letters*, *20*(2), 167-170.

Zhang, M., Xu, Y., Lv, J., Yang, L., Jiang, X., He, G., & Sun, Z. (2014). Capability of coupled CdSe/TiO_2 heterogeneous structure for photocatalytic degradation and photoconductivity. *Nanoscale Research Letters*, *9*(1), 1-7.

Zhang, Y., Fu, W., Yang, H., Qi, Q., Zeng, Y., Zhang, T., & Zou, G. (2008). Synthesis and characterization of TiO_2 nanotubes for humidity sensing. *Applied Surface Science*, *254*(17), 5545–5547.

Zhao, J., Wang, X., Chen, R., & Li, L. (2005). Fabrication of titanium oxide nanotube arrays by anodic oxidation. *Solid State Communications*, *134*(10), 705–710.

Zhu, K., Vinzant, T. B., Neale, N. R., & Frank, A. J. (2007). Removing structural disorder from oriented TiO_2 nanotube arrays: Reducing the dimensionality of transport and recombination in dye-sensitized solar cells. *Nano Letters*, *7*(12), 3739–3746.

Zhu, Y., Li, H., & Koltypin, Y. (2001). Sonochemical synthesis of titania whiskers and nanotubes. *Chemical Communications*, *2001*(c), 2616–2617.