SYNTHESIS AND CHARACTERIZATION OF IRON OXIDE THIN FILMS FOR USE IN ELECTRICAL DEVICES

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Juan Pablo Gonzalez
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The Undersigned Faculty Committee Approves the

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Synthesis and Characterization of Iron Oxide Thin Films for Use in Electrical Devices

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DEDICATION

I would like to dedicate this thesis to Emma “Carmelita” Gonzalez who is the best mom in the whole world.
Melius tarde, quam nunquam.
ABSTRACT OF THE THESIS

Synthesis and Characterization of Iron Oxide Thin Films for Use in Electrical Devices
by
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We have developed a novel method of preparation of homogeneous transparent iron oxide thin films based on the thermal decomposition of iron tris-2,2’-bipyridine complexes. The resulting films were characterized with optical spectroscopy, optical and scanning electron microscopy and their crystal structure was established with X-ray powder diffraction and Raman spectroscopy. The film morphology is defined by the choice of the iron precursor and the method allows for both mono- and multilayer deposition, effectively providing control over film thickness. Addition of tris-2,2’-bipyridine complexes of other metals on the stage of film deposition provides a convenient path towards film doping. Obtained iron oxide films were also tested as photoanodes in dye-sensitized solar cells.
TABLE OF CONTENTS

ABSTRACT ............................................................................................................................. vi
LIST OF TABLES ..................................................................................................................... x
LIST OF FIGURES ................................................................................................................. xi
LIST OF ABBREVIATIONS ................................................................................................ xiii
ACKNOWLEDGEMENTS ................................................................................................... xiv

CHAPTER

1 INTRODUCTION: IRON OXIDES ..............................................................................1
   1.1 Forms of Oxidized Iron ......................................................................................1
       1.1.1 Hematite ....................................................................................................2
       1.1.2 Maghemite ...............................................................................................3
       1.1.3 Magnetite ..................................................................................................5
       1.1.4 Wüstite ......................................................................................................5
       1.1.5 Beta-Fe₂O₃ ................................................................................................6
       1.1.6 Epsilon-Fe₂O₃ ...........................................................................................6
       1.1.7 Amorphous Fe₂O₃ .....................................................................................7
       1.1.8 Goethite ....................................................................................................7
       1.1.9 Protohematite and Hydrohematite ............................................................8
       1.1.10 Ferrihydrite .............................................................................................8
       1.1.11 Distinguishing Between Different Crystalline Forms of Iron Oxide ...............................................................................................................9
   1.2 Iron Oxide Thin Films in Electrical Devices .....................................................9
   1.3 Iron Oxide Films Doped with Cobalt, Nickel, and Oxides .........................10
   1.4 Known Methods of Preparation of Iron Oxide Thin Films ........................11
       1.4.1 Synthesis of Hematite Thin Films ...........................................................11
       1.4.2 Synthesis of Maghemite Thin Films .........................................................12
       1.4.3 Synthesis of Magnetite Thin Films ...........................................................12
       1.4.4 Synthesis of Amorphous Fe₂O₃ Thin Films ............................................12
1.4.5 Iron (II) 2',2'-tris-bipyridyl Thin Films ..................................................13

2 EXPERIMENTAL SECTION .....................................................................................14
   2.1 Chemicals .........................................................................................................14
   2.2 Substrate Cleaning ...........................................................................................14
   2.3 Synthesis of Iron (II) tris-2,2’-bipyridyl Perchlorate .......................................14
   2.4 Synthesis of Iron (II) tris-2,2’-bipyridyl Chloride ...........................................15
   2.5 Synthesis of Iron (II) tris-2,2’-bipyridyl Tetrfluoroborate ..............................15
   2.6 Synthesis of Cobalt (II) tris-2,2’-bipyridyl Perchlorate ....................................16
   2.7 Synthesis of Cobalt (II) tris-2,2’-bipyridyl Chloride ........................................16
   2.8 Synthesis of Nickel (II) tris-2,2’-bipyridyl Perchlorate ....................................17
   2.9 Preparation of Iron (III) Oxide Thin Films .....................................................17
   2.10 Preparation of Doped Iron Oxide (Fe2O3-MxOy) Thin Films ........................18
   2.11 Deposition of “Bulk” Iron (III) Oxide on Substrates .....................................18
   2.12 Raman Spectroscopy ....................................................................................18
   2.13 Optical Characterization ................................................................................19
   2.14 Optical Microscopy .......................................................................................19
   2.15 X-Ray Powder Diffraction ..........................................................................19
   2.16 Morphological Characterization of Iron (III) Oxide Thin Films by
       Scanning Electron Microscopy .................................................................20
   2.17 Film Thickness Estimation by UV-vis Spectroscopy ....................................20

3 RESULTS AND DISCUSSION ..................................................................................21
   3.1 Morphology of Iron (III) Oxide Thin Films ....................................................21
       3.1.1 Optical Microscopy and SEM of Fe(bipy)3X2 and Fe2O3 Films .............21
       3.1.2 Optical Properties ...................................................................................25
       3.1.3 Fe2O3 Monolayer Films .........................................................................28
       3.1.4 Film Thickness Estimation .....................................................................30
       3.1.5 Crystal Structure of Iron Oxide Films ....................................................31
       3.1.6 Raman Spectroscopy ............................................................................32
       3.1.7 Effect of Aging ......................................................................................34
       3.1.8 Raman Analysis of Bulk Sample ............................................................34
   3.2 Multilayer Iron Oxide Films .............................................................................34
       3.2.1 SEM of Multilayer Films .........................................................................35
<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.2.2</td>
<td>Optical Properties of Multilayer Thin Films</td>
<td>35</td>
</tr>
<tr>
<td>3.2.3</td>
<td>XRD of Multilayer Films</td>
<td>40</td>
</tr>
<tr>
<td>3.2.4</td>
<td>Raman Spectroscopy of Multilayer Films</td>
<td>41</td>
</tr>
<tr>
<td>3.3</td>
<td>Preliminary Results on Iron (III) Oxide Thin Films Doped with Ni and Co</td>
<td>42</td>
</tr>
<tr>
<td>3.3.1</td>
<td>Optical Properties Doped Fe₂O₃ Films</td>
<td>42</td>
</tr>
<tr>
<td>3.3.2</td>
<td>Raman Analysis of Doped Fe₂O₃ Films</td>
<td>42</td>
</tr>
<tr>
<td>3.4</td>
<td>Applications of Iron Oxide Thin Films in Dye-Sensitized Solar Cells</td>
<td>44</td>
</tr>
<tr>
<td>3.4.1</td>
<td>Solar Cell Fabrication</td>
<td>45</td>
</tr>
<tr>
<td>3.4.2</td>
<td>Final Assembly and Performance Testing</td>
<td>46</td>
</tr>
<tr>
<td>3.4.3</td>
<td>Performance Testing</td>
<td>46</td>
</tr>
<tr>
<td>3.4.4</td>
<td>Device Characteristics</td>
<td>47</td>
</tr>
<tr>
<td>3.5</td>
<td>Conclusions</td>
<td>47</td>
</tr>
<tr>
<td>REFERENCES</td>
<td></td>
<td>49</td>
</tr>
</tbody>
</table>
LIST OF TABLES

Table 3.1. UV-Vis Data for Fe(bipy)$_3$X$_2$. Film Thickness Estimate ........................................23
Table 3.2. Summary of Raman Peak Data for Single Layer Fe$_2$O$_3$ Films Prepared from Fe(bipy)$_3$X$_2$ ..................................................................................................................33
Table 3.3. Summary of Raman Peak Data for Bulk Fe$_2$O$_3$ Prepared from Fe(bipy)$_3$X$_2$........33
# LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1</td>
<td>Teflon holder loaded with FTO substrates and placed in the tightly fitting beaker (top cover is removed and not shown in the picture).</td>
<td>15</td>
</tr>
<tr>
<td>3.1</td>
<td>General scheme for Fe₂O₃ single layer thin film preparation. Red layers are Fe(bipy)₃X₂ and yellow layers are Fe₂O₃.</td>
<td>21</td>
</tr>
<tr>
<td>3.2</td>
<td>Transmission optical microscopy images of: (a-c) Fe(bipy)₃X₂ thin films on glass; (a'-c') Fe₂O₃ film obtained by heating of the corresponding Fe(bipy)₃X₂ films at 330 °C.</td>
<td>22</td>
</tr>
<tr>
<td>3.3</td>
<td>Transmission optical microscopy images of films obtained by spin coating of 0.0800 M Fe(bipy)₃Cl₂ solution in MeOH at: (a) 600 rpm (b) 1200 rpm; (c) 2400 rpm; (d) 3600 rpm; (e) 4800 rpm, and (f) 6000 rpm.</td>
<td>24</td>
</tr>
<tr>
<td>3.4</td>
<td>UV-Vis absorption spectra of Fe₂O₃ monolayer films taken at five different spots.</td>
<td>25</td>
</tr>
<tr>
<td>3.5</td>
<td>(a) Transmission optical microscopy image of: Fe(bipy)₃(BF₄)₂ thin film.</td>
<td>26</td>
</tr>
<tr>
<td>3.6</td>
<td>SEM images of Fe₂O₃ films on FTO obtained from: (a) Fe(bipy)₃(ClO₄)₂; (b) Fe(bipy)₃Cl₂.</td>
<td>26</td>
</tr>
<tr>
<td>3.7</td>
<td>UV-Vis absorption spectra of the Fe(bipy)₃X₂ thin film on glass taken at five different spots.</td>
<td>27</td>
</tr>
<tr>
<td>3.8</td>
<td>UV-Vis absorption spectra of 16.6 , 3.32, 49.8, 66.2 µM Fe(bipy)₃X₂ solutions.</td>
<td>28</td>
</tr>
<tr>
<td>3.9</td>
<td>UV-Vis absorption spectra of Fe₂O₃ monolayer films prepared by heating corresponding Fe(bipy)₃X₂ films at: (a) 250°C and (b) 550 °C. (c) Comparison of UV-Vis spectra of Fe₂O₃ films obtained from Fe(bipy)₃(BF₄)₂ by heating at 250°C and 550°C.</td>
<td>29</td>
</tr>
<tr>
<td>3.10</td>
<td>XRD patterns of: (a) Fe₂O₃ monolayer films and (b) bulk Fe₂O₃ films obtained from Fe(bipy)₃X₂ by heating at 550 °C.</td>
<td>32</td>
</tr>
<tr>
<td>3.11</td>
<td>Raman spectrum of: (a) Fe₂O₃ monolayer films and (b) bulk Fe₂O₃ films obtained from Fe(bipy)₃X₂ by heating at 550 °C.</td>
<td>34</td>
</tr>
<tr>
<td>3.12</td>
<td>General scheme for Fe₂O₃ multilayer film preparation.</td>
<td>35</td>
</tr>
<tr>
<td>3.13</td>
<td>SEM images of a (a) bare FTO surface.; thermally decomposed Fe(bipy)₃(ClO₄)₂ thin film on FTO. (b) 1-layer, (c) 2-layers, (d) 3-layers.</td>
<td>36</td>
</tr>
<tr>
<td>3.14</td>
<td>SEM images of a (a) bare FTO surface.; thermally decomposed Fe(bipy)₃(ClO₄)₂ thin film on FTO.</td>
<td>37</td>
</tr>
</tbody>
</table>
Figure 3.15. UV-Vis absorption spectrum of successive layer growth of a Fe$_2$O$_3$ thin film on glass using layers of decomposed Fe(bipy)$_3$X$_2$ at (left) 330 °C and (right) 550 °C: (a, a') X = ClO$_4^-$, (b, b') X = BF$_4^-$, (c, c') X = Cl$. UV-Vis. ..................38

Figure 3.16. Raman spectra of Fe$_2$O$_3$ multilayer films annealed at 330 °C (left): Raman spectra of Fe$_2$O$_3$ films annealed at 550 °C (right). ...........................................39

Figure 3.17. XRD patterns of Fe$_2$O$_3$ multilayer films annealed at 550 °C: (a) X = ClO$_4^-$, (b) X = BF$_4^-$, (c) X = Cl$. (d) XRD of amorphous, $\alpha$- and $\gamma$-phase Fe$_2$O$_3$ annealed at various temperatures. .................................................41

Figure 3.18. General scheme for MO$_x$-doped Fe$_2$O$_3$ film preparation. .................................42

Figure 3.19. UV-Vis spectra of pure Fe$_2$O$_3$ monolayer, Fe$_2$O$_3$ monolayer doped with 50% Ni$^{2+}$ and 50% Co$^{2+}$, and pure Co$_3$O$_4$ and NiO monolayers annealed at 550 °C. ...........................................................................................................43

Figure 3.20. Raman spectra of Fe$_2$O$_3$ monolayer films doped with: (a) Co; and (b) Ni. ............43

Figure 3.21. (Left) A schematic drawing and a photograph of the setup used for sensitization of metal oxide films. ...............................................................................................................45

Figure 3.22. Comparison of I-V curves for FTO|Fe$_2$O$_3$| I$^-$/I$_3^-$ | 6nm Pt |FTO (unsensitized) and FTO|Fe$_2$O$_3$|N$_3$| I$^-$/I$_3^-$ | 6nm Pt |FTO cells at different light intensity levels (L1-L4). .................................................................48
# LIST OF ABBREVIATIONS

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Meaning</th>
</tr>
</thead>
<tbody>
<tr>
<td>ACN</td>
<td>Acetonitrile</td>
</tr>
<tr>
<td>$A_{\text{max}}$</td>
<td>Absorption maximum</td>
</tr>
<tr>
<td>Fe(bipy)$_3$X$_2$</td>
<td>Iron (II) tris-$2'2'$-bipyridyl salt where $X = \text{Cl}^-$, $\text{ClO}_4^-$, or $\text{BF}_4^-$</td>
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<tr>
<td>Fe$_2$O$_3$</td>
<td>Iron (III) oxide</td>
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<tr>
<td>Fe$_3$O$_4$</td>
<td>Magnetite</td>
</tr>
<tr>
<td>FeOOH</td>
<td>Ferric oxyhydroxide</td>
</tr>
<tr>
<td>Fh</td>
<td>Ferrihydrite</td>
</tr>
<tr>
<td>FTO</td>
<td>Fluorine-tin oxide</td>
</tr>
<tr>
<td>LED</td>
<td>Light emitting diode</td>
</tr>
<tr>
<td>M(bipy)$_3$X$_2$</td>
<td>metal (II) tris-$2'2'$-bipyridyl salt where $X = \text{Cl}^-$, $\text{ClO}_4^-$, or $\text{BF}_4^-$</td>
</tr>
<tr>
<td>MeOH</td>
<td>Methanol</td>
</tr>
<tr>
<td>M$_x$O$_y$</td>
<td>Metal oxide</td>
</tr>
<tr>
<td>NC</td>
<td>Nanocrystal/ nanocrystalline</td>
</tr>
<tr>
<td>NP</td>
<td>Nanoparticle</td>
</tr>
<tr>
<td>PTFE</td>
<td>Polytetrafluoroethylene</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
</tr>
<tr>
<td>TM</td>
<td>Transmission mode</td>
</tr>
<tr>
<td>$T_M$</td>
<td>Morrin temperature</td>
</tr>
<tr>
<td>$T_N$</td>
<td>Néel temperature</td>
</tr>
<tr>
<td>UV-vis</td>
<td>Ultra violet-visible</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
</tr>
<tr>
<td>$\alpha$-Fe$_2$O$_3$</td>
<td>Hematite</td>
</tr>
<tr>
<td>$\gamma$-Fe$_2$O$_3$</td>
<td>Maghemite</td>
</tr>
</tbody>
</table>
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CHAPTER 1

INTRODUCTION: IRON OXIDES

1.1 FORMS OF OXIDIZED IRON

Iron is the most abundant metal on earth. This element has been known since antiquity and played an instrumental role in the development of our civilization as the foundation of countless structural material components. Oxides of iron (besides their applications as pigments)\(^1\) and related processes of corrosion, have long been perceived as an inevitable nuisance. In recent years, however, iron oxides have demonstrated themselves as increasingly viable materials for advanced applications in such diverse fields as medicine,\(^2,3\) biology,\(^4,5\) catalysis,\(^6,7\) photovoltaics,\(^8\) and as combustible gas sensors\(^9,10\) to name a few.

Oxidized iron can be classified as anhydrous or hydrated. There are fifteen iron oxides, oxide hydroxides, and hydroxides known to date. The most common anhydrous oxides of iron are trivalent oxides of iron, which constitute four crystalline phases.\(^11\) In nature, iron (III) oxides exist as the minerals hematite (\(\alpha\)-\(\text{Fe}_2\text{O}_3\)) and maghemite (\(\gamma\)-\(\text{Fe}_2\text{O}_3\)). Both hematite and maghemite exist in bulk and nanocrystalline forms.\(^12\) The two other forms rarely (if ever) observed in nature are the \(\beta\)-phase and \(\varepsilon\)-phase \(\text{Fe}_2\text{O}_3\), which exist only in nanocrystalline form.\(^13\) Besides crystalline phases of \(\text{Fe}_2\text{O}_3\), amorphous \(\text{Fe}_2\text{O}_3\) phase is also known to exist.\(^12\) In addition to trivalent iron oxides, there is an iron (II) oxide (\(\text{FeO}\)), occurring in nature as the mineral wüstite. Naturally occurring wüstite is often bound to \(\text{Fe}_2\text{O}_3\) to form a mineral called magnetite with the formula \(\text{FeO}\cdot\text{Fe}_2\text{O}_3\), or \(\text{Fe}_3\text{O}_4\).

In the presence of water ferric oxides are hydrated forming products with the general formula \(\text{Fe}_2\text{O}_3\cdot x(\text{OH})_{2x}\) which is often simplified as \(\text{FeO(OH)}\) or \(\text{FeOOH}\).\(^11\) As naturally occurring minerals, hydrated ferric oxides are found as the thermodynamically favored \(\alpha\)-phase (goethite), as the \(\beta\)-phase (akaganéite) and as the \(\gamma\)-phase (lepidocrocite). The \(\delta\)-phase of \(\text{FeO(OH)}\) called feroxyhyte has been observed in the high pressure, low temperature environment of the deep Pacific Ocean.\(^14\) Feroxyhyte alters spontaneously to goethite upon exposure to air. \(\text{Fe}_5\text{HO}_8 \cdot 4 \text{H}_2\text{O}\) is also known to exist as the poorly crystalline phase called ferrihydrite.
A characteristic of the iron oxide system is the variety of possible interconversions between the different phases. In the presence of oxygen, goethite and hematite are thermodynamically the most stable compounds in this system and are therefore the end members of many transformation routes. Transformations of Fe$_2$O$_3$ can be induced by mechanical or thermal treatment. Mechanical activation can be achieved either by high pressure treatment or by milling, while thermal treatment involves isothermal or dynamic heating. The mechanism of Fe$_2$O$_3$ transformation depends not only on the applied physicochemical conditions but also on the form of the ferric oxide sample (crystals, nanopowder, nanocomposite, thin film, coated particles, etc.). Other factors that have a significant effect on the outcome of the transformation include the internal properties of the particles such as structure and degree of crystallinity. External parameters such as coatings, deposition over matrices, degree of particle aggregation, and the particles’ size distribution can also play a significant role in the phase transition of iron oxide.

Properties of iron oxides such as IR spectra, magnetism, and solvation may be influenced by their morphology and size. Iron oxides can be tuned to a particular application. Certain morphologies are desirable for industrial applications. Needles of maghemite are required for magnetic tapes because they can be orientated in a strong magnetic field during the manufacturing process and this reduces background noise during recording. On the other hand, iron oxide pigments for use in paints should be cubic because they tend to orient themselves with the brush stroke. The range of shapes and sizes displayed by iron oxides reflects, to a large extent, the growth environment.

1.1.1 Hematite

In its mineralogical form, hematite is steel-gray, white to gray-white, with a bluish tint, in reflected light, with characteristic deep blood-red internal reflections. Nanocrystalline α-Fe$_2$O$_3$ is red. The α-Fe$_2$O$_3$ crystal structure is a rhombohedrally centered hexagonal cell of the corundum type. α-Fe$_2$O$_3$ belongs to the space group $R \bar{3}c$. The basal plane of the α-Fe$_2$O$_3$ crystal structure contains two interpenetrating magnetic sublattices. Below the Morin threshold $\sim$250 K ($T_M$) both bulk and pure α-Fe$_2$O$_3$ without cation substitution) behave as an ideal antiferromagnet with the magnetic moments lying along the electric field gradient (oriented nearly along the α-Fe$_2$O$_3$ $c$-crystallographic axis). At $\sim$260 K, its electron spins are
reoriented by \( \sim 90^\circ \) so as to lie approximately in the \( \alpha\text{-Fe}_2\text{O}_3 \) basal plane.\(^{19,20}\) \( \alpha\text{-Fe}_2\text{O}_3 \) is also antiferromagnetic below the \( (T_M) \) Morin threshold, and only weakly ferromagnetic before the Néel temperature \( (T_N) \) of about 950 K, after which hematite becomes paramagnetic.\(^{13}\) The magnetic features of hematite, including the temperature values of magnetic transitions, can be largely influenced by numerous factors, such as pressure, external magnetic fields, lattice defects, presence of impurities, surface phenomena and, in particular, ion substitution, and the size of particles.\(^{12}\) Historically, hematite has been widely used since antiquity as a red pigment and as jewelry material. Hematite is the most stable of all the iron oxides and behaves as an n-type semiconductor at ambient conditions.\(^{21}\) In the last few decades, hematite has been investigated for novel applications such as detection of oxygen gas\(^{21}\) and other volatile organic compounds.\(^{13,21,22}\) Hematite-based sensors change surface resistivity in the presence of the gasses; as a water redox catalyst,\(^{23}\) and as a photovoltaic material\(^{24}\) among others. \( \alpha\text{-Fe}_2\text{O}_3 \) has some significant advantages as a photoelectrode for solar cells: for example hematite has a bandgap of 2.10 eV for bulk form \( \alpha\text{-Fe}_2\text{O}_3 \) and 2.2 eV for the nanocrystalline form;\(^{24}\) hematite is also highly resistant to corrosion, and commercially available at a relatively low cost.

### 1.1.2 Maghemite

Maghemite (\( \gamma\text{-Fe}_2\text{O}_3 \)) is a red-brown\(^{25}\) compound and is the second most stable polymorph of iron (III) oxide. The band gap of bulk \( \gamma\text{-Fe}_2\text{O}_3 \) is 2.43 eV and 2.22 eV for the nanocrystalline form. Of the known \( \text{Fe}_2\text{O}_3 \) polymorphs, \( \gamma\text{-Fe}_2\text{O}_3 \) is regarded as the most practically important and useful due to its simple synthesis and the interesting magnetic characteristics of its nanosized objects.\(^{13}\) Maghemite occurs naturally in soils as a weathering product of magnetite (\( \text{Fe}_3\text{O}_4 \)), to which it is structurally related.\(^{11}\) Like \( \text{Fe}_3\text{O}_4 \), maghemite contains cations in two nonequivalent crystallographic sites: the tetrahedral and octahedral positions. Unlike \( \text{Fe}_3\text{O}_4 \), the crystal structure of \( \gamma\text{-Fe}_2\text{O}_3 \) features vacant cation sites, which usually occur in octahedral positions to compensate for its increased positive charge.\(^{13}\) Both \( \text{Fe}^{2+} \) and \( \text{Fe}^{3+} \) cations are present in \( \text{Fe}_3\text{O}_4 \), whereas in maghemite all the iron cations are in trivalent state. The charge neutrality of the magnetite/maghemite cell is guaranteed by the presence of cation vacancies.\(^{26}\) This cation vacancy therefore results in at least three different crystal symmetries for \( \gamma\text{-Fe}_2\text{O}_3 \): (i) cubic vacancy-disordered, (ii) cubic vacancy-ordered, and
a (iii) tetragonal structure with tetragonal structure with a threefold doubling along the c-axis and perfectly ordered vacancies.

The cubic-vacancy-disordered $\gamma$-Fe$_2$O$_3$ belongs to the $Fd3m$ space group, the same as spinel, and has a theoretical composition of $(\text{Fe}^{+3})_8[\text{Fe}^{+3}_{5/6} \square_{1/6}]_16\text{O}_{32}$, where $\square$ is a vacant position. Due to the two vacancies in cubic vacancy-ordered maghemite, $\gamma$-Fe$_2$O$_3$ belongs to the space groups $P4_12_12$), which was first suggested by Oosterhout and Rooijmans as the most stable structure for maghemite and was experimentally verified by Shmakov et al. Density functional studies also agree that the space group $P4_12_12$, which corresponds to tetragonal symmetry, is the most thermodynamically preferred situation in the bulk material due to the minimal Coulomb repulsion between neighbor Fe$^{+3}$ ions. It should be noted however that deviation from the $P4_12_12$ configuration is very much possible because low temperature growth of $\gamma$-Fe$_2$O$_3$ is does not presuppose an equilibrium growth of the crystals, and the surface effects in nanocrystals could contribute to deviations from an ideal ordering of the vacancies.

Contrasting with antiferromagnetic hematite, bulk maghemite exhibits ferromagnetic ordering with a high net magnetic moment of 2.5 $\mu_B$ per formula unit, which together with its chemical stability and low cost led to its wide application as magnetic pigment in electronic recording media since the late 1940's. Magnetic recording media typically involves an emulsion of ferromagnetic particles less coated on a plastic ribbon.

Susceptibility and magnetization measurements at room and low temperatures indicate superparamagnetic behavior for nanocrystalline maghemite. Field cooled and zero field magnetization data indicate that the system is not a spin glass. The magnetic anisotropy is two orders of magnitude larger than the magnetocrystalline anisotropy of bulk $\gamma$-Fe$_2$O$_3$, suggesting that the total anisotropy energy is dominated by contributions (e.g., stress induced) other than the magnetocrystalline anisotropy. $\gamma$-Fe$_2$O$_3$ in nanocrystalline form is irreversibly converted to hematite at high pressures (21.3-26.4 GPa). Due to the special magnetic properties of nanosized $\gamma$-Fe$_2$O$_3$, this material has proved very useful for applications where specifically targeted magnetic response is desired such as in magnetic resonance imaging.
1.1.3 Magnetite

Magnetite (Fe₃O₄) is a common magnetic iron oxide that has a cubic inverse spinel structure (space group \( Fd3m \)) with oxygen forming a fcc closed packing and Fe cations occupying interstitial tetrahedral sites and octahedral sites. In its mineralogical form, magnetite is black, gray with brownish tints in reflected light. Magnetite contains iron in both divalent and trivalent states. As a result, the compound exhibits unique electric and magnetic properties based on the transfer of electrons between Fe\(^{2+}\) and Fe\(^{3+}\) within the octahedral sites. Magnetite is metastable and will convert to maghemite under exposure to temperatures typically around 200°C. Further heating to above 400°C will produce \( \alpha-\text{Fe}_2\text{O}_3 \). Hematite can reduce back to magnetite by reacting with hydrogen gas elevated temperatures and pressures. It is interesting to note that magnetite is only thermodynamically stable in its bulk form.

Its particle dispersions have been widely used as ferrofluid in rotary shaft sealing, oscillation damping, and position sensing. The use of properly coated magnetite nanoparticles in clinical medicine has also intensified. With proper surface coating, these magnetic nanoparticles can be dispersed into water, forming water-based suspensions. Such a suspension can interact with an external magnetic field and be positioned to a specific area, facilitating magnetic resonance imaging for medical diagnosis and AC magnetic field-assisted cancer therapy. All these technological and medical applications require that the nanoparticles are superparamagnetic with sizes smaller than 20 nm and the overall particle size distribution is narrow so that the particles have uniform physical and chemical properties.

1.1.4 Wüstite

Wüstite, Fe\(_x\)O is a nonstoichiometric phase of iron divalent iron with a known stability range from \( x = 0.83 \) to 0.96 above 560 °C. Nearly stoichiometric samples of FeO were found to arrange the Fe and O atoms monoclinic lattice with space group \( C2/m \). At pressures of >75 GPa, a new monoclinic modification of FeO has been observed (space group \( P2_1/m \)). The high pressure structure is closely related to that of cubic sodium chloride as a distortion of the lattice. The mineralogical form of this compound is often along with deposits of hematite, maghemite and hydrated iron oxides. Natural wüstite has a brown to
gray appearance. Prior to structural investigations of iron oxides at the nanoscale, wüstite was typically prepared by heating iron and magnetite in sealed vessels, and was known to be stable only above 560–570 °C. Below this temperature it decomposes via a two-step mechanism into $\alpha$-Fe and magnetite, Fe$_3$O$_4$.\textsuperscript{11,39,41} Because wüstite is nonstoichiometric, Fe$_x$O is expected to have many defects with an ordered distribution of iron vacancies.\textsuperscript{42} Fe$_x$O can be oxidized to magnetite and finally to maghemite, $\gamma$-Fe$_2$O$_3$. All three compounds are based on an approximately face-centered cubic structure of oxygen. The transformation between the three different phases is thought to be determined by the diffusion of Fe$^{2+}$ and Fe$^{3+}$ ions within the oxygen sublattice and electron transfer between iron ions of different valence. The wealth of the system is enriched by the occurrence of nonstoichiometry in all three phases.

1.1.5 Beta-Fe$_2$O$_3$

$\beta$-Fe$_2$O$_3$ is a very rare polymorph of iron (III) oxide its natural abundance has yet to be reported. $\beta$-Fe$_2$O$_3$ exhibits a body-centered cubic “bixbyite” structure and crystallizes in the $Ia\bar{3}$ space group with $a = 9.393$ Å. In $\beta$-Fe$_2$O$_3$, the Fe$^{3+}$ ions occupy two nonequivalent octahedral crystallographic sites. $\beta$-Fe$_2$O$_3$ is the only iron (III) oxide polymorph that exhibits paramagnetic behavior at room temperature; its Néel magnetic transition temperature is between 100 and 119 K. Below this temperature, $\beta$-Fe$_2$O$_3$ is antiferromagnetically ordered. Because it is thermodynamically unstable, it is transformed into either $\alpha$-Fe$_2$O$_3$\textsuperscript{43-45} or $\gamma$-Fe$_2$O$_3$ on heating, depending on the precise nature of the nanoparticles. To date, $\beta$-Fe$_2$O$_3$ has found few applications.

1.1.6 Epsilon-Fe$_2$O$_3$

$\varepsilon$-Fe$_2$O$_3$ is a dark brown magnetic phase of iron (III) oxide.\textsuperscript{46} $\varepsilon$-phase Fe$_2$O$_3$ is a phase not usually observed in nature. Synthetically, $\varepsilon$-phase occurs only in the form of nanostructures whose yield abundance tends to be low.\textsuperscript{12} Popovoci et al. demonstrated however, that a sol-gel synthesis (>93% yield) of $\varepsilon$-Fe$_2$O$_3$ nanospheres could be stabilized up to 1600 K in the pores of a silica matrix.\textsuperscript{16} The epsilon polymorph has been reported in some plants as biogenic nanoparticles\textsuperscript{47} and it has been found as a thermal decomposition product of almandine garnets\textsuperscript{48} and iron-rich clays.\textsuperscript{49} The crystal structure of $\varepsilon$-Fe$_2$O$_3$ is an orthorhombic structure (space group = $Pna\bar{2}1$).\textsuperscript{50} The asymmetric unit consists of Fe$_4$O$_6$, and four asymmetric units comprise the unit cell, which is expressed as Fe$_{16}$O$_{24}$.\textsuperscript{51} The magnetic
properties of $\epsilon$-Fe$_2$O$_3$ are not yet wholly understood. $\epsilon$-Fe$_2$O$_3$ has been long known to exhibit rather large magnetic anisotropy.$^{52}$

### 1.1.7 Amorphous Fe$_2$O$_3$

Amorphous Fe$_2$O$_3$ is a metastable phase of iron (III) oxide. If nanopowdered amorphous Fe$_2$O$_3$ is heated under air, maghemite is the primary crystallization product after low temperature heating (~290°C).$^{53}$ After heating amorphous Fe$_2$O$_3$ to higher temperatures (>340°), $\alpha$-Fe$_2$O$_3$ is the most reported product.$^{54}$ Amorphous iron (III) oxide is formed from very small particles, <5 nm in diameter.$^{55}$ In amorphous Fe$_2$O$_3$, Fe$^{3+}$ ions are surrounded by oxygen octahedra with the respective symmetry axes randomly orientated in a nonperiodic lattice.$^{56}$ Results obtained from Mössbauer spectroscopy and magnetic susceptibility measurements show that amorphous Fe$_2$O$_3$ is paramagnetic at temperatures above $T_N = 80$ K with a magnetic moment of 2.5 $\mu$B per atom of iron.$^{57}$ Amorphous Fe$_2$O$_3$ has generated much interest as an advanced material in recent years, especially in applications where a large, mesoporous surface area is desired over a well-defined crystal structure. Amorphous iron oxide shows substantial industrial potential in magnetic memory storage, surface sorption, catalysis, and in thin film solar cells.$^{54}$ Amorphous Fe$_2$O$_3$ has a potential of using it as a light absorber in solar cells. It absorbs light from 295 to 565 nm, which accounts for 38% of the photons at air mass (AM) 1.5.$^{58}$

### 1.1.8 Goethite

Named after Johann von Goethe, goethite occurs in rocks and throughout the various compartments of the global ecosystem. Goethite has the orthorhombic structure of diaspora, thus the structure of goethite is based on an arrangement of O atoms in an hexagonal close packing, with Fe$^{3+}$ ions occupying half of the octahedral sites.$^{59}$ Goethite is also known as $\alpha$-FeOOH is associated in the space group $Pbnm$.$^{60}$ Goethite is one of the thermodynamically most stable iron oxides at ambient temperature and is, therefore, either the first oxide to form or the end member of many transformations. In massive crystal aggregates goethite is dark brown or black, whereas the powder is yellow and responsible for the color of many rocks, soils and ochre deposits.$^{11}$ Goethite has a Neel temperature of 400 K,$^{61}$ and is therefore antiferromagnetically ordered at room temperature. Goethite turns into hematite around 280-290°C.$^{62}$
1.1.9 Protohematite and Hydrohematite

Although hematite remains the most thermodynamically favored phase of the anhydrous iron oxides, defects in the crystallinity of the sample due to the synthetic conditions, could result in the formation of a metastable and poorly crystalline phase of hematite called protohematite. One such route to protohematite is from thermal decomposition of goethite at low temperatures (>250 °C) before less than one half of the stoichiometric water content in goethite is expelled. Under pressure, mechanical, chemical activation, or thermal treatment above 1100°C, protohematite transforms into the highly crystalline R 3c α-Fe2O3. The vibrational spectrum of protohematite is characterized through intense absorption bands at 308, 445, and 530 cm⁻¹.

A comparison of the spectrum of protohematite with the spectra of other known modifications of iron oxide suggests that some iron cations have an effective tetrahedral environment. This structure of protohematite is responsible for its higher catalytic activity compared to hematite. The protohematite-hematite phase transition is initiated by heating above ~1000 °C, by pressure application, or by mechanochemical activation.

A compositionally-related isomorph of protohematite is hydrohematite. Hydrohematite is a low-temperature product of hydrothermal decomposition of goethite. Hydrohematite contains a number of lattice bound OH- groups replacing the oxygen atoms with the number of iron vacancies sufficient to keep electroneutrality. The IR vibrational spectrum of hydrohematite displays weak OH stretching and deformation vibrations. The Fe-O fundamental vibrations are shifted to the low frequencies.

1.1.10 Ferrihydrite

Although a well-known nanomineral, ferrihydrite (Fh) has no known crystalline counterpart formed in the laboratory or found in nature. Ferrihydrite belongs to the group of ferric oxyhydroxides and is characterized by high dispersion, poor crystallinity and low stability. As such, the basic crystal structure and physical properties of ferrihydrite including density, composition, and magnetic properties have remained controversial and a definite space group assignment has not been possible. A variety of structural models have been proposed for ferrihydrite but all have proven difficult to confirm unequivocally by conventional crystallographic techniques. The best stoichiometry for disordered Fh to date
assumes formula \((\text{Fe}_{8.2}\text{O}_{8.5}(\text{OH})_{7.4} + 3 \text{H}_2\text{O})\).\(^{74}\) Ferrihydrite can take two forms, 2-line and 6-line, characterized by 2-line and 6-line XRD powder patterns, respectively. 2-line Fh decomposes to hematite via maghemite, whereas the 6-line phase transforms directly to hematite.\(^{75}\) Ferrihydrite is unstable against dehydration even at temperatures below 100°C.\(^{76}\) In natural environments Fh occurs in sediments, soils and weathering crusts, being formed through precipitation from Fe-rich oxidized solutions.\(^{11}\)

### 1.1.11 Distinguishing Between Different Crystalline Forms of Iron Oxide

Several established methods for the differentiation of the crystalline forms of iron oxide can often be employed. X-ray powder diffraction (XRD) may be used to identify the crystal structure of an unknown material as well as the average spacings between rows of atoms. XRD however is usually not enough to differentiate a mixture of various \(\text{Fe}_2\text{O}_3\) phases because hematite, maghemite, and magnetite have many overlapping peaks in their XRD profile. When XRD analysis is coupled with Raman spectroscopy, a clearer compositional picture emerges, and composition can be differentiated.\(^{34}\) Amorphous phase \(\text{Fe}_2\text{O}_3\) cannot be definitively distinguished by XRD either. Electron diffraction analysis (via TEM) can also be used to corroborate the presence of an amorphous phase over a small area as evidenced by the absence of diffraction rings.\(^{77}\) Amorphous \(\text{Fe}_2\text{O}_3\) may also be easily distinguished with Mössbauer spectroscopy.\(^{54}\)

### 1.2 Iron Oxide Thin Films in Electrical Devices

In recent years advanced applications for thin films of iron oxide have become a subject of ongoing research due to their electrical and optical properties.\(^{78}\) Hematite, wüstite, maghemite are n-type semiconductors while magnetite displays metallic-like properties.\(^{11}\)

In the case of most iron oxides with semiconductor properties, electron excitation can be achieved by irradiation with visible light below wavelengths of 560 nm (~2-2.2 eV).\(^{78}\) This indirect bandgap makes \(\text{Fe}_2\text{O}_3\) a seemingly efficient light collector with peak absorptivity exceeding \(10^5 \text{ cm}^{-1}\). However the incorporation of iron oxide for photovoltaic applications is hampered by the notoriously low efficiencies.\(^{79,80}\) The poor efficiency of \(\text{Fe}_2\text{O}_3\) photoanodes has been attributed to a low rate constant of water oxidation by surface trapped holes\(^{81,82}\) and a short hole diffusion length in hematite\(^{82}\) (2-20 nm) which allows only
holes created close to the electrolyte interface to oxidize water. Since the light penetration length in \( \alpha-\text{Fe}_2\text{O}_3 \) is of the order of 100 nm \((\alpha = 1.6 \times 10^7 \text{ m}^{-1} \text{ at } 500 \text{ nm})\), most holes are created in the bulk and will recombine with electrons before having reached the surface.\(^7^9\) It has also been suggested that collecting 90% of incident photons with energy greater than the indirect gap would require a relatively thick film (~1 µm).\(^8^1\) Still, iron oxide is an especially attractive as a photoanode due to its abundance, stability, and environmental compatibility. Recent research has shown that doping iron oxides with p-type impurities\(^8^4-^8^7\) as well as deposition of multiple thin layers over single layers\(^7^9\) increased the inherently low photocurrents.

### 1.3 Iron Oxide Films Doped with Cobalt, Nickel, and Oxides.

Many of the applications that exist for iron oxides have also been investigated and developed for other metal oxides. Considerable research effort in recent years has been dedicated to investigating the photoelectrical performance of mixed metal oxides films.

Cobalt forms two common oxides: CoO and Co\(_3\)O\(_4\). CoO converts to Co\(_3\)O\(_4\) if heated to around 600-700 °C. Heating above 900 °C converts Co\(_3\)O\(_4\) to CoO.\(^8^8\) These two compositions thus exist in equilibrium. On their own, cobalt oxides have a wide range of industrial applications including in Li\(^+\) ion batteries,\(^8^9,^9^0\) as CO oxidation catalysts,\(^9^1\) as a magnetic recording material,\(^9^2\) and as gas sensors.\(^8^9,^9^1\) Cobalt oxides are p-type semiconductors. CoO, which often has a deep blue color, has a band gap of 2.4 eV. Co\(_3\)O\(_4\) is a black-colored solid. It has two optical band gaps, 2.2 and 1.5 eV. The first band gap of Co\(_3\)O\(_4\) can be associated to O\(_2^-\)→Co\(^{2+}\) charge-transfer process (basic optical band gap energy, or valence to conduction band excitation), while the second one to O\(_2^-\)→Co\(^{3+}\) charge transfer (Co\(^{3+}\) level is located below the conduction band). Cobalt oxides make a p-n junction when coupled with Fe\(_2\)O\(_3\) and have been shown to enhance the poor photocurrents normally found in pure Fe\(_2\)O\(_3\).\(^7^9,^9^3\)

Nickel (II) oxide is often found as a pale green salt. It is a relatively cheap material with a high thermodynamic stability.\(^9^4\) Nickel oxides have found use in rechargeable Li\(^+\) batteries.\(^9^5,^9^6\) Because nickel oxide is an electrochromic material,\(^9^7\) it is found in glazing and smart windows.\(^9^8\) Another major area is the use of nickel oxide as a cathode in molten carbonate fuel cells.\(^1^0^0,^1^0^1\) NiO is can also be used in sensing volatile compounds such as
formaldehyde and hydrogen. Electrically, NiO is a p-type semiconductor with a band gap of 3.1-3.8 eV. Systems that incorporate a NiO-Fe$_2$O$_3$ lattice create a p-n junction. NiO has been found to enhance the Fe$_2$O$_3$ thin film as photoanodes for water oxidation and thin film solar cell applications. NiO-Fe$_2$O$_3$ systems have also been investigated as thick film gas sensors.

It follows that the incorporation of dopants such as Co$_x$O$_y$, and NiO, as well as successive film layering creates novel design strategies to enhance the performance of Fe$_2$O$_3$ photoanodes, which is particularly limited by electron-hole recombination losses. P-doping enhances electron depletion within the Fe$_2$O$_3$ photoelectrode while still ensuring sufficient conductivity through the film to allow electron extraction without large ohmic losses.

1.4 KNOWN METHODS OF PREPARATION OF IRON OXIDE THIN FILMS

General approach to synthesizing Fe$_2$O$_3$ thin films is to deposit a precursor film layer and to oxidize it into Fe$_2$O$_3$. The precursor film may be a layer of elemental iron, an iron salt, or an organometallic complex. Single crystal films of Fe$_2$O$_3$ have used ultra-high vacuum epitaxial methods of deposition and Chemical Vapor Deposition (CVD) of iron organometallic species such as Fe(CO)$_5$, which are known to result in high-quality single-crystal films. Such high vacuum methods however are often impractical or economically unattractive. More cost-effective methods such as spin coating salt solutions can come with potential drawbacks such as counter ion contaminants such as NO$_3^-$ and SO$_4^{2-}$. Organometallic routes may involve the handling highly toxic organometallic species like Fe(CO)$_5$ or the explosive [Fe(O$^-$-Bu)$_3$]$_2$. The oxidation step offers certain control over the desired crystallographic phase because hematite tends to be the most stable thermodynamic phase at higher temperatures, while gamma-, amorphous- and oxyhydroxide phases tend to be favored at relatively lower temperatures.

1.4.1 Synthesis of Hematite Thin Films

α-Fe$_2$O$_3$ thin films have been synthesized by the high temperature thermal decomposition of iron (III) chloride hexahydrate films in air. According to this method, a pure hematite thin film could not be synthesized below 1000 °C. Such high temperatures
would lead to substantially degraded the FTO and glass substrates. Hematite films are achievable well below 1000°C, but are not necessarily going to be of uniform composition. Grätzel and Duret thermally decomposed thin films of ferric acetylacetonate deposited by both Spray Pyrolysis (SP) and Ultrasonic Spray Pyrolysis (USP) around 450 °C, but both heating methods produced hematite films with magnetite impurities.6

1.4.2 Synthesis of Maghemite Thin Films

\(\gamma\)-phase Fe\(_2\)O\(_3\) thin films can be deposited by spin coating solution of iron (III) nitrate dissolved in ethylene glycol and calcinating the resulting film at 600 °C.118 Bersani et al. obtained maghemite films by coating glass substrates with 0.3 M iron (III) nitrate solution in methoxyethanol, followed by annealing at 300 °C.119 Maghemite thin films can also be synthesized by chemical vapor deposition of iron onto a substrate. The iron film is then heated in a muffle furnace at 350 °C where it oxidizes to \(\gamma\)-phase Fe\(_2\)O\(_3\).116

1.4.3 Synthesis of Magnetite Thin Films

Pure magnetite thin films tend to be synthetically challenging because Fe\(_3\)O\(_4\) is less stable than gamma or alpha phase. Layer by layer assembly of Fe\(_3\)O\(_4\) films can be made by electrodepositing stabilized magnetite particles at ambient conditions.120 Another method involves sputtering using a pure Fe target, followed a highly controlled exposure to oxygen.121 Thick (5 mm) films of magnetite (Fe\(_3\)O\(_4\)) films can be grown by flowing a mixture of O\(_2\)/N\(_2\) for 20 h on lipid monomolecular layers of arachic acid spread on an aqueous solution of FeCl\(_2\).122

1.4.4 Synthesis of Amorphous Fe\(_2\)O\(_3\) Thin Films

Amorphous thin films of iron (III) oxide have been created by thermal decomposition of an aerosol upon a heated substrate (thin plate of fused quartz). The aerosol was generated by pneumatically or ultrasonically atomizing a solution of FeCl\(_3\) (10 wt. %) in butyl acetate.56 Amorphous Fe\(_2\)O\(_3\) films were also produced by a conventional sputter deposition using a Fe\(_2\)O\(_3\) target method under high sputter gas (Ar) pressure at a substrate temperature of -196 °C.57 Srivasta et al. showed that a mesoporous layer of amorphous Fe\(_2\)O\(_3\) could be precipitated using an ultrasonic horn to irradiating iron(III) ethoxide and cetyltrimethylammonium bromide (CTAB) as an inorganic precursor and surfactant in
alkaline conditions. Deposition of amorphous iron(III)-oxide films was also achieved via a cathodic bias in a 0.1 M hydrated ammonium iron(II) sulfate ((NH₄)₂Fe(SO₄)₂·6H₂O) solution at −1.6 V versus Ag/AgCl.

### 1.4.5 Iron (II) 2’,2’-tris-bipyridyl Thin Films

To the best of our knowledge, thermal decomposition of Fe(bipy)₃X₂ films has not been previously used for the preparation of iron oxide thin films. Trisbipyridine complexes tend to have very high solubility in water as well as aprotic polar organic solvents such as acetonitrile, and small weight alcohols. This solubility profile of transition metal bipyridyl complexes make them great candidate materials for thin film deposition by spin coating. Bipyridine complexes tend to be straightforward to synthesize and have varying degrees of stability in normal atmosphere. When deposited as organometallic thin films on electrodes, metal-bipyridine complexes exhibit diode behavior. Some similar compounds such as Os(bipy)₃(ClO₄)₂, Ru(bipy)₃(ClO₄)₂ and Ru(bipy)₃(BF₄)₂ produced homogeneous films when spin coated from acetonitrile solutions. These films deposited on ITO have been studied as thin film light-emitting diodes.

In this work we report a simple yet effective way to grow pure or doped iron (III) oxides on glass and fluoridated tin-oxide-covered glass (FTO) via thermal decomposition of thin films of various iron trisbipyridine (Fe(bipy)₃X₂) complexes. This method offers advantages over other approaches in that this technique allows preparation of transparent homogeneous high-quality thin films of iron (III) oxide of a desired thickness without the need for costly apparatus or toxic precursors.
CHAPTER 2

EXPERIMENTAL SECTION

2.1 CHEMICALS

2,2’ bipyridine (bipy, 99%, Alfa Aesar), iron(II) perchlorate hexahydrate, (Fe(ClO₄)₂·6H₂O, reagent grade, Alfa Aesar), iron(II) chloride tetrahydrate (FeCl₂·4H₂O, reagent grade, Alfa Aesar), cobalt (II) chloride hexahydrate, (CoCl₂·6H₂O, reagent grade, EMD), nickel (II) chloride hexahydrate (NiCl₂·6H₂O, reagent grade, Alfa Aesar), sodium carbonate (Na₂CO₃, reagent grade, EMD), perchloric acid (HClO₄, 60%, Fischer, reagent grade), tetrafluoroboric acid (HBF₄, 48%, Alfa Aesar), isopropanol (99%, EMD), acetonitrile (ACN, 99%, EMD), methanol (MeOH, 99%, EMD), 18 MΩ water (Barnstead EASYpure compact ultrapure water system) were used as received without any further purification before the synthesis.

2.2 SUBSTRATE CLEANING

Microscope slide glass (VWR) or fluoridated tin oxide coated glass (FTO, Pinkerton Glass) substrates (slides) were placed into the specially designed PTFE substrate holder sonicated for 20 minutes in isopropanol (Figure 2.1).

The substrates were then rinsed with deionized water for at least four times, then rinsed once with 18 MΩ water. The cleaned substrates were placed in a closed Petri dish and dried in the oven at 120°C for ~8 h.

2.3 SYNTHESIS OF IRON (II) TRIS-2,2’-BIPYRIDYL PERCHLORATE

0.0814 g (0.112 mmol) of iron (II) perchlorate hexahydrate was added to a vial containing 0.05591 g (0.3584 mmol) of 2,2’ bipyridine. 2 mL of acetonitrile was added as a reaction solvent. The mixture was stirred to produce a dark red (almost black) suspension. The dark red crystals were collected, recrystallized in water or ACN (recrystallization in water produced greater yields) and dried in air at room temperature overnight.
2.4 SYNTHESIS OF IRON (II) TRIS-2,2’-BIPYRIDYL CHLORIDE

0.201 g (1.01 mmol) of FeCl₂·4H₂O was added to a vial containing a 0.5126 g (3.285 mmol) of 2,2’ bipyridine. 2.00 mL of MeOH was added as a reaction solvent. The mixture was then stirred to produce a blood red solution of Fe(bipy)₃Cl₂. The newly formed Fe(bipy)₃Cl₂ solution was recrystallized in ACN and passed through a vacuum filtration apparatus under a piece of filter paper. The purified crystals were allowed to air dry at room temperature overnight.

2.5 SYNTHESIS OF IRON (II) TRIS-2,2’-BIPYRIDYL TETRFLUOROBORATE

A minimal amount of MeOH (sufficient to dissolve the FeCl₂·4H₂O) was added to a vial containing 0.6099 g (3.079 mmol) of FeCl₂·4H₂O. Water was not used to dissolve FeCl₂·4H₂O because it forms a highly acidic solution, which interferes with the ligand substitution step of the synthesis. A second vial contained slurry of 0.3577 g (3.376 mmol) of Na₂CO₃ in 50-100 mL of 18 MΩ water. A black precipitate of FeCO₃ was formed upon mixing the Na₂CO₃ slurry and FeCl₂ solution. The black precipitate was collected, rinsed with 18 MΩ water and transferred into a new vial. A minimal volume of HBF₄ was added
drop-wise until the black precipitate of FeCO₃ was almost completely dissolved (not to allow excess of HBF₄). Gaseous CO₂ was evolved during this reaction and a pale yellow solution of Fe(BF₄)₂ was formed. A solution of 1.5333 g (9.8288 mmol) of bipy in a small volume of ACN was added to Fe(BF₄)₂ solutions to produce a dark red solution. The solution was filtered using a 0.2 µm PTFE syringe filter and rotovapped to dryness. Dark red solid was then twice recrystallized in water. Needle-like shiny crystals of Fe(bipy)₃(BF₄)₂ were collected.

2.6 SYNTHESIS OF COBALT (II) tris-2,2’-bipyridyl PERCHLORATE

0.5123 g of CoCl₂ · 6H₂O (2.153 mmol) of was added to a vial containing 0.5 - 1.0 mL 18 MΩ water. To a second vial, a slurry of 0.2813 g (2.654 mmol) of Na₂CO₃ in a minimal amount of 18 MΩ water was prepared. The two reagent vials were mixed together in a third vial, which resulted in a violet-colored slurry of CoCO₃. The CoCO₃ slurry was filtered via a vacuum filtration apparatus and washed with 18 MΩ. The CoCO₃ was transferred to a new vial where HClO₄ was carefully added dropwise to the CoCO₃ solids until no more bubbling was observed. A lower concentration of HClO₄ than the one reported may be better suited because the cobalt is easily oxidized by HClO₄. To the resulting solution of Co(ClO₄)₂, 1.321 g (6.890 mmol) of tris-2,2’-bipyridine in 1.0 mL of MeOH was added to the Co(ClO₄)₂ and allowed to react. The mixture was washed with cold 18 MΩ water and passed through a vacuum filtration apparatus, which yielded green-brown flaky crystals of Co(bipy)₃(ClO₄)₂. The resulting crystals were allowed to air dry overnight. Co(bipy)₃(ClO₄)₂ was used without any further purification.

2.7 SYNTHESIS OF COBALT (II) tris-2,2’-bipyridyl CHLORIDE

0.6112 g (2.568 mmol) of CoCl₂ · 6 H₂O was added to a vial containing 1.2886 g (8.251 mmol) of 2,2’ bipyridine. ~2.00 mL of MeOH was added as a reaction solvent. The mixture was then stirred to produce a dark-yellow-brown solution of Co(bipy)₃Cl₂. The newly formed Co(bipy)₃Cl₂ solution was recrystallized in ACN and passed through a vacuum filtration apparatus under a piece of filter paper. The purified crystals were allowed to air dry at room temperature overnight.
2.8 SYNTHESIS OF NICKEL (II) TRIS-2,2'-BIPYRIDYL PERCHLORATE

0.5001 g (2.103 mmol) of nickel (II) chloride hexahydrate was added to a vial containing 0.5 - 1.0 mL 18 MΩ water. To a second vial, a slurry of 0.2685 g (2.533 mmol) of Na2CO3 in a minimal amount of 18 MΩ water was prepared. The two reagent vials were mixed together in a third vial, which resulted in pale-colored slurry of NiCO3. The NiCO3 slurry was filtered via a vacuum filtration apparatus and washed with 18 MΩ. The NiCO3 was transferred to a new vial where HClO4 was carefully added dropwise to the NiCO3 solids until no more bubbling was observed. To the resulting solution of Ni(ClO4)2, 1.0902 g (6.980 mmol) white solution forms of tris-2,2'-bipyridine in 1.0 mL of MeOH was added to the Ni(ClO4)2. Initially a milky white solution forms, which yields ruby red precipitates. The solution was gently heated to evaporate the solvents. The precipitates were added to a vial containing ~1.0 mL of MeOH or ACN and were left overnight. This resulted in pale red crystals of Ni(bipy)3(ClO4)2 when the mixture passed through a vacuum filtration apparatus. The resulting crystals were washed with cold MeOH or ACN and allowed to air dry overnight. Ni(bipy)3(ClO4)2 was used without any further purification.

2.9 PREPARATION OF IRON (III) OXIDE THIN FILMS

A ~0.08 M solution of Fe(bipy)3(ClO4)2 was made by adding a 0.0350 g (48.4 µmol) of Fe(bipy)3(ClO4)2 to 0.60 mL of ACN. A ~0.08 M solution of Fe(bipy)3(BF4)2 was made by adding a 0.0313 g (44.8 µmol) of Fe(bipy)3(BF4)2 to 0.56 mL of ACN. A ~0.08 M solution of Fe(bipy)3Cl2 was made by adding a 0.0350 g (58.8 µmol) of Fe(bipy)3Cl2 to 0.74 mL of MeOH. All solutions were filtered by passing them through a 0.2 µm PTFE membrane syringe filter prior to spin coating. 25.0 µL of a solution was delivered via volumetric pipette to the substrate while spinning at 1000-2000 rpm using a Laurell Technologies Corporation WS-400A-6NPP/LITE spin coater. Alternatively, two drops of the same solution were delivered to the substrate using a Pasteur pipette. The substrate was allowed to spin for up to one additional minute after the solution was delivered. A magenta-colored, thin film of Fe(bipy)3X2 remained on the substrate. Using a cotton swab wetted with acetonitrile, two edge sections of the film were carefully removed so as to expose a region the substrate not covered with film for improved contrast in optical microscopy imaging. The substrate with Fe(bipy)3X2 was then heated in a furnace (Lindberg Blue M Box, Thermo Scientific) at
550°C. The temperature was increased at 1 °C/min rate. The films were kept at 550 °C for one hour and then were cooled to room temperature using 1 °C/min cooling rate. A transparent pale yellow-brown thin film of Fe₂O₃ was left behind on the substrate.

### 2.10 Preparation of Doped Iron Oxide (Fe₂O₃-MₓOₙ) Thin Films

0.08 M solutions of Co(bipy)₃Cl₂, and Ni(bipy)₃(ClO₄)₂, were made in ~0.5 mL of MeOH or ACN using the method described for Fe(bipy)₃X₂. 250 µL of the Co(bipy)₃Cl₂ in MeOH and Ni(bipy)₃(ClO₄)₂ in ACN and solution was mixed with an equal volume of 0.08 M Fe(bipy)₃Cl₂ in MeOH and Fe(bipy)₃(ClO₄)₂ in ACN, respectively. The result was a 0.08 M solution of (50%/50%) Fe(bipy)₃X₂/ M(bipy)₃X₂ in ~0.5 mL of solvent. 25.0 µL of the spiked Fe(bipy)₃(ClO₄)₂ solutions were delivered via volumetric pipette to the substrate while spinning at 1200 rpm using a Laurell Technologies Corporation WS-400A-6NPP/LITE spin coater. The substrates with Fe(bipy)₃X₂-M(bipy)₃X₂ were then was then heated in a furnace (Lindberg Blue M Box, Thermo Scientific) at 550°C. The temperature was increased at 1 °C/min rate. The films were kept at 550 °C for one hour and then were cooled to room temperature using 1 °C/min cooling rate. Films of MₓOₙ-Fe₂O₃ were left behind on the substrate. Co(bipy)₃Cl₂, and Ni(bipy)₃(ClO₄)₂ were chosen because Co(bipy)₃(ClO₄)₂ had relatively low solubility in ACN and would saturate below the desired concentration of 0.08 M.

### 2.11 Deposition of “Bulk” Iron (III) Oxide on Substrates

~100 µL aliquots of concentrated Fe(bipy)₃X₂ solutions or suspensions were drop-casted onto the glass substrates and left to dry in air. The substrates then were heated in a furnace at 550°C using the same protocol as for thin films. The resulting orange-brownish films were analyzed using Raman microscopy and XRD.

### 2.12 Raman Spectroscopy

Raman spectroscopy was performed on a Thermo Scientific DXR Raman microscope using OMNIC software and 532 nm laser. Laser frequency calibration was performed prior to the measurements by using a polystyrene film sample. Spectra were taken after a laser beam (0.5 – 5 mW) was focused on the film-air interface of a sample using 50x objective. For
blank spectra of glass the laser was focused at the front glass-air interface and Raman spectra were taken in the area of the slide not covered with the film at the same conditions. The power delivered from the laser is capable of spanning 0.5 mW to 10.0 mW. Samples were analyzed using 2.0 mW laser power unless otherwise noted for 10 scans lasting 30 seconds each. Following spectra acquisition the spots of the sample illuminated with the laser were inspected to verify that there was no visible damage to sample. Spectra then were corrected by subtracting the blank Raman spectrum of glass using OMNIC software.

2.13 Optical Characterization
UV-vis absorbance spectra of solutions and thin films were collected using a Cary Varian Bio 50 spectrophotometer. Spectra for solutions were measured in a quartz 1.00 cm (optical path) cuvette. Spectra of thin films were obtained by attaching the glass substrate to the wall of the cuvette holder using double adhesive tape. Spectra of at least five different regions of the same film were taken to obtain a representative spectrum.

2.14 Optical Microscopy
The optical microscopy was performed using a Nikon Eclipse TE-2000-U Microscope equipped with 4x, 10x, 40x and 100x objectives. All presented images were taken using the 10x magnification lens (unless noted otherwise) and AmScope digital MU-300 USB CCD camera with proprietary software for digital image capture.

2.15 X-Ray Powder Diffraction
The X-ray diffraction patterns were obtained on a Phillips X’ Pert Pro X-Ray Diffractometer located at the Geology Department at San Diego State University. The tension voltage was set to 45 kV and 40 mA using Cu-Kα radiation (λ = 1.54187 Å) in the range of 0° to 70° using a 10 mm brass mask. 20-hour scans were used to obtain proper signal-to-noise ratio.
2.16 MORPHOLOGICAL CHARACTERIZATION OF IRON (III) OXIDE THIN FILMS BY SCANNING ELECTRON MICROSCOPY

Morphological analysis of the Fe$_2$O$_3$ films was done on a FEI-Quanta 450 scanning electron microscope. The acceleration voltage was 20 kV and a working distance of 11 mm was used. ~5-nm platinum layer was sputtered onto Fe$_2$O$_3$ films before SEM analysis.

2.17 FILM THICKNESS ESTIMATION BY UV-VIS SPECTROSCOPY

Thickness of Fe(bipy)$_3$X$_2$ thin films can be estimated using Beer’s law. This estimate is based on several approximations: (1) extinction coefficients of Fe(bipy)$_3$X$_2$ in solution and in films are the same; (2) the measured absorbance signal has minimal contributions from film reflectance and scattering. Beer’s law:

\[ A = \varepsilon CN \]  

(2.1)

where $A$ is the absorption at the peak absorption wavelength, $C$ is the molar concentration of the analyte, $\varepsilon$ is extinction coefficient and $N$ is the length of the analyte sample (usually cuvette length). Using the extinction coefficient of a film solution it is possible to approximate the film thickness on a transparent substrate if Beer’s law is solved this time for the path length, $N$.

Molar concentration in solid is determined by the density $\rho$ and molecular weight $M$:

\[ C = \frac{\rho}{M} \]  

(2.2)

Substituting Equation 2.2 into Beer’s law and solving for the film thickness $N_{film}$ we obtain:

\[ N_{film} = \frac{AM}{\varepsilon \rho} \]  

(2.3)

Extinction coefficients of Fe(bipy)$_3$Cl$_2$, Fe(bipy)$_3$(ClO$_4$)$_2$, and Fe(bipy)$_3$(BF$_4$)$_2$ were determined from Beer’s plots in MeOH (Fe(bipy)$_3$Cl$_2$) or ACN (Fe(bipy)$_3$(ClO$_4$)$_2$, Fe(bipy)$_3$(BF$_4$)$_2$) solutions. UV/Vis spectra were measured for solutions prepared by successive additions of 5.0 µL aliquots of 0.0100 M stock solutions into cuvette ($N = 1.0$ cm) with 3.00 mL of solvent. The in a Cary 50 UV/Vis Spectrometer. The slopes of $A$ vs. $C$ plots were taken as extinction coefficients and used for film thickness estimation.
CHAPTER 3

RESULTS AND DISCUSSION

3.1 MORPHOLOGY OF IRON (III) OXIDE THIN FILMS

Our method of preparation of iron (III) oxide thin films is based on thermal decomposition of spin coated Fe(bipy)$_3$X$_2$ thin films in air (Figure 3.1). When spin coated from ACN solutions, Fe(bipy)$_3$(ClO$_4$)$_2$ and Fe(bipy)$_3$(BF$_4$)$_2$ form continuous transparent homogeneous films. Fe(bipy)$_3$Cl$_2$ is poorly soluble in ACN and therefore can be spin coated from MeOH solutions. The resulting Fe(bipy)$_3$Cl$_2$ films are discontinuous island films. After heating at 300-550°C in air, Fe(bipy)$_3$X$_2$ is converted into iron (III) oxide and the oxide films’ morphology is defined by the morphology of their parent films.

![Figure 3.1. General scheme for Fe$_2$O$_3$ single layer thin film preparation. Red layers are Fe(bipy)$_3$X$_2$ and yellow layers are Fe$_2$O$_3$.](image)

$X = \text{Cl}_2, \text{ClO}_4, \text{BF}_4$

bipy = \[
\begin{array}{c}
\text{N} \\
\text{N}
\end{array}
\]

3.1.1 Optical Microscopy and SEM of Fe(bipy)$_3$X$_2$ and Fe$_2$O$_3$ Films

Figure 3.2 shows optical microscopy images of Fe$_2$O$_3$ and their parent Fe(bipy)$_3$X$_2$ films. Films from both Fe(bipy)$_3$(ClO$_4$)$_2$ and Fe(bipy)$_3$(BF$_4$)$_2$ are continuous besides few defects near film edges. Films from Fe(bipy)$_3$Cl$_2$ are discontinuous with the average island size around 10-20 µm and the estimated average inter-island gap size was between 1-10 µm (Figure 3.2). The average thickness of this film was estimated to be ~200 nm (Table 3.1).
Figure 3.2. Transmission optical microscopy images of: (a-c) Fe(bipy)$_3$X$_2$ thin films on glass; (a’-c’) Fe$_2$O$_3$ film obtained by heating of the corresponding Fe(bipy)$_3$X$_2$ films at 330 °C. Counterion X for Fe(bipy)$_3$X$_2$ films is shown in lower right part of (a-c). For all the images film edges or defects were purposely chosen so the contrast between film and glass substrate could be easily seen. Same region of films are shown prior (a-c) and after (a’-c’) heating.
### Table 3.1. UV-Vis Data for Fe(bipy)_3X_2 Film Thickness Estimate

<table>
<thead>
<tr>
<th>Material</th>
<th>Molar mass (g/mol)</th>
<th>Extinction coefficient (M(^{-1}) cm(^{-1}))</th>
<th>Crystalline density (g/cm(^3))</th>
<th>Film thickness estimate (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe(bipy)_3(ClO_4)_2</td>
<td>723.3</td>
<td>13512</td>
<td>1670</td>
<td>155 ± 8</td>
</tr>
<tr>
<td>Fe(bipy)_3(BF_4)_2</td>
<td>698.0</td>
<td>14775</td>
<td>1670/</td>
<td>135 ± 3</td>
</tr>
<tr>
<td>Fe(bipy)_3Cl_2</td>
<td>595.3</td>
<td>11636</td>
<td></td>
<td>202 ± 67</td>
</tr>
</tbody>
</table>

The size of the islands and the space between them can be controlled by spin rate, to increase the film’s coverage and homogeneity. Figure 3.3 shows the optical micrographs of Fe\(_2\)O\(_3\) films obtained from Fe(bipy)_3Cl_2 by spin coating at various rates. Higher spin rates showed smaller grain sizes with smaller inter-island gaps (Figure 3.3). The most homogenous X = Cl\(^-\) film was seen at 6000 rpm, which was also the maximum rate that the spin coater could sustain. Higher spin rates were experimentally unnecessary for the films obtained from Fe(bipy)_3(ClO_4)_2 and Fe(bipy)_3(BF_4)_2 because they were already quite smooth at 1200 rpm.

The films made from Fe(bipy)_3(ClO_4)_2 and Fe(bipy)_3(BF_4)_2 resulted in visibly smooth and continuous textures (Figure 3.2 a, b). This was evidenced by the little variability in their absorbance spectra when the film was sampled at five different spots on the substrate. These monolayers had a calculated film thickness of 117 ± 6 nm and 100 ± 2 nm (Table 3.1), respectively. The small error in the reported confidence interval for both of these samples is consistent with their high degree of homogeneity. After heating, the resulting Fe\(_2\)O\(_3\) films have morphology similar to their parent Fe(bipy)_3X_2 films (Figure 3.2).

The films obtained from Fe(bipy)_3(ClO_4)_2 and Fe(bipy)_3(BF_4)_2 resulted in visibly smooth and continuous textures with few defects. Besides optical microscopy data, this was evidenced by the little variability in their absorbance spectra when the films were sampled at five different spots on the substrate (Figure 3.4).

The films from Fe(bipy)_3(BF_4)_2 were continuous but tended to show signs of cracking scale-like patterns when annealed at higher temperatures (Figure 3.5). This effect was more often seen in thicker films prepared with Fe(bipy)_3(BF_4)_2 solutions of greater than 0.08 M concentration or at lower than 1200 rpm spin rates.
Figure 3.3. Transmission optical microscopy images of films obtained by spin coating of 0.0800 M Fe(bipy)$_3$Cl$_2$ solution in MeOH at: (a) 600 rpm (b) 1200 rpm; (c) 2400 rpm; (d) 3600 rpm; (e) 4800 rpm, and (f) 6000 rpm. For all the images film edges were purposely chosen so the contrast between film and glass substrate could be easily seen.
Figure 3.4. UV-Vis absorption spectra of Fe₂O₃ monolayer films taken at five different spots. The films were prepared by heating Fe(bipy)₃X₂ films at 300 °C. (a) X = ClO₄⁻, (b) X = BF₄⁻, (c) X = Cl⁻.

SEM shows that Fe₂O₃ films obtained from Fe(bipy)₃(ClO₄)₂ have features smaller than 20 nm (Figure 3.6a). Fe₂O₃ films obtained from Fe(bipy)₃Cl₂ have island structure (Figure 3.6b). Overall, spin coating solutions of Fe(bipy)₃(ClO₄)₂ in ACN produced the most continuous and defect free Fe₂O₃ films according to both SEM and optical microscopy data.

3.1.2 Optical Properties

UV-Vis spectra of Fe(bipy)₃X₂ films on glass are analogous to the spectra of Fe(bipy)₃X₂ solutions besides a small 5-20 nm red shift (compare Figure 3.7 with Figure 3.8). Absolute absorbance values obtained for Fe(bipy)₃(BF₄)₂ and Fe(bipy)₃(ClO₄)₂ films are similar
Figure 3.5. (a) Transmission optical microscopy image of: Fe(bipy)$_3$(BF$_4$)$_2$ thin film. (a’) reflectance mode optical microscopy of the thermally decomposed Fe(bipy)$_3$(BF$_4$)$_2$ thin film annealed at 550 °C showing signs of cracking. Reflectance mode was chosen for better contrast.

Figure 3.6. SEM images of Fe$_2$O$_3$ films on FTO obtained from: (a) Fe(bipy)$_3$(ClO$_4$)$_2$; (b) Fe(bipy)$_3$Cl$_2$. The Fe(bipy)$_3$X$_2$ films were heated at 450°C prior to imaging. In (a) film edge is purposely chosen so the contrast between the film and FTO support could be better seen.
Figure 3.7. UV-Vis absorption spectra of the Fe(bipy)$_3$X$_2$ thin film on glass taken at five different spots. (a) X = ClO$_4^-$, (b) X = BF$_4^-$, (c) X = Cl$^-$. (d) UV-Vis absorption spectra of the Fe(bipy)$_3$Cl$_2$ thin films on glass spin-coated at various rates. Indicating that spin coating of the solutions with the same concentration produces the films of comparable thickness. While the absolute absorbance values of Fe(bipy)$_3$Cl$_2$ films are greater, it is not due to the larger film thickness but rather a result of noticeable scattering of the films. Little spot-to-spot variability in spectra intensity of Fe(bipy)$_3$(BF$_4$)$_2$ and Fe(bipy)$_3$(ClO$_4$)$_2$ films is in agreement with homogeneity of this films observed in optical microscopy and SEM (Figure 3.4 a, b). Comparatively larger deviation in UV-Vis spectra of Fe(bipy)$_3$Cl$_2$ films is likely at least in part due to the effects of unpredictable light scattering observed in these films (Figure 3.7c). Figure 3.7d shows that when spin-coating of Fe(bipy)$_3$Cl$_2$ is carried out at the maximum spin rate (6000 rpm), the resulting film spectra
Figure 3.8. UV-Vis absorption spectra of 16.6, 32.3, 49.8, 66.2 µM Fe(bipy)$_3$X$_2$ solutions. (a) X = ClO$_4^-$ in ACN (b) X = BF$_4^-$ in ACN, (c) X = Cl$^-$ in MeOH. (d) Beer plots for solutions of Fe(bipy)$_3$X$_2$.

showed the least amount of scattering (seen as the background absorbance at >600 nm wavelengths). This is probably cannot be explained by just a decrease in film thickness since the absorbance at 550 nm maximum does not noticeably change with increasing spin rate.

3.1.3 Fe$_2$O$_3$ Monolayer Films

When the films of Fe(bipy)$_3$X$_2$ are thermally decomposed at 250-550 °C, their intense magenta color changes to a pale dirty-yellow color, which is characteristic of iron (III) oxides. Interestingly, the iron oxide films from Fe(bipy)$_3$Cl$_2$ dramatically decrease their optical scattering to the point where they become nearly indistinguishable from Fe$_2$O$_3$ films.
prepared from Fe(bipy)$_3$(BF$_4$)$_2$ and Fe(bipy)$_3$(ClO$_4$)$_2$ (Figure 3.9). The absolute absorbance at 300 nm for all three films is very similar (~0.02) showing that the film thicknesses of these films are very close.

![Figure 3.9](image)

Figure 3.9. UV-Vis absorption spectra of Fe$_2$O$_3$ monolayer films prepared by heating corresponding Fe(bipy)$_3$X$_2$ films at: (a) 250°C and (b) 550°C. (c) Comparison of UV-Vis spectra of Fe$_2$O$_3$ films obtained from Fe(bipy)$_3$(BF$_4$)$_2$ by heating at 250°C and 550°C. (d) UV–Vis absorption spectra of nanocrystalline γ-Fe$_2$O$_3$ nanoparticles dispersed in chloroform and water. Source: Miyoshi, H.; Yoneyama, H. J. Chem. Soc., Faraday Trans. 1989, 85, 1873.

For the monolayers made from decomposed Fe(bipy)$_3$(BF$_4$)$_2$ at 250°C, the absorption tail was measured to have a negative absorbance value below above 580 nm (Figure 3.9a, c). Negative absorbance values are consistent with anti-reflective coatings. This implies that the film absorbs less than the glass substrate at those wavelengths. The shape of UV-Vis spectra of Fe$_2$O$_3$ films depends on both the annealing temperature and the film
precursor. When Fe$_2$O$_3$ films initially prepared by heating the Fe(bipy)$_3$X$_2$ films at 250° C are later annealed at 550° C, the absorbance at 600-800 nm remains unchanged for the film prepared from Fe(bipy)$_3$(ClO$_4$)$_2$, decreases for the film prepared from Fe(bipy)$_3$Cl$_2$, and increases for the film prepared from Fe(bipy)$_3$(BF$_4$)$_2$ (Figure 3.9a, Figure 3.9b). The reasons for such behavior are unclear. It is known that higher annealing temperatures improve the crystallinity of the film, so the light scattering observed as an absorbance background at 600-800 nm should increase but this is observed only for the Fe$_2$O$_3$ films prepared from Fe(bipy)$_3$(BF$_4$)$_2$. If the film in nanocrystalline, its band gap should decrease, and the absorbance should show a red shift as the average size of crystals increases when annealing temperature increases. Such red shift is observed only for the films prepared from Fe(bipy)$_3$(BF$_4$)$_2$.

Using the Tauc relation: 
\[
\left(\alpha - h\nu\right)^{1/n} = A(h\nu - E_g), \]
where $A$ is a constant, $\alpha$ is the absorption coefficient near the absorption edge, and $n$ is the exponent ($n = -1/2$ or 2 for direct or indirect transition), the band gap energies, $E_g$, were calculated. From the intercept of the straight line at $\alpha = 0$ in the plot of $\alpha h\nu$ versus $h\nu$, the band gaps for films are within 2-2.1 eV, which are consistent with the literature values of 2-2.2 eV.

Comparison with Figure 3.9d the UV-Vis spectra in Figure 3.9a-c also reveal that all the monolayers annealed at 330 °C are composed of nanocrystalline γ-phase Fe$_2$O$_3$. The absorption onset of the spectra of the monolayer films occur around 600 nm. Because of the quantum size effect, this value is blue-shifted about 100 nm compared to Fe$_2$O$_3$ bulk powder.

### 3.1.4 Film Thickness Estimation

UV-Vis spectra of Fe(bipy)$_3$X$_2$ solutions are very similar (Figure 3.8). Using the extinction coefficients for Fe(bipy)$_3$X$_2$, extracted from Beer’s plots (Figure 3.8d) and Equation 3, an estimate for the average film thickness can be calculated. The Fe(bipy)$_3$(ClO$_4$)$_2$ monolayer film was found to have an estimated thickness of ~155 nm, while the Fe(bipy)$_3$(BF$_4$)$_2$ monolayer had an estimated thickness of ~135 nm. There is a sizable error interval for the films from Fe(bipy)$_3$Cl$_2$ due to their lack of homogeneity. The estimate of ~140-260 nm is consistent with the observed optical and SEM data. It is difficult to evaluate the thickness of Fe(bipy)$_3$Cl$_2$ films since the large contribution from Rayleigh
scattering observed as broadband background declining from 600 nm toward longer wavelengths obscures the true value of the film absorbance (Figure 3.7c). However, the difference in absorbance at 540 nm (peak) and 440 nm (valley) is comparable to the corresponding value for Fe(bipy)$_3$(BF$_4$)$_2$ and Fe(bipy)$_3$(ClO$_4$)$_2$ films showing that Fe(bipy)$_3$Cl$_2$ film thickness is of the same order of magnitude. Given that the Fe(bipy)$_3$Cl$_2$ films can be measured to have an approximately 50% higher $A_{\text{max}}$ than the X = ClO$_4^-$ and BF$_4^-$ films at the same deposition conditions, the estimated thickness values are also in agreement with Beer’s law. The largest source of uncertainty in estimating average film thicknesses of Fe(bipy)$_3$Cl$_2$ and Fe(bipy)$_3$(BF$_4$)$_2$ is the assumption that the density of these complexes is similar to the density of Fe(bipy)$_3$(ClO$_4$)$_2$. Despite the lack of literature data on the density of Fe(bipy)$_3$Cl$_2$ and Fe(bipy)$_3$(BF$_4$)$_2$ we believe that our film thickness estimates are within 20% error since the similar Fe(bipy)$_3^{2+}$ compounds all have densities within 1.5-1.7 g/cm$^3$.

3.1.5 Crystal Structure of Iron Oxide Films

Monolayer Fe$_2$O$_3$ films obtained by heating their parent Fe(bipy)$_3$X$_2$ films at 550 °C have no distinct XRD peaks and their shape is very similar to XRD pattern of the blank glass sample (Figure 3.10a). The only observable difference in the films’ XRD patterns is a slightly increased background at greater values of 2$\theta$ for the film obtained from Fe(bipy)$_3$Cl$_2$. The lack of peaks in XRD patterns indicates very poor crystallinity in those films and suggests that these films consists of amorphous or nanocrystalline Fe$_2$O$_3$. It is not trivial to distinguish between amorphous and nanocrystalline Fe$_2$O$_3$ using XRD. Based on Raman spectroscopy analysis, we believe that the obtained films are mainly nanocrystalline $\gamma$-Fe$_2$O$_3$ rather than the amorphous iron (III) oxide.

Figure 3.10b shows XRD patterns of Fe$_2$O$_3$ films obtained by heating of thick, drop-casted films of Fe(bipy)$_3$X$_2$ at exactly the same conditions as monolayer films of the same compounds. Unlike their monolayer analogs, these films are crystalline with hematite as the dominant form. Besides hematite, the films prepared from Fe(bipy)$_3$Cl$_2$ and Fe(bipy)$_3$(BF$_4$)$_2$ (and in lesser extent the films from Fe(bipy)$_3$(ClO$_4$)$_2$) contain detectable amount of $\gamma$-Fe$_2$O$_3$ or Fe$_3$O$_4$ as evidenced by the peaks at 31° and 45°. In general, it is difficult to distinguish between the $\gamma$-Fe$_2$O$_3$ and Fe$_3$O$_4$ phases based solely on XRD since their known XRD patterns
Figure 3.10. XRD patterns of: (a) Fe$_2$O$_3$ monolayer films and (b) bulk Fe$_2$O$_3$ films obtained from Fe(bipy)$_3$X$_2$ by heating at 550 °C.

are almost identical.$^{138}$ The obvious difference in crystallinity of monolayer and bulk Fe$_2$O$_3$ films suggests that a certain critical film thickness is necessary to yield crystals large enough to be detected by XRD.

3.1.6 Raman Spectroscopy

Tables 3.2 and 3.3 contain detailed comparison of observed Raman spectra of Fe$_2$O$_3$ monolayer and bulk films with literature data. The monolayer films are all nanocrystalline maghemite. This is evidenced by a medium intense broad peak ~695 cm$^{-1}$, which is consistent with literature spectra for $\gamma$-Fe$_2$O$_3$. Maghemite spectra may show two smaller humps at 506, 350 cm$^{-1}$.\textsuperscript{139,140} At the film defects (see e.g. brown dots observed in Figure 3.2) or edges there are occasional $\alpha$-Fe$_2$O$_3$ (hematite) impurities (data not shown).

Ferric oxyhydroxides are excluded as possible compositions for both monolayers and bulk samples due to the absence of OH-stretches in the > 3000 cm$^{-1}$ region (Figure 3.11a,b).

Fe$_3$O$_4$ is also ruled as the dominant film composition in both the monolayer films as well as the bulk controls. Magnetite has a similar profile to maghemite which includes a diagnostic medium intense peak ~665 cm$^{-1}$ corresponding to the A$_{1g}$ mode of magnetite. Fe$_3$O$_4$ may also contain two additional small characteristic peaks occurring about 310 and 550 cm$^{-1}$.\textsuperscript{6} These correspond to Fe$_3$O$_4$ T$_{2g}$ and E$_g$ vibrational modes respectively.

The conclusion that the films are all $\gamma$-Fe$_2$O$_3$ is consistent with the fact that gamma-phase Fe$_2$O$_3$ is the likeliest product to form from poorly crystalline Fe$_2$O$_3$.\textsuperscript{55}
### Table 3.2. Summary of Raman Peak Data for Single Layer Fe₂O₃ Films Prepared from Fe(bipy)₃X₂

<table>
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<tr>
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<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>T₂g**</td>
<td>310</td>
<td>310</td>
<td>310</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>E₉*</td>
<td>350 (m)</td>
<td>358</td>
<td>332±1</td>
<td>348±4 (s)</td>
<td>336±6</td>
<td></td>
</tr>
<tr>
<td>T₂g</td>
<td>512 (b)</td>
<td>505</td>
<td>522±2</td>
<td>523±3</td>
<td>529±7</td>
<td></td>
</tr>
<tr>
<td>A₁g**</td>
<td>550</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A₁g*</td>
<td>665</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A₁g</td>
<td>664 (b)</td>
<td>689±3 (m)</td>
<td>686±3 (m)</td>
<td>684±3 (m)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>726 (m)</td>
<td>708 (m)</td>
<td>705±3</td>
<td>729±4</td>
<td>728±5</td>
<td></td>
</tr>
</tbody>
</table>

*Maghemite
**Magnetite

Note: (s) = sharp, (m) = medium broad, (b) = broad. The most intense peak is in bold and the second most intense is underlined.

### Table 3.3. Summary of Raman Peak Data for Bulk Fe₂O₃ Prepared from Fe(bipy)₃X₂

<table>
<thead>
<tr>
<th>Vibrational mode</th>
<th>Duret &amp; Grätzel (2005)</th>
<th>De Faria &amp; Lopez (2007)</th>
<th>Hanesch (2009)</th>
<th>This work Bulk Fe₂O₃ when X = Cl⁻</th>
<th>This work Bulk Fe₂O₃ when X = ClO₄⁻</th>
<th>This work Bulk Fe₂O₃ when X = BF₄⁻</th>
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</thead>
<tbody>
<tr>
<td>A₁g*</td>
<td>224 (s)</td>
<td>227 (s)</td>
<td>225 (s)</td>
<td>218±3 (s)</td>
<td>220±2 (s)</td>
<td>218±3 (s)</td>
</tr>
<tr>
<td>E₉*</td>
<td>244 (s)</td>
<td>246 (s)</td>
<td>245 (s)</td>
<td>240±1 (s)</td>
<td>240±1 (s)</td>
<td>243±1 (s)</td>
</tr>
<tr>
<td>E₉*</td>
<td>292 (s)</td>
<td>293 (s)</td>
<td>290 (s)</td>
<td>282±5 (s)</td>
<td>286±3 (s)</td>
<td>282±4 (s)</td>
</tr>
<tr>
<td>E₉*</td>
<td>409 (s)</td>
<td>412 (s)</td>
<td>412 (s)</td>
<td>396±6 (s)</td>
<td>401±3 (s)</td>
<td>401±5 (s)</td>
</tr>
<tr>
<td>A₁g*</td>
<td>499 (s)</td>
<td>498 (s)</td>
<td>500 (s)</td>
<td>489±5 (s)</td>
<td>492±4 (s)</td>
<td>496±2 (s)</td>
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<tr>
<td>E₉*</td>
<td>612 (m)</td>
<td>610 (m)</td>
<td>611 (m)</td>
<td>597±8 (m)</td>
<td>600±4 (m)</td>
<td>598±6 (m)</td>
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<tr>
<td>A₁g**</td>
<td>656 (m)</td>
<td>667 (m)</td>
<td>654±5 (m)</td>
<td>655±1 (m)</td>
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<td>Two-phonon scattering*</td>
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<td>1322 (s)</td>
<td><strong>1321 (m)</strong></td>
<td><strong>1298±8 (m)</strong></td>
<td><strong>1305±6 (m)</strong></td>
<td><strong>1309±4 (m)</strong></td>
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</tbody>
</table>

*Hematite
**Magnetite

Note: (s) = sharp, (m) = medium broad, (b) = broad. The most intense peak is in bold and the second most intense is underlined.
3.1.7 Effect of Aging

In order to test the hypothesis that the iron oxide thin films would not absorb water and hydrate to form goethite or ferrihydrite, the three films annealed at 550°C were studied using Raman spectrometry. The Raman spectra newly annealed films were compared spectra of the same sample exactly one week later (data not shown). Ten measurements were made each week respectively, but no new compositional differences were found. This suggests that the films composition is stable well after the annealing process.

3.1.8 Raman Analysis of Bulk Sample

Raman analysis of the bulk material annealed at 550 °C showed hematite as the dominant composition of the bulk samples, with instances of magnetite and/or maghemite impurity phases also present (Figure 3.11). Seven phonon lines are expected in the Raman spectrum of hematite, namely two $A_{1g}$ modes (225 and 498 cm$^{-1}$) and five $E_g$ modes (247, 293, 299, 412 and 613 cm$^{-1}$). Measurements from the bulk samples irrespective of the precursor Fe(bipy)$_3$X$_2$ material are in close agreement the XRD measurements.

3.2 MULTILAYER IRON OXIDE FILMS

The general strategy of iron (III) oxide monolayer films is based on thermal decomposition of Fe(bipy)$_3$X$_2$ monolayer thin films outlined in Figure 3.1. Multilayer Fe$_2$O$_3$ films are prepared similarly by repeating spin-coating/heating step multiple times until the
desired thickness is achieved (Figure 3.12). The multilayer film can be later annealed in the furnace if the phase conversion or increase in crystallinity is needed.

![Diagram of Fe(bipy)$_3$X$_2$ and Fe$_2$O$_3$ multilayer film preparation.]

**Figure 3.12.** General scheme for Fe$_2$O$_3$ multilayer film preparation. Red layers are Fe(bipy)$_3$X$_2$ and yellow layers are Fe$_2$O$_3$.

### 3.2.1 SEM of Multilayer Films

Figure 3.13 and Figure 3.14 show that a bare FTO surface can be coated by successive layers of Fe$_2$O$_3$. This is evidenced by the appearance of a coating that charges in response to the electron raster beam: Fe$_2$O$_3$ is less conductive than the bare FTO control. Figure 3.14 shows that the layers of Fe$_2$O$_3$ have very small grain sizes, which agrees with the SEM of the monolayer films.

### 3.2.2 Optical Properties of Multilayer Thin Films

Every monolayer of thermally decomposed Fe(bipy)$_3$Cl$_2$ thin films was found to have the same kind of UV-Vis absorption profile when the annealing temperature was 330 °C. Figure 3.9d suggests that the composition of these films was nanocrystalline γ-Fe$_2$O$_3$. Their UV-Vis spectra suggest that all samples have the same composition at these conditions (Figure 3.15 a, b, c). The given that the absorption onset becomes increasingly red-shifted for the films annealed at 550 °C with the number of Fe$_2$O$_3$ layers, this suggests that the more layers the larger the average Fe$_2$O$_3$ grain size (Figure 3.15 a’, b’, c’). Bulk hematite’s absorption onset is closer to 600 nm, than nanocrystalline hematite, which is closer to 500
Thus the UV-Vis spectra reveal that the thicker films, irrespective of the counterion, tend to approach bulk crystallinity when annealed at the higher temperatures.

The optical properties of the multilayer Fe$_2$O$_3$ films when X = ClO$_4^-$ are similar to the ones from when X = BF$_4^-$. Both types of films resisted crystallographic conversions to hematite when annealed at 550 °C until the eighth and fourth layer respectively. For Fe$_2$O$_3$ multilayer films from Fe(bipy)$_3$(ClO$_4$)$_2$. The absorption tail at ~580 nm, which diminishes steadily for the 1-, 2-, and 4-layer films, remains mostly constant through 800 nm in the case of the 8-layer film. The 8-layer sample also had a highly reflective (almost mirror) appearance that was not present in the oxidized Fe(bipy)$_3$Cl$_2$ or Fe(bipy)$_3$(BF$_4$)$_2$ films.

For the monolayer film, the absorption tail after 580 nm is slightly negative, implying that this film is also anti-reflective. This behavior was seen in the multilayer films though the
negative absorption values start at increasingly higher wavelengths as the layer thickness increases. The 8-layer oxidized Fe(bipy)$_3$(BF$_4$)$_2$ film had no mirror-like appearance possibly due to the appearance of α-Fe$_2$O$_3$ as the dominant composition (Figure 3.16b`).

Unlike the other two precursor films, there is a well-defined peak at~320 nm, as opposed to a shoulder as seen in the thicker samples of oxidized Fe(bipy)$_3$(ClO$_4$)$_2$ or broad peak, which can be seen in the thinner films from decomposed Fe(bipy)$_3$(ClO$_4$)$_2$ and Fe(bipy)$_3$(BF$_4$)$_2$ (Figure 3.15). When the Fe$_2$O$_3$ films from Fe(bipy)$_3$Cl$_2$ were reannealed at 550 °C, the 8-layer samples went from a dirty yellow to orange-red color. The UV-Vis
Figure 3.15. UV-Vis absorption spectrum of successive layer growth of a Fe$_2$O$_3$ thin film on glass using layers of decomposed Fe(bipy)$_3$X$_2$ at (left) 330 °C and (right) 550°C: (a, a') X = ClO$_4^-$, (b, b') X = BF$_4^-$, (c, c') X = Cl$. UV-Vis.
Figure 3.16. Raman spectra of Fe$_2$O$_3$ multilayer films annealed at 330°C (left): Raman spectra of Fe$_2$O$_3$ films annealed at 550°C (right).
spectrum for this film shows a peak around 450 nm which is consistent with different grain sizes of hematite. Because hematite was already confirmed in the films above two layers when X = Cl⁻, the difference. The UV-Vis spectra for the 4-layer film unequivocally shows a completely different composition before and after the reannealing at 550 °C because two peaks appear where there used to be broad shoulder.

The 2-layer X = Cl⁻ sample also became slightly orange in color, while the monolayer film had almost no color change. The color change to orange-red is consistent with the appearance of the α-Fe₂O₃ phase, which is consistent with the results seen in Figure 3.16c’.

### 3.2.3 XRD of Multilayer Films

XRD measurements on the multilayer thin films are consistent with the results from Raman analysis suggesting that after a critical thickness, the gamma phase converts to hematite (Figure 3.17). This result was observed in all the films because their bulk spectra were that of α-Fe₂O₃. The films from Fe(bipy)₃(ClO₄)₂ were also measured to have very weak Fe₂O₃ signals below four layers though the 8-layer spectrum does match the corresponding bulk material profile, thereby confirming hematite as the composition. Both the Fe(bipy)₃²⁺ films from the perchlorate and chloride solutions generated a weak maghemite signal as early as two layers when X = Cl⁻ and at four layers when X = ClO₄⁻ in the form of a small but distinguishable peak at 31°. Normally this peak alone cannot be used to distinguish maghemite from hematite because maghemite is expected to have additional peaks at 41° and 53°. The disappearance of the 31° peak in the subsequent layers (and appearance in the respective XRD bulk spectra) further supports the conclusion that maghemite turns to hematite after a critical layer thickness irrespective of the counter ion used in the film solution. The reappearance of the maghemite peak at 31° in the bulk sample also suggests that the bulk materials may have had a small maghemite impurity phase. The XRD measurements on the multilayer films from Fe(bipy)₃(BF₄)₂ do not definitively confirm the Fe₂O₃ crystallographic phase with this technique alone. In fact the XRD patterns suggest that the crystallinity in these multilayer films is quite poor. Amorphous phase Fe₂O₃ is ruled out of the multilayer film compositions when X = BF₄⁻ because the Raman measurements support the conclusion that maghemite was the dominant composition.
Figure 3.17. XRD patterns of Fe₂O₃ multilayer films annealed at 550 °C: (a) X = ClO₄⁻, (b) X = BF₄⁻, (c) X = Cl⁻. (d) XRD of amorphous, α- and γ-phase Fe₂O₃ annealed at various temperatures. Source: Phu, N. D.; Ngo, D. T.; Hoang, L. H.; Luong, N. H.; Chau, N.; Hai, N. H. J. Phys. D-Appl. Phys. 2011, 44, 345002.

3.2.4 Raman Spectroscopy of Multilayer Films

The Raman spectra results suggest that γ-phase Fe₂O₃ thin films are thermally stable before a critical thickness threshold is met (Figure 3.16). If the threshold is met or exceeded, hematite thin films are the favored product during high temperature annealing. Figure 3.16a-b’ shows that when X = ClO₄⁻ and X = BF₄⁻, the films were composed of γ-phase at all thicknesses if the annealing temperature was 330 °C. When those films were annealed at 550 °C, the film’s phase changed to α-phase by 8 layers when X = ClO₄⁻ and 4 layers when X =
BF₄⁻ Figure 3.16c-c’ show that when X = Cl⁻, α–phase impurities were detected as early as 4-layers for the films annealed at 330 °C and as at 2-layers when they were annealed at 550 °C.

### 3.3 Preliminary Results on Iron (III) Oxide Thin Films Doped with Ni and Co

The general strategy for the deposition of doped iron (III) oxide monolayer films is based on the same thermal decomposition of Fe(bipy)₃X₂ monolayer thin films outlined in Figure 3.1. In Figure 3.18 however, a Fe(bipy)₃X₂ solution of known molarity is mixed with a M(bipy)₃X₂ solution of a predetermined molar volume in order to achieve a desired level of doping in the metal oxide film.

![Figure 3.18. General scheme for MOₓ-doped Fe₂O₃ film preparation. Red layers are Fe(bipy)₃X₂ and yellow layers are MOₓ-doped Fe₂O₃.](image)

M = Co, Ni, Cu

#### 3.3.1 Optical Properties Doped Fe₂O₃ Films

UV-Vis measurements confirm that it is possible to mix a Fe(bipy)₃X₂ solution with a Co(bipy)₃X₂ or a Ni(bipy)₃X₂ to create a desired amount of doping in the resulting thermally decomposed film. Figure 3.19 shows that the annealed MOₓ film (M = Co, Ni) will incorporate the dopant metal oxide into its composition. This is evidenced by the 50% doped films’ spectra that show that they approach a profile similar to that of the pure Fe₂O₃. The results also suggest that using the general deposition method described herein may also be extended to more metal oxide systems.

#### 3.3.2 Raman Analysis of Doped Fe₂O₃ Films

Raman spectroscopy confirmed that the composition of the doped iron oxide thin films incorporated the Co³⁺, and Ni²⁺ impurities into a gamma-phase Fe₂O₃ monolayer lattice as seen in Figure 3.20. The γ-phase of Fe₂O₃ was observed as an expected medium-broad
Figure 3.19. UV-Vis spectra of pure Fe$_2$O$_3$ monolayer, Fe$_2$O$_3$ monolayer doped with 50% Ni$^{2+}$ and 50% Co$^{2+}$, and pure Co$_3$O$_4$ and NiO monolayers annealed at 550°C.

Figure 3.20. Raman spectra of Fe$_2$O$_3$ monolayer films doped with: (a) Co; and (b) Ni.

peak ~685 cm$^{-1}$ with a small hump at ~305 cm$^{-1}$. The absence of hematite diagnostic peaks around 220 and 280 cm$^{-1}$ for example, also show that the α-phase Fe$_2$O$_3$ is not favored by the presence of the other metal ions for a monolayer.

The pure cobalt oxide films were determined to contain mostly trivalent cobalt oxide. CoO has sharp peaks ~690 cm$^{-1}$ and 480 cm$^{-1}$ \cite{144,145} which can make it tricky when differentiating it from Co$_3$O$_4$. Raman spectrum of Co$_3$O$_4$ is characterized by sharp peaks around 693, 624, 523, 485, and 197 cm$^{-1}$ \cite{145-147} which were observed, though they were
shifted lower by about 10 cm$^{-1}$, suggesting a very small grain size. Raman spectra of CoO have a broad hump extending from about 450-650 cm$^{-1}$ which was present in the measurements of the pure cobalt oxide film. It was expected that CoO would not be present in appreciable amounts because CoO is the preferred phase above annealing temperatures of 900 °C. Figure 3.20a shows that the 50%/50% Fe$_2$O$_3$-Co$_3$O$_4$ films incorporated iron oxide in the gamma-phase due to the broad peak around 680 cm$^{-1}$ that blends with the sharp peak of Co$_3$O$_4$.

The films from pure Ni(bipy)$_3$(ClO$_4$)$_2$ showed that the composition was that of signs of nickel (III) in the form of NiOOH. Figure 3.20 shows characteristic peaks of NiOOH at 462 and 570 wavenumbers. The films from 50% Fe(bipy)$_3$(ClO$_4$)$_2$/50% Ni(bipy)$_3$(ClO$_4$)$_2$ were found to contain nickel ferrite, NiFe$_2$O$_4$. Nickel ferrite bulk material where Ni$^{2+}$ and Fe$^{3+}$ ions exist in a ferromagnetic ternary oxide that lattice with cubic spinel-type structure. Figure 3.20b shows that the film from Ni(bipy)$_3$(ClO$_4$)$_2$ has peaks at 295, 463, and 684 cm$^{-1}$ which are characteristic for NiFe$_2$O$_4$.

The results from Raman spectroscopy demonstrate a Fe$_2$O$_3$ system can be doped create a crystal at least up to 50% doping with a Co$^{2+}$ or Ni$^{2+}$ impurity.

### 3.4 APPLICATIONS OF IRON OXIDE THIN FILMS IN DYE-SENSITIZED SOLAR CELLS

In the most conventional solid-state semiconductor (e.g. silicon) -based solar cells, the photoelectrons are generated and charge-transported by the same material. This double functionality imposes serious limitations on the choice of the solar cell material and elevates its cost. A new type of solar cell material design is based on the general ideas of dye-sensitised solar cells (DSSC). DSSCs detach the task of the photoelectron generation from the task of the charge separation – the electrons are produced by a photosensitive dye, while their conduction is provided by a band-gap base semiconductor, such as titania. A broad industrial implementation of DSSCs, however, is still hampered by three main reasons: cost of the dye, efficiency, and stability. The most efficient up-to-date dyes for DSSC are ruthenium-based (such as N3 dye, Figure 3.21), which makes them extremely expensive. Despite the relatively high quantum efficiency of DSSC, the solar-to-electric power conversion efficiency does not exceed 11-12% due to the energy losses in the band-gap material and in the electrodes. One of the factors preventing the use of inexpensive and more
stable sensitizers such as metal oxide thin films in DSSCs is a relatively high position of conduction band in titania. Fe₂O₃ is a semiconductor whose conduction band lies by 0.5 eV lower than that of TiO₂ and therefore in principle can be used instead of TiO₂ in DSSCs. This chapter describes the proof-of-principle experiments utilizing Fe₂O₃ thin films as DSSCs’ anodes.

3.4.1 Solar Cell Fabrication

FTO with deposited monolayer Fe₂O₃ film obtained from Fe(bipy)₃(ClO₄)₂ was immersed into ~1 mM solution of N3 dye in isopropanol for 14 hours. Two thin glass slides
supported the Fe₂O₃ off of the bottom surface of the Petri dish. This creates a thin gap between the Fe₂O₃ and the bottom of the Petri dish, creating capillary forces that draw the dye into the Fe₂O₃ layer (Figure 3.21). After the 14 hour time period, the Fe₂O₃ film was rinsed in a 50/50 acetone/isopropanol bath to remove any physisorbed N3 dye.

### 3.4.2 Final Assembly and Performance Testing

Fe₂O₃-coated FTO electrode modified with N3 dye was prepared as it was described. The counter electrode was made by sputtering ~12 nm layer of Pt onto FTO. The two electrodes were sealed together with thermal melt polymer film (150 µm thick Surlyn, DuPont). After a lot of trial and error it was found that the best sealing was done at 135°C for 10 minutes. A beaker or Petri dish is placed over the cells to create an “oven” effect and is critical for reliable sealing. Before being removed from the hot plate to cool, pressure is applied to the top surface of the cell to help minimize air bubbles between the Surlyn and glass substrate. The electrolyte can be added to the cell once it has cooled. A syringe is used to inject the electrolyte solution into the cell. This is a delicate process as it is very easy to trap a bubble in the cell which is very difficult to remove.

### 3.4.3 Performance Testing

Two methods have been used in this study to test the performance of the solar cells. In one method, conventional 150W 1.0 AM solar simulator IV System (Newport) was used. Since it was not always available and operational, another home-built simulator based on the high vapor pressure Hg lamp source of the Nikon Eclipse inverted microscope and Autolab (PGSTAT100, Eco Chemie) potentiostat was constructed and used for solar cell testing (Figure 3.21).

In the results sections the levels of light are listed as no light (nl), for ambient lighting condition, and levels L1-L4, for the different levels available from the microscope light source. This method of performance testing is not capable of directly computing the efficiency of the cell precisely; however it was very useful for comparison of cells and finding relative efficiency.
### 3.4.4 Device Characteristics

To the best of our knowledge the films of Fe$_2$O$_3$ has never been tested as DSSC’s anode. So before sensitizing thin films of Fe$_2$O$_3$ with any new sensitizers we have to test whether these films can be sensitized in principle. N3 dye and other components of conventional DSSCs are good candidates for this purpose.

Figure 3.22 shows that N3 dye clearly can sensitize the Fe$_2$O$_3$. However the efficiency for such cells does not exceed 0.02 %. Such low efficiency is probably due to low carrier mobility in Fe$_2$O$_3$ comparing to the one of TiO$_2$. It should be noted that this relatively low efficiency was obtained for undoped Fe$_2$O$_3$ and the thin film morphology and surface area were not optimized for adsorption of the maximum amount of sensitizer. If the electrical properties can be improved by using doped films and the amount of the adsorbed dye can be increased by using multilayered films with optimized surface area, efficiencies of these cells could be significantly improved.

### 3.5 CONCLUSIONS

We were able to synthesize high quality γ- and α-Fe$_2$O$_3$ thin films through a simple and straightforward method using readily available and inexpensive reagents. The simplicity and level of control available with our method makes it a potentially economically viable process for the deposition of iron oxide films on various substrates. Both thickness and morphology may be tuned to the requirements of a particular application. Our films may also be tuned to have a certain range of optical and electrical properties including reflectivity and color absorption. Iron oxide films prepared by our method have the appropriate bandgap and mesoporous structure that make them potentially useful in fabricating dye-sensitized thin film solar cells using various kinds of dyes. Our synthetic and deposition method provides convenient routes for doping iron oxide films with various transition metals such as Co, and Ni thereby opening an even broader range of potential applications.
Figure 3.22. Comparison of I-V curves for FTO|Fe$_2$O$_3$| I$^-$/I$_3^-$ | 6nm Pt | FTO (unsensitized) and FTO|Fe$_2$O$_3$|N3| I$^-$/I$_3^-$ | 6nm Pt | FTO cells at different light intensity levels (L1-L4).
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78. Maji, S. K.; Mukherjee, N.; Mondal, A.; Adhikary, B. Polyhedron 2012, 33, 145.


