UNIVERSITI PUTRA MALAYSIA

SYNTHESIS AND CHARACTERIZATION OF ZINC OXIDE NANORODS SENSITISED BY Bi_2S_3, Ag_2S and Ag_2S-Bi_2S_3 FOR PHOTOELECTROCHEMICAL APPLICATION

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By

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September 2020

DEDICATION

In appreciation of their love, sacrifices, faith, and endless goodness I would like to dedicate this thesis to
my dear father may god have mercy on his soul and mother,
my beloved husband, Saleh,
and
our daughters, Lana, Jowana and Nada.

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of the requirement for the degree of Doctor of Philosophy

SYNTHESIS AND CHARACTERIZATION OF ZINC OXIDE NANORODS SENSITISED BY Bi_2S_3, Ag_2S AND Ag_2S-Bi_2S_3 FOR PHOTOELECTROCHEMICAL APPLICATION

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This study focuses on the synthesis and characterisation of zinc oxide nanorods sensitised by narrow bandgap energy metal chalcogenides for photoelectrochemical application. Zinc oxide (ZnO) is a promising oxide semiconductor for photoelectrochemical application. Although it is very efficient in absorbing UV light, its wide bandgap is not ideal for visible light absorption. To solve this problem, heterostructures of the nanocomposite semiconductors such as bismuth sulfide/zinc oxide (Bi_2S_3/ZnO), silver sulfide/zinc oxide (Ag_2S/ZnO) and bismuth sulfide /silver sulfide/ zinc oxide (Bi_2S_3/Ag_2S/ZnO), are proposed to be the alternative conversion medium, as they could possibly harvest larger spectrum of sunlight. There are a variety of modification methods can be applied during the synthesis in order to increase the overall photoconversion efficiency of these nanocomposites such as deposition of sensitised narrow band gap energy materials on the surface of ZnO nanorod arrays. The deposition is expected to result in the modification of the electronic interface and facilitating charge carrier transfer between the coated material and the host semiconductor. In this study, ZnO nanoparticles seed layer (NPs) was prepared by sol-gel spin coating technique followed by heat-treatment at different temperatures to optimise the nucleation. ZnO nanorod arrays (NRAs) were then grown through a simple, facile hydrothermal method. The effect of hydrothermal growth temperature and duration were optimised to ensure achieving the high aspect ratio of ZnO NRAs. Bi_2S_3/ZnO NRAs/ITO, Ag_2S/ZnO NRAs/ITO were prepared using successive ionic layer adsorption and reaction (SILAR) method. In addition, considering the effect of various parameters on formation of Bi_2S_3/ZnO NRAs and Ag_2S/ZnO NRAs nanocomposite, the synthesis was carried out with variation of SILAR cycles number, dipping time, concentration of cationic precursor, pH, and annealing temperature. The formation of ZnO nanorods and Bi_2S_3 was noticed when the colour of the samples changed from colourless to white for ZnO, and dark brown for Bi_2S_3/ZnO. The powder X-ray diffraction (XRD) analysis verified that the synthesised ZnO NRAs sample has

hexagonal phase while Bi_2S_3 has an orthorhombic crystal structure. The deposited photosensitiser has no effect on the host material structure. The small nanoparticles of Bi_2S_3 on ZnO NRAs was observed by field emission scanning electron microscopy (FE-SEM). The red shifted absorbance spectra of the UV-visible spectrophotometry were observed after depositing Bi_2S_3 on ZnO NRAs. On the other hand, the transmission electron microscopy (TEM) provided the estimated average particle size of the Bi_2S_3 /ZnO nanoparticles heterostructure followed by determination of lattice fringe (d-spacing) from high-resolution transmission electron microscopy (HR-TEM). Bi_2S_3/ZnO NRAs nanocomposite synthesised at optimum condition gave a maximum photocurrent density of 2.76 mA/cm^2 and photoconversion efficiency of 3.17% which was 13 times greater than the plain ZnO NRAs (0.25%). The combination of wide bandgap energy (ZnO) with narrow bandgap energy semiconductor caused bending of different Fermi-level positions. Thus, the photogenerated electrons can be transferred easily from conduction band of Bi_2S_3 to the conduction band of ZnO while the holes transferred from the valance band of ZnO NRAs to the valance band of Bi_2S_3. Furthermore, the formation of ZnO nanorods and Ag_2S was observed as the colour of the samples changed from colourless to white for ZnO NRAs and dark brownish colour for the Ag_2S/ZnO sample. XRD, FE-SEM and UV-visible spectrophotometry analyses showed that the samples synthesised had a monoclinic phase, red shifted on the absorption edge of Ag_2S/ZnO NRAs/ITO. Additionally, ternary nanocomposite thin film Bi_2S_3/Ag_2S/ZnO NRAs has been optimised via controlling SILAR cycle number, dipping time, and annealing temperature. Results showed that due to its narrow bandgap, Bi_2S_3 and Ag_2S deposited samples were able to harvest more light compared to plain ZnO NRAs. In comparison with ZnO NRAs/ITO PEC electrode with a bandgap of 3.22 eV, Bi_2S_3/ZnO /ITO and Ag_2S/ZnO/ITO showed much smaller bandgaps of 1.95 eV, 1.78 eV, respectively. This cascading bands gap alignment decreased the chance for electron-hole recombination and enhanced the efficiency of electrons collection. The photoelectrochemical performance of the bare ZnO nanorods, Bi_2S_3/ZnO, Ag_2S/ZnO was examined under the illumination of a simulated visible light. The enhancement of photoconversion efficiency was observed to be 3.17% for Bi_2S_3/ZnO, 2.33% for Ag_2S/ZnO and 12.63% for Bi_2S_3/Ag_2S /ZnO compared to plain ZnO nanorods sample of only 0.25%.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Doktor Falsafah

SINTESIS DAN PENCIRIAN ROD NANO ZINK OKSIDA DIPEKA OLEH Bi_2S_3, Ag_2S DAN Ag_2S-Bi_2S_3 UNTUK APLIKASI FOTOELEKTROKIMIA

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Kajian ini memberi tumpuan kepada sintesis dan pencirian rod nano zink oksida yang dipeka oleh logam kalkogenida berluang tenaga sempit untuk aplikasi fotoelektrokimia. Zink oksida (ZnO) adalah semikonduktor oksida yang berpotensi untuk aplikasi fotoelektrokimia. Walaupun sangat berkesan untuk menyerap cahaya UV, luang tenaganya yang besar adalah tidak sesuai untuk penyerapan cahaya nampak. Untuk menyelesaikan masalah ini, semikonduktor komposit nano heterostruktur seperti bismut sulfida /zink oksida (Bi_2S_3/ZnO), argentum sulfida /zink oksida (Ag_2S/ZnO) dan bismut sulfida/argentum sulfida/zink oksida, (Bi_2S_3/Ag_2S/ZnO) dicadangkan sebagai medium penukaran alternatif kerana berpotensi menyerap spektrum solar pada julat yang lebih besar. Terdapat pelbagai cara pengubahsuaian yang boleh digunakan semasa proses sintesis bagi memastikan kecekapan keseluruhan penukaran tenaga cahaya komposit nano ini dapat ditingkatkan seperti pemendapan bahan luang tenaga sempit terpeka pada permukaan barisan rod nano ZnO. Pengenapan ini dijangka menghasilkan pengubahsuaian antara muka elektronik dan membantu pemindahan pembawa cas antara bahan enapan dan semikonduktor hos. Dalam kajian ini, lapisan benih partikel nano ZnO (NPs) disediakan melalui teknik salutan berputar sol-gel diikuti oleh rawatan haba pada suhu yang berbeza untuk mengoptimumkan penukleusan. Barisan rod nano ZnO kemudiannya ditumbuhkan melalui kaedah hidroterma yang mudah dan ringkas. Kesan suhu dan tempoh pertumbuhan hidroterma dioptimumkan untuk mendapatkan nisbah aspek ZnO NRA_S yang tinggi. Bi_2S_3/ZnO NRAs/ITO, Ag_2S/ZnO NRAs /ITO telah disediakan menggunakan kaedah penjerapan dan tindak balas lapisan ionik berturut (SILAR). Tambahan itu, dengan mengandaikan kesan pelbagai parameter ke atas pembentukan komposit nano Bi_2S_3/ZnO dan Ag_2S/ZnO NRAs /ITO, sintesis telah dijalankan dengan variasi bilangan kitaran SILAR, masa pencelupan, kepekatan prekursor kationik, pH, dan suhu penyepuhlindapan. Pembentukan rod nano ZnO dan Bi_2S_3 dapat dikesan apabila warna sampel berubah daripada tidak berwarna kepada putih untuk ZnO, dan coklat gelap untuk Bi_2S_3/ZnO. Analisis pembelauan X-ray

(XRD) mengesahkan bahawa sampel ZnO NRAs yang disintesis mempunyai fasa heksagonal manakala Bi_2S_3 mempunyai struktur kristal ortorombik. Pemeka tenaga cahaya yang dienapkan tidak memberi kesan terhadap struktur bahan hos. Struktur partikel nano Bi_2S_3 yang kecil di atas ZnO NRAs telah diperhatikan melalui mikroskopi pengimbasan elektron pancaran medan (FE-SEM). Peralihan merah spektrum penyerapan dapat diperhatikan daripada spektrum UV-nampak selepas pengenapan Bi_2S_3 pada ZnO NRAs. Sementara itu, mikroskopi transmisi elektron (TEM) memberi anggaran purata saiz partikel Bi_2S_3/ZnO heterostruktur diikuti penentuan jarak pinggiran kekisi (d-spacing) daripada mikroskopi transmisi elektron beresolusi tinggi (HR-TEM). Komposit nano Bi_2S_3/ZnO NRA yang disintesis pada keadaan optimum memberikan ketumpatan arus tenaga cahaya maksimum pada 2.76 mA/cm^2 dan kecekapan penukaran tenaga cahaya sebanyak 3.17% iaitu 13 kali lebih baik daripada ZnO NRAs kosong (0.25%). Gabungan semikonduktor ZnO berluang tenaga luas dengan semikondukor berluang tenaga sempit telah menhasilkan lenturan posisi aras Fermi yang berlainan. Oleh itu, elektron terjana tenaga cahaya dapat dipindahkan dengan mudah daripada jalur konduksi Bi_2S_3 ke jalur konduksi ZnO sementara lubang dipindahkan dari jalur valensi ZnO NRAs ke jalur valensi Bi_2S_3. Seterusnya, pembentukan rod nano ZnO dan Ag_2S diperhatikan apabila warna sampel berubah daripada tidak berwarna kepada putih untuk ZnO NRAs dan warna coklat gelap untuk sampel Ag_2S/ZnO. Analisis XRD, FE-SEM dan spektrofotometri UV-nampak menunjukkan sampel yang disintesis mempunyai fasa monoklinik, dan teralih merah pada hujung penyerapan bagi Ag_2S/ZnO NRAs/ITO. Sebagai tambahan, filem nipis komposit nano ternari Bi_2S_3/Ag_2S/ZnO NRAs telah dioptimumkan melalui kawalan bilangan kitaran SILAR, masa pencelupan dan suhu penyepuhlindapan. Keputusan mendapati luang tenaga yang sempit menyebabkan sampel yang dienapkan Bi_2S_3 dan Ag_2S dapat menyerap lebih banyak cahaya berbanding dengan ZnO NRAs kosong. Sebagai perbandingan dengan elektrod PEC ZnO NRAs/ITO berluang tenaga 3.22 eV, Bi_2S_3/ZnO/ITO dan Ag_2S/ZnO/ITO menunjukkan luang tenaga yang lebih kecil iaitu masing-masing 1.95 eV dan 1.78 eV. Penurunan berurutan luang jalur ini mengurangkan peluang untuk penggabungan semula elektron-lubang dan meningkatkan kecekapan pengumpulan elektron. Prestasi fotoelektrokimia rod nano ZnO, Bi_2S_3/ZnO, Ag_2S/ZnO diperhatikan di bawah sinaran cahaya nampak simulasi. Peningkatan kecekapan penukaran tenaga cahaya yang diperhatikan ialah 3.17% untuk Bi_2S_3/ZnO, 2.33% untuk Ag_2S/ZnO dan 12.63% untuk Bi_2S_3/Ag_2S/ZnO berbanding rod nano ZnO dengan hanya 0.25%.

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TABLE OF CONTENTS

		Page
ABSTRACT		i
ABSTRAK		iii
ACKNOWLEDGEMENTS		v
APPROVAL		vii
DECLARATION		ix
LIST OF TABLES		xiv
LIST OF FIGURES		xvi
LIST OF ABBREVIATIONS		xxviii

CHAPTER

1	**INTRODUCTION**		1
	1.1	Background of the Study	1
	1.2	Problem Statement	3
	1.3	Study Objectives	4
	1.4	Significance of the Study	5
	1.5	Scope of the Study	5
2	**LITERATURE REVIEW**		7
	2.1	Introduction	7
	2.2	Properties of nanomaterials	8
		2.2.1 One-dimensional Metal-oxide Nanostructures	8
		2.2.2 Heterostructured-semiconductor	9
	2.3	Photoelectrochemical cell	11
		2.3.1 Fundamental principles of photoelectrochemical cells	12
		2.3.2 The Quantum Confinement Theory in nano scaled semiconductor	16
	2.4	Properties of zinc oxide (ZnO)	18
	2.5	Approaches in synthesising zinc oxide thin film	20
	2.6	Synthesis of ZnO nanorod arrays	22
		2.6.1 Vapour phase deposition	23
		2.6.2 Metal organic chemical vapour deposition (MOCVD)	23
		2.6.3 Chemical bath deposition (CBD)	24
		2.6.4 Pulse laser deposition (PLD)	24
		2.6.5 Electrodeposition (ED)	25
		2.6.6 Hydrothermal Method (HT)	25
	2.7	Synthesis methods of sensitised semiconductors	27
	2.8	Bismuth sulfide properties	31
	2.9	Previous works on Bi_2S_3/metal oxide semiconductor	32
	2.10	Silver sulphide properties	37
	2.11	Previous work on Ag_2S/ metal oxide semiconductor	38
	2.12	Previous work on Bi_2S_3/Ag_2S	40

3	**METHODOLOGY**		43
	3.1	Introduction	43
	3.2	Synthesis methods	43
	3.3	Chemical reagents	45
	3.4	Preparation of ZnO nanoparticles via sol-gel spin coating technique	45
	3.5	Preparation of ZnO nanorod arrays (NRAs) using hydrothermal method (HT)	46
	3.6	Preparation of Bi_2S_3/ZnO NRAs nanocomposites via (SILAR) method	47
	3.7	Preparation of Ag_2S/ZnO NRAs nanocomposites via (SILAR) method	48
	3.8	Fabrication of Bi_2S_3/ Ag_2S/ZnO NRAs nanocomposites via SILAR method	49
	3.9	Characterisation techniques	50
		3.9.1 Ultraviolet- visible (UV-Vis) spectroscopy	50
		3.9.2 Powder X-ray diffraction (XRD)	51
		3.9.3 Raman spectroscopy	53
		3.9.4 Field emission scanning electron microscopy (FE-SEM) analysis	53
		3.9.5 Transmission electron microscopy (TEM)	54
		3.9.6 Energy dispersive X-ray spectroscopy	55
		3.9.7 X-ray photoelectron spectroscopy (XPS)	55
		3.9.8 Photoelectrochemical performance (PEC)	56
4	**ZnO NANOSTRUCTURES LAYER**		60
	4.1	Introduction	60
	4.2	Sol-gel spin coating deposition of ZnO nanoparticles (NPs) seed layer	60
	4.3	Hydrothermal growth of ZnO nanorod arrays (NRAs)	66
		4.3.1 Effect of growth temperature on ZnO NRAs	67
		4.3.2 Effect of growth time on ZnO NRAs	76
5	**SYNTHESIS AND CHARACTERIZATION OF Bi_2S_3/ZnO NRAs FOR PHOTOELECTROCHEMICAL APPLICATION**		85
	5.1	Introduction	85
	5.2	Effect of varying SILAR cycles number	85
	5.3	Effect of SILAR dipping time	91
	5.4	Effect of varying cationic concentration	96
	5.5	Effect of varying pH of cationic precursor	102
	5.6	Effect of annealing temperature	107
6	**SYNTHESIS AND CHARACTERIZATION OF Ag_2S/ZnO NRAs FOR PHOTOELECTROCHEMICAL APPLICATION**		122
	6.1	Introduction	122
	6.2	Effect of varying SILAR cycle number	122
	6.3	Effect of SILAR dipping time	128
	6.4	Effect of varying cationic concentration	134
	6.5	Effect of varying pH of cationic precursor	138

6.6 Effect of annealing temperature 143

7 SYNTHESIS AND CHARACTERIZATION OF $Bi_2S_3/Ag_2S/$ ZnO NRAs FOR PHOTOELECTROCHEMICAL APPLICATION 156
7.1 Introduction 156
7.2 Effect of SILAR cycles 156
7.3 Effect of dipping time 161
7.4 Effect of varying annealing temperature 166
7.5 Comparison between ZnO NRAs, Bi_2S_3/ZnO NRAs, Ag_2S/ ZnO NRAs and Bi_2S_3/Ag_2S /ZnO NRAs/ITO 176

8 CONCLUSIONS 188
8.1 Conclusions 188
8.2 Recommendations for future work 190

REFERENCES 191
APPENDICES 209
BIODATA OF STUDENT 222
LIST OF PUBLICATIONS 223

LIST OF TABLES

Table		Page
2.1	Classification of quantum confined structures	17
2.2	Overview on Bi_2S_3/ZnO and Ag_2S/ZnO thin films used for photoelectrochemical cells	42
3.1	Chemicals materials and solvents used throughout this work	45
3.2	Parameters studied in Bi_2S_3/ZnO/ ITO via SILAR method	48
3.3	Parameters studied in Ag_2S/ZnO/ ITO via SILAR method	49
3.4	Parameters studied in Bi_2S_3/Ag_2S/ZnO NRAs/ITO	49
3.5	Compounds and their JCPDS reference codes	52
4.1	The particle size values of ZnO NPs seed layer at various annealing temperatures	62
4.2	Values of photo conversion efficiency (η%) of ZnO NPs seed layer at different annealing temperatures	66
4.3	Summarised data depicting the XRD patterns of aligned ZnO NRAs/ ITO	68
4.4	Summarised data of the FE-SEM images (thickness, diameter, and aspect ratio), E_g values, and photocurrent density of aligned ZnO NRAs/ ITO	71
4.5	Summarised data from FE-SEM images of ZnO/ITO NRAs at 110 ºC for different growth time	77
4.6	Comparative study for synthesised ZnO NRAs /ITO at different hydrothermal growth temperature, growth time and different methods for seed layer fabrication	84
5.1	Photocurrent density and photoconversion efficiency values of Bi_2S_3/ ZnO NRAs at different cationic concentration	100
5.2	The calculated C.B. and V.B. position values of various constructions of nanostructure	121
6.1	The photoelectrochemical conversion efficiency of Ag_2S/ZnO NRAs/ ITO at different dipping time	134
6.2	The conduction band and valance band position of Ag_2S/ZnO NRAs at different annealing temperatures	155

7.1 EDS data of Bi_2S_3/ZnO/ITO; Ag2S/ZnO/ITO; and Bi2S3/Ag2S/ZnO /ITO 181

7.2 Comparison of binding energy of Bi_2S_3/ZnO, Ag_2S/ZnO and Bi_2S_3/Ag_2S/ZnO 182

7.3 Comparison of optical properties calculated C.B. and V.B. positions of bare ZnO NRAs/ITO, Bi_2S_3/ZnO NRAs/ITO, Ag_2S/ZnO NRAs/ITO, and Bi_2S_3/Ag_2S /ZnO NRAs/ITO 184

LIST OF FIGURES

Figure		Page
2.1	Diagram illustrates the heterostructured-alignment process in which C. B and V.B. symbolise the valence band and conduction band, respectively. (a) Type I band alignment: ”Straddling” ; (b) Type II staggered gap and (c) Type III broken gap	10
2.2	Energy band diagram for a n-type semiconductor (a) before contact; (b) after dark-equilibration; (c) illuminated-equilibration of Fermi levels at the semiconductor/ electrolyte interface and presence of band-bending and space charged layer (SCL)	14
2.3	Density of states presented in different confinement configurations	17
2.4	Demonstration of ZnO crystal structures: (a) cubic rock salt, (b) cubic zinc blend and (c) hexagonal wurtzite structure. The colored blue and yellow spheres symbolise zinc and oxygen atoms, respectively (Özgür et al., 2018)	19
2.5	ZnO's typical wurtzite crystal structure (Rodnyi & Khodyuk, 2011)	19
2.6	Schematic diagram of methods which are used in ZnO thin film synthesis	20
2.7	Sol-gel coating methods: (a) dip-coating and (b) spin-coating	22
2.8	Schematic diagram deposition SILAR growth. (i) adsorption of precursor KLp on the substrate surface and the formation of the electrical double layer; (ii) rinsing step; (iii) reaction of KLp surface species with the precursor A$L^{'}$q and (iv) rinsing(II)	30
2.9	Schematic drawing of the orthorhombic crystal structure of Bi_2S_3	32
2.10	Diagrammatic illustrations of (i) monoclinic acantite (α-Ag_2S); (ii) cubic argentite (β-Ag_2S) structure	38
3.1	Schematic diagram of research flowchart	44
3.2	Schematic diagram of the preparation of ZnO NPs seed layer by sol - gel spin coating	46
3.3	Schematic diagram of the preparation of ZnO NRAs by hydrothermal method	47
3.4	Diagram of preparation Bi_2S_3/ZnO NRAs nanoparticles via SILAR method of cationic and anionic precursor (•=Bi^{3+} and •= S^{2-})	48
3.5	The schematic diagram of X-ray diffraction	52

3.6 Set-up for photoelectrochemical experiments 58

4.1 Field emission scanning electron microscopy (FE-SEM) images of ZnO NPs (seed layer) with two different magnifications (×50,000 and × 100,000) annealed at different temperatures of (a) 300 ºC; (b) 350 ºC; (c) 400 ºC; (d) 450 ºC 61

4.2 X-ray diffractogram of ZnO NPs at different annealing temperatures of: (a) plain ITO;(b) 300 ºC; (c) 350 ºC; (d) 400 ºC; and (e) 450 ºC 63

4.3 The absorbance spectra of ZnO NPs at the different annealing temperatures of: (a) 300 ºC; (b) 350 ºC; (c) 400 ºC; and (d) 450 ºC 63

4.4 Bandgap energy curves of ZnO NPs at the different annealing temperatures of: (a) 300 °C; (b) 350 °C; (c) 400° C; and (d) 450 °C 64

4.5 Linear sweep voltammograms of ZnO/ITO NPs (seed layers) prepared at the different annealing temperatures at scan rate of 20 mV/s from -0.5 V to +1.0 V: (a) 300 ºC; (b) 350 ºC; (c) 400 ºC; (d) 450 ºC 65

4.6 The graph of photocurrent density (J_{ph}) at +0.5 V applied voltage vs. Ag/AgCl plotted against the annealing temperature of ZnO/ITO NPs (seed layers) 66

4.7 X-ray diffraction of ZnO NRAs/ITO at different hydrothermal growth temperatures for 4 hours (a) ITO substrate; (b) 80 °C; (c) 90 °C; (d) 100 °C; (e) 110 °C and (f) 120 °C. The inset of figure represents the (002) peak plotted from 34° to 35.5° 68

4.8 Top view and cross section FE-SEM images of ZnO NRAs/ITO grown for 4 hours at different hydrothermal temperatures: (a) 80 °C;(b) 90°C; (c) 100 °C; (d) 110 °C; and (e) 120 °C 70

4.9 ZnO NRAs growth temperature vs. change in length, diameter, and aspect ratio (insets) 72

4.10 The absorbance spectra of ZnO NRAs/ITO grown for 4 hours at different hydrothermal temperatures: (a) 80 °C; (b) 90 °C; (c) 100 °C; (d) 110 °C and (e) 120 °C 73

4.11 The Tauc plot $(\alpha hv)^2$ versus energy (hv) of ZnO NRAs/ITO grown for 4 hours at different hydrothermal temperatures: (a) 80 °C; (b) 90 °C; (c) 100 °C; (d) 110 °C and (e) 120 °C 74

4.12 Linear sweep voltammograms of (a) ZnO NPs (seed layer); ZnO NRAs /ITO synthesised at different hydrothermal temperatures (b) 80 °C; (c) 90 °C; (d) 100 °C; (e) 110 °C and (f) 120 °C for 4 hours obtained at the scan rate of 20 mVs^{-1} at the applied potentials from -0.5 V to +1.0 V under illumination intensity of 100 $mWcm^{-2}$ in 0.1 M Na_2S and 0.1 M Na_2SO_3 electrolyte 75

4.13 Photocurrent density (J_{ph}) (mA/cm^2) plotted against growth temperature (°C) at applied potential of +0.5V vs. Ag/AgCl 76

4.14 X-ray diffractograms of ZnO NRAs prepared at 110 °C using hydrothermal method at different growth times: (a) ITO substrate; (b) 1h;(c) 2h; (d) 3h; (e) 4h; and (f) 5h. The inset of figure represents the (002) peak plotted from 34° to 35° 77

4.15 Top view and cross section FE-SEM images of ZnO NRAs/ITO grown at 110 °C for different growth time: (a) 1h; (b) 2h; (c) 3h; (d) 4h; and (e) 5h 78

4.16 The absorbance spectra of ZnO NRAs/ITO grown at 110 °C via hydrothermal method at different growth time: (a) 1h;(b) 2h; (c) 3h; (d) 4h; and (e) 5h 79

4.17 The Tauc plot $(\alpha h\nu)^2$ versus energy ($h\nu$) ZnO NRAs/ITO grown at 110 °C via hydrothermal method at different growth time: (a) 1h;(b) 2h; (c) 3h; (d) 4h; and (e) 5h 80

4.18 Graph of optical bandgap energy of ZnO NRAs prepared via hydrothermal method at 110 °C against the growth time 81

4.19 Linear sweep voltammograms of: (a) ZnO NPs (seed layer); ZnO NRAs/ITO synthesised at 110 °C using hydrothermal method at different growth time: (b) 1h;(c) 2h; (d) 3h; (e) 4h; and (f) 5h obtained at the scan rate of 20 mVs^{-1} at the applied potentials from -0.5 V to 1.0 V under illumination intensity of 100 mWcm^{-2} in 0.1 M Na_2S and 0.1 M Na_2SO_3 electrolyte 82

4.20 Photo conversion efficiency values ZnO NRAs/ITO synthesised at 110 °C using hydrothermal method at different growth time: (a) 1h;(b) 2h; (c) 3h; (d) 4h; and (e) 5h under illumination intensity of 100 m Wcm^{-2}in 0.1M Na_2S and 0.1M Na_2SO_3 electrolyte system 83

5.1 X-ray diffraction of: (a) ZnO NRAs, Bi_2S_3/ZnO NRAs/ITO at different SILAR cycles of (b) 3 cycles; (c) 5 cycles; (d) 7 cycles; (e) 9 cycles; (f) 11 cycles 86

5.2 (A) UV-Vis Spectra; (B) bandgap energy curves of: (a) ZnO NRAs/ ITO and Bi_2S_3/ZnO NRAs/ITO prepared at different SILAR cycles (b) 3 cycles; (c) 5 cycles; (d) 7 cycles ;(e) 9 cycles; (f) 11 cycles and the inset plot shows the optical band gap energy at different SILAR cycles 87

5.3 Different magnification(×25,000 and ×50,000) FE-SEM images of (a) pristine ZnO NRAs and ZnO nanorods decorated with Bi_2S_3 nanoparticles for (b) 3 cycles; (c) 7 cycles; (d) 11 cycles. Cross-sectionals of the samples a, c is shown in the insets of the figures 88

5.4 Energy dispersive X-ray (EDX) spectra of Bi_2S_3/ZnO NRAs/ITO heterostructure at (a) 3 cycles; (b) 7 cycles of Bi_2S_3/ZnO NRAs/ITO heterostructure. Inset shows the tabulated EDX data in atomic% of the corresponding films 89

5.5 Linear sweep voltammograms obtained at the scan rate of 20 mV s^{-1} at applied potentials from -0.5V to +1.0 V under illumination intensity of 100 $mWcm^{-2}$ in 0.1M Na_2S and Na_2SO_3 electrolyte for: (a) bare ZnO NRAs/ITO; Bi_2S_3/ZnO NRAs/ITO at different SILAR cycles number: (b) 3 cycles; (c) 5 cycles; (d) 7 cycles; (e) 9 cycles; (f) 11 cycles 90

5.6 Photoconversion efficiency as a function of applied voltage versus (Ag/AgCl) of: (a) bare ZnO NRAs/ITO; (b) Bi_2S_3/ZnO NRAs prepared at 7 SILAR cycles under illumination intensity of 100 $mWcm^{-2}$ in 0.1M Na_2SO_3 and 0.1M Na_2S electrolyte mixture 91

5.7 FE-SEM images of: (a) ZnO NRAs/ITO and Bi_2S_3/ZnO NRAs/ITO prepared at different dipping time (b) 20 s;(c) 60 s; (d) 100 s Cross sectional images of (a) and (c) are shown in insets of the figures 92

5.8 X-ray diffraction of: (a) ZnO NRAs; Bi_2S_3/ZnO NRAs/ITO at different dipping time of (b) 20 s; (c) 40 s; (d) 60 s; (e) 80 s; (f) 100 s 93

5.9 (A) UV-Vis Spectra; (B) bandgap energy curves of: (a) ZnO NRAs/ ITO and Bi_2S_3/ZnO NRAs/ITO prepared at different dipping time (b) 20 s;(c) 40 s; (d) 60 s ;(e) 80 s; (f) 100 s and the inset plot shows the optical band gap energy values at different dipping time 94

5.10 Linear sweep voltammograms obtained at the scan rate of 20 mV s^{-1} at applied potentials from -0.5V to +1.0 V under illumination intensity of 100 $mWcm^{-2}$ in 0.1M Na_2S and Na_2SO_3 electrolyte for: (a) bare ZnO NRAs/ITO; Bi_2S_3/ZnO NRAs/ITO at different dipping time (b) 20 s; (c) 40 s; (d) 60 s ;(e) 80 s; (f) 100 s 95

5.11 Photoconversion efficiency as a function of applied voltage versus (Ag/AgCl) of Bi_2S_3/ZnO NRAs prepared with different dipping time: (a) 20 s;(b) 40 s; (c) 60 s ;(d) 80 s; (e) 100 s under illumination intensity of 100 $mWcm^{-2}$ in 0.1M Na_2SO_3 and 0.1M Na_2S electrolyte mixture 96

5.12 X-ray diffraction of: (a) ZnO NRAs ; Bi_2S_3/ZnO NRAs/ITO at different cationic concentration of (b) 1 mM;(c) 3 mM; (d) 5 mM; (e) 8 mM; (f) 10 mM 97

5.13 FE-SEM images of (a) bare ZnO NRAs, ZnO NRAs decorated with Bi_2S_3 nanoparticles at different cationic concentration (b) 1 mM; (c) 3 mM; (d) 10 mM. Cross-sectional images of bare ZnO NRAs (a), higher magnification (×50,000) of (b),(c),(d) is shown in the insets of the figures 98

5.14 (A) UV-Vis spectra; (B) the bandgap energy curves of: (a) ZnO NRAs /ITO and Bi_2S_3/ZnO NRAs/ITO prepared at different cationic concentration (b) 1 mM;(c) 3 mM ; (d) 5 mM ;(e) 8 mM; (f) 10 mM. The optical band gap energy values at different cationic concentrations is shown in the insets of figure 99

5.15 Linear sweep voltammograms obtained at the scan rate of 20 mV s^{-1} at applied potentials from -0.5 V to +1.0 V under illumination intensity of 100 $mWcm^{-2}$ in 0.1M Na_2S and Na_2SO_3 electrolyte for: (a) bare ZnO NRAs/ITO; Bi_2S_3/ZnO NRAs/ITO at different cationic concentration : (b) 1 mM; (c) 3 mM; (d) 5 mM; (e) 8 mM; (f) 10 mM 101

5.16 Photoconversion efficiency values as a function of applied voltage vs. Ag/AgCl of Bi_2S_3/ZnO NRAs at different cationic concentration: (a) 1mM; (b) 3mM; (c) 5 mM; (c) 8 mM; (d) 8 Mm; (e) 10 mM, under illumination intensity (100 mW cm^{-2}) in 0.1 M Na_2S and 0.1 M Na_2SO_3 102

5.17 X-ray diffraction patterns of: (a) ZnO NRAs; Bi_2S_3/ZnO NRAs/ITO with different pH cationic precursor: (b) 1.3;(c) 2.3; (d) 3.3; (e) 4.3; (f) 5.3 103

5.18 FE-SEM images of: ZnO NRAs (a) ;Bi_2S_3/ZnO NRAs/ITO with different cationic pH: (b) 1.3; (c) 2.3; (d) 3.3; (e) 4.3; (f) 5.3 104

5.19 (A) UV-Vis spectra and (B) the optical bandgap Eg energy curves of: (a) ZnO NRAs/ITO and Bi_2S_3/ZnO NRAs/ITO prepared at different pH cationic (b) 1.3; (c) 2.3 ; (d) 3.3 ; (e) 4.3; (f) 5.3. The optical band gap energy values at different cationic pH is shown in the insets of figure 105

5.20 Linear sweep voltammograms obtained at the scan rate of 20 mVs^{-1} at applied potentials from -0.5 V to +1.0 V under illumination intensity of 100 $mWcm^{-2}$ in 0.1M Na_2S and Na_2SO_3 electrolyte for: (a) bare ZnO NRAs/ITO; Bi_2S_3/ZnO NRAs/ITO at different cationic pH: (b) 1.3; (c) 2.3; (d) 3.3; (e) 4.3; (f) 5.3 106

5.21 Photoconversion efficiency values of (a) ZnO NRAs/ITO; Bi_2S_3/ZnO NRAs/ITO as a function of applied voltage vs. Ag/AgCl of at different pH cationic: (b) 1.3; (c) 2.3; (d) 3.3; (e) 4.3; (f) 5.3 under illumination intensity (100 mW cm^{-2}) in 0.1 M Na_2S and 0.1 M Na_2SO_3 107

5.22 X-ray diffraction of: (a) ZnO NRAs/ITO; Bi_2S_3/ZnO NRAs/ITO at various annealing temperatures: (b) as deposited, (c) 100 ºC; (d) 200 ºC; (e) 300 ºC; (f) 400 ºC; (g) 500 ºC. The inset of figure represents the peaks plotted from 2θ 25°to 33° 108

5.23 Raman spectra of (a) ZnO NRAs; (b) Bi_2S_3/ZnO NRAs annealed at 300 °C for 1h in N_2 gas flow 109

5.24 XPS spectra of Bi_2S_3/ZnO/ITO heterostructure annealed at 300 ºC: (a) the overall spectra Bi_2S_3/ZnO/ITO; (b) Bi 4f and S 2p spectra; (c) O 1s spectra and (d) Zn 2p spectra 110

5.25 (A) UV-Vis spectra; (B) the optical bandgap energy curves of: (a) ZnO NRAs/ITO; (b) Bi_2S_3/ZnO NRAs/ITO as-deposited and Bi_2S_3/ZnO NRAs/ITO annealed at (c) 100 ºC;(d) 200 ºC ; (e) 300 ºC ;(f) 400 ºC; (g) 500 ºC 111

5.26 FE-SEM images at two different magnification (×25,000 and ×50,000) of: (a) ZnO NRAs, (b) as-prepared Bi_2S_3/ZnO NRAs, Bi_2S_3/ZnO NRAs at different annealing temperatures (c) 200 °C; (d) 300 °C; (e) 400 °C. (f) 500 °C. Cross sectional images of (a) and (d) are shown in the insets of the figures 113

5.27 (a) The SAED pattern of plain ZnO NRAs; (b) The SAED pattern of Bi_2S_3/ZnO NRAs annealed at 300 ºC for 1 h in N_2 flow; (c) TEM image of plain ZnO NRAs; (d) TEM image of the optimal sample Bi_2S_3/ZnO NRAs annealed at 300 ºC for 1 h in N_2 flow 114

5.28 FFT patterns for Bi_2S_3/ZnO obtained from the selected area in HRTEM image under 5 nm scale 115

5.29 The EDS pattern and elemental mapping (EELS) of the optimum sample Bi_2S_3/ZnO NRAs/ITO annealed at 300 °C for 1h under N_2 air flow 116

5.30 Linear sweep voltammograms of (a) as-deposited Bi_2S_3/ZnO NRAs, and Bi_2S_3/ZnO NRAs annealed at (b) 100 ºC; (c) 200 ºC; (d) 300 ºC; (e) 400 ºC; (f) 500 ºC for 1h, obtained at the scan rate of 20 mVs^{-1} at the applied potential from -0.5V to +1.0 V under illumination intensity (100 mW cm^{-2}) in 0.1 M of Na_2S and 0.1 M of Na_2SO_3 electrolyte 118

5.31 Photoconversion efficiency as a function of applied voltage versus (Ag/AgCl) of: Bi_2S_3/ZnO NRAs prepared at different annealing temperatures: (a) as-deposited; (b) 100 °C; (c) 200 °C; (d) 300 °C; (e) 400 °C; (f) 500 °C at illumination intensity of 100 $mWcm^{-2}$ in 0.1M Na_2SO_3 and 0.1M Na_2S electrolyte mixture 119

5.32 Schematic band alignment of the heterostructured Bi_2S_3/ZnO NRAs /ITO binary nanostructure 120

6.1 FE-SEM images at two different magnification (×25,000 and × 50,000) of (a) ZnO NRAs, Ag_2S/ZnO NRAs prepared at different SILAR cycles: (b) 4 cycles; (c) 6 cycles; (d) 8 cycles; (e) 12 cycles 123

6.2 Photographic image of Ag_2S/ZnO NRAs samples at different SILAR cycle numbers: (a) 4cycles; (b) 6 cycles; (c) 8 cycles; (d) 10 cycles; (e) 12 cycles 124

6.3 X-ray diffractogram of: (a) bare ZnO NRAs; Ag_2S/ZnO NRAs/ITO prepared at different SILAR cycles: (b) 4 cycles; (c) 6 cycles; (d) 8 cycles; (e) 10 cycles and (f) 12 cycles 125

6.4 (A) UV-Vis Spectra; (B) the optical bandgap energy curves of: (a) ZnO NRAs/ITO; Ag_2S/ZnO NRAs/ITO prepared at different SILAR cycles: (b) 4 cycles; (c) 6 cycles; (d) 8 cycles; (e) 10 cycles and (f) 12 cycles 126

6.5 Linear sweep voltammograms obtained at the scan rate of 20 mV s^{-1} at applied potentials from -0.5 V to +1.0 V under illumination intensity of 100 $mWcm^{-2}$ in 0.1M Na_2S and Na_2SO_3 electrolyte for: (a) bare ZnO NRAs/ITO; Ag_2S/ZnO NRAs/ITO prepared at different SILAR cycles: (b) 4 cycles; (c) 6 cycles; (d) 8 cycles; (e) 10 cycles and (f) 12 cycles 127

6.6 Photoconversion efficiency values as a function of applied voltage vs. Ag/AgCl of Ag_2S/ ZnO NRAs at different SILAR cycles: (a) 4 cycles; (b) 6 cycles; (c) 8 cycles; (d) 10 cycles; (f) 12 cycles under illumination intensity (100 mW cm^{-2}) in mixture of 0.1 M Na_2S and Na_2 SO_3 128

6.7 FE-SEM images at two different magnification (×25,000 and ×50,000) of (a) ZnO NRAs, Ag_2S/ZnO NRAs prepared at different dipping time: (b) 20 s; (c) 60 s; (d) 80 s;(e) 100 s 130

6.8 XRD patterns of: (a) ZnO nanorods decorated with Ag_2S nanoparticles with different dipping time: (b) 20 s; (b) 40 s; (c) 60 s; (d) 80 s; (f) 100 s 131

6.9 (A) UV-Vis Spectra; (B) bandgap energy curves of (a) ZnO NRAs/ ITO and Ag_2S/ZnO NRAs/ITO prepared at different dipping time : (b) 20 s; (b) 40 s; (c) 60 s; (d) 80 s; (f) 100 s The inset of Figure A shows the E_g changes at different dipping time 132

6.10 Linear sweep voltammograms obtained at the scan rate of 20 mVs^{-1} at applied potentials from -0.5V to +1.0 V under illumination intensity of 100 $mWcm^{-2}$ in 0.1 M Na_2S and Na_2SO_3 electrolyte for: (a) ZnO NRAs/ITO; Ag_2S/ZnO NRAs/ITO at different dipping time : (b) 20 s; (c) 40 s; (d) 60 s; (e) 80 s; (f) 100 s 133

6.11 XRD patterns of (a) ZnO nanorods decorated with Ag_2S nanoparticles at different cationic concentration: (b) 0.01 M; (c) 0.02 M; (d) 0.04 M; (e) 0.06M; (f) 0.08 M 135

6.12 FE-SEM images of (a) bare ZnO NRAs; and ZnO nanorods decorated with Ag_2S nanoparticles , (b) 0.01 M; (c) 0.02 M; (d) 0.06 M; (e) 0.08 M at different magnifications (×25,000 and ×50,000) 136

6.13 (A) UV-Vis Spectra; (B) bandgap energy curves of: (a) ZnO NRAs/ ITO and Ag_2S/ZnO NRAs/ITO prepared at different cationic concentration: (b) 0.01 M; (c) 0.02 M; (d) 0.04 M; (e) 0.06 M; (f) 0.08 M. Eg values at different cationic concentration is shown in the insets of figure 137

6.14 Linear sweep voltammograms obtained at the scan rate of 20 mV s^{-1} at applied potentials from -0.5 V to +1.0 V under illumination intensity of 100 $mWcm^{-2}$ in 0.1M Na_2S and Na_2SO_3 electrolyte for: (a) ZnO NRAs/ITO; Ag_2S/ZnO NRAs/ITO at various cationic concentration: (b) 0.01 M; (c) 0.02 M; (d) 0.04 M; (e) 0.06 M;(f) 0.08 M 138

6.15 XRD patterns of (a) : pure ZnO NRAs and Ag_2S/ZnO NRAs at different cationic pH;(b) 3; (c) 4; (d) 5; (e) 6; (f) 7 139

6.16 FE-SEM images of bare ZnO NRAs (a), and ZnO nanorods decorated with Ag_2S nanoparticles at different pH: (b) 3; (c) 4; (d) 5; (e) 6; (f) 7 at (×25,000 and ×50,000) magnification 140

6.17 (A) UV-Vis spectra; (B) bandgap energy curves of: (a) ZnO NRAs/ ITO and Ag_2S/ZnO NRAs/ITO prepared at different cationic pH: (b) 3; (c) 4; (d) 5; (e) 6; (f) 7. Eg values at different cationic pH is shown in the insets of figure 141

6.18 Linear sweep voltammograms obtained at the scan rate of 20 mVs^{-1} at applied potentials from -0.5 V to +1.0 V under illumination intensity of 100 $mWcm^{-2}$ in 0.1M Na_2S and Na_2SO_3 electrolyte for: (a) ZnO NRAs/ITO; Ag_2S/ZnO NRAs/ITO at various cationic pH: (b) 3; (c) 4; (d) 5; (e) 6; (f) 7 142

6.19 Photoconversion efficiency values as a function of applied voltage vs. Ag/AgCl of Ag_2S/ZnO NRAs at different $AgNO_3$ pH: (a) 3; (b) 4; (c) 5; (d) 6; (e) 7 under illumination intensity (100 mW cm^{-2}) in mixture of 0.1 M Na_2S and of Na_2 SO_3 143

6.20 XRD patterns of (a) : pure ZnO NRAs and Ag_2S/ZnO NRAs at different annealing temperatures: (b) as-deposited; (c) 100 ºC; (d) 200 ºC;(e) 300 ºC; (f) 400 ºC and (g) 500 ºC for 1 h with heating rate of 2 degree/ min in N_2 atmosphere 144

6.21 The EDS spectra of Ag_2S/ZnO NRAs annealed at 400°C for 1 h with heating rate of 2 degree/min in N_2 atmosphere 145

6.22 High resolution XPS spectrum of Ag_2S/ZnO NRAs/ITO-400 ºC for 1 h with heating rate of 2 degree/min in N_2 atmosphere - survey spectrum 146

6.23 XPS spectra of Zn-2p (a); (b) O-1s; (c) Ag-3d; (d) S-2p elements in Ag_2S/ZnO/ITO annealed at 400 ºC 147

6.24 Raman spectra of the optimum sample Ag_2S/ZnO NRAs/ITO annealed at 400 ºC for 1 h with heating rate of 2 degree/min in N_2 atmosphere 148

6.25 FE-SEM images of (a) bare ZnO NRAs, ZnO NRAs decorated with Ag_2S nanoparticles annealed at different temperatures (b) as-deposited ; (c) 100 ºC; (d) 200 ºC; (e) 400 ºC; (f) 500ºC. Higher magnification is shown in the inset of figure 149

6.26 (a) TEM images and (b) HRTEM images of the optimal sample of Ag_2S/ZnO NRAs annealed at 400 ˚C for 1 h with heating rate of 2 degree/min in N_2 atmosphere 150

6.27 (A) UV-Vis Spectra; (B) the optical bandgap energy curves of: (a) ZnO NRAs/ITO; (b) Ag_2S/ZnO NRAs/ITO as-deposited and Ag_2S/ ZnO NRAs/ITO annealed at (c) 100 ºC;(d) 200 ºC ; (e) 300 ºC; (f) 400 ºC; (g) 500 ºC. Eg values at different annealing temperatures is shown in the inset of figure 151

6.28 Linear sweep voltammograms of (a) bare ZnO NR; (b) as -deposited Ag_2S/ZnO NRAs/ITO, and Ag_2S/ZnO NRAs/ITO annealed at (c) 100 ºC; (d)200 ºC; (e) 300 ºC; (f) 400 ºC; (g) 500 ºC for 1 h, obtained at the scan rate of 20 mV s^{-1} at the applied potential from -0.5 V to + 1.0 V under illumination intensity (100 mW/ cm^2) in 0.1 M Na_2S and 0.1 M Na_2SO_3 electrolyte 152

6.29 Photoconversion efficiency values as a function of applied voltage vs. Ag/AgCl of Ag_2S/ZnO NRAs/ITO at different annealing temperatures: (a) as -deposited; (b) 100 ºC; (b) 200 ºC; (c) 300 ºC; (d) 400 ºC; (f) 500 ºC for 1 h, under illumination intensity (100 mW/cm^2) in 0.1 M Na_2S and 0.1 M Na_2SO_3 153

6.30 Schematic band alignment of Ag_2S/ZnO NRAs binary heterostructure photoanode 154

7.1 XRD patterns of (a): pure ZnO NRAs and Bi_2S_3/Ag_2S/ZnO NRAs /ITO at different SILAR cycles : (b) 1 cycle; (c) 3 cycles; (d) 5 cycles; (e) 7 cycles; (f) 9 cycles 157

7.2 (A) UV-Vis spectra; (B) the optical bandgap energy curves of: (a) ZnO NRAs/ITO; (b) Bi_2S_3/Ag_2S/ZnO NRAs/ITO prepared at different SILAR cycles : (b) 1 cycle; (c) 3 cycles; (d) 5 cycles;(e) 7 cycles; (f) 9 cycles. Eg values at different SILAR cycles is shown in the inset of figure 158

7.3 Linear sweep voltammograms of (a) bare ZnO NR; (b) as -deposited Ag_2S/ZnO NRAs/ITO; (c) Ag_2S/ZnO NRAs/ITO annealed 400 ºC; and Bi_2S_3/Ag_2S/ZnO NRAs/ITO prepared at different SILAR cycles at (d) 1 cycle; (e) 3 cycles; (f) 5 cycles;(g) 7 cycles; (h) 9 cycles. obtained at the scan rate of 20 mV s^{-1} at the applied potential from -

0.5 V to + 1.0 V under illumination intensity (100 mW/ cm^2) in 0.1 M Na_2S and 0.1 M Na_2SO_3 electrolyte 159

7.4 Photoconversion efficiency values as a function of applied voltage vs. Ag/AgCl of: (a) ZnO NRAs; (b) Ag_2S/ZnO NRAs/ITO-400 ºC; Bi_2S_3/Ag_2S/ZnO NRAs/ITO prepared at different SILAR cycles at (c) 1 cycle; (d) 3 cycles; (e) 5 cycles;(f) 7 cycles; (g) 9 cycles under illumination intensity (100 mW/cm^2) in 0.1 M Na_2S and 0.1 M Na_2SO_3 160

7.5 FE-SEM images of: (a) Ag_2S/ZnO NRAs-400 ºC, Bi_2S_3/Ag_2S/ZnO NRAs/ITO prepared at different SILAR cycles at (b) 1 cycle; (c) 3 cycles; (d) 5 cycles;(e) 7 cycles; (f) 9 cycles. Higher magnification (×50,000) of the images is in the insets of figures 161

7.6 XRD patterns of (a): pure ZnO NRAs and Bi_2S_3/Ag_2S/ZnO NRAs/ITO at different dipping time: (b) 5 s; (c) 10 s; (d) 15 s;(e) 20 s; (f) 25 s 162

7.7 (A) UV-Vis Spectra; (B) the optical bandgap energy curves of: (a) ZnO NRAs/ITO; (b) Bi_2S_3/Ag_2S/ZnO NRAs/ITO prepared at different dipping time: (b) 5 s; (c) 10 s; (d) 15 s;(e) 20 s; (f) 25 s. Eg values at different dipping time is shown in the inset of figure 163

7.8 Linear sweep voltammograms of (a) bare ZnO NR; (b) as -deposited Ag_2S/ZnO NRAs/ITO; (c) Ag_2S/ZnO NRAs/ITO annealed 400 ºC; and Bi_2S_3/Ag_2S/ZnO NRAs/ITO prepared at different dipping time: (d) 5 s; (e) 10 s; (f) 15 s;(g) 20 s; (h) 25 s obtained at the scan rate of 20 m V s^{-1} at the applied potential from -0.5 V to +1.0 V under illumination intensity (100 mW/ cm^2) in mixture of 0.1 M Na_2S and M Na_2SO_3 electrolyte 164

7.9 Photoconversion efficiency values as a function of applied voltage vs. Ag/AgCl of (a) bare ZnO NRAs; (b) Ag_2S/ZnO NRAs-400 ºC; Bi_2S_3/Ag_2S/ZnO NRAs/ITO prepared at different dipping time: (c) 5 s; (d) 10 s; (e) 15 s;(f) 20 s; (g) 25 s under illumination intensity (100 mW/cm^2) in 0.1 M Na_2S and 0.1 M Na_2SO_3 165

7.10 FE-SEM images of (a) Ag_2S/ZnO NRAs/ITO annealed 400 ºC; and Bi_2S_3/Ag_2S/ZnO NRAs/ITO prepared at different dipping time: (b) 5 s; (c) 10 s; (d) 15 s;(e) 20 s; (f) 25 s. ×50,000 magnification of the images is in the insets of figures 166

7.11 FE-SEM images of (a): bare ZnO NRAs and Bi_2S_3/Ag_2S/ZnO NRAs /ITO electrode synthesised at different annealing temperatures: (b) as-deposited; (c) 100 ºC; (d) 200 ºC; (e) 400 ºC; (f) 500 ºC for 1h with heating rate of 2degree/min in N_2 atmosphere. Magnification (×50,000 is shown in the insets of figures 168

7.12 EDS pattern and elemental mapping (EELS) of $Bi_2S_3/Ag_2S/ZnO$ NRAs /ITO annealed at 400 ºC 1h with heating rate of 2 degree/min in N_2 atmosphere 169

7.13 (a) TEM and (b) HR-TEM image of the optimum sample Bi_2S_3/Ag_2S /ZnO NRAs/ITO annealed at 400 ºC for 1 h in N_2 atmosphere 170

7.14 XPS spectra of $Bi_2S_3/Ag_2S/ZnO$ NRAs/ITO heterostructure (optimal sample annealed at 400 ºC): (a) the XPS survey spectra of $Bi_2S_3/Ag_2S/ZnO/ITO$; (b) Zn 2p spectra ; (c) O 1s spectra; (d) Bi 4f and S 2p spectra; (e) Ag 3d spectra 171

7.15 XRD diffractogram of : (a) ZnO NRAs/ITO; $Bi_2S_3/Ag_2S/ZnO$ NRAs /ITO prepared at different annealing temperatures : (b) as-deposited; (c) 100 ºC; (d) 200 ºC; (e) 300 ºC; (f) 400 ºC; (g) 500 ºC 172

7.16 (A) UV-Vis spectra; (B) bandgap energy curves of: (a) ZnO NRAs/ ITO; (b) $Bi_2S_3/Ag_2S/ZnO$ NRAs/ITO-as deposited; (c) 100 ºC; (d) 200 ºC;(e) 300 ºC; (f) 400 ºC; (g) 500 ºC for 1 h in N_2 air. The changes in optical band gap energy values at different annealing temperatures is shown in the inset of figure 173

7.17 Linear sweep voltammograms obtained at the scan rate of 20 mVs^{-1} at applied potentials range from -0.5 V to +1.0 V under illumination intensity of 100 $mWcm^{-2}$ in 0.1M Na_2S and Na_2SO_3 electrolyte for: (a) ZnO NRAs and $Bi_2S_3/Ag_2S/ZnO$ NRAs/ITO at different annealing temperatures :(b) as-deposited; (c) 100 ºC; (d) 200 ºC;(e) 300 ºC; (f) 400 ºC; (g) 500 ºC for 1 h in N_2 air 174

7.18 Photoconversion efficiency as a function of applied voltage versus (Ag/AgCl) of: (a) bare ZnO NRAs/ITO; Bi_2S_3(7)/Ag_2S (6)/ZnO NRAs/ITO at different annealing temperatures :(b) as-deposited; (c) 100 ºC; (d) 200 ºC; (e) 300 ºC; (f) 400 ºC; (g) 500 ºC for 1 h in N_2 air under illumination intensity of 100 $mWcm^{-2}$ in 0.1M Na_2SO_3 and 0.1M Na_2S electrolyte mixture 175

7.19 Schematic of the relative energy levels and ideal cascade band structure in Bi_2S_3/Ag_2S /ZnO NRAs/ITO heterostructure ternary system 176

7.20 X-ray diffractogram of: (a) bare ZnO NRAs; (b) Bi_2S_3/ZnO NRAs/ ITO; (c) Ag_2S/ZnO NRAs; (d) Bi_2S_3/Ag_2S /ZnO NRAs/ITO 177

7.21 Plane view FE-SEM images with cross-sectional of: (a-b) bare ZnO NRAs; (c-d) Bi_2S_3/ZnO NRAs/ITO; (e-f) Ag_2S/ZnO NRAs/ITO; (g-h) Bi_2S_3/Ag_2S /ZnO NRAs/ITO 178

7.22 TEM images of : (a) bare ZnO NRAs; (b) Bi_2S_3/ZnO NRAs/ITO; (c) Ag_2S/ZnO NRAs/ITO; (d) Bi_2S_3/Ag_2S /ZnO NRAs/ITO 179

7.23 HRTEM image of : (a) Bi_2S_3/ZnO NRAs/ITO; (b) Ag_2S/ZnO NRAs /ITO; (c) Bi_2S_3/Ag_2S /ZnO NRAs/ITO 180

7.24 EDS patterns of: (a) Bi_2S_3/ZnO NRAs/ITO; (b) Ag_2S/ZnO NRAs /ITO; (c) Bi_2S_3/Ag_2S /ZnO NRAs/ITO 181

7.25 UV-Vis spectra of : (a) bare ZnO NRAs/ITO; (b) Bi_2S_3/ZnO NRAs /ITO; (c) Ag_2S/ZnO NRAs/ITO; (d) Bi_2S_3/Ag_2S /ZnO NRAs/ITO 183

7.26 Optical bandgap energy curves of: (a) bare ZnO NRAs/ITO; (b) Bi_2S_3 /ZnO NRAs/ITO; (c) Ag_2S/ZnO NRAs/ITO; (d) Bi_2S_3/Ag_2S /ZnO NRAs/ITO 183

7.27 Linear sweep voltammograms of : (a) bare ZnO NRAs/ITO; (b) Bi_2S_3 /ZnO NRAs/ITO; (c) Ag_2S/ZnO NRAs/ITO; (d) Bi_2S_3/Ag_2S /ZnO NRAs/ITO under illumination intensity of 100 mWcm^{-2} in 0.1M Na_2SO_3 and 0.1M Na_2S electrolyte mixture 185

7.28 Photoconversion efficiency values as a function of applied voltage versus Ag/AgCl of : (a) bare ZnO NRAs/ITO; (b) Bi_2S_3/ZnO NRAs /ITO; (c) Ag_2S/ZnO NRAs/ITO; (d) Bi_2S_3/Ag_2S /ZnO NRAs/ITO under illumination intensity (100 mW cm^{-2}) in 0.1 M Na_2S and 0.1 M Na_2SO_3 electrolyte 186

7.29 Plot of photoconversion efficiency values versus of : bare ZnO NRAs /ITO; Bi_2S_3/ZnO NRAs/ITO; Ag_2S/ZnO NRAs/ITO; Bi_2S_3/Ag_2S /ZnO NRAs/ITO 187

LIST OF ABBREVIATIONS

NRs	Nanorods
NRAs	Nanorods Arrays
NPs	Nanoparticles
PEC	Photoelectrochemical
UV-Vis	Ultraviolet-visible spectroscopy
EDS	Energy Dispersive X-Ray Spectroscopy
XRD	X-ray diffraction
FE-SEM	Field Emission Scanning Electron Microscopy
XPS	X-ray photoelectron spectroscopy
TEM	Transmission Electron Microscopy
HR-TEM	High Resolution-Transmission Electron Microscopy
SAED	Selected Area Electron Diffraction
EELS	Electron Energy Loss Spectrometer
ITO	Indium Tin Oxide
E_g	Optical bandgap energy
C.B.	Conduction band
V.B.	Valence band
e	Electron
h	Hole
J_{ph}	Photocurrent density
V_{app}	Voltage applied
LSV	Linear Sweep Voltammetry
Red.	Redaction
Ox.	Oxidation
WE	Working electrode

CE	Counter electrode
RE	Reference electrode
HMTA	Hexamethylenetetramine
DEA	Diethanolamine
ED	Electrodeposition
CBD	Chemical bath deposition
SILAR	Successive ionic layer adsorption and reaction
DIW	Deionised water

CHAPTER 1

INTRODUCTION

1.1 Background of the Study

The main urgent energy issue is to concentrate on identifying the resources in the generation and supply of energy that can substitute fossil fuels to meet the world's tremendous energy consumption. Renewable energy resources such as geothermal and tidal power and other renewable energy resources possibilities like wind power, biofuels, hydropower, and solar energy should be considered as potential replacements by the turn of the century. Since the amount of energy usage almost parallels the rate of economic growth and private satisfaction, it is clear that humanity's survival at the current developmental rate will depend on appropriate and adequate energy accessibility. Current circumstances call for contamination-free and less costly sources of energy that can be sourced by harnessing solar energy (Islam et al., 2020) to avoid more crisis in the environment. The most attractive possibility is solar-based energy because it is available in abundance to the extent of ten thousand times the total annual energy use. Furthermore, it will also neither affect the equalisation of our planet's heat energy nor will it cause any contamination.

Several technologies have efficiently utillised the spectrum of visible light, namely photovoltaic (Mishra & Tiwari, 2020), photochemical, photoelectrochemical, and the photothermal cells (Manassen et al., 1976). A number of review articles (Ahmed & Dincer, 2019; Rattanawarinchai et al., 2018; Kumar et al., 2017) have been published in the field of photoelectrochemical conversion. For two to three decades, many attempts have been made with separate solar conversion systems. As a result of the emergence of the field of photoelectrochemistry, the connection between photovoltaic devices and electrochemical devices was established and consequential developments such as photoelectrochemical solar cells (PECs) were used to further strengthen the field (Li et al., 2013).

Among the above methods, photoelectrochemical cells have lately achieved popularity as an inexpensive technique to convert solar energy into chemical then electrical energy to achieve high conversion efficiency. Furthermore, one of the interesting study elements in this sector is the search for cost-effective materials for the photoelectrodes. Therefore, several attempts were made to increase the quality performance of the photoanode materials.

Currently, the study of semiconductor nanomaterials has been reinforced as a photoanode in photoelectrochemical cells and is growing rapidly. In addition, owing to their outstanding structural flexibility along with other appealing characteristics, metal oxide semiconductor nanomaterials have gained more attention. The metal oxide nanostructures achieve appealing characteristics due to their bulk, such as chemical sensing, photoelectrochemical efficiency, and photodetection, as well as characteristics associated with their highly anisotropic geometry and size confinement (Lu et al., 2006). The composites of novel and traditional characteristics with distinctive nanostructure impacts make the investigation of novel metal oxide nanostructures a quiet remarkable topic in research and development from both an essential and a wide-ranging viewpoint. Due to its distinctive features, simple crystallisation at low temperature, elevated electron mobility, its wide optoelectronic applications, Zinc oxide (ZnO) has received significant recognition among distinct metal oxides. In particular, ZnO nanostructures (NSs) are deeply focused as they can be synthesised with distinct morphologies through various methods (Xu & Wang, 2011). Several decades of research have resulted in numerous methods of synthesising ZnO nanostructure as well as sensitizing ZnO. One of the most prevalent methods is the successive ionic layer adsorption and reaction (SILAR) method, hydrothermal (HT) technique and sol-gel spin coating (Holi et al., 2019; Nikam et al., 2015; Saleem et al., 2012).

The one-dimensional ZnO nanorods (NRAs) structure has been extensively studied, particularly among diversified nanostructures, as it offers a wide surface area. A large surface area is the main factor in achieving high effectiveness in PEC applications (Desai et al., 2020). ZnO properties such as, wide bandgap energy (3.37 eV), 60 meV strong exciton energy, 300 $cm^2\ v^{-1}.s^{-1}$ high electronic mobility that drawn the attention of the research community extend back to 1935, specifically in the application sector for low wavelength optoelectronics energy. Despite its many strengths over ZnO nanorods as a broad direct bandgap semiconductor, however ZnO's applications in optoelectronics are limited by the unavailability of visible light harvesting (Xu et al., 2020). ZnO nanorods should, therefore, be altered to enhance the absorption harvest in the visible light spectrum. This can be accomplished by sensitising the surface to adjust the comparatively large bandgap. Great efforts have been made through different methods, such as organic dye doping (Norton et al., 2004), synthesising heterostructure (Kumar et al., 2017), dye sensitisation (Kilic, 2019) and sensitisation by using narrow bandgap energy chalcogenide materials (Khot et al., 2015). Due to their strong absorption coefficient, high stability, flexible bandgap and great matching bandgap with visible range, narrow bandgap energy metal chalcogenide semiconductors have been selected among the afore-mentioned approaches (Zhao et al., 2019).

Since their implementation in optoelectronic systems, narrow bandgap metal chalcogenide are promising candidates for sensitising ZnO nanorods. Narrow bandgap energy metal chalcogenide semiconductors such as bismuth sulphide (Bi_2S_3) and silver sulphide (Ag_2S) could be appropriate photosensitisers for ZnO NRAs to manufacture photo-electrodes that can use both the characteristics of wide and narrow bandgap energy materials and enhance the hosting material's light-harvesting capability. Due to its narrow optical bandgap inset 1.3 ~1.7 eV and a wide range of electronic device applications, Bi_2S_3 was adopted as a reliable photosensitizer (Arumugam et al., 2018). Ag_2S is also appropriate for qualifying as a non-toxic, narrow bandgap energy of 0.9 ~1.05 eV which makes it an efficient photovoltaic semiconductor material (Holi et al., 2018). As a result, composite materials (i.e. small bandgap bases / metal oxide) based semiconductor nanofilms have become essential for enhancing the effectiveness of photoconversion due to their high conversion, electrolyte system stability, low-cost production, and flexibility. Due to their affordable synthesis and low used amount of starting materials, thin films nanomaterials are favoured, which implies large-scale manufacturing. It should be noted that the properties of photoelectrochemical cells (PECs) for nanocomposite materials can be significantly improved by (i) controlling the ZnO NRAs preparation condition to improve the aspect ratio to accommodate the photosensitiser; (ii) ZnO sensitisation with narrow band gap materials such as Bi_2S_3 and Ag_2S to increase its ability to absorb more visible light.

1.2 Problem Statement

ZnO is the most promising contender because of its high earth plenty, nontoxicity as well as exceptional physical and chemical features for diverse photovoltaic uses. Many of these applications have used thin film ZnO nanostructure which is considered an ideal alternative to the high costly single crystal, silicon-based photoelectrochemical cells. ZnO is a typical II–VI semiconductor compound with a hexagonal phase of wurtzite, which has excellent electronic and optical properties. This is expressed in its properties such as 3.37 eV wide bandgap energy and substantial 60 meV excitonic binding energy at room temperature compared to other materials with a wide bandgap energy such as TiO_2. However, ZnO's wide bandgap energy absorbs only a small portion of visible spectrum of light. Sensitising the surface of ZnO nanorods can increase the visible light harvesting. Sensitising the ZnO NRAs surface can be achieved with doping organic dyes, using nanocomposite materials, or doping with narrow bandgap materials. Since several sensitises involving organic dyes have been widely studied, inorganic metal chalcogenide with narrow bandgap energy values have gained significant attention among researchers owing to their excellent absorption over a wide wavelength range, great stability, adjustable bandgap, and high conversion efficiency. Numerous studies have indicated sensitization of ZnO nanorods employing inorganic chalcogenide semiconducting nanoparticles like CdS (Nikam et al., 2016), PbS (Li Xianchang et al., 2016), Ag_2S (Holi et al., 2018), Cu_2O (Messaoudi et al., 2015), CdSe (Nikam et al., 2018), and Bi_2S_3 (Velanganni et al., 2018) by employing various approaches which shows a range of possible uses and a remarkable enhancement in their outcomes compared to the intrinsic structure.

Among the metal chalcogenide narrow band materials described above, such as bismuth sulphide (Bi_2S_3) and silver sulphide (Ag_2S) can then be used efficiently to improve the photo response of ZnO NRAs. It is well known that both Bi_2S_3 and Ag_2S have suitable E_gs within the visible light spectrum and can be regarded as proper materials for enhancing the ZnO light harvesting. Therefore, their narrow bandgap energy may efficiently expand the ZnO absorption range from the UV region to the visible light spectrum region. Additionally, the two narrow band metal chalcogenides have been used to co-sensitise ZnO to enhance the alignment of the bandgaps reflecting significant improvement in optical and electrical properties. However, one of the most essential problems that can be faced when using sensitiser materials with narrow band gap energy, is the high rate of electron-hole pairs recombination caused by a strong exciton binding energy.

The literature review indicates that the performance of binary photoanodes of Bi_2S_3/ZnO and Ag_2S/ZnO fabricated by SILAR method needs more investigations to improve the ability of the photoconversion efficiency of PEC. Moreover, there is no report so far on deposition of the ternary construction of Bi_2S_3/Ag_2S/ZnO for photoelectrochemical applications. Hydrothermal approach and successive ionic layer adsorption and reaction (SILAR) method have been used for synthesis of ZnO NRAs and nanocomposite samples, respectively. The two methods are simple, inexpensive, low preparation temperature, controllable preparation parameters and eco-friendly, all of which encourage large industrial production. This study introduces an essential contribution for improving bandgap structure using binary, ternary nanocomposite for PECs application via simplified methods.

1.3 Study Objectives

In a world where natural resources are not abundant and our dependence on them continues to grow, great interest has always been shown in finding new technology that can support our demands without the consumption of non-renewable resources. One of the most promising areas is photovoltaic devices-photoelectrochemical cells. Semiconductor nanomaterials have drawn much attention as a promising candidate for the research and development of the highly converted photoelectrochemical cell. Nanocomposite semiconductors such as Bi_2S_3/ZnO, Ag_2S/ ZnO and Bi_2S_3/Ag_2S / ZnO have traditionally demonstrated significant flexibility in their fundamental features. Bi_2S_3 and Ag_2S nanomaterials have been extensively discussed due to their distinctive photoelectronic, photochemical and photocatalytic properties that are totally different from their bulk counterparts, their characteristics are critically dependent on the particle shape, size, and surface composition.

This research involves fundamental research on synthesis of nanostructure, surface modification and application of nano thin film semiconductors for clean and environmentally-friendly energy conversion.

This project aims to use two convenient low-cost techniques to synthesise binary heterostructured Bi_2S_3/ZnO/ITO, Ag_2S/ZnO/ITO, and ternary Bi_2S_3/Ag_2S/ZnO/ITO photoanode for photoelectrochemical applications. Simple and low-cost hydrothermal method has been used for fabricating ZnO NRAs while SILAR method has been used to deposit narrow band gap energy-based metal chalcogenides on ZnO NRAs. Moreover, increasing the aspect ratio of ZnO NRAs by adjusting the distribution of nucleation sites and controlling the temperature, the growth period is one of the imperative keys for high conversion efficiency. In addition, the morphological, compositional structure, optical features and photoelectrochemical performance of the electrodes have been researched carefully.

The clearly defined objectives of this research are:

1. To improve the surface area of the ZnO nanostructure layers via controlling the annealing temperature of ZnO NPs seed layer, controlling growth temperature and growth time of ZnO NRAs by using sol-gel spin coating technique and hydrothermal method, respectively.
2. To enhance ZnO nanostructure's structural, optical and photoelectrochemical characteristics by depositing Bi_2S_3 and Ag_2S as binary nanocomposite heterostructure into ZnO using the SILAR technique and to characterise the optical, morphological and photoelectrochemical performance of binary photoanodes
3. To fabricate and characterise Bi_2S_3 and Ag_2S as co-sensitised ZnO nanorods to improve the alignment of bandgaps to achieve improved optical characteristics and photoelectrochemical efficiency.
4. To evaluate the photoconversion efficiencies of photoelectrochemical cells with different fabricated photoanodes ZnO NPs/ITO, ZnO NRAs/ITO, binary heterostructured Bi_2S_3/ZnO/ITO, Ag_2S/ZnO/ITO, and ternary heterostructured Bi_2S_3/Ag_2S/ZnO/ITO.

1.4 Significance of the Study

Global warming and climate change are aspects of great concern as we move further forward into the 21st century. As world energy consumption increases and fossil fuel reserves decline, clean and renewable energy sources have never been more demanded. Studies on renewable energy sources, which are plentiful, environmentally sustainable, renewable, and cost-effective, increased dramatically due to rising energy demand and limitations on existing energy sources such as coal, oil, and natural gas. Solar energy clearly shows the greatest promise represented by the three most prevalent sources of renewable energy. The sun radiates have sufficient energy over an hour to power the Earth for one year. A world map with horizontal solar irradiation globally shows that sunlight can power almost every country to meet their individual energy needs. The rapid increase in research of solar energy has generated some prominent trends in recent years. Effectiveness of the commercial panel has risen, while expenditure has decreased proportionately. Due to their streamlined production and high photoconversion efficiency, photoelectrochemical cells based on photosensitised narrow-band materials are considered one of the most important options for using abundant solar energy. This research would yield an important contribution to the ongoing search for ZnO nanostructure sensitisers in order to improve light harvesting for photoelectrochemical applications.

1.5 Scope of the Study

In this study, two different hierarchical hybrid materials are developed by simple successive ionic layer adsorption and reaction (SILAR) method and their morphological structures, optical and electrical properties effects on the photoelectrochemical cells performance are investigated extensively. Zinc oxide is used as a template for the growth of binary and ternary hierarchical nanostructures on ITO substrates. In all instances, the acquired heterostructure binary photoanode is fabricated through three basic steps: (i) preparation of high density ZnO nanoparticles seed layer via sol-gel spin coating; (ii) synthesising optimised well-aligned ZnO nanorod arrays using simplified hydrothermal method; (iii) photosensitising ZnO NRAs using narrow bandgap energy metal chalcogenides with SILAR technique. The motivation of this research is the investigating the effect of Bi_2S_3 and Ag_2S modifying the surface of ZnO NRAs on their performance as a photoanode in photoelectrochemical cells. Control of the production condition of Bi_2S_3/ZnO NRAs/ITO, Ag_2S/ZnO NRAs/ITO arrays such as SILAR cycle number, dipping time, cationic concentration, pH, and annealing temperature is essential to enhance the ability of photosensitised-ZnO NRAs to harvest visible light. This thesis is divided into eight chapters: Chapter one includes the research background, problem statement, and study objectives, followed by study significance, and then study scope, which concludes the chapter. Chapter two highlights the working principles of semiconductor electrodes in photoelectrochemical cells and related literature on methods of thin film synthesis heterostructure and characterization techniques. Chapter three outlines the methods and processes used in this study. All the fabrication procedures for ZnO NPs/ITO seed layer, ZnO NRAs/ITO arrays, binary heterostructure (Bi_2S_3/ZnO/ITO, Ag_2S/ZnO/ITO, and ternary structure) and several preparations adjusting variables are described and explained. Chapter four includes the data analysis and discussion of the findings and the outcomes of the experiments related to ZnO nanoparticles seed layers and ZnO NRAs. Chapter five and six include the data analysis and findings discussion of binary heterostructured photoanode which are Bi_2S_3/ZnO NRAs and Ag_2S/ZnO NRAs/ITO, respectively. While chapter seven includes the data analysis and discussion of results of the ternary heterostructure Bi_2S_3/Ag_2S/ZnO NRAs/ITO. The comparison between the plain ZnO NRAs, binary and ternary nanocomposite photoanode has been presented in chapter seven too. Chapter eight presents the conclusions drawn from the research and finally makes recommendations for further related research.

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