



UNIVERSITI PUTRA MALAYSIA

***ELECTROCHEMICAL PREPARATION AND CHARACTERISATION OF
ZINC OXIDE AND POLY(3,4-ETHYLENEDIOXYTHIOPHENE)/ZINC OXIDE
THIN FILMS***

ABDUL HADI BIN ISMAIL

FS 2016 31



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THIN FILMS**

By

ABDUL HADI BIN ISMAIL

**Thesis submitted to the School of Graduate Studies, Universiti Putra Malaysia, in
fulfilment of the Requirement for the Degree of Master of Science**

March 2016



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DEDICATION

Dedicated to my parents, family, supervisory committees and friends for love, support, motivation, inspiration and encouragements



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Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfillment of the requirements for the degree of Master of Science

ELECTROCHEMICAL PREPARATION AND CHARACTERISATION OF ZINC OXIDE AND POLY(3,4-ETHYLENEDIOXYTHIOPHENE)/ZINC OXIDE THIN FILMS

By

ABDUL HADI ISMAIL

March 2016

Chairman : Yusran Sulaiman, PhD
Faculty : Science

The physical, chemical and electrochemical properties of zinc oxide (ZnO) and poly(3,4-ethylenedioxythiophene)/zinc oxide (PEDOT/ZnO) film electrode that were prepared electrochemically were studied. ZnO was electrodeposited on ITO glass substrate by applying five different electrodeposition potentials (-1.0 V, -1.3 V, -1.5 V, -1.7 V and -2.0 V), three different concentrations of the precursor solution (70 mM, 80 mM and 90 mM) and bath temperature (70 °C, 80 °C and 90 °C). The specific capacitance of the ZnO samples were observed to increase when the applied electrodeposition potential is increased from -1.3 V to -1.5 V. However, the specific capacitance is found to decrease when the applied electrodeposition potential is further increased to -1.7 V. PEDOT was potentiostatically deposited on the optimised hexagonal flake-like ZnO-covered ITO glass substrate by applying three different potentials (1.0 V, 1.25 V and 1.5 V) where under these circumstances, the effect of varying electropolymerisation potentials were studied. The optical band gap of each of the PEDOT/ZnO composites prepared were noticed to be within the range of 3.40 eV to 3.45 eV which were in between the optical band gap values of sole PEDOT and ZnO. The presence of both materials was asserted from XRD, FTIR and Raman spectroscopy analysis where all of the corresponding peaks for each of the materials in the spectra were assigned. SEM revealed the flake-like hexagonal morphology of ZnO which is in agreement with the XRD analysis. While the PEDOT morphology was discerned with round-shaped granular morphology where the average grain size decreased with the electropolymerisation potentials. The resistance of charge transfer of PEDOT/ZnO thin film is directly proportional to the electropolymerisation potential while on the specific capacitance was inversely proportional. The composite exhibit both PEDOT and ZnO unique properties that can be used as a multi-functional material in various potential applications.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk Ijazah Sarjana Sains

PENYEDIAAN SECARA ELEKTROKIMIA DAN PENCIRIAN FILEM ZINK OKSIDA DAN POLI(3,4-ETILENADIOKSITIOFINA)/ZINK OKSIDA

Oleh

ABDUL HADI ISMAIL

Mac 2016

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Sifat-sifat fizikal, kimia dan elektrokimia zink oksida (ZnO) dan poli(3,4-etilenadioksitiofina)/zink oksida (PEDOT/ZnO) filem elektrod yang disediakan secara elektrokimia telah dikaji. ZnO dielektroenap ke atas substrat kaca ITO dengan menggunakan lima keupayaan elektroenapan (-1.0 V, -1.3 V, -1.5V, -1.7 V dan -2.0 V), perubahan kepekatan bahan pemula (70 mM, 80 mM and 90 mM) dan suhu elektrolit yang berbeza (70 °C, 80 °C and 90 °C). Kapasiti spesifik sampel-sampel ZnO didapati meningkat dengan peningkatan keupayaan electroenapan dari -1.3 V sehingga -1.5 V. Namun demikian, nilai kapasiti spesifik didapati menurun dengan peningkatan keupayaan electroenapan kepada -1.7 V. PEDOT telah disediakan secara potentiostatik ke atas ZnO optimum yang menutupi permukaan substrat kaca ITO dengan menggunakan tiga keupayaan yang berbeza (1.0 V, 1.25 V dan 1.5 V) di mana dengan keadaan ini, kesan perubahan nilai keupayaan elektropemolimeran telah dikaji. Nilai jurang optik untuk setiap komposit PEDOT/ZnO didapati mempunyai nilai jurang optik dalam lingkungan 3.40 eV hingga 3.45 eV. Nilai-nilai ini berada di dalam lingkungan nilai jurang optik PEDOT dan ZnO tunggal. Kehadiran PEDOT dan ZnO telah disahkan daripada analisis pembelauan tenaga sinaran-X (XRD), spektroskopi Fourier infra merah (FTIR) dan spektroskopi Raman di mana setiap puncak yang bersesuaian dengan setiap bahan-bahan tersebut telah ditentukan. Daripada analisis mikroskopi imbasan elektron (SEM), morfologi kepingan heksagon ZnO telah diketahui dan ia adalah bersamaan dengan analisis XRD yang telah dilakukan. Morfologi PEDOT menunjukkan bentuk butiran bulat dengan purata saiz butiran didapati berkurang dengan pengurangan keupayaan elektropemolimeran. Rintangan pemindahan cas PEDOT/ZnO adalah berkadar terus dengan keupayaan elektropemolimeran. Didapati ia berkadar songsang dengan nilai kapasiti spesifik. Komposit yang telah disediakan mempunyai ciri unik kedua-dua bahan PEDOT dan ZnO yang boleh digunakan sebagai bahan pelbagai fungsi di dalam pelbagai aplikasi yang berpotensi.

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I certify that a Thesis Examinations Committee has met on March 29, 2016 to conduct the final examination of Abdul Hadi Bin Ismail on his thesis entitled “Electrochemical Preparation and Characterisation Of Zinc Oxide And Poly(3,4-Ethylenedioxythiophene)/Zinc Oxide Thin Films” in accordance with the Universities and University Colleges Act 1971 and the Constitution of the Universiti Putra Malaysia [P.U.(A) 106] 15 March 1988. The committee recommends that the student be awarded the Master of Science.

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TABLE OF CONTENTS

	Page
ABSTRACT	i
ABSTRAK	ii
ACKNOWLEDGEMENTS	iii
APPROVAL	iv
DECLARATION	vi
LIST OF ABBREVIATIONS	x
LIST OF SYMBOLS	xii
LIST OF FIGURES	xiii
LIST OF TABLES	xviii
CHAPTER	
1	INTRODUCTION
	1.1 Background of study 1
	1.2 Problem statement 2
	1.3 Objectives of Research 2
	1.4 Significance of study 3
2	LITERATURE REVIEW
	2.1 Theory of semiconductor 4
	2.1.1 Zinc oxide 6
	2.1.2 Properties and applications of Zinc oxide 6
	2.1.3 Synthesis methods of ZnO thin film 7
	2.1.3.1 Electrochemical deposition technique 7
	2.1.3.2 Metal–Organic Chemical Vapor Deposition technique 10
	2.1.3.3 Molecular Beam Epitaxy 11
	2.2 Conducting polymers 12
	2.2.1 Properties of Conducting polymers 13
	2.2.1.1 Electrical-conducting properties 13
	2.2.1.2 Optical properties 13
	2.2.1.3 Wettability 14
	2.2.2 Poly(3,4-ethylenedioxythiophene) (PEDOT) 14
	2.3 Fundamentals of fabrication of organic/inorganic thin film composites 15
	2.4 Synthesis of PEDOT/ZnO thin film composites 16
	2.5 Applications of PEDOT/ZnO thin film composites 18
3	METHODOLOGY
	3.1 Chemicals and reagents 19
	3.2 Electrochemical deposition of ZnO thin film 19
	3.3 Electrochemical deposition of PEDOT/ZnO thin film composite 19
	3.4 Characterisations of ZnO and PEDOT/ZnO thin film composite 20
	3.4.1 X–Ray Diffraction analysis 20
	3.4.2 Scanning electron microscopy 20

3.4.3	Raman spectroscopy	20
3.4.4	Cyclic voltammetry and electrochemical impedance spectroscopy	20
3.4.5	Fourier transform infrared	21
3.4.6	Ultraviolet/Visible (UV/Vis)	21
4	RESULTS AND DISCUSSION	
4.1	Electrochemical deposition of ZnO	22
4.1.1	XRD analysis of ZnO	24
4.1.1.1	Effect of varying electrodeposition potentials	24
4.1.1.2	Effect of varying precursor concentration	32
4.1.1.3	Effect of varying bath temperature	38
4.1.2	Scanning electron microscopy analysis of ZnO	43
4.1.2.1	Effect of varying electrodeposition potentials	43
4.1.2.2	Effect of varying precursor concentration	49
4.1.2.3	Effect of varying bath temperature	51
4.1.3	Cyclic voltammetry of ZnO films	53
4.1.4	Electrochemical impedance spectroscopy of ZnO	55
4.2	Electrochemical deposition of PEDOT/ZnO films	58
4.2.1	XRD analysis of PEDOT/ZnO films	60
4.2.2	SEM analysis of PEDOT/ZnO films	61
4.2.3	Fourier transform infrared of PEDOT/ZnO films	62
4.2.4	Raman Spectroscopy of PEDOT/ZnO films	63
4.2.5	UV-vis analysis of PEDOT/ZnO films	65
4.2.6	Cyclic voltammetry and EIS analysis of PEDOT/ZnO films	67
5	CONCLUSIONS AND RECOMMENDATIONS	72
	REFERENCES	74
	BIODATA OF STUDENT	88
	PUBLICATIONS	89

LIST OF ABBREVIATIONS

Ag/AgCl	Silver/Silver chloride
C_f	Final current
C_i	Initial current
C_{int}	Intermediate current
CNT	Carbon nanotube
CNT/PANI	Carbon nanotube/Polyaniline
CPs	Conducting polymers
Cu K_α	Copper K-alpha emission line
CV	Cyclic voltammetry
ECD	Electrochemical deposition technique
EDOT	3,4-ethylenedioxythiophene
EIS	Electrochemical impedance spectroscopy
FTIR	Fourier transform infrared
FWHM	Full width half maximum
GaN/Sapphire	Gallium nitride on sapphire
ICPs	Intrinsically conducting polymers
IO	Inorganic-organic
ITO	Indium tin oxide
JCPDS	Joint Committee on Powder Diffraction Standards
MBE	Molecular beam epitaxy
MOCVD	Metal–Organic chemical vapor deposition
<i>n</i> -ZnO/ <i>p</i> -PEDOT	<i>n</i> -doped Zinc oxide on <i>p</i> -doped Poly(3,4-ethylenedioxythiophene)

OCP	Open circuit potential
OI	Organic-inorganic
P(TTPP)	Poly(2,5-di(thiophen-2-yl)-1-(4-(thiophen-3-yl)phenyl)-1-H-pyrrole)
PANI	Polyaniline
PEDOT	Poly(3,4-ethylenedioxythiophene)
PEDOT/ZnO	Poly(3,4-ethylenedioxythiophene) on Zinc oxide
PEDOT:PSS	Poly(3,4-ethylenedioxythiophene) doped Poly(styrene sulfonate)
<i>p</i> -Si/ <i>n</i> -ZnO	<i>p</i> -doped Silicon on <i>n</i> -doped Zinc oxide
RF-sputtering	Radio frequency-sputtering
SCE	Saturated calomel electrode
SEM	Scanning electron microscopy
TC(<i>hkl</i>)	Texture coefficient
UATR	Attenuated total reflectance
UV light	Ultraviolet light
UV-vis	Ultraviolet-visible
XRD	X-ray diffraction
ZnO/PEDOT:PSS	Zinc oxide/ Poly(3,4-ethylenedioxythiophene) doped Poly(styrene sulfonate)
λ_{\max}	Maximum wavelength
CPE	Constant phase element
PZ 1V	PEDOT/ZnO electropolymerised at 1 V
PZ 1.25V	PEDOT/ZnO electropolymerised at 1.25 V
PZ 1.5V	PEDOT/ZnO electropolymerised at 1.5 V
ZnO [<i>x</i> mM, <i>y</i> °C, <i>z</i> V]	ZnO sample prepared from <i>x</i> mM of precursor solution, <i>y</i> °C of bath temperature, <i>z</i> V of electrodeposition potential

LIST OF SYMBOLS

θ	Theta	$^{\circ}$
R_s	Resistance of solution	Ω
C_{dl}	Double layer capacitance	F
R_{ct}	Resistance of charge transfer	Ω



LIST OF FIGURES

Figure		Page
2.1	Differences of the energy band gap of (a) Insulators, (b) Semiconductors and (c) Conductors and the position of the Fermi level (E_f) of each type of the material	5
2.2	The position of the Fermi level (E_f) for an (a) <i>n</i> -type and a (b) <i>p</i> -type semiconductors	5
2.3	General schematic diagram of ECD technique	9
2.4	Illustration of the growth of ZnO plates vertical to the ITO glass substrate during the electrochemical process	9
2.5	Schematic visualisation of the experimental set-ups for the growth of ZnO nanowires by MOCVD technique	11
2.6	Functional schematic of a basic MBE system	12
2.7	Backbone structure of PEDOT	14
4.1	Typical cyclic voltammetry scan obtained for the deposition of ZnO on bare ITO glass substrate by using scan rate = 0.1 Vs ⁻¹ at three different concentrations and bath temperature	22
4.2	Typical chronoamperometric curve related to the growth of ZnO on ITO glass substrate	23
4.3	XRD spectra of ZnO electrodeposited at fixed electrodeposition potential (-1.0 V) at different concentration of precursor solutions and different cell temperatures. Peaks labelled with “♦”, “♣” and “∇” correspond to the peaks of ITO glass substrate, Zn(OH) ₂ and metallic Zn, respectively	25
4.4	XRD spectra of ZnO electrodeposited at fixed precursor concentration of 70 mM Zn(NO ₃) ₂ .xH ₂ O in 0.1 M KCl and at (A) 70 °C, (B) 80 °C, (C) 90 °C of bath temperature for (a) -2.0 V, (b) -1.7 V, (c) -1.5 V and (d) -1.3 V of electrodeposition potentials. Peaks labelled with “♦”, “♣” and “♠” correspond to the peaks of ITO glass substrate, Zn(OH) ₂ and ZnO, respectively.	27

- 4.5 XRD spectra of ZnO electrodeposited at fixed precursor concentration of 80 mM $\text{Zn}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$ in 0.1 M KCl and at (A) 70 °C, (B) 80 °C, (C) 90 °C of bath temperature for (a) -2.0 V, (b) -1.7 V, (c) -1.5 V and (d) -1.3 V of electrodeposition potentials. Peaks labelled with “♦”, “♣” and “♠” correspond to the peaks of ITO glass substrate, $\text{Zn}(\text{OH})_2$ and ZnO, respectively. 28
- 4.6 XRD spectra of ZnO electrodeposited at fixed precursor concentration of 90 mM $\text{Zn}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$ in 0.1 M KCl and at (A) 70 °C, (B) 80 °C, (C) 90 °C of bath temperature for (a) -2.0 V, (b) -1.7 V, (c) -1.5 V and (d) -1.3 V of electrodeposition potentials. Peaks labelled with “♦”, “♣” and “♠” correspond to the peaks of ITO glass substrate, $\text{Zn}(\text{OH})_2$ and ZnO, respectively. 29
- 4.7 XRD spectra of ZnO electrodeposited at fixed electrodeposition potential of -1.3 V vs Ag/AgCl and at (A) 70 °C, (B) 80 °C, (C) 90 °C of bath temperature for varied precursor concentration of (a) 90 mM, (b) 80 mM and (c) 70 mM of $\text{Zn}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$ in 0.1 M KCl. Peaks labelled with “♦”, “♣” and “♠” correspond to the peaks of ITO glass substrate, $\text{Zn}(\text{OH})_2/\text{Zn}_5(\text{OH})_8\text{Cl}_2$ and ZnO, respectively. 33
- 4.8 XRD spectra of ZnO electrodeposited at fixed electrodeposition potential of -1.5 V vs Ag/AgCl and at (A) 70 °C, (B) 80 °C, (C) 90 °C of bath temperature for varied precursor concentration of (a) 90 mM, (b) 80 mM and (c) 70 mM of $\text{Zn}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$ in 0.1 M KCl. Peaks labelled with “♦”, “♣” and “♠” correspond to the peaks of ITO glass substrate, $\text{Zn}(\text{OH})_2/(\text{Zn}_5(\text{OH})_8\text{Cl}_2)$ and ZnO, respectively. 34
- 4.9 XRD spectra of ZnO electrodeposited at fixed electrodeposition potential of -1.7 V vs Ag/AgCl and at (A) 70 °C, (B) 80 °C, (C) 90 °C of bath temperature for varied precursor concentration of (a) 90 mM, (b) 80 mM and (c) 70 mM of $\text{Zn}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$ in 0.1 M KCl. Peaks labelled with “♦”, “♣” and “♠” correspond to the peaks of ITO glass substrate, $\text{Zn}(\text{OH})_2/(\text{Zn}_5(\text{OH})_8\text{Cl}_2)$ and ZnO, respectively. 35
- 4.10 XRD spectra of ZnO electrodeposited at fixed electrodeposition potential of -2.0 V vs Ag/AgCl and at (A) 70 °C, (B) 80 °C, (C) 90 °C of bath temperature for varied precursor concentration of (a) 90 mM, (b) 80 mM and (c) 70 mM of $\text{Zn}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$ in 0.1 M KCl. Peaks labelled with “♦”, “♣” and “♠” correspond to the peaks of ITO glass substrate, $\text{Zn}(\text{OH})_2/(\text{Zn}_5(\text{OH})_8\text{Cl}_2)$ and ZnO, respectively. 37

- 4.11 XRD spectra of ZnO electrodeposited at fixed electrodeposition potential of -1.3 V vs Ag/AgCl and at (A) 70 mM, (B) 80 mM, (C) 90 mM of precursor concentration of $\text{Zn}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$ in 0.1 M KCl for varied bath temperature of (a) 90 °C, (b) 80 °C and (c) 70 °C. Peaks labelled with “♦”, “♣” and “♠” correspond to the peaks of ITO glass substrate, $\text{Zn}(\text{OH})_2$, $(\text{Zn}_5(\text{OH})_8\text{Cl}_2)$ and ZnO, respectively. 39
- 4.12 XRD spectra of ZnO electrodeposited at fixed electrodeposition potential of -1.5 V vs Ag/AgCl and at (A) 70 mM, (B) 80 mM, (C) 90 mM of precursor concentration of $\text{Zn}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$ in 0.1 M KCl for varied bath temperature of (a) 90 °C, (b) 80 °C and (c) 70 °C. Peaks labelled with “♦”, “♣” and “♠” correspond to the peaks of ITO glass substrate, $\text{Zn}(\text{OH})_2/(\text{Zn}_5(\text{OH})_8\text{Cl}_2)$ and ZnO, respectively. 40
- 4.13 XRD spectra of ZnO electrodeposited at fixed electrodeposition potential of -1.7 V vs Ag/AgCl and at (A) 70 mM, (B) 80 mM, (C) 90 mM of precursor concentration of $\text{Zn}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$ in 0.1 M KCl for varied bath temperature of (a) 90 °C, (b) 80 °C and (c) 70 °C. Peaks labelled with “♦”, “♣” and “♠” correspond to the peaks of ITO glass substrate, $\text{Zn}(\text{OH})_2/(\text{Zn}_5(\text{OH})_8\text{Cl}_2)$ and ZnO, respectively. 41
- 4.14 XRD spectra of ZnO electrodeposited at fixed electrodeposition potential of -2.0 V vs Ag/AgCl and at (A) 70 mM, (B) 80 mM, (C) 90 mM of precursor concentration of $\text{Zn}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$ in 0.1 M KCl for varied bath temperature of (a) 90 °C, (b) 80 °C and (c) 70 °C. Peaks labelled with “♦”, “♣” and “♠” correspond to the peaks of ITO glass substrate, $\text{Zn}(\text{OH})_2/(\text{Zn}_5(\text{OH})_8\text{Cl}_2)$ and ZnO, respectively. 42
- 4.15 SEM images of ZnO samples taken at X3,000 magnification at fixed cell temperature of 70°C at varied electrodeposition potential of (a)–(c) -1.3 V, (d)–(f) -1.5 V and (g)–(i) -1.7 V and at varied precursor concentrations of (a), (d), (g) 70 mM, (b), (e), (h) 80 mM and (c), (f), (i) 90 mM of $\text{Zn}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$ mixed with 0.1 M KCl 45
- 4.16 SEM images of ZnO samples taken at X3,000 magnification at fixed cell temperature of 80°C at varied electrodeposition potential of (a)–(c) -1.3 V, (d)–(f) -1.5 V and (g)–(i) -1.7 V and at varied precursor concentrations of (a), (d), (g) 70 mM, (b), (e), (h) 80 mM and (c), (f), (i) 90 mM of $\text{Zn}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$ mixed with 0.1 M KCl 46

4.17	SEM images of ZnO samples taken at X3,000 magnification at fixed cell temperature of 90°C at varied electrodeposition potential of (a)–(c) -1.3 V, (d)–(f) -1.5 V and (g)–(i) -1.7 V and at varied precursor concentrations of (a), (d), (g) 70 mM, (b), (e), (h) 80 mM and (c), (f), (i) 90 mM of Zn(NO ₃) ₂ .xH ₂ O mixed with 0.1 M KCl	48
4.18 (A)-(D)	CV for selected ZnO samples in the potential range of -0.5 and 0.5 V with the scan rate of 0.1 Vs ⁻¹ in 0.1 M KCl aqueous solution	54
4.19	Nyquist plots for ZnO. Full lines indicate the fitting of the equivalent circuits.	56
4.20	Equivalent circuit used to fit the experimental Nyquist plots for the selected ZnO samples. CPE, <i>R_{ct}</i> and <i>R_s</i> stand for constant phase element, resistance of charge transfer and resistance of solution, respectively.	57
4.21	Cyclic voltammogram of 0.01 M EDOT and 0.1 M LiClO ₄ on the prepared ZnO within the scan range of -0.5V to 2.0V	59
4.22	The oxidative polymerisation mechanism of PEDOT	59
4.23	XRD spectra for sample (a) ZnO [80 mM, 80°C, -1.5 V] (b) PZ 1V (c) PZ 1.25V (d) PZ 1.5V and (e) P which represents the sample of PEDOT on bare ITO glass substrate	60
4.24	SEM images for sample ZnO [80 mM, 80°C, -1.5 V], P 1V, P 1.25V, P 1.5V, PZ 1V, PZ 1.25V and PZ 1.5V each taken at X5000 magnification. Smaller images for sample Z, PZ 1V, PZ 1.25V and PZ 1.5V were taken at X3000 magnification	62
4.25	FTIR spectra of (a) ZnO [80 mM, 80°C, -1.5 V], (b) PEDOT and (c) PEDOT/ZnO thin film prepared on ITO glass substrate.	63
4.26	Raman spectra of (a) PZ, (b) P and (c) ZnO [80 mM, 80°C, -1.5 V] thin film prepared on ITO glass substrate.	64
4.27	UV-vis spectra for (a) ZnO [80 mM, 80°C, -1.5 V], PZ 1V, PZ 1.25V and PZ 1.5V and (b) sample P 1.0 V, P 1.25 V and P 1.5 V	66
4.28	CV for (a) ZnO [80 mM, 80°C, -1.5 V], PZ 1V, PZ 1.25V and PZ 1.5V and (b) P 1 V, P 1.25 V and P 1.5 V in the potential range of -0.5 to 0.5 V with the scan rate of 0.1 Vs ⁻¹ in 0.1 M KCl aqueous solution	68

4.29	Nyquist plots for (a) ZnO [80 mM, 80°C, -1.5 V], PZ 1V, PZ 1.25V and PZ 1.5V and (b) P 1V, P 1.25V and P 1.5V Full lines indicate the fitting of the equivalent circuits.	70
4.30	Equivalent circuit used to fit the experimental Nyquist plots for (a) PZ 1V, PZ 1.25V and PZ 1.5 V and (b) P 1V, P 1.25V and P 1.5V	71



LIST OF TABLES

Table		Page
4.1	Charge values of selected ZnO samples obtained from the chronoamperometric curves	24
4.2	The average crystallite size of each selected samples of varied parameters with standard deviation calculated for each average values.	31
4.3	Areal capacitance and evaluated data from the fitted equivalent circuit for the selected ZnO samples	58
4.4	Raman peaks for sample PZ 1V, PZ 1.25V and PZ 1.5V	64
4.5	Band gap energies, specific areal capacitance and evaluated data from the fitted equivalent circuit for sample ZnO, P 1 V, P 1.25 V, P 1.5 V, PZ 1V, PZ 1.25V and PZ 1.5V	67

CHAPTER 1

INTRODUCTION

1.1 Background of study

Extensive effort has been made recently to develop new electrode materials for various types of applications. Efforts on study of hybrid organic-inorganic materials have been continuously made recently resulting from its capability to provide positive and highly beneficial outcomes (Gómez-Romero, 2001). New inventions have been explored from time to time commenced from the stage of maturity of this research discipline. In particular, this field has focused on the formulation of functionality in the hybrid/composite materials while on the contrary, ameliorated control and comprehension of the processing, chemistry and the microstructure of the materials system has divulged advanced prospects in dealing with a more complex materials (Gómez-Romero and Sanchez, 2005). Integration of organic and inorganic materials is broadening the scope in seeking for new materials where the combinations were ranged from non-complex mixtures of bulk materials to merge the properties of individual organic and inorganic constituents (Yoshida *et al.*, 2009).

The pioneered work on the discovery of conducting polymer in 1977 by Shirakawa, MacDiarmid and Heeger has initiated a new era of technologically important conducting polymers which has led to a lot of works on its applications (Shirakawa *et al.*, 1977). Poly(3,4-ethylenedioxythiophene) (PEDOT) is among the one of intriguing conducting polymers which consist of organic elements that has unique electrochemical, electrical and optical characteristics. Currently, PEDOT plays a dominant role in electric, electronic and antistatic applications (Kateb *et al.*, 2013, Kirchmeyer and Reuter, 2005).

On the other hand, in the past decades, semiconductor nanostructures have engaged substantial attentions due to its captivating electronic and optical properties (Tong *et al.*, 2015, Wang and Herron, 1991). Amidst the semiconductor materials, zinc oxide (ZnO) is a direct wide band gap semiconductor with a large exciton binding energy of 60 meV is a material of exceptional electrical properties that possess a wide range of applications (Tong *et al.*, 2015, Wadowska *et al.*, 2013). The synergistic effects between different materials in a hybrid or composite system are hypothetically complex, but will offer massive potential for energy applications. Opportunities in scrutinising novel combinations of these materials, control and fundamental electrochemical properties of these complex systems are wide open for further inventions and improvements (Gómez-Romero *et al.*, 2010, Rodriguez-Moreno *et al.*, 2014).

1.2 Problem statement

A combination of organic-inorganic materials constitutes different interface which consequently resulting in prominent advantages and restrictions. The ultimate obstacle in combining these two distinct materials is to keep or elevate the foremost characteristics of individual species while annihilating their notable limitations (Gómez-Romero, 2001). The growing interest on the importance of fabrication of conducting polymer-inorganic composite materials is currently overwhelming. The properties of the conducting polymer (organic component) or the inorganic component can be adjusted from the synergism between the properties of the individual components in the composite (Chen *et al.*, 2013). ZnO as a type of semiconductor oxides with a wide band gap ranging from less than 3.1 eV to 3.55 eV (Marotti *et al.*, 2004, Pauporté and Lincot, 2000) with and a large exciton binding energy of 60 meV (Singh *et al.*, 2013, Skompska and Zarebska, 2014, Wadowska *et al.*, 2013, Wei *et al.*, 2013) at room temperature (Chettah and Abdi, 2013, Çoban *et al.*, 2013) has been subjected to a renewed interest for numerous applications related to its excellent electrical and optical characteristics (Chettah and Abdi, 2013). Pertaining to the organic materials, poly(3,4-ethylenedioxythiophene) (PEDOT) is currently the most eminent type of conducting polymer due to its high stability, moderate band gap (Wang and Wong, 2006) and low redox potential (Selvaganesh *et al.*, 2007) has great potential in organic electronics field (Döbbelin *et al.*, 2009). The combination of PEDOT and ZnO is therefore offers an interesting option to fabricate p-n junctions composite (Döbbelin *et al.*, 2009). The performance of the composite material is closely imparted to its properties, which is exceedingly affected by corresponding fabrication parameters (Chen *et al.*, 2013). Thus, the optimisation of a set of various electrochemical deposition parameters upon the fabrication of PEDOT/ZnO thin film composite is principally important upon the detailed study on its morphological, physical, chemical and electrochemical properties with regard to its potential applications for supercapacitors and solar cells.

1.3 Objectives of Research

The following are the objectives of this study:

1. To prepare ZnO thin film via potentiostatic technique.
2. To evaluate and optimise the effect growth parameters (electrodeposition potentials, precursor concentrations and bath temperature) on the physical, chemical and electrochemical properties of ZnO and PEDOT/ZnO thin films.
3. To characterise the prepared ZnO and PEDOT/ZnO composite using scanning electron microscopy (SEM), X-ray diffraction (XRD), Fourier transform infrared (FTIR), Raman spectroscopy, ultraviolet-visible (UV-Vis), cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS).

1.4 Significance of study

This study was performed to synthesise PEDOT/ZnO thin film composite as a multifunctional material with great potentials for a number of potential applications. By retaining the advantages of both organic and inorganic materials, the composite which where synthesised via a low cost and low temperature electrochemical route certainly will offer impressive options in energy, electrical and optical applications.



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