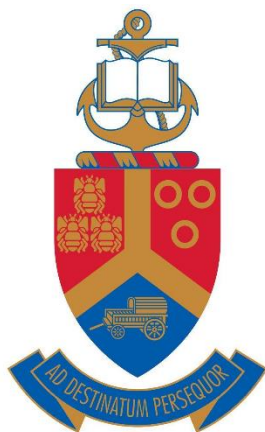


Synthesis and characterization of nanostructured hematite for photoelectrochemical water splitting

By

Justine Sageka Nyarige



**Submitted in partial fulfilment of the requirements
for the degree**

**Doctor of Philosophy (PhD) in Physics
in the**

Faculty of Natural and Agricultural Sciences

Department of Physics

University of Pretoria

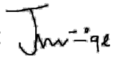
Supervisor: Prof MM Diale

Co-supervisor: Prof TPJ Krüger

February 2021

Declaration

I, **JUSTINE SAGEKA NYARIGE**, declare that the thesis, I hereby submit for the degree of Doctor of Philosophy (PhD) in Physics at the University of Pretoria, is my work and has not been submitted previously by me for a degree at this or any other institution. Any work of others that have been drawn upon is duly acknowledged in the text, and a list of references is presented at the end of every chapter.

Signature: 

Date: 15th February, 2021

Student number: 18389075

Abstract

This study aims to synthesize nanostructured hematite films using spray pyrolysis at different deposition temperatures. L-arginine was used to transform the irregular shaped nanoparticles to uniform nanospheres by chemical bath deposition at 90°C for 48 h. We also investigated the variation of L-arginine: iron precursor concentrations from 1:1 to 3:1, respectively. Likewise, hematite films doped with zinc (Zn), silver (Ag), and Zn/Ag were synthesized using spray pyrolysis. All the films were annealed at temperatures ranging from 450 to 500°C for complete hematite phase transformation.

The films were used as photoanodes in photoelectrochemical (PEC) water splitting experiments. X-ray diffraction confirmed the formation of the corundum hexagonal structure of hematite with $R\bar{3}C$ space group. Raman spectroscopy further confirmed the polycrystalline hematite symmetry with two E_g and five A_{1g} vibrational phonon modes. UV-Vis absorption showed a variation of absorbance with bandgaps that ranged from 2.10 to 1.90 eV. Scanning electron microscopy reported the shape transformation of nanoparticles to nanospheres that ranged in size from 6 to 100 nm. The study showed that the nanostructured films synthesized at temperatures of 430 and 400°C have the highest photocurrent densities of 6 and 1.52 μAcm^{-2} , respectively. There was an improvement of the photocurrent density from 6.4 to 10 μAcm^{-2} after the transformation of pristine irregularly shaped hematite nanoparticles to spherical hematite. However, on the variation of L-arginine: iron precursor concentrations, a photocurrent of 9.8 μAcm^{-2} was obtained for 3:1 sample. Also, an improvement of photocurrent from 17 to 89 μAcm^{-2} was observed for films prepared at 30 and 50 mM iron precursor concentration, respectively. In addition, there was a significant increase in the photocurrent density from 40 to 813 μAcm^{-2} for pristine and Zn/Ag hematite films, respectively. Ultrafast transient absorption spectroscopy was used to study the electron-hole recombination rates and lifetimes. The results indicated four lifetimes obtained from global analysis with a reduction in the electron-hole recombination rate in the femtosecond and nanosecond range, both for L-arginine/hematite and doped samples. From this study, we were able to prove that the nanostructured and doped hematite films had a longer charge carrier lifetime compared to bulk hematite.

List of Abbreviations

PEC	Photoelectrochemical
CBE	Conduction band edge
VBE	Valence Band Edge
AM	Air mass
STH	Solar-to-Hydrogen
SCLJ	Semiconductor liquid junction
NHE	Near hydrogen electrode
HER	Hydrogen evolution reaction
OER	Oxygen evolution reaction
NPs	Nanoparticles
EIS	Electrochemical impedance spectra
RHE	Reversible hydrogen electrode
LSV	Linear scan voltammetry
RE	Reference electrode
CE	Counter electrode
WE	Working electrode
M-S	Mott Schottky
OD	Optical density
GSB	Ground state bleach
SE	Stimulated emission
ESA	Excited state absorption

WLG	White light generation
SVD	Singular value decomposition
EADS	Evolution associated difference spectra
CBD	Chemical bath deposition
FTO	Fluorine doped tin oxide
XRD	X-ray diffraction
FE-SEM	Field Emission scanning electron microscopy
TEM	Transmission electron microscopy
EDS	Energy dispersive X-ray spectroscopy
NLC	National laser centre
CSIR	Council for scientific and industrial research
RMS	Root mean square
AFM	Atomic force microscopy
ΔA	Difference absorption
CPE	Constant phase element
RC	Resistance capacitance

Dedication

To my lovely wife Caroline Gesare my siblings David Atika, Dorca Atika, Verah Mocheche, Felix Oiroka, Slyviah Nyaboke, Enosh Mogire, Cliff Matagi, Lilian Rianga, James Rianga and Esther Kerubo for unwavering support and prayers.

&

To my lovely parents, Nathan Nyarige, Callen Nyanduko, Stephen Nyareru and Rebecca Moraa for ensuring that I achieve my ultimate dreams as a Scientist

Acknowledgements

I will like to thank the Almighty God for the protection and the strength that He bestowed upon me during this research period. Without His blessings, all things may not have worked as planned.

I will like to express my gratitude to Prof Mmantsae Moche Diale for her supervision and generous support, advice, and guidance, positive criticism and significant contribution to my PhD. She has been a pillar and more than a supervisor in my research. I thank her for her determination and encouragement all the time.

I thank Prof Tjaart P.J. Krüger for his co-supervision and positive criticism on my work. I also extend this gratitude to Prof Chis Theron, the Head of Physics Department. My sincere gratitude also goes to Dr Nolwazi Nombona for her generous support during our weekly group meetings and accessing the Department of Chemistry labs. I thank Chemistry Department for allowing me to use XRD and UV-Vis equipment. I will like to also thank the microscopy lab for help in SEM and EDX measurements.

I acknowledge the entire Clean and Green energy and Semiconductor research groups for their constructive criticism that made this work possible. The research group meeting organized by Prof Diale was of much help to me. I also thank all members of the Department of Physics for their encouragement and moral support.

Special thanks to the National Laser Centre (NLC) rental pool program for allowing us to make use of the ultrafast transient absorption spectroscopy (UTAS) at the Council for Scientific and Industrial Research (CSIR). Special thanks go to Dr Alexander Paradzah and Mr Justin Harrison for taking the time to teach me in on the principles of UTAS. I also thank the Laser Research Institute (LRI) at the University of Stellenbosch for organizing the African Laser Centre (ALC) student workshops.

I am thankful to my wife, Mrs Caroline Gesare Sageka and the entire family for the love, encouragement, motivation and patience during my entire period as a PhD student.

Finally, I would like to thank the African Laser Centre, University of Pretoria, the National Research Foundation (NRF) grant No#N0115/115463 (SARChI, M.D.), for the financial assistance, attending of local and international conferences.

Table of Contents

Declaration.....	ii
Abstract.....	iii
List of Abbreviations	iv
Dedication	vi
Acknowledgements	vii
List of Figures.....	xi
List of Tables	xvi
1 Introduction.....	1
1.1 Background and Motivation.....	1
1.2 Why L-arginine/hematite nanostructures	3
1.3 Aims and objectives	4
1.4 Structure of the thesis	5
References	6
2 Hematite nanostructures for photoelectrochemical water splitting	8
2.1 Introduction	8
2.2 Working principle of a PEC cell in water splitting	8
2.3 Properties of a suitable photoelectrode in PEC water splitting.....	9
2.4 Crystal structure of hematite	10
2.5 Structure of L-arginine	12
2.6 Nanostructured hematite in PEC water splitting.....	13
2.6.1 Hematite nanorods	14
2.6.2 Hematite nanotubes.....	16
2.6.3 Hematite nanowires	17
2.6.4 Hematite nanosheets	18
2.6.5 Hematite nanoflakes.....	19
2.6.6 Hematite nanoparticles.....	20
2.7 Synthesis and preparation methods of hematite nanostructures.....	24
2.7.1 Sol-Gel method	24
2.7.2 Hydrothermal technique.....	26
2.7.3 SILAR method	27
2.7.4 Dip coating method.....	28

2.7.5	Chemical Precipitation.....	30
2.7.6	Surfactant-controlled method.....	31
2.7.7	Electrochemical deposition method.....	31
2.7.8	Spray pyrolysis.....	33
	References	35
3	Experimental.....	42
3.1	Introduction	42
3.2	Substrate cleaning	42
3.3	Synthesis of hematite nanoparticles	42
3.4	Synthesis of L-arginine/hematite nanospheres.....	43
3.5	Synthesis of hematite nanoparticles at different precursor concentration and temperatures.	45
3.6	Zn, Ag and Zn/Ag surface-doped hematite nanostructures.....	45
3.7	Characterization of hematite nanostructures	46
3.7.1	X-ray diffraction	46
3.7.2	Raman spectroscopy	48
3.7.3	Scanning Electron Microscopy	49
3.7.4	Energy-dispersive X-ray Spectroscopy.....	50
3.7.5	Photoelectrochemical study	51
3.7.6	Ultraviolet-Visible (UV-VIS) spectroscopy	52
3.7.7	Ultrafast transient absorption spectroscopy	54
	References	56
4	Results and discussion.....	57
4.1	Introduction	57
4.2	Structural and optical properties of hematite and L-arginine/hematite nanostructures prepared by thermal spray pyrolysis	57
4.2.1	X-ray diffraction analysis	57
4.2.2	Raman spectroscopy	59
4.2.3	Variation of thickness with temperature.	61
4.2.4	Surface morphology and topography.....	62
4.2.5	Optical studies.....	66
4.2.6	Photocurrent measurements	68

4.3	Effects of L-arginine concentration on hematite nanostructures synthesized by spray pyrolysis and chemical bath deposition	69
4.3.1	Structural properties.....	69
4.3.2	Surface morphology and elemental analysis.....	74
4.3.3	Optical properties.....	77
4.3.4	Photocurrent density measurements	79
4.3.5	Ultrafast transient absorption spectroscopy	79
4.4	Influence of precursor concentration and deposition temperature on the photoactivity of hematite electrodes for water splitting.	87
4.4.1	X-ray diffraction	87
4.4.2	Optical properties.....	89
4.4.3	Surface morphology of hematite nanoparticles	90
4.4.4	Photocurrent measurements	93
4.4.5	Mott-Schottky analysis	94
4.5	Surface-doped hematite nanostructures for the efficient photoelectrochemical water splitting.....	96
4.5.1	Structural analysis.....	96
4.5.2	Surface morphology.....	98
4.5.3	Optical properties.....	98
4.5.4	Photocurrent-voltage (I-V) measurements.....	100
4.5.5	Electrochemical impedance measurements.	101
4.5.6	Ultrafast transient absorption spectroscopy	105
	References	114
5	Conclusion and future work	119
5.1	Conclusion.....	119
5.2	Future work	122
	Appendix	123
	List of publications	123

List of Figures

Figure 1.1.1. Conduction band edge (CBE) and valence band edge (VBE) of the semiconductors with respect to H^+/H_2O and O_2/H_2O redox potentials.	3
Figure 2.2.1. Schematic diagram of photoelectrochemical cell in use for water splitting.	9
Figure 2.4.1. Schematic crystal structure of (a) hexagonal unit cell structure, and (b) rhombohedral primitive cell structure. Red represents oxygen, while grey is iron [2].	11
Figure 2.4.2. Schematic diagram of the electronic structure of hematite.	12
Figure 2.5.1. Structure of L-arginine, characterised by a side chain comprised of a three-carbon straight chain ending with a guanidino group ($HNCNHNH_2$) shown on the right, covalently bound to the, amine (blue) and carboxylic (red) functional groups on the left.	12
Figure 2.6.1. Schematic structure of (i) bulk hematite, (ii) dendrites, (iii) nanoparticles, (iv) mesoporous, (v) nanorods, (vi) nanotubes, (vii) nanosheets, (viii) nanocones, and (ix) cauliflower nanostructured hematite [2].	13
Figure 2.7.1. Schematic diagram of sol-gel used in the preparation of hematite.	25
Figure 2.7.2. Schematic diagram of the hydrothermal method used in growing hematite nanorods.	27
Figure 2.7.3. Schematic diagram of the SILAR method.	28
Figure 2.7.4. Schematic diagram of a dip-coating method.	29
Figure 2.7.5. Schematic diagram of the chemical precipitation method.	30
Figure 2.7.6. Schematic diagram of the electrochemical deposition method.	32
Figure 3.3.1. The schematic diagram for thermal spray pyrolysis used for the preparation of hematite thin films at different deposition temperatures.	43
Figure 3.4.1. The schematic diagram for chemical bath deposition used to prepare L-arginine/hematite nanospheres at a temperature of $90^\circ C$ for 48 h.	44
Figure 3.6.1. The architecture of nanostructures of surface doped hematite ($\alpha-Fe_2O_3:Zn$, $\alpha-Fe_2O_3:Ag$, and $\alpha-Fe_2O_3:Zn/Ag$) thin films prepared by spray pyrolysis.	46
Figure 3.7.1. (a) Schematic arrangement of XRD components, (b) shows the XRD intensity versus 2θ angles spectra of the actual measurement obtained from our sample.	47
Figure 3.7.2. Schematic diagram of the Raman microspectroscopy setup.	49
Figure 3.7.3. Schematic diagram of a scanning electron microscope.	50

Figure 3.7.4. Schematic diagram of (a) a photoelectrochemical cell with three electrodes (CE, WE and RE) inserted in 1 M NaOH used as the electrolyte. Hematite was used as a WE, Ag/AgCl as RE, and a platinum mesh as the CE; (b) A VersaSTAT 3F potentiostat was used for electrochemical measurements; and (c) A computer with the VersaStudio program was used to run the experiments.	52
Figure 3.7.5. Schematic layout of the UV-Vis spectrophotometer.	53
Figure 3.7.6. Schematic diagram of the pump-probe spectroscopy setup at the NLC used in performing ultrafast experiments on hematite nanostructures.	54
Figure 4.2.1. X-ray diffraction patterns of (a) hematite nanostructured films synthesized using spray pyrolysis at different temperatures (280 - 430°C), (b) (104) and (110) phases of hematite.	58
Figure 4.2.2. Raman spectra of nanostructured hematite at temperatures of 280, 330, 380, and 430°C prepared by spray pyrolysis, L-Arg/ α -Fe ₂ O ₃ transformed using chemical bath deposition.	60
Figure 4.2.3 (b-f) 226 and 245 cm ⁻¹ deconvoluted Raman peaks of hematite NPs and L-Arg/ α -Fe ₂ O ₃ nanospheres, (g) Raman peak positioning of the ~225 and ~245 cm ⁻¹ modes vs. deposition temperature of hematite films.	61
Figure 4.2.4. (a) Cross-section micrograph images estimating the thickness using FE-SEM for hematite films deposited at 280, 330, 380, and 430°C using spray pyrolysis. A scale of 200 nm (red bars) was used, and hematite films thickness on the substrate were estimated using the purple lines by matching them with the scale bar, (b) thickness against temperature for hematite thin films at 45 s deposition time, 1.5 × 10 ⁵ Pa spray pressure, and 50 mM of concentration.	62
Figure 4.2.5. (a) FE-SEM images of hematite NPs prepared at temperatures of 280, 330, 380 and 430°C using spray pyrolysis at a precursor concentration of 50 mM, and 1.5 × 10 ⁵ Pa spray pressure, (b) a Gaussian fitting of hematite NPs distribution. (c) AFM RMS roughness of hematite NPs at 430°C. (d) as-deposited images of α -Fe ₂ O ₃ samples.	63
Figure 4.2.6. (a) FE-SEM image of hematite nanospheres using chemical bath deposition at 90°C for 48 h, (b) Gaussian fit of hematite nanosphere grain size distribution.	64
Figure 4.2.7. Heterogeneous nucleation of L-Arg/ α -Fe ₂ O ₃ nanospheres; (i) Hematite NPs synthesized using spray pyrolysis at 430°C, (ii) CBD of FeCl ₃ .6H ₂ O and L-arginine at a bath temperature of 90°C for 48 h, (iii) iron (III) hydroxide formed that underwent heterogeneous	

nucleation in step (iv). The nucleation is uniformly distributed, as shown in (v) to form hematite nanospheres in (vi). (b) AFM surface RMS roughness of as-prepared L-Arg/ α -Fe₂O₃ nanospheres.

..... 66

Figure 4.2.8. (a) The transmittance of hematite thin films synthesized at temperatures of 280, 330, 380, and 430°C by spray pyrolysis, (b) transmittance of L-Arg/ α -Fe₂O₃ prepared by CBD at a bath temperature of 90°C for 48 h, (c) a plot of $(\alpha h\nu)^{0.5}$ against $h\nu$ for hematite nanostructured films prepared at different temperatures (280 - 430°C. The inset presents the optical absorbance L-Arg/ α -Fe₂O₃ and pristine hematite thin films, (d) $(\alpha h\nu)^{0.5}$ versus $h\nu$ for L-Arg/ α -Fe₂O₃ and pristine thin films hematite (prepared at 430°C)..... 67

Figure 4.2.9. Photocurrent density of pristine hematite prepared at different temperatures (280-430°C) using spray pyrolysis, and L-Arg/ α -Fe₂O₃ thin film synthesized using CBD at a bath temperature of 90°C for 48 h, scan rate of 50 mVs⁻¹ and 1 M NaOH as the electrolyte. 68

Figure 4.3.1. XRD spectra of hematite nanoparticles prepared by CSP and L-Arg/Fe₂O₃ nanospheres synthesized by CBD for 1:1, 2:1, and 3:1 of L-arginine: FeCl₃.6H₂O, respectively.

..... 70

Figure 4.3.2. FWHM variation of pristine α -Fe₂O₃ and L-Arg/ α -Fe₂O₃ nanostructures of 1:1, 2:1 and 3:1 of L-arginine: FeCl₃.6H₂O respectively..... 71

Figure 4.3.3. Raman spectroscopy of hematite nanoparticles and L-Arg/ α -Fe₂O₃ nanospheres prepared at 1:1, 2:1, and 3:1 of L-arginine: FeCl₃.6H₂O precursor concentrations respectively. 73

Figure 4.3.4. Scanning electron microscopy images of L-Arg/ α -Fe₂O₃ nanoparticles synthesized by chemical bath deposition at 90°C for 48 h and spray pyrolysis (at 430°C). The EDX spectra showing the elemental composition is presented below the morphology of each sample..... 74

Figure 4.3.5. L-Arg/Fe₂O₃ and pristine Fe₂O₃ nanostructures' grain size distribution analysed using ImageJ. 75

Figure 4.3.6. Histogram by wt % of hematite nanoparticles and L-Arg/ α -Fe₂O₃ nanospheres as obtained from EDX..... 77

Figure 4.3.7. A variation of absorbance of pristine α -Fe₂O₃ and L-Arg/ α -Fe₂O₃ nanostructured thin films, prepared by both spray pyrolysis and chemical bath deposition. 78

Figure 4.3.8. Photocurrent density plots for L-Arg/ α -Fe₂O₃ and pristine α -Fe₂O₃ films. The scan rate of 0.05 Vs⁻¹ and 1 M of NaOH as the electrolyte..... 79

Figure 4.3.9. Ultrafast transient absorption spectra displayed as a two-dimensional colour map for (a) pristine α -Fe ₂ O ₃ , (b) 1:1, (c) 2:1 and (d) 3:1 of L-arginine: FeCl ₃ .6H ₂ O precursor concentrations, respectively. The samples were excited at 387.5 nm.	80
Figure 4.3.10. Difference absorption spectra at selected delay times for (a) pristine α -Fe ₂ O ₃ , (b) 1:1, (c) 2:1 and (d) 3:1 of L-arginine: FeCl ₃ .6H ₂ O precursor concentrations, respectively.	81
Figure 4.3.11. Kinetic traces at selected wavelengths (570, 600 and 620 nm) of (a) pristine α -Fe ₂ O ₃ (b) 1:1, (c) 2:1 and (d) 3:1 of L-arginine: FeCl ₃ .6H ₂ O precursor concentrations, respectively. The fitting was done between 1 and 100 ps.....	82
Figure 4.3.12. Evolution associated difference spectra with associated decay lifetimes obtained from global analysis using Glotaran software for (a) pristine α -Fe ₂ O ₃ , (b) 1:1, (c) 2:1 and (d) 3:1 of L-arginine: FeCl ₃ .6H ₂ O precursor concentrations, respectively.	85
Figure 4.4.1. X-ray diffraction patterns of hematite nanoparticles synthesized at different precursor concentration and deposition temperatures.....	87
Figure 4.4.2. Lattice constants, and crystallite sizes for hematite nanoparticles at different deposition temperatures (250, 340, 400°C) and precursor concentrations (30, 40, 50 mM). The inset in Figure 4.4.2 (a and b) shows the variation of crystallite sizes with concentrations and temperature, respectively	88
Figure 4.4.3. The absorption edge of hematite thin films at different (a) precursor concentrations, and (b) deposition temperatures using spray pyrolysis,. (b) Corresponding energy bandgaps of hematite thin films prepared by spray pyrolysis.	89
Figure 4.4.4. Scanning electron micrographs of hematite NPs deposited at different precursor concentrations and deposition temperatures.	91
Figure 4.4.5. Occurrence frequency of hematite NPs prepared at different temperatures and precursor concentrations.	92
Figure 4.4.6. Variation in grain sizes of hematite NPs for different (a) precursor concentrations, and (b) deposition temperatures.....	92
Figure 4.4.7. Photocurrent density curves for hematite thin films prepared at (a) different precursor concentration, and (b) different deposition temperatures. A 50 mVs ⁻¹ linear scan rate was used in the potential range of 0 to 1 V.	93

Figure 4.4.8. Mott-Schottky plots for nanostructured hematite films at different deposition temperature and precursor concentrations using a frequency of 10 kHz under dark measurements.	95
Figure 4.5.1. X-ray diffraction patterns of pristine α -Fe ₂ O ₃ , α -Fe ₂ O ₃ :Zn, α -Fe ₂ O ₃ :Ag, and α -Fe ₂ O ₃ :Zn/Ag thin films.	97
Figure 4.5.2. Surface morphology using SEM for pristine α -Fe ₂ O ₃ , α -Fe ₂ O ₃ :Zn, α -Fe ₂ O ₃ :Ag, and α -Fe ₂ O ₃ :Zn/Ag thin films.	98
Figure 4.5.3. Optical studies of (a) pristine α -Fe ₂ O ₃ , (b) α -Fe ₂ O ₃ :Zn, (c) α -Fe ₂ O ₃ :Ag, and (d) α -Fe ₂ O ₃ :Zn/Ag thin films.	99
Figure 4.5.4. Photocurrent-voltage measurements pristine α -Fe ₂ O ₃ , α -Fe ₂ O ₃ :Zn, α -Fe ₂ O ₃ :Ag, and α -Fe ₂ O ₃ :Zn/Ag thin films.	100
Figure 4.5.5. Mott-Schottky plots of pristine α -Fe ₂ O ₃ , α -Fe ₂ O ₃ :Zn, α -Fe ₂ O ₃ :Ag, and α -Fe ₂ O ₃ :Zn/Ag thin films, with a frequency of 10 kHz in the potential range between -0.2 and 0.5 V.	101
Figure 4.5.6. (a) Electrochemical impedance spectra of pristine α -Fe ₂ O ₃ , α -Fe ₂ O ₃ :Zn, α -Fe ₂ O ₃ :Ag, and α -Fe ₂ O ₃ :Zn/Ag thin films using 1 M NaOH electrolyte, with the inset showing the equivalent circuit, (b) the EIS Nyquist plot of the fitted and experimental results of pristine α -Fe ₂ O ₃ as obtained from EIS spectrum analyser.	103
Figure 4.5.7. Comparisons of the current densities at 1.23 V vs. RHE and 1.41 V vs. RHE and the donor densities of pristine α -Fe ₂ O ₃ , α -Fe ₂ O ₃ :Zn, α -Fe ₂ O ₃ :Ag, and α -Fe ₂ O ₃ :Zn/Ag photoanodes.	105
Figure 4.5.8. Two-dimensional colour map of pristine α -Fe ₂ O ₃ , α -Fe ₂ O ₃ :Zn, α -Fe ₂ O ₃ :Ag, and α -Fe ₂ O ₃ :Zn/Ag obtained from femtosecond transient absorption spectroscopy.	106
Figure 4.5.9. The difference in absorption at selected delay times for pristine, α -Fe ₂ O ₃ , α -Fe ₂ O ₃ :Zn, α -Fe ₂ O ₃ :Ag, and α -Fe ₂ O ₃ :Zn/Ag.	107
Figure 4.5.10. Kinetic traces at selected wavelengths (570, 600 and 620 nm) for pristine α -Fe ₂ O ₃ , α -Fe ₂ O ₃ :Zn, α -Fe ₂ O ₃ :Ag, and α -Fe ₂ O ₃ :Zn/Ag samples. The fitting was done between 1 and 100 ps.	108
Figure 4.5.11. Evolution associated difference spectra (EADS) with associated decay lifetimes for pristine α -Fe ₂ O ₃ , α -Fe ₂ O ₃ :Zn, α -Fe ₂ O ₃ :Ag, and α -Fe ₂ O ₃ :Zn/Ag samples shown with each spectrum's associated decay lifetime.	111

List of Tables

Table 4.2.1. Crystallite sizes and FWHM of hematite nanostructures synthesized by both spray pyrolysis and chemical bath deposition.	59
Table 4.3.1. Average crystallite sizes, dislocation densities, and micro-strains of pristine α -Fe ₂ O ₃ and L-Arg/ α -Fe ₂ O ₃ nanostructures.	72
Table 4.3.2. Summary of the lifetimes and amplitudes (A_1 and A_2) obtained from fitting the kinetic traces at 570, 600, and 620 nm of pristine (a) α -Fe ₂ O ₃ (b) 1:1, (c) 2:1, and (d) 3:1 of L-arginine: FeCl ₃ .6H ₂ O precursor concentrations, respectively.....	83
Table 4.3.3. Decay lifetimes of hematite nanostructures obtained from global analysis.....	86
Table 4.4.1. Summary of the structural, optical and electrical properties of the hematite nanostructures prepared at different temperatures and precursor concentrations.....	94
Table 4.4.2. Summary of the donor density and flat band potential of hematite nanostructures at different temperatures and precursor concentrations.....	96
Table 4.5.1. Equivalent circuit fitting values obtained from the fitted data for the pristine α -Fe ₂ O ₃ , α -Fe ₂ O ₃ :Zn, α -Fe ₂ O ₃ :Ag, and α -Fe ₂ O ₃ :Zn/Ag thin films.	104
Table 4.5.2. Summary of the lifetimes and amplitudes (A_1 and A_2) obtained from fitting the kinetic traces at 570, 600, and 620 nm for (a) pristine α -Fe ₂ O ₃ , (b) α -Fe ₂ O ₃ :Zn, (c) α -Fe ₂ O ₃ :Ag, and (d) α -Fe ₂ O ₃ :Zn/Ag samples.	108
Table 4.5.3. Summary of the photocurrents densities, lifetimes and donor densities of pristine α -Fe ₂ O ₃ , α -Fe ₂ O ₃ :Zn, α -Fe ₂ O ₃ :Ag, and α -Fe ₂ O ₃ :Zn/Ag samples.....	113

1 Introduction

1.1 Background and Motivation

The global energy demand has been on the rise due to increase in world population and industrialization. The annual energy consumption is estimated at 17.7 TW, with fossil fuels being the primary source, accounting for 87 % of the total energy produced [1, 2]. However, burning of fossils releases carbon dioxide and other greenhouse gases to the environment, leading to climate change. On the other hand, solar energy is free, abundant, renewable, clean and green. Solar energy irradiating the earth at any given moment is approximately 1.4×10^5 TW which is higher by four orders of magnitude of the global energy consumption [3]. Efficient use of solar energy will therefore help reduce the CO₂ emission and hence saving the environment. Solar energy can be converted to electrical energy and subsequently stored as a fuel in the form of hydrogen [4]. One of the approaches that have been used in the production of hydrogen is photoelectrochemical (PEC) water splitting. This technology produces hydrogen (H₂) and stores it in the form of chemical bonds using semiconductors [5].

The PEC water splitting was first reported by Fujishima and Honda in 1972 using crystalline TiO₂ [6]. However, low efficiency of 0.1 % was reported due to TiO₂ absorbing in the UV region of the electromagnetic spectrum. Since then, different semiconductors have been used as photoelectrodes for hydrogen production. This includes Cadmium sulfide (CdS), Copper(I)oxide (Cu₂O), Zinc oxide (ZnO), Gallium phosphate (GaP), Gallium Arsenide (GaAs), among others.

Cadmium sulfide (CdS) for instance has been observed as a suitable photocatalytic material due to its bandgap of 2.4 eV, valence band position of +1.7 V, and conduction band position of -0.7 V

[7]. Moreover, CdS has a long diffusion length of a micrometre range compared to other materials. However, the material suffers anodic photo corrosion due to photogeneration accumulation of the electrons and holes on the surface that results from the poor oxygen kinetics. Gallium Arsenide (GaAs) whose bandgap is 1.42 eV, has electron and hole mobilities of $9.2 \times 10^3 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ and $4.0 \times 10^2 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$, respectively. A high photocurrent has been reported from GaAs despite being less stable [8]. Copper(I)oxide (Cu_2O) has also been reported as a photocathode in PEC water splitting due to its direct bandgap of 2.0 eV and conduction band position of -1.1 V. However Cu_2O suffers electron-hole recombination and stability [9]. Gallium phosphide (GaP) can also be a suitable material since it absorbs in the visible region with a bandgap of 2.3 eV, but its instability limits the PEC applications [10]. Zinc oxide (ZnO) in the PEC water splitting has led to low photocurrent production despite having other desirable properties. This is due to the wide bandgap of 3.37 eV [11]. Other metal oxides that have been applied for PEC application includes tungsten trioxide (WO_3), bismuth vanadate (BiVO_4), and hematite ($\alpha\text{-Fe}_2\text{O}_3$) [12, 13].

Hematite, as a photoanode in PEC water splitting has attracted much attention compared to other semiconductors due to its desirable properties. The semiconductor has a favourable bandgap that ranges from 1.9 to 2.2 eV [14-16]. Additionally, the valence band edge straddles well the oxygen oxidation potential, initiating the oxygen evolution reaction without any bias [17]. Hematite can theoretically produce a photocurrent density of 12.6 mAcm^{-2} under AM 1.5 G illumination and solar-to-hydrogen (STH) of 15.5 % [18]. The semiconductor is stable in aqueous solutions and non-toxic. Besides, hematite is also abundant since oxygen and iron are the first and fourth most abundant elements on earth, respectively [19, 20]. Furthermore, the production of hematite does not require high-cost technology.

However, hematite has not been fully exploited for PEC production due to a few drawbacks. This includes short electron-hole diffusion length of 2 - 20 nm that leads to high recombination rates, poor electrical conductivity limiting the mobility of the charge carriers before recombination takes place, and poor oxygen evolution kinetics [21-23]. Figure 1.1.1 presents the band edge positions of some of the semiconductors used in PEC water splitting.

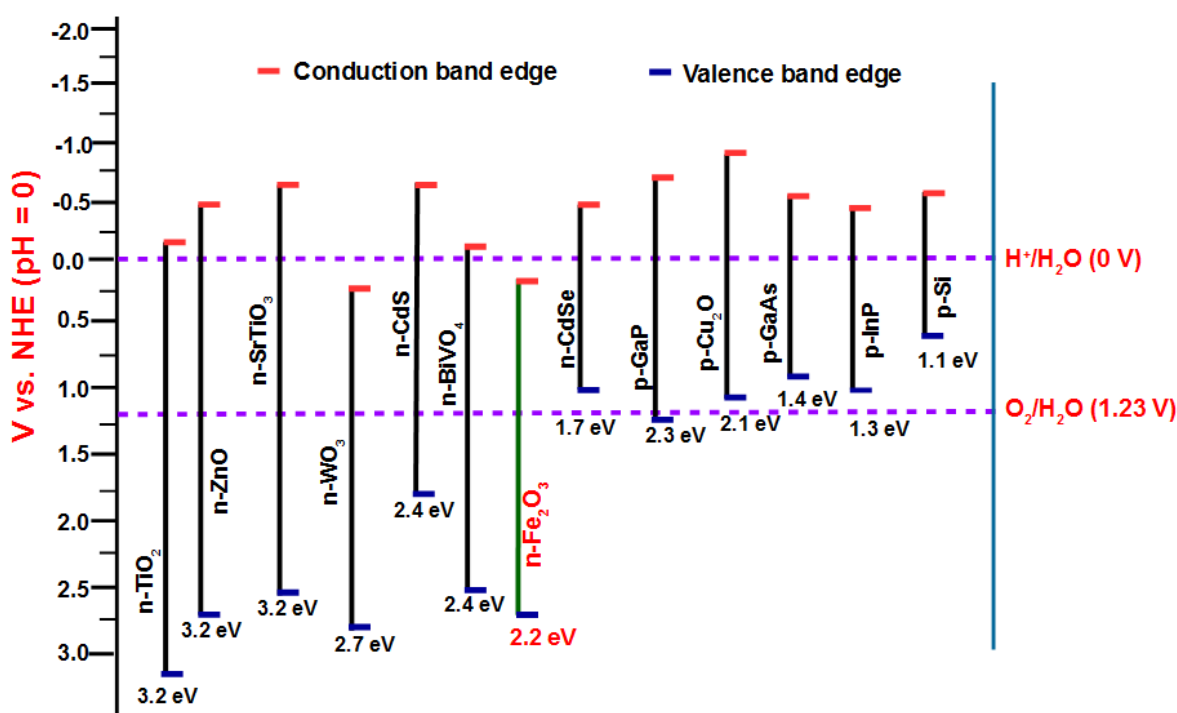


Figure 1.1.1. Conduction band edge (CBE) and valence band edge (VBE) of the semiconductors with respect to $\text{H}^+/\text{H}_2\text{O}$ and $\text{O}_2/\text{H}_2\text{O}$ redox potentials.

1.2 Why L-arginine/hematite nanostructures

Nanostructured hematite has been reported to improve the photocurrent production by enhancement of the surface area of the films. The reduction of the grain sizes of the nanostructures improves the carrier collection. However, some of the nanostructures like nanoparticles have been

reported to have high surface energy. Different approaches have been used for modification of these nanostructures. One of the ways that have brought more attention to the modification of nanostructured materials is by use of biominerals like L-arginine and L-alanine as capping agents. The capping agents reduce the agglomeration of the formed nanostructures and minimize surface energy [24]. L-arginine is an amino acid characterized by a positively charged guanidino group with three carbon chains. L-arginine was used in this study as a capping agent, in transforming the shape of the nanostructures. The motivation behind L-arginine was to obtain hematite nanostructures with a well-defined shape. Unlike other amino acids, L-arginine has strong basic properties that can be compared to that of sodium hydroxide. This has been discussed in detail in the subsequent chapters.

1.3 Aims and objectives

The thesis aims to synthesize and characterize pristine hematite, L-arginine/hematite, and doped hematite nanostructures for photoelectrochemical water splitting. The objectives are as follows:

To study the:

- i. Structural, optical and electrical properties of L-arginine/hematite nanostructures prepared by thermal spray pyrolysis
- ii. Effect of precursor concentrations on L-arginine/hematite nanostructures prepared by spray pyrolysis and chemical bath deposition.
- iii. Influence of deposition temperature and precursor concentration on the photoactivity of pristine hematite nanostructures.
- iv. Performance of zinc (Zn) doped, silver (Ag) doped, and Zn/Ag-doped hematite nanostructured films in photocurrent production.

- v. Recombination rates of pristine hematite, L-arginine/hematite, and doped hematite nanostructures using ultrafast transient absorption spectroscopy.

1.4 Structure of the thesis

This thesis is divided into five (5) chapters as follows:

Chapter 1 presents the motivation and background of the research, aim, and objectives and the structure of the thesis.

Chapter 2 reports the literature review on the working principle of a PEC cell, the structure of hematite and L-arginine, trends of hematite nanostructures, synthesis and preparation methods of hematite.

Chapter 3 reports on the experimental methods employed in the synthesis and characterization of pristine, doped, and L-arginine/hematite nanostructures for PEC applications.

Chapter 4 discusses the results obtained from the experiments of hematite nanostructures.

Chapter 5 concludes and recommends possible future work.

References

- [1] P.-Q. Wang, Y. Bai, P.-Y. Luo, J.-Y. Liu, Graphene–WO₃ nanobelt composite: Elevated conduction band toward photocatalytic reduction of CO₂ into hydrocarbon fuels, *Catalysis Communications*, 38 (2013) 82-85.
- [2] S. Saritaş, E. Turgut, M. Kundakci, B. Gürbulak, M. Yildirim, Compared with α -Fe₂O₃ and ZnXFe₃-XO₄ thin films grown by Chemical Spray Pyrolysis, *Int J Sens Netw Data Commun*, 6 (2017) 2.
- [3] A.A. Malek, M. Hasanuzzaman, N. Abd Rahim, Prospects, progress, challenges and policies for clean power generation from biomass resources, *Clean Technologies and Environmental Policy*, DOI (2020) 1-25.
- [4] A. Kay, I. Cesar, M. Grätzel, New benchmark for water photooxidation by nanostructured α -Fe₂O₃ films, *Journal of the American Chemical Society*, 128 (2006) 15714-15721.
- [5] A.J. Bard, M.A. Fox, Artificial photosynthesis: solar splitting of water to hydrogen and oxygen, *Accounts of Chemical Research*, 28 (1995) 141-145.
- [6] A. Fujishima, K. Honda, TiO₂ photoelectrochemistry and photocatalysis, *Nature*, 238 (1972) 37-38.
- [7] Y. Xu, W. Zhao, R. Xu, Y. Shi, B. Zhang, Synthesis of ultrathin CdS nanosheets as efficient visible-light-driven water splitting photocatalysts for hydrogen evolution, *Chemical Communications*, 49 (2013) 9803-9805.
- [8] D. Kang, J.L. Young, H. Lim, W.E. Klein, H. Chen, Y. Xi, B. Gai, T.G. Deutsch, J. Yoon, Printed assemblies of GaAs photoelectrodes with decoupled optical and reactive interfaces for unassisted solar water splitting, *Nature Energy*, 2 (2017) 17043.
- [9] A. Paracchino, N. Mathews, T. Hisatomi, M. Stefik, S.D. Tilley, M. Grätzel, Ultrathin films on copper (I) oxide water splitting photocathodes: a study on performance and stability, *Energy & Environmental Science*, 5 (2012) 8673-8681.
- [10] S. Hu, M.R. Shaner, J.A. Beardslee, M. Lichterman, B.S. Brunschwig, N.S. Lewis, Amorphous TiO₂ coatings stabilize Si, GaAs, and GaP photoanodes for efficient water oxidation, *Science*, 344 (2014) 1005-1009.
- [11] M. Liu, C.-Y. Nam, C.T. Black, J. Kamcev, L. Zhang, Enhancing water splitting activity and chemical stability of zinc oxide nanowire photoanodes with ultrathin titania shells, *The Journal of Physical Chemistry C*, 117 (2013) 13396-13402.
- [12] T.W. Kim, Y. Ping, G.A. Galli, K.-S. Choi, Simultaneous enhancements in photon absorption and charge transport of bismuth vanadate photoanodes for solar water splitting, *Nature communications*, 6 (2015) 1-10.
- [13] Z. Zhang, P. Wang, Highly stable copper oxide composite as an effective photocathode for water splitting via a facile electrochemical synthesis strategy, *Journal of Materials Chemistry*, 22 (2012) 2456-2464.
- [14] Y. Lin, G. Yuan, S. Sheehan, S. Zhou, D. Wang, Hematite-based solar water splitting: challenges and opportunities, *Energy & Environmental Science*, 4 (2011) 4862-4869.
- [15] A. Duret, M. Grätzel, Visible light-induced water oxidation on mesoscopic α -Fe₂O₃ films made by ultrasonic spray pyrolysis, *The Journal of Physical Chemistry B*, 109 (2005) 17184-17191.
- [16] C. Jorand Sartoretti, B.D. Alexander, R. Solarska, I.A. Rutkowska, J. Augustynski, R. Cerny, Photoelectrochemical oxidation of water at transparent ferric oxide film electrodes, *The Journal of Physical Chemistry B*, 109 (2005) 13685-13692.

- [17] T. Lindgren, L. Vayssieres, H. Wang, S.-E. Lindquist, Photo-oxidation of water at hematite electrodes, *Chemical Physics of Nanostructured Semiconductors*, DOI (2003) 83-110.
- [18] A.G. Tamirat, J. Rick, A.A. Dubale, W.-N. Su, B.-J. Hwang, Using hematite for photoelectrochemical water splitting: a review of current progress and challenges, *Nanoscale Horizons*, 1 (2016) 243-267.
- [19] C. Song, J. Zhang, Electrocatalytic oxygen reduction reaction, PEM fuel cell electrocatalysts and catalyst layers, Springer 2008, pp. 89-134.
- [20] C.E. Lankford, B.R. Byers, Bacterial assimilation of iron, *CRC Critical Reviews in Microbiology*, 2 (1973) 273-331.
- [21] H.-J. Ahn, M.-J. Kwak, J.-S. Lee, K.-Y. Yoon, J.-H. Jang, Nanoporous hematite structures to overcome short diffusion lengths in water splitting, *Journal of Materials Chemistry A*, 2 (2014) 19999-20003.
- [22] J. Glasscock, P. Barnes, I. Plumb, A. Bendavid, P. Martin, Structural, optical and electrical properties of undoped polycrystalline hematite thin films produced using filtered arc deposition, *Thin Solid Films*, 516 (2008) 1716-1724.
- [23] A.T. Paradzah, K.D. Maabong, H.M. Elnour, A. Singh, M. Diale, T.P. Krüger, Identification of Exciton–Exciton Annihilation in Hematite Thin Films, *The Journal of Physical Chemistry C*, 123 (2019) 18676-18684.
- [24] S. Talwatkar, Y. Tamgadge, A. Sunatkari, A. Gambhire, G. Muley, Amino acids (L-arginine and L-alanine) passivated CdS nanoparticles: synthesis of spherical hierarchical structure and nonlinear optical properties, *Solid state sciences*, 38 (2014) 42-48.

2 Hematite nanostructures for photoelectrochemical water splitting

2.1 Introduction

Nanostructured hematite materials have recently been used as photoanodes in the photoelectrochemical water splitting. The nanostructures have shown a significant improvement in photoactivity as compared to the bulk hematite. This chapter explains the working principle of a PEC cell, crystal structure of hematite and L-arginine, synthesis and preparation methods of hematite, different hematite nanostructures, and their applications in PEC water splitting.

2.2 Working principle of a PEC cell in water splitting

Water splitting is a chemical reaction, where hydrogen and oxygen gases are produced by breaking water molecules, using photoelectrochemical cell. This has been reported as a greener method of obtaining hydrogen gas compared to the steam reformation of natural gas [1]. The PEC cell, shown in Figure 2.2.1, requires a semiconductor (photoanode/photocathode) to be used as a working electrode, a reference, and counter electrodes. During the water splitting process, the absorption of light with an energy greater than the bandgap of the semiconductor anode/cathode takes place. This generates the electron-hole (e^- - h^+) pairs used as charge carriers. For n-type semiconductors in contact with a common electrolyte, a space charge depletion layer is formed at the semiconductor/liquid junction (SCLJ). The electrons and holes are then spatially separated due to the electric field created inside the space-charge region promoted by band-bending [2]. The holes (h^+) in the valence band diffuse and migrate to the SCLJ where oxygen evolution reaction occurs. Electrons (e^-) on the other hand are promoted into the conduction band of the semiconductor and drive away from the SCLJ. The e^- are thereafter transported to the anode towards the back contact and conveyed by the external circuit to the cathode (e.g platinum) where water reduction (hydrogen evolution reaction) takes place to produce H_2 [3]. From Eqn 2.2.1, for one molecule of oxygen gas to be produced, four holes are required. This is an uphill process, and the reaction is endoenergetic, with a Gibbs free energy, $\Delta G = 237.2 \text{ kJ mol}^{-1}$, for every mole of H_2O utilised. This is equivalent to the minimum potential of $E_{O_2/H_2O}^o = 1.23 \text{ V}$ vs. normal hydrogen electrode (NHE) at $pH = 0$. In

Eqn 2.2.2, a zero potential ($E_{H^+/H_2}^o = 0$ V) at NHE is needed for the reduction of water to hydrogen gas.

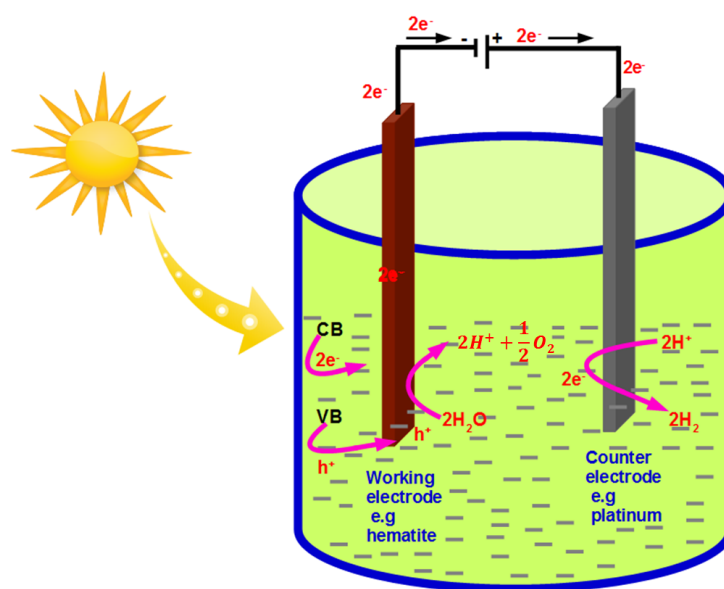


Figure 2.2.1. Schematic diagram of photoelectrochemical cell in use for water splitting.

2.3 Properties of a suitable photoelectrode in PEC water splitting

For the PEC water splitting to take place effectively, the photoelectrode should have the desirable properties. The material should have the bandgap that absorbs in the visible region. From the solar spectrum, ~5 % of sunlight consists of UV (300 - 400 nm), 43 % is the visible light (400 - 700 nm) and 52 % is the infrared region (700 - 2500 nm). Under the standard conditions, and based on Eqn 2.2, an appropriate semiconductor to drive this process should have a bandgap (E_g) > 1.23 eV for the conversion of H_2O into H_2 and O_2 [4]. The required energy bandgap for PEC water splitting using the photoelectrodes has been reported to range from 1.6 to 2.4 eV [5]. Another property for

a suitable photoelectrode is the efficient transportation of the separated charges. This reduces the electron-hole recombination from taking place before the PEC water splitting. The choice of this material, therefore, depends on properties like electron and hole mobility, intrinsic to the semiconductor and the crystallinity. The photoelectrode material should also be stable under alkaline conditions. Most of the materials are not stable under alkaline conditions, and these lead to more surface reaction kinetics, resulting in electron-hole recombination, hence limiting its application.

The valence band edge (VBE) and conduction band edge (CBE) must straddle the potentials for hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) to sufficiently take place [2]. For HER and OER to adequately take place without recombination, the charge carriers (e^- - h^+) must travel to the liquid junction, and the reaction has to take place on the surface of the semiconductor. The band edge positions of these materials will also determine the photo corrosion. For instance, if the valence band potential is below the anodic photo corrosion potential, then anodic corrosion will take place. At the same time, when the conduction band is above the photo corrosion potential, cathodic decomposition potential occurs. For example, materials like ZnO, CdS, and BiVO_4 whose actual decomposition depends on the pH can undergo anodic decomposition. In contrast, materials like TiO_2 cannot undergo the same process since it is dynamically stable. The cost and abundance of photoelectrode should also be one of the critical considerations. This will enhance an easy scale-up for the actual solar fuel devices.

2.4 Crystal structure of hematite

Hematite, a stable oxide of iron is an n-type semiconductor under ambient conditions. The structure of hematite has two formulas in a unit cell. This includes primitive rhombohedral and trigonal-hexagonal unit cells. Trigonal-hexagonal unit cell structure has the arrangement of oxygen and iron atoms, a space group, $R\bar{3}C(D_{3d}^6)$, with corundum ($\alpha\text{-Al}_2\text{O}_3$) [6]. The corresponding lattice parameters for this structure are $a = b = 0.5034$ nm, $c = 1.3750$ nm and each unit cell has six formula units [2]. Besides, the hexagonal closed packed (hcp) lattice along (001) direction contains the arrangement of cations (Fe^{3+}) and anions (O^{2-}) [7].

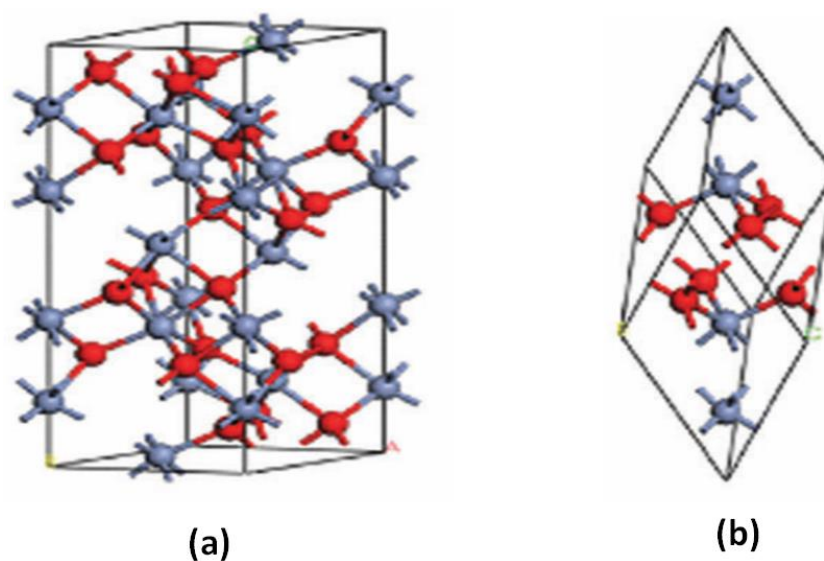


Figure 2.4.1. Schematic crystal structure of (a) hexagonal unit cell structure, and (b) rhombohedral primitive cell structure. Red represents oxygen, while grey is iron [2].

The method used to prepare hematite nanostructures influences the morphology and grain sizes. The grain size and temperature also affect the magnetic properties of hematite becoming weakly ferromagnetic at low temperatures and paramagnetic above 956 K. At 260 K (Morin Temperature, T_M), hematite undergoes a magnetic transition to antiferromagnetic [8]. Hematite suffers from poor conductivity which is in the order of $10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ at room temperature. This conductivity is associated with valence alternation of $\text{Fe}^{3+}/\text{Fe}^{2+}$ on spatially localized 3d orbitals, affecting the separation of charge efficiency. The poor conductivity is also due to polaron hopping [2, 9]. The optical absorption band of hematite ranges from the UV to the NIR regions. In terms of its electronic structure, hematite has O 2p and Fe 3d orbitals. Fe^{3+} experiences three types of optical transitions. This includes ligand-to-metal charge transfer transitions from O (2p), the non-bonding valence band, to Fe (3d) ligand filled orbitals, d-d transition, and simultaneous pair excitations from two adjacent Fe^{3+} cations occupying the sites [10, 11]. Hematite has both direct and indirect bandgaps. The optical properties of hematite can also be influenced by the preparation method due to variation of crystallinity. Figure 2.4.2 gives a summary of the electronic structure of hematite.

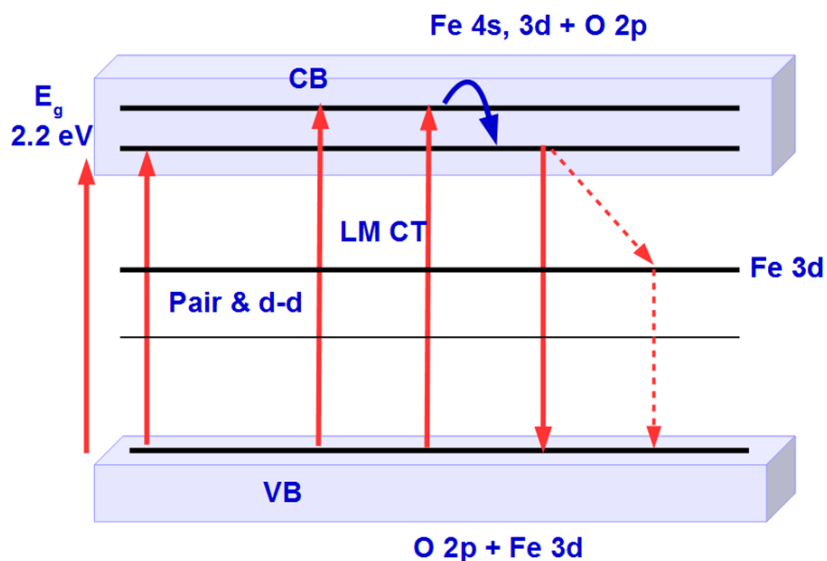


Figure 2.4.2. Schematic diagram of the electronic structure of hematite.

2.5 Structure of L-arginine

L-arginine (L-Arg) is one of the essential amino acids in biological organisms. The strong basicity of the guanidino group ($pK_a = 12.5$) of the L-Arg molecule enables it to perform various functions in living matter [12]. L-Arg has the chemical formula $C_6H_{14}N_4O_2$, as shown in Figure 2.5.1

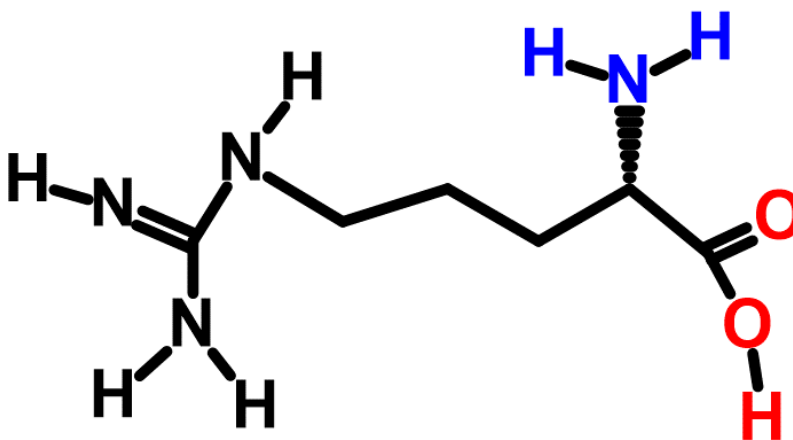


Figure 2.5.1. Structure of L-arginine, characterised by a side chain comprised of a three-carbon straight chain ending with a guanidino group ($HNCNHNH_2$) shown on the right, covalently bound to the, amine (blue) and carboxylic (red) functional groups on the left.

The symmetry of L-Arg has the lattice parameters $a = 0.976$ nm, $b = 1.602$ nm, $c = 0.558$ nm, $\beta = 98.1^\circ$, and a space group of $P2_1$ [13]. L-Arg has a melting point of 260°C , the boiling point of 368°C , it is highly soluble in water and slightly soluble in ethanol. Due to these properties, L-Arg has been used as a capping agent in the growth of various nanostructures like hematite and cadmium sulfide NPs for different applications [14, 15].

2.6 Nanostructured hematite in PEC water splitting

Nanostructuring is one of the approaches reported by various researchers to improve the efficiency of PEC water splitting, and encouraging results have been obtained. Nanostructured hematite such as nanoparticles, nanowires, nanotubes, nanobelts, urchinlike, elliptic superstructures, nanospheres, and nanorods have been reported, as shown in Figure 2.6.1[16-23].

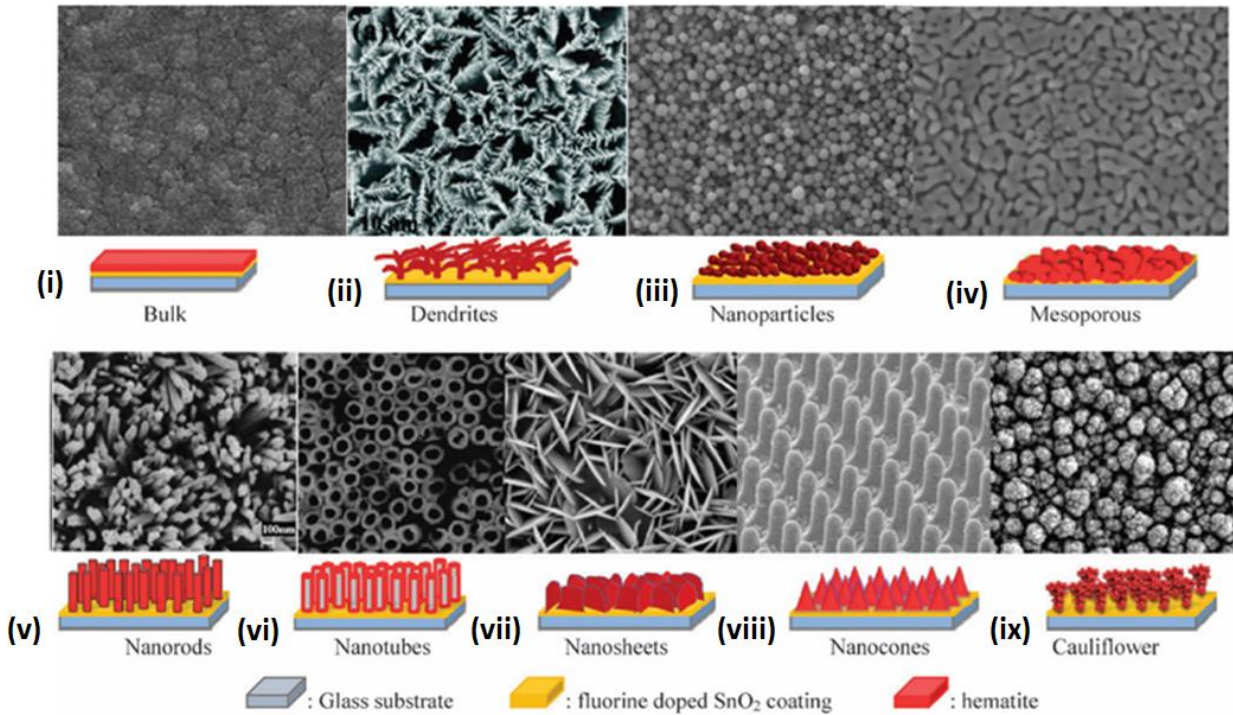


Figure 2.6.1. Schematic structure of (i) bulk hematite, (ii) dendrites, (iii) nanoparticles, (iv) mesoporous, (v) nanorods, (vi) nanotubes, (vii) nanosheets, (viii) nanocones, and (ix) cauliflower nanostructured hematite [2].

2.6.1 Hematite nanorods

Different researchers have reported on nanorods (NRs) for PEC applications. For example, Morris and co-workers reported the activation of hematite nanorods by controlling the annealing conditions using chemical bath deposition [24]. These nanorods had a diameter that ranged from 100 to 400 nm with an increase in PEC performance by 100 fold from what other researchers had reported. The improved PEC performance was a result of the change in the surface morphology and the addition of tin (Sn) from fluorine-doped tin oxide (F:SnO₂) that was used as the substrate. Sn, therefore, underwent surface doping at high annealing temperatures. In another study, Vitor and co-workers reported highly oriented nanorods that were synthesized by a single chemical route [25]. This involved a short reaction time at low temperatures. Their study obtained a photocurrent density of 0.9 mAcm⁻² at 0.4 V vs. Ag/AgCl. Besides, the produced nanorod films had a thickness of ~450 nm [25]. Gurudayal and co-workers, on the other hand, reported a study where they improved the efficiency of hematite nanorods by doping with manganese (Mn) using the hydrothermal method. From their results, there was a significant improvement of the current density of 1.6 mAcm⁻² at 1.23 V vs. RHE, which was 75 % higher than that of pristine hematite which had a photocurrent of 3.2 mAcm⁻² at 1.8 V vs. RHE. This change in photocurrent was due to the increase in the donor density and the suppression of the recombination of the electrons and holes [26]. Tantalum (Ta) doped hematite nanorods were also reported by Yanming and co-workers using the facile solution growth method [27]. The prepared photoanodes produced a current density of 0.53 mAcm⁻², 3.5 times higher than the pristine hematite. The increase in the photocurrent in their case was attributed to the increase in donor density as a result of the Ta doping.

Hematite NRs doped with titanium (Ti) have been reported to increase the band bending and carrier density [28]. The nanorod films prepared exhibited a high photocurrent of 2.28 mAcm⁻² at 1.23 V vs. RHE and 4.18 mAcm⁻² at 1.70 V vs. RHE. Besides, the α -Fe₂O₃:Ti produced a steady current for 3 h that ranged from 1.9 to 2.2 mAcm⁻² in a strongly alkaline solution [28]. Degao and co-workers have reported vertically aligned hematite nanorods with high crystallinity [29]. This was achieved by employing antimony doped tin oxide nanoparticles on the FTO substrate for the vertical growth of the nanorods. A current density of 2.12 mAcm⁻² at 1.23 V vs. RHE and 3.34 mAcm⁻² at 1.5 V vs. RHE was obtained from these nanorods, which is one of the highest reported

photocurrents of unmodified hematite nanorods [29]. The vertical nanorods were also reported by Chee and co-workers. The group also reported core-shell hematite nanorods prepared by both spray pyrolysis and chemical bath deposition. The photoactivity was observed to be 1.2 mAcm^{-2} at 1.23 V vs. RHE, which was twice that of pristine hematite [30].

In another study, atomic layer deposition was used to grow ultrathin TiO_2 on hematite nanorods prepared by the hydrothermal technique [31]. The samples were annealed at 650°C and the results showed an improvement in the current density of 1.9 mAcm^{-2} at 1.23 V vs. RHE, and 2.5 mAcm^{-2} at 1.8 V vs. RHE [31]. From the electrochemical impedance spectra (EIS) results, it was further shown that surface charge mediated transfer existed at the electrolyte/semiconductor interface, leading to an improvement in the current density [31]. In another study, Shaohua and co-workers reported on the modification of hematite nanorods by surface doping using silver (Ag). The higher photoelectrochemical performance was observed on the $\text{Fe}_2\text{O}_3/\text{Ag}_x\text{Fe}_{2-x}\text{O}_3$ as compared to the pristine samples [32]. In addition, there was an increase in incident-photon-to-current efficiency (IPCE) from 2.2 to 8.8 % at 1.23 V vs. RHE for 400 nm. The improved photocurrent performance was due to the increase in the surface oxidation reaction kinetics resulting from the Ag surface doping on hematite nanorods [32].

Hematite nanorods that have been co-doped with Ruthenium (Ru) using the doctor blade method have been reported by Xueli and co-workers [33]. The samples were annealed in air at 700°C . From this study, a current density of 5.7 mAcm^{-2} at 1.23 V vs. RHE and high IPCE with an onset potential of anodic photocurrent of 0.7 V vs. RHE. These improvements were a result of the high carrier concentration and mobility from the Ru doping that reduced the surface defects which act as recombination centres for the electrons and holes generated [33]. Recently, Wang and co-workers reported an improvement in the photocurrent production of hematite nanorods by monodoping with Sn and co-doping with Cobalt (Co) [34]. Their results revealed that Sn monodoping produced a photocurrent density of 0.93 mAcm^{-2} at 1.23 V vs. RHE under 1 sun illumination (A.M 1.5 G) while the co-doping further improved the photocurrent to 1.25 mAcm^{-2} at 1.23 V vs. RHE. There was also an observed cathodic shift of $\sim 140 \text{ mV}$ for the co-doped photoanode from $\sim 100 \text{ mV}$ for the monodoped sample [34]. This improvement in photocurrent density of the co-doped and monodoped samples was due to an increase in the carrier density resulting from Sn doping. At

the same time, surface kinetics of the oxygen reaction was improved by Cobalt co-doping on the hematite nanorods [34].

2.6.2 Hematite nanotubes

Hematite nanotubes (NTs) are one-dimensional (1D) nanostructures and are promising photoanode materials that have shown some significant improvement in photocurrent density. These nanotubes have been explored by different researchers. Zhongai's research group has reported hematite nanotubes prepared by a two-step electrochemical anodization method [35]. The NTs produced had a thickness of 2 μm , 40 nm pore diameter, and 10 nm wall thickness. Under the illumination of 1 sun (A.M 1.5 G), maximum photoconversion efficiencies of 0.51 % and 0.60 % were obtained at 0.3 V. These NTs also showed a significant PEC performance under illumination [35]. Nanotubular anodized hematite photoanodes have also been reported by Chong and co-workers [36]. Their research found that the iron foil substrate purity used to fabricate these nanotubes and nanoporous structure using the electrochemical anodization approach affect the performance [36]. Moreover, impurities like manganese (Mn) and thermal thickness affect the PEC performance. The morphology of these NTs was also affected by the presence of Mn.

Mao's research group presented a comparative study of the synthesized nanorods and nanotubes [37]. An electrochemical method was used to prepare the vertically aligned nanostructures using a gold (Au) substrate. From their results, a better photoresponse and enhanced photocurrent of the NTs in comparison to NRs were obtained [37]. Besides, the onset potential shifted negatively, and better charge transfer was observed on the NTs compared to NRs from the EIS measurements. Potentiostatic anodization of the iron foil method was also used in the synthesis of hematite NTs [38]. The NTs produced were vertically oriented with a pore diameter of 30 - 80 nm and 10 nm thickness [38]. There was an increase in photocurrent density with a change in bath temperature. Schebler and co-workers reported the growth of hematite NTs using ultrasound-assisted anodization of iron substrates. The obtained NTs had a diameter range of 40 - 50 nm and 20 - 30 nm thickness [19]. These photoelectrodes obtained a maximum IPCE value in the range of 350 and 375 nm, with 45 % obtained at 375 nm [19].

In another study, Mushove and co-workers reported hematite NTs synthesized by chemical anodization of iron foil. From the results, there was an increase of the IPCE at 350 nm by a factor

of 3 for the wavelike NTs compared to those of single-layered ones. The IPCE increment was also dependent on the surface area of the electrochemical. Mohapatra's research group also reported electrochemical anodization of hematite NTs. From their results, there was a high charge transport that was ~40 - 50 times higher than for nanoparticles. An increase in the charge transport was a result of the ultrathin NTs that ranged between 5 - 7 nm thickness and 2 - 3 μm in length. This led to an enhanced photocurrent density of the NTs compared to nanoparticles [39].

2.6.3 Hematite nanowires

Nanowires (NWs) have also been reported by different researchers in the enhancement of photocurrent density by increasing the diffusion length before charge recombination takes place. Ling and co-workers reported hematite nanowires prepared by sintering akaganeite in the air at 550°C for 2 h [40]. Hematite NW produced the highest photocurrent of 3.37 mAcm^{-2} at 1.50 V vs. RHE. The photocurrent enhancement was due to an increase in the donor density resulting from V_o (Fe^{2+}) formation. This creation of V_o was due to the presence of chlorine and an oxygen-deficient environment during the sintering process [40]. Franking and co-workers, on the other hand, reported hematite NWs that were prepared by thermal oxidation of air. The NWs were later doped with Ti and zirconium (Zr). Their results showed an improvement in the photocurrent, and this was attributed to the Ti doping that changed the electronic structure of the surface [41]. A two-step annealing process reported by Ling and co-workers has shown an improvement in the photocurrent [42]. In their study, pure nitrogen gas (N_2) at 350°C was used for annealing $\beta\text{-FeOOH}$ nanowires synthesized using the hydrothermal method. This led to the formation of magnetite, which was later converted to hematite in air. The change in phase of hematite from magnetite led to an improvement in donor density increasing electrical conductivity. The NWs annealed at 350°C produced higher photocurrent than those annealed at 550°C. Significantly, there was a three-fold increase in photocurrent when the NWs were doped with Sn for films annealed at 350°C [42]. In another study, nickel oxide (NiO) nanosheets were used to cover hematite NWs [43]. The NiO/ $\alpha\text{-Fe}_2\text{O}_3$ nanosheets enhanced the photocurrent by 43.5 % to that of undoped hematite due to proton reduction. Pristine hematite produced a current density of 2.3 μAcm^{-2} , while NiO/ $\alpha\text{-Fe}_2\text{O}_3$ reported 3.3 μAcm^{-2} at 1.23 V vs. RHE [43]. Li and co-workers have reported nanostructured hematite NWs that were treated using fire, followed by cobalt-phosphate (Co-Pi) co-catalyst. The results showed a photocurrent of 2.63 mAcm^{-2} at 1.23 V vs. RHE, that was stable and constant for 10 h [44].

Another study conducted by Tang and co-workers reported a multi-layered NWs that used indium doped tin oxide (ITO) as the substrate, with the architecture of ITO/Fe₂O₃/Fe₂TiO₅/FeNiOOH. The NWs reported an improvement in the photocurrent production from 0.205 to 2.20 mAcm⁻² at 1.23 V vs. RHE. The improvement in the photocurrent was due to atomic addition of Fe₂TiO₅ that regulated the surface states [18]. Recently, a study by Urbain and co-workers have reported hematite NWs coated with Fe₂TiO₅, previously reported by Tang and co-workers using ITO as the substrate. Besides, the NWs were decorated by FeNiOOH nanodots, producing a tandem approach photoelectrode. This tandem device showed an improvement in solar-to-hydrogen (STH) by 27 % and a prolonged photocurrent of 4.6 mAcm⁻² for 28 h [45].

2.6.4 Hematite nanosheets

Hematite nanosheets are 2D nanostructures that have been explored in the improvement of the PEC performance. For example, Liu and co-workers have reported hematite nanosheets doped with Germanium (Ge) using laser ablation. From their results, it was found that circular nanosheets with a thickness that ranged between 10 and 200 nm were formed, while a 30 - 40 nm thickness was obtained for 5 at % doped nanosheets. The doping further reduced the E_g and improvement in the PEC performance [46]. Besides, the group also reported hematite nanosheets in another study that were vertically aligned to the FTO substrate using the hydrothermal method. Ge doped nanosheets had a thickness of < 10 nm with (001) preferred orientation. A current density of 1.4 mAcm⁻² at 1.23 V vs. RHE, which was 50 times more than for pristine hematite was produced [47]. Chemical vapour deposition (CVD) was used to prepare FeOCl nanosheets using FTO as the substrate [48]. The FeOCl nanosheets were then converted to hematite nanosheets by annealing at high temperature. These photoelectrodes recorded a high photocurrent density of 0.33 mAcm⁻² at 1.23 V vs. RHE to that of pristine hematite which produced only 0.088 mAcm⁻² at 1.23 V vs. RHE. Peerakiatkhajohn and co-workers, on the other hand, reported hematite nanosheets prepared by the anodization method and thereafter modified with Co-Pi and Ag nanoparticles [49]. The photoanodes were able to produce a current density of 4.68 mAcm⁻² at 1.23 V vs. RHE, which corresponds to 0.55 % STH. The enhancement in the current density was due to an improvement in the light-harvesting which led to more charge transfer taking place, and this was a result of Ag NPs. Besides, the electron-hole recombination was reduced by the Co-Pi catalyst [49].

In another study conducted by Ji and co-workers, ferrihydrite nanosheets which were vertically aligned to the FTO and grown using one-step solvothermal methods were reported. These nanosheets had a thickness of 10 and 40 nm branch length [50]. Upon annealing the ferrihydrite nanosheets at 550°C, they were successfully converted to hematite nanosheets and later doped with Ti. The Ti:Fe₂O₃ reported a current density of 1.79 mAcm⁻² at 1.6 V vs. RHE. Additionally, there was an increase in donor density and charge transfer due to Ti doping. Xie and co-workers reported Ti:Fe₂O₃ decorated by cadmium sulphide NPs. Just like the previous study of Ji and co-workers, there was an improvement in the conductivity of hematite through Ti doping. Besides, charge separation was enhanced by the addition of CdS NPs, leading to a 6-fold increase in the photocurrent density to that of undoped hematite at 0.2 V vs. Ag/AgCl. There was also a cathodic shift in the onset potential to 500 mV [51].

In another attempt to improve the PEC performance of hematite nanosheets, indium ion (I³⁺) was used as a dopant [52]. The treatment of the nanosheets using I³⁺ increased the performance of these photoelectrodes 2.6 times to that of pristine hematite at 1.23 V vs. RHE. The enhancement of the current density was a result of higher absorption of light due to an increase in the surface area. Besides, the treatment led to an increase in donor density, charge separation, and transfer [52]. Bu and co-workers have also recently reported amorphous cerium (Ce) phosphate (Ce_xPO₄) on phosphorous doped hematite (P-Fe₂O₃) [53]. A Ce_xPO₄ co-catalyst was used to enhance kinetic reactions for oxygen and reduce electron-hole recombination. From their results, a photocurrent density of more than 1.24 mAcm⁻² at 1.23 V vs. RHE, that was 3.5 times and 1.4 times higher than the pristine nanosheets and P-Fe₂O₃ respectively.

2.6.5 Hematite nanoflakes

Ultrathin hematite nanoflakes (NFs) have been reported to improve the PEC performance. For example, hematite NFs doped with Sn were reported by Wang and co-workers. The results showed that annealing the NFs at 1000°C for 10 s led to the production of a photocurrent of 1.1 mAcm⁻² at 1.23 V vs. RHE, with a maximum of 1.6 mAcm⁻² at 1.60 V vs. RHE [54]. The maintenance of the morphology by fast direct heating led to the current enhancement. Rajendran and co-workers in their study used the hydrothermal method to prepare vertically aligned NFs. The NFs annealed at 300°C reported a higher photocurrent performance of 2 mAcm⁻² at 2.2 V vs. RHE and reduction in flat band potential than those annealed at 600°C [55]. In another research done by Wang and

co-workers, hematite NFs were decorated with gold (Au) NPs. This led to a higher photocurrent of 2.0 mAcm^{-2} at 1.6 V vs. RHE and a cathodic shift of the onset potential to 0.6 V. This increase was due to the Au NPs that increased the optical absorption by acting as plasmonic photosensitizers [56].

There was a morphological transformation of hematite NRs to hematite NFs using electrochemical induction that was reported by Liu and co-workers. The NFs had an average diameter of 100 nm and 10 nm thickness. Additionally, there was an increase in the surface area of the NFs from the NRs, further enhancing the charge separation. These NFs recorded a photocurrent that was three times higher than the NRs [57]. Wang and co-workers have reported platinum (Pt) and FeOOH nanolayers grown on hematite NFs. The photoanode produced a 2.0 mAcm^{-2} at 1.23 V vs. RHE and 3.2 mAcm^{-2} at 1.5 V vs. RHE that was an improvement from the pristine hematite. This improvement was attributed to the enhanced charge separation due to the suppression of the surface electron-hole recombination centres [58].

2.6.6 Hematite nanoparticles

A lot of studies have been carried out on hematite nanoparticles (NPs) as suitable photoanodes for PEC water splitting. However, the NPs, mesoporous, and dendrite hematite have been reported to suffer e^-h^+ recombination due to the large grain sizes obtained, limiting the transport of these charge carriers [2]. Different approaches have been made to counter this challenge. For example, Tilley and co-workers improved the PEC performance by modification of the surface of the nanostructured film using iridium oxide (IrO_2) as a catalyst [59]. Electrophoresis was used to deposit IrO_2 on the surface of hematite NPs. Their results showed an improvement in the onset potential from 1.0 to 0.8 V vs. RHE. This was also accompanied by the increase in the plateau current from 3.45 to 3.75 mAcm^{-2} and a photocurrent density of 3 mAcm^{-2} at 1.23 V vs. RHE under 1 sun irradiation [59]. In addition, there was over 50 % in the IPCE at 320 nm that was higher than the previously reported values (46 and 14 % at 320 nm).

Le Formal and co-workers reported improvement in the photoactivity of the hematite NPs prepared by spray pyrolysis. The samples had an average thickness of 12.3 nm and were able to absorb 25 % of incident light at 400 nm [60]. The group recorded a photocurrent density of 0.55 mAcm^{-2} at 1.4 V vs. RHE, with a 1.07 V vs. RHE onset potential. Besides, the absorbed-photon-to-current

efficiency (APCE) of 30 % at 350 nm and 1.43 V was also reported while untreated FTO substrate reported no photoactivity [60]. In another study, mesoporous NPs prepared using solution-based colloidal methods were reported by Sivula and co-workers. The nanostructured hematite films were able to realize a photocurrent density of 0.56 mAcm^{-2} at 1.23 V vs. RHE, under AM 1.5 G and 100 mWcm^{-2} [61]. Further, this photoactivity was improved by increasing the annealing temperature up to 800°C . This was due to the change in the optical properties where the absorption coefficient was raised by a factor of 2 as a result of the change in particle size [61]. The hydrothermal technique has been used to synthesize hematite nanocubes using L-arginine as the capping agent [15]. Bora and workers in the same study reported a photocurrent density of $218 \mu\text{Acm}^{-2}$ at 1.23 V vs. RHE. This improvement was mainly due to optical change and an increase in the surface area of the modified films [62].

In another study, Mao and co-workers reported the heterojunction where hematite NPs were grown on top of tungsten trioxide (WO_3). Their results showed an increase in the absorption from 480 to 600 nm when hematite NPs were coated on WO_3 film [63]. The hematite NPs/ WO_3 films were able to produce a maximum current density of 0.91 mAcm^{-2} at 1.23 V vs. RHE, with a solar-to-hydrogen (STH) conversion efficiency of 0.5 % at 0.6 V - 0.7 V vs. Pt [63].

Hisatomi and co-workers reported improvement of photocurrent performance of hematite NPs by using gallium oxide (Ga_2O_3) of 2 nm thickness as under layers [64]. The Ga_2O_3 underlayers were deposited by atomic layer deposition. The films were further doped with antimony tin oxide nanoparticles that showed further improvement in photocurrent production and a shift in the onset potential from 1.1 to 0.9 V vs. RHE for modified and unmodified hematite respectively [64]. Also, niobium pentaoxide (Nb_2O_5) as the underlayers were reported by Hisatomi's group to improve the performance of the photoanodes in PEC production. From this study, 40 % APCE at 1.43 V vs. RHE, with a current density of 1.16 mAcm^{-2} was obtained using Nb_2O_5 underlayers [65]. Colloidal electrophoretic deposition processing was used to produce hematite NPs as reported by Zong and co-workers. In their study, the hematite photoelectrodes recorded a high current density of 1.1 mAcm^{-2} at 1.23 V vs. RHE under the normal standard conditions [66].

Another study conducted by Du and co-workers reported a low turn-on voltage of 0.62 V vs. RHE that was achieved by the modification of hematite with NiFeO_x layer [67]. This reduction in potential was a result of the increase in the voltage without the decrease in efficiency. Marelli and

co-workers reported an improvement of the current density using hematite nanostructures synthesized by plasma-enhanced chemical vapour deposition (PE-CVD). The group obtained nanoplatelets with (001) orientation having a length that ranged between 350 - 750 nm, and 10 nm width for the nanobranches [68]. The photoelectrodes produced the highest photocurrent density of 1.39 mAcm^{-2} at 1.55 V vs. RHE. Yang and co-workers conducted another study by depositing an ultrathin layer of TiO_2 of $\sim 0.04 \text{ nm}$ on top of hematite NPs using atomic layer deposition (ALD) [69]. From their results, there was a reduction in the negative fluence by surface states due to the TiO_2 layer. Besides, there was a significant improvement in the current density for the passivated films. However, the electron-hole recombination of these films remained a considerable challenge to them.

To address the short electron-hole diffusion length of hematite, Yoon and co-workers coupled hematite NPs with 3D graphene inverse opal (3D-GIO) conducting substrate [70]. The low-temperature condition was used to grow the GIO on the FTO substrate. The nanostructured films composed of hematite/GIO produced a current density of 1.62 mAcm^{-2} at 1.5 V vs. RHE that was ~ 1.4 higher than the pristine hematite [70]. Also, there was a reduction in electron-hole and faster electron transfer from the EIS and IPCE plots. This resulted from the short distance created between the conduction electrode and active material. Shipu and co-workers have reported hematite NPs prepared by atmospheric chemical vapour deposition (APCVD) and doped using Ti. The films recorded a photocurrent density of 0.9 mAcm^{-2} at 0.6 V vs. SCE. The results further showed a higher photocurrent of Ti foil films to that of TiO_2 or FTO as substrate [71]. Han and workers, on the other hand, reported the cauliflowers with agglomerated nanoparticles using a laser ablation method. Their results revealed higher photocurrent, which was 34 % higher on the $\text{Ti:Fe}_2\text{O}_3\text{-SiO}_2$ films to that of $\text{Ti:Fe}_2\text{O}_3$. This improvement was due to the extensive longer electron lifetime and large surface area of the nanoparticles [72].

Xu and co-workers modified nanostructured hematite by using zinc (Zn) and cobalt (Co) double-layered hydroxide (LDH) [73]. The grain size of the nanoparticles produced ranged from 60 - 130 nm with some aggregations taking place. Their results revealed an improvement in the photocurrent from 1.27 mAcm^{-2} to 1.73 mAcm^{-2} at 1.5 V vs. RHE for pristine hematite and Zn-Co hematite, respectively [73]. This was 45 % improvement in comparison to the hematite samples doped with Ti and 36 % from the pristine hematite. This improvement could be due to the

introduction of the Zn-Co LDH shell. In another study, Kondofersky and co-workers reported the influence in scaffold doping density on hematite nanoparticles using SnO_2 and Sb as the dopants [74]. From their results, it was shown that $\text{SnO}_2\text{:Sb}$ produced the highest dark photocurrent characteristics. This could result from the highly conducting scaffold that led to oxygen evolution. However, these scaffolds ($\text{SnO}_2\text{:Sb}$) gave the same current density under illumination, an indication that $\text{SnO}_2\text{:Sb}$ can be a good absorber material [74]. Yu and co-workers reported a decrease in the applied potential to initiate the PEC reaction by using a nanostructured ferric oxyhydroxide (FeOOH) by photo-electrodeposition on the hematite surface [75]. A four times increase in photocurrent at 1.23 V vs. RHE and onset cathodically shifting to 140 mV in comparison with the pristine hematite was observed.

The research done by Dongyu and co-workers revealed a novel strategy of synthesizing the NiFeO_x and hematite doped with Ti using hydrothermal and spin-coating techniques, respectively. The EIS results showed lowest onset potential for 30 mM NiFe precursor treatment and an increase in the current density from 0.998 mAcm^{-2} for pristine hematite to 1.126 mAcm^{-2} at 1.23 V vs. RHE which was 12.7 % increment [76]. Moreover, due to NiFeO_x modification, there was an increase in the photocurrent since the overpotentials were lowered. For the development of high-performance photoelectrodes, nanopores were incorporated into the large hematite single-crystal sizes reported by Wang and co-workers [77]. These films were able to produce a photocurrent density of 0.61 mAcm^{-2} at 1.23 V vs. RHE under AM 1.5 G illumination, and this was 20 times higher than those of solid crystals. The improvement of the photocurrent was also due to enhanced charge separation and high light absorption [77].

A research conducted by Yang and co-workers revealed that electron-hole recombination of nanostructured hematite could be suppressed by the acid treatment [78]. This was evidenced by the improvement in the charge separation that further led to an increase in the produced photocurrent. By use of the acid, the detrapping rate was increased leading to the minimization of the recombination of electrons and holes on the surface, and this was confirmed by transient absorption (TA) spectroscopy and transient photocurrent (TPC) measurements [78]. More recently, Primc and co-workers have reported the doping of hematite NPs with TiO_2 [79]. The samples were further doped with tantalum (Ta). This modification led to a photocurrent current density of 2.2 mAcm^{-2} at 1.23 V vs. RHE. This improvement in the current was due to the Ta

doping and formation of the blocking layer by the rutile $\text{TiO}_2\text{-Fe}_2\text{O}_3$ [79]. In another study, nanostructured hematite films were doped with sulphur (S). The doping led to the reduction of Fe^{3+} to Fe^{2+} , increasing the vacancy sites for oxygen. This enhanced the polaron hopping resulting from higher charge carrier mobility hence reducing the electron-hole recombination. These photoelectrodes led to the production of current density 4 times that of pristine hematite [80].

In a recent study, doping of titanium on the nanostructured hematite was reported by Diale's research group. Their results produced a photocurrent of 0.72 mAcm^{-2} at 1.23 V vs. RHE, 2 times higher than that of pristine hematite which had a 0.30 mAcm^{-2} at 1.23 V vs. RHE. The improvement of the photocurrent was attributed to charge separation enhancement resulting from Ti doping [81].

2.7 Synthesis and preparation methods of hematite nanostructures

For the last two decades or so, different methods have been used in the synthesis of nanostructured hematite. Synthesis of hematite involves mixing methods, temperature, concentration of the solutions, pH choice, and the rate of oxidation [82]. Growth, adsorption of impurities, aggregation, and nucleation determines the morphology of the particles. During synthesis, hematite is prepared by the transformation of another iron oxide precursor [83]. The method chosen for the synthesis of hematite, therefore, has a significant influence on their properties. Several techniques have been used for the solution-based synthesis of hematite nanostructures and colloids. Some of the synthesis and methods of preparation of hematite are explained in the following sub-sections.

2.7.1 Sol-Gel method

Sol-gel is one of the wet chemical processes used in colloidal dispersion synthesis of inorganic and organic materials. The method allows the good formation of metal oxides at low temperatures. Sol-gel involves the conversion of the metal alkoxide or metal precursors. The condition of the preparation, pH, ion source and nature of precursors gives the structure of nano oxides formed. Figure 2.7.1 presents a summary of the sol-gel method.

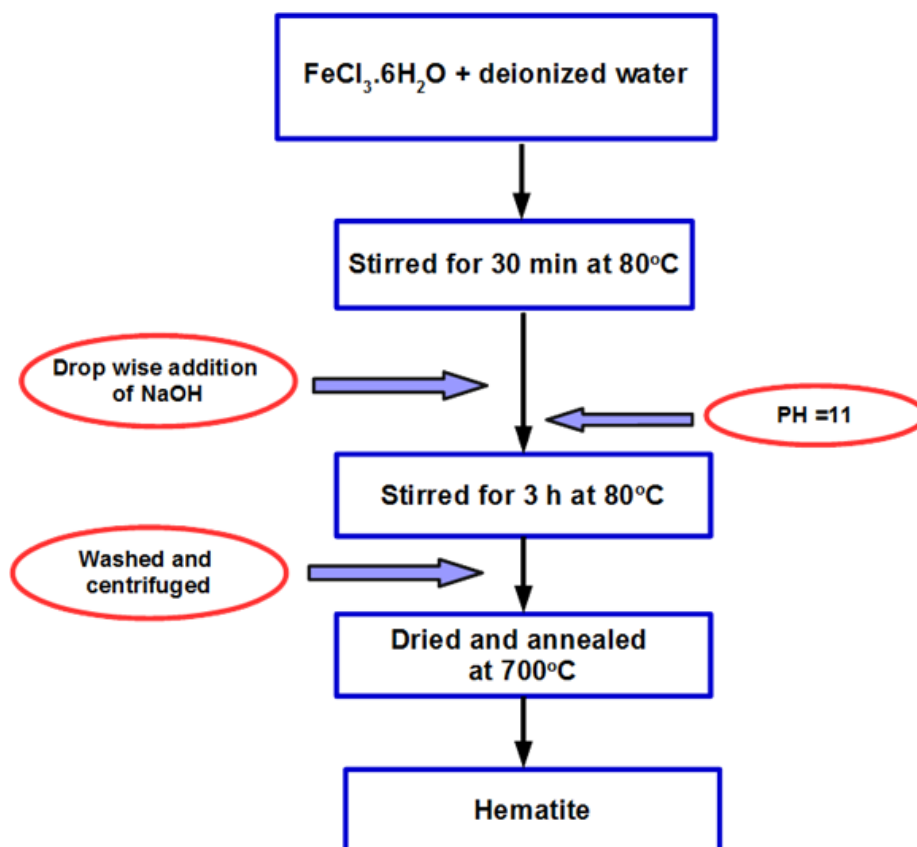


Figure 2.7.1. Schematic diagram of sol-gel used in the preparation of hematite

Some of the advantages of sol-gel technique include processing of materials with low temperature, materials made can be tailored for a given application by having a reasonable process control, and homogeneous solutions are achieved hence good production of materials can be obtained. Various parameters that influence the type of gel produced have been reported [84]. Sugimoto and co-workers reported the synthesis of hematite using the Sol-Gel technique by mixing FeCl_3 in NaOH to obtain ferric hydroxide gel that was used during condensation [85]. The gel was aged for 100°C for 8 days, and it obtained cubic $\alpha\text{-Fe}_2\text{O}_3$. A two-step phase transformation reaction involving precipitation of $\text{Fe}(\text{OH})_3$ gel to $\beta\text{-FeOOH}$ and finally to $\alpha\text{-Fe}_2\text{O}_3$ took place [85]. Hydrolysis of Fe^{3+} is the widely used method in the synthesis of iron oxyhydroxide, but several weeks are needed for the ageing of the Sol prepared using KOH or NaOH solutions and the ferric precursors [86]. During oxidation of $\alpha\text{-Fe}_2\text{O}_3$ from ferrous salt in the air, various oxides of iron can be obtained (Fe_3O_4 , $\gamma\text{-FeOOH}$, $\alpha\text{-FeOOH}$, and $\alpha\text{-Fe}_2\text{O}_3$), depending on the temperature of annealing. In another research, Domingo and co-workers reported, $\gamma\text{-FeOOH}$, and Fe_3O_4 , $\alpha\text{-FeOOH}$, with different

synthesis conditions and morphological properties. This obtained circular goethite after oxidation at temperatures of 60 and 80°C [82]. Bersani and co-workers, on the other hand, prepared iron oxide films using two Sol-Gel syntheses of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ that were studied using Raman spectroscopy. The films produced from this study revealed the maghemite ($\gamma\text{-Fe}_2\text{O}_3$) peaks that were annealed at 500°C to produce hematite ($\alpha\text{-Fe}_2\text{O}_3$) peaks [87]. Better homogeneity of the films was obtained as a result of the disappearance of maghemite peaks.

2.7.2 Hydrothermal technique

This technique involves the heterogeneous reaction of using mineralizers, temperature, and high pressure. Different oxides of iron can be obtained using hydrothermal. The type of oxide produced is dependent on the pH and temperature. For instance, Chistensen reported the use of amorphous iron (III) hydroxide in the production of goethite and hematite at different temperatures and pressure. At high pH (10.5 - 10.8), goethite was formed while hematite was obtained at low pH (0.8-2.6) from their results. At the higher temperature of $>150^\circ\text{C}$, $\alpha\text{-FeOOH}$ decomposed to $\alpha\text{-Fe}_2\text{O}_3$ [88]. Axe and co-workers investigated the rate of crystallization by thermal decomposition of amorphous iron (III) hydroxide to hematite and goethite [89]. Hydrolysis of aqueous FeCl_3 has been reported by Saric's group, with the main focus on effects of urotropin (hexamethylenetetramine, $\text{C}_6\text{H}_{12}\text{N}_4$) on the microstructural and chemical properties of iron oxide powders [90].

Solvothermal and hydrothermal synthesis of magnetite and hematite respectively have been reported by Liang and co-workers, through which hematite was prepared at different temperatures. From their findings, hematite prepared at a temperature of 420°C had a small particle size of 40 nm as compared to the one prepared at a temperature of 350°C that had 60 nm particle size [91]. In another study, hematite nanorods prepared by hydrogen peroxide and ferrous sulphate through the hydrothermal process was reported by Dong and co-workers. From their findings, a low reaction temperature of 150°C produced goethite and high reaction temperature of 200°C produced hematite [23]. Munawar and co-workers, on the other hand, reported the growth and characterization of hematite prepared by the hydrothermal method wherein, FeCl_3 and NH_4OH were synthesized at high temperatures. The concentration of Fe^{3+} (16 mM) and NH_4OH (40 mM) obtained good crystals of hematite with 100 nm particle size, with a reaction temperature of 120°C [92]. Figure 2.7.2 presents a schematic hydrothermal method.

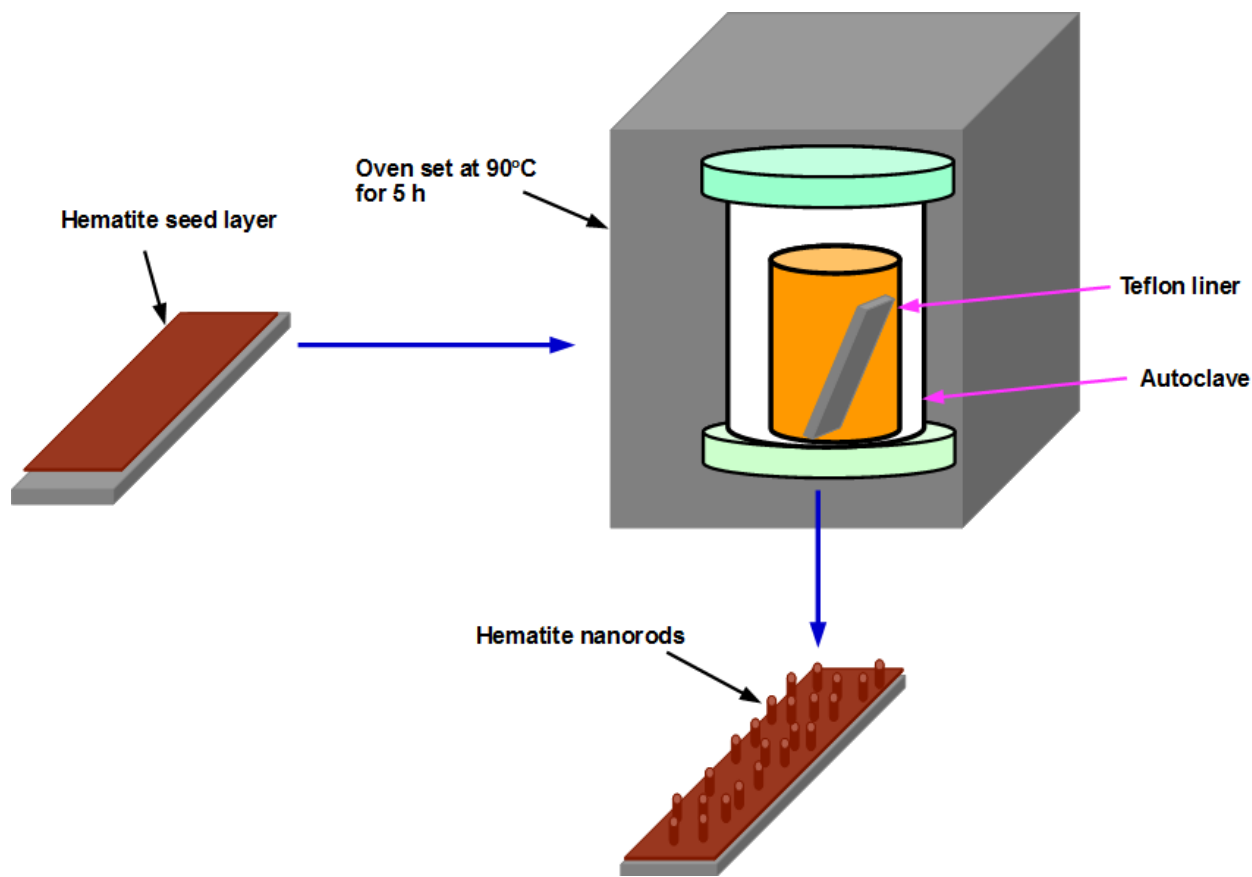


Figure 2.7.2. Schematic diagram of the hydrothermal method used in growing hematite nanorods.

2.7.3 SILAR method

SILAR is an abbreviation of Successive Ionic Layer Adsorption and Reaction. SILAR method is used for the adsorption and reaction from the precursor solutions and rinsing after every immersion or dipping with distilled water to avoid the reaction between the precursors (precipitation). The SILAR method is, therefore based on the adsorption and reaction of the surface at the substrate surface. In each reaction or adsorption, there is a rinsing step that enables the heterogeneous reaction between a solid phase and ions in the solution. The thickness of the layer grown during the SILAR is dependent on the number of cycles. One cycle forms a monolayer film. For the growth mechanisms, three critical steps are involved: Specific adsorption of the most strongly adsorbed ion in the compound to be grown by substrate immersion in a solution of cationic precursors is the first step. This is then followed by rinsing with distilled water to remove the

excess solution. Finally, the chemical reaction between the adsorbed anion and substrate takes place. This is illustrated in Figure 2.7.3.

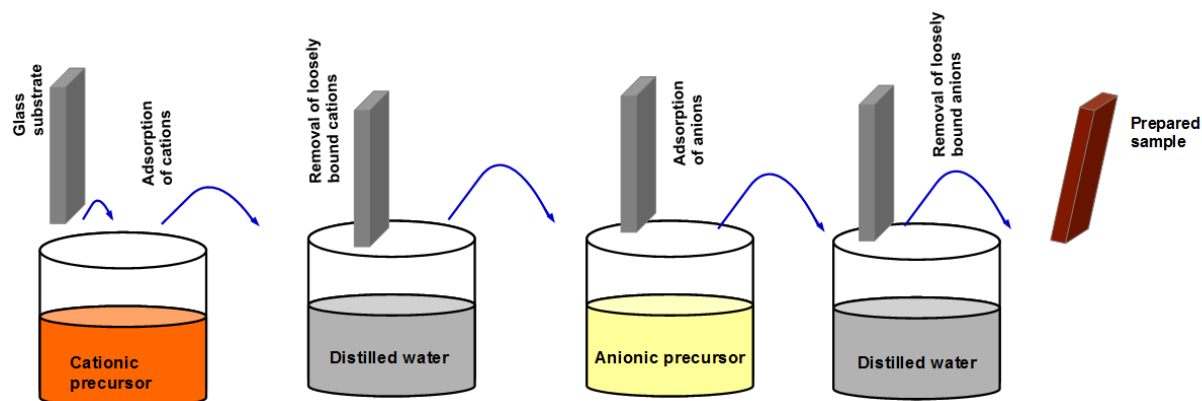


Figure 2.7.3. Schematic diagram of the SILAR method

Hematite films prepared by SILAR technique for PEC water-splitting have been reported by Abel and co-workers [93]. $\text{Fe}(\text{NO})_3 \cdot 9\text{H}_2\text{O}$ and NaOH were used as cations and anions respectively with deionized water for rinsing. The thickness of the prepared films increased as the number of cycles increased from 30 cycles to 120 cycles. The increase in the number of cycles and Ti doping led to a maximum current production of 10 mAcm^{-2} . Nanostructured hematite films grown by SILAR technique have been reported by Ubale and co-workers, using $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and NaOH as cations and anion precursors [94]. Films prepared by the SILAR showed crystalline nature when observed by X-ray diffraction. Film thickness increased from 156 to 251 nm, as the number of cycles was increased. This, in turn, led to a decrease in resistivity from 11.76×10^2 to $9.46 \times 10^2 \text{ } \Omega\text{cm}^{-1}$. Films further showed n-type conductivity with an increase in efficiency from 37.5 to 87.50 %.

2.7.4 Dip coating method

Dip coating is one of the simplest methods used in the preparation of thin films. It consists of a beaker with a solution of the precursor to be deposited. The substrate is dipped into the precursor container while varying the withdrawal speed, as shown in Figure 2.7.4.

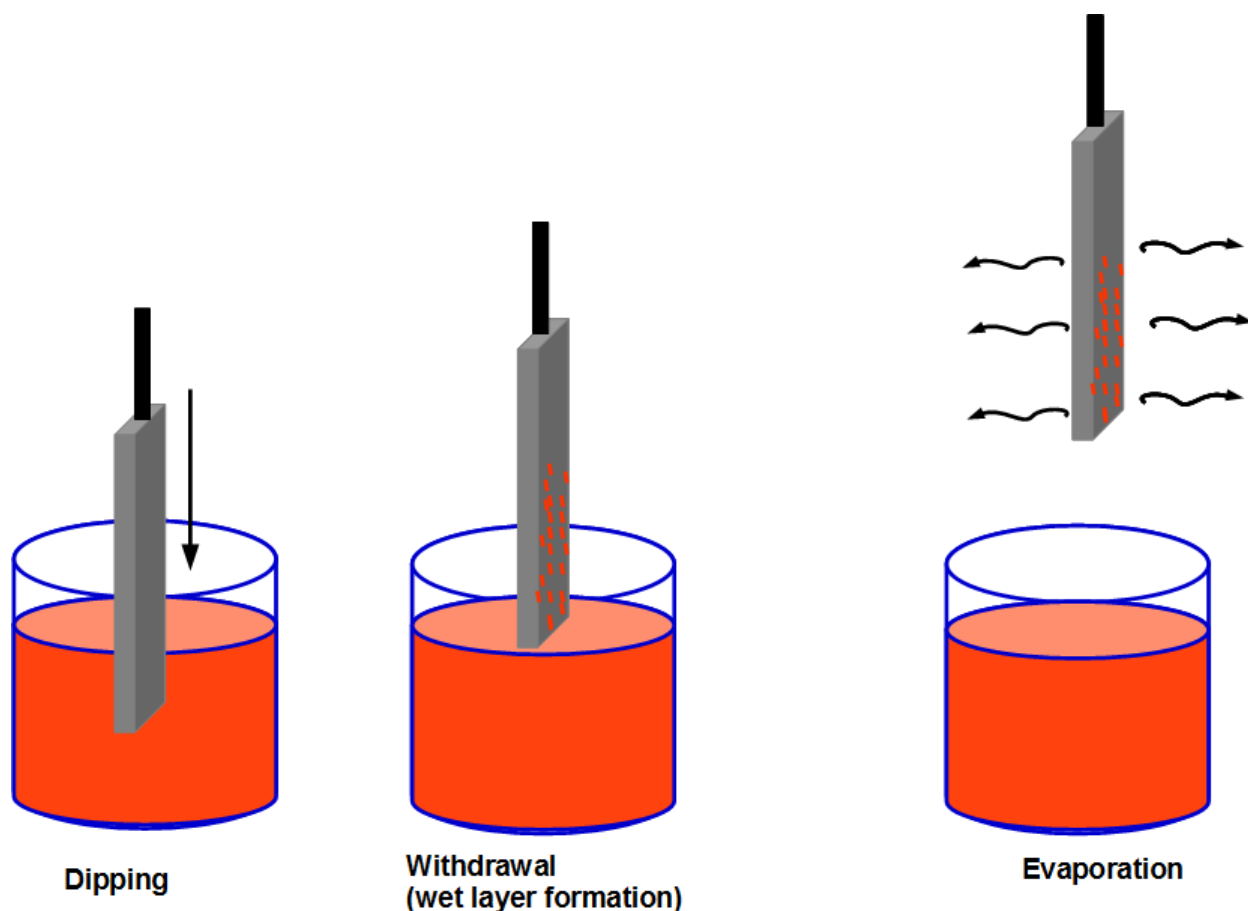


Figure 2.7.4. Schematic diagram of a dip-coating method

Hematite thin films have been prepared by the dip-coating method. For example, Orel and co-workers reported the preparation of hematite by dip coating from the sols of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and ammonium hydroxide precursors. The films prepared contained small particle sizes of $< 100 \text{ \AA}$ in diameter. These hematite films were used for electrochromism that was not experienced when the films were annealed at higher temperatures of 500°C . This was due to the formation of large grain sizes of $> 270 \text{ \AA}$. Preparation of hematite for water splitting by the dip-coating was reported by Bora and co-workers, using $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, oleic acid, and stearic acid ($\text{C}_{18}\text{H}_{36}\text{O}_2$) as the initial precursors. The films prepared were annealed at a temperature range of 300 and 900°C to obtain the hematite phase [95]. In another study, Hu's group reported the dip coating of Silicon doped hematite photoanodes. The precursors used were iron nitrate, oleic acid and orthosilicate (TEOS) that was used as a dispersion agent. The prepared samples were treated with heat at temperatures

between 500 and 760°C. This produced mesoporous films with a photocurrent density of $>1 \text{ mAcm}^{-2}$ and a roughness factor of 17 [96].

2.7.5 Chemical Precipitation

Precipitation is one of the simplest methods of obtaining hematite nanoparticles. The preparation of oxides of iron (FeOOH , Fe_3O_4 or $\alpha\text{-Fe}_2\text{O}_3$) is by forming a suspension used for ageing that is prepared by the addition of an alkali such as KOH . During the precipitation method, a large number of nanoparticles can be synthesized. The only challenge in precipitation is the control of the particle size. Precipitation involves two stages: Creation of supersaturation due to the concentration of the species and surface growth of the nuclei on the substrate through the diffusion process. Figure 2.7.5 summarizes the chemical precipitation method. During the synthesis of iron oxide, several parameters are varied to control the magnetic characteristics, size, and surface properties.

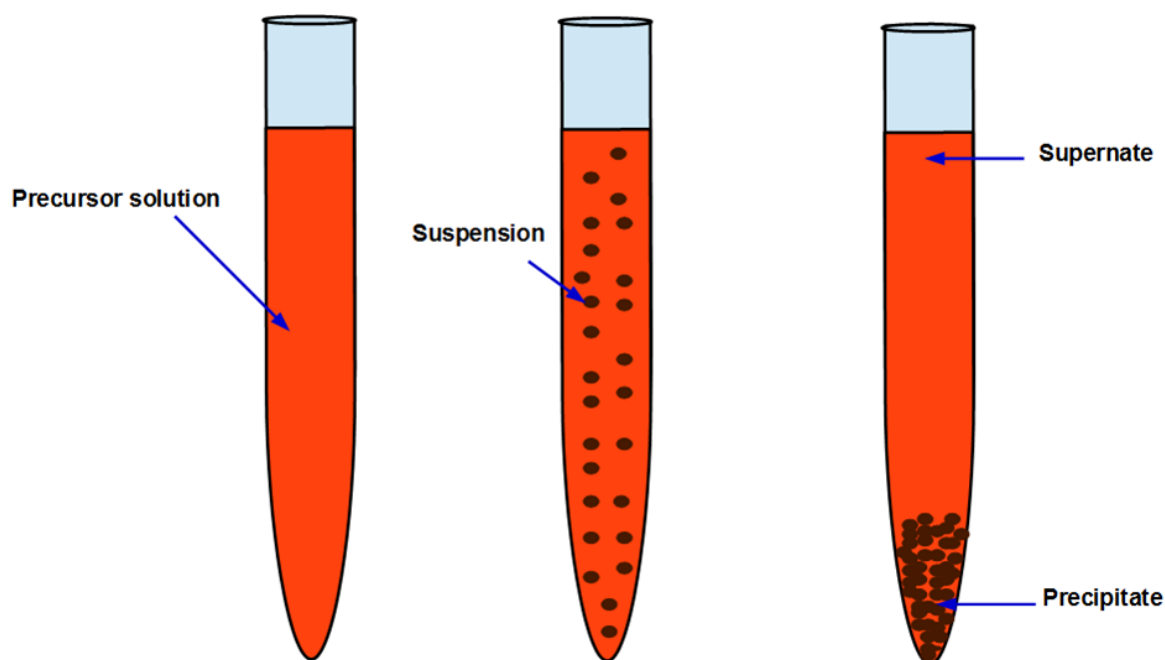


Figure 2.7.5. Schematic diagram of the chemical precipitation method.

Supermagnetic hematite films that were prepared using the precipitation method were first reported by Massart and co-workers. This was done using alkaline precipitation of FeCl_2 and FeCl_3 . In another study, Raming and co-workers have reported magnetic properties of nano-sized hematite using ferric salts dissolved in hydrochloric acid at a temperature of 100°C [97]. This was

done by dissolving $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ in double distilled water at room temperature followed by the addition of hydrochloric (HCl) acid as the temperature was increased to 100°C , with one-day heating. The solution was stirred and left for 1 week for the suspension to form. Centrifugation of the suspension was done to obtain a clear supernatant while the sediments were washed with distilled water. The steps were repeated until the required chloride without powder was obtained. This was later analysed using a transmission electron microscope (TEM) to obtain the size of the particles formed.

2.7.6 Surfactant-controlled method

The surfactant method uses neutral or charged template molecules. Controlled hydrolysis and precipitation of iron cations to obtain iron/surfactant arrays have been reported by Tolbert and co-workers [98]. The surfactants were obtained by mixing of iron (III) salt solution with sodium n-alkyl sulphates. This preparation was done at room temperature. The addition of ammonia to FeCl_3 with the mixing of sodium n-alkyl produced iron oxyhydroxide [99]. Inorganic ions like phosphate, chloride, or sulphate have a strong influence on particle shape and size while the morphology is affected by the long-chain surfactant templates. Liu and co-workers synthesized $\alpha\text{-Fe}_2\text{O}_3$ nanotubes and nanorods using different surfactants [100]. Further, the addition of butanol as a solvent and carbide as the base obtained quality products at a temperature of 150°C .

2.7.7 Electrochemical deposition method

Electrochemical is one of the environmentally friendly methods used in the preparation of thin films with no pollution. The technique, however, uses platinum as the electrode that is costly and cannot be used in aqueous solution. Figure 2.7.6 presents a simple electrochemical deposition.

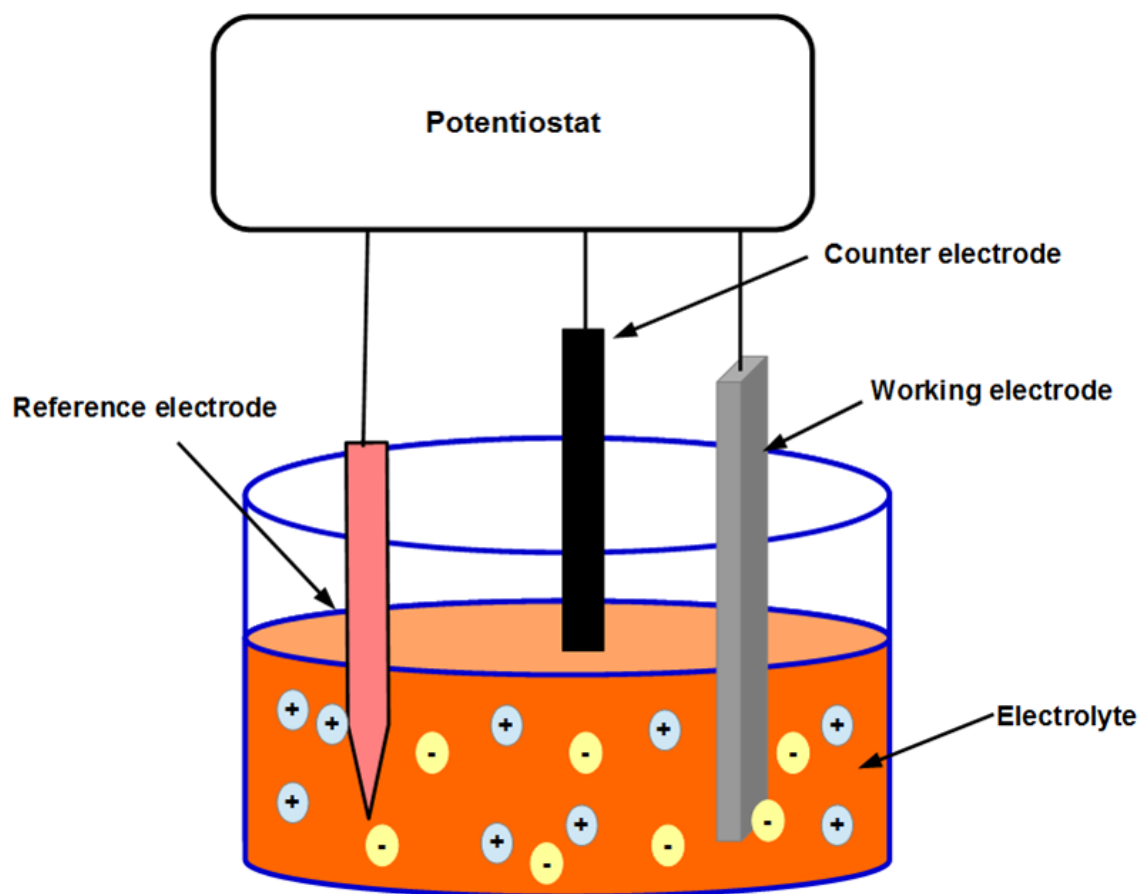


Figure 2.7.6. Schematic diagram of the electrochemical deposition method.

The nano-sized $\alpha\text{-Fe}_2\text{O}_3$ particles prepared by electrochemical deposition have been reported by Zhang and co-workers, where cathode and anode used were stainless steel plates. A two-step electrochemical anodization has been used to prepare hematite nanotube arrays using NH_4F as the organic electrolyte. The iron foils were first cleaned by degreasing using ethanol in the sonicator and distilled water for rinsing. Fe and Pt foils were used as the anode and cathode, respectively [35]. Electrochemical formation of iron oxyhydroxide $(\text{FeOH})_3$ has been reported by Kazemi and co-workers. Oxyhydroxide was then converted to hematite by thermal treatment at a temperature of 520°C in air. Three electrodes were used (platinum as the counter electrode, saturated calomel electrode as the reference electrode, and hematite on FTO as the working electrode). The films obtained showed nanostructured morphology, as observed by a scanning electron microscope [101]. Fauziatul and co-workers, on the other hand, reported the magnetic properties of hematite

prepared by electro-oxidation of iron in the water. The iron used in the electro-oxidation was prepared by electroplating of the iron plate in FeSO_4 solution [102].

2.7.8 Spray pyrolysis

Spray pyrolysis is one of the chemical methods used for the deposition of thin films. It involves spraying an aqueous solution, containing soluble salt of the components of the required compound on a heated glass/metal substrate. Spray pyrolysis consists of a solution container, substrate heater, temperature controller, and an atomizer [103]. For the decomposition of a metallic compound to occur, the precursor must be sprayed onto a pre-heated substrate at high temperatures. The droplets in the form of spray are carried out of the nozzle onto the pre-heated substrate by the carrier gas, that can either be compressed air or nitrogen gas. Among the advantages of this method include (i) the method is easy to set up, (ii) a solution to be sprayed is soluble and contains a salt with the desired constituents, (iii) large areas of thin films can be prepared, and (iv) various parameters can be optimized and hence the variation of the stoichiometry of the films produced. The only disadvantage of this method is that it cannot produce very thin films if several layers of iron salt used as a precursor is sprayed on a pre-heated substrate [104].

Spray pyrolysis on hematite films was first reported by Misho and co-workers using iron nitrate as the precursor with double distilled water as the solvent [105]. The substrate temperature used was 300°C , spray time of 15 s, spray height of 35 cm, spray rate of $10\text{ cm}^3/\text{min}$, and 3 min as the period before the spray process was done. The optical characterization of the films was done with the estimation of the bandgap. Duret and co-workers have reported hematite films prepared by ultrasonic spray pyrolysis. The prepared films had a mesoscopic leaflet type structure. The films deposited on FTO were used as electrodes in the tandem cell that was used for solar water splitting. The structural properties of the samples were studied using XRD, and the films were reported to have a thickness ranging from 5 to 10 nm. The mesoscopic leaflets allowed faster diffusion of light in the visible region, fastening the water-splitting process by reducing the distance required for the photo-generated holes to reach the electrolyte before recombination [105].

Physico-chemical, optical and electrical characterization of hematite films prepared by spray pyrolysis have also reported by Dghoughi and co-workers. FeCl_3 dissolved in deionized water with a concentration of 0.05 M was used as a precursor. Spray rate was varied from $1.5 - 6\text{ cm}^3/\text{min}$ and

substrate temperature of 400 - 500°C on a clean glass substrate. Compressed air was used as the carrier gas with the deposition time of 5 - 7 min. The diameter of the nozzle was fixed at 0.5 mm and the deposition height of 40 cm. The films were analysed for photoelectrochemical performance. Diale's research group conducted a recent study on hematite thin films prepared by spray pyrolysis. The study investigated the effect of spray volume, tetraethoxysilicate and post-annealing. Ultrafast transient absorption spectroscopy studies indicated that larger spray volume, tetraethoxysilicate, and post-annealing slower electron-hole recombination [106].

In another study, Laser-assisted spray pyrolysis has been reported in the thin film fabrication where it has produced nanocrystalline coatings and powders. In laser spray pyrolysis, the droplets interact with a continuous laser beam as they come out of the nozzle as compared to the thermal spray pyrolysis where the decomposition and reaction take place on the hot substrate. Witanachchi and co-workers reported α -Fe₂O₃ and TiO₂ nanoparticle coating prepared by laser spray pyrolysis [107]. In their setup, iron pentacarbonyl Fe(CO)₅ was used as the precursor, and sulphur hexafluoride (SF₆) was used as a carrier gas. The laser (3W CO₂) was focused above the orifice tube and used to heat the aerosol before reaching the substrate. The gas flow meter (SF₆) was used to control the speed and flow rate of the aerosol. Nitrogen gas was used to maintain the forward flow of the aerosol. Toluene was used as a solvent for hematite and TiO₂, and the precursors were deposited at a substrate temperature of 300°C. This led to evaporation of toluene and Pentacarbonyliron that have boiling points of 93 and 103°C respectively, with a decomposition temperature of 200°C. The heating by the CO₂ laser-produced smaller particles of 60 nm as compared to the films that were prepared without the CO₂ laser. The concentration of the precursor was varied from 0.1 to 0.05 M that led to the reduction of the particle size from 60 to 48 nm.

References

- [1] S.J. Moniz, S.A. Shevlin, D.J. Martin, Z.-X. Guo, J. Tang, Visible-light driven heterojunction photocatalysts for water splitting—a critical review, *Energy & Environmental Science*, 8 (2015) 731-759.
- [2] A.G. Tamirat, J. Rick, A.A. Dubale, W.-N. Su, B.-J. Hwang, Using hematite for photoelectrochemical water splitting: a review of current progress and challenges, *Nanoscale Horizons*, 1 (2016) 243-267.
- [3] A.A. Ismail, D.W. Bahnemann, Photochemical splitting of water for hydrogen production by photocatalysis: a review, *Solar Energy Materials and Solar Cells*, 128 (2014) 85-101.
- [4] M.G. Walter, E.L. Warren, J.R. McKone, S.W. Boettcher, Q. Mi, E.A. Santori, N.S. Lewis, Solar water splitting cells, *Chemical reviews*, 110 (2010) 6446-6473.
- [5] J.R. Bolton, S.J. Strickler, J.S. Connolly, Limiting and realizable efficiencies of solar photolysis of water, *Nature*, 316 (1985) 495-500.
- [6] T. Lindgren, L. Vayssieres, H. Wang, S.-E. Lindquist, Photo-oxidation of water at hematite electrodes, *Chemical Physics of Nanostructured Semiconductors*, DOI (2003) 83-110.
- [7] N.Y. Dzade, A. Roldan, N.H. De Leeuw, A density functional theory study of the adsorption of benzene on hematite (α -Fe₂O₃) surfaces, *Minerals*, 4 (2014) 89-115.
- [8] J.G. Kim, K.H. Han, C.H. Lee, J.Y. Jeong, K.H. Shin, Crystallographic and magnetic properties of nanostructured hematite synthesized by the sol-gel process, *Journal-Korean Physical Society*, 38 (2001) 798-802.
- [9] F. Morin, Electrical properties of α -Fe₂O₃ and α -Fe₂O₃ containing titanium, *Physical Review*, 83 (1951) 1005.
- [10] D.M. Sherman, T.D. Waite, Electronic spectra of Fe³⁺ oxides and oxide hydroxides in the near IR to near UV, *American Mineralogist*, 70 (1985) 1262-1269.
- [11] R.M. Cornell, U. Schwertmann, *The iron oxides: structure, properties, reactions, occurrences and uses*, John Wiley & Sons 2003.
- [12] T. Mallik, T. Kar, G. Bocelli, A. Musatti, Synthesis, crystal structure and solubility of C₆H₁₄N₄O₂, C₄H₄O₄, 2H₂O, *Science and Technology of Advanced Materials*, 6 (2005) 508.
- [13] E. Courvoisier, P.A. Williams, G.K. Lim, C.E. Hughes, K.D. Harris, The crystal structure of l-arginine, *Chemical Communications*, 48 (2012) 2761-2763.
- [14] S. Talwatkar, Y. Tamgadge, A. Sunatkari, A. Gambhire, G. Muley, Amino acids (L-arginine and L-alanine) passivated CdS nanoparticles: synthesis of spherical hierarchical structure and nonlinear optical properties, *Solid state sciences*, 38 (2014) 42-48.
- [15] H. Cao, G. Wang, J.H. Warner, A.A. Watt, Amino-acid-assisted synthesis and size-dependent magnetic behaviors of hematite nanocubes, *Applied Physics Letters*, 92 (2008) 013110.
- [16] J.S. Nyarige, T.P. Krüger, M. Diale, Structural and optical properties of hematite and L-arginine/hematite nanostructures prepared by thermal spray pyrolysis, *Surfaces and Interfaces*, 18 (2020) 100394.
- [17] Z. An, J. Zhang, S. Pan, F. Yu, Facile template-free synthesis and characterization of elliptic α -Fe₂O₃ superstructures, *The Journal of Physical Chemistry C*, 113 (2009) 8092-8096.
- [18] P. Tang, H. Xie, C. Ros, L. Han, M. Biset-Peiró, Y. He, W. Kramer, A.P. Rodríguez, E. Saucedo, J.R. Galán-Mascarós, Enhanced photoelectrochemical water splitting of hematite

- multilayer nanowire photoanodes by tuning the surface state via bottom-up interfacial engineering, *Energy & Environmental Science*, 10 (2017) 2124-2136.
- [19] R. Schebler, L.A. Ballesteros, H. Gómez, P. Grez, R. Córdova, E. Muñoz, R. Schebler, J. Ramos-Barrado, E.A. Dalchiele, Electrochemically grown self-organized hematite nanotube arrays for photoelectrochemical water splitting, *Journal of The Electrochemical Society*, 161 (2014) H903-H908.
- [20] Y.M. Zhao, Y.H. Li, R.Z. Ma, M.J. Roe, D.G. McCartney, Y.Q. Zhu, Growth and characterization of iron oxide nanorods/nanobelts prepared by a simple iron–water reaction, *Small*, 2 (2006) 422-427.
- [21] A.G. Tamirat, W.-N. Su, A.A. Dubale, C.-J. Pan, H.-M. Chen, D.W. Ayele, J.-F. Lee, B.-J. Hwang, Efficient photoelectrochemical water splitting using three dimensional urchin-like hematite nanostructure modified with reduced graphene oxide, *Journal of Power Sources*, 287 (2015) 119-128.
- [22] J.S. Nyarige, T.P. Krüger, M. Diale, Effects of L-arginine concentration on hematite nanostructures synthesized by spray pyrolysis and chemical bath deposition, *Physica B: Condensed Matter*, 581 (2020) 411924.
- [23] Y. Dong, H. Yang, R. Rao, A. Zhang, Selective synthesis of α -FeOOH and α -Fe₂O₃ nanorods via a temperature controlled process, *Journal of nanoscience and nanotechnology*, 9 (2009) 4774-4779.
- [24] R. Morrish, M. Rahman, J.D. MacElroy, C.A. Wolden, Activation of hematite nanorod arrays for photoelectrochemical water splitting, *ChemSusChem*, 4 (2011) 474-479.
- [25] V.A. de Carvalho, R.A.d.S. Luz, B.H. Lima, F.N. Crespilho, E.R. Leite, F.L. Souza, Highly oriented hematite nanorods arrays for photoelectrochemical water splitting, *Journal of Power Sources*, 205 (2012) 525-529.
- [26] S.Y. Chiam, M.H. Kumar, P.S. Bassi, H.L. Seng, J. Barber, L.H. Wong, Improving the efficiency of hematite nanorods for photoelectrochemical water splitting by doping with manganese, *ACS applied materials & interfaces*, 6 (2014) 5852-5859.
- [27] Y. Fu, C.-L. Dong, Z. Zhou, W.-Y. Lee, J. Chen, P. Guo, L. Zhao, S. Shen, Solution growth of Ta-doped hematite nanorods for efficient photoelectrochemical water splitting: a tradeoff between electronic structure and nanostructure evolution, *Physical Chemistry Chemical Physics*, 18 (2016) 3846-3853.
- [28] D. Wang, H. Chen, G. Chang, X. Lin, Y. Zhang, A. Aldalbahi, C. Peng, J. Wang, C. Fan, Uniform doping of titanium in hematite nanorods for efficient photoelectrochemical water splitting, *ACS applied materials & interfaces*, 7 (2015) 14072-14078.
- [29] D. Wang, Y. Zhang, C. Peng, J. Wang, Q. Huang, S. Su, L. Wang, W. Huang, C. Fan, Crystallinity Engineering of Hematite Nanorods for High-Efficiency Photoelectrochemical Water Splitting, *Advanced Science*, 2 (2015) 1500005.
- [30] P.M. Chee, P.P. Boix, H. Ge, F. Yanan, J. Barber, L.H. Wong, Core–shell hematite nanorods: a simple method to improve the charge transfer in the photoanode for photoelectrochemical water splitting, *ACS applied materials & interfaces*, 7 (2015) 6852-6859.
- [31] X. Li, P.S. Bassi, P.P. Boix, Y. Fang, L.H. Wong, Revealing the role of TiO₂ surface treatment of hematite nanorods photoanodes for solar water splitting, *ACS applied materials & interfaces*, 7 (2015) 16960-16966.

- [32] S. Shen, J. Zhou, C.-L. Dong, Y. Hu, E.N. Tseng, P. Guo, L. Guo, S.S. Mao, Surface engineered doping of hematite nanorod arrays for improved photoelectrochemical water splitting, *Scientific reports*, 4 (2014) 6627.
- [33] X. Guo, L. Wang, Y. Tan, Hematite nanorods Co-doped with Ru cations with different valence states as high performance photoanodes for water splitting, *Nano Energy*, 16 (2015) 320-328.
- [34] J. Wang, C. Du, Q. Peng, J. Yang, Y. Wen, B. Shan, R. Chen, Enhanced photoelectrochemical water splitting performance of hematite nanorods by Co and Sn co-doping, *International Journal of Hydrogen Energy*, 42 (2017) 29140-29149.
- [35] Z. Zhang, M.F. Hossain, T. Takahashi, Self-assembled hematite (α -Fe₂O₃) nanotube arrays for photoelectrocatalytic degradation of azo dye under simulated solar light irradiation, *Applied Catalysis B: Environmental*, 95 (2010) 423-429.
- [36] C.Y. Lee, L. Wang, Y. Kado, M.S. Killian, P. Schmuki, Anodic nanotubular/porous hematite photoanode for solar water splitting: substantial effect of iron substrate purity, *ChemSusChem*, 7 (2014) 934-940.
- [37] A. Mao, K. Shin, J.K. Kim, D.H. Wang, G.Y. Han, J.H. Park, Controlled synthesis of vertically aligned hematite on conducting substrate for photoelectrochemical cells: nanorods versus nanotubes, *ACS applied materials & interfaces*, 3 (2011) 1852-1858.
- [38] T.J. LaTempa, X. Feng, M. Paulose, C.A. Grimes, Temperature-dependent growth of self-assembled hematite (α -Fe₂O₃) nanotube arrays: rapid electrochemical synthesis and photoelectrochemical properties, *The Journal of Physical Chemistry C*, 113 (2009) 16293-16298.
- [39] S.K. Mohapatra, S.E. John, S. Banerjee, M. Misra, Water photooxidation by smooth and ultrathin α -Fe₂O₃ nanotube arrays, *Chemistry of Materials*, 21 (2009) 3048-3055.
- [40] Y. Ling, G. Wang, J. Reddy, C. Wang, J.Z. Zhang, Y. Li, The influence of oxygen content on the thermal activation of hematite nanowires, *Angewandte Chemie International Edition*, 51 (2012) 4074-4079.
- [41] R. Franking, L. Li, M.A. Lukowski, F. Meng, Y. Tan, R.J. Hamers, S. Jin, Facile post-growth doping of nanostructured hematite photoanodes for enhanced photoelectrochemical water oxidation, *Energy & Environmental Science*, 6 (2013) 500-512.
- [42] Y. Ling, G. Wang, H. Wang, Y. Yang, Y. Li, Low-temperature activation of hematite nanowires for photoelectrochemical water oxidation, *ChemSusChem*, 7 (2014) 848-853.
- [43] L. Li, H. Dai, D. Luo, S. Wang, X. Sun, Nickel Oxide Nanosheets for Enhanced Photoelectrochemical Water Splitting by Hematite (α -Fe₂O₃) Nanowire Arrays, *Energy Technology*, 4 (2016) 758-763.
- [44] Y. Li, H. Chen, Facile fire treatment of nanostructured hematite with an enhanced photoelectrochemical water splitting performance, *Journal of Materials Chemistry A*, 4 (2016) 14974-14977.
- [45] F. Urbain, P. Tang, V. Smirnov, K. Welter, T. Andreu, F. Finger, J. Arbiol, J.R. Morante, Multilayered Hematite Nanowires with Thin-Film Silicon Photovoltaics in an All-Earth-Abundant Hybrid Tandem Device for Solar Water Splitting, *ChemSusChem*, 12 (2019) 1428-1436.
- [46] J. Liu, C. Liang, G. Xu, Z. Tian, G. Shao, L. Zhang, Ge-doped hematite nanosheets with tunable doping level, structure and improved photoelectrochemical performance, *Nano Energy*, 2 (2013) 328-336.

- [47] J. Liu, Y. Cai, Z. Tian, G. Ruan, Y. Ye, C. Liang, G. Shao, Highly oriented Ge-doped hematite nanosheet arrays for photoelectrochemical water oxidation, *Nano Energy*, 9 (2014) 282-290.
- [48] C.W. Wang, S. Yang, H.B. Jiang, H. Yang, Chemical Vapor Deposition of FeOCl Nanosheet Arrays and Their Conversion to Porous α -Fe₂O₃ Photoanodes for Photoelectrochemical Water Splitting, *Chemistry–A European Journal*, 21 (2015) 18024-18028.
- [49] P. Peerakiathajohn, J.H. Yun, H. Chen, M. Lyu, T. Butburee, L. Wang, Stable hematite nanosheet photoanodes for enhanced photoelectrochemical water splitting, *Advanced Materials*, 28 (2016) 6405-6410.
- [50] M. Ji, J. Cai, Y. Ma, L. Qi, Controlled growth of ferrihydrite branched nanosheet arrays and their transformation to hematite nanosheet arrays for photoelectrochemical water splitting, *ACS applied materials & interfaces*, 8 (2016) 3651-3660.
- [51] X. Xie, K. Li, W.-D. Zhang, Photoelectrochemical properties of Ti-doped hematite nanosheet arrays decorated with CdS nanoparticles, *RSC advances*, 6 (2016) 74234-74240.
- [52] X. Bu, G. Wang, Y. Tian, Foreign In³⁺ treatment improving the photoelectrochemical performance of a hematite nanosheet array for water splitting, *Nanoscale*, 9 (2017) 17513-17523.
- [53] X. Bu, Y. Gao, S. Zhang, Y. Tian, Amorphous cerium phosphate on P-doped Fe₂O₃ nanosheets for efficient photoelectrochemical water oxidation, *Chemical Engineering Journal*, 355 (2019) 910-919.
- [54] L. Wang, C.Y. Lee, A. Mazare, K. Lee, J. Müller, E. Spiecker, P. Schmuki, Enhancing the Water Splitting Efficiency of Sn-Doped Hematite Nanoflakes by Flame Annealing, *Chemistry–a European journal*, 20 (2014) 77-82.
- [55] R. Rajendran, Z. Yaakob, M. Pudukudy, M.S.A. Rahaman, K. Sopian, Photoelectrochemical water splitting performance of vertically aligned hematite nanoflakes deposited on FTO by a hydrothermal method, *Journal of alloys and compounds*, 608 (2014) 207-212.
- [56] L. Wang, X. Zhou, N.T. Nguyen, P. Schmuki, Plasmon-Enhanced Photoelectrochemical Water Splitting Using Au Nanoparticles Decorated on Hematite Nanoflake Arrays, *ChemSusChem*, 8 (2015) 618-622.
- [57] T. Liu, Y. Ling, Y. Yang, L. Finn, E. Collazo, T. Zhai, Y. Tong, Y. Li, Investigation of hematite nanorod–nanoflake morphological transformation and the application of ultrathin nanoflakes for electrochemical devices, *Nano Energy*, 12 (2015) 169-177.
- [58] L. Wang, Y. Yang, Y. Zhang, Q. Rui, B. Zhang, Z. Shen, Y. Bi, One-dimensional hematite photoanodes with spatially separated Pt and FeOOH nanolayers for efficient solar water splitting, *Journal of Materials Chemistry A*, 5 (2017) 17056-17063.
- [59] S.D. Tilley, M. Cornuz, K. Sivula, M. Grätzel, Light-induced water splitting with hematite: improved nanostructure and iridium oxide catalysis, *Angewandte Chemie International Edition*, 49 (2010) 6405-6408.
- [60] F. Le Formal, M. Grätzel, K. Sivula, Controlling photoactivity in ultrathin hematite films for solar water-splitting, *Advanced Functional Materials*, 20 (2010) 1099-1107.
- [61] K. Sivula, R. Zboril, F. Le Formal, R. Robert, A. Weidenkaff, J. Tucek, J. Frydrych, M. Gratzel, Photoelectrochemical water splitting with mesoporous hematite prepared by a solution-based colloidal approach, *Journal of the American Chemical Society*, 132 (2010) 7436-7444.

- [62] D.K. Bora, A. Braun, R. Erni, G. Fortunato, T. Graule, E.C. Constable, Hydrothermal treatment of a hematite film leads to highly oriented faceted nanostructures with enhanced photocurrents, *Chemistry of Materials*, 23 (2011) 2051-2061.
- [63] A. Mao, J.K. Kim, K. Shin, D.H. Wang, P.J. Yoo, G.Y. Han, J.H. Park, Hematite modified tungsten trioxide nanoparticle photoanode for solar water oxidation, *Journal of Power Sources*, 210 (2012) 32-37.
- [64] T. Hisatomi, J. Brillet, M. Cornuz, F. Le Formal, N. Tétreault, K. Sivula, M. Grätzel, A Ga_2O_3 underlayer as an isomorphic template for ultrathin hematite films toward efficient photoelectrochemical water splitting, *Faraday discussions*, 155 (2012) 223-232.
- [65] T. Hisatomi, H. Dotan, M. Stefik, K. Sivula, A. Rothschild, M. Graetzel, N. Mathews, Enhancement in the performance of ultrathin hematite photoanode for water splitting by an oxide underlayer, *Advanced Materials*, 24 (2012) 2699-2702.
- [66] X. Zong, S. Thaweesak, H. Xu, Z. Xing, J. Zou, G.M. Lu, L. Wang, A scalable colloidal approach to prepare hematite films for efficient solar water splitting, *Physical Chemistry Chemical Physics*, 15 (2013) 12314-12321.
- [67] C. Du, X. Yang, M.T. Mayer, H. Hoyt, J. Xie, G. McMahon, G. Bischooping, D. Wang, Hematite-based water splitting with low turn-on voltages, *Angewandte Chemie International Edition*, 52 (2013) 12692-12695.
- [68] M. Marelli, A. Naldoni, A. Minguzzi, M. Allieta, T. Virgili, G. Scavia, S. Recchia, R. Psaro, V. Dal Santo, Hierarchical hematite nanoplatelets for photoelectrochemical water splitting, *ACS applied materials & interfaces*, 6 (2014) 11997-12004.
- [69] X. Yang, R. Liu, C. Du, P. Dai, Z. Zheng, D. Wang, Improving hematite-based photoelectrochemical water splitting with ultrathin TiO_2 by atomic layer deposition, *ACS applied materials & interfaces*, 6 (2014) 12005-12011.
- [70] K.-Y. Yoon, J.-S. Lee, K. Kim, C.H. Bak, S.-I. Kim, J.-B. Kim, J.-H. Jang, Hematite-based photoelectrochemical water splitting supported by inverse opal structures of graphene, *ACS applied materials & interfaces*, 6 (2014) 22634-22639.
- [71] S. Li, P. Zhang, X. Song, L. Gao, Ultrathin Ti-doped hematite photoanode by pyrolysis of ferrocene, *International journal of hydrogen energy*, 39 (2014) 14596-14603.
- [72] H.S. Han, S. Shin, J.H. Noh, I.S. Cho, K.S. Hong, Heterojunction $\text{Fe}_2\text{O}_3\text{-SnO}_2$ Nanostructured Photoanode for Efficient Photoelectrochemical Water Splitting, *JOM*, 66 (2014) 664-669.
- [73] D. Xu, Y. Rui, Y. Li, Q. Zhang, H. Wang, Zn-Co layered double hydroxide modified hematite photoanode for enhanced photoelectrochemical water splitting, *Applied Surface Science*, 358 (2015) 436-442.
- [74] I. Kondofersky, H.K. Dunn, A. Müller, B. Mandlmeier, J.M. Feckl, D. Fattakhova-Rohlfing, C. Scheu, L.M. Peter, T. Bein, Electron collection in host-guest nanostructured hematite photoanodes for water splitting: the influence of scaffold doping density, *ACS applied materials & interfaces*, 7 (2015) 4623-4630.
- [75] Q. Yu, X. Meng, T. Wang, P. Li, J. Ye, Hematite films decorated with nanostructured ferric oxyhydroxide as photoanodes for efficient and stable photoelectrochemical water splitting, *Advanced Functional Materials*, 25 (2015) 2686-2692.
- [76] D. Xu, Y. Rui, V.T. Mbah, Y. Li, Q. Zhang, H. Wang, Binary nickel and iron oxide modified Ti-doped hematite photoanode for enhanced photoelectrochemical water splitting, *International Journal of Hydrogen Energy*, 41 (2016) 873-881.

- [77] C.W. Wang, S. Yang, W.Q. Fang, P. Liu, H. Zhao, H.G. Yang, Engineered hematite mesoporous single crystals drive drastic enhancement in solar water splitting, *Nano letters*, 16 (2016) 427-433.
- [78] Y. Yang, M. Forster, Y. Ling, G. Wang, T. Zhai, Y. Tong, A.J. Cowan, Y. Li, Acid treatment enables suppression of electron–hole recombination in hematite for photoelectrochemical water splitting, *Angewandte Chemie International Edition*, 55 (2016) 3403-3407.
- [79] D. Primc, M. Bärtsch, D. Barreca, G. Carraro, C. Maccato, C. Sada, M. Niederberger, Doping of TiO₂ as a tool to optimize the water splitting efficiencies of titania–hematite photoanodes, *Sustainable Energy & Fuels*, 1 (2017) 199-206.
- [80] H. Bemana, S. Rashid-Nadimi, Effect of sulfur doping on photoelectrochemical performance of hematite, *Electrochimica Acta*, 229 (2017) 396-403.
- [81] K. Maabong, A.G. Machatine, B.S. Mwankemwa, A. Braun, D.K. Bora, R. Toth, M. Diale, Nanostructured hematite thin films for photoelectrochemical water splitting, *Physica B: Condensed Matter*, 535 (2018) 67-71.
- [82] C. Domingo, R. Rodríguez-Clemente, M. Blesa, Morphological properties of α -FeOOH, γ -FeOOH and Fe₃O₄ obtained by oxidation of aqueous Fe (II) solutions, *Journal of colloid and interface science*, 165 (1994) 244-252.
- [83] A.S. Baker, A.S. Brown, M.A. Edwards, J.S. Hargreaves, C.J. Kiely, A. Meagher, Q.A. Pankhurst, A structural study of haematite samples prepared from sulfated goethite precursors: the generation of axial mesoporous voids, *Journal of Materials Chemistry*, 10 (2000) 761-766.
- [84] C. Cannas, D. Gatteschi, A. Musinu, G. Piccaluga, C. Sangregorio, Structural and magnetic properties of Fe₂O₃ nanoparticles dispersed over a silica matrix, *The Journal of Physical Chemistry B*, 102 (1998) 7721-7726.
- [85] T. Sugimoto, K. Sakata, Preparation of monodisperse pseudocubic α -Fe₂O₃ particles from condensed ferric hydroxide gel, *Journal of colloid and interface science*, 152 (1992) 587-590.
- [86] C. Pascal, J. Pascal, F. Favier, M. Elidrissi Moubtassim, C. Payen, Electrochemical synthesis for the control of γ -Fe₂O₃ nanoparticle size. Morphology, microstructure, and magnetic behavior, *Chemistry of materials*, 11 (1999) 141-147.
- [87] D. Bersani, P. Lottici, A. Montenero, Micro-Raman investigation of iron oxide films and powders produced by sol–gel syntheses, *Journal of Raman spectroscopy*, 30 (1999) 355-360.
- [88] A. IRL, Hydrothermal preparation of goethite and haematite from amorphous iron (III) hydroxide, *Acta Chem. Scand*, 22 (1968).
- [89] A.N. Chistensen, T.R. Jensen, C.R. Bahl, E. DiMasi, Nano size crystals of goethite, α -FeOOH: Synthesis and thermal transformation, *Journal of Solid State Chemistry*, 180 (2007) 1431-1435.
- [90] A. Šarić, K. Nomura, S. Popović, N. Ljubešić, S. Musić, Effects of urotropin on the chemical and microstructural properties of Fe-oxide powders prepared by the hydrolysis of aqueous FeCl₃ solutions, *Materials Chemistry and Physics*, 52 (1998) 214-220.
- [91] M.-T. Liang, S.-H. Wang, Y.-L. Chang, H.-I. Hsiang, H.-J. Huang, M.-H. Tsai, W.-C. Juan, S.-F. Lu, Iron oxide synthesis using a continuous hydrothermal and solvothermal system, *Ceramics International*, 36 (2010) 1131-1135.

- [92] M. Khalil, J. Yu, N. Liu, R.L. Lee, Hydrothermal synthesis, characterization, and growth mechanism of hematite nanoparticles, *Journal of Nanoparticle Research*, 16 (2014) 2362.
- [93] A.J. Abel, I. Garcia-Torregrosa, A.M. Patel, B. Opanont, J.B. Baxter, SILAR-deposited hematite films for photoelectrochemical water splitting: effects of Sn, Ti, thickness, and nanostructuring, *The Journal of Physical Chemistry C*, 119 (2015) 4454-4465.
- [94] A. Ubale, M. Belkhedkar, Size dependent physical properties of nanostructured α -Fe₂O₃ thin films grown by successive ionic layer adsorption and reaction method for antibacterial application, *Journal of Materials Science & Technology*, 31 (2015) 1-9.
- [95] D.K. Bora, Hematite and its hybrid nanostructures for photoelectrochemical water splitting: how do properties affect functionality, *University_of_Basel*, 2012.
- [96] Y. Hu, D.K. Bora, F. Boudoire, F. Häussler, M. Graetzel, E.C. Constable, A. Braun, A dip coating process for large area silicon-doped high performance hematite photoanodes, *Journal of Renewable and Sustainable Energy*, 5 (2013) 043109.
- [97] T. Raming, A.J. Winnubst, C.M. van Kats, A. Philipse, The synthesis and magnetic properties of nanosized hematite (α -Fe₂O₃) particles, *Journal of Colloid and Interface Science*, 249 (2002) 346-350.
- [98] S.H. Tolbert, P. Sieger, G.D. Stucky, S.M. Aubin, C.-C. Wu, D.N. Hendrickson, Control of inorganic layer thickness in self-assembled iron oxide/surfactant composites, *Journal of the American Chemical Society*, 119 (1997) 8652-8661.
- [99] G. Wirnsberger, K. Gatterer, P. Behens, Novel synthetic pathways to layered iron (hydro) oxyhydroxide–surfactant composites, *Journal of materials chemistry*, 8 (1998) 1509-1510.
- [100] L. Liu, H.-Z. Kou, W. Mo, H. Liu, Y. Wang, Surfactant-assisted synthesis of α -Fe₂O₃ nanotubes and nanorods with shape-dependent magnetic properties, *The Journal of Physical Chemistry B*, 110 (2006) 15218-15223.
- [101] N. Kazemi, A. Maghsoudipour, T. Ebadzadeh, Electrochemical preparation of hematite nanostructured films for solar hydrogen production, *EPJ Web of Conferences*, EDP Sciences, 2012, pp. 02007.
- [102] F. Fajarah, H. Setyawan, A. Nur, I.W. Lenggoro, Thermal stability of silica-coated magnetite nanoparticles prepared by an electrochemical method, *Advanced Powder Technology*, 24 (2013) 507-511.
- [103] T. Vimalkumar, K. Vijayakumar, Highly conductive and transparent ZnO thin film using Chemical Spray Pyrolysis technique: Effect of doping and deposition parameters, *Cochin University of Science & Technology*, 2011.
- [104] J.B. Mooney, S.B. Radding, Spray pyrolysis processing, *Annual review of materials science*, 12 (1982) 81-101.
- [105] A. Duret, M. Grätzel, Visible light-induced water oxidation on mesoscopic α -Fe₂O₃ films made by ultrasonic spray pyrolysis, *The Journal of Physical Chemistry B*, 109 (2005) 17184-17191.
- [106] S. Congolo, M. Madito, A. Paradzah, A. Harrison, H. Elnour, T. Krüger, M. Diale, Reduction of recombination rates due to volume increasing, annealing, and tetraethoxysilicate treatment in hematite thin films, *Applied Nanoscience*, DOI (2020) 1-11.
- [107] S. Witanachchi, G. Dedigamuwa, P. Mukherjee, Laser-assisted spray pyrolysis process for the growth of TiO₂ and Fe₂O₃ nanoparticle coatings, *Journal of materials research*, 22 (2007) 649-654.

3 Experimental

3.1 Introduction

Hematite nanoparticles were synthesized using spray pyrolysis at different deposition temperatures and precursor concentrations. Some of these thin films were used as a seed layer for the transformation of the nanoparticles to nanospheres using L-arginine (L-Arg) molecule by chemical bath deposition. Also, the synthesis of the surface doped hematite using Zn, Ag and Zn/Ag prepared by spray pyrolysis is presented in this chapter.

3.2 Substrate cleaning

Fluorine doped tin oxide (FTO) of dimensions 1.5 cm x 3 cm used as substrates, were first soaked for 10 min in a solution containing sodium hydroxide (NaOH) and sodium stearate ($C_{17}H_{35}COONa$) that was 0.5 M. This was done to etch the surface of the dirt. They were later scrubbed one by one to ensure the dirt had been removed. Thereafter, deionized (DI) water was used to rinse the substrates. The rinsed substrates were then transferred to a beaker containing ethanol and agitated in an ultrasonic cleaner for 10 min at room temperature. This was followed by rinsing with DI before transferring the substrates to another beaker containing acetone solution. Using the same pre-set conditions, the substrates were agitated in the ultrasonic for 10 min. This was done to ensure that grease has been completely removed from the substrates, which were then rinsed with DI water and dried with nitrogen (N_2) gas.

3.3 Synthesis of hematite nanoparticles

Chemical spray pyrolysis (CSP) was used to deposit hematite nanoparticles, as shown in Figure 3.3.1. Iron (III) nitrate nonahydrate, $Fe(NO_3)_3 \cdot 9H_2O$, (Sigma Aldrich, AR, 99.99%) was used as the precursor chemical. 50 mM of $Fe(NO_3)_3 \cdot 9H_2O$ solution using DI water as solvent was prepared and stirred with a magnetic bead for 4 min to obtain a homogeneous solution that was later transferred to the solution container for CSP. The $Fe(NO_3)_3 \cdot 9H_2O$ solution was then sprayed onto the pre-heated FTO substrates using N_2 as the carrier gas and a spray pressure of 3.0×10^5 Pa. The deposition temperatures of 280, 330, 380, and 430°C were used. A flow rate of 10 ml/min was

maintained during spraying. Besides, these nanostructured hematite films were prepared using the nozzles of 1, 0.5, 0.3, and 0.2 mm for optimization. The substrate to nozzle distance of 28 cm was used with the spray time of 45 s. The films were after that annealed using Lindberg furnace at 450°C in air for 1 h. These films were used as a seed layer for the transformation of NPs to nanospheres using the chemical bath deposition.

The following care was taken into consideration after thin film deposition; (i) the prepared films were transferred to a relatively hot surface. This enhanced gradual cooling to avoid cracking of the glass substrate before any characterization. Films transferred to a cold surface immediately from the hotplate cracked because of the rapid temperature change. (ii) After setting the required temperature, the set up was left for 5 min for stabilization before the start of the deposition, (iii) the melting point of the chemicals to be deposited were established before deposition. This enabled the temperature that was used during deposition not to exceed the temperature of the melting point of the materials.

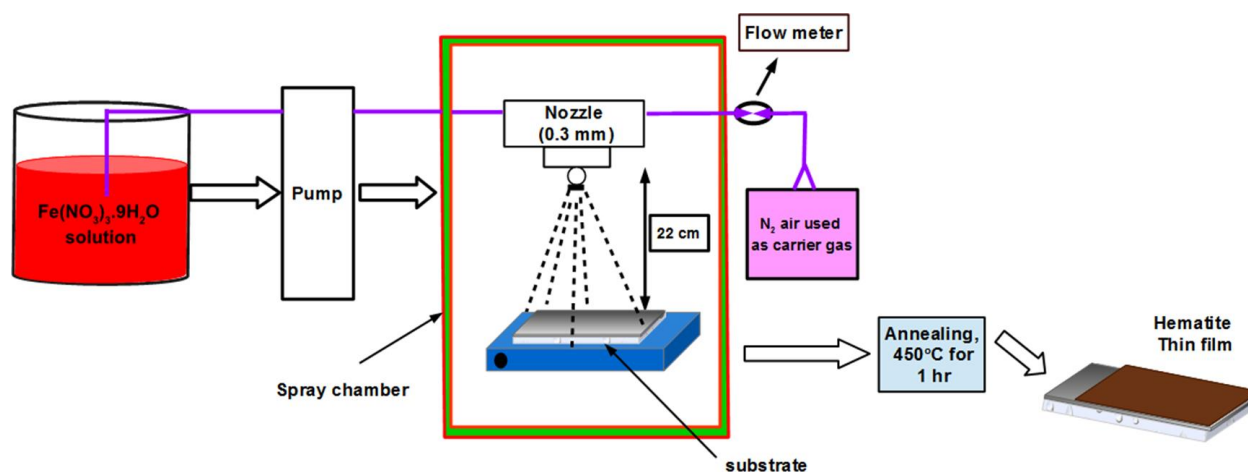


Figure 3.3.1. The schematic diagram for thermal spray pyrolysis used for the preparation of hematite thin films at different deposition temperatures.

3.4 Synthesis of L-arginine/hematite nanospheres

Chemical bath deposition (CBD) method was used in the preparation of L-Arg/ α - Fe_2O_3 nanospheres. Hematite NPs prepared by CSP at 430°C were used as seed layers, with equimolar

solutions of DI water and L-arginine. 25 ml of 50 mM iron (III) chloride hexahydrate, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, (Sigma Aldrich, AR, 99.99%) was used to obtain solution A with DI water as the solvent while solution B was prepared by dissolving 25 ml of L-arginine, $\text{C}_6\text{H}_{14}\text{N}_4\text{O}_2$, (Sigma Aldrich, AR, 99.99%) in DI water. After that, drop-wise addition of solution B to solution A was done with a copious stirring. This ensured a homogeneous solution was obtained that was used as the precursor. The precursor was then loaded in the beaker and first pre-heated to 90°C using the hot plate before loading the hematite seed layer substrates. CBD was used to transform the NPs into nanospheres, as shown in Figure 3.4.1.

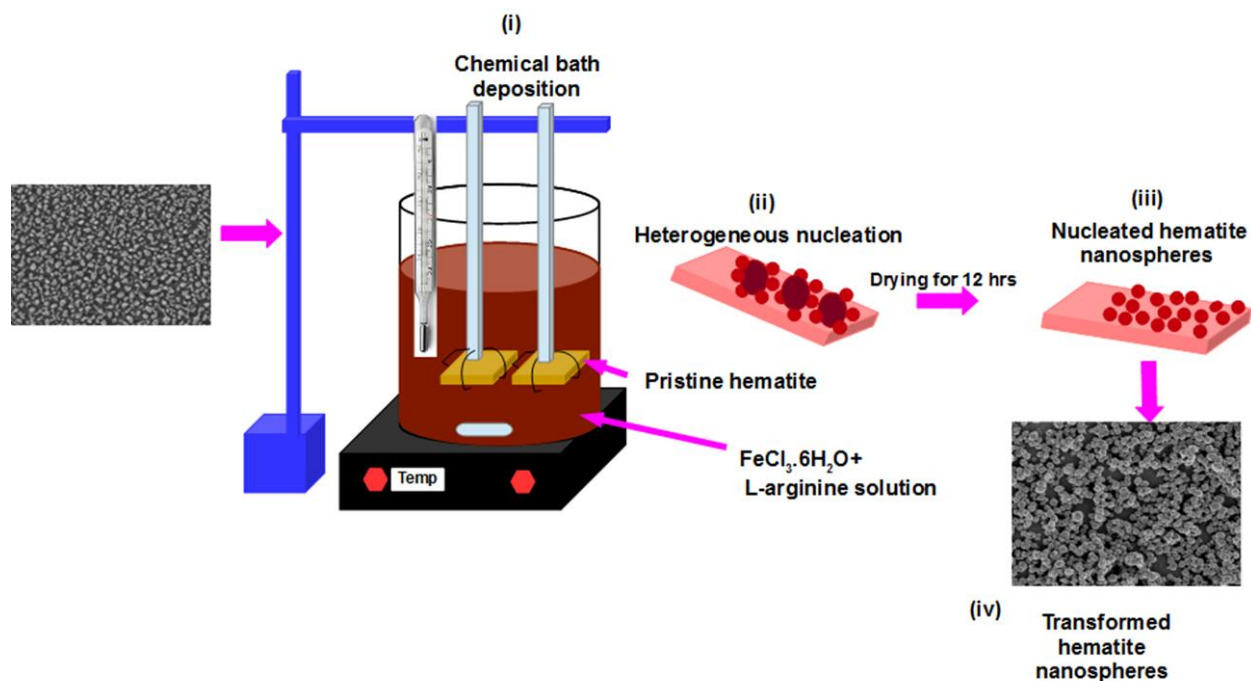


Figure 3.4.1. The schematic diagram for chemical bath deposition used to prepare L-arginine/hematite nanospheres at a temperature of 90°C for 48 h.

The seeded layer of hematite was kept facing down; suspension maintained by the use of non-releasable nylon cable ties. The uncoated side of the substrate was covered using a non-reactive heat resistant tape. The experimental set up was maintained for 48 h with the pre-set conditions. The same conditions and parameters were used for the synthesis of L-Arg/ α - Fe_2O_3 nanospheres using different precursor concentrations of L-arginine. L-arginine: $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ precursor

concentration ratios of 2:1 and 3:1 respectively were used. After the 48 h, the samples were cleaned with DI water, and ethanol then left to dry at room temperature for 12 h.

3.5 Synthesis of hematite nanoparticles at different precursor concentration and temperatures

Different precursor concentrations (30, 40 and 50 mM) of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ were used to synthesize hematite nanoparticles by CSP at 280°C , with a nozzle diameter of 0.3 mm, 45 s spray time, deposition height of 22 cm, and spray pressure of 2.2×10^5 Pa. On the other hand, a different set of samples of hematite thin films were also prepared with the same pre-set CSP parameters using deposition temperatures of 250, 340, and 400°C , with 50 mM of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ as the precursor concentration. All the samples were annealed at 450°C for 1 h and left to cool to room temperature for characterization.

3.6 Zn, Ag and Zn/Ag surface-doped hematite nanostructures

Chemical spray pyrolysis was used to synthesize zinc doped ($\alpha\text{-Fe}_2\text{O}_3\text{:Zn}$), silver doped ($\alpha\text{-Fe}_2\text{O}_3\text{:Ag}$) and zinc/silver co-doped hematite ($\alpha\text{-Fe}_2\text{O}_3\text{:Zn/Ag}$) at a deposition temperature of 430°C . The cleaned FTO films were first used to deposit the seed layer at 430°C , followed by annealing at 450°C for 1 h. The cooled samples were later used as seed layers for surface doping of Zn, Ag and Zn/Ag. The solutions of zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, Sigma Aldrich, AR, 99 %) and silver nitrate ($\text{Ag}(\text{NO}_3)$, Sigma Aldrich, AR, 99 %) were used as the precursor dopants, with a doping concentration of 0.5 wt %. These precursor dopants were then mixed separately with 50 mM of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ at room temperature for 10 min to obtain a uniform solution. For the $\alpha\text{-Fe}_2\text{O}_3\text{:Zn/Ag}$, solutions of 0.5 wt % of the precursor dopants ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Ag}(\text{NO}_3)$) were added to a beaker containing 50 mM of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and stirred to maintain uniformity. The solution was then sprayed on top of pre-heated seeded hematite samples using spray pyrolysis for 20 s at 430°C to create a thin nanostructured doped hematite layer. All the samples were annealed at 450°C in air and left to cool to room temperatures for 12 h. The annealing of these samples was done separately to avoid possible contamination at high temperatures. The architecture of the prepared samples is shown in Figure 3.6.1.

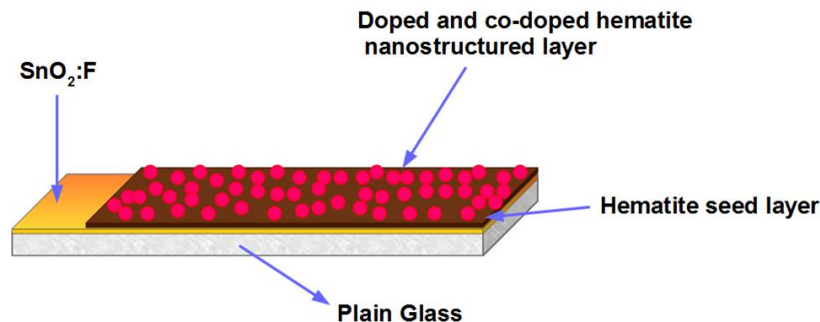


Figure 3.6.1. The architecture of nanostructures of surface doped hematite ($\alpha\text{-Fe}_2\text{O}_3\text{:Zn}$, $\alpha\text{-Fe}_2\text{O}_3\text{:Ag}$, and $\alpha\text{-Fe}_2\text{O}_3\text{:Zn/Ag}$) thin films prepared by spray pyrolysis.

3.7 Characterization of hematite nanostructures

3.7.1 X-ray diffraction

X-ray diffraction (XRD) is a non-destructive technique used to study the structural properties of hematite nanostructures. Some of the properties that can be investigated using XRD include orientation of the material, crystallite size, phase, micro-strain, defects in materials, and lattice parameters. In addition, XRD can give more information if the material prepared is crystalline or amorphous and has unit cell dimensions. The setup uses Co, Cu, Mo, and Cr as the target materials, producing X-rays at a specific wavelength. The monochromatic beam produces X-rays that are collimated and directed on the sample. The intensity of the X-rays is recorded when the detector and the sample are rotated. The distribution of the atoms in the lattice determines the intensity of the peaks [1]. The interaction of the incident rays produces constructive interference at an angle θ with the sample. For this to happen, Bragg's law, $n\lambda = 2d \sin \theta$, has to be satisfied where n is an integer, d the spacing between the diffraction planes and λ is the wavelength of radiation, while θ represents the incident angle [2]. The detector records the X-ray signal that is converted to a count rate and then directed to the output device such as a computer or printer. Some of the main parts of an XRD setup are shown in Figure 3.7.1 (a).

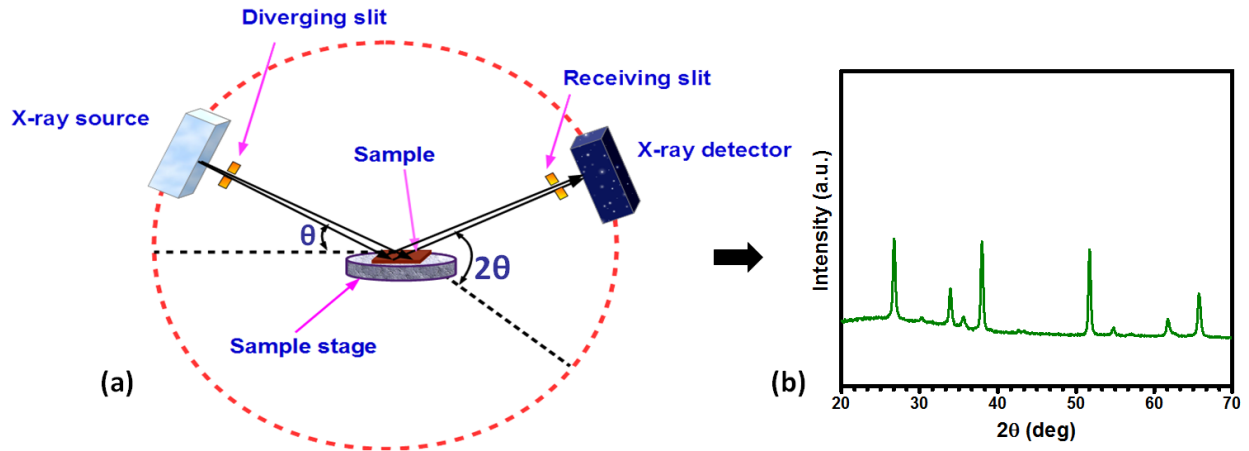


Figure 3.7.1. (a) Schematic arrangement of XRD components, (b) shows the XRD intensity versus 2θ angles spectra of the actual measurement obtained from our sample.

Debye-Scherrer's formula shown in the equation has been used to calculate the crystallite size

$$D = \frac{k\lambda}{\beta \cos \theta} \quad 3.7.1$$

where D is the average crystallite size, k is the shape factor, λ the wavelength of radiation, β is the full-width at half maximum (FWHM), and the θ is the Bragg angle. For this study, a German Bruker D2 Phaser X-ray diffractometer with a $\text{CuK}\alpha$ radiation ($1.5418 \text{ \AA}$) source, and a 2θ range of 20° to 80° was used. The diffraction peaks to d-spacing were then used for identification of our samples with the standard reference patterns (JCPDS file no. 03-0664).

Since hematite has a hexagonal structure, the lattice parameters $a = b$ and c were calculated using,

$$\frac{1}{d_{hkl}^2} = \frac{4}{3a^2} (h^2 + k^2 + hk) + \frac{l^2}{c^2} \quad 3.7.2$$

where a , b and c are lattice parameters while h , k and l are Miller indices. The Miller indices (hkl) present a parallel plane having a spacing of d_{hkl} . Micro-strain (ε) on the other hand was calculated using the Williamson-Hall model equation,

$$\varepsilon = \frac{\beta}{4 \sin \theta} \quad 3.7.3$$

and dislocation density (δ) obtained using

$$\delta = \frac{1}{D^2} \quad 3.7.4$$

where D is the average crystallite size of the material.

3.7.2 Raman spectroscopy

Raman spectroscopy is a non-destructive technique that gives information about the molecular interaction of materials, chemical structure and crystallinity. It relies on inelastic scattering of electromagnetic radiation by molecules or atoms. This inelastic scattering leads to the scattering of the photons with different frequency from the incident photons. The scattering processes that can occur are Rayleigh, Stokes and anti-Stokes scattering, the former being an elastic process, while the latter two are inelastic processes. In Stokes scattering, the material absorbs energy and the emitted photon has a lower energy than the incident photon, whereas in anti-Stokes scattering the material loses energy and the emitted photon has a higher energy than the absorbed photon. Stokes scattering is the most probable process to occur compared to anti-Stokes, and hence the Raman spectral measurements are Stokes measurement plots of the intensity of the scattered photon as a function of the difference between the incident and scattered photon energy (i.e. Raman shift typically expressed in wavenumbers) [3]. The laser provides a monochromatic light beam that excites the molecules. The light travels from the light source to the beam expander and the Rayleigh filter, which is a dichroic beam splitter that acts as a short-pass filter. It is then reflected off a mirror into a microscope where it is directed onto the sample. The scattered light is collected and then directed by a focusing mirror onto a grating where it is dispersed. The dispersed light is then focused into a detector. A focusing mirror is after that used to direct the scattered light to the grating where dispersion takes place, and finally to the detector [4]. For this study, Raman results obtained were measured using a WITec alpha300 RAS+ confocal Raman microscope with a 532 nm excitation laser.

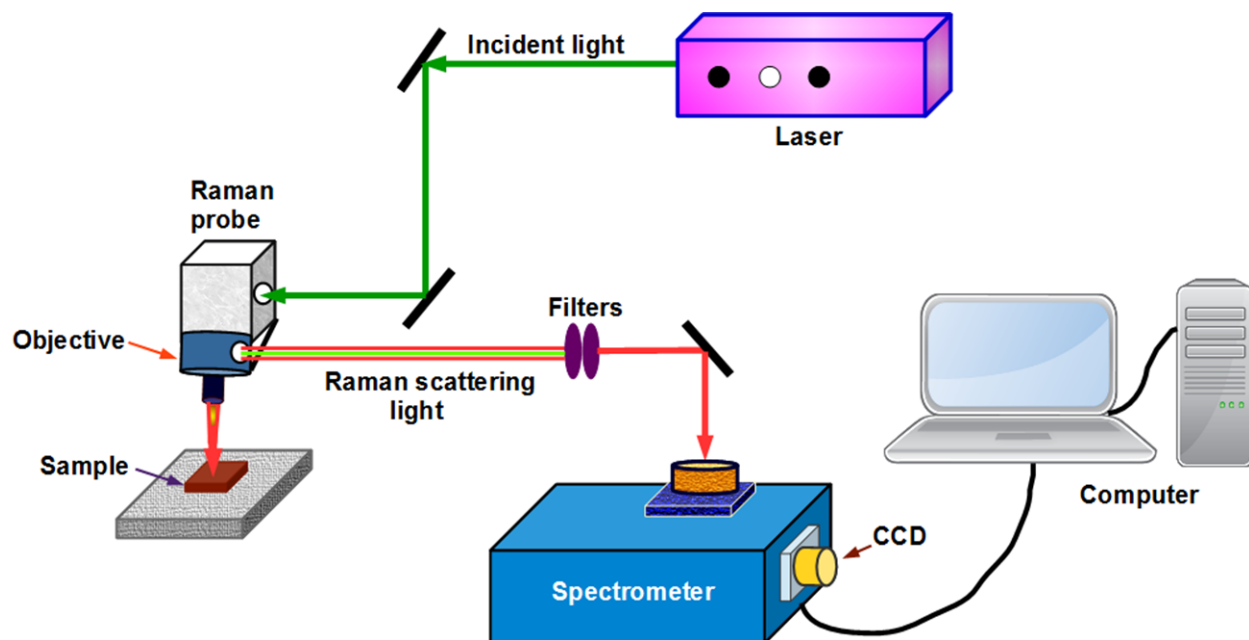


Figure 3.7.2. Schematic diagram of the Raman microspectroscopy setup.

3.7.3 Scanning Electron Microscopy

Scanning electron microscopy (SEM) in Figure 3.7.3 has been widely used to study the morphology and topography of the samples by scanning the surface of the sample using a high energy beam of electrons. SEM uses magnetic lenses to focus the electrons to a spot. The main components of the SEM are the source of electrons (tungsten filament is used as an electron gun), column for electron beam generation, vacuum pump, optics (lens, apertures, and deflectors), detectors, monitor and control balance [5]. The electrons are focused on the spot (with a nano-range diameter) surface of the sample, whereby they are absorbed, reflected or excite the surface electrons to release secondary electrons, Auger electrons, Bremsstrahlung X-rays or backscattered electrons [6]. The secondary or backscattered electrons are the main ones used when performing SEM measurements because of their low energies. The number of secondary electrons determines the brightness of the signal [7].

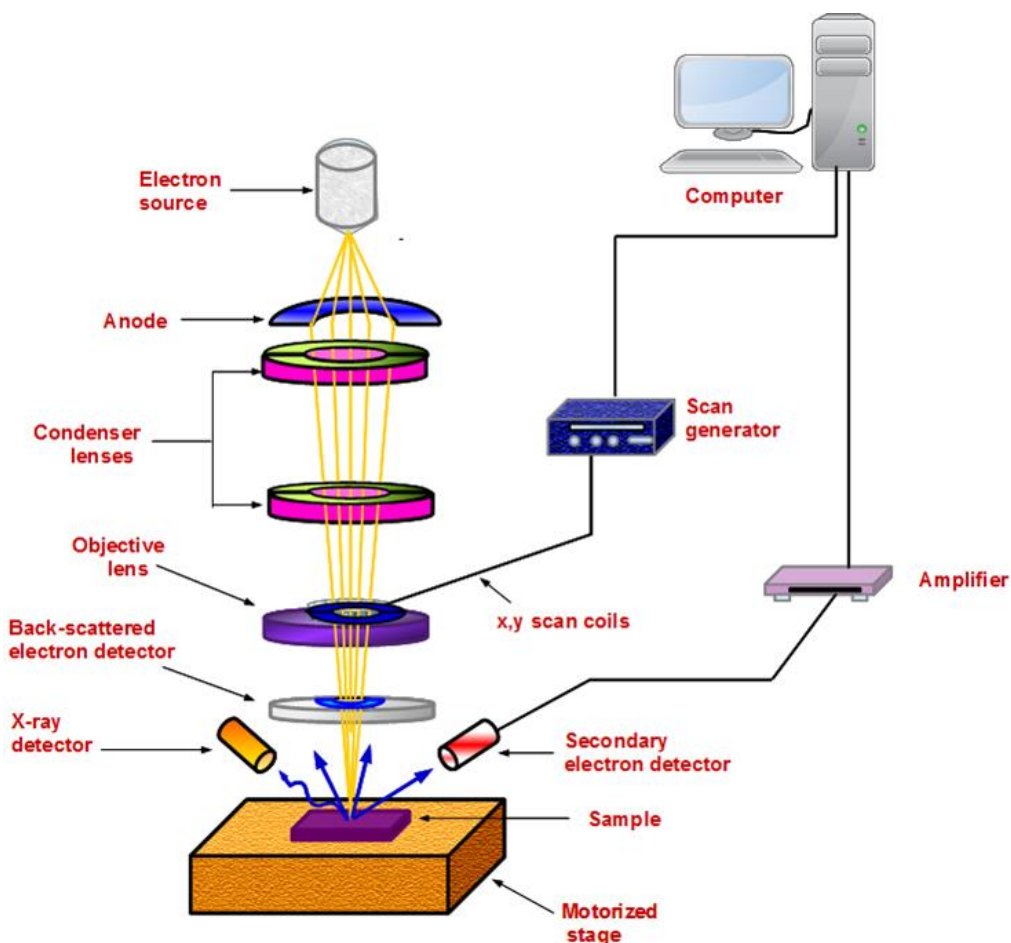


Figure 3.7.3. Schematic diagram of a scanning electron microscope.

In this study, the surface morphology and thickness of hematite nanostructures were obtained using a field emission scanning electron microscope (Zeiss Crossbeam 540 FESEM-Microscopes), operating at 2 kV. Before the actual loading of the samples into the SEM machine, they were first coated using carbon to enhance the surface conductivity. Carbon coating reduces the charging effect that leads to the deflection of the incoming electron beam.

3.7.4 Energy-dispersive X-ray Spectroscopy

Energy-dispersive X-ray spectroscopy (EDS) is used to determine the elemental composition of a material. It is typically coupled with SEM or transmission electron microscopy (TEM). The EDS detector then separates X-rays of various elements into an energy spectrum. Through this separation, the abundance of the elements in the material is obtained. Also, when performing EDS,

an elemental composition map can be obtained from the point analyser at a given spot size/area. The spectrum for EDS has a plot of the peak intensity (X-ray count) against energy (keV) [6]. The peak location on the x-axis is then converted into atoms representing the energy changes, and this is shown using a computer program. EDS (Oxford instruments) coupled with SEM, operating at 15 kV using Aztec 3.0 SP1 software was used for the elemental composition in this study. The time for each analysis was set to 10 min.

3.7.5 Photoelectrochemical study

The PEC performance of hematite was determined using a work station with three electrodes. This includes the working electrode (WE), the counter electrode (CE) and a reference electrode (RE) that were connected to the potentiostat and the computer. For this study, VersaSTAT 3F, from Princeton Applied Research U.S.A with a three-electrode system was used to measure the LSV, M-S and impedance Nyquist plots. NaOH (pH of 13.6), a platinum mesh as the CE, a hematite film as the WE, and Ag/AgCl in 3 M KCl as the RE, all inserted into a “cappuccino cell” were used for our study. The setup is shown in Figure 3.7.4. A scan rate of 50 mVs⁻¹ was used for both dark and light measurements. For light measurements, simulated sun (AM 1.5 G) was irradiated to the hematite thin film (WE) with a defined area of 0.49 cm², using a solar simulator (LSC 100 W Xenon lamp). The light intensity of 100 mWcm⁻² that was used during the measurements was adjusted using the detector (Newport). A voltage range of 0 and 1 was used for LSV measurements. Dark measurements were run first before the measurements of the actual sample. Using the LSV curves, the amount of photocurrent produced can be obtained when a simulated light intensity equivalent to 1 sun is irradiated to the semiconductor (WE) with a known area (cm² or mm²) using Eqn 3.7.5.;

$$J = \frac{I}{A} \quad 3.7.5$$

where J is the current density, I the current measured from the potentiostat and A the area of the working electrode/semiconductor. The obtained potentials can then be converted to the reversible hydrogen electrode using the Nernst Eqn,

$$E_{RHE} = E_{(Ag/AgCl)} + 0.059 \text{ pH} + E_{(Ag/AgCl)}^o \quad 3.7.6$$

where $E_{(Ag/AgCl)}$ is the potential measured against the reference electrode, $E^{\circ}_{(Ag/AgCl)}$ is 0.205 V at room temperature (25°C). Also, the pH of the electrolyte (NaOH, KOH or Na₂SO₄) is taken into consideration [9]. A potential that ranged from -0.2 to 1 V with a frequency of 10 kHz to 1 Hz was used to perform Nyquist plots for impedance measurements and Mott-Schottky curves under dark conditions.

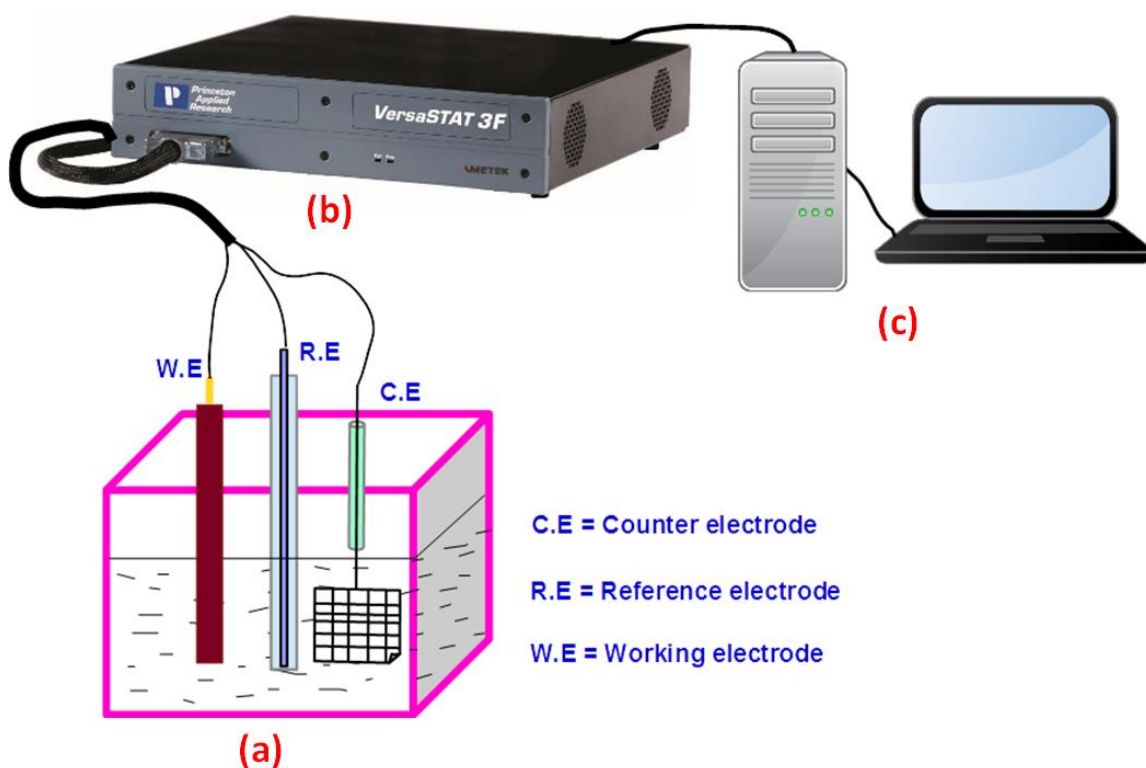


Figure 3.7.4. Schematic diagram of (a) a photoelectrochemical cell with three electrodes (CE, WE and RE) inserted in 1 M NaOH used as the electrolyte. Hematite was used as a WE, Ag/AgCl as RE, and a platinum mesh as the CE; (b) A VersaSTAT 3F potentiostat was used for electrochemical measurements; and (c) A computer with the VersaStudio program was used to run the experiments.

3.7.6 Ultraviolet-Visible (UV-VIS) spectroscopy

Ultraviolet-Visible (UV-Vis) spectroscopy is a technique used to measure light absorption of a sample. Electromagnetic rays in the visible (400 - 700 nm) and ultraviolet (200 - 400 nm) ranges

are used to illuminate the sample. The light is either transmitted, reflected or absorbed by the sample. This is analysed through measuring the intensity of light before the sample (I_o) and after the sample (I). The absorbance A of the sample is related to the transmittance ($T = \frac{I}{I_o}$), through the following expression:

$$A = -\log T \quad 3.7.7$$

In this study, absorbance measurements of hematite nanostructures were obtained using a Cary 100 Bio UV-Vis spectrophotometer. Before the actual measurements, baseline correction was done using two clean blank FTO substrates. After the zero and baseline correction, $\alpha\text{-Fe}_2\text{O}_3$ thin films were placed in one of the sample holders, with the coated side facing the light source. The other FTO substrate was left in the sample holder throughout the measurement as a reference. The bandgap was then estimated using the onset absorption and Tauc's Eqn [10].

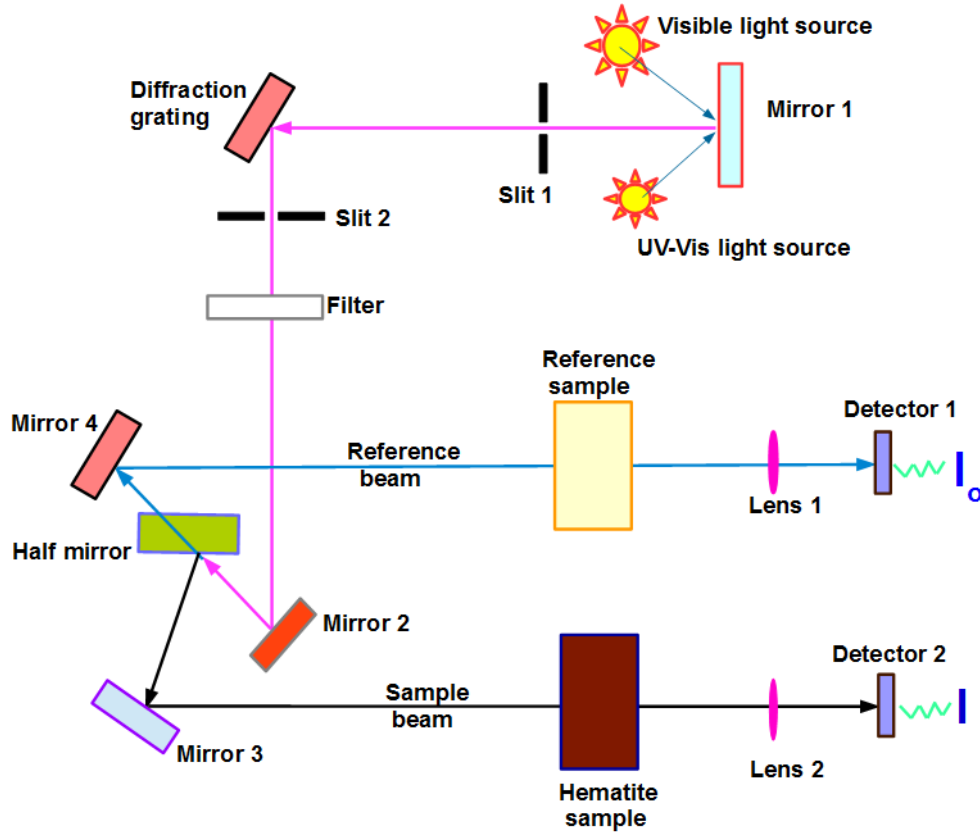


Figure 3.7.5. Schematic layout of the UV-Vis spectrophotometer.

3.7.7 Ultrafast transient absorption spectroscopy

An ultrafast transient absorption (pump-probe) spectroscopy setup at the National Laser Centre (NLC) of the Council for Scientific and Industrial Research (CSIR) was used in this study. The setup contains a CPA-2110 fiber-seeded Ti: Sapphire regenerative amplified laser system. The laser has the following specifications: 1 mJ pulse energy, a pulse width of 150 fs, 1 kHz repetition rate, and a peak wavelength of 775 nm.

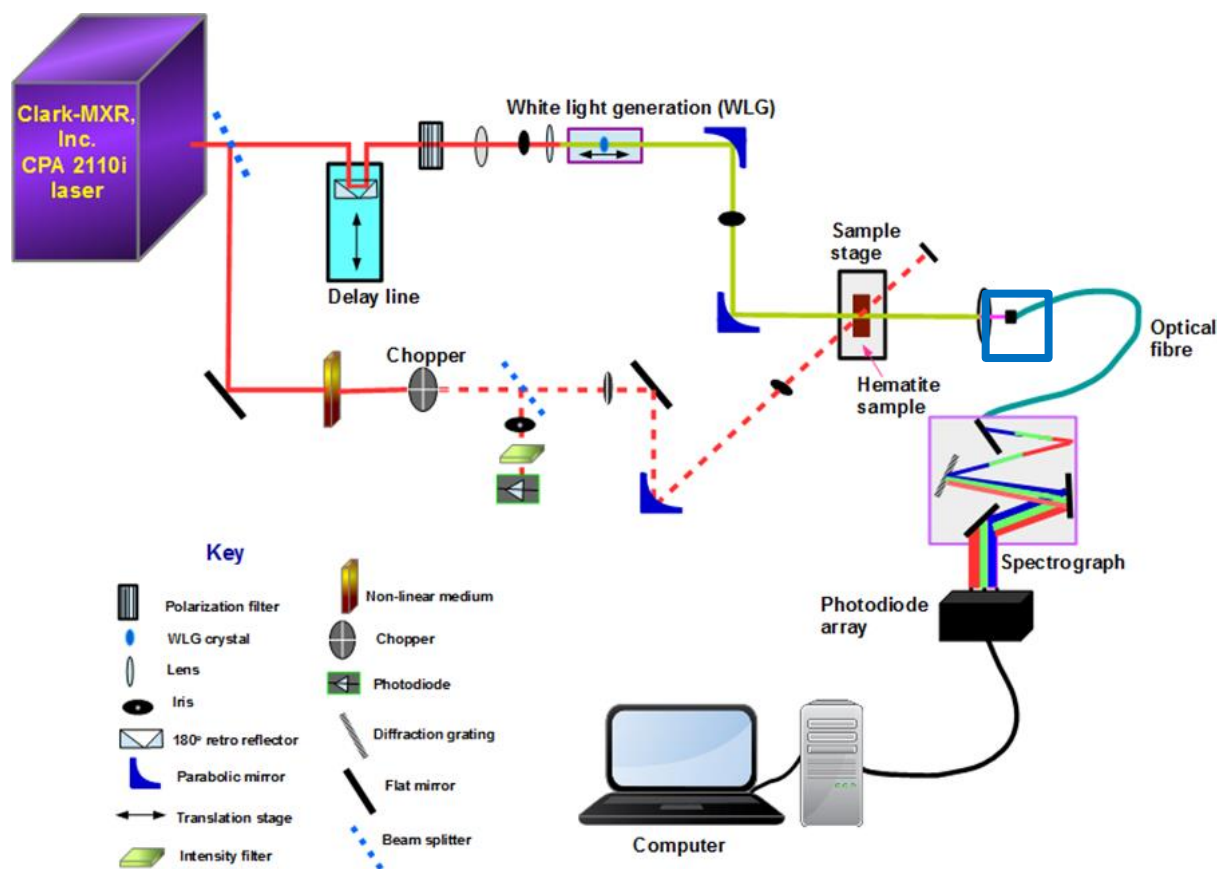


Figure 3.7.6. Schematic diagram of the pump-probe spectroscopy setup at the NLC used in performing ultrafast experiments on hematite nanostructures.

A fundamental beam with power of ~ 800 mW, centred at 775 nm was produced from our laser system. The beam was split into pump and probe beams using a beam splitter, as shown in Figure 3.7.6 in the ratio of 70:30, representing 565 mW for the probe beam and 235 mW for the pump

beam. The pump beam was then sent to β -barium borate (BBO) crystal for frequency doubling by producing a 387.5 nm centred beam, having a FWHM bandwidth of ~ 4 nm. A chopper placed in the pump beam was used to enable “pumped” and “unpumped” measurements. The probe beam was directed to a 2 ns delay line that has a motorized stage to achieve different delay times. From the delay line, the probe beam was attenuated and focused into the sapphire crystal for production of a white light continuum that has a wavelength range of 430 to 700 nm. This white light was used as the probe beam in the experiment, and focused to overlap temporally and spatially with the pump beam at the sample. Difference absorption ($\Delta A = A_{\text{pumped}} - A_{\text{unpumped}}$) spectra were obtained from these measurements. Beyond the sample, the pump beam was blocked using a pinhole while the probe beam was focused into an optical fibre and dispersed onto a CMOS sensor to capture the transmitted spectra. A custom-written MATLAB code was used in performing the measurements. Global analysis using Glotaran software was then used to analyse the data to obtain the decay lifetimes and evolution associated difference spectra (EADS) of hematite nanostructures [11]. This was done using a sequential model since it gives a more realistic description of the charge recombination in semiconductors like hematite than a parallel decay model.

References

- [1] A. Bunaciu, gabriela Udriștioiu, E.; Aboul-Enein, HY; Gabriela Udr Stioiu, E.; Aboul-Enein, Crit. Rev. Anal. Chem, 45 (2015) 289-299.
- [2] H.P. Klug, L.E. Alexander, X-ray diffraction procedures: for polycrystalline and amorphous materials, X-Ray Diffraction Procedures: For Polycrystalline and Amorphous Materials, 2nd Edition, by Harold P. Klug, Leroy E. Alexander, pp. 992. ISBN 0-471-49369-4. Wiley-VCH, May 1974., DOI (1974) 992.
- [3] T. Thompson, The fundamentals of Raman spectroscopy, Electro Opt, 2 (2012) 2.
- [4] K.J. Ember, M.A. Hoeve, S.L. McAughtrie, M.S. Bergholt, B.J. Dwyer, M.M. Stevens, K. Faulds, S.J. Forbes, C.J. Campbell, Raman spectroscopy and regenerative medicine: a review, NPJ Regenerative medicine, 2 (2017) 1-10.
- [5] R.F. Egerton, The Scanning Electron Microscope, Physical Principles of Electron Microscopy: An Introduction to TEM, SEM, and AEM, Springer International Publishing, Cham, 2016, pp. 121-147.
- [6] J.I. Goldstein, D.E. Newbury, J.R. Michael, N.W. Ritchie, J.H.J. Scott, D.C. Joy, Scanning electron microscopy and X-ray microanalysis, Springer2017.
- [7] B. Inkson, Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) for materials characterization, Materials characterization using nondestructive evaluation (NDE) methods, Elsevier2016, pp. 17-43.
- [8] S. Nasrazadani, S. Hassani, Modern analytical techniques in failure analysis of aerospace, chemical, and oil and gas industries, Handbook of Materials Failure Analysis with Case Studies from the Oil and Gas Industry, Elsevier2016, pp. 39-54.
- [9] E.S. Cho, M.J. Kang, Y.S. Kang, Enhanced photocurrent density of hematite thin films on FTO substrates: effect of post-annealing temperature, Physical Chemistry Chemical Physics, 17 (2015) 16145-16150.
- [10] R.-b. Cao, X.-q. Chen, W.-h. Shen, Z. Long, A facile route to synthesize nano-hematite colloid, Materials Letters, 65 (2011) 3298-3300.
- [11] J. Snellenburg, S. Liptonok, R. Seger, K. Mullen, I. Van Stokkum, Glotaran: A Java-based graphical user interface for the R package TIMP, DOI (2012).

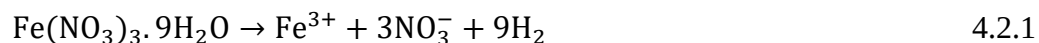
4 Results and discussion

4.1 Introduction

In this section, the results obtained from the synthesis of hematite nanoparticles using thermal spray pyrolysis are presented. This was done at elevated temperatures, varied from 280 to 430°C. Hematite thin films prepared at 430°C were used as the seed layer for the transformation of nanoparticles to nanospheres using L-arginine, by chemical bath deposition. A comparative study on the effect of iron precursor concentration and deposition temperatures on photoactivity water splitting is also presented. Hematite that was individually surface-doped with Zn, Ag and co-doped with Zn/Ag for PEC water improvement is also reported in this chapter. Finally, ultrafast transient absorption spectroscopy on pristine α -Fe₂O₃, L-Arg/ α -Fe₂O₃ and surface-doped hematite was performed to study their decay lifetimes and transient absorption spectra

4.2 Structural and optical properties of hematite and L-arginine/hematite nanostructures prepared by thermal spray pyrolysis

Hematite underwent a phase transformation whereby Fe(NO₃)₃·9H₂O and water provided Fe³⁺ and OH⁻ respectively to produce iron (III) hydroxide (Fe(OH)₃). This (Fe(OH)₃) was annealed in air at 450°C for 1 h for phase transformation to α -Fe₂O₃ according to the following Eqns:



Yadav and co-worked have reported similar results in the study of hematite nanostructures using FeCl₃ as the precursor [1].

4.2.1 X-ray diffraction analysis

Figure 4.2.1 presents the X-ray diffraction (XRD) of the hematite NPs crystal structure for the 2θ range of between 20° and 70°. All the phases confirmed hematite with the corundum structure,

having lattice constants of $a = b = 0.5034$ nm and $c = 1.3750$ nm, and a space group $R\bar{3}C$ matching with JCPDS file no. 84-0311 [1, 2]. Besides, the Miller indices of (012), (104), (110), (113), (024), (116), (122), and (124) were indexed at 25.5° , 33.3° , 35.3° , 41° , 49° , 54° , 57° , and 63° , respectively. The corundum structure of hematite is characterized by (104) and (110) phases, which were also reported in all our samples to be the most intense. The growth of these phases was perpendicular to the crystallographic planes, a clear indication of the application of these thin films in the photoelectrochemical water splitting [3].

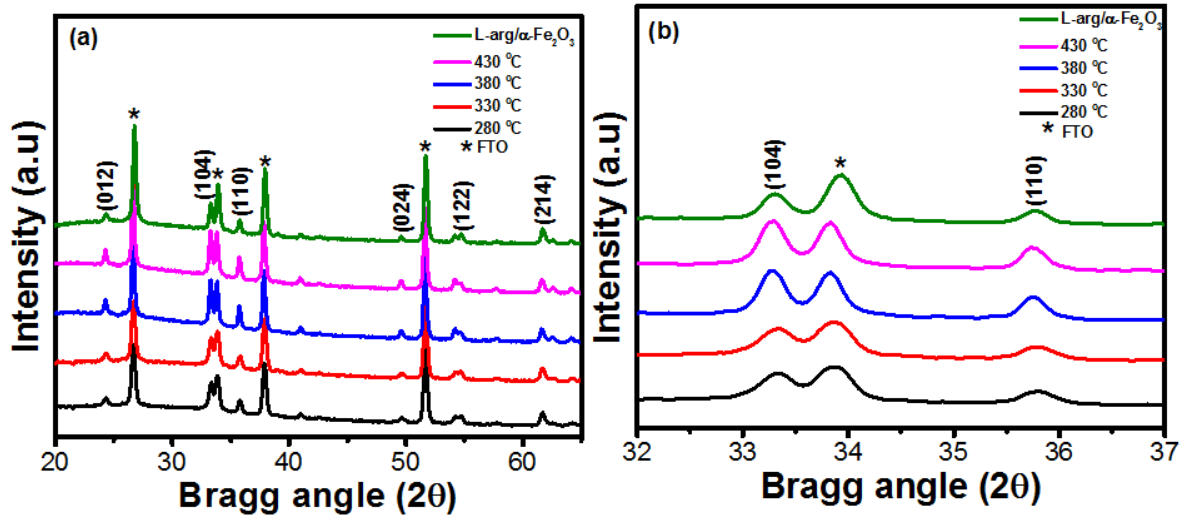


Figure 4.2.1. X-ray diffraction patterns of (a) hematite nanostructured films synthesized using spray pyrolysis at different temperatures (280 - 430°C), (b) (104) and (110) phases of hematite.

Origin Pro software was used to calculate the full width at half maximum (FWHM), with the fitting done using the dominant phases of hematite (110 and 104). Further, crystallite sizes were then calculated using Debye-Scherrer's formula,

$$D = \frac{0.9\lambda}{\beta \cos \theta} \quad 4.2.4$$

where D is the crystallite size, λ wavelength of the radiation (0.15418 nm, CuK α), β is the FWHM and θ the 2-theta angles for the (110) and (104) peaks [5]. From this calculation, crystallite sizes that ranged between 21 and 46 nm were obtained, as shown in Table 4.2.1

Table 4.2.1. Crystallite sizes and FWHM of hematite nanostructures synthesized by both spray pyrolysis and chemical bath deposition.

Sample	FWHM (°)	Crystal size of 104 peak (nm)	FWHM (°)	Crystal size of 110 peak (nm)
280°C	0.3238	29.38	0.2370	40.10
330°C	0.3356	28.35	0.2561	38.03
380°C	0.3875	24.54	0.3031	32.14
430°C	0.4473	21.26	0.2736	35.57
L-Arg/ α -Fe ₂ O ₃	0.3497	27.22	0.2136	45.61

The deposition temperature affected the crystallite size of nanostructured hematite films, whereby large grains were formed at low temperatures (280°C) leading to the broadening of the peaks. This was due to rapid evaporation at higher temperatures (380 and 430°C) resulting in deposition of the precursor in the vapour form. In contrast, at low temperature (280 and 330°C) most of the precursor deposition was in liquid form since the evaporation was limited. The crystallite size for L-Arg/ α -Fe₂O₃ nanospheres was observed to increase slightly, and this could be due to erosion of the hematite layer during the growth process. There was an observed shift of the angular Bragg peaks to higher 2θ angles (Figure 4.2.1 b), resulting from grain size unit cell decrease with an increase in deposition temperature. Also, at higher deposition temperatures, the imposition of the surface stress on hematite nanospheres and NPs was increased. The change in crystallite size can therefore lead to a change in structure, stress, stoichiometry and strain of the materials [6].

4.2.2 Raman spectroscopy

Figure 4.2.2 presents Raman spectroscopy of hematite thin films with the sample scan that ranged from 200 and 1450 cm⁻¹. The synthesized hematite thin films were all polycrystalline as revealed

by sharp and strong vibrational modes. The 225 and 500 cm^{-1} peaks are assigned to A_{1g} while the 245, 291, 300, 409, and 609 cm^{-1} modes were assigned to E_g vibrational modes [7]. The 660 cm^{-1} peak was associated with the longitudinal optical (LO) mode of hematite. On the other hand, the 1312 cm^{-1} peak, which is at a wavenumber twice that of the LO mode, observed in all the samples was due to the two-phonon (magnon) scattering mode (2LO) [8, 9]. There was an observed Raman shift, leading to the 2LO mode not having the exact wavenumber with the LO mode as the deposition temperature was varied from 280 to 430°C. Raman spectra intensity peaks of L-Arg/ α - Fe_2O_3 sample were observed to increase compared to the pristine hematite samples, and this was due to the change in the crystal size.

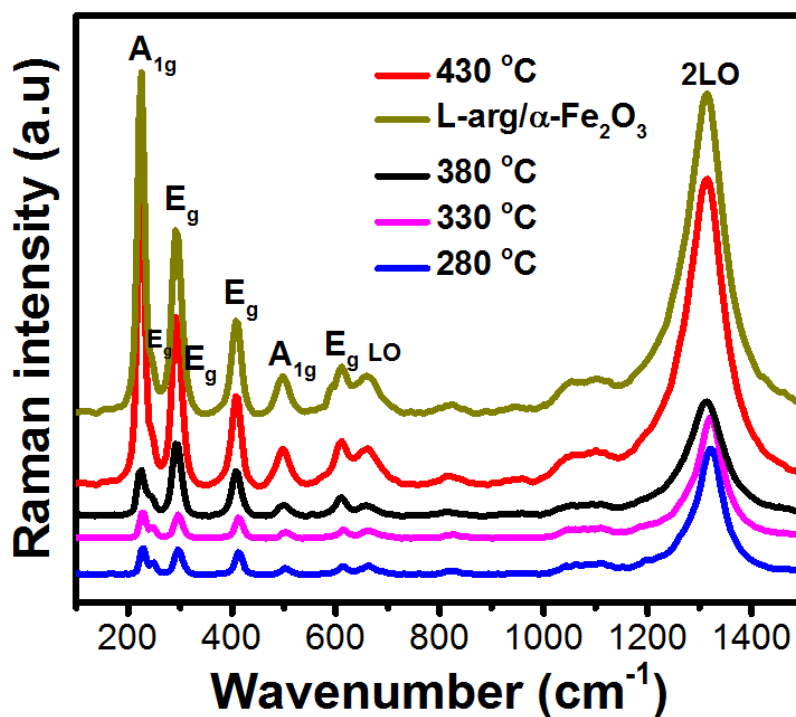


Figure 4.2.2. Raman spectra of nanostructured hematite at temperatures of 280, 330, 380, and 430°C prepared by spray pyrolysis, L-Arg/ α - Fe_2O_3 transformed using chemical bath deposition.

There was a vibrational overlap of 225 cm^{-1} (A_{1g}) and 245 cm^{-1} (E_g) modes, hence the deconvolution was necessary to reveal these peaks as shown in Figure 4.2.3 (a-e). Besides, there was a red-shifting of these two vibrational modes with an increase in the temperature of deposition from 280 - 430°C. This was due to the induced transformations resulting from the thermal expansions, affecting the vibrational energy and population of different phonon mode levels [10].

The variation of half widths(Γ) at different deposition temperatures also led to the red-shifting of these vibrational phonon modes [11]. Besides, there was a peak broadening as the deposition temperature increased from 280 to 430°C and this resulted from the phonon-phonon scattering caused by anharmonic terms [11]. The Raman effect observed is also due to the change of phases from magnetite to maghemite since they have different crystallographic structures. However, the peaks of maghemite and magnetite were not observed in all our synthesized samples, and all the phases were consistent with the XRD findings. Figure 4.2.4 (f) shows a non-linear Raman shift with the variation of the deposition temperature.

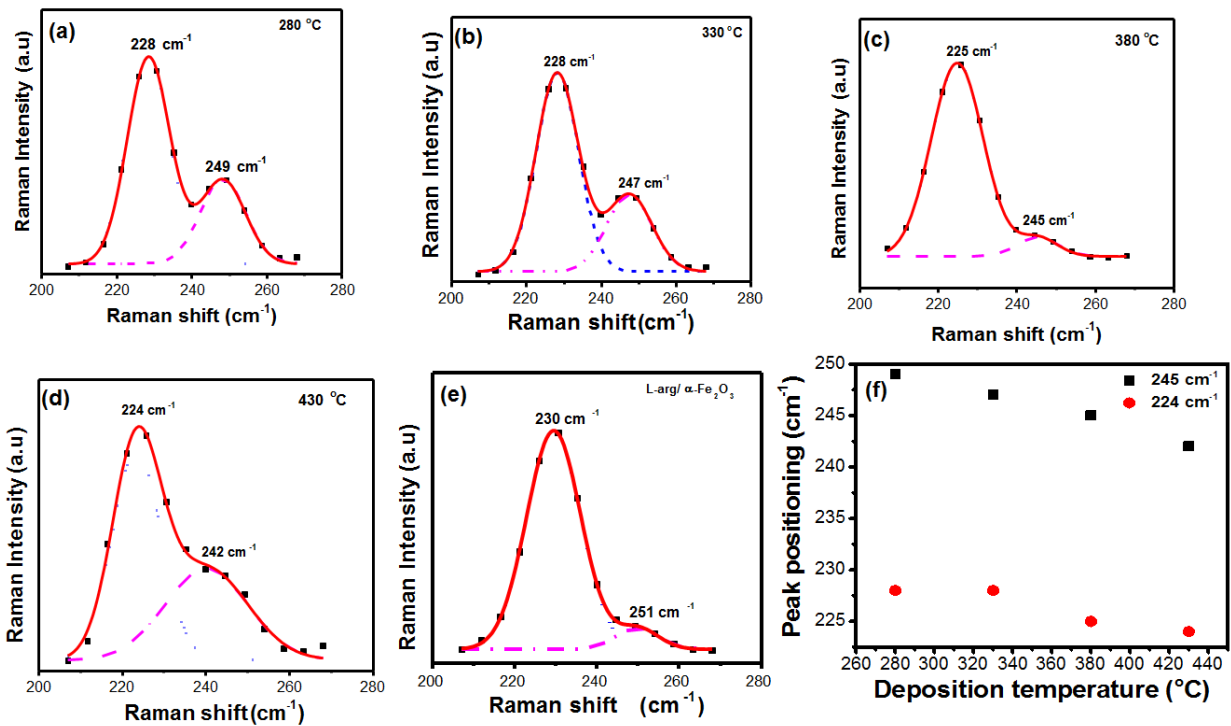


Figure 4.2.3 (b-f) 226 and 245 cm⁻¹ deconvoluted Raman peaks of hematite NPs and L-Arg/ α -Fe₂O₃ nanospheres, (g) Raman peak positioning of the ~225 and ~245 cm⁻¹ modes vs. deposition temperature of hematite films.

4.2.3 Variation of thickness with temperature.

An average cross-section was used to measure the thickness of hematite nanostructured films using field emission scanning electron microscopy (FE-SEM). The thickness obtained excluded the fluorine-doped tin oxide (FTO) layer, which was on top of the soda-lime glass. From the

measurements, the thickness was observed to decrease as the deposition temperature increased from 280 to 430°C, as shown in Figure 4.2.4 (a). This was due to a high growth rate at low temperatures resulting from deposition taking place in liquid form since most of the iron precursor solution was landing on the FTO substrate. However, at higher temperatures, more evaporation of the precursor took place, leading to vapour deposition of the precursor as it was landing on the substrate. This led to thin films (~240 nm for films deposited at 430°C) as shown in Figure 4.2.4 (a). The variation of thickness with temperature can be summarized in Figure 4.2.4 (b).

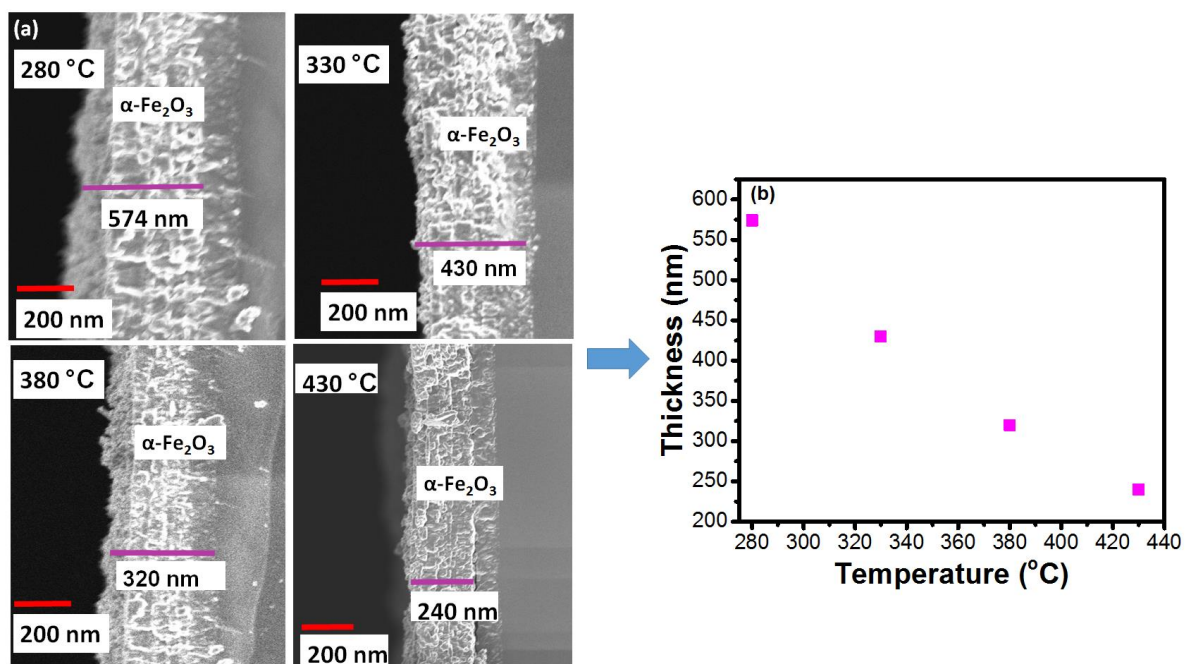


Figure 4.2.4. (a) Cross-section micrograph images estimating the thickness using FE-SEM for hematite films deposited at 280, 330, 380, and 430°C using spray pyrolysis. A scale of 200 nm (red bars) was used, and hematite films thickness on the substrate were estimated using the purple lines by matching them with the scale bar, (b) thickness against temperature for hematite thin films at 45 s deposition time, 1.5×10^5 Pa spray pressure, and 50 mM of concentration.

4.2.4 Surface morphology and topography

4.2.4.1 Hematite nanoparticles

Figure 4.2.5 represents the surface morphology and topography of hematite NPs at different temperatures. There was an observed decrease in the grain size as the temperature of deposition was increased from 280 to 430°C, as shown in Figure 4.2.5 (a) which was obtained using FE-SEM. The change in grain size could be due to a crystallinity change to polycrystalline from amorphous at high and low deposition temperatures, respectively. From the ImageJ software, the average grain sizes were estimated on a given area on the film surface. The films deposited at 280°C had an average grain size of 100 ± 0.5 nm, while 41 ± 0.5 nm was obtained for films deposited at 430°C. Since hematite suffers from short electron-hole diffusion lengths of 2-20 nm, [12], the small grain size could therefore facilitate the charge carriers (e^-h^+) to travel to the semiconductor surface before recombination takes place during the PEC process. Duret and co-workers have reported similar results on the synthesis of hematite nanostructures using ultrasonic spray pyrolysis using ferric acetylacetonate dissolved in ethanol as the precursor [13]. From their findings, the nanostructures had an average diameter that ranged from 50.0 to 100 ± 0.5 nm, with a current density of $1.07 \mu\text{A}/\text{cm}^2$ at 1.23 V vs. RHE.

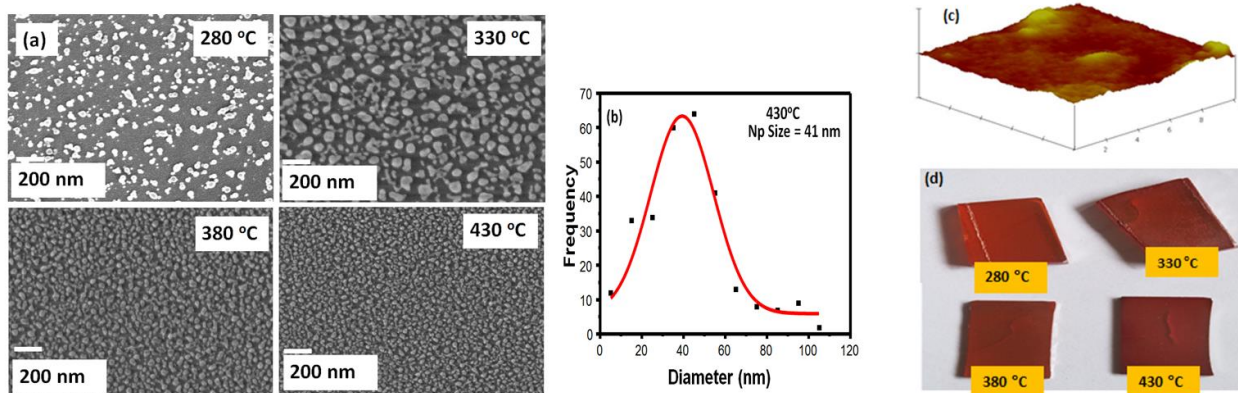


Figure 4.2.5. (a) FE-SEM images of hematite NPs prepared at temperatures of 280, 330, 380 and 430°C using spray pyrolysis at a precursor concentration of 50 mM, and 1.5×10^5 Pa spray pressure, (b) a Gaussian fitting of hematite NPs distribution. (c) AFM RMS roughness of hematite NPs at 430°C. (d) as-deposited images of $\alpha\text{-Fe}_2\text{O}_3$ samples.

Atomic force microscopy (AFM) was employed in the study of the surface roughness and topography for the nanostructured hematite film prepared at 430°C, a temperature used to

transform NPs to nanospheres as will be discussed in Section 4.2.4.2. From AFM measurements presented in Figure 4.2.5 (c), a homogeneous morphology and root mean square (RMS) roughness of 35 nm as estimated using Gwydion software was obtained. Figure 4.2.5 (d) presents the actual hematite films on FTO, which were brown as obtained from spray pyrolysis.

4.2.4.2 L-arginine/hematite nanostructures

Films prepared at 430°C were used as seed layers in the transformation of hematite NPs to nanospheres using chemical bath deposition, with a constant bath temperature of 90°C for 48 h. This was done using L-arginine ($C_6H_{14}N_4O_2$), which is an amino acid. The grain size of L-Arg/ α - Fe_2O_3 nanospheres is shown in Figure 4.2.6 (a), obtained from FE-SEM measurements.

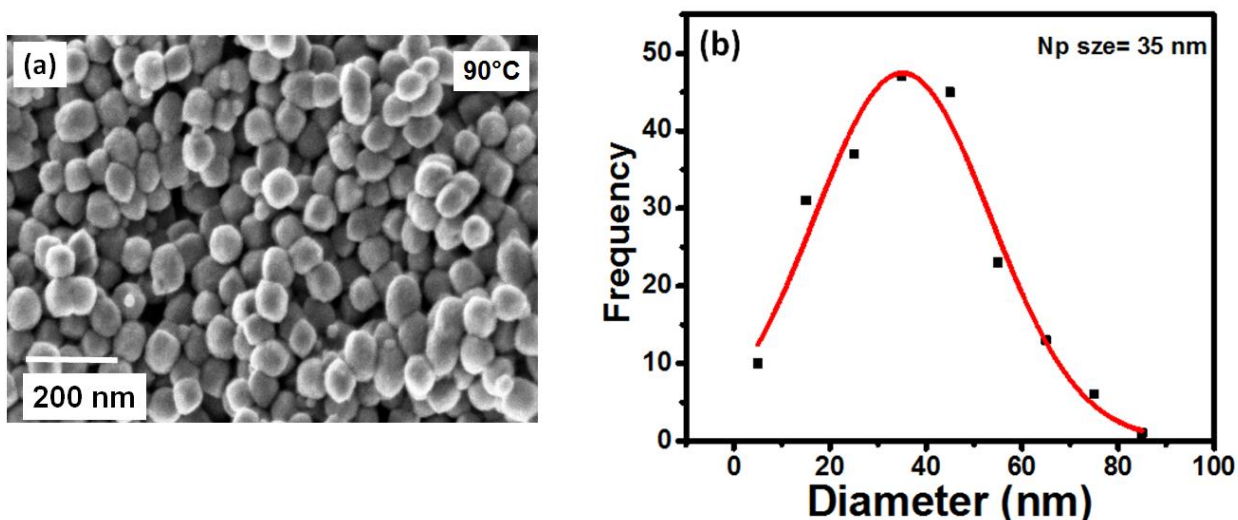
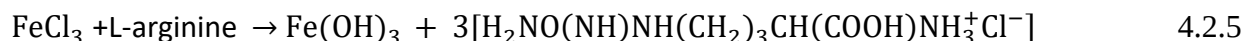


Figure 4.2.6. (a) FE-SEM image of hematite nanospheres using chemical bath deposition at 90°C for 48 h, (b) Gaussian fit of hematite nanosphere grain size distribution.

The grain sizes were observed to be roughly spherical and uniformly distributed on the surface of the film. The 35.0 ± 0.5 nm average grain size was obtained using ImageJ, as shown in Figure 4.2.6 (b). The growth of the uniform spherical size and shape was probably influenced by the fundamental nature of L-arginine that creates a suitable seeding medium for crystal growth. It was also due to the equimolar solutions of L-arginine and $FeCl_3 \cdot 6H_2O$ used during the transformation process, leading to a uniform interaction between the two solutions. Iron (III) hydroxide ($Fe(OH)_3$)

that produced a uniform transformation of hematite NPs to nanospheres was formed through this interaction process. Eqn 4.2.5 represents the formation of $(\text{Fe}(\text{OH})_3)$, where the second term on the reactant side is the L-arginine molecule, while on the product side, iron (III) hydroxide (first term) and a waste product (last term) were formed [14].



The $\text{Fe}(\text{OH})_3$ went through the process of heterogeneous nucleation on the seeded layer of hematite NPs, forming an akaganeite ($\beta\text{-FeO}_{0.833}(\text{OH})_{1.167}\text{Cl}_{0.167}$) phase, which has the octahedral structure consisting of hydrogen bonds [15]. The unstable oxide of iron (akaganeite) was then oxidized at high temperatures in the air to form $\alpha\text{-Fe}_2\text{O}_3$ nanospheres, presented in Eqn 4.2.6. The formed $\alpha\text{-Fe}_2\text{O}_3$ nanospheres were then nucleated and distributed on the whole surface of pristine hematite, forming uniform nanospheres of equal diameter.



Figure 4.2.7 gives a summary of the heterogeneous process that took place during the transformation process.

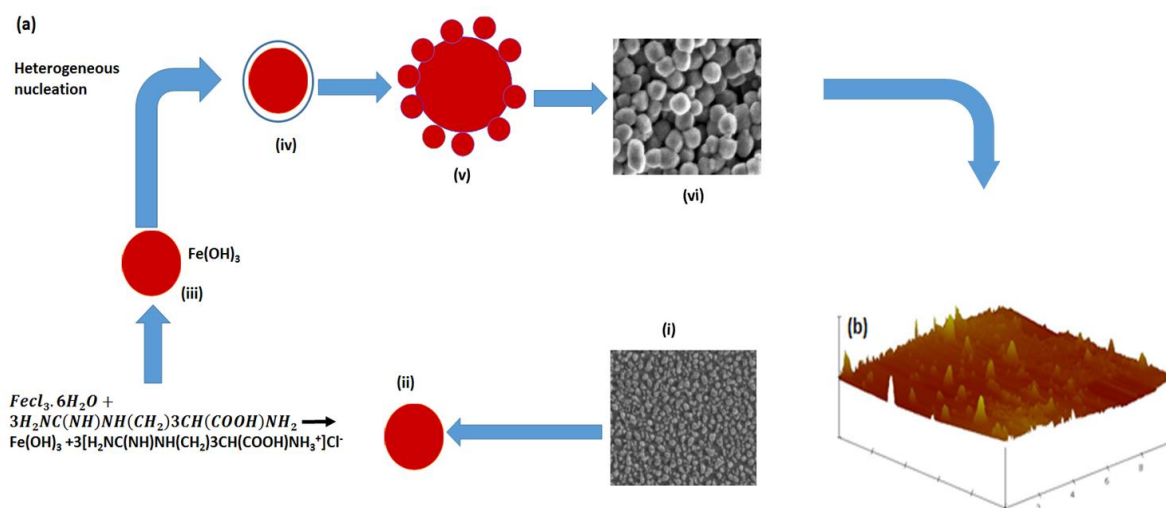


Figure 4.2.7. Heterogeneous nucleation of L-Arg/ α -Fe₂O₃ nanospheres; (i) Hematite NPs synthesized using spray pyrolysis at 430°C, (ii) CBD of FeCl₃.6H₂O and L-arginine at a bath temperature of 90°C for 48 h, (iii) iron (III) hydroxide formed that underwent heterogeneous nucleation in step (iv). The nucleation is uniformly distributed, as shown in (v) to form hematite nanospheres in (vi). (b) AFM surface RMS roughness of as-prepared L-Arg/ α -Fe₂O₃ nanospheres.

4.2.5 Optical studies

UV-Vis spectroscopy was used to measure the optical properties of hematite thin films in the wavelength range of 350 - 800 nm to obtain the absorbance and transmittance, later used to estimate the energy bandgap. From Figure 4.2.8 (a), an average transmittance of ~47 % was obtained for all the films at a wavelength of 550 nm. This low transmittance resulted from more absorbance due to several layers of hematite during the spray pyrolysis deposition process. Besides, this transmittance was also observed to increase with the rise in deposition temperatures, from ~44 to ~56 % for 280 and 430°C samples respectively (Figure 4.2.8 a), due to a decrease in film thickness at higher temperatures. These results agree with the Lambert-Beer law [16]. For L-Arg/ α -Fe₂O₃ film, there was an observed decrease in transmittance from ~56 % (hematite film deposited at 430°C) to ~49 %. This could result from a slight increase in film thickness during the transformation process where hematite film was used as a seed layer. Tauc's equation was used in the estimation of the bandgap from transmittance measurements:

$$(\alpha h\nu)^{\frac{1}{2}} = A(h\nu - E_g)^m \quad 4.2.7$$

where α represents the absorption coefficient, $h\nu$ the photon energy, A is the effective mass of holes and electrons constant, m is 2 for allowed indirect transition, and $\frac{1}{2}$ for allowed direct transition [17]. For the indirect bandgap of hematite, a plot of $(\alpha h\nu)^{0.5}$ against $h\nu$ was used from Tauc relation as shown in Figure 4.2.8 (c).

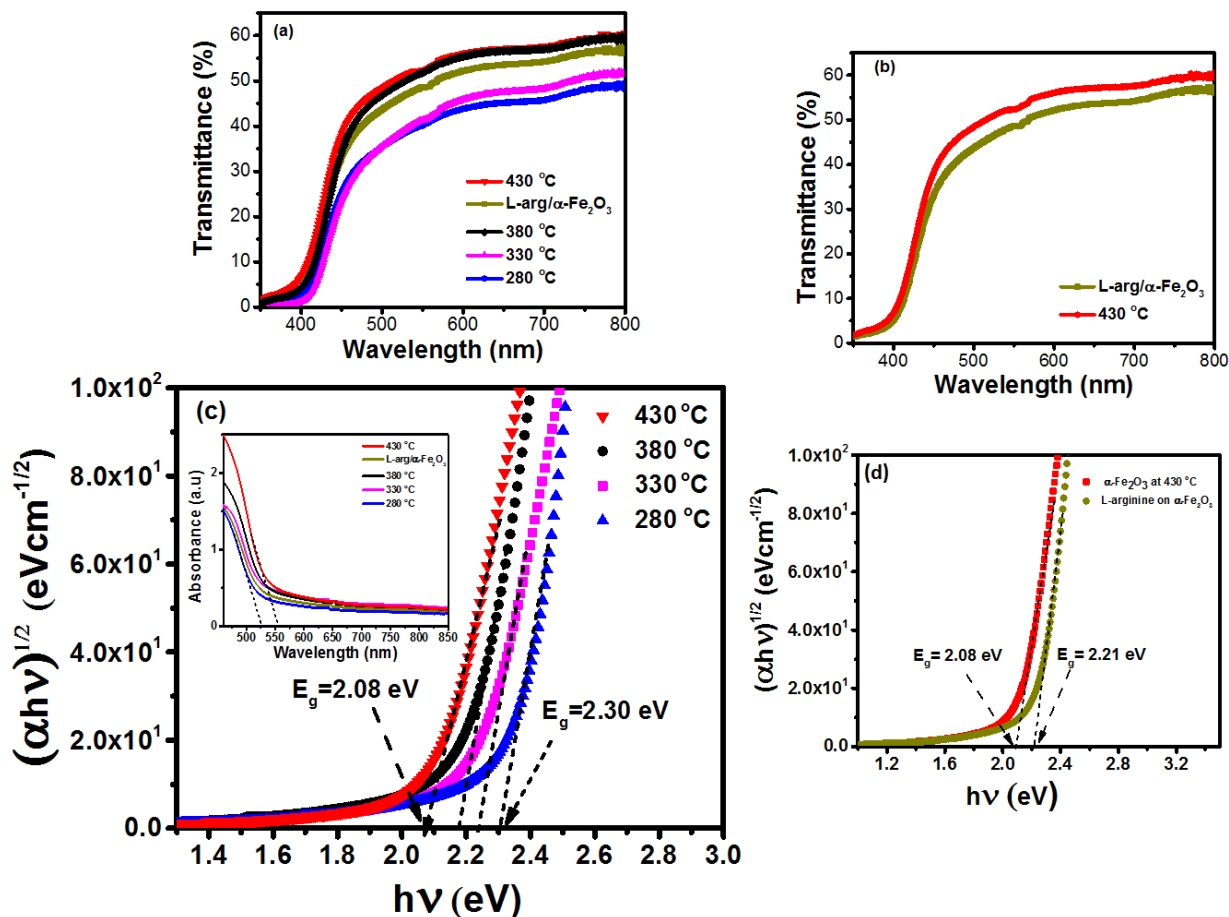


Figure 4.2.8. (a) The transmittance of hematite thin films synthesized at temperatures of 280, 330, 380, and 430°C by spray pyrolysis, (b) transmittance of L-Arg/ α -Fe₂O₃ prepared by CBD at a bath temperature of 90°C for 48 h, (c) a plot of $(\alpha h\nu)^{0.5}$ against $h\nu$ for hematite nanostructured films prepared at different temperatures (280 - 430°C). The inset presents the optical absorbance L-Arg/ α -Fe₂O₃ and pristine hematite thin films, (d) $(\alpha h\nu)^{0.5}$ versus $h\nu$ for L-Arg/ α -Fe₂O₃ and pristine thin films hematite (prepared at 430°C).

An indirect bandgap that ranged from 2.30 eV (280°C sample) to 2.08 eV (430°C sample) was obtained (Figure 4.2.8 c). From these results, it can further be observed that there was a decrease in bandgap as the temperature of deposition was increasing from 280 to 430°C. This could be due to the increase in the inter-atomic spacing, leading to a reduction in electron potential. This, therefore, creates an advantage to our prepared films for PEC applications as more solar energy in the visible region is absorbed by the smaller bandgap of 2.08 eV (596 nm). The absorbance spectra for both the pristine hematite and L-Arg/ α -Fe₂O₃ nanostructures is presented in the inset of Figure 4.2.8 (c). This absorbance was found to be in the range of 1.90 and 2.20 eV using onset estimation, similar to what we obtained using Tauc's equation, and what Bora and co-workers

have reported [18]. The comparison of the bandgap of pristine hematite and L-Arg/ α -Fe₂O₃ is presented in Figure 4.2.8 (d). The bandgap increased from 2.08 to 2.21 eV for pristine hematite at 430°C and L-Arg/ α -Fe₂O₃ thin films, respectively, and this could be due to the change in thickness during the transformation process using CBD. The effect, therefore, could have led to a change in the grain boundary barrier height [19].

4.2.6 Photocurrent measurements

The potentiostat (VersaSTAT 3 F, U.S.A) work station was used to measure the photocurrent density (J) using Ag/AgCl as the reference electrode, a platinum mesh as the counter electrode, and prepared nanostructured hematite films as the working electrode. The hematite sample was irradiated with 1.5 G simulated solar light, based on a Xe lamp with a focus area of 0.49 cm². 1 M sodium hydroxide (NaOH) was used as electrolyte during the linear scan voltammetry (LSV) measurements in the PEC. The LSV measurements were recorded using a voltage range of 0 and 1 V with a scan rate of 0.05 Vs⁻¹ as presented in Figure 4.2.9.

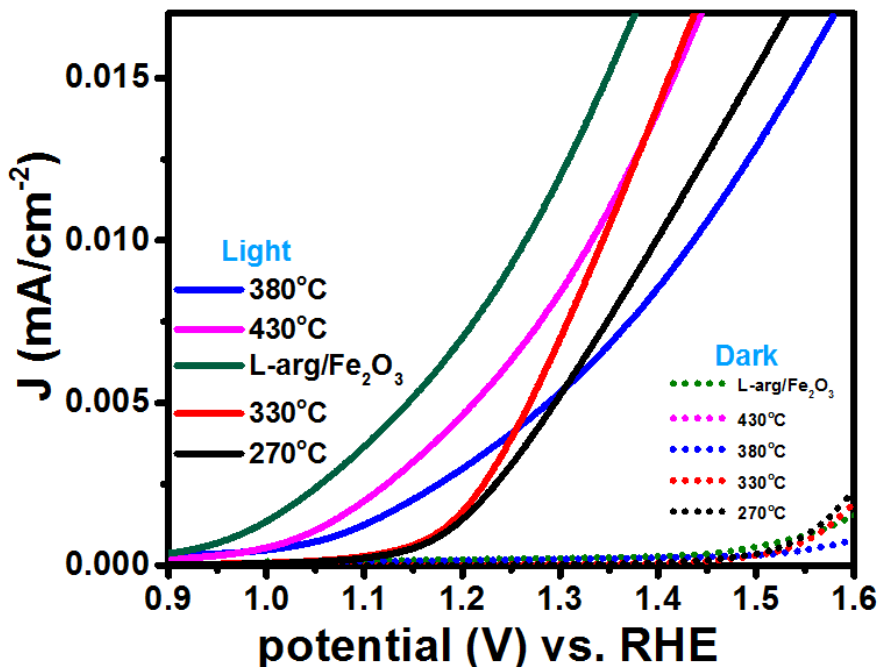
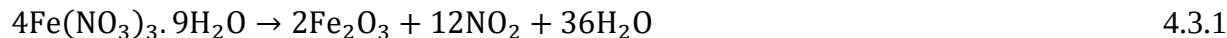


Figure 4.2.9. Photocurrent density of pristine hematite prepared at different temperatures (280-430°C) using spray pyrolysis, and L-Arg/ α -Fe₂O₃ thin film synthesized using CBD at a bath temperature of 90°C for 48 h, scan rate of 50 mVs⁻¹ and 1 M NaOH as the electrolyte.

The highest photocurrent density for L-Arg/ α -Fe₂O₃ thin films of 10 μAcm^{-2} , at 1.23 eV vs. RHE was recorded. On the other hand, the pristine hematite films prepared at different deposition temperature produced a photocurrent density of 6.4, 4.3, 4.0, and 2.8 μAcm^{-2} at 1.23 eV vs. RHE for samples prepared at 430, 380, 330, and 280°C, respectively. Additionally, a cathodic shift was observed for L-Arg/ α -Fe₂O₃ films from 1.13 to 0.91 V. Bora and co-workers have reported related current-voltage (I-V) using a hydrothermal technique [20]. Despite the drawbacks of hematite for its poor conductivity, pristine hematite can show some promising improvement through nanostructuring. However, for higher photocurrent density to be obtained, other approaches such as doping with elements like Zn and Cu can increase the donor density [21, 22].

4.3 Effects of L-arginine concentration on hematite nanostructures synthesized by spray pyrolysis and chemical bath deposition

During the spray pyrolysis, iron oxyhydrate Fe(OH)₃ was formed, and later underwent a phase transformation during annealing to form hematite according to the Eqn 4.3.1.



4.3.1 Structural properties

XRD was used to study the structure of the synthesized L-Arg/hematite through a 2θ angle that ranged between 20 and 70°, as shown in Figure 4.3.1.

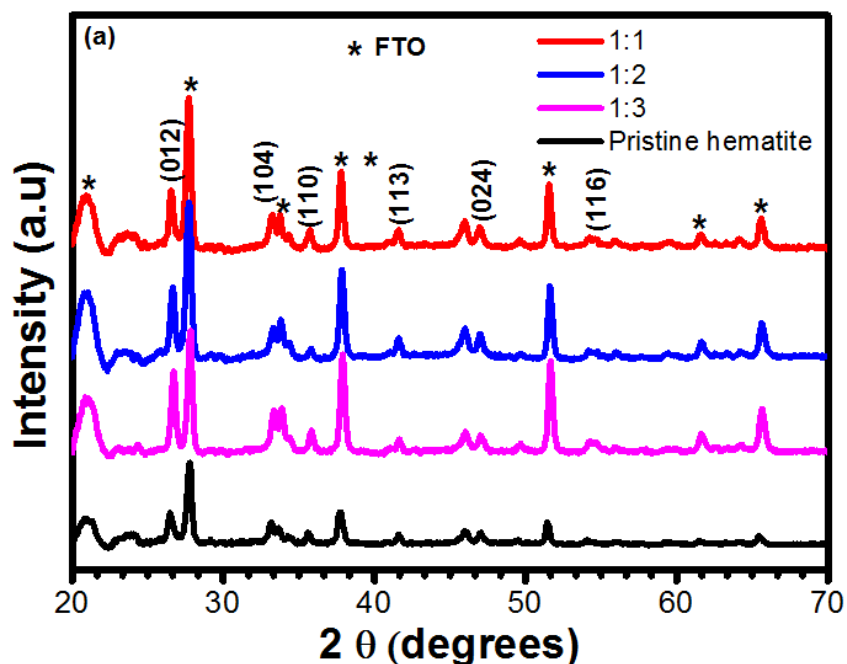


Figure 4.3.1. XRD spectra of hematite nanoparticles prepared by CSP and L-Arg/Fe₂O₃ nanospheres synthesized by CBD for 1:1, 2:1, and 3:1 of L-arginine: FeCl₃.6H₂O, respectively.

The (104) and (110) indexed at 33.3° and 35.5° that are associated with hematite were the dominant peaks. These peaks further confirm the corundum structure of hematite with space group $R\bar{3}C$. Besides, the lattice parameters of hematite thin films were calculated using these dominant peaks (104 and 110). The average lattice constant for these nanostructures, $a = b$ (for hexagonal structures) was 5.021 Å, and $c = 13.749$ Å. These parameters were similar to the standard lattice parameters for hematite using the JCPDS file no. 33-0664 [23]. There was an observable high intensity of (012) indexed at 25.6° that was predominant to other phases, further confirming the perfect lattice fringes in hematite. The purity of the films was further confirmed since no other diffraction peaks for other phases of iron were observed. Other researchers have reported similar results whereby the hematite films were synthesized using a hydrothermal technique for application in gas sensing [24, 25].

Using Debye Scherrer's equation, crystallite sizes of these hematite nanostructures were obtained. The crystallite size the hematite thin films decreased as the 2θ (Bragg angle) was increased, a former attributed to the increase in the crystallinity with the variation of the precursor

concentration from 1:1 to 3:1. The change in crystallite size could also be due to the difference in the geometrical shape of these nanospheres (*vide infra*). Also, a study on the comparison of the full width at half maximum (FWHM) analysed from Origin Pro on hematite nanostructures was reported as shown in Figure 4.3.2. There was a non-linear increase in the FWHM as the Bragg angle was increased from 20 to 58°. This might have resulted from the finite crystal size at large angles, micro-strain, dislocations, and defects that took place during the growth of the films and calcination process [26].

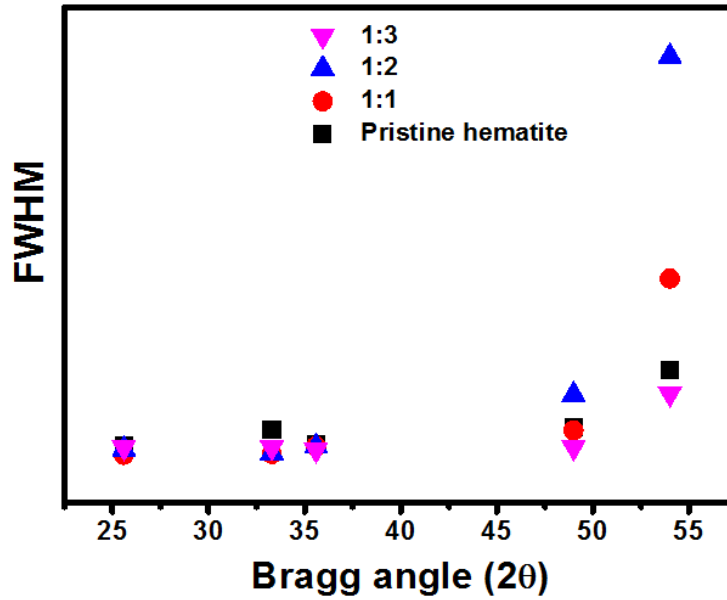


Figure 4.3.2. FWHM variation of pristine α -Fe₂O₃ and L-Arg/ α -Fe₂O₃ nanostructures of 1:1, 2:1 and 3:1 of L-arginine: FeCl₃.6H₂O respectively.

A non-linear relationship between the aperture of the detector and the d-spacing could have also resulted in the broadening of the FWHM. To further analyse the structure of these films, the micro-strains were calculated using the Williamson-Hall equation.

$$\varepsilon = \frac{\beta}{4 \sin \theta} \quad 4.3.2$$

where ε is the micro-strain, and β is the FWHM [27]. On the other hand, the dislocation density equation was used to obtain the defects in our nanostructured films,

$$\delta = \frac{1}{D^2} \quad 4.3.3$$

where D is the crystallite size and δ the dislocation density [28]. There was an increase in micro-strain and dislocation density as the L-arginine: $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ was varied from 1:1 to 3:1, respectively (see Table 4.3.1). The stacking layers of different layers during deposition and imperfections could have led to the high dislocation density of $1.60 \times 10^{-4} \text{ nm}^{-2}$. In addition, L-Arg/ α - Fe_2O_3 nanostructures deposited at 1:1, 2:1 and 3:1 of L-arginine: $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ precursor concentrations were observed to have a dislocation density of 1.10×10^{-4} , 1.16×10^{-4} and $1.21 \times 10^{-4} \text{ nm}^{-2}$ respectively (Table 4.3.1).

Table 4.3.1. Average crystallite sizes, dislocation densities, and micro-strains of pristine α - Fe_2O_3 and L-Arg/ α - Fe_2O_3 nanostructures.

Sample type	Average crystallite size (nm)	Dislocation density ($\times 10^{-4} \text{ nm}^{-2}$)	Micro-strain ($\times 10^{-4}$)
Pristine	25.02	1.60	1.73
1:1	31.67	1.10	1.44
2:1	29.43	1.16	1.61
3:1	28.79	1.21	1.67

The increase in the dislocation density can be attributed to the rise in the locking stress, whereby there was oxygen diffusion during the transformation process. Toromo and co-workers have posted similar results on their study on oxygen concentration effect in silicon during direct solidification [29]. The crystallinity and vibrational phonon modes of hematite NPs and nanospheres were further confirmed using Raman spectroscopy with green laser light of 532 nm (Figure 4.3.3). The irreducible representations for the optical modes in the crystal are represented by the Eqn 4.3.4,

$$\Gamma_{\text{vib}} = 2A_{1g} + 2A_{1u} + 3A_{2g} + 2A_{2u} + 5E_g + 4E_u \quad 4.3.4$$

where A_{1g} , A_{1u} , A_{2g} , E_g and E_u represents the irreducible optical modes of hematite structure [30].

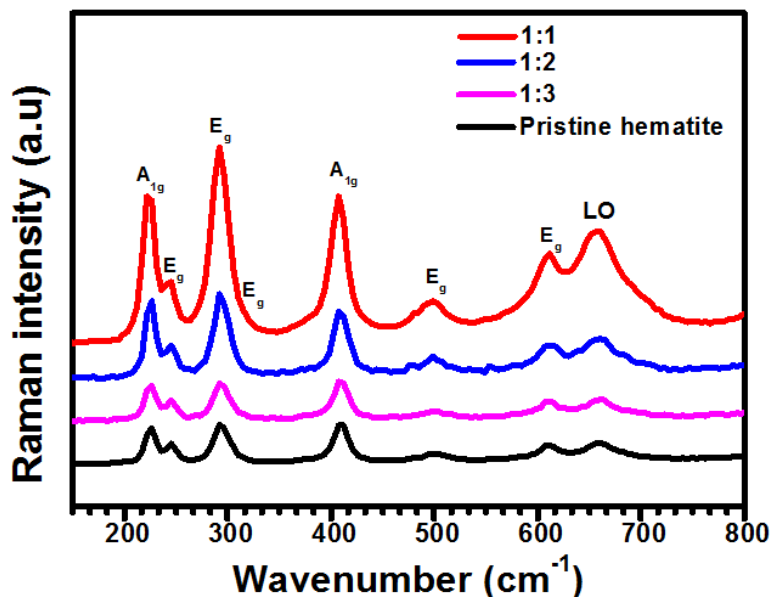


Figure 4.3.3. Raman spectroscopy of hematite nanoparticles and L-Arg/ α -Fe₂O₃ nanospheres prepared at 1:1, 2:1, and 3:1 of L-arginine: FeCl₃.6H₂O precursor concentrations respectively.

From Figure 4.3.3, all the symmetric vibrational modes of hematite were observed. Hematite has a corundum structure, and for this structure, group theory proposes seven first-order Raman-active vibrational modes at the centre of the Brillouin zone. Hematite has two A_{1g} modes at 243 cm⁻¹ and 409 cm⁻¹ and five E_g modes at 226, 240, 293, 500, and 609 cm⁻¹ which were all observed both on nanoparticles and nanospheres thin films. Also, the ferromagnetic property of hematite was confirmed with the 656 cm⁻¹, longitudinal optical (LO), mode. Further, the intensity of the 1:1 of L-arginine: FeCl₃.6H₂O sample was observed to be higher as compared to the other samples. This could be attributed to the equal interactions of hydrogen and carbon bonds, leading to the uniform vibrational modes. Besides, the Raman peaks of L-arginine were not observed on the L-Arg/ α -Fe₂O₃ nanospheres samples, a further confirmation of the purity of the hematite nanospheres during the transformation process.

4.3.2 Surface morphology and elemental analysis

The NPs obtained were irregular in shape. The shape however changed from irregular NPs to uniform nanospheres, evenly distributed on the FTO film as shown in Figure 4.3.4. The average grain size of 41 ± 0.5 nm for pristine α -Fe₂O₃ NPs was obtained (Figure 4.2.5). This was analysed using the ImageJ, Gaussian fitting and histogram.

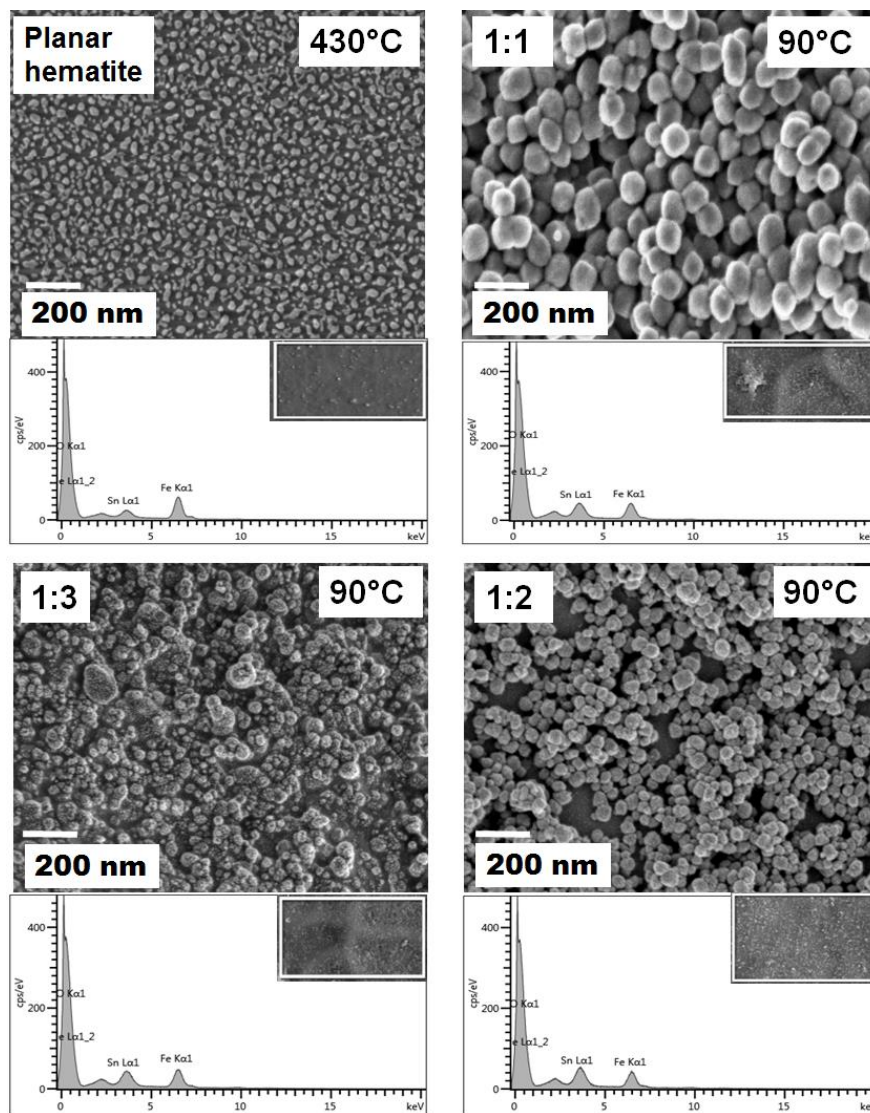


Figure 4.3.4. Scanning electron microscopy images of L-Arg/ α -Fe₂O₃ nanoparticles synthesized by chemical bath deposition at 90°C for 48 h and spray pyrolysis (at 430°C). The EDX spectra showing the elemental composition is presented below the morphology of each sample.

From Figure 4.3.5, there was a decrease in grain size for L-Arg/Fe₂O₃ as the precursor concentrations of L-arginine was varied from 1:1 to 3:1, with that of iron salt (FeCl₃.6H₂O). The average grain size obtained was 35.0 ± 0.5 nm for 1:1, 8.0 ± 0.5 nm for 2:1 and 6.0 ± 0.5 nm for 3:1 of L-arginine: FeCl₃.6H₂O precursor concentrations respectively. This decrease in grain size could probably have resulted from the suitable seeding medium for crystal growth that is created by the strong basic nature of L-arginine (C₆H₁₄N₄O₂).

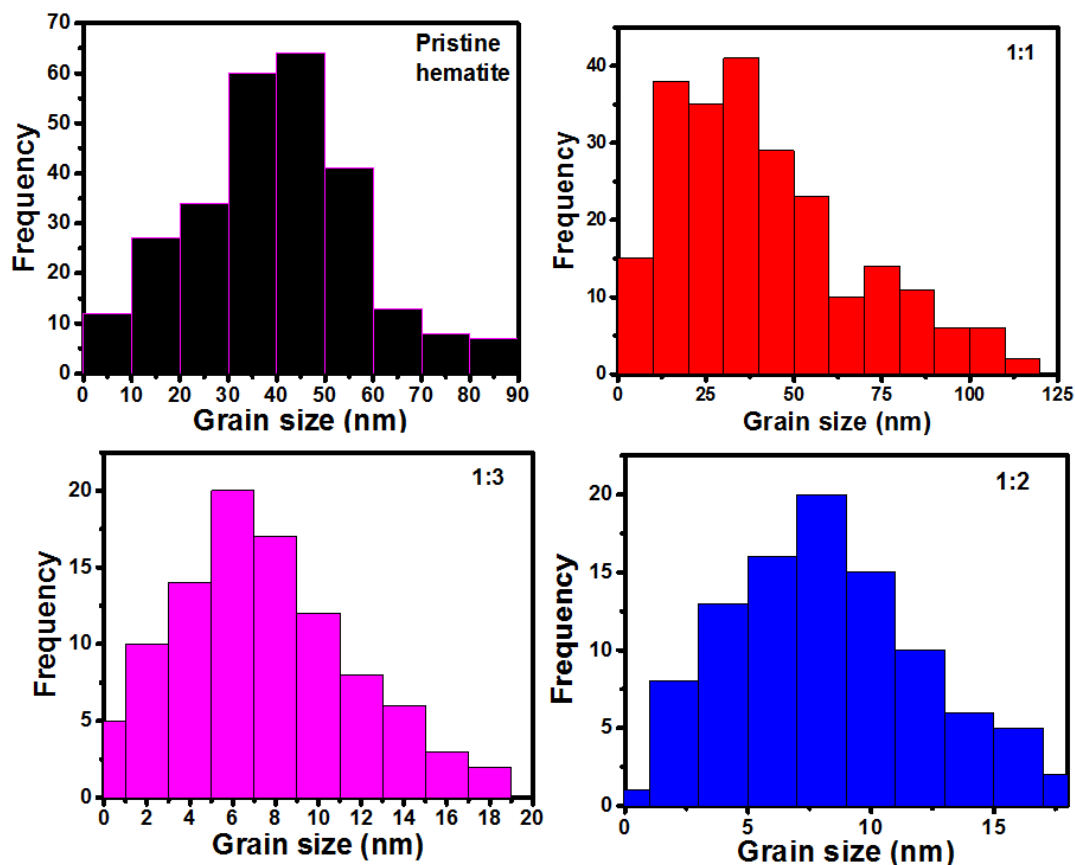


Figure 4.3.5. L-Arg/Fe₂O₃ and pristine Fe₂O₃ nanostructures' grain size distribution analysed using ImageJ.

The full reaction that takes place in the transformation of NPs to nanospheres is presented in Eqns 4.3.5-4.3.7. Step II in Eqn 4.3.6 shows the formation of akageneite (β -FeO_{0.833}(OH)_{1.167}Cl_{0.167}). This iron phase (akageneite) has an octahedral crystal structure [14, 31]. The akageneite that is an unstable phase of iron is finally transformed to α -Fe₂O₃, as shown in the last step of Eqn 4.3.7.



A high rate of heterogeneous nucleation on the seeded hematite layer could have led to the grain size transformation shown in Figure 4.3.4. This transformation was also possible due to the L-arginine, a structure-directing agent resulting from its -NH₂ and -COOH functional groups. The hydrogen bond can explain enhanced interaction between akageneite and L-arginine between the surface of L-arginine and akageneite [31]. The grains and crystallite size obtained reported a general trend, although their sizes were not similar. This was due to different approaches used in estimation whereby for crystallite size, Scherrer's formula from XRD was used, while for grain size, ImageJ was employed. Reduction in grain size could also result from the micro-strain, dislocation density and other defects, which were confirmed by the peak broadening at large 2θ angles.

To study the elemental composition and stoichiometry on the samples, energy dispersive X-ray (EDX) analysis was used. Figure 4.3.4 shows the EDX images at the bottom of the surface morphology micrographs. It can be confirmed that only the predominant signals of iron (Fe) and oxygen (O) were present, which is in agreement from Frydrych and co-workers on their study on the synthesis of hematite using thermal decomposition of solid FeCl₃·6H₂O as the precursor [32]. The K-line of iron (Fe) is shown by the line at 6.42 keV, while 0.53 keV represents the K-line of oxygen (O) [32]. The L-line, however, was found to be closer to oxygen K-line for all samples. This could be attributed to the composition of oxygen since it was predominant in all the samples. A possible split of the L-shell could have taken place into 1 and 2 to accommodate the oxygen composition population of all the L-Arg/α-Fe₂O₃ nanosphere samples and pristine Fe₂O₃ [33]. Tin (Sn) signals were also predominant from the results since the FTO was used as the substrate. The weight percentage composition of Fe and O forming hematite at different precursor concentrations is presented in Figure 4.3.6.

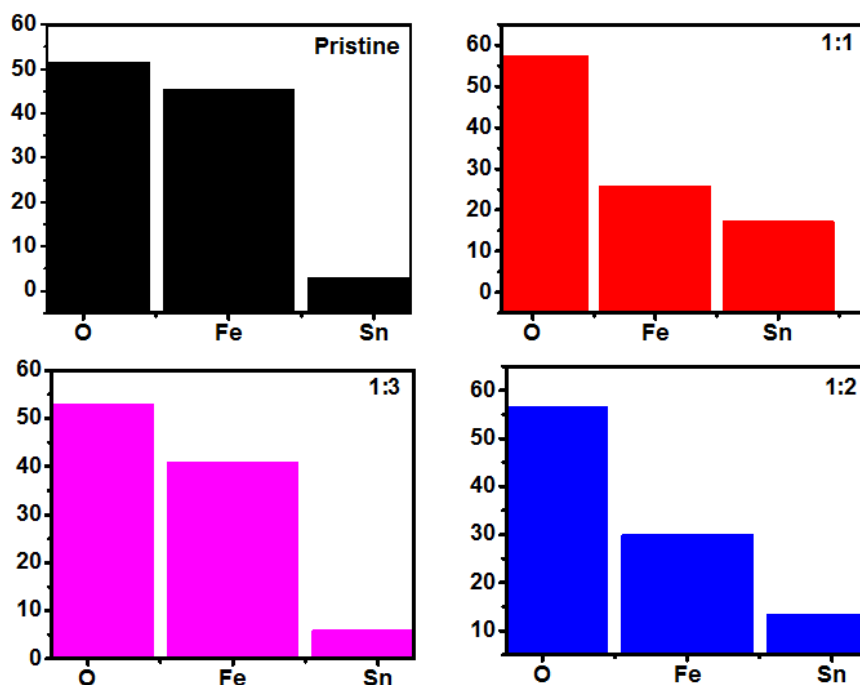


Figure 4.3.6. Histogram by wt % of hematite nanoparticles and L-Arg/ α -Fe₂O₃ nanospheres as obtained from EDX.

EDX further confirmed the purity of the synthesized nanostructures since no other elements were present from Figure 4.3.4 and 4.3.6, and this is in agreement with the structural properties (XRD and Raman) reported in section 4.3.1. There was a variation of the percentage, as shown in Figure 4.3.6, and this was majorly due to the change of the precursor concentration. Similar results have been reported by Ubale and co-workers on their synthesis of nanocrystalline hematite using Successive Ionic Adsorption and Reaction (SILAR) method [34].

4.3.3 Optical properties

The absorbance of pristine Fe₂O₃ NPs and L-Arg/ α -Fe₂O₃ nanosphere thin films were obtained from the UV-Vis spectroscopy. From Figure 4.3.7, a blue-shift was observed as the precursor concentration was increased from 1:1 to 3:1 of L-arginine: FeCl₃.6H₂O, respectively.

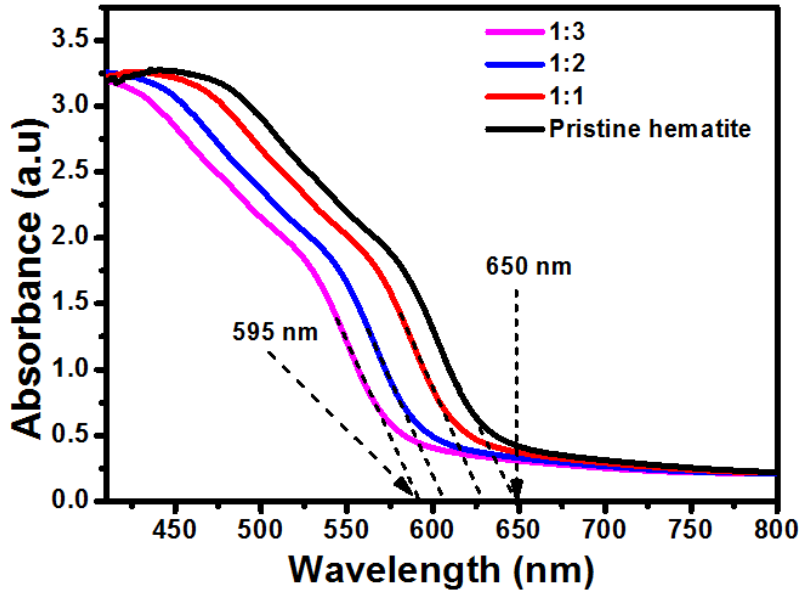


Figure 4.3.7. A variation of absorbance of pristine $\alpha\text{-Fe}_2\text{O}_3$ and L-Arg/ $\alpha\text{-Fe}_2\text{O}_3$ nanostructured thin films, prepared by both spray pyrolysis and chemical bath deposition.

This absorbance was almost linear in the red region of the solar spectrum. The onset absorption band edge of these nanostructured films ranged from 595 to 650 nm, with d-d being the main transition in these regions [35]. There was also a high absorption of all the samples in the visible region, with the absorption tail extending to 670 nm. Further, an extrapolation of the tangent line at the onset region of the absorbance was used to estimate the optical bandgap of these nanostructured thin films. This was achieved by using the photon equation,

$$E_g(\text{eV}) = \frac{1240}{\lambda(\text{nm})} \quad 4.3.8$$

where λ is the wavelength of the absorbance. The bandgap values of 1.91, 1.96, 2.04, and 2.08 eV were obtained for pristine $\alpha\text{-Fe}_2\text{O}_3$, 1:1, 2:1, and 3:1 for L-arginine: $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ respectively. Other researchers have reported a similar bandgap range using Tauc's equation [36, 37]. L-arginine growth on the seed layer did not affect the transition of electrons since the indirect movement to Fe^{3+} d from valence band was still maintained. Additionally, although the d-d transitions are spin forbidden, their occurrence can sometimes take place, with a finite transition and they can become allowed by other means like the magnetic coupling of electron spins nearer to Fe^{3+} of the crystalline hematite [38].

4.3.4 Photocurrent density measurements

The Potentiostat work station (VersaSTAT 3F, USA) was used in the measurements of linear scan voltammetry (LSV). A photocurrent density (I-V) was then obtained using AM 1.5 G simulated sun, as discussed in chapter 3, section 3.7.5. From Figure 4.3.8, a low I-V for pristine α -Fe₂O₃ of 1.6×10^{-3} mA/cm² at 1.23 V vs. RHE was obtained. On the other hand, photocurrent densities of 2.7×10^{-3} , 5.4×10^{-3} , and 9.8×10^{-3} mA/cm² at 1.23 V vs. RHE were measured. From this study, L-arginine reported higher photocurrent, which was a six-fold increase from the pristine α -Fe₂O₃ thin film. This was enhanced by a good absorption of the solar spectrum in the visible region, small grain size and polycrystallinity of these nanostructured films.

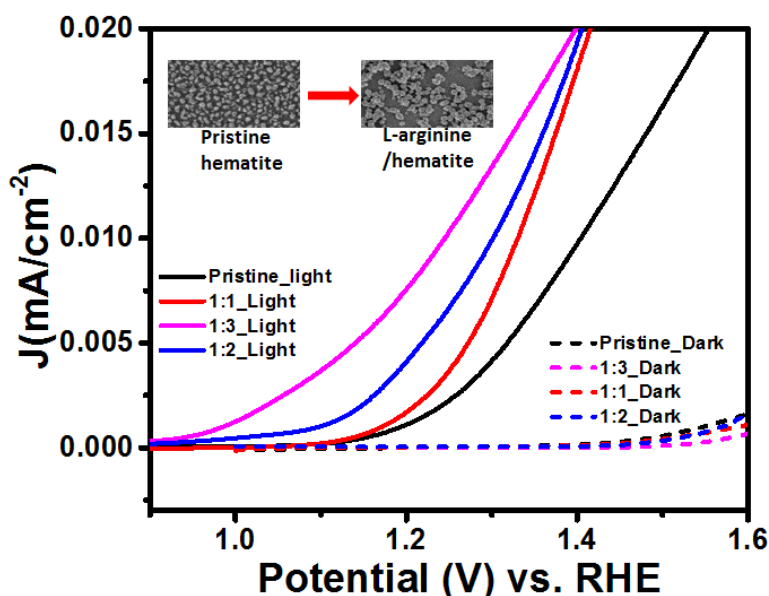


Figure 4.3.8. Photocurrent density plots for L-Arg/ α -Fe₂O₃ and pristine α -Fe₂O₃ films. The scan rate of 0.05 Vs⁻¹ and 1 M of NaOH as the electrolyte.

4.3.5 Ultrafast transient absorption spectroscopy

A two-dimensional colour map of the difference absorption (ΔA), with selected delay times, is presented in Figure 4.3.9. The signals obtained from any transient absorption spectroscopy (TAS) measurements include ground state bleach (GSB), excited-state absorption (ESA), and stimulated

emission (SE). From Figure 4.3.9, the intensity of the 3:1 of L-arginine: $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ precursor concentration sample was strongly peaked as compared to pristine hematite, 1:1 and 2:1 of L-arginine: $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ precursor concentration samples. The 570 nm centered positive band was observed for all samples.

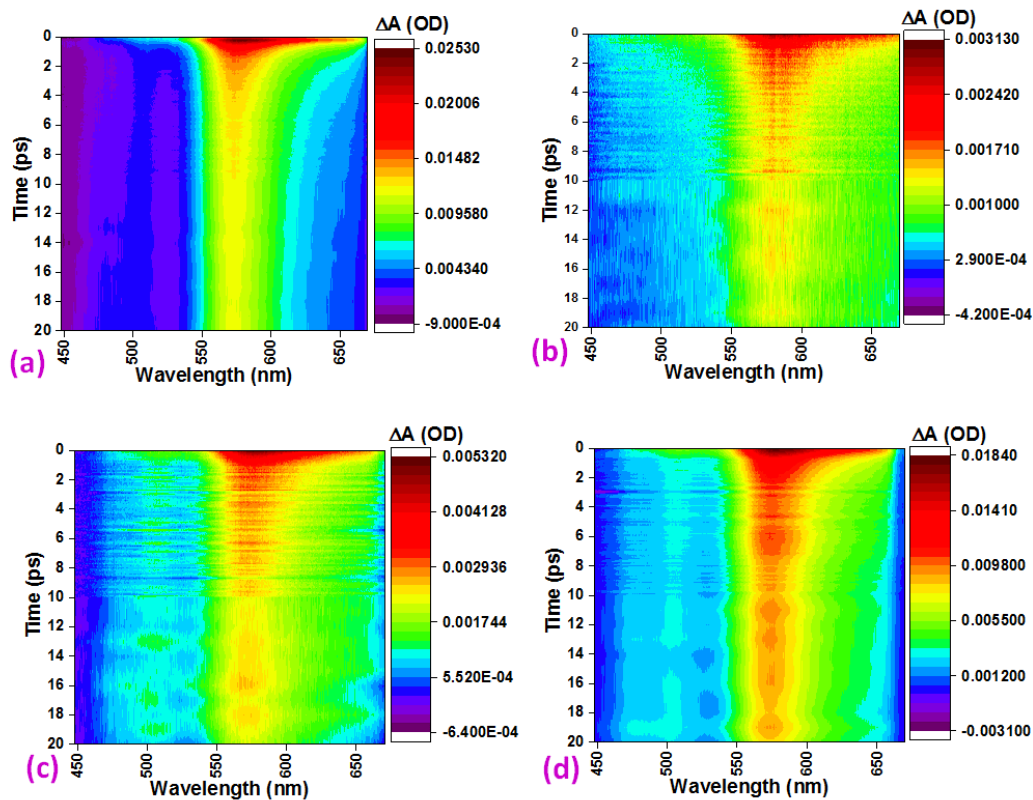


Figure 4.3.9. Ultrafast transient absorption spectra displayed as a two-dimensional colour map for (a) pristine $\alpha\text{-Fe}_2\text{O}_3$, (b) 1:1, (c) 2:1 and (d) 3:1 of L-arginine: $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ precursor concentrations, respectively. The samples were excited at 387.5 nm.

The difference in absorbance (ΔA), also known as the difference in optical density (OD) between the pumped and unpumped samples, at selected wavelength, is presented in Figure 4.3.10. The maximum peak (570 nm) was attributed to excited state absorption, specifically probe light absorption from the photoexcited holes in the valence band and photoexcited electrons in the conduction band [39]. However, a study conducted by Hayes *et al.* [40] contradicted what other researchers have reported in literature and concluded that the positive band centred at 570 nm is thermal rather than electronic in origin. Hayes and co-workers compared the optical transient

absorption spectrum of hematite with the thermal difference spectrum obtained through subtracting the steady-state spectra recorded at 500 K and 300 K [40]. They observed striking similarities in the two spectra, especially at the ~ 570 nm centred band suggesting that the peak is thermal in origin. They suggested from the measurements that the spectra of hematite are dominated by lattice expansion and thermal distortions. However, according to Mia *et al.*, the distortions in hematite can also be induced by photoexcited charge carriers in the form of polarons [41]. This peak at 570 nm is speculated to be due to the hole polarons associated with the Fe^{4+} species that can be generated by either heat, photoexcitation or electrical bias [41]. The distorted lattice gradually returns to its ground-state form as holes are consumed through recombination. The ESA feature has also been reported to result from the presence of intra-bandgap states in hematite thin films [42].

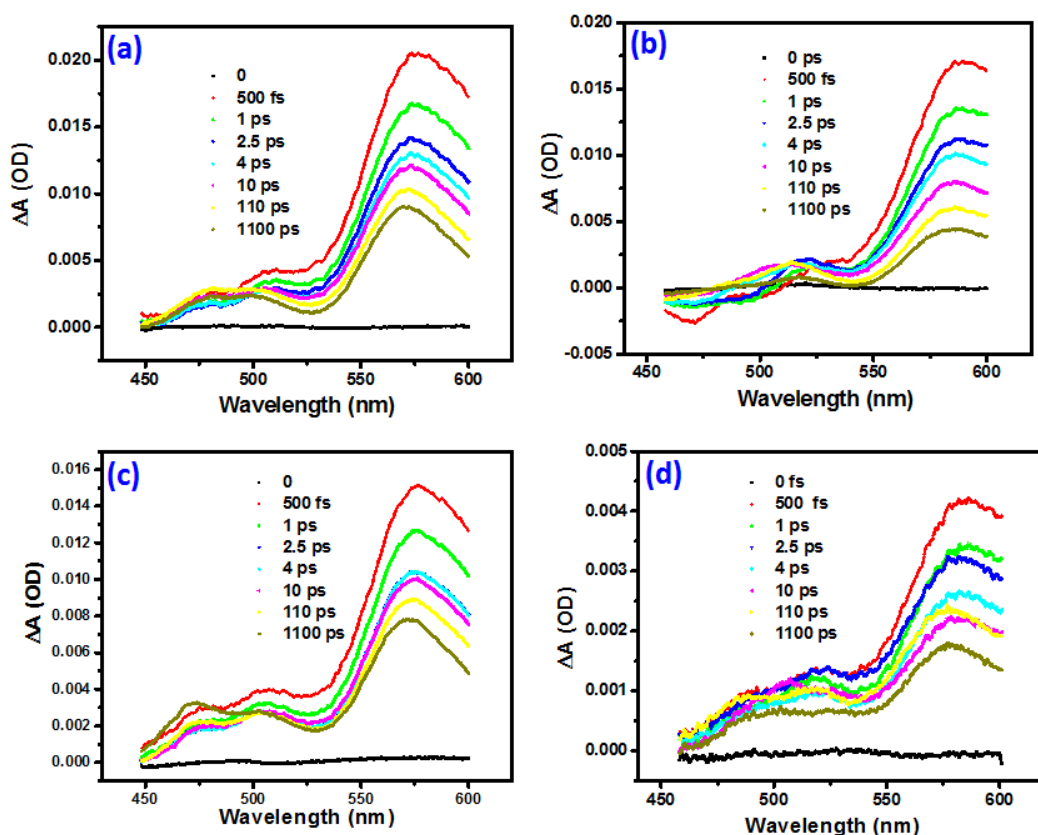


Figure 4.3.10. Difference absorption spectra at selected delay times for (a) pristine $\alpha\text{-Fe}_2\text{O}_3$, (b) 1:1, (c) 2:1 and (d) 3:1 of L-arginine: $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ precursor concentrations, respectively.

Kinetic traces at selected wavelengths (570, 600, 620 nm) were plotted to study the decay rates of the ESA feature, as shown in Figure 4.3.11. From the kinetic trace analysis, there was a fast growth

of all the signals to the maximum, taking place on a timescale of < 150 fs. The decay of the positive band was fast initially but later slowed down after 1.5 ps, forming a long tail that decayed on a much longer timescale. The traces were fitted using a biexponential decay function, $\Delta A = A_1 e^{-t/\tau_1} + A_2 e^{-t/\tau_2}$ where ΔA is the difference absorption, t is the delay time, τ_1 and τ_2 are the decay lifetimes, and A_1 and A_2 are the corresponding amplitudes. The obtained decay lifetimes from the individual spectra correlate with the associated lifetimes obtained from the evolution associated difference spectra, shown in Table 4.3.3, where τ_1 and τ_2 ranged in fs and ps, respectively. The values of A_1 and A_2 indicate that most of the ΔA amplitudes decay at the slower rate (τ_2) in all the samples. Interestingly, the slower rate is more dominant for the 2:1 and 3:1 samples as shown by the larger values of A_2 . Summaries of the lifetimes and amplitudes from the fitted traces are shown in Tables 4.3.2 (a-d).

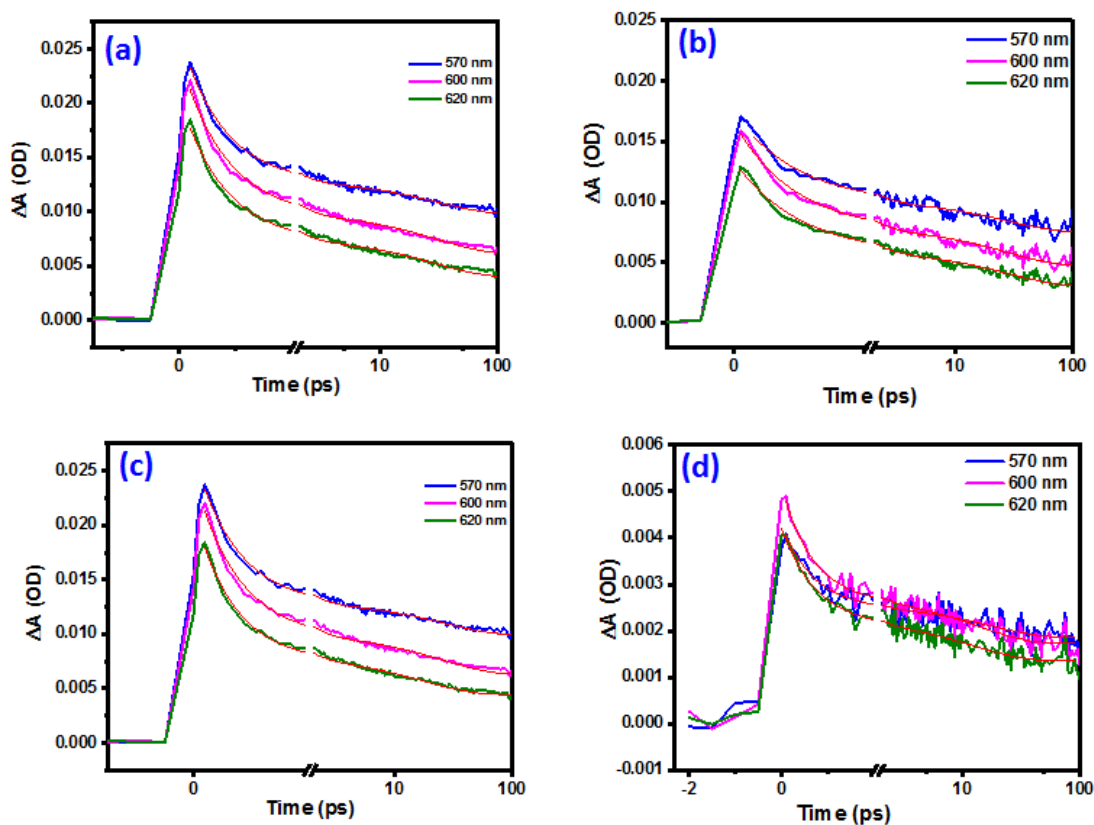


Figure 4.3.11. Kinetic traces at selected wavelengths (570, 600 and 620 nm) of (a) pristine α - Fe_2O_3 (b) 1:1, (c) 2:1 and (d) 3:1 of L-arginine: $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ precursor concentrations, respectively. The fitting was done between 1 and 100 ps

Table 4.3.2. Summary of the lifetimes and amplitudes (A_1 and A_2) obtained from fitting the kinetic traces at 570, 600, and 620 nm of pristine (a) α -Fe₂O₃ (b) 1:1, (c) 2:1, and (d) 3:1 of L-arginine: FeCl₃.6H₂O precursor concentrations, respectively

a) Pristine hematite sample

Wavelength (nm)	A_1 ($\times 10^{-3}$)	τ_1 (fs)	A_2 ($\times 10^{-3}$)	τ_2 (ps)
570	1.39	571	3.10	12
600	1.52	592	4.00	9
620	1.37	595	3.70	10

b) 1:1 sample

Wavelength (nm)	A_1 ($\times 10^{-3}$)	τ_1 (fs)	A_2 ($\times 10^{-3}$)	τ_2 (ps)
570	1.35	938	2.30	28
600	1.49	909	3.20	29
620	1.34	978	3.50	27

c) 2:1 sample

Wavelength (nm)	A₁ ($\times 10^{-3}$)	τ_1 (fs)	A₂ ($\times 10^{-3}$)	τ_2 (ps)
570	2.38	746	9.70	26
600	3.70	764	8.20	25
620	2.50	692	7.90	17

d) 3:1 sample

Wavelength (nm)	A₁ ($\times 10^{-3}$)	τ_1 (fs)	A₂ ($\times 10^{-3}$)	τ_2 (ps)
570	1.80	668	7.00	22
600	2.40	648	6.10	18
620	2.00	729	8.90	13

Global and target analysis (Glutaran) software was used to determine the electron-hole recombination timescales of the nanostructured hematite films, using a four-component sequential model. The requirement of four components was determined by means of singular value decomposition (SVD) of the raw data. Figure 4.3.12 presents the evolution associated difference spectra (EADS) obtained from a global analysis of all the samples. The EADS obtained describe

the spectral evolution of the whole system and not that of an individual spectrum or state. The analysis gave four associated lifetimes for each of the samples.

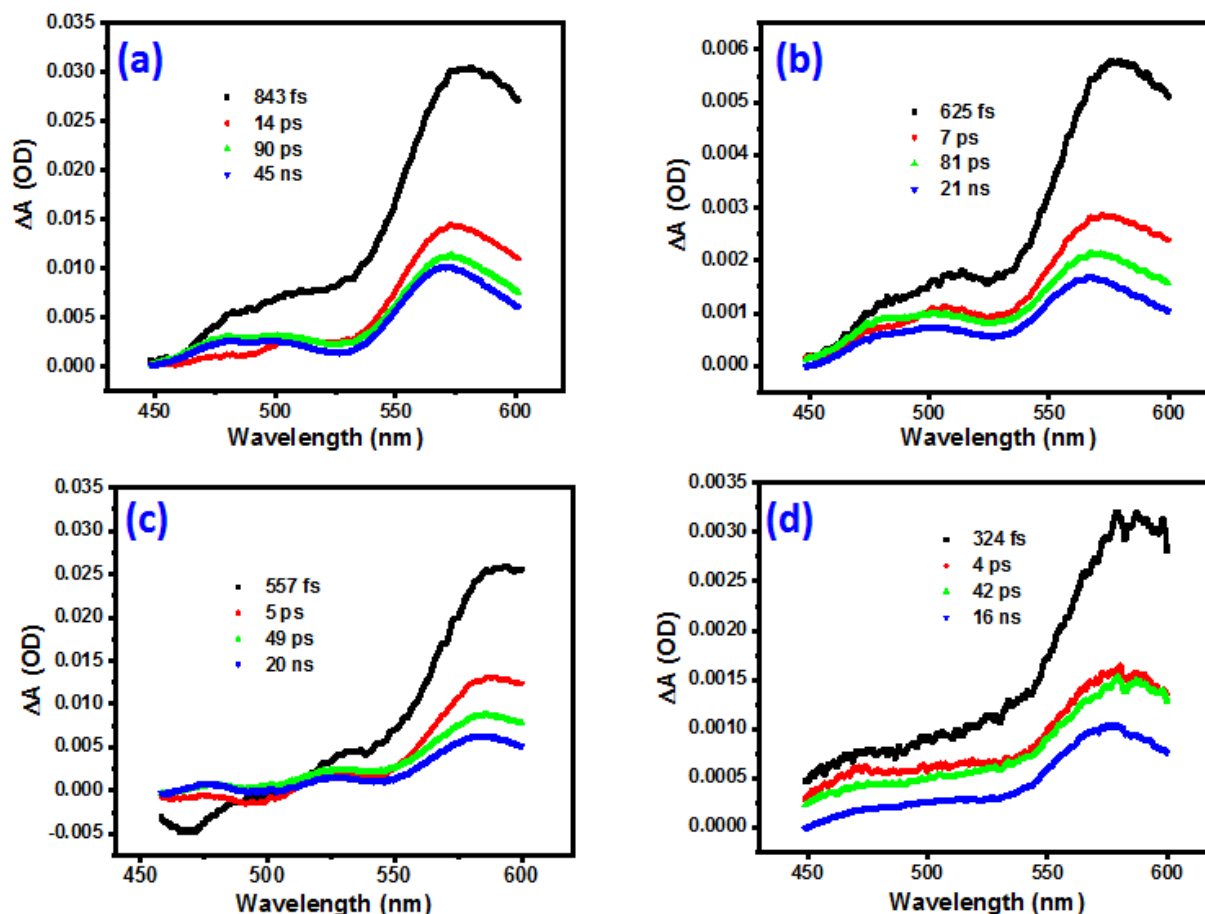


Figure 4.3.12. Evolution associated difference spectra with associated decay lifetimes obtained from global analysis using Glotaran software for (a) pristine α - Fe_2O_3 , (b) 1:1, (c) 2:1 and (d) 3:1 of L-arginine: $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ precursor concentrations, respectively.

The electron-hole recombination rates associated with lifetimes obtained from EADS analysis are presented in Table 4.3.3. From this study, the electron-hole recombination timescales taking place in hematite samples were assigned to different systems. The first lifetime (τ_1), which ranged from 813 fs to 324 fs for pristine hematite and 3:1 of L-arginine: $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ precursor concentrations samples, respectively, was attributed to hole cooling. This lifetime is assigned to hot electrons and holes tending to relax to the respective band edges. This process is very fast, hence taking place on an ultrafast timescale. During this process, the electrons relax to the conduction band minimum

while the holes relax to the top of the valence band. The second lifetime (τ_2), on the other hand, was in the ps range (4 - 14 ps) and is attributed to charge carrier (e^-h^+) recombination and trapping by mid-gap states. A previous study has shown that the mid-gap, Fe $d-d$, states and oxygen defects in hematite increase the recombination in hematite, limiting its efficiency in PEC applications [43].

The recombination of the electrons and holes trapped by mid-gap states contributes to the third lifetime (τ_3). This recombination obtained from our study ranged from 42 ps for 3:1 of L-arginine: FeCl₃.6H₂O precursor concentrations sample to 90 ps for pristine hematite. Also, τ_3 could be due to the recombination resulting from valence band holes and conduction band electrons [44]. The fourth lifetimes (τ_4) are in the ns range (16 - 45 ns) and are associated with recombination taking place by the electrons that undergo backflow from the FTO [45]. This is a slower process compared to other processes, hence it has a longer timescale in the order of ns.

Table 4.3.3. Decay lifetimes of hematite nanostructures obtained from global analysis.

Lifetime	Pristine Hematite	L-Arg/α-Fe₂O₃ (1:1)	L-Arg/α-Fe₂O₃ (2:1)	L-Arg/α-Fe₂O₃ (3:1)
τ_1	843 fs	625 fs	557 fs	324 fs
τ_2	14 ps	7 ps	5 ps	4 ps
τ_3	90 ps	81 ps	49 ps	42 ps
τ_4	45 ns	21 ns	20 ns	16 ns

From this study, there was a general trend of reduction in the lifetime from pristine hematite NPs to L-Arg/ α -Fe₂O₃ as the precursor concentration of L-arginine was increased. These changes were majorly due to a decrease in grain size. A larger surface area to volume ratio dictates that electrons spend more time near the particle surface at which they can be trapped by surface states, hence decreasing the lifetime.

4.4 Influence of precursor concentration and deposition temperature on the photoactivity of hematite electrodes for water splitting.

4.4.1 X-ray diffraction

Figure 4.4.1 presents the X-ray diffraction patterns for the hematite nanostructures prepared at different precursor concentrations (30, 40, and 50 mM), and deposition temperatures (250, 340, and 400°C). All the samples were confirmed to be hematite, having the corresponding peaks indexed in the right 2θ angles and no additional impurities. Further, the dominance of the (012), (104) and (110) phases compared to other phases like (113), (024), (116), (214) was observed in all the samples. The dominant peaks (012, 104, and 110) characterize the corundum structure of hematite, having a space group of $R\bar{3}C$ as reported earlier.

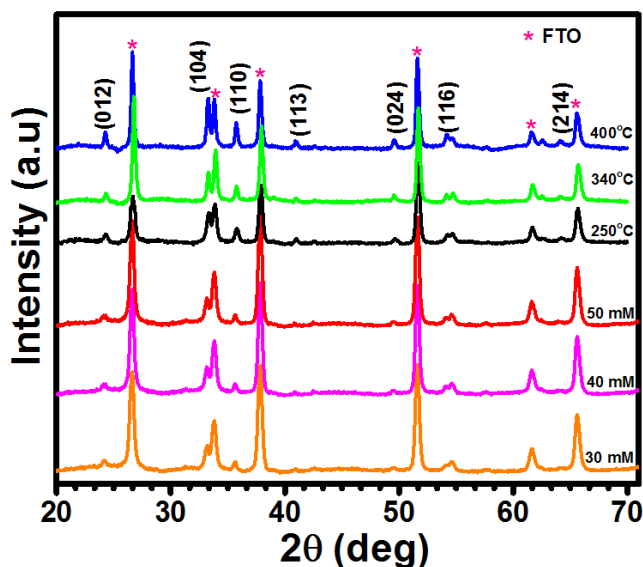


Figure 4.4.1. X-ray diffraction patterns of hematite nanoparticles synthesized at different precursor concentration and deposition temperatures.

Debye Scherrer's Eqn 4.2.4 was used to calculate the crystallite size of the samples [46]. From this analysis, there was an increase in the crystallite size from 23.05 to 29.92 nm for samples prepared at different precursor concentrations (30 to 50 mM) while a reduction in crystallite size was found for samples prepared at different temperatures (250 to 400°C) from 38.11 to 23.97 nm.

This trend is shown on the inset in Figure 4.4.2. This increase and decrease in the crystallite sizes can be a result of crystallinity as the concentration and temperature were varied. The lattice parameters for all the samples were obtained using the dominant peaks, (012, 104, 110), Eqns 4.4.1, and 4.4.2:

$$2d_{hkl} \sin \theta = n\lambda \quad 4.4.1$$

and

$$\frac{1}{d_{hkl}^2} = \frac{4}{3a^2} (h^2 + k^2 + hk) + \frac{l^2}{c^2} \quad 4.4.2$$

where d^2 represents the inter-planar spacing between the crystals and the planes, and (hkl) is the Miller indices. Samples prepared at different precursor concentrations had average lattice parameters, $a = b = 5.0681 \text{ \AA}$ and $c = 13.6934 \text{ \AA}$. For different deposition temperature samples, the lattice parameters were $a = b = 5.0172 \text{ \AA}$, and $c = 13.6527 \text{ \AA}$. The results obtained from this study agree with the standard lattice parameters of $a = 5.0346 \text{ \AA}$ and $c = 13.7520 \text{ \AA}$ from JCPDS file no. 03-0664 for hematite. The influence of the substrate (FTO) on the growth of the nanostructured hematite layer could have led to the small variation of the lattice parameters from the standard ones. Sharma and co-workers have reported a similar trend of the reversal in the lattice parameters contraction of hematite nanoparticles [47].

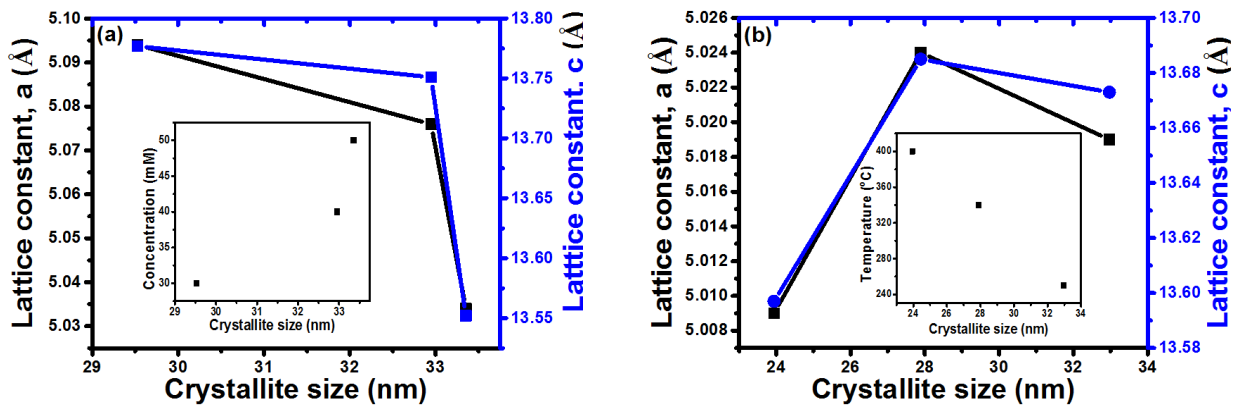


Figure 4.4.2. Lattice constants, and crystallite sizes for hematite nanoparticles at different deposition temperatures (250, 340, 400°C) and precursor concentrations (30, 40, 50 mM). The inset in Figure 4.4.2 (a and b) shows the variation of crystallite sizes with concentrations and temperature, respectively

4.4.2 Optical properties

UV-Vis spectroscopy was used in the measurement of the absorbance of these hematite nanostructures prepared at different temperatures and precursor concentrations. There was a relatively high absorbance of these films in the visible region, as shown in Figure 4.4.3 (a).

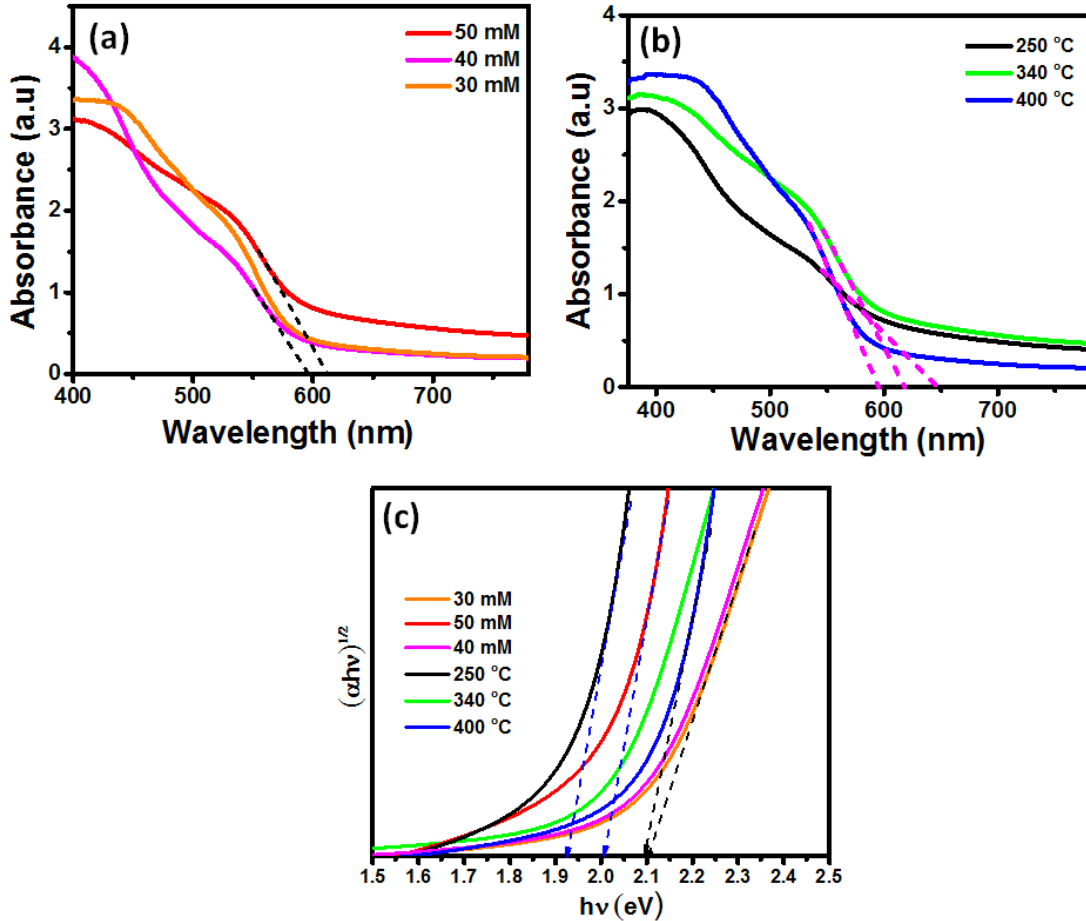


Figure 4.4.3. The absorption edge of hematite thin films at different (a) precursor concentrations, and (b) deposition temperatures using spray pyrolysis. (c) Corresponding energy bandgaps of hematite thin films prepared by spray pyrolysis.

A slight red-shifting in the absorbance onset was observed for the 30 and 50 mM samples, while a blue shift occurred for the 40 mM film. For the samples prepared at different deposition temperatures, a blue-shift was observed with an increase in temperature (250 - 400 °C), as presented in Figure 4.4.3 (b). The blue-shifting of the absorbance was due to the change in grain

size as the precursor concentration and temperatures were varied, which is explained in Section 4.4.3. To estimate the optical bandgap (E_g), Tauc's Eqn (Eq. 4.4.3) was used, and E_g estimated in Figure 4.4.3 (c).

$$(\alpha h\nu)^n = A(h\nu - E_g) \quad 4.4.3$$

where α is the absorption coefficient, $h\nu$ the incident photon energy, A is a constant, E_g the energy bandgap of that material, and n the nature of transition wherein it is 2 for direct bandgap and for indirect transition, n is $\frac{1}{2}$. A plot of $(\alpha h\nu)^{1/2}$ vs. $h\nu$ with extrapolation of the linear part gives an indirect bandgap while $(\alpha h\nu)^2$ vs. $h\nu$ gives a direct bangap [48].

A bandgap decrease from 2.10 to 1.99 eV for different precursor concentration samples (30, 40, and 50 mM) was obtained. This reduction in bandgap could be due to the grain sizes increase with the variation of precursor concentration. At the same time, the deposition temperature of 280°C used in preparing the three samples was maintained constant. On the other hand, samples prepared at different temperatures (250 - 400°C) reported an increase in bandgap from 1.92 eV for 250°C sample to 2.09 eV for the 400°C sample, under a constant precursor concentration of 50 mM. This was attributed to the small grain size achieved at high temperatures leading to the quantum confinement effect. According to Fondell and co-workers, the optical properties of hematite, with grains of nm scale (< 20 nm) are affected by the quantum confinement effect. During this process, the grain size of the materials is less than the Bohr electron-hole radius [49, 50]. This spatially confines the wave function of the charge carriers leading to an increase in the optical bandgap as grain size decreases [49, 51]. The rise in the inter-atomic spacing as the temperature was increased from 250 to 400°C could have led to an increase in the bandgap resulting from the phonon-electron interaction enhancement [52]. Lassoued and co-workers have reported similar results on the synthesis of hematite nanostructures at different precursor concentrations using chemical bath deposition, obtaining grain sizes that ranged from 21 to 82 nm [2].

4.4.3 Surface morphology of hematite nanoparticles

The morphology of α -Fe₂O₃ NPs prepared at different deposition temperatures and precursor concentrations is presented in Figure 4.4.4. There was an observed increase in grain size with the variation of precursor concentrations from 30 to 50 mM. This could be attributed to the agglomeration of the precursor (Fe(NO₃)₂·9H₂O) during the deposition. This aggregation could have

further led to agglomerations, leading to an increase in the grain size at higher precursor concentrations (50 mM). The size of the formed NPs was further limited due to the formation of iron nuclei, and this is similar to Fouad and co-workers on their study of hematite deposited using precipitation. Their study reported the effects of precursor concentrations on the crystallinity, grain size, lump formation and morphology of hematite nanoparticles. Besides, they found out that more agglomeration and lumps of grain sizes occurred as the precursor concentration was increased.

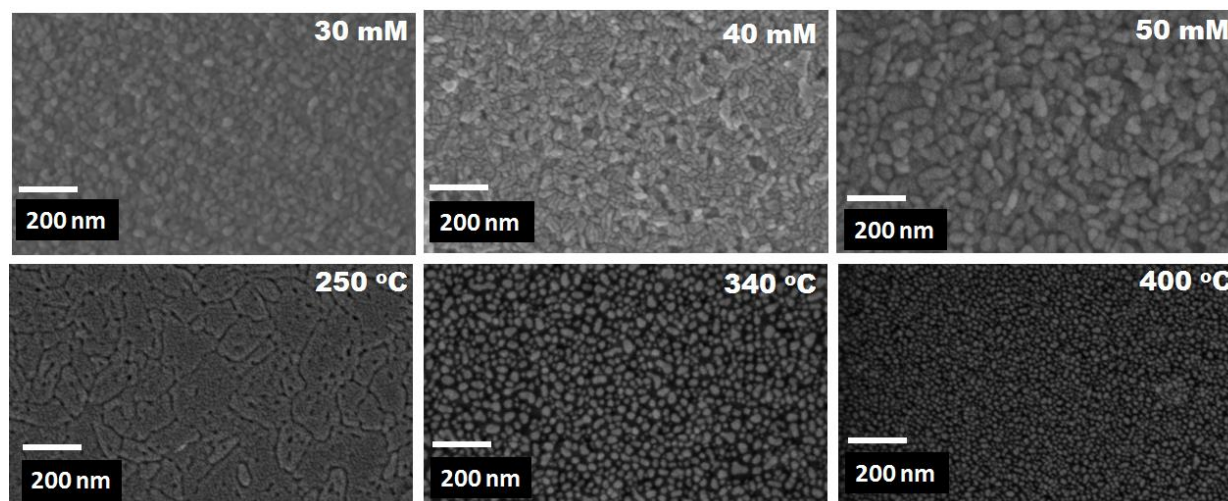


Figure 4.4.4. Scanning electron micrographs of hematite NPs deposited at different precursor concentrations and deposition temperatures.

ImageJ was used to study the occurrence frequency of the grain sizes at different precursor concentrations and deposition temperatures, as shown in Figure 4.4.5. From this analysis, the grain sizes that ranged from 33 to 14 nm for 250 and 400°C, respectively, were obtained. The decrease in the grain sizes was due to high levels of evaporation occurring at high temperatures leading to many depositions occurring in vapour form. This was converse to the samples prepared at lower temperatures since much of the precursor was landing on the precursor in liquid form. We have reported a similar study on the structural and optical properties of L-arginine/hematite nanostructures prepared by both spray pyrolysis and chemical bath deposition [4].

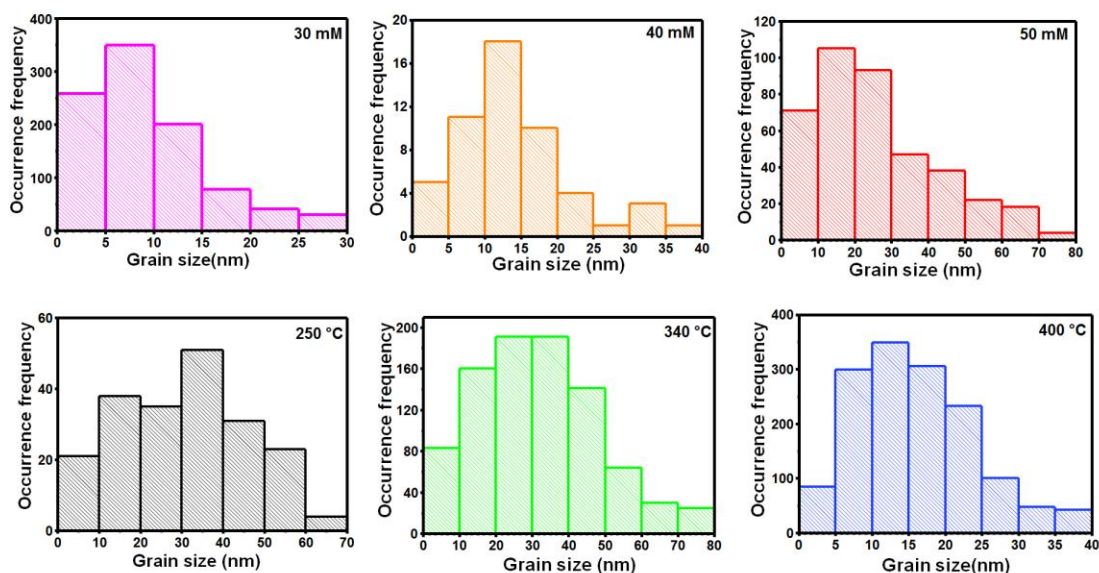


Figure 4.4.5. Occurrence frequency of hematite NPs prepared at different temperatures and precursor concentrations.

The average grain size of samples prepared at different precursor concentrations increased from 7 to 19 nm, as shown in Figure 4.4.5. Figure 4.4.6 presents the trend observed as the parameters (concentration and temperature) were varied for hematite NPs. A near-linear trend can be observed for different precursor concentrations and deposition temperatures.

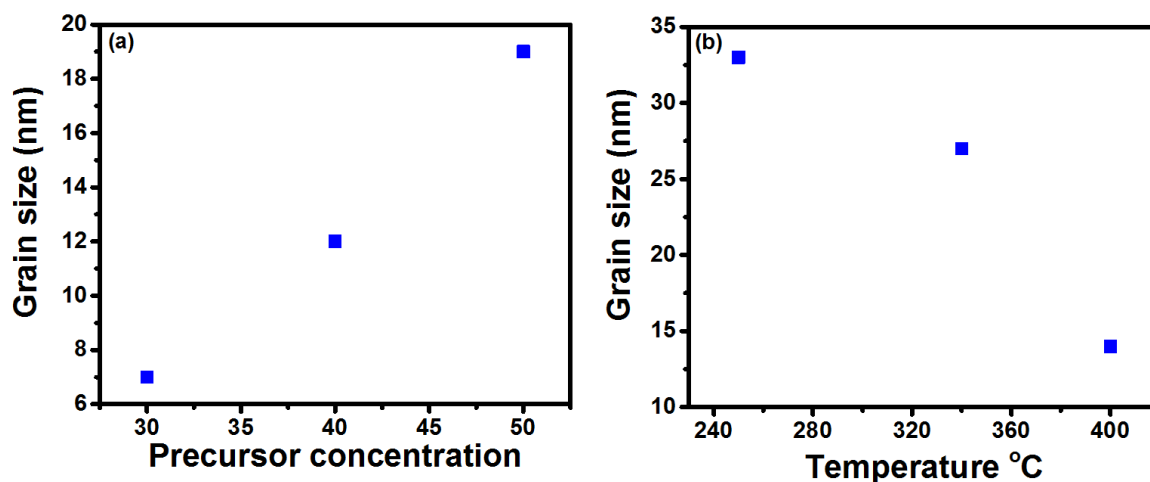


Figure 4.4.6. Variation in grain sizes of hematite NPs for different (a) precursor concentrations, and (b) deposition temperatures.

4.4.4 Photocurrent measurements

A potentiostat workstation was used in the measurement of photocurrent under simulated 1 sun irradiation, as shown in Figure 4.4.7. The highest photocurrent of $89 \mu\text{Acm}^{-2}$ at 1.23 V vs. RHE for the sample prepared using a 50 mM precursor concentration was obtained. This photocurrent was, however, observed to reduce to 53 and $17 \mu\text{Acm}^{-2}$ for the 40 and 30 mM precursor concentrations samples, respectively. On the other hand, a photocurrent density of 1.52, 1.03, and $0.78 \mu\text{Acm}^{-2}$ was produced for 400, 340, and 250°C samples, respectively. These photocurrents obtained for different temperatures were, however, lower than those at different precursor concentrations. This could be attributed to the differences in thickness, limiting the charge transfers from the FTO substrate to the top layer of hematite.

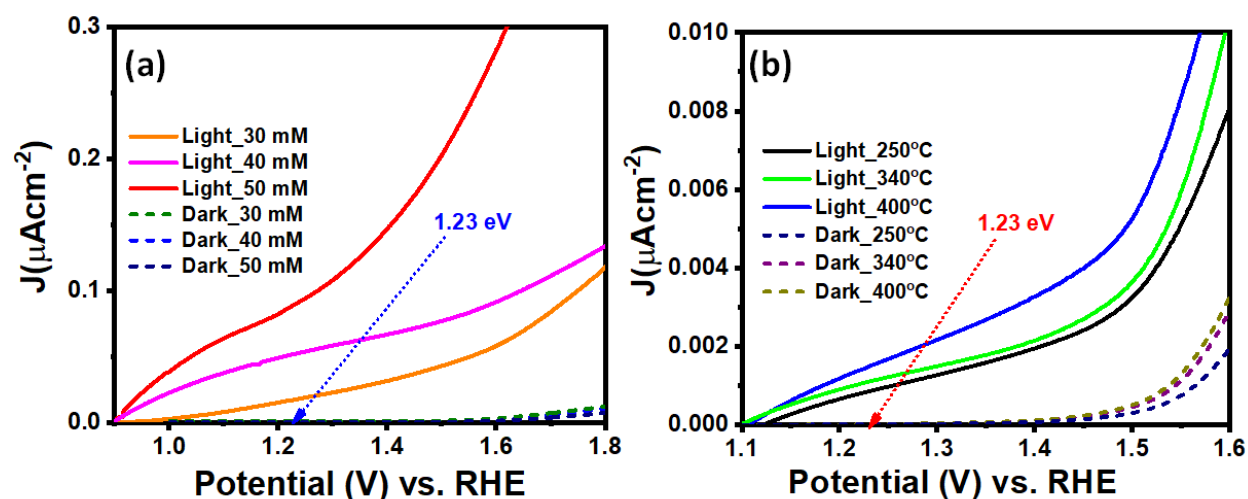


Figure 4.4.7. Photocurrent density curves for hematite thin films prepared at (a) different precursor concentration, and (b) different deposition temperatures. A 50 mVs^{-1} linear scan rate was used in the potential range of 0 to 1 V.

However, despite the nanostructuring of these samples, the obtained photocurrent densities were relatively low, and hematite, due to its poor conductivity, required further surface modification like doping to improve its carrier mobility. There was negligible dark current (Figure 4.4.7 a, b) up to a potential of 1.61 V vs. RHE and 1.52 V vs. RHE for different precursor concentrations and

deposition temperatures, respectively, where oxygen evolution starts. Table 4.4.1 gives a summary of the properties of the hematite obtained from this study.

Table 4.4.1. Summary of the structural, optical and electrical properties of the hematite nanostructures prepared at different temperatures and precursor concentrations.

Sample	Average crystal size (nm)	Lattice constant (a)	Lattice constant (b)	E _g (eV)	Photocurrent density (μAcm ⁻²)
30 mM	23.05	5.09	13.75	2.10	17
40 mM	27.63	5.03	13.75	2.06	53
50 mM	29.92	5.03	13.77	1.99	89
250°C	38.11	5.01	13.69	1.91	1.52
340°C	32.89	5.02	13.67	2.00	1.03
400°C	23.97	5.01	13.68	2.09	0.78

4.4.5 Mott-Schottky analysis

Mott-Schottky (M-S) analysis was done under dark conditions using a frequency of 10 kHz. The analysis was then done to obtain a flat band potential and donor density using Eqn 4.4.3:

$$\frac{1}{C_{sc}^2} = \left(\frac{2}{\epsilon \epsilon_0 q N_D} \right) \left(V - V_{FB} - \frac{K_B T}{q} \right) \quad 4.4.3$$

where C is the space charge capacitance, q the charge of the electron, ϵ the dielectric constant of hematite which has been reported to be 80 [53], ϵ_0 the dielectric permittivity of vacuum, N_D is the carrier density, V is the applied potential with the reference electrode, V_{FB} is the flat band

potential, k is the Boltzmann constant, and T is the room temperature [54]. From Figure 4.4.8, the slope on the linear part was used to obtain the donor density while the extrapolation of the intercept of the straight line with the x-axis (applied potential, V) estimated the flat band potential.

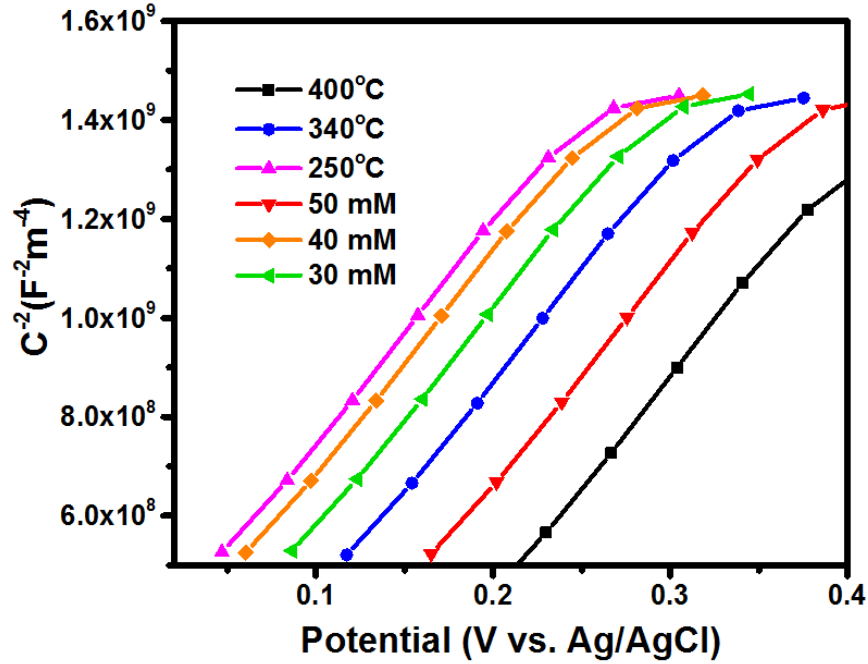


Figure 4.4.8. Mott-Schottky plots for nanostructured hematite films at different deposition temperature and precursor concentrations using a frequency of 10 kHz under dark measurements.

From the analysis, the positive slopes were obtained for all the samples, an indication that they were n-type semiconductors. Nanostructured hematite film prepared at 250°C produced the lowest E_{FB} of 0.045 V. All other samples had a flat band potential which was in the range of 0.044 and 0.213 V (for 400°C deposited sample). The films had a donor density in the range of 10^{18} cm^{-3} . Samples deposited at 50 mM precursor concentration and 400°C had donor densities of 3.98×10^{18} and $4.34 \times 10^{18} \text{ cm}^{-3}$ respectively, which was a slight increase from other samples. The obtained N_D is similar to what Lopes and co-workers have reported in their evaluation of the role of the film thickness using impedance spectroscopy [55]. The increase in donor density in our case could have resulted from the change in thickness, since much of deposition for high-temperature samples (400°C) was taking place in vapour form. Due to the poor conductivity of hematite, there is limited transfer of the charges for the thicker samples, which also explains the low PEC performance by

these samples. Aiwu and co-workers have given similar reports on the effect of thickness of the films prepared by hydrothermal synthesis for solar water splitting [56]. Table 4.4.2 presents a summary of the donor density and flat band potential that was obtained from this study.

Table 4.4.2. Summary of the donor density and flat band potential of hematite nanostructures at different temperatures and precursor concentrations.

Sample	Donor density ($\times 10^{18} \text{ cm}^{-3}$)	Flat band potential (V)
30 mM	2.09	0.084
40 mM	2.27	0.058
50 mM	3.98	0.162
250°C	1.95	0.045
340°C	3.77	0.116
400°C	4.34	0.213

4.5 Surface-doped hematite nanostructures for the efficient photoelectrochemical water splitting

4.5.1 Structural analysis

XRD was used to confirm the crystal structure of pristine $\alpha\text{-Fe}_2\text{O}_3$, $\alpha\text{-Fe}_2\text{O}_3\text{:Zn}$, $\alpha\text{-Fe}_2\text{O}_3\text{:Ag}$, and $\alpha\text{-Fe}_2\text{O}_3\text{:Zn/Ag}$ thin films. From the results in Figure 4.5.1, all the phases of hematite were confirmed with the correct indexing in their 2θ angles. There was, however, a decrease in the peak

intensity of the doped samples from the pristine hematite (Figure 4.5.1). The (110) phase was observed in all the samples. However, it can be observed that the intensity of the (110) phase in α -Fe₂O₃:Zn/Ag and α -Fe₂O₃:Ag samples was relatively higher than that of α -Fe₂O₃:Zn sample. The high intensity of this peak relative to other phases gives more information about the vertical orientation of the (001) plane for the samples. Besides, the (001) phase has been reported to favour the photoanode activity, resulting from improvement in the electron transport of the doped samples. The faster electron transport that has been reported for the (001) plane could also result from the improved conductivity relative to other planes due to doping. A similar study has been reported by Mirbagheri and co-workers using Zn and Ti-doped hematite films for PEC water oxidation using electro-deposition technique [57]. The peaks of Zn or Ti were not detected in their study.

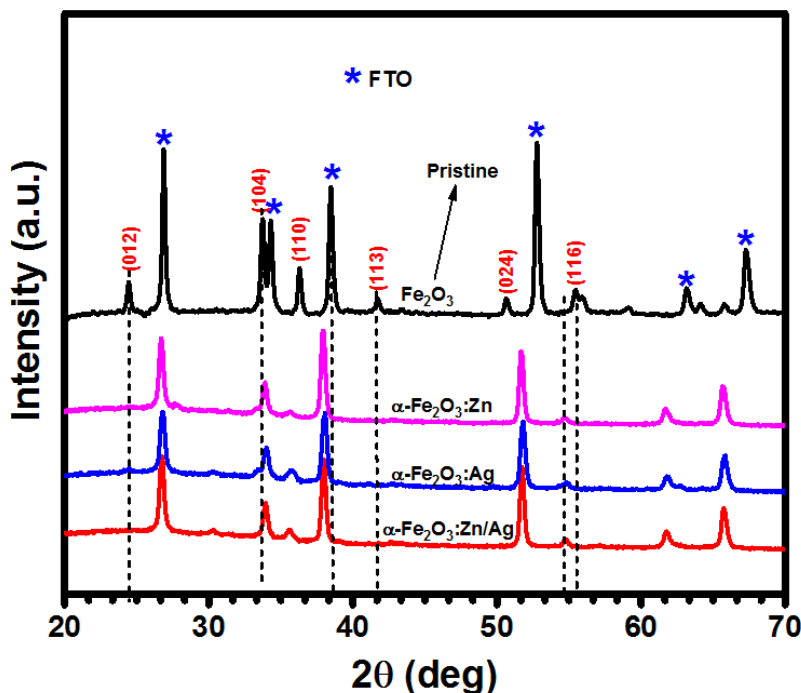


Figure 4.5.1. X-ray diffraction patterns of pristine α -Fe₂O₃, α -Fe₂O₃:Zn, α -Fe₂O₃:Ag, and α -Fe₂O₃:Zn/Ag thin films.

Interestingly, there was a peak shift to lower 2θ angles for α -Fe₂O₃:Zn, α -Fe₂O₃:Ag, and α -Fe₂O₃:Zn/Ag samples. This might have also led to an increase in the lattice parameters resulting from the increase in the ionic radius of Ag⁺ (0.115 nm), and Zn²⁺ (0.074 nm) compared to Fe³⁺

(0.064 nm), and O^{2-} (0.140 nm), which had an ultimate effect (increase) on the Coulombic repulsion between the ion charges [58].

4.5.2 Surface morphology

The pristine $\alpha\text{-Fe}_2\text{O}_3$, $\alpha\text{-Fe}_2\text{O}_3\text{:Zn}$, $\alpha\text{-Fe}_2\text{O}_3\text{:Ag}$, and $\alpha\text{-Fe}_2\text{O}_3\text{:Zn/Ag}$ thin films revealed a nanoporous NPs, with the grain sizes distributed evenly on the surface of the film as shown in Figure 4.5.2. Rod-like structures were, however, observed for the $\alpha\text{-Fe}_2\text{O}_3\text{:Ag}$ samples (Figure 4.5.2 c), with pores that were having almost the same diameter. From the ImageJ analysis, the average grain size for all the samples was found to be < 30 nm. The small grain size is preferably right to counter the short hole diffusion that hematite faces (2 -20 nm), which further leads to high electron-hole recombination, hence reducing its PEC performance [59].

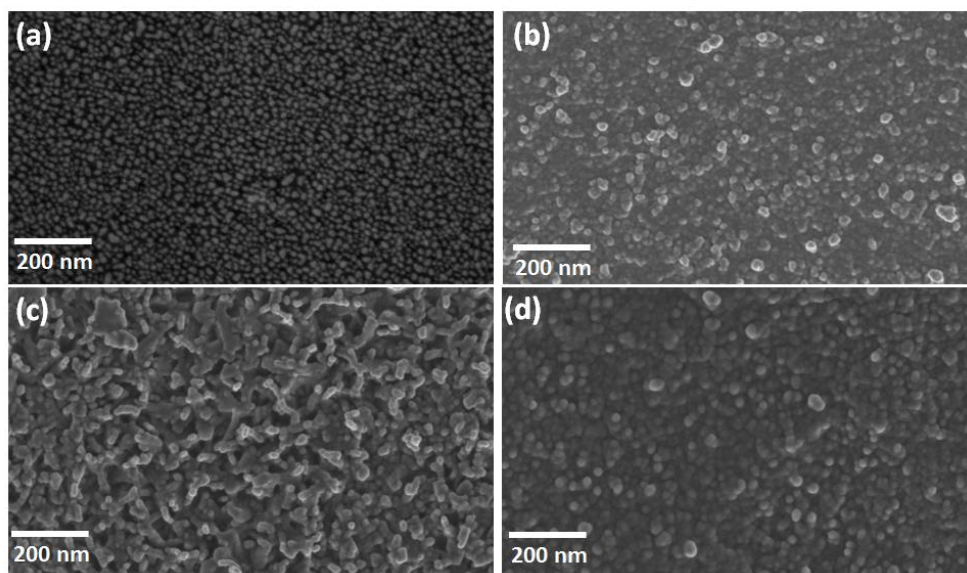


Figure 4.5.2. Surface morphology using SEM for pristine $\alpha\text{-Fe}_2\text{O}_3$, $\alpha\text{-Fe}_2\text{O}_3\text{:Zn}$, $\alpha\text{-Fe}_2\text{O}_3\text{:Ag}$, and $\alpha\text{-Fe}_2\text{O}_3\text{:Zn/Ag}$ thin films.

4.5.3 Optical properties

From the UV-Vis measurements of pristine $\alpha\text{-Fe}_2\text{O}_3$, $\alpha\text{-Fe}_2\text{O}_3\text{:Zn}$, $\alpha\text{-Fe}_2\text{O}_3\text{:Ag}$, and $\alpha\text{-Fe}_2\text{O}_3\text{:Zn/Ag}$ thin films, there was high absorbance in the visible region with the onset absorbance ranging from 592 to 681 nm, presented in Figure 4.5.3. There was, however, a slight blue-shifting of the $\alpha\text{-Fe}_2\text{O}_3\text{:Zn}$, $\alpha\text{-Fe}_2\text{O}_3\text{:Ag}$, and $\alpha\text{-Fe}_2\text{O}_3\text{:Zn/Ag}$ thin films compared to pristine $\alpha\text{-Fe}_2\text{O}_3$, which is

shown in the inset in Figure 4.5.3. This could be attributed to the decrease in thickness during surface doping. Research has shown that unlike thick films that present a single transition, thinner films like the ones obtained in this study can have three transitions. These transitions indicate the presence of intermediate energy levels that further relates to the electrons closer to the conduction band trapped [60]. A strong interaction between the substrate and the film that can lead to stress could have led to the origin of the intermediate levels.

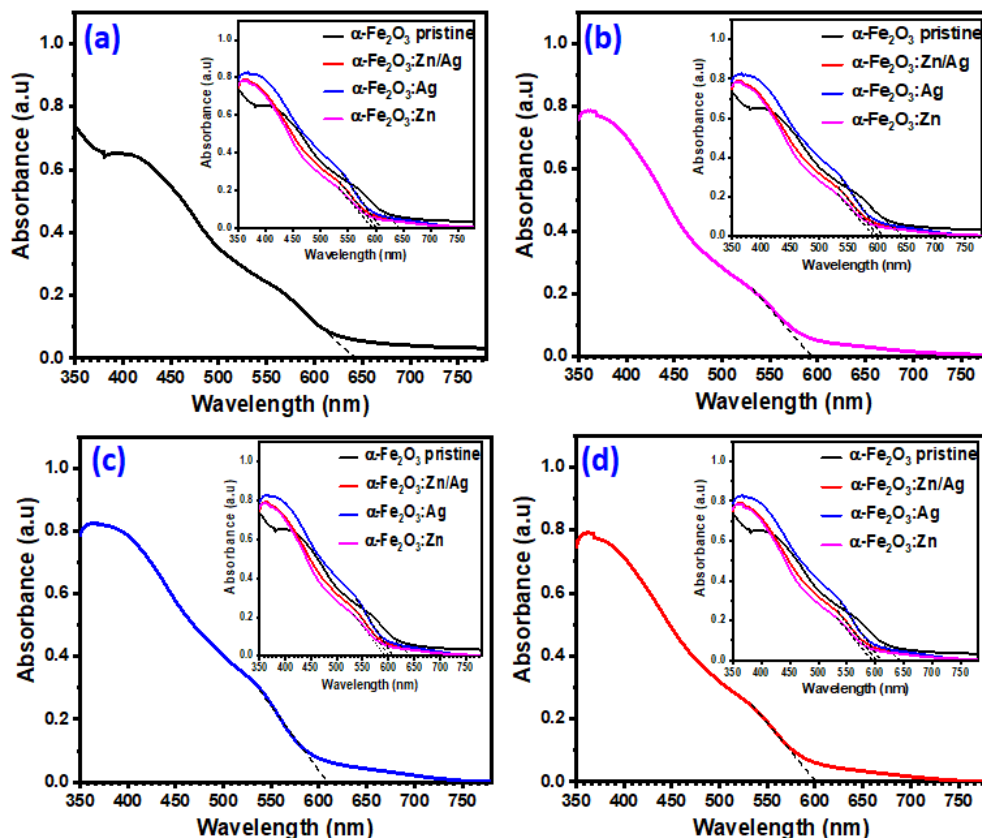


Figure 4.5.3. Optical studies of (a) pristine $\alpha\text{-Fe}_2\text{O}_3$, (b) $\alpha\text{-Fe}_2\text{O}_3\text{:Zn}$, (c) $\alpha\text{-Fe}_2\text{O}_3\text{:Ag}$, and (d) $\alpha\text{-Fe}_2\text{O}_3\text{:Zn/Ag}$ thin films.

From these optical studies, the bandgaps were estimated using the onset absorbance with the use of the photon energy equation described in Section 4.3.3. The absorbance in the visible region from Figure 4.5.3 was mainly due to the Fe^{3+} d-d transitions. Maximum absorbance at around 400 nm is attributed to the ligand-to-metal charge transfer (LMCT) from O (2p) orbitals to Fe^{3+} $2t_{2g}$ and $3e_g$ orbitals [61]. There were also some weak absorption features observed in the UV region

from the d-d transitions since they are spin-forbidden [62]. Bandgaps of pristine $\alpha\text{-Fe}_2\text{O}_3$, $\alpha\text{-Fe}_2\text{O}_3\text{:Zn}$, $\alpha\text{-Fe}_2\text{O}_3\text{:Ag}$ and $\alpha\text{-Fe}_2\text{O}_3\text{:Zn/Ag}$ were obtained as 1.8, 2.1, 2.0, and 2.1 eV, respectively, which falls in the standard bandgap of hematite as reported in Sections 4.2.5, 4.3.3, and 4.4.2.

4.5.4 Photocurrent-voltage (I-V) measurements

Figure 4.5.4 presents the I-V measurements of pristine $\alpha\text{-Fe}_2\text{O}_3$, $\alpha\text{-Fe}_2\text{O}_3\text{:Zn}$, $\alpha\text{-Fe}_2\text{O}_3\text{:Ag}$, and $\alpha\text{-Fe}_2\text{O}_3\text{:Zn/Ag}$ thin films using the potentiostat workstation described earlier and 1 M NaOH as the electrolyte. The focused area that was irradiated by the simulated sun was 0.49 cm^2 . From the analysis, photocurrents of 0.033, 0.160, 0.270, and 0.470 mAcm^{-2} at 1.23 V vs. RHE for pristine $\alpha\text{-Fe}_2\text{O}_3$, $\alpha\text{-Fe}_2\text{O}_3\text{:Zn}$, $\alpha\text{-Fe}_2\text{O}_3\text{:Ag}$, and $\alpha\text{-Fe}_2\text{O}_3\text{:Zn/Ag}$, respectively, were obtained.

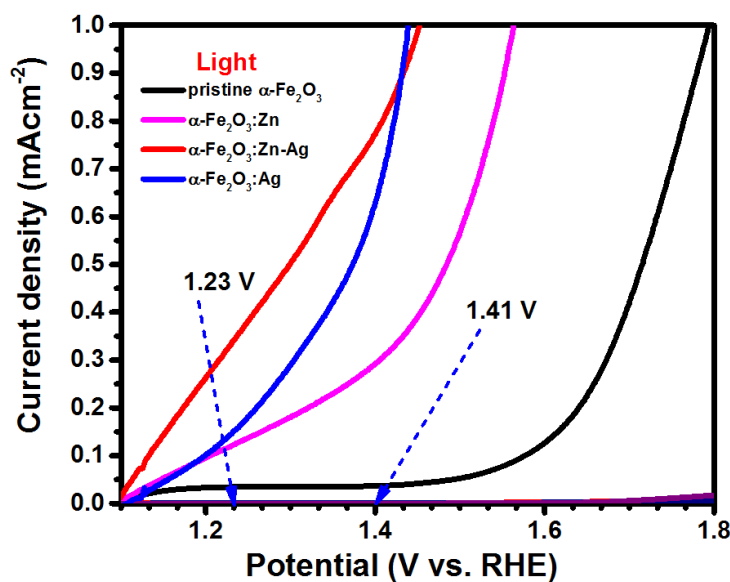


Figure 4.5.4. Photocurrent-voltage measurements pristine $\alpha\text{-Fe}_2\text{O}_3$, $\alpha\text{-Fe}_2\text{O}_3\text{:Zn}$, $\alpha\text{-Fe}_2\text{O}_3\text{:Ag}$, and $\alpha\text{-Fe}_2\text{O}_3\text{:Zn/Ag}$ thin films.

A significant increase in the photocurrent was observed for the $\alpha\text{-Fe}_2\text{O}_3\text{:Zn/Ag}$ from the pristine $\alpha\text{-Fe}_2\text{O}_3$ one. Additionally, at a potential of 1.41 V vs. RHE, photocurrent densities of 0.040, 0.305, 0.689, and 0.813 mAcm^{-2} for pristine $\alpha\text{-Fe}_2\text{O}_3$, $\alpha\text{-Fe}_2\text{O}_3\text{:Zn}$, $\alpha\text{-Fe}_2\text{O}_3\text{:Ag}$, and $\alpha\text{-Fe}_2\text{O}_3\text{:Zn/Ag}$ thin films were recorded. This was a significant improvement of ~ 1.8 times from 1.23 V vs. RHE for the $\alpha\text{-Fe}_2\text{O}_3\text{:Zn}$, $\alpha\text{-Fe}_2\text{O}_3\text{:Ag}$, and $\alpha\text{-Fe}_2\text{O}_3\text{:Zn/Ag}$ samples.

The improvements in the photocurrent density for the $\alpha\text{-Fe}_2\text{O}_3\text{:Zn}$, $\alpha\text{-Fe}_2\text{O}_3\text{:Ag}$, and $\alpha\text{-Fe}_2\text{O}_3\text{:Zn/Ag}$ from pristine $\alpha\text{-Fe}_2\text{O}_3$ could be attributed to the increase in the donor density. Also, there were a cathodic shift in the onset absorbance to ~ 80 mV for pristine $\alpha\text{-Fe}_2\text{O}_3$ and $\alpha\text{-Fe}_2\text{O}_3\text{:Zn/Ag}$ samples. The improvement in the photocurrent could also have resulted from the reduction in the formation of the surface trap states for $\alpha\text{-Fe}_2\text{O}_3\text{:Zn}$, $\alpha\text{-Fe}_2\text{O}_3\text{:Ag}$, and $\alpha\text{-Fe}_2\text{O}_3\text{:Zn/Ag}$ samples as compared to the pristine $\alpha\text{-Fe}_2\text{O}_3$, hence enhancing the transient lifetimes [58]. On the other hand, there is low electron mobility for the pristine hematite sample, leading to low photocurrent production.

4.5.5 Electrochemical impedance measurements.

Mott-Schottky (M-S) plots were performed on the pristine $\alpha\text{-Fe}_2\text{O}_3$, $\alpha\text{-Fe}_2\text{O}_3\text{:Zn}$, $\alpha\text{-Fe}_2\text{O}_3\text{:Ag}$, and $\alpha\text{-Fe}_2\text{O}_3\text{:Zn/Ag}$ thin films to study their electronic properties using capacitance (C) vs. potential measurements with a frequency of 10 kHz in a potentiostat workstation as shown in Figure 4.5.5. The M-S slopes for all the samples were observed to be positive, an indication that the pristine $\alpha\text{-Fe}_2\text{O}_3$, $\alpha\text{-Fe}_2\text{O}_3\text{:Zn}$, $\alpha\text{-Fe}_2\text{O}_3\text{:Ag}$, and $\alpha\text{-Fe}_2\text{O}_3\text{:Zn/Ag}$ samples still showed n-type properties. Eqn 4.4.3 was used to calculate the carrier densities (N_D) and flat band potential (E_{FB}).

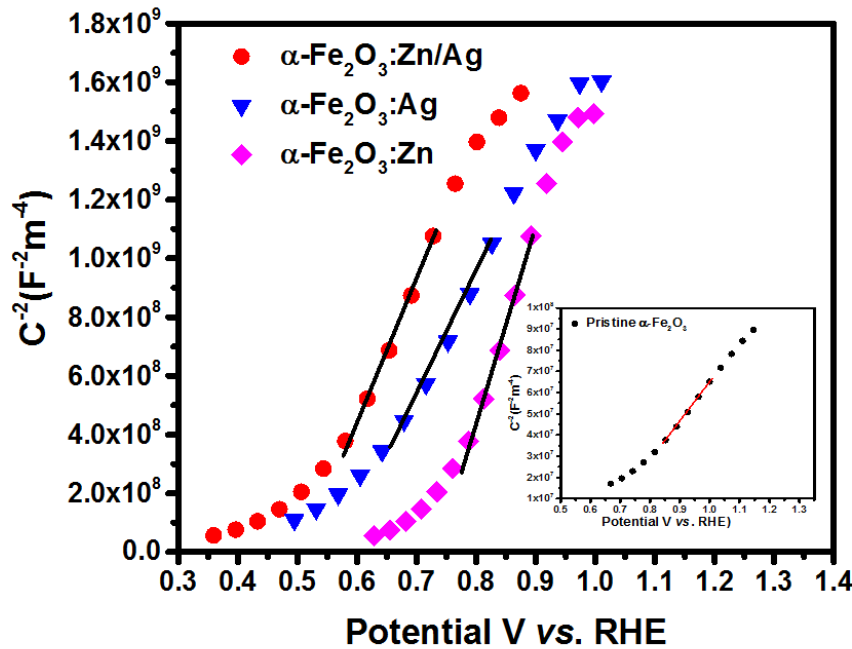


Figure 4.5.5. Mott-Schottky plots of pristine $\alpha\text{-Fe}_2\text{O}_3$, $\alpha\text{-Fe}_2\text{O}_3\text{:Zn}$, $\alpha\text{-Fe}_2\text{O}_3\text{:Ag}$, and $\alpha\text{-Fe}_2\text{O}_3\text{:Zn/Ag}$ thin films, with a frequency of 10 kHz in the potential range between -0.2 and 0.5 V.

From the M-S analysis, flat band potentials of 0.74, 0.68, 0.53 and 0.44 V vs. RHE for pristine $\alpha\text{-Fe}_2\text{O}_3$, $\alpha\text{-Fe}_2\text{O}_3\text{:Zn}$, $\alpha\text{-Fe}_2\text{O}_3\text{:Ag}$, and $\alpha\text{-Fe}_2\text{O}_3\text{:Zn/Ag}$ thin films were obtained. The E_{FB} values obtained were related to the photocurrents measured since the E_{FB} and onset potential usually are almost equal from the theoretical perspective [63]. A cathodic shift of E_{FB} was observed for pristine $\alpha\text{-Fe}_2\text{O}_3$, $\alpha\text{-Fe}_2\text{O}_3\text{:Zn}$, $\alpha\text{-Fe}_2\text{O}_3\text{:Ag}$, with $\alpha\text{-Fe}_2\text{O}_3\text{:Zn/Ag}$ revealing the highest shift of 29 V. Additionally, the donor densities of 9.39×10^{19} , 3.83×10^{20} , 3.90×10^{20} , and $3.91 \times 10^{21} \text{ cm}^{-3}$ for pristine $\alpha\text{-Fe}_2\text{O}_3$, $\alpha\text{-Fe}_2\text{O}_3\text{:Zn}$, $\alpha\text{-Fe}_2\text{O}_3\text{:Ag}$, and $\alpha\text{-Fe}_2\text{O}_3\text{:Zn/Ag}$ samples, respectively, were obtained. There was a significant increase in the donor density for the $\alpha\text{-Fe}_2\text{O}_3\text{:Zn/Ag}$ from pristine $\alpha\text{-Fe}_2\text{O}_3$.

This increase in donor density and the cathodic shifting of the flat band potential could have led to the photocurrent improvement as a result of the enhancement in the conductivity. Further, the improvements could have also led to the transfer of surface electrons that further reduces the charge recombination and favouring the low onset potential [64]. The reported results in this work are almost consistent with Xi and co-workers on their study of the surface treatment of hematite photoanodes using zinc acetate for water oxidation [65]. Besides, the results show that doping with Zn, Ag and Zn/Ag did not change hematite to photocathode from photoanode. This means that the oxygen evolution reaction (OER) still took place on the prepared photoelectrodes.

Electrochemical impedance spectra (EIS) was performed on our samples for further studying their electrochemical behaviour using a three-electrode configuration. The impedance (Z) was determined using Ohms law:

$$Z(\omega) = \frac{V(t)}{I(t)} \quad 4.4.1$$

where $V(t) = V_o + V_m \sin(\omega t)$ and $I(t) = I_o + I_m \sin(\omega t + \theta)$, with I_o and V_o representing the *dc* steady-current and bias potentials that flow when performing the EIS experiments. The maximum voltage obtained and the sinusoidal current is represented by V_m and I_m while θ is the phase angle [66]. Figure 4.5.6 presents the EIS Nyquist plots for pristine $\alpha\text{-Fe}_2\text{O}_3$, $\alpha\text{-Fe}_2\text{O}_3\text{:Zn}$, $\alpha\text{-Fe}_2\text{O}_3\text{:Ag}$, and $\alpha\text{-Fe}_2\text{O}_3\text{:Zn/Ag}$ thin films.

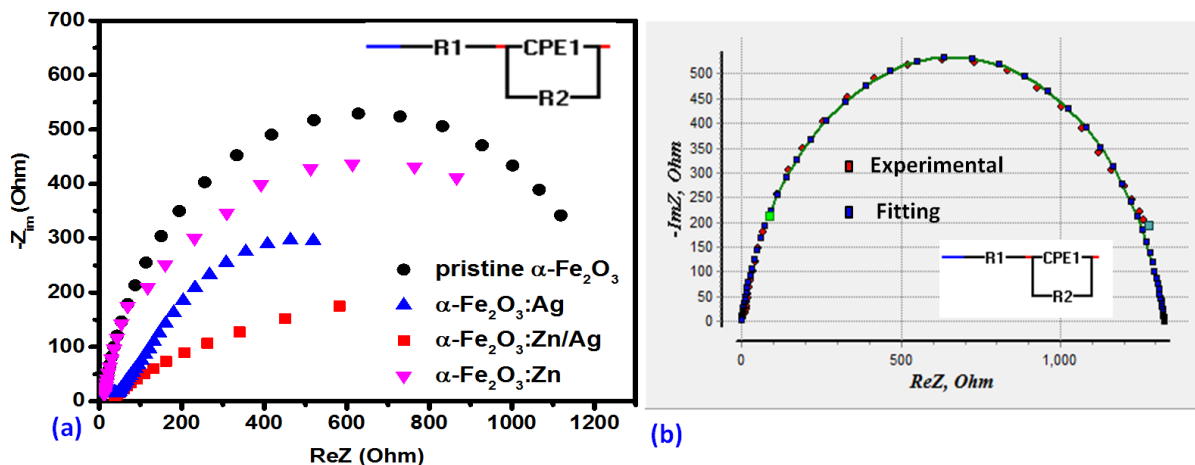


Figure 4.5.6. (a) Electrochemical impedance spectra of pristine $\alpha\text{-Fe}_2\text{O}_3$, $\alpha\text{-Fe}_2\text{O}_3\text{:Zn}$, $\alpha\text{-Fe}_2\text{O}_3\text{:Ag}$, and $\alpha\text{-Fe}_2\text{O}_3\text{:Zn/Ag}$ thin films using 1 M NaOH electrolyte, with the inset showing the equivalent circuit, (b) the EIS Nyquist plot of the fitted and experimental results of pristine $\alpha\text{-Fe}_2\text{O}_3$ as obtained from EIS spectrum analyser.

The curve for pristine hematite from Figure 4.5.6 had the highest diameter, while $\alpha\text{-Fe}_2\text{O}_3\text{:Zn/Ag}$ has the least. Besides, the n-type semiconductor/electrolyte for a PEC system is typically presented by the largest semicircle, which was in agreement with our results [63]. This also indicates that there was high resistance for the undoped hematite compared to doped ones. Additionally, the improved photocurrent measurements for the $\alpha\text{-Fe}_2\text{O}_3\text{:Zn/Ag}$ compared to pristine hematite can further be explained by the small-diameter [57]. This gives further evidence of the improvement of the photocurrent for $\alpha\text{-Fe}_2\text{O}_3\text{:Zn/Ag}$ compared to the pristine hematite. During doping, OER barrier is reduced by a reduction of the charge transfer barrier at the electrolyte/semiconductor interface [67]. To further interpret the EIS results, equivalent circuits were performed using EIS spectral analyser software, and the simulated values presented in Table 4.5.1. Equivalent circuits give more information on charge transport and trapping at the interface of the semiconductor and the electrolyte.

The resistance-capacitance (RC) circuit that consists of FTO resistance, R_s , represented by R1 in the inset of Figure 4.5.6, constant phase element (CPE1), and charge transfer resistance, R_{ct} , represented by R2, were used to fit the results of the pristine $\alpha\text{-Fe}_2\text{O}_3$, $\alpha\text{-Fe}_2\text{O}_3\text{:Zn}$, $\alpha\text{-Fe}_2\text{O}_3\text{:Ag}$, and $\alpha\text{-Fe}_2\text{O}_3\text{:Zn/Ag}$ samples. From the fitting results obtained (Table 4.5.1), a reduction in charge transfer resistance for the $\alpha\text{-Fe}_2\text{O}_3\text{:Zn}$, $\alpha\text{-Fe}_2\text{O}_3\text{:Ag}$, and $\alpha\text{-Fe}_2\text{O}_3\text{:Zn/Ag}$ samples from the pristine

one was observed. The high resistance on the semiconductors from this study can be assigned to the $\alpha\text{-Fe}_2\text{O}_3$ /electrolyte interface. This is due to the opposition to the flow of the minority carriers from the hematite layer to oxidize water, the major cause being the poor conductivity of hematite and the recombination centres created by particle boundaries [64, 69].

The lowest R_{ct} observed in the $\alpha\text{-Fe}_2\text{O}_3\text{:Zn/Ag}$ sample explains the higher photocurrents obtained as compared with the pristine hematite. Also, the $\alpha\text{-Fe}_2\text{O}_3\text{:Zn/Ag}$ samples revealed the lowest space charge capacitance at the electrolyte/semiconductor interface. At the same time, there was also an observable change in CPE for $\alpha\text{-Fe}_2\text{O}_3\text{:Zn/Ag}$, $\alpha\text{-Fe}_2\text{O}_3\text{:Zn}$, and $\alpha\text{-Fe}_2\text{O}_3\text{:Ag}$ from pristine $\alpha\text{-Fe}_2\text{O}_3$, which further explains the small semicircle that was obtained for these photoelectrodes. As such, the decrease in CPE indicates the formation of a high charge transfer gradient when the dopants are introduced.

Table 4.5.1. Equivalent circuit fitting values obtained from the fitted data for the pristine $\alpha\text{-Fe}_2\text{O}_3$, $\alpha\text{-Fe}_2\text{O}_3\text{:Zn}$, $\alpha\text{-Fe}_2\text{O}_3\text{:Ag}$, and $\alpha\text{-Fe}_2\text{O}_3\text{:Zn/Ag}$ thin films.

Sample	R1 (Ωcm^{-1})	CPE1 ($\times 10^{-6} \text{ Fcm}^{-2}$)	R2 (Ωcm^{-1})
Pristine $\alpha\text{-Fe}_2\text{O}_3$	57.858	7.7	1162.8
$\alpha\text{-Fe}_2\text{O}_3\text{:Zn}$,	53.198	7.5	808.5
$\alpha\text{-Fe}_2\text{O}_3\text{:Ag}$	50.401	7.4	753.5
$\alpha\text{-Fe}_2\text{O}_3\text{:Zn/Ag}$	50.287	4.2	749.8

During the water splitting process, high space charge capacitance is reported mostly for the bulk and undoped samples, leading to low current-voltage densities [69]. The comparisons of the current densities at 1.23 V vs. RHE and 1.41 V vs. RHE donor density is shown in Figure 4.5.7.

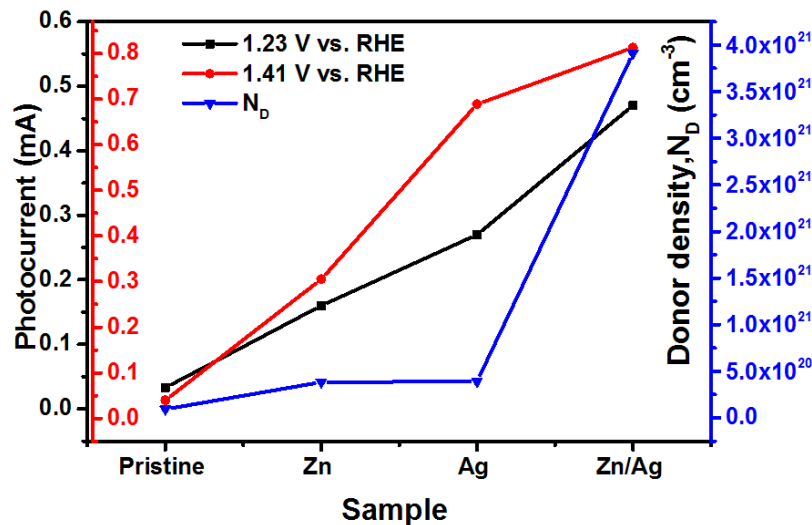


Figure 4.5.7. Comparisons of the current densities at 1.23 V vs. RHE and 1.41 V vs. RHE and the donor densities of pristine $\alpha\text{-Fe}_2\text{O}_3$, $\alpha\text{-Fe}_2\text{O}_3\text{:Zn}$, $\alpha\text{-Fe}_2\text{O}_3\text{:Ag}$, and $\alpha\text{-Fe}_2\text{O}_3\text{:Zn/Ag}$ photoanodes.

4.5.6 Ultrafast transient absorption spectroscopy

Two-dimensional colour maps of the difference absorption (ΔA) of pristine $\alpha\text{-Fe}_2\text{O}_3$, $\alpha\text{-Fe}_2\text{O}_3\text{:Zn}$, $\alpha\text{-Fe}_2\text{O}_3\text{:Ag}$, and $\alpha\text{-Fe}_2\text{O}_3\text{:Zn/Ag}$ obtained from ultrafast transient absorption spectroscopy are presented in Figure 4.5.8 for delay times up to 180 ps. The colour maps in Figure 4.5.8 (a)-(d) show an excited state absorption (ESA) band centred at 570 nm. This ESA band was present from zero delay time and does not completely decay even up to 1.1 ns, as shown in Figure 4.5.9 for all samples.

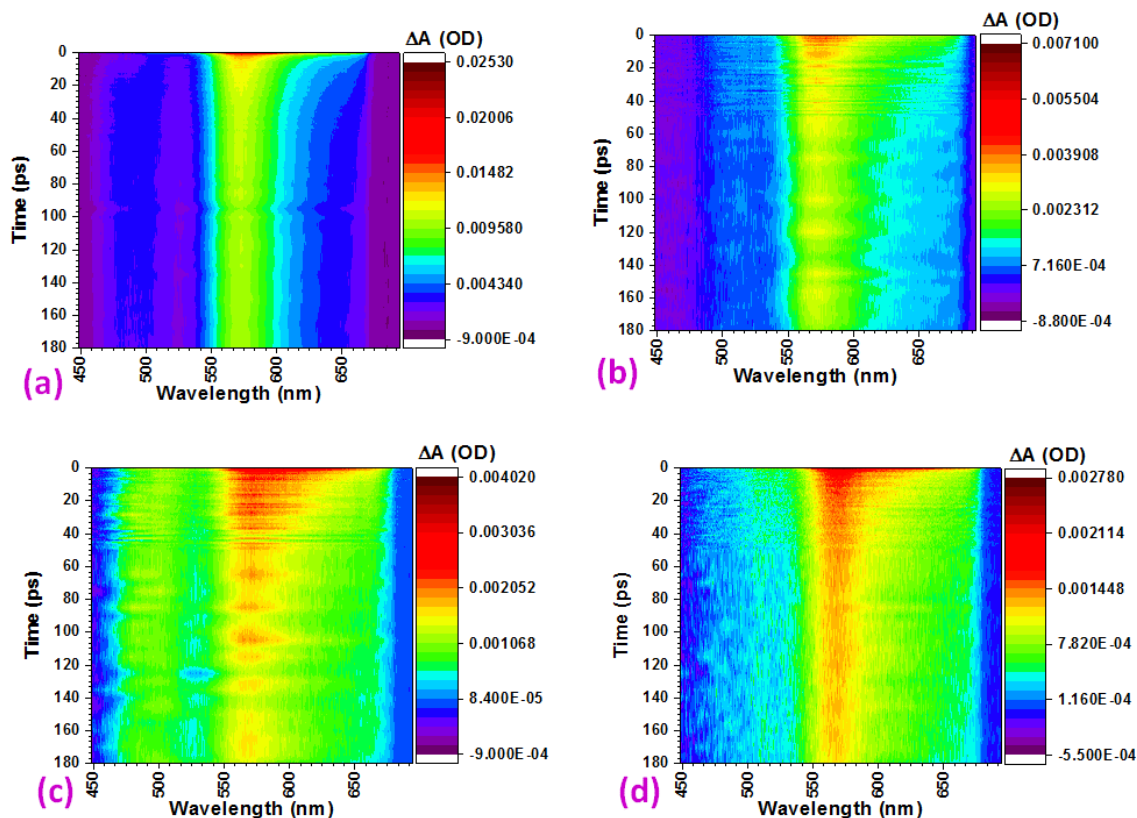


Figure 4.5.8. Two-dimensional colour map of pristine $\alpha\text{-Fe}_2\text{O}_3$, $\alpha\text{-Fe}_2\text{O}_3\text{:Zn}$, $\alpha\text{-Fe}_2\text{O}_3\text{:Ag}$, and $\alpha\text{-Fe}_2\text{O}_3\text{:Zn/Ag}$ obtained from femtosecond transient absorption spectroscopy.

Although the doping does not necessarily improve the lifetimes of the charge carriers as reported previously by Morris and co-workers [70], the nanostructured morphology of the samples synthesized had a significant impact since the average grain size of $\alpha\text{-Fe}_2\text{O}_3\text{:Zn/Ag}$, $\alpha\text{-Fe}_2\text{O}_3\text{:Zn}$, $\alpha\text{-Fe}_2\text{O}_3\text{:Ag}$, and pristine $\alpha\text{-Fe}_2\text{O}_3$ was < 30 nm. For the pump-probe measurements, ΔA at selected delay times are shown in Figure 4.5.9. There is a broad, positive band that peaks at 570 nm and extends beyond 650 nm. The positive band (570 nm) is present throughout our experimental time window showing that this feature decays slowly. The photoexcitation of holes in the valence band and electrons in the conduction band that accompanied the probe light absorption might have also led to the rise of the band.

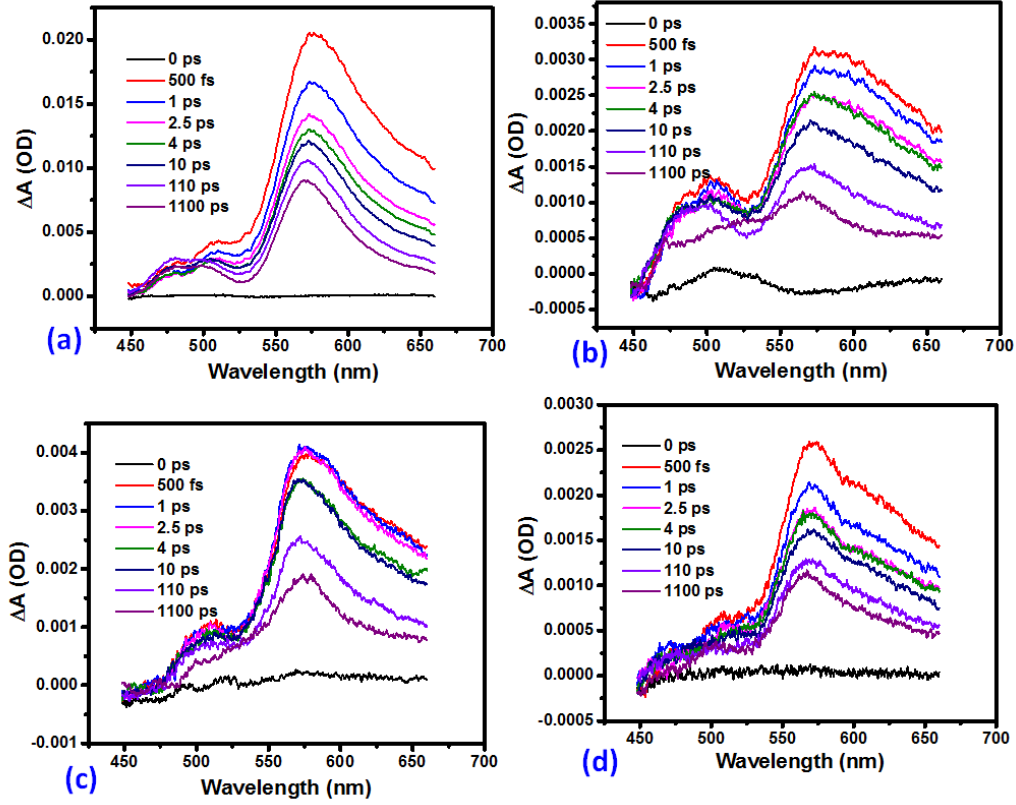


Figure 4.5.9. The difference in absorption at selected delay times for pristine, α -Fe₂O₃, α -Fe₂O₃:Zn, α -Fe₂O₃:Ag, and α -Fe₂O₃:Zn/Ag.

To further explain the electron-hole recombination resulting from the decay of the positive band (570 nm peak) kinetic traces at selected wavelengths in the range of 450 and 670 nm were extracted. In Figure 4.5.10, the signals can be observed to have grown to the maximum value in the transient time scale (< 150 fs) and decayed faster for the first ~ 2 ps before slowing down. A two-exponential function was used to fit the traces as shown in Figure 4.5.10. The obtained lifetimes from the fitting is shown in Tables 4.5.1 (a-d) using $\Delta A = A_1 e^{-t/\tau_1} + A_2 e^{-t/\tau_2}$ biexponential equation where ΔA is the difference absorption, t is the delay time and τ_1 and τ_2 are the decay lifetimes. The decay lifetimes obtained from the individual spectra ranged from fs to ps. This correlates well with the associated lifetimes obtained from evolution associated decay spectra which is displayed in Table 4.5.3. The values of A_1 and A_2 obtained in Table 4.5.2 indicate that most of the ΔA amplitudes decays at the slower rate (τ_2) in all the samples.

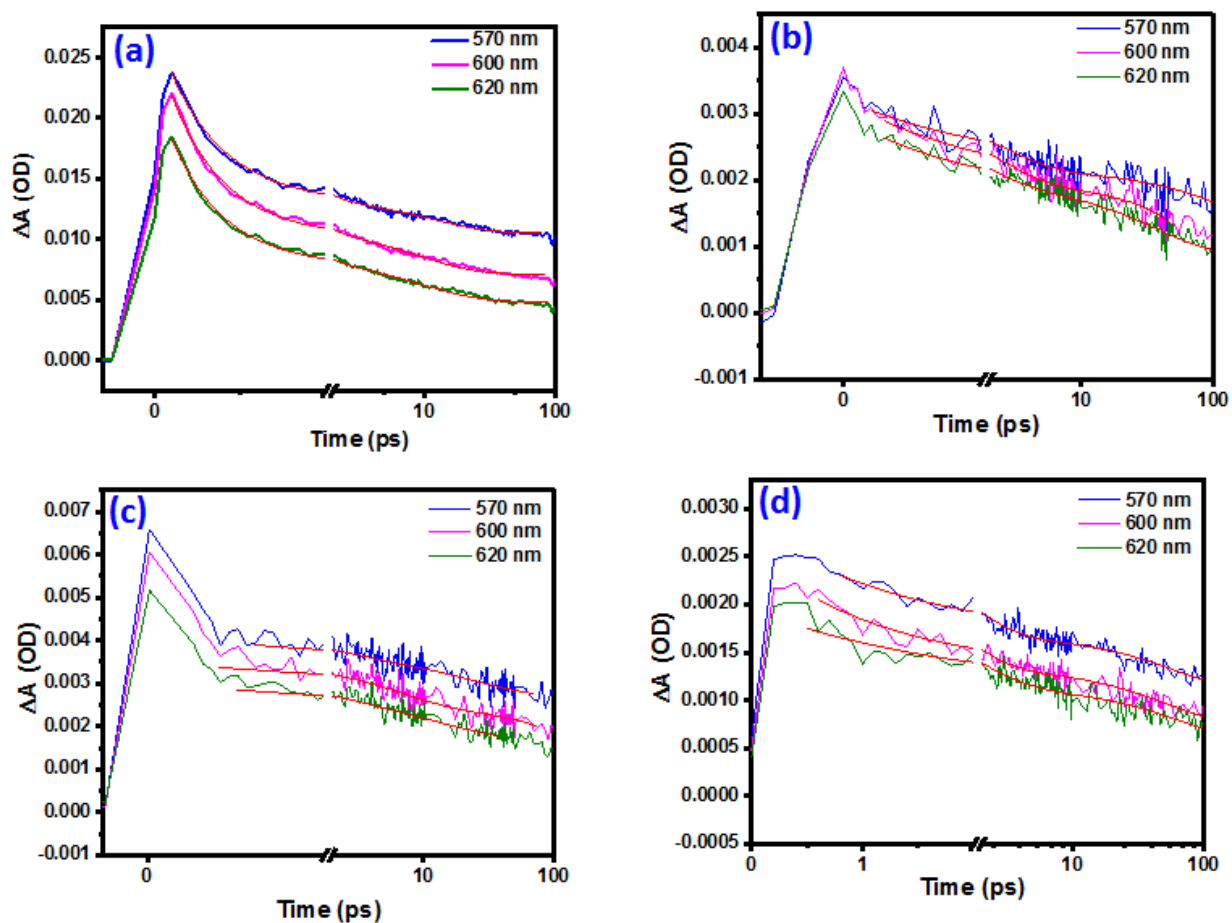


Figure 4.5.10. Kinetic traces at selected wavelengths (570, 600 and 620 nm) for pristine $\alpha\text{-Fe}_2\text{O}_3$, $\alpha\text{-Fe}_2\text{O}_3\text{:Zn}$, $\alpha\text{-Fe}_2\text{O}_3\text{:Ag}$, and $\alpha\text{-Fe}_2\text{O}_3\text{:Zn/Ag}$ samples. The fitting was done between 1 and 100 ps.

Table 4.5.2. Summary of the lifetimes and amplitudes (A_1 and A_2) obtained from fitting the kinetic traces at 570, 600, and 620 nm for (a) pristine $\alpha\text{-Fe}_2\text{O}_3$, (b) $\alpha\text{-Fe}_2\text{O}_3\text{:Zn}$, (c) $\alpha\text{-Fe}_2\text{O}_3\text{:Ag}$, and (d) $\alpha\text{-Fe}_2\text{O}_3\text{:Zn/Ag}$ samples.

a) Pristine hematite sample

Wavelength (nm)	A ₁ ($\times 10^{-3}$)	τ_2 (fs)	A ₂ ($\times 10^{-3}$)	τ_2 (ps)
570	2.29	575	4.13	12
600	1.18	592	3.18	9
620	2.47	595	3.78	10 ps

b) α -Fe₂O₃:Zn sample

Wavelength (nm)	A ₁ ($\times 10^{-3}$)	τ_1 (fs)	A ₂ ($\times 10^{-3}$)	τ_2 (ps)
570	1.07	892	9.78	8
600	1.28	744	5.54	14
620	1.14	601	9.51	11

c) α -Fe₂O₃:Ag sample

Wavelength (nm)	A ₁ ($\times 10^{-3}$)	τ_1 (fs)	A ₂ ($\times 10^{-3}$)	τ_2 (ps)
570	3.54	668 fs	7.59	15
600	1.05	648 fs	4.33	11
620	3.97	729 fs	4.35	13

d) α -Fe₂O₃:Zn-Ag sample

Wavelength (nm)	A ₁ ($\times 10^{-3}$)	τ_1 (fs)	A ₂ ($\times 10^{-3}$)	τ_2 (ps)
570	1.16	822	2.27	12
600	1.88	751	5.45	10
620	3.63	834	6.07	9

Global analysis was performed to determine the electron-hole dynamics (e-h relaxation to the respective band edges, electron trapping by defects and e-h recombination) for pristine α -Fe₂O₃, α -Fe₂O₃:Zn, α -Fe₂O₃:Ag, and α -Fe₂O₃:Zn/Ag samples. This was done using a four-component sequential model described elsewhere [71, 72]. The requirement of four components was determined by means of singular value decomposition of the raw data. The evolution associated difference spectra (EADS) with associated decay lifetimes for the pristine α -Fe₂O₃, α -Fe₂O₃:Zn,

α -Fe₂O₃:Ag, and α -Fe₂O₃:Zn/Ag samples were obtained from the analysis, and are shown in Figure 4.5.11. These lifetimes ranged from femtosecond to nanosecond timescales. The shape of the nanostructures does not affect the lifetime of the samples on the picosecond scale [70, 73].

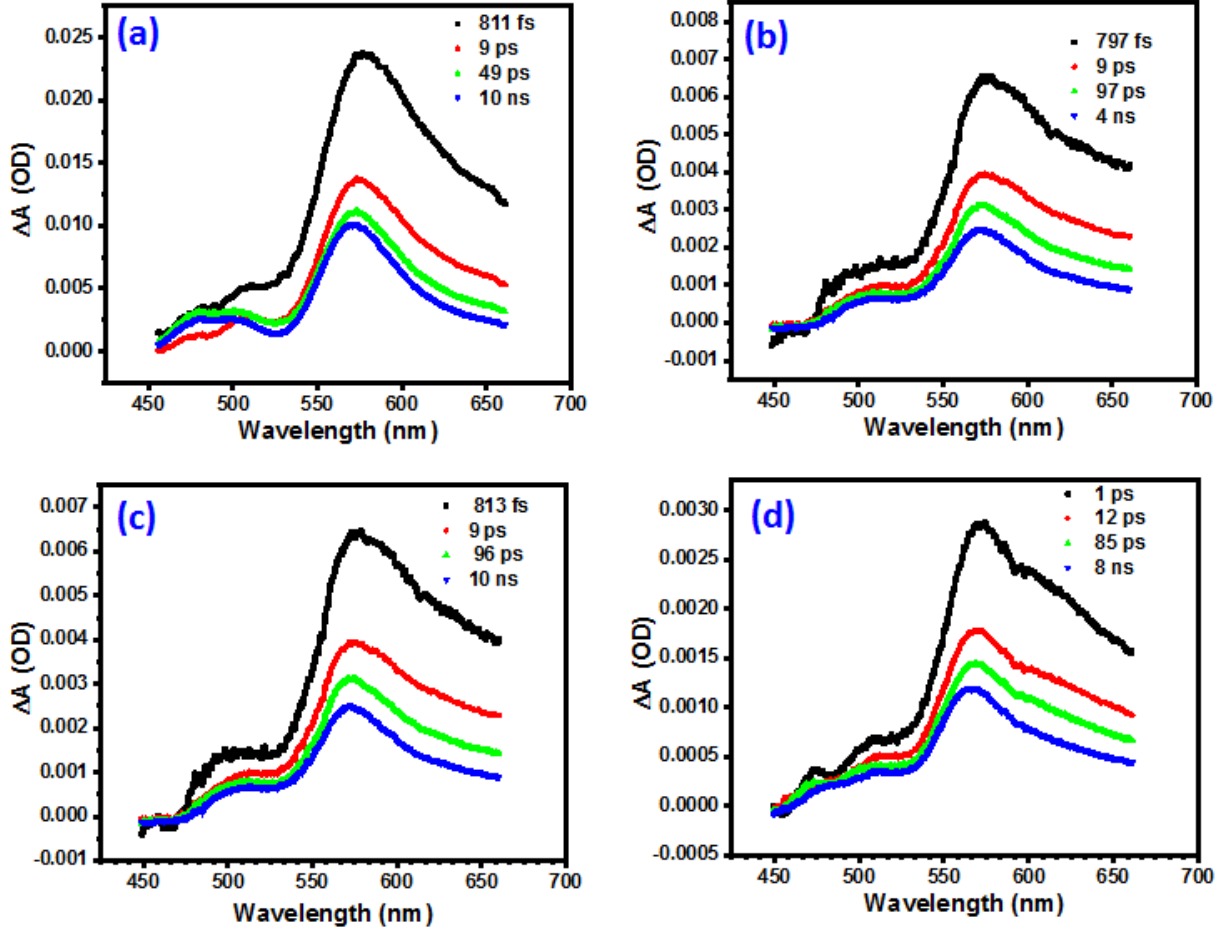


Figure 4.5.11. Evolution associated difference spectra (EADS) with associated decay lifetimes for pristine α -Fe₂O₃, α -Fe₂O₃:Zn, α -Fe₂O₃:Ag, and α -Fe₂O₃:Zn/Ag samples shown with each spectrum's associated decay lifetime.

During the process of excitation from the ground to excited states, creation of hot electrons and holes takes place. The electrons later thermalize and relax to the bottom of the conduction band while the holes relax to the top of the valence band, and the whole process happens on a femtosecond timescale [44]. This process was associated with the first lifetime, τ_1 (Table 4.5.3). The τ_1 values obtained ranged from 797 fs to 1 ps for pristine α -Fe₂O₃ and α -Fe₂O₃:Zn/Ag samples,

respectively. Besides the relaxation of the hot electrons and holes, the decay lifetime (τ_1) can also result from electron-hole recombination.

On the other hand, recombination of the thermalized electron states, having the holes from the trap states and valence band, can take place. The process takes place in the picosecond range corresponding to the second (τ_2) and third (τ_3) lifetimes in our study. The τ_2 lifetimes ranged from 9 to 12 ps, while τ_3 ranged from 49 and 97 ps for pristine α -Fe₂O₃ and α -Fe₂O₃:Zn/Ag respectively. Also, the low trap state densities could have been probably present from the Mott-Schottky plots even though hematite suffers from poor conductivity that results from the valence alternation of the Fe³⁺/Fe²⁺ valence on spatially localized 3d orbitals, affecting the separation of charge efficiency [74]. This could result from the strong coupling between the conduction band and the trap states. Additionally, oxygen vacancies, which are the primary defects in hematite, might have also led to a high density of these trap states [75]. There was not much change observed in the XRD structure of hematite during doping. However, the slight variation in these lifetimes for α -Fe₂O₃:Zn, α -Fe₂O₃:Ag, and α -Fe₂O₃:Zn/Ag from pristine α -Fe₂O₃ could be due to differences in the grain sizes. Since there was a reduction of the 570 nm amplitude (Figure 4.5.9.3 a-d), we can also associate these lifetimes with e⁻-h⁺ recombination.

The fourth lifetime was on a ns timescale. One possible cause of these lifetimes is the recombination between conduction band electrons and valence band holes. These electrons and holes that recombine on this timescale consist of electrons that undergo backflow from the FTO. This is possible due to the 0.19 eV energetic difference between the FTO and hematite. The dopants (Zn, Ag and Zn/Ag) might have, however, suppressed the process but not prohibiting it completely. This could have probably resulted from the sufficient electric field and band bending, but more studies on the same still need to be done. Table 4.5.3 gives a summary of the current density (J), donor density and lifetimes obtained from this study.

Table 4.5.3. Summary of the photocurrents densities, lifetimes and donor densities of pristine α -Fe₂O₃, α -Fe₂O₃:Zn, α -Fe₂O₃:Ag, and α -Fe₂O₃:Zn/Ag samples.

Sample	J (1.23 V) (mAcm ⁻²)	J (1.41 V) (mAcm ⁻²)	τ_1 (fs)	τ_2 (ps)	τ_3 (ps)	τ_4 (ns)	N_D (cm ⁻³)
Pristine α -Fe ₂ O ₃	0.033	0.040	811	9	49	10	9.39×10^{19}
α -Fe ₂ O ₃ :Zn	0.160	0.305	797	9	97	4	3.83×10^{20}
α -Fe ₂ O ₃ :Ag	0.270	0.609	813	9	96	10	3.90×10^{20}
α -Fe ₂ O ₃ :Zn/Ag	0.470	0.813	1000	12	85	8	3.91×10^{21}

References

- [1] A.A. Yadav, Preparation and electrochemical properties of spray deposited α -Fe₂O₃ from nonaqueous medium for supercapacitor applications, *Journal of Materials Science: Materials in Electronics*, 27 (2016) 12876-12883.
- [2] A. Lassoued, B. Dkhil, A. Gadri, S. Ammar, Control of the shape and size of iron oxide (α -Fe₂O₃) nanoparticles synthesized through the chemical precipitation method, *Results in physics*, 7 (2017) 3007-3015.
- [3] T. Mariño-Otero, M. Oliver-Tolentino, M.A. Aguilar-Frutis, G. Contreras-Martínez, E. Pérez-Cappe, E. Reguera, Effect of thickness in hematite films produced by spray pyrolysis towards water photo-oxidation in neutral media, *international journal of hydrogen energy*, 40 (2015) 5831-5836.
- [4] J.S. Nyarige, T.P. Krüger, M. Diale, Structural and optical properties of hematite and L-arginine/hematite nanostructures prepared by thermal spray pyrolysis, *Surfaces and Interfaces*, 18 (2020) 100394.
- [5] B. Hall, D. Zanchet, D. Ugarte, Estimating nanoparticle size from diffraction measurements, *Journal of applied crystallography*, 33 (2000) 1335-1341.
- [6] J. Morales, J. Tirado, M. Macias, Changes in crystallite size and microstrains of hematite derived from the thermal decomposition of synthetic akaganéite, *Journal of Solid State Chemistry*, 53 (1984) 303-312.
- [7] M. Mahadik, S. Shinde, K. Rajpure, C. Bhosale, Photocatalytic oxidation of Rhodamine B with ferric oxide thin films under solar illumination, *Materials Research Bulletin*, 48 (2013) 4058-4065.
- [8] D. Bersani, P. Lottici, A. Montenero, Micro-Raman investigation of iron oxide films and powders produced by sol–gel syntheses, *Journal of Raman spectroscopy*, 30 (1999) 355-360.
- [9] M.F. Hassan, M.M. Rahman, Z.P. Guo, Z.X. Chen, H.K. Liu, Solvent-assisted molten salt process: A new route to synthesise α -Fe₂O₃/C nanocomposite and its electrochemical performance in lithium-ion batteries, *Electrochimica Acta*, 55 (2010) 5006-5013.
- [10] S. Xie, E. Iglesia, A.T. Bell, Effects of temperature on the Raman spectra and dispersed oxides, *The Journal of Physical Chemistry B*, 105 (2001) 5144-5152.
- [11] G. Lucazeau, Effect of pressure and temperature on Raman spectra of solids: anharmonicity, *Journal of Raman Spectroscopy*, 34 (2003) 478-496.
- [12] M. Barroso, S.R. Pendlebury, A.J. Cowan, J.R. Durrant, Charge carrier trapping, recombination and transfer in hematite (α -Fe₂O₃) water splitting photoanodes, *Chemical Science*, 4 (2013) 2724-2734.
- [13] A. Duret, M. Grätzel, Visible light-induced water oxidation on mesoscopic α -Fe₂O₃ films made by ultrasonic spray pyrolysis, *The Journal of Physical Chemistry B*, 109 (2005) 17184-17191.
- [14] H. Cao, G. Wang, J.H. Warner, A.A. Watt, Amino-acid-assisted synthesis and size-dependent magnetic behaviors of hematite nanocubes, *Applied Physics Letters*, 92 (2008) 013110.
- [15] D.K. Bora, A. Braun, R. Erni, G. Fortunato, T. Graule, E.C. Constable, Hydrothermal treatment of a hematite film leads to highly oriented faceted nanostructures with enhanced photocurrents, *Chemistry of Materials*, 23 (2011) 2051-2061.

- [16] A.S. Hassanien, A.A. Akl, Optical characteristics of iron oxide thin films prepared by spray pyrolysis technique at different substrate temperatures, *Applied Physics A*, 124 (2018) 752.
- [17] M.F. Silva, L.A. de Oliveira, M.A. Ciciliati, L.T. Silva, B.S. Pereira, A.A.W. Hechenleitner, D.M. Oliveira, K.R. Pirola, F.F. Ivashita, A. Paesano Jr, Nanometric particle size and phase controlled synthesis and characterization of γ -Fe₂O₃ or (α + γ)-Fe₂O₃ by a modified sol-gel method, *Journal of Applied Physics*, 114 (2013) 104311.
- [18] D.K. Bora, Hematite and its hybrid nanostructures for photoelectrochemical water splitting: how do properties affect functionality?, *University_of_Basel*, 2012.
- [19] Y. Liu, Y.-X. Yu, W.-D. Zhang, Photoelectrochemical properties of Ni-doped Fe₂O₃ thin films prepared by electrodeposition, *Electrochimica Acta*, 59 (2012) 121-127.
- [20] D.K. Bora, Hematite and its hybrid nanostructures for photoelectrochemical water splitting: how do properties affect functionality, *University_of_Basel*, 2012.
- [21] V.R. Satsangi, S. Kumari, A.P. Singh, R. Shrivastav, S. Dass, Nanostructured hematite for photoelectrochemical generation of hydrogen, *International Journal of Hydrogen Energy*, 33 (2008) 312-318.
- [22] E.L. Tsege, T.S. Atabaev, M.A. Hossain, D. Lee, H.-K. Kim, Y.-H. Hwang, Cu-doped flower-like hematite nanostructures for efficient water splitting applications, *Journal of Physics and Chemistry of Solids*, 98 (2016) 283-289.
- [23] X. Liu, G. Qiu, A. Yan, Z. Wang, X. Li, Hydrothermal synthesis and characterization of α -FeOOH and α -Fe₂O₃ uniform nanocrystallines, *Journal of alloys and compounds*, 433 (2007) 216-220.
- [24] X. Rao, X. Su, C. Yang, J. Wang, X. Zhen, D. Ling, From spindle-like β -FeOOH nanoparticles to α -Fe₂O₃ polyhedral crystals: shape evolution, growth mechanism and gas sensing property, *CrystEngComm*, 15 (2013) 7250-7256.
- [25] M. Tadić, N. Čitaković, M. Panjan, Z. Stojanović, D. Marković, V. Spasojević, Synthesis, morphology, microstructure and magnetic properties of hematite submicron particles, *Journal of alloys and compounds*, 509 (2011) 7639-7644.
- [26] M. Somaraj, N. John, N.J. Tharayil, S. Usha, Effect of Temperature on the Optical and Antioxidant Properties of Bio and Organic Synthesised Hematite Nanoparticles, *IOP Conference Series: Materials Science and Engineering*, IOP Publishing, 2018, pp. 012017.
- [27] M.L. Meier, Measuring crystallite size using X-ray diffraction, the Williamson-Hall method, Department of Chemical Engineering and Materials Science, University of California, DOI (2005).
- [28] J. Ayers, The measurement of threading dislocation densities in semiconductor crystals by X-ray diffraction, *Journal of Crystal Growth*, 135 (1994) 71-77.
- [29] T. Ide, H. Harada, Y. Miyamura, M. Imai, S. Nakano, K. Kakimoto, Relationship between dislocation density and oxygen concentration in silicon crystals during directional solidification, *Crystals*, 8 (2018) 244.
- [30] S. Porto, R. Krishnan, Raman effect of corundum, *The Journal of Chemical Physics*, 47 (1967) 1009-1012.
- [31] K. Ståhl, K. Nielsen, J. Jiang, B. Lebech, J.C. Hanson, P. Norby, J. van Lanschot, On the akaganéite crystal structure, phase transformations and possible role in post-excavational corrosion of iron artifacts, *Corrosion science*, 45 (2003) 2563-2575.
- [32] J. Frydrych, L. Machala, M. Hermanek, I. Medrik, M. Mashlan, J. Tucek, J. Pechousek, V.K. Sharma, A nanocrystalline hematite film prepared from iron (III) chloride precursor, *Thin Solid Films*, 518 (2010) 5916-5919.

- [33] D.E. Newbury*, N.W. Ritchie, Is scanning electron microscopy/energy dispersive X-ray spectrometry (SEM/EDS) quantitative?, *Scanning*, 35 (2013) 141-168.
- [34] A. Ubale, M. Belkhedkar, Size dependent physical properties of nanostructured α -Fe₂O₃ thin films grown by successive ionic layer adsorption and reaction method for antibacterial application, *Journal of Materials Science & Technology*, 31 (2015) 1-9.
- [35] S. Shinde, R. Bansode, C. Bhosale, K. Rajpure, Physical properties of hematite α -Fe₂O₃ thin films: application to photoelectrochemical solar cells, *Journal of Semiconductors*, 32 (2011) 013001.
- [36] S. Piccinin, The band structure and optical absorption of hematite (α -Fe₂O₃): a first-principles GW-BSE study, *Physical Chemistry Chemical Physics*, 21 (2019) 2957-2967.
- [37] S.Y. Chiam, M.H. Kumar, P.S. Bassi, H.L. Seng, J. Barber, L.H. Wong, Improving the efficiency of hematite nanorods for photoelectrochemical water splitting by doping with manganese, *ACS applied materials & interfaces*, 6 (2014) 5852-5859.
- [38] D.M. Sherman, T.D. Waite, Electronic spectra of Fe³⁺ oxides and oxide hydroxides in the near IR to near UV, *American Mineralogist*, 70 (1985) 1262-1269.
- [39] A.T. Paradzah, K.D. Maabong, H.M. Elnour, A. Singh, M. Diale, T.P. Krüger, Identification of Exciton–Exciton Annihilation in Hematite Thin Films, *The Journal of Physical Chemistry C*, 123 (2019) 18676-18684.
- [40] D. Hayes, R.G. Hadt, J.D. Emery, A.A. Cordones, A.B. Martinson, M.L. Shelby, K.A. Fransted, P.D. Dahlberg, J. Hong, X. Zhang, Electronic and nuclear contributions to time-resolved optical and X-ray absorption spectra of hematite and insights into photoelectrochemical performance, *Energy & Environmental Science*, 9 (2016) 3754-3769.
- [41] T.J. Miao, J. Tang, Characterization of charge carrier behavior in photocatalysis using transient absorption spectroscopy, *The Journal of Chemical Physics*, 152 (2020) 194201.
- [42] M. Barroso, C.A. Mesa, S.R. Pendlebury, A.J. Cowan, T. Hisatomi, K. Sivula, M. Grätzel, D.R. Klug, J.R. Durrant, Dynamics of photogenerated holes in surface modified α -Fe₂O₃ photoanodes for solar water splitting, *Proceedings of the National Academy of Sciences*, 109 (2012) 15640-15645.
- [43] A.G. Joly, J.R. Williams, S.A. Chambers, G. Xiong, W.P. Hess, D.M. Laman, Carrier dynamics in α -Fe₂O₃ (0001) thin films and single crystals probed by femtosecond transient absorption and reflectivity, *Journal of applied physics*, 99 (2006) 053521.
- [44] N.J. Cherepy, D.B. Liston, J.A. Lovejoy, H. Deng, J.Z. Zhang, Ultrafast studies of photoexcited electron dynamics in γ - and α -Fe₂O₃ semiconductor nanoparticles, *The Journal of Physical Chemistry B*, 102 (1998) 770-776.
- [45] A.T. Paradzah, M. Diale, K. Maabong, T.P. Krüger, Use of interfacial layers to prolong hole lifetimes in hematite probed by ultrafast transient absorption spectroscopy, *Physica B: Condensed Matter*, 535 (2018) 138-142.
- [46] J. Hargreaves, Some considerations related to the use of the Scherrer equation in powder X-ray diffraction as applied to heterogeneous catalysts, *Catalysis, Structure & Reactivity*, 2 (2016) 33-37.
- [47] M. Sharma, S. Murugavel, D.K. Shukla, F.M. De Groot, Reversal in the Lattice Contraction of α -Fe₂O₃ Nanoparticles, *The Journal of Physical Chemistry C*, 122 (2018) 9292-9301.
- [48] F. Morin, Electrical properties of α -Fe₂O₃ and α -Fe₂O₃ containing titanium, *Physical Review*, 83 (1951) 1005.

- [49] M. Fondell, T.J. Jacobsson, M. Boman, T. Edvinsson, Optical quantum confinement in low dimensional hematite, *Journal of Materials Chemistry A*, 2 (2014) 3352-3363.
- [50] C. Garoufalidis, P. Pouloupoulos, N. Bouropoulos, A. Barnasas, S. Baskoutas, Growth and optical properties of Fe₂O₃ thin films: A study of quantum confinement effects by experiment and theory, *Physica E: Low-dimensional Systems and Nanostructures*, 89 (2017) 67-71.
- [51] C. Luna, A.D. Cuan-Guerra, E.D. Barriga-Castro, N.O. Núñez, R. Mendoza-Reséndez, Confinement and surface effects on the physical properties of rhombohedral-shape hematite (α -Fe₂O₃) nanocrystals, *Materials Research Bulletin*, 80 (2016) 44-52.
- [52] P.K. Sarswat, M.L. Free, Demonstration of a sol-gel synthesized bifacial CZTS photoelectrochemical cell, *physica status solidi (a)*, 208 (2011) 2861-2864.
- [53] J.H. Kennedy, K.W. Frese Jr, Flatband Potentials and Donor Densities of Polycrystalline α -Fe₂O₃ Determined from Mott-Schottky Plots, *Journal of the Electrochemical Society*, 125 (1978) 723.
- [54] A. Hankin, F.E. Bedoya-Lora, J.C. Alexander, A. Regoutz, G.H. Kelsall, Flat band potential determination: avoiding the pitfalls, *Journal of Materials Chemistry A*, 7 (2019) 26162-26176.
- [55] T. Lopes, L. Andrade, F. Le Formal, M. Gratzel, K. Sivula, A. Mendes, Hematite photoelectrodes for water splitting: evaluation of the role of film thickness by impedance spectroscopy, *Physical Chemistry Chemical Physics*, 16 (2014) 16515-16523.
- [56] A. Pu, J. Deng, Y. Hao, X. Sun, J. Zhong, Thickness effect of hematite nanostructures prepared by hydrothermal method for solar water splitting, *Applied surface science*, 320 (2014) 213-217.
- [57] N. Mirbagheri, D. Wang, C. Peng, J. Wang, Q. Huang, C. Fan, E.E. Ferapontova, Visible light driven photoelectrochemical water oxidation by Zn-and Ti-doped hematite nanostructures, *Acs Catalysis*, 4 (2014) 2006-2015.
- [58] B.A. Aragaw, C.-J. Pan, W.-N. Su, H.-M. Chen, J. Rick, B.-J. Hwang, Facile one-pot controlled synthesis of Sn and C codoped single crystal TiO₂ nanowire arrays for highly efficient photoelectrochemical water splitting, *Applied Catalysis B: Environmental*, 163 (2015) 478-486.
- [59] T.-P. Ruoko, K. Kaunisto, M. Bärtsch, J. Pohjola, A. Hiltunen, M. Niederberger, N.V. Tkachenko, H. Lemmetyinen, Subpicosecond to second time-scale charge carrier kinetics in hematite-titania nanocomposite photoanodes, *The journal of physical chemistry letters*, 6 (2015) 2859-2864.
- [60] F.L. Souza, K.P. Lopes, E. Longo, E.R. Leite, The influence of the film thickness of nanostructured α -Fe₂O₃ on water photooxidation, *Physical Chemistry Chemical Physics*, 11 (2009) 1215-1219.
- [61] L.A. Marusak, R. Messier, W.B. White, Optical absorption spectrum of hematite, α -Fe₂O₃ near IR to UV, *Journal of Physics and Chemistry of Solids*, 41 (1980) 981-984.
- [62] J. Tossell, D. Vaughan, K. Johnson, The electronic structure of rutile, wustite, and hematite from molecular orbital calculations, *American Mineralogist: Journal of Earth and Planetary Materials*, 59 (1974) 319-334.
- [63] J.Y. Kim, H. Jun, S.J. Hong, H.G. Kim, J.S. Lee, Charge transfer in iron oxide photoanode modified with carbon nanotubes for photoelectrochemical water oxidation: an electrochemical impedance study, *International journal of hydrogen energy*, 36 (2011) 9462-9468.

- [64] M. Li, J. Deng, A. Pu, P. Zhang, H. Zhang, J. Gao, Y. Hao, J. Zhong, X. Sun, Hydrogen-treated hematite nanostructures with low onset potential for highly efficient solar water oxidation, *Journal of Materials Chemistry A*, 2 (2014) 6727-6733.
- [65] L. Xi, P.S. Bassi, S.Y. Chiam, W.F. Mak, P.D. Tran, J. Barber, J.S.C. Loo, L.H. Wong, Surface treatment of hematite photoanodes with zinc acetate for water oxidation, *Nanoscale*, 4 (2012) 4430-4433.
- [66] K. Gelderman, L. Lee, S. Donne, Flat-band potential of a semiconductor: using the Mott–Schottky equation, *Journal of chemical education*, 84 (2007) 685.
- [67] Q. Yu, X. Meng, T. Wang, P. Li, J. Ye, Hematite films decorated with nanostructured ferric oxyhydroxide as photoanodes for efficient and stable photoelectrochemical water splitting, *Advanced Functional Materials*, 25 (2015) 2686-2692.
- [68] J.Y. Kim, J.-W. Jang, D.H. Youn, J.Y. Kim, E.S. Kim, J.S. Lee, Graphene–carbon nanotube composite as an effective conducting scaffold to enhance the photoelectrochemical water oxidation activity of a hematite film, *Rsc Advances*, 2 (2012) 9415-9422.
- [69] J.Y. Kim, G. Magesh, D.H. Youn, J.-W. Jang, J. Kubota, K. Domen, J.S. Lee, Single-crystalline, wormlike hematite photoanodes for efficient solar water splitting, *Scientific reports*, 3 (2013) 2681.
- [70] B.C. Fitzmorris, J.M. Patete, J. Smith, X. Mascorro, S. Adams, S.S. Wong, J.Z. Zhang, Ultrafast transient absorption studies of hematite nanoparticles: the effect of particle shape on exciton dynamics, *ChemSusChem*, 6 (2013) 1907-1914.
- [71] I.H. Van Stokkum, D.S. Larsen, R. Van Grondelle, Global and target analysis of time-resolved spectra, *Biochimica et Biophysica Acta (BBA)-Bioenergetics*, 1657 (2004) 82-104.
- [72] J. Snellenburg, S. Liptonok, R. Seger, K. Mullen, I. Van Stokkum, Glotaran: A Java-based graphical user interface for the R package TIMP, DOI (2012).
- [73] H. Fan, G. You, Y. Li, Z. Zheng, H. Tan, Z. Shen, S. Tang, Y. Feng, Shape-controlled synthesis of single-crystalline Fe₂O₃ hollow nanocrystals and their tunable optical properties, *The Journal of Physical Chemistry C*, 113 (2009) 9928-9935.
- [74] A.G. Tamirat, J. Rick, A.A. Dubale, W.-N. Su, B.-J. Hwang, Using hematite for photoelectrochemical water splitting: a review of current progress and challenges, *Nanoscale Horizons*, 1 (2016) 243-267.
- [75] C. Leygraf, M. Hendewerk, G. Somorjai, The preparation and selected properties of Mg-doped p-type iron oxide as a photocathode for the photoelectrolysis of water using visible light, *Journal of Solid State Chemistry*, 48 (1983) 357-367.

5 Conclusion and future work

5.1 Conclusion

The present study was based on the synthesis of pristine hematite, L-arginine/hematite and doped hematite nanostructured films whose main application was in photoelectrochemical water splitting. For the first time, we were also able to transform hematite nanoparticles (NPs) to nanospheres using L-arginine as the capping agent, with improved photocurrent densities.

In section 4.2, chemical spray pyrolysis was successfully used to synthesize hematite NPs using FTO as the substrate. The samples were deposited at elevated temperatures (280, 330, 380 and 430°C), and later used as seed layers for the transformation of NPs to nanospheres. This was performed using L-arginine under chemical bath deposition at a constant temperature of 90°C for 48 h. The surface morphology analysis using scanning electron microscopy reported grain sizes of 100 nm for the lowest temperature (280°C) sample, 41 nm, and 35 nm for the 430°C and L-arginine/hematite samples respectively. Besides, there was an observed decrease in thickness using cross-section measurements from the SEM. X-ray diffraction and Raman spectroscopy were used to study the structural properties of these films. From the XRD studies, all the hematite phases, indexed in the respective 2θ angles were reported. Raman spectroscopy, on the other hand, revealed all the seven lattice vibrational modes of hematite (two A_{1g} and five E_g). A maximum average transmittance of ~47 % at 550 nm was obtained for all the pristine hematite films, while the L-arginine/hematite film had a transmittance of ~49 %. The optical bandgap of these films were 2.30, 2.20, 2.18 and 2.08 eV, for samples deposited at 280, 330, 380 and 430°C respectively. There was a slight increase in the bandgap of pristine hematite at 430 °C that was used to transform the NPs to nanospheres from 2.08 to 2.21eV for L-arginine/hematite.

Photocurrents of 10, 6.4, 4.3, 4.0, and 2.8 μAcm^{-2} at 1.23 V vs. RHE for 280, 330, 380 and 430°C and L-arginine/hematite respectively were obtained. From this study, a 1.5 fold increase in the photocurrent was obtained for L-arginine/hematite from pristine hematite film at 430°C. Also, there was an observed cathodic shift in the onset of the photocurrent for L-arginine/hematite, 430 and 380°C films from ~1.13 V to ~0.91 V. Although hematite is a poor conductor in nature, the L-arginine/hematite and pristine nanostructured films have observed to record some improvement in the current densities.

In section 4.3, different precursor concentrations of L-arginine were used to transform the NPs to nanospheres using CBD. XRD results confirmed a corundum structure of hematite with a space group of $R\bar{3}C$. Further, Raman spectroscopy also confirmed the lattice vibrational modes of hematite indexed in their right wavenumbers. On the other hand, the SEM studies revealed morphologies of nanospheres of different grain sizes. Besides, the grain size was observed to reduce as the precursor concentration was increased from 1:1 to 3:1 of L-arginine/FeCl₃.6H₂O precursor concentrations samples, respectively. The average grain size obtained reduced from 41.0 to 6.0 nm for pristine hematite and 3:1 of L-arginine: FeCl₃.6H₂O precursor concentrations samples, respectively. Energy-dispersive X-ray further confirmed the purity of hematite with iron and oxygen as the prominent faces dominant.

The films were absorbing in the visible region with a bandgap range of 1.91 and 2.08 eV for pristine hematite prepared at 430°C and 3:1 of L-arginine: FeCl₃.6H₂O precursor concentrations samples. Current densities of 1.6×10^{-3} , 2.7×10^{-3} , 5.4×10^{-3} , and 9.8×10^{-3} mAcm⁻² at 1.23 V vs. RHE for pristine hematite at 430°C, 1:1, 2:1 and 3:1 of L-arginine: FeCl₃.6H₂O precursor concentrations samples respectively were produced. From this study, L-arginine reported higher photocurrent that was a six-fold increase from the pristine α -Fe₂O₃ thin film. This was enhanced by a good absorption of the solar spectrum in the visible region, small grain size and polycrystallinity of the nanostructured films.

Transient absorption spectroscopy reported four lifetimes obtained from the Global analysis of the raw data matrix using singular value decomposition and sequential component. The first lifetimes in the femtosecond range (843 to 324 fs) were associated with the hot electrons and holes tending to relax to their respective band edges. Second lifetimes that ranged from 4 to 14 ps were attributed to the charge carriers (e⁻-h⁺) recombination and trapping by mid-gap states. The recombination of the electrons and holes trapped by the mid-gap states contributes to the third lifetime that ranged from 90 to 42 ps. The fourth lifetimes that was in ns range, (16 - 45 ns), were associated with the recombination taking place from the electrons that undergo backflow from the FTO substrate to the hematite samples. From this study, there was a general trend of reduction in the lifetime from pristine hematite film to L-Arg/ α -Fe₂O₃ as the precursor of L-arginine was increased. These changes were majorly due to a decrease in grain size. A larger surface area to volume ratio dictates

that electrons spend more time near the particle surface at which they can be trapped by surface states hence increasing the lifetime.

In section 4.4, XRD studies confirmed nanostructured hematite films prepared at different precursor concentrations (30, 40, 50 mM) and deposition temperature (250, 340 and 400°C) with the main peaks (012), (110) and (104) indexed at 25.5°, 33.3° and 35.5° respectively. Crystallite sizes that ranged from 23.05 and 29.92 nm for different precursor concentrations and 23.97 and 38.11 nm for different deposition temperatures were obtained. The grain sizes obtained from SEM ranged from 7 to 19 nm for 30 and 50 mM precursor concentrations, while a range of 33 and 14 nm was obtained for 250 and 400°C respectively. The films were absorbing in the visible region with an onset absorbance that ranged from 590 nm (2.10 eV) to 680 (1.80 eV) nm for different precursor concentrations and temperatures. The 50 mM precursor concentration sample recorded the highest photocurrent density of 89 μAcm^{-2} . Other photocurrents obtained were 53, 17, 1.52, 1.03, and 0.78 μAcm^{-2} for 40 mM, 30 mM, 400, 340 and 250°C samples. From the Mott-Schottky analysis, a donor density of $\sim 10^{18} \text{ cm}^{-3}$ was obtained for all the samples, with a flat band potential that ranged from 0.082 V to 0.214 V vs. Ag/AgCl.

Section 4.5 reports the improvement of the photocurrent by surface-doping of hematite with Zn, Ag and co-doping with Zn/Ag as the dopants. The purity of the hematite phase was still maintained after doping as confirmed using XRD. However, there was a slight shift of the hematite peaks to the lower 2θ angles. The films had bandgaps of 1.9, 2.1, 2.0 and 2.1 eV for pristine hematite, $\alpha\text{-Fe}_2\text{O}_3\text{:Zn}$, $\alpha\text{-Fe}_2\text{O}_3\text{:Ag}$ and $\alpha\text{-Fe}_2\text{O}_3\text{:Zn/Ag}$ respectively. From the Mott-Schottky analysis, the doped and undoped hematite revealed n-type properties. Also, there was a three-fold increase in donor density and cathodic shift of -29 V for the $\alpha\text{-Fe}_2\text{O}_3\text{:Zn/Ag}$ sample from pristine $\alpha\text{-Fe}_2\text{O}_3$ one.

The $\alpha\text{-Fe}_2\text{O}_3\text{:Zn/Ag}$ sample produced the lowest diameter from the electrochemical impedance spectra analysis compared to the pristine $\alpha\text{-Fe}_2\text{O}_3$. This shows a faster charge transfer was taking place, a further indication that oxygen evolution reaction barrier was reduced by surface doping. A reduction of the charge transfer at the electrode interface was confirmed by the equivalent circuit. An improvement of photocurrent that was >1.8 times was observed for $\alpha\text{-Fe}_2\text{O}_3\text{:Zn}$, $\alpha\text{-Fe}_2\text{O}_3\text{:Ag}$, and $\alpha\text{-Fe}_2\text{O}_3\text{:Zn/Ag}$ from the pristine $\alpha\text{-Fe}_2\text{O}_3$ sample. The highest photocurrent density of 0.470 mAcm^{-2} at 1.23 V vs. RHE was obtained for the $\alpha\text{-Fe}_2\text{O}_3\text{:Zn/Ag}$. At the same time, $\alpha\text{-Fe}_2\text{O}_3\text{:Zn/Ag}$ further recorded higher current densities of 0.813 mAcm^{-2} at 1.41 V vs. RHE

whereas 0.033 and 0.040 mAcm⁻² that were the lowest for pristine α -Fe₂O₃, were recorded at potentials of 1.23 V vs. RHE 1.41 V vs. RHE respectively.

Four lifetimes that followed a general reduction trend were obtained from the TAS analysis ranging from fs to ps. The first lifetime resulted from the hot air electrons cooling back to the bottom of conduction band edge and top of valence band edge. The second and third lifetimes that were in picosecond range were due to the trap states and mid bandgaps leading to electron-hole recombination. The fourth lifetime, on the other hand, which was slower than other lifetimes (ns range) were due to the recombination of electrons transferred from the back of the FTO substrate.

5.2 Future work

We have successfully been able to synthesize, characterize and apply nanostructured hematite films in the photoelectrochemical water splitting. A substantial improvement of photocurrent for the L-arginine/hematite, doped and surface co-doped hematite nanostructures compared to pristine hematite was attained.

From the present study, some of the gaps that need to be addressed include investigation of the effect of the deposition height, spray pressure, and nozzle diameter variation during spray pyrolysis of hematite thin films on the photocatalytic applications. More study on the transformation of hematite nanoparticles to nanospheres at different growth times, which will give a better understanding of the exact time the transformation starts to occur also needs to be investigated. Since L-arginine has strong alkaline properties, the effect of varying the pH can also be an area that needs further research. Besides, the L-arginine/hematite and surface co-doped hematite have shown promised photocurrent density results; therefore, more studies need to be done on the L-arginine/surface co-doped hematite thin films. We believe there will be a further improvement in the properties of these nanostructures and photocurrent enhancement.

Appendix

List of publications

1. **Justine Sageka Nyarige**, Tjaart P.J Kruger and Mmantsae Diale “Structural and optical properties of hematite and L-arginine/hematite nanostructures prepared by thermal spray pyrolysis” Surfaces and interfaces 18 (2020) 100394 <https://doi.org/10.1016/j.surfin.2019.100394>
2. **Justine Sageka Nyarige**, Tjaart P.J Kruger and Mmantsae Diale “Effects of L-arginine concentration on hematite nanostructures synthesized by spray pyrolysis and chemical bath deposition” Physica B:Physics of Condensed Matter 581 (2020) 411924 <https://doi.org/10.1016/j.physb.2019.411924>
3. **Justine Sageka Nyarige**, Tjaart P.J Kruger and Mmantsae Diale “Influence of precursor concentration and deposition temperature on the photoactivity of hematite electrodes for water splitting” Materials Today communications 25 (2020) 101459 <https://doi.org/10.1016/j.mtcomm.2020.101459>
4. **Justine Sageka Nyarige**, Tjaart P.J Kruger and Mmantsae Diale “Ultrafast transient absorption studies of surface-doped hematite nanostructures for efficient photoelectrochemical water splitting” (in Draft)
5. E. R. Ollotu, **J. S. Nyarige**, N. R. Mlyuka , M. E. Samiji · M. Diale “Properties of ITO thin films rapid thermally annealed in different exposures of nitrogen gas” Journal of Materials Science: Materials in Electronics <https://doi.org/10.1007/s10854-020-04192-y>