
William B. Ingler Jr.

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For Direct Water Photoelectrolysis

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Presented By

William B. Ingler Jr.

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Name: William B. Ingler Jr.


Degree: Doctorate of Philosophy

Date: April 14, 2005

Approved:

Shahed U. M. Khan, Ph.D.
Dissertation Advisor
Associate Professor of Chemistry
Department of Chemistry and Biochemistry, Duquesne University

Approved:

Jeffry D. Madura, Ph.D.
Professor of Chemistry
Chairman of the Department of Chemistry and Biochemistry
Department of Chemistry and Biochemistry, Duquesne University

Approved:

Jeffrey D. Evaneck, Ph.D.
Associate Professor of Chemistry
Department of Chemistry and Biochemistry, Duquesne University

Approved:

David W. Wright, Ph.D.
Outside Reader
Assistant Professor of Chemistry
Vanderbilt University, Nashville, TN.

Approved:

David W. Seybert, Ph.D.
Professor of Chemistry
Dean of the Bayer School of Natural and Environmental Sciences
Department of Chemistry and Biochemistry, Duquesne University
Preface

This dissertation is the culmination of four and a half years of research. The work is presented here represents the culmination of hundreds of samples and an unending dedication for discovery and finding what has yet to be seen by others. I would say yet to be created, but all the work has already been done for us, we are simply refining the work, so that we and others may understand what was always there for us. It is by nature that we are curious, and it is that curiosity that makes us strive ever harder to understand the environment around us. In all facets of life there are mysteries still not understood by anyone, and it is the place of the scientist in society to explore and investigate and yet undocumented part of that environment. I set forth in my pursuit of this dissertation to explore and understand but one infinitesimal aspect of electrochemistry at large. It is my hope that my insights and new understandings bring insight to others, especially friends and colleagues in the field.

There is so much to be done on this project and I have only turned over a few stones to see the beginnings of what can be a very fruitful venture. I would hope that this work is pursued by myself or others in the future, it is this drive towards imagination, which makes us better as society.

William B. Ingler Jr.

Department of Chemistry and Biochemistry
Bayer School of Natural and Environmental Sciences
Duquesne University, Pittsburgh, PA, U.S.A. 15282

Abstract

My Ph.D. Dissertation describes (1) the influence of metal dopants on the spray pyrolytic synthesis of p-type and n-type iron(III) oxide thin film semiconductors, (2) the fabrication of carbon-modified (CM) n-type titanium dioxide, and (3) various self-driven photoelectrochemical cells (PEC) for water splitting. (1) Stable thin films of Fe$_2$O$_3$ was the first goal pursued in this work. Various metal dopants were investigated to ascertain their viability as good dopant for iron(III) oxide. These metals included copper, zinc, and magnesium. This was followed by investigating metals that could improve the conductivity of n-type iron(III) oxide, which included indium, iodine, manganese, and calcium. Research showed that zinc improved p-type characteristics the best, and considerably improved stability of p-type iron(III) oxide in acidic media. Indium-doped n-type iron(III) oxide showed improvement in photocurrent response over naturally-doped iron(III) oxide; however, there was a loss in the onset potential, which proved vital for developing a self-driven PEC. Importantly, the use of 1-pentanol as the spray solution solvent instead of ethanol improved the onset potential and photoresponse of n-type iron(III) oxide which helped to fabricate a self-driven p-type/n-type iron(III) oxide PEC for water splitting. (2)
Carbon-modified n-type titanium dioxide electrodes were found to be extremely valuable towards fabrication of self-driven water splitting PEC, because the addition of carbon into the titanium dioxide crystal structure provided it with the ability to absorb light much further into the visible spectrum. Unmodified titanium dioxide can only absorb ~13% of the total solar power (100 mW/cubic cm) of Air Mass (AM) 1.5; in other words wavelengths of light from ultraviolet to 414 nm. Carbon modification of n-type titanium dioxide allows it to absorb up to 535 nm, or ~30% of the total solar power. (3) The most important part of this work is the fabrication of a self-driven PEC for water splitting using zinc-doped p-type iron(III) oxide and naturally-doped n-type iron(III) oxide; carbon-modified n-type titanium dioxide and zinc-doped p-type iron(III) oxide; and p-type gallium indium phosphide and carbon-modified n-type titanium dioxide.
Foreword

I would like to give my sincere thanks to my dissertation advisor, Dr. Shahed U. M. Khan, for his continual guidance, support, and advice over the 11 years that he has been a friend and mentor for me as I have moved from a bachelor’s degree, to a master’s degree, and now to ultimate level of achievement for which I can be bestowed with at Duquesne, which is my Doctorate of Philosophy in Chemistry. I would also like to thank the other members on my dissertation committee, Dr. Jeffrey D. Evanseck, Dr. Jeffry D. Madura, and Dr. David W. Wright, who early on gave me the direction to achieve my goals, and helped to expand and learn more during my studies towards my dissertation.

I would like to thank my parents, Susan A. Ingler and William B. Ingler Sr., for whom none of this would have been possible, if not for their financial and moral support that they have given me during my studies. I would also like to gratefully thank the Department of Chemistry and Biochemistry and the Bayer School of Natural and Environmental Sciences for their financial support during my dissertation studies.

I would also like to thank the rest of the faculty at Duquesne, who in their entirety helped to advance my understanding of chemistry as whole with the graduate courses that I took. I would also like to thank the graduate students who have passed through Duquesne during my time there, especially Sejal Iyer and Lisa Pasierb, who undying support helped me during the toughest of times, all the while moving forward with my research. It is through friendships bonded for a lifetime that we gain peace and a deeper understanding of what we can do with the help of so many others.

I would like to acknowledge the support of Dr. John Baltrus at the National Energy and Technology Laboratory and the Department of Energy for X-ray photoelectron spectroscopy analysis of zinc-doped p-Fe₂O₃ samples, and Robert Hengstebeck and Dr. Carlos Patano at Penn State University at State College for X-ray photoelectron spectroscopy analysis of magnesium-doped p-Fe₂O₃ and iodine-doped n-Fe₂O₃ samples. Dr. Lucian Diamandescu who was a visiting professor in the Department of Physics at Duquesne University for his invaluable help in peak identification of X-ray diffraction data for all powder X-ray diffraction data presented. Dr. John Turner and the National Renewable Energy Laboratory in Golden, CO. for the p-GaInP₂ used for the study of p-GaInP₂ and CM-n-TiO₂. Yasser Shaban, a graduate student in Dr. Khan’s lab, for providing the CM-n-TiO₂ used in the study of p-GaInP₂ and CM-n-TiO₂. Additionally, I would like to thank Dan Bodnar and Dave Hardesty for their technical expertise and instrumental maintenance that kept things running, so that I could complete my research. Also, Mr. Ian Welsh and the departmental office staff for the help in ordering chemicals and other laboratory needs that it took to keep the lab running.
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1. INTRODUCTION

The field of water photoelectrolysis using semiconductor electrodes has seen several advances over the past 30 years, but the greatest need is still the ability to produce a stable and low cost semiconductor with a low band gap; therefore, being able to absorb a large amount of photons from the solar spectrum. Most of the modern innovations have sought to raise the limits of the photon absorption range of TiO$_2$. The study of photoelectrochemical (PEC) systems has been a well-studied area since Fujishima and Honda identified the process of photosplitting of water in 1972. Since that time, electrochemists and material scientists have devoted large amounts of time and money in government labs and academia to devise an efficient PEC system to generate H$_2$ gas to be used as a viable clean energy source. This is in contrast to the current major energy sources of fossil fuels and coal. Fossil fuels and coal have the unwanted effects of CO$_2$ and CO production, which are greenhouse gases, and sulfur and nitrogen oxides, which are associated with acid rain. On the other hand, the combustion of H$_2$ gas will produce H$_2$O, which can be renewed with a PEC system to reproduce H$_2$ and O$_2$ gas. This is the renewable energy storage cycle associated with PEC systems; whereas, fossil fuels and coal are non-renewable in that once they are consumed they cannot be regenerated for reuse.

In that first system, TiO$_2$ electrodes were illuminated with uv light and a small external bias was applied and it was seen to be very stable. Many modifications have taken place to improve the original TiO$_2$ system. The drawback of a PEC system involving TiO$_2$ is that it can absorb only uv light, which is only 5% of the solar spectrum (Figure 1.1). This is due to its large band gap energy of 3 - 3.2 eV. Iron(III) oxide (Fe$_2$O$_3$) is a low cost semiconductor having stability and can absorb most of the visible light in the solar spectrum. Iron(III) oxide has a band gap of 2.0 to 2.1 eV; therefore, it can absorb solar radiation from 620 to
295 nm, which comprises 38% of solar spectrum at air mass (AM) 1.5. Fe₂O₃ utilizes 38% of the solar spectrum, which makes it an ideal semiconductor based solely on its ability to absorb solar radiation deep into the visible spectrum. In the search for a better semiconductor, the major drawbacks have been the low stability and photocorrosion of semiconductors, because low band gap semiconductors are in general unstable.

To use semiconductors as possible photoelectrodes, their viability depends on their ability to absorb enough sunlight (to split water efficiently) and as well as their stability against photocorrosion. The U.S. Department of Energy has set a 10% efficiency benchmark, which is the accepted worldwide standard. Some semiconductor systems have met this 10% efficiency barrier. One such discovery is the system developed by Khaselev and Turner in which they demonstrated a monolithic solar cell that can be used as a PEC that has a water-splitting efficiency of 12.4%. However, this system involves p-GaInP₂ as a top layer, which is not stable for more than 24 hours in basic environments, or 2 to 3 days in an acidic environment. On the other hand, TiO₂ (which is a stable system) is inefficient due to it’s a large band gap energy (i.e., 3 – 3.2 eV). This makes n-TiO₂ a poor absorber of sunlight, consequently its photoconversion efficiency is less than optimal (~1.0%). However, attempts were made to reduce the band gap of n-TiO₂. For example, it was found by Asahi et al that a nitrogen containing TiO₂ had a lower band gap to absorb visible light in the solar spectrum. Recently, it was discovered a carbon-modified (CM)-n-TiO₂ photocatalyst can photochemically split water to hydrogen and oxygen with a maximum photoconversion efficiency of 8.35%. As was stated above, carbon modification of n-TiO₂ has lowered the band gap to absorb in the visible spectrum, which contains 45% of solar photons as shown in Figure 1.1.
Figure 1.1. NREL Standard of AM 1.5 (Direct Filter). The two lines represent 388 nm and 414 nm, which correspond to band gaps of 3.0 eV and 3.2 eV (for n-TiO$_2$), respectively. The last line represents 620 nm, or a band gap of 2.0 eV for n-Fe$_2$O$_3$.

The band bending in a p-type semiconductor, for example p-Fe$_2$O$_3$, and the direction of electron movement in a p-Fe$_2$O$_3$/Pt PEC is shown in Figure 1.2. For a p-type semiconductor like Fe$_2$O$_3$, the band-edges of the conduction and valence bands are bent downward, and the Fermi level is just above the valence band. Conversely, for a n-type semiconductor, the band-edges of the conduction and valence bands are bent upward, and the Fermi level is just below the conduction band as shown in Figure 1.3. A general set-up of a combination of p-type and n-type semiconductors is shown in Figure 1.4.
The energy difference between the conduction band and the valence band is called the band gap. This energy difference must be overcome by an electron being photoexcited from the valence band to the conduction band. The magnitude of the band gap is related to the nature of materials. Above a band gap of 4.0 eV, a material is considered to be an insulator. Almost everything below a band gap of 4.0 eV is considered to be a semiconductor. The last class of materials is metals, which have little or no band gap separation, because the conduction band and the valence band are in close contact with each other.

When a semiconductor electrode is illuminated by a light source or directly by solar radiation that can provide the electrode with photonic energy (hν) greater than its band gap energy (E$_g$), then an electron from the valence band will be excited into the conduction band, and correspondently, a positively charged hole will be left in the valence band.

**Figure 1.2.** Water splitting reactions on the surface of the p-Fe$_2$O$_3$ thin film semiconductor under illumination with a platinum metal counter electrode.
Figure 1.3. An illustration of water splitting reactions on the surface of the n-TiO$_2$ thin film semiconductor under illumination with a platinum metal counter electrode is shown.

The n-type semiconductor (e.g., n-TiO$_2$, n-Fe$_2$O$_3$) has upward band-bending, therefore the electron that is excited from the valence band to the conduction band, moves downhill to the back of electrode and moves to the counter-electrode and the holes move to the surface and react with species in the solution as shown in Figures 1.3 and 1.4. So, on the surface of the n-type semiconductor, the following reaction takes place for water splitting:
Hydrogen from water (4 electron–hole transfer reaction):

\[ \text{4H}_2\text{O} \rightarrow \text{4H}^+ + 4\text{OH}^- \quad (1.1) \text{ in solution} \]

\[ \text{CM-n-TiO}_2 \text{ (photoanode) + sunlight} \rightarrow 4\text{h}^+ + 4\text{e}^- \quad (1.2) \text{ at photoanode} \]

\[ 4\text{ OH}^- + 4\text{h}^+ \rightarrow \text{O}_2 + 2\text{H}_2\text{O} \quad (1.3) \text{ at photoanode} \]

\[ \text{4H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2 \quad (1.4) \text{ at cathode} \]

Eqs. (1) - (4) give the overall reaction as,

\[ \text{H}_2\text{O} + \text{CM-nTiO}_2 \text{ (photocatalyst) + sunlight} \rightarrow \text{H}_2 + \frac{1}{2} \text{O}_2 \quad (1.5) \]

CM-n-TiO\textsubscript{2} and n-Fe\textsubscript{2}O\textsubscript{3} are visible light absorbing semiconductors, and hence are expected to split water efficiently. The primary method of synthesis of n-Fe\textsubscript{2}O\textsubscript{3} was spray pyrolysis\textsuperscript{68,78-83}. However, plasma-sprayed p-Fe\textsubscript{2}O\textsubscript{3} has been looked at as an option\textsuperscript{84}. Other methods of preparation of p-Fe\textsubscript{2}O\textsubscript{3} semiconductors have included sol-gel methods\textsuperscript{85-89}, vacuum deposition, and nanowire or quantum wire vacuum deposition\textsuperscript{90-95}. 
Figure 1.4. An illustration of water splitting reactions on the surfaces of the p- and n-Fe$_2$O$_3$ thin film semiconductor photoelectrodes is shown under illumination.

Characterization of p- and n-Fe$_2$O$_3$ and CM-n-TiO$_2$ includes determination of photocurrent–potential dependence and open-circuit voltage using methods reported earlier.$^{8,96-99}$ Other methods of characterization are X-ray diffraction (XRD),$^{100,101}$ scanning electron microscopy (SEM), uv-vis absorption and monochromatic photocurrent density for band gap determination,$^{102}$ and capacitance measurements for Mott-Schottky calculations.

Earlier Fe$_2$O$_3$ was studied as a semiconductor photocatalyst in various forms, which include pressed pellets,$^{97,103-117}$ nanoparticles synthesized by sol-gel techniques,$^{94,118}$ single crystal and ceramic electrodes,$^{63,73,96,119}$ electrodes made by argon sputtering,$^{26,120}$ and spray pyrolysis deposition (SPD).$^{8,9,17,30,55,68,69,121}$ Most studies on p-type doping of iron oxide were carried out by
magnesium dopant, including studies utilizing calcium, nickel, and copper as p-type dopants. However, no synthesis of p-type Fe₂O₃ thin films by spray pyrolytic deposition (SPD) using zinc, copper, calcium, or nickel doping were performed earlier to study their photoresponse towards water splitting reaction; but there was one study that formed zinc ferrite films by spraying a spray solution that contained iron(III) nitrate and zinc nitrate. Nevertheless, this study did not examine the photoelectrochemical properties and optimization of the films, but focused only on the materials and surface chemistry of the films. There were two other methods that incorporated zinc dopant, one of which a mixed solution on an alumina substrate was deposited and then dried and calcinated and another in which powders of ferric oxide and zinc oxide were mixed and pressing the powders into pellets.

Thin films of n-Fe₂O₃ (with no added metal dopant) have been extensively studied with reported photoconversion efficiencies of up to 2% for water-splitting. An efficient p-Fe₂O₃ semiconductor can be coupled with an n-Fe₂O₃ to replace the platinum metal counter electrode utilized in most studies. Theoretically, a tandem n-Fe₂O₃/p-Fe₂O₃ system will need less external bias potential than is required to split water using n-Fe₂O₃ / Pt system. Furthermore, SPD synthesized transparent p-Fe₂O₃ thin films can be utilized in tandem with an n-i-p Si solar cell in order to develop a self-driven monolithic hydrogen producing system.

Some applications include the use of n-TiO₂ in wet solar cells and for the photodegradation of organics present in polluted water and air under ultraviolet (UV) light (wavelength, λ < 400 nm) illumination, the energy of which exceeds the band gap energy of 3.0 eV in the rutile crystalline form of n-TiO₂. Photoelectrodes that are (i) highly stable, (ii) inexpensive, (iii) have a conduction band minimum which is higher than the H₂/H₂O level and a valence band maximum which is lower than the H₂O/O₂ level, and (iv) can absorb most of the
photons of the solar spectrum are most suitable for efficient photosplitting of water to hydrogen, a source of abundant clean energy. Although both the anatase and rutile forms of titanium oxide [n-TiO₂] meet conditions (i)–(iii), they are poor absorbers of photons in the solar spectrum. Several attempts have been made earlier to lower the band gap energy of n-TiO₂ by transition metal doping¹³⁴-¹³⁷ and reducing it by hydrogen.¹³⁸,¹³⁹ But no noticeable change in band gap energy of n-TiO₂ was observed.

A carbon-modified (CM) n-TiO₂ was synthesized by flame oxidation of Ti metal sheet in an attempt to lower its band gap energy so that it can absorb the uv and most of the visible light of solar spectrum, while at the same time retaining its stability.
Very popular semiconductors for the study of water splitting reactions are TiO$_2$ and Fe$_2$O$_3$. These two semiconductor electrodes have enjoyed a large amount scientific interest. Titanium dioxide has a large band gap of 3.0 to 3.2 eV, and its band gap covers the energy region for both the O$_2$ and H$_2$ redox couples as shown in Figure 1.5. But, efficient water splitting is not possible with TiO$_2$ due to its large band gap and without the application of a minimum amount of bias potential. To these ends, several modifications have been employed to overcome this problem, which include incorporation of other atoms in the titanium dioxide structure, such as carbon$^7$, nitrogen$^6$, and sulfur$^{21}$. Though the band gap of Fe$_2$O$_3$ is optimal, it has a common problem that its band gap does not cover the energy region of O$_2$ and H$_2$ redox couples (see Figure 1.5) and as well as its conductivity is very low.
To characterize the semiconductor materials the photoconversion efficiency ($\%\varepsilon_{\text{photo}}$), total conversion efficiency ($\%\varepsilon_{\text{total}}$), flatband potential, $V_{\text{fb}}$, donor density, $N_d$, acceptor density, $N_a$, quantum efficiency, $\eta(\lambda)$, and band gap calculations can be performed using the following equations:

**A. Photoconversion Efficiency for a Non-Self-Driven PEC**

For the PEC for which an external bias is needed, the calculation of photoconversion efficiency can be calculated using the equation given as $^7,8,34$

\[
%\varepsilon_{\text{photo}} = \frac{(\text{total power output}) - (\text{electrical power input})}{(\text{light power input})} \times 100 \quad (1.6)
\]

or it can alternatively be written as,

\[
%\varepsilon_{\text{photo}} = \left[ j_p \left( E^{\circ}_{\text{rev}} - |E_{\text{app}}| \right)/I_0 \right] \times 100 \quad (1.7)
\]

where $j_p$ is the photocurrent density, $E^{\circ}_{\text{rev}}$ is the standard state reversible potential, which is 1.23 V for water splitting reaction and $|E_{\text{app}}|$ is the absolute value of applied potential at the photoanode or photocathode that can be expressed as $^7,8$

\[
E_{\text{app}} = E_{\text{meas}} - E_{\text{aoc}} \quad (1.8)
\]

where $E_{\text{meas}}$ is the potential with respect to the reference electrode (e.g., SCE) at which photocurrent was measured and $E_{\text{aoc}}$ is the electrode potential at open circuit conditions with
respect to the same reference electrode and under the same illumination conditions used for the photocurrent measurements.

Non-self-driven photoelectrochemical cells (PEC) cannot generate enough photopotential to overcome the reversible potential for the reaction ($E_{\text{rev}}^o$). Therefore, an applied potential ($E_{\text{app}}$) has to be administered for the reaction to proceed forward, thereby overcoming the $E_{\text{rev}}^o$ thermodynamic barrier that exists for the reaction (e.g., water splitting reaction). Consequently, for a non-self-driven PEC, instead of $E_{\text{rev}}^o$, a value of potential ($E_{\text{rev}}^o - |E_{\text{app}}|$) is used (see Equation 1.7) to determine the photoconversion efficiency.

**B. Total Conversion Efficiency or Photoconversion Efficiency for a Self-Driven PEC**

The calculation of total conversion efficiency ($\%\varepsilon_{\text{total}}$) can be carried out using the equation given as,$^8,^9,^{34},^{140}$

$$\%\varepsilon_{\text{total}} = \left(\frac{\text{total power output}}{\text{light power input}}\right) \times 100 \quad (1.9)$$

or it can alternatively be written as,

$$\%\varepsilon_{\text{total}} = \left[ j_p (E_{\text{rev}}^o / I_o) \right] \times 100 \quad (1.10)$$

which also includes the electrical power input contribution. Note that this equation can be used also for the calculation of photoconversion efficiency for the self-driven PEC.
C. Flatband Potential and Doping Density from Mott-Schottky Equation

The flatband potential (E_{fb}) for a given semiconductor can be calculated from the intercept of a Mott-Schottky plot (1/C^2 vs E_{meas}) using the following equation,\(^\text{8,35,141-143}\)

\[
\frac{1}{C^2} = \left(\frac{2}{\epsilon \epsilon_0 N}ight) \left(Z_i \left(E_{\text{meas}} - E_{\text{fb}}\right) - \frac{kT}{e}\right)
\]

(1.11)

where C is the capacitance, \(\epsilon\) is the dielectric constant of the semiconductor, \(\epsilon_0\) is the permittivity of the vacuum, N represents the acceptor density in a p-type semiconductor and the donor density in a n-type semiconductor, E_{meas} is the measured electrode potential at which capacitance was measured, Z_i is +1 for donors and -1 for acceptors, and kT/e_0 is the temperature-dependent term in the Mott-Schottky equation.

D. Quantum Efficiency

The quantum efficiency under monochromatic light illumination, \(\eta(\lambda)\) can be considered using the following relationship,\(^\text{8,9,144}\)

\[
\eta(\lambda) = \frac{j_p(\lambda)}{e_o I_o(\lambda)}
\]

(1.12)

where \(j_p(\lambda)\) is the monochromatic photocurrent density, \(e_o\) is the electronic charge, and \(I_o(\lambda)\) is the flux of incident photon at wavelength, \(\lambda\).
E. Band Gap Calculations

The band gap energy, $E_g$, of a semiconductor can be determined using the following equation,8,15,145-150

$$\eta(\lambda)hv = A(hv - E_g)^n$$

(1.13)

where $A$ is a constant, $hv$ is the wavelength dependent energy of light, and $n$ equals $\frac{1}{2}$ for allowed direct transitions, 2 for allowed indirect transitions, and $\frac{3}{2}$ for direct forbidden transitions. The allowed direct transition of an electron from the valence band to the conduction band by light energy ($hv$) is not phonon (generated from lattice vibrations) assisted because such a transition does not require any momentum change, since momentum is conserved. In the case of the allowed indirect transition, it involves changes in energy and momentum. Momentum is conserved from phonon interaction because light photons do not make changes in the momentum.150,151

F. Scherer’s Calculations

From the XRD data the crystal size can be calculated from the diffraction peaks by using Scherer’s equation as shown below,152

$$D = \frac{(0.9\lambda)}{(\beta \cos \theta)}$$

(1.14)

where $D$ is the average crystal size in nm, $\lambda$ is the radiation wavelength (0.15405 nm), $\beta$ is the corrected half-width at half-maximum intensity, and $\theta$ is the diffraction peak angle.
The focus in this dissertation was to study the synthesis of both p-type and n-type Fe$_2$O$_3$ by incorporation of various metal dopants using spray pyrolytic deposition (SPD), synthesis of carbon-modified n-TiO$_2$ by flame oxidation of titanium metal sheets, and the study of their photoresponse towards water electrolysis. The conditions and parameters were optimized for the efficient water splitting. Then, p-Fe$_2$O$_3$ and n-Fe$_2$O$_3$ were used in the form of a tandem PEC to generate a self-driven system. Also, other combinations such as p-Fe$_2$O$_3$/CM-n-TiO$_2$ and p-GaInP$_2$/CM-n-TiO$_2$ were studied in this work with p-GaInP$_2$ were obtained from the National Renewable Energy Laboratory (NREL) to develop a self-driven PEC for water splitting.
2. EXPERIMENTAL

A. Preparation of n-Fe₂O₃ Thin Films by Spray Pyrolysis Deposition (SPD)

P-type and n-type Fe₂O₃ semiconductors were prepared by spray pyrolysis methods and were described earlier in detail. Spray solutions of various concentrations (0.09 – 0.12 M) of iron(III) chloride hexahydrate (FeCl₃·6H₂O; ACS Grade, Acros Organics) were made in 100% ethanol (Pharmco Products Inc.; 200 Proof) with various concentrations of metal ions (0.0022 to 0.0132M) in the form of indium chloride hydrate (InCl₃·xH₂O; Alfa Aesar), iodine (I₂, Alfa Aesar), manganese(II) nitrate tetrahydrate (Mn(NO₃)₂·4H₂O, Aldrich), manganese(II) acetate tetrahydrate (C₄H₆O₄Mn·4H₂O, Acros Organics), or calcium chloride dehydrate (CaCl₂·2H₂O, Acros Organics). The concentration ratios of FeCl₃·6H₂O and dopant compound were found to be critical for the synthesis of both n-type and p-type Fe₂O₃ thin films with optimum properties. Optically transparent thin films of conducting tin-oxide coated glass (100 Ω cm², 3.175 mm thick Pyrex glass, Swift Glass Company, Elmira, NY) were used as substrates. A portion of the tin-oxide coated glass substrate was covered with aluminum foil to keep it free from Fe₂O₃ deposition for use as an electrical contact.

A Thermolyne Corp. K-type Thermocouple (PM20700, Series 405) was used to measure and maintain the temperature of the glass substrate placed on a Fisher Scientific hotplate. The temperature was varied from 380 to 420°C. An area of ~ 1.0 cm² on the tin-oxide coated glass surface was exposed to the spray solution of iron(III) oxide and dopant compound in absolute ethanol. A custom Pyrex 250 mL round-bottom flask with two spray attachments on the glassware was used to spray the solution as shown in Figure 2.1. These attachments consist of two buret-like tips that point at each other at a 90° angle, which is discussed in detail in a prior work. The lower buret serves to deliver the ethanolic solution and the other buret tip acts as the point at
which the carrier gas flows to atomize the ethanolic solution. The pressure of the carrier gas (oxygen) was maintained at 138 kPa. Five minutes breaks were allowed between each spray period of 10 s to maintain a constant temperature on the substrate surface.

![Figure 2.1](image)

**Figure 2.1.** A diagram showing the position of the sprayer with respect to the hot plate on which the glass substrate was heated.

We used iron chloride as the precursor for the formation of $\alpha$-$\mathrm{Fe}_2\mathrm{O}_3$, because other possible compounds had various drawbacks. When iron nitrates were used in the spray solution, the favored products are $\mathrm{Fe}_3\mathrm{O}_4$ and $\gamma$-$\mathrm{Fe}_2\mathrm{O}_3$,\textsuperscript{94,118} which have very low conductivity to be effective semiconductors. Iron acetylacetonate favors the formation of $\alpha$-$\mathrm{Fe}_2\mathrm{O}_3$,\textsuperscript{17,68} which was reported to be the most conductive form of $\mathrm{Fe}_2\mathrm{O}_3$, but was found to be rather soft and dissolved in acidic
media too easily and was considered unsatisfactory for use as a semiconductor in the form of thin films. Iron chloride was our precursor of choice, because it favors formation of a polycrystalline form of $\alpha$- and $\gamma$-Fe$_2$O$_3$. Iron pentacarbonyl has also been seen to favor a polycrystalline formation, but the temperature for fabrication is not in a favorable temperature range with the dopant materials.

B. Fabrication of p-type Fe$_2$O$_3$ by Incorporation of Metal Dopants

The synthesis of p-type Fe$_2$O$_3$ depends upon the inclusion of atoms that have at least one more electron on the metal atom. In other words, if we are producing p-type iron(III) oxide, Fe$_2$O$_3$, which is a $+3$ state, then we need to use an atom that is a $+2$ state, such as copper(II), Cu$^{2+}$, magnesium, Mg$^{2+}$, or zinc, Zn$^{2+}$. In order to find suitable metals and compounds for use as dopant materials, there are several properties that need to be considered. These properties include the melting point and the boiling point of the precursor compound, the oxidation state being used, the solubility of the synthesized compound(s) in acidic and basic solvents. We also need to consider the melting and boiling points of the compound(s) being formed. Several metal atoms such as copper, zinc, magnesium, tin, cadmium, calcium, manganese, cobalt, zirconium, and nickel were considered, whose $+2$ state are correspondently available. Some of these metals were studied in the past such as magnesium, calcium, manganese, and tin. Calcium and manganese were reported earlier as p-type dopant, however work in optimizing with these two atoms was fruitless, and they eventually were identified as n-type dopants. The compounds studied for calcium and manganese were calcium acetate (melting point (m.p.) = dec 160°C, Fisher Scientific), calcium chloride dehydrate (m.p. = dec 175 °C, Fisher Scientific), manganese(II) acetate tetrahydrate (m.p. = 80°C, Fisher Scientific), manganese(II) nitrate hydrate (m.p. = dec
30°C, Aldrich), manganese(II) nitrate tetrahydrate (m.p. = dec 37.1°C, Fisher Scientific), and manganese(II) nitrate hexahydrate (m.p. = dec 28°C, Aldrich).

Along the way, several suitable compounds of zinc, copper, and magnesium. Magnesium was identified p-type dopant of iron(III) oxide. In this work, we utilized magnesium(II) nitrate hexahydrate, Mg(NO₃)₂·6H₂O, Fisher Scientific (m.p. = dec. 95°C). For copper and zinc, copper sulfate pentahydrate (m.p. = dec 110°C), copper(II) nitrate hemipentahydrate (m.p. = 114°C, b.p = dec 170°C), zinc chloride dihydrate (m.p. = 170°C), and zinc nitrate hexahydrate (m.p. = dec 36°C) were studied. It was found that the nitrates for each metal generated the best p-Fe₂O₃ thin film electrodes.

Also, cadmium and tin should have theoretically provided good results because they have complimentary physical properties that closely match those of iron as well as the +2 state; however, the work done with cadmium nitrate tetrahydrate (m.p. = 59.5°C) and tin(II) chloride dihydrate (m.p. = dec 37°C) were used, but did not generate p-Fe₂O₃.

For the study of these compounds, there were several parameters that needed to be optimized each time. These parameters were the temperature of substrate, spray time, concentration of dopant precursor compound, carrier gas (oxygen) pressure, sprayer distance, and the angle of spray. There were other parameters that could be looked at including the continual spray on solution and electrolyte solution. Time constraints did not allow varying of the electrolyte solution. Continuous sprays, instead of 5 min breaks between 10 s sprays on the substrate, were carried out with reduced spray gas pressure, which produced layers on which droplets of solution overcooled the substrate. Hence, continuous sprays proved to be unrealistic with the experimental set-up being used. A sprayer that atomizes at lower pressures would be needed to do a continuous spray deposition.
C. Fabrication of Carbon Modified (CM)-n-TiO$_2$

We thermally oxidized a 0.25 mm thick Ti metal sheet (Strem Co.) in the presence of combustion products, CO$_2$ and steam (H$_2$O) in a natural gas flame with controlled amounts of oxygen added at a flow rate of \( \sim 350 \) ml min$^{-1}$. The flame temperature, measured with a digital pyrometer (Thermolyne Co.), was maintained close to 850$^{\circ}$C by controlling the flow rates of natural gas and oxygen. The best photoresponse was obtained with a pyrolysis time of 13 min. The CM-n-TiO$_2$ films were dark gray; whereas, the n-TiO$_2$ films prepared in an electric tube furnace under the same oxygen flow rate, at the same temperature, and time of pyrolysis (considered here as a reference sample of n-TiO$_2$ film) were very light gray.

D. Uv-vis Spectroscopic Measurements

UV-vis spectra of p-type and n-type Fe$_2$O$_3$ and CM-n-TiO$_2$ were recorded using a Varian Cary 1E uv-visible Spectrophotometer with a Varian GRID 386is-25 microprocessor and a Dell Optiplex PC. The samples were run in a Labsphere (model DRA-CA-30I) with a reflectance standard (I.D. USRS-99-010). The samples were standardized with an indium-doped tin oxide-coated glass substrate and its spectrum was used as the baseline and CM-n-TiO$_2$ was standardized with a titanium metal sheet. The spectra of all samples were measured in a wavelength range between 190 and 800 nm using double reverse reflectance.

E. Measurement of Photocurrent

Anodic and cathodic properties of the films were evaluated using a scanning potentiostat (EG&G Princeton Applied Research model 362) with an X-Y recorder (EG&G Houston model RE0092) controlling the potential of the working electrode in a three electrode cell with a 1.0 mm quartz window to minimize the loss of light through scattering. A Keithley multimeter was used
to monitor the photocurrent and measure electrode potential at open circuit conditions prior to scanning each sample. Fifteen minute intervals were The three electrode cell consisted of the Fe$_2$O$_3$ thin films (p-and n-type) as the working electrode, a platinum gauze as the counter electrode, and saturated calomel electrode (SCE, Fisher Scientific) as reference electrode. The electrolyte solution of 1.0 M NaOH solution for n-Fe$_2$O$_3$/Pt and 0.5 M H$_2$SO$_4$ for p-Fe$_2$O$_3$/Pt cells were used. 5 M KOH was used for CM-n-TiO$_2$/Pt cells The potential range of working electrode was from +1.0 to -0.1 V/SCE (for p-type) in the cathodic (negative) direction and -0.5 to +0.7 V/SCE in the anodic (positive) direction at a scan rate of 50 mV/sec. For CM-n-TiO$_2$, the potential range was -1.0 to +0.2 V/SCE in the anodic direction.

The surface of the n-Fe$_2$O$_3$ thin film electrode was illuminated with a light intensity of 40.0 mW/cm$^2$ from a 150 W xenon arc lamp (Kratos model LH 150/1). The intensity of the light was measured with a digital radiometer (International Light, model IL 1350). A monochromator (Kratos model GM100) with a 1.4 mm aperture was used to generate the light at a particular wavelength. A “hot” mirror from Edmund Electronics was used to reduce the excess IR radiation (which is not present in AM 1.5 solar radiation) from the xenon arc lamp.

**F. X-Ray Diffraction Spectra Measurements**

X-ray diffraction (XRD) patterns were measured by a Rigaku X-ray diffractometer. The scans were collected in the range from 28° to 70° (2θ) by use of copper Kα radiation ($\lambda = 1.5405$ Å) operating at 30 kV and 25 mA. The samples were run with a continuous scan at a rate of 0.100 degrees per minute with a recording period of 0.024 degrees. $\alpha$-Fe$_2$O$_3$ (Alfa Aesar), $\gamma$-Fe$_2$O$_3$ (Alfa Aesar), MgO (Fisher Chemical), ZnO (Alfa-Aesar), In$_2$O$_3$ (Alfa-Aesar), CuO (Sargeant-Welch), I$_2$ (Alfa-Aesar), MnO$_2$ (Acros Organics), CaO (Spectrum Chemical), and In$_2$O$_3$ (Alfa-Aesar) were scanned as references and compared with the XRD data of SPD produced p-type and n-type Fe$_2$O$_3$.
thin film samples. For CM-n-TiO₂ (flame-made) XRD were compared to n-TiO₂ (oven-made). A peak-fitting program (PowderCell 2.0) was able to correctly identify the peaks.

G. Scanning Electron Microscopy (SEM) and Energy Dispersive Analysis by X-rays (EDAX)

Scanning electron microscopy (SEM) was performed using a CamScan series 4 microscope operating at 50 kV with a tungsten filament on specimens upon which conductive carbon tape was used to make a contact with the conductive tin oxide surface to an aluminum sample deck. An electron microprobe attached to the SEM unit used in energy dispersive analysis by X-rays (EDAX) mode was employed to obtain information on the amount and presence of Fe₂O₃, Fe₂MgO₄, CuFe₂O₄, InFeO₃, I₂, Fe₂MnO₄, Fe₂CaO₄, or ZnFe₂O₄ in the metal-doped p- and n-Fe₂O₃ samples. The EDAX analysis was done with a Princeton GammaTech Inc. integrated microanalyzer software package.

H. X-ray Photoelectron Spectroscopic Measurements

X-ray photoelectron spectroscopic (XPS) measurements were carried out using a Leybold LHS-10 spectrometer with a magnesium Kα (1253.6 eV) X-ray source at a pass energy of 100 eV. The pressure in the analysis chamber was typically 2×10⁻⁸ torr. The spectra were curve-fitted using a damped non-linear least-squares fitting program (LOGAFIT).¹⁵⁶

I. Ac Impedance Measurements

The ac impedance of p-type or n-type Fe₂O₃ thin films was measured using an EG&G Two-Phase Lock-In Analyzer (model 5208) linked to an EG&G Potentiostat/Galvanostat (model 273). These two instruments were computer controlled by an EG&G hardware module (model 378) that
automatically was set to adjust the phase angle during each measurement. The ac amplitude was set to 10 mV for all measurements. For these measurements, the thin film electrode was the working electrode, platinum gauze was counter electrode and a SCE reference electrode was used. All measurements were carried out in 0.01 M H₂SO₄ (for p-type) and 0.5 M NaOH (for n-type) solutions in the dark.

The capacitance, C, was calculated using the following expression of impedance, Z, for a series capacitor-resistor model,

\[ Z = Z' + iZ'' \] (2.1)

where \( Z' \) is the real part of the impedance and \( Z'' \) is the imaginary part of the impedance, and \( i = (-1)^{1/2} \). The capacitance, C, can be obtained by using,

\[ Z'' = \frac{-i}{\omega C} \] (2.2)

where \( \omega = 2\pi f \) and \( f \) = the ac frequency in Hertz. The values of \( Z'' \) at different ac frequencies were obtained from Nyquist (\( Z'' \) versus \( Z' \)) plots generated from the measured data of impedance, \( |Z| \).

J. Calculations of Current Density for Metal Islet Electrodeposition

For the deposition of 6.0 µg of a metal per 1 cm², we need to know the amount of current to pass for 1 s for an electrode surface of 1 cm² using HMClₓ•xH₂O solution. We used the following equation:
\[ m = \left( \frac{i \times t_{\text{sec}}}{n \times F} \right) \times M \quad (2.3) \]

where \( m \) is the mass of electrocatalyst being deposited (6.08 µg), \( I \) is the current in amps that needs to be applied for electrocatalyst deposition, \( t_{\text{sec}} \) is the time used for deposition (1 or 2 s), \( n \) is the number of electrons transferred for the deposition of \( M \) (For Au\(^{3+}\) ion, \( n = 3 \) is used), \( F \) is the Faraday constant, and \( M \) is the molar mass of the catalyst metal (e.g., Au, Pt, etc.).

Solving Equation 2.3, for Au we find that \( i \) equals 8.936 mA/cm\(^2\); therefore, we needed to pass 8.936 mA current for 1 s or 4.468 mA for 2 s on an electrode area of 1 cm\(^2\). Hence, we would need to run a potentiostat in a 10 mA range while applying 0.4468 V, which would equal 4.468 mA/cm\(^2\) for a total application time of 2 s for Au deposition.

If the surface area is not 1 cm\(^2\), but 0.2 cm\(^2\), then we need to pass a current density of 250 µA/cm\(^2\). We need to use 250 µA/cm\(^2\)× 0.2 cm\(^2\), which equals -50 µA/sec or -25 µA for 2 s. A potentiostat is generally run in current mode during electrocatalyst deposition.

Electrodeposition of platinum was done with 0.1 M hydrogen hexachloroplatinate (IV) hydrate, where \( n = 4 \) was used in Equation 2.3. The electrodeposition was done on various samples from -400 to +500 µA/cm\(^2\). Electrodeposition of gold was done with 0.1 M hydrogen tetrachloroaurate(III) trihydrate. The electrodeposition was done on various samples from -400 to +500 µA/cm\(^2\). Electrodeposition of ruthenium was done with 0.1 M ruthenium(III) chloride hydrate, where \( n = 3 \) was used. The electrodeposition was done on various samples from +100 to +300 µA/cm\(^2\). Electrodeposition of nickel was done with 0.1 M nickel chloride hexahydrate, where \( n = 2 \) was used. The electrodeposition was done on various samples from +100 to +300 µA/cm\(^2\). All p-type semiconductor substrate electrodeposition was done under illumination of light at 100 mW/cm\(^2\).
3. Results and Discussion

3.1. Photoresponse of Spray Pyrolytically Synthesized Magnesium-doped Iron(III) oxide (p-Fe₂O₃) Thin Film Electrodes

A. Photocurrent-Potential Dependence

The results of photocurrent-potential dependence were optimized with respect to several parameters, including spray distance, angle of spray, temperature of substrate, carrier gas (i.e., O₂) pressure, spray solution (iron(III) chloride) concentration, dopant concentration, and spray time. We found a spray distance of 0.5 meter at an angle of 90° with respect to substrate surface and a carrier gas (oxygen) pressure of 138 kPa with 0.0132 M magnesium dopant and 0.11 M FeCl₃ solution to be the optimum conditions. The temperature of the tin oxide-coated glass substrate was varied from 380 to 420°C. The magnesium nitrate concentration was varied by an interval of 0.0055 M from magnesium concentrations that ranged from 0.011 to 0.0132 M.

Figure 3.1. Photocurrent density versus measured potential ($E_{\text{meas}}$, V/SCE) for p-Fe$_2$O$_3$ samples synthesized using different total spray times at a substrate temperature of 390°C under an illumination intensity of 40 mW/cm$^2$ from a 150 W Xe arc lamp. 0.0132 M magnesium doping in 0.11M iron(III) chloride spray solution in pure ethanol was used for the synthesis of p-Fe$_2$O$_3$. The dark current for the samples is also shown. The dark current was found to be identical for all samples shown.

Figure 3.1 shows the dependence of photocurrent density ($j_P$) as a function of measured potential ($E_{\text{meas}}$, V/SCE) for samples prepared at various spray times (80, 90, 100, 110, 120, 130, and 140 s) having 10 s spray periods. These samples were made at an optimal temperature of 390°C. The highest photocurrent density of 0.21 mA/cm$^2$ at 0.2 V/SCE at a light intensity of 40 mW/cm$^2$ from a 150 W Xe arc lamp was observed at the p-Fe$_2$O$_3$ thin film electrode synthesized using a total spray time of 130 s. These results show an upward trend for the samples prepared using a total spray time up to 130 s and then a sharp decline in photocurrent was observed for the sample prepared using a total spray time of 140 s. This behavior can be attributed to the fact that at lower spray times, the thickness of the film is not thick enough to absorb enough light. However, at higher spray times beyond 130 s, the quality and the conductivity of the films decline and as a result, the photocurrent density decreases.
The maximum photoconversion efficiency (\(\% \varepsilon_{\text{photo}}\)) as a function of total spray time is shown in Figure 3.2. The percent photoconversion efficiency (for \(j_p\) at \(E_{\text{meas}} = +0.2\) V/SCE) as a function of total spray time for different spray periods are shown in Figure 3.2. The maximum results of photoconversion efficiency for each of the three spray periods are outlined in Table 3.1. The thin films prepared using 8 s spray periods show lower photoresponse compared to those of 10 s spray periods. The 8 s spray period needed more sprays and layers compared to the 10 s spray period. This is likely to be responsible for the generation of lower quality thin films for the 8 s spray period compared to those fabricated by 10 s spray period. The thin films prepared using 15 s spray periods showed a substantial decrease in efficiency, which may be due to overcooling of the substrate compared to 8 and 10 s spray periods.

Figure 3.3 shows the total conversion efficiency (\(\% \varepsilon_{\text{total}}\)). The thin films were prepared using 8 (♦), 10 (▲), and 15 (■) s spray periods under 150 W xenon light illumination of 40.0 mW/cm². The films prepared using 10 s spray period showed 1% highest total conversion efficiency. The films prepared by using 8 s spray period have comparable results with approximately 0.9% maximum total conversion efficiency. However, the low quality film prepared by using 15 s spray time period showed a much lower result of total conversion efficiency of \(~0.45\%\).
Figure 3.2. Photoconversion efficiency versus total spray time for different spray periods: 8 (♦), 10 (▲), and 15 (■) s. Substrate temperature of 390°C for 8 and 10 s spray periods and 400°C for 15 s spray periods were used. Error bars are shown for a 95% confidence limit (CL) or a 2σ level of error with n = 4. All error bars presented hereafter are at a 95% confidence limit unless stipulated otherwise.

Figure 3.3. Total conversion efficiency, %ε_{total}, as a function of measured potential, E_{meas} (V/SCE) for 8 (♦), 10 (▲), and 15 (■) s spray periods. Substrate temperature of 390°C for 8 and 10 s spray periods and 400°C for 15 s spray periods were used.
Table 3.1. Percent photoconversion and total conversion efficiencies for water splitting at magnesium-doped p-Fe₂O₃ thin film electrodes prepared using various spray periods.

<table>
<thead>
<tr>
<th>Spray Period</th>
<th>Number of Sprays</th>
<th>$E_{aoc}$ vs SCE (V)</th>
<th>$E_{app} = (E_{meas} - E_{aoc})$ for $E_{meas} = +0.2$ V/SCE</th>
<th>$%\varepsilon_{\text{photo}}$</th>
<th>$%$ Total Conversion Efficiency‡</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>16</td>
<td>+0.88 V</td>
<td>-0.68 V</td>
<td>0.25%</td>
<td>0.84%</td>
</tr>
<tr>
<td>10</td>
<td>13</td>
<td>+0.81 V</td>
<td>-0.61 V</td>
<td>0.33%</td>
<td>0.99%</td>
</tr>
<tr>
<td>15</td>
<td>9</td>
<td>+0.82 V</td>
<td>-0.62 V</td>
<td>0.15%</td>
<td>0.42%</td>
</tr>
</tbody>
</table>

‡ At $E_{app} = -0.6$ V/SCE

Photocurrent density ($j_P$, mA/cm²) and the corresponding photoconversion efficiency ($\%\varepsilon_{\text{photo}}$) as a function of applied potential ($E_{app}$) for spray periods of 8 (♦), 10 (▲), and 15 (■) s are shown in Figures 3.4a and 3.4b, respectively. Photocurrent densities (Figure 3.4a), measured at +0.2 V/SCE and at an illumination intensity of 40 mW/cm², were found to be 0.18 mA/cm², 0.21 mA/cm², and 0.10 mA/cm², for the films prepared using 8, 10 and 15 s spray periods, respectively. The maximum photoconversion efficiencies (Figure 3.4b) were found to 0.25%, 0.33%, and 0.15% for 8, 10, and 15 s spray periods, respectively. The corresponding $E_{app}$ at these maximum efficiencies were -0.68, -0.61, and -0.62 V versus $E_{aoc}$ for samples prepared using 8, 10, and 15 s spray periods, respectively. The electrode potential at the open circuit under the same illumination of 40 mW/cm² were found to be +0.88, +0.81, and +0.82 V/SCE for the samples prepared using 8, 10, and 15 s, respectively. These results are summarized in Table 3.1. The discrepancies can be attributed to a mismatch in 15 layers at 8 s spray periods compared to 13 layers at 10 s spray periods. However, during the preparation of thin films by spray pyrolysis using 15 s spray period, the substrate temperature decreased to a greater extent and consequently the film quality declined.
Figures 3.4a & 3.4b. Photocurrent density ($j_P$, mA/cm$^2$) (a) and percent photoconversion efficiency ($\% \varepsilon_{\text{photo}}$) vs measured potential, $E_{\text{meas}}$ (V/SCE) (b) at p-Fe$_2$O$_3$ electrodes prepared using 8 (♦), 10 (▲), and 15 (■) s spray periods. 0.0132 M magnesium doping in 0.11M iron(III) chloride spray solution in pure ethanol was used for the production of p-Fe$_2$O$_3$. The electrode potentials at the open circuit, $E_{\text{aoc}}$ (a) were $+0.88$, $+0.81$, and $+0.82$V vs SCE for p-Fe$_2$O$_3$ prepared using 8 (♦), 10 (▲), and 15 (■) s spray periods, respectively. Substrate temperatures of 390°C for 8 and 10 s spray periods and 400°C for 15 s spray periods were used.

B. Reproducibility of Photoresponse

An important hallmark to thin film fabrication is the reproducibility of the synthesis of any given semiconductor. To test the reproducibility of magnesium-doped p-Fe$_2$O$_3$ thin films, eight samples were synthesized at the optimum conditions of 390°C for 130 s total spray time with 10 s spray periods using a spray solution of 0.11 M FeCl$_3$ and 0.0132 M Mg(NO$_3$)$_2$ in absolute ethanol. Photocurrents of these samples were measured in 0.5 M H$_2$SO$_4$ electrolyte using a light intensity
of 40.0 mW/cm². The electrode potentials of these samples at open circuit conditions were found to be +0.85 ± 0.05 V/SCE.

**Figure 3.5** shows the photocurrent density ($j_P$, mA/cm²) versus measured potential, $E_{\text{meas}}$ (V/SCE). All eight samples had a constant set of values. At $+0.2$ V/SCE, the samples had a fairly constant value for maximum photocurrent density, which represented also the maximum efficiency point. An average photocurrent density of 0.208 mA/cm² was found at $+0.2$ V/SCE for these samples. These data points correspond to a standard deviation ($\sigma$) of $\pm 0.00287$ mA/cm². This indicates a good reproducibility by spray pyrolytically synthesizing p-Fe₂O₃ thin films in the present work.

![Figure 3.5](image_url)

**Figure 3.5.** The photocurrent density versus the measured potential ($E_{\text{meas}}$) of eight p-Fe₂O₃ films synthesized by SPD under identical conditions are shown to test reproducibility. The conditions used on the eight samples were 10 s spray intervals with 130 s total spray time, 0.11 M FeCl₃ and 0.0132 M Mg(NO₃)₂ in absolute ethanol, pyrolysis temperature of 390°C, electrolyte solution of 0.5 M H₂SO₄, and a light intensity of 40.0 mW/cm² from a 150 W Xe arc lamp. All samples had the electrode potential of $+0.85 \pm 0.05$ V/SCE at open circuit conditions.
C. The Effect of Substrate Temperature

The most important parameter for spray pyrolytic synthesis of efficient p-Fe$_2$O$_3$ semiconductors was found to be the temperature of the substrate. Samples were fabricated initially at substrate temperatures of 385°C, 400°C, 415°C, etc. with 15 ± 2°C variation to have a rough range of the optimum temperature. The temperature was then varied by 5 ± 1°C from 380°C to 415°C. This resulted in an increased accuracy in finding the optimum temperature for the synthesis of better quality p-Fe$_2$O$_3$ thin films. Maximum photocurrent efficiencies versus substrate temperature (°C) for 10 s spray periods are shown in Figure 3.6. There is a distinct peak in the efficiency (~0.33%) at 390°C, with a sharp decline when the temperature was decreased or increased by 5°C. The photocurrent density decreased approximately 50% when the temperature was increased from 390°C by 5°C to 395°C. At temperatures below 390°C, it is most likely that the iron and magnesium are not fully oxidized and various partially oxidized states of iron and magnesium exist along with fully oxidized Fe$_2$O$_3$ and Fe$_2$MgO$_4$, or more likely that the structure are more amorphous at lower temperatures. At temperatures above 390°C, the dramatic lowering in photocurrent is likely due to the smoothing of the surface and hence reduction of effective surface area was as demonstrated in a prior work. This indicates that the temperature of the substrate plays a vital role in fabricating the best quality p-Fe$_2$O$_3$ by SPD, or for that fact any fabrication process.
Figure 3.6. Maximum photoconversion efficiency versus temperature (°C) of the glass substrate for p-Fe₂O₃ thin films prepared using 10 s spray periods having a total spray time of 130 s.

D. The Effect of Dopant Concentration

The effect of magnesium dopant concentration on photocurrent and photoconversion efficiencies is shown in Figure 3.7. The concentration of magnesium dopant was varied while keeping the iron concentration fixed at 0.11 M FeCl₃·6H₂O. Like substrate temperature the doping concentration was found to be just as vital for better photoresponse. The magnesium dopant concentration of 0.0132 M was found to be optimum (Figure 3.7). If the dopant concentrations were decreased by 0.5%, the photocurrent and photoconversion efficiency both went down more than 50%, and if the dopant concentration were increased by 0.5%, the photocurrent and photoconversion efficiency decreased more than 60%. This large effect on photocurrent and photoconversion efficiency demonstrates the importance of the optimization of parameters for the synthesis of efficient p-Fe₂O₃ thin films by magnesium doping.
Figure 3.7. The effects of magnesium dopant concentration on photocurrent and photoconversion efficiencies. The concentration of magnesium dopant was varied keeping iron concentration constant at 0.11 M FeCl₃·6H₂O.

E. Uv-vis Spectroscopic Results

Figure 3.8 shows the uv-vis spectroscopic data for an optimized magnesium-doped p-type Fe₂O₃ semiconductor. The absorption spectrum exhibits a high degree of absorption in the uv region, which extends into the visible region, with a tail extending to 568 nm. The threshold of absorption at 568 nm (2.19 eV) is in approximate agreement with the band gap value of 2.2 eV for undoped Fe₂O₃. This sample was synthesized using the optimum conditions which include 10 s spray periods with 130 s total spray time, using 0.11 M FeCl₃ and 0.0132 M Mg(NO₃)₂ in absolute ethanol as the sprat solution and a pyrolysis temperature of 390°C.
Figure 3.8. Uv-vis reflectance data for magnesium-doped p-Fe$_2$O$_3$ thin film electrodes.

F. X-Ray Diffraction Results

Figure 3.9 shows X-ray diffraction (XRD) plots of magnesium-doped p-type iron(III) oxide (p-Fe$_2$O$_3$) thin film electrodes of optimum properties. The peaks on the plots were identified as $\alpha$-Fe$_2$O$_3$ (a), In$_2$O$_3$ (b), and iron(III) magnesium oxide, Fe$_2$MgO$_4$ (c). These peaks indicate that spray pyrolytically synthesized p-Fe$_2$O$_3$ have mixed structures of $\alpha$-iron(III) oxide, as well as the presence of Fe$_2$MgO$_4$. The In$_2$O$_3$ was from the indium-doped tin oxide substrate. A peak-fitting program (PowderCell 2.0) was able to correctly identify the peaks.

The average crystal size was 4.96 nm for $\alpha$-Fe$_2$O$_3$ and 0.30 nm for Fe$_2$MgO$_4$. With the low amount of magnesium precursor added to the spray solution, there is a low amount of material available for crystal formation, thus the crystals are more than a factor of ten times smaller than the Fe$_2$O$_3$ crystals.
Figure 3.9. X-ray diffraction (XRD) plots of magnesium-doped p-type iron(III) oxide (p-Fe$_2$O$_3$) thin film electrodes. The peaks on the plots were identified as $\alpha$-Fe$_2$O$_3$ (a), In$_2$O$_3$ (b), and magnesium iron(III) oxide, MgFe$_2$O$_4$ (c).

It was reported earlier$^{68,94,111,118,120}$ that the best Fe$_2$O$_3$ semiconductors are of mixed states. Our magnesium-doped thin films are of mixed states, $\alpha$-Fe$_2$O$_3$ and Fe$_2$MgO$_4$. The presence of Fe$_2$MgO$_4$ in the XRD plots clearly shows the presence of magnesium dopant in the thin film.$^{82}$ Pure $\alpha$-state iron(III) oxide semiconductors have very poor conductivity and have shown almost zero photocurrent.$^{68,94,111,118,120}$ Hence, these mixed structures of $\alpha$-Fe$_2$O$_3$ and Fe$_2$MgO$_4$ of spray pyrolytically synthesized samples are responsible for higher photocurrent densities as compared to earlier results.$^{108,111,116,158}$
G. Photoresponse of Electro catalyst Deposited p-Type Iron(III) Oxide Thin Films towards Water Splitting

Electrodeposition of electrocatalysts have been done on n-type Fe₂O₃ in prior publications, but none have been done on p-type Fe₂O₃. Electrodeposition was carried out by the same method outlined earlier. Various metals islets of platinum, gold, ruthenium, and nickel were deposited galvonstatically at a various current densities. The samples were illuminated with the xenon lamp at 100 mW/cm² during electrodeposition.

![Photoresponse of Electro catalyst Deposited p-Type Iron(III) Oxide Thin Films towards Water Splitting](image)

**Figure 3.10.** Photocurrent density, \( j_p \), versus measured potential, \( E_{\text{meas}} \) (V/SCE), at magnesium-doped p-Fe₂O₃ for platinum, gold, ruthenium, and nickel photoelectrodeposited samples in 0.5 M H₂SO₄ solution. Electrodeposition was carried out at -250 µA/cm².
Figure 3.11. Photoconversion efficiencies for platinum, gold, ruthenium, and nickel deposition at -250 μA/cm² for one second on magnesium-doped p-Fe₂O₃. The fabrication conditions include: substrate temperature of 390°C; spray time of 90 s; spray solvent of absolute ethanol; dopant concentration of 0.01265 M Mg(NO₃)₂ and electrolyte solution of 0.5 M H₂SO₄. The open circuits are as follows: zero second = +0.924 V; one second of metal deposition = +0.923 V.

Figure 3.10 shows the photocurrent density for magnesium-doped p-Fe₂O₃ without electrocatalyst and then with 1 s of deposition of platinum, gold, ruthenium, and nickel. Platinum and gold did not improve photoresponse, but reduced it. Ruthenium electrocatalyst had little effect, except at voltages close to zero. The only positive electrocatalyst was nickel, which showed a minimal improvement in photocurrent density at all measured voltages. Figure 3.11 shows photoconversion efficiency for the same samples. The results are almost identical to photocurrent density; however, ruthenium showed a slightly higher than expected photoconversion efficiency.
3.2. Photoresponse of Spray Pyrolytically Synthesized Copper-Doped p-Fe₂O₃ Thin Film Electrodes towards Water Splitting

A. Photocurrent Density-Potential Dependence

Figure 3.12 shows the dependence of photocurrent density, jₚ, as a function of measured potential (Eₘₑₐₛ, V/SCE) for samples prepared by various spray times (70, 80, 90, 100, and 110 s) using 10 s spray periods. These samples were made at an optimal temperature of 395°C. The photocurrent densities for each sample were found to increase up to 0.0 V/SCE, and then the photocurrent became zero when the potential becomes more cathodic to -0.1 V/SCE. This was because at this cathodic potential, the dark current became dominant due to reduction of Fe₂O₃ and its consequent partial degradation. Hence, no limiting photocurrent was observed as shown in Fig. 3.12.

B. Photocurrent Density-Spray Time Dependence

Figure 3.13 shows the dependence of photocurrent density, jₚ, as a function of spray time at a measured electrode potential of 0.0 V/SCE. It is observed that photocurrent density increases with an increase in spray time and then decreases beyond 100 s total spray time. This behavior can be attributed to the fact that with an increase in spray time the thickness of the films increases, which will then allow the sample to absorb more light photons and as a result the photocurrent density increases. However, with an increase in the spray time beyond 100 s, the photoresponse of the film decreased considerably due to a mismatch of too many layers beyond an optimum number of layers (i.e., 10 layers for these samples) and consequently an increase in the resistivity of the film.

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This change in the film quality was observed when its color changed from yellow to reddish-brown when it was prepared using more than 100 s total spray time.

![Figure 3.12.](image)

**Figure 3.12.** Photocurrent density, $j_P$, at light intensity of 40.0 mW/cm$^2$ versus measured potential ($E_{\text{meas}}$, V/SCE) for copper-doped p-Fe$_2$O$_3$ samples produced for various total spray times at a substrate temperature of 395°C. 0.01155 M Cu$^{2+}$ doping in 0.11M iron(III) chloride spray solution in pure ethanol was used for the synthesis of p-Fe$_2$O$_3$. The electrode potential at open circuit conditions was found to vary from +0.70 to +0.75 V/SCE in 0.5 M H$_2$SO$_4$ electrolyte. The dark current results are also shown and were the same for all samples.

C. The Effect of Substrate Temperature

Photocurrent density, $j_P$, versus the temperature of the substrate on the hot plate is shown in **Figure 3.14.** It shows a maxima at a substrate temperature of 395°C. It is observed that a small change in substrate temperature makes a large difference in photoresponse in terms of photocurrent density, $j_P$. Note that the photocurrent density at each temperature corresponds to its optimum molar concentration (0.0110 to 0.0132 M) of Cu$^{2+}$ dopant. Though substrate temperature and the copper dopant concentration were found critical in synthesizing optimum quality p-Fe$_2$O$_3$ thin films, no simple trends were found between them.
**Figure 3.13.** Photocurrent density, $j_P$, at copper-doped $p$-$\text{Fe}_2\text{O}_3$ electrodes at an illumination intensity of 40 mW/cm$^2$ and at a potential of 0.0 V/SCE versus spray time. A substrate temperature of 395°C was used to synthesize these thin films. A 0.5 M $\text{H}_2\text{SO}_4$ was used as the electrolyte. An optimum copper dopant concentration of 0.01155 M was used to synthesize these thin films.

**Figure 3.14.** Photocurrent density, $j_P$, at a copper-doped $p$-$\text{Fe}_2\text{O}_3$ thin film electrode (at an illumination intensity of 40 mW/cm$^2$ at an electrode potential of 0.0 V/SCE) versus temperature of substrate surface. At each temperature, the optimum copper dopant concentration (0.01155M) was utilized using a total spray time of 100 s. 0.5 M $\text{H}_2\text{SO}_4$ was used as the electrolyte.
Figure 3.15. Photocurrent density (at 0.0 V/SCE) at copper-doped p-Fe$_2$O$_3$ thin film electrode versus Cu$^{2+}$ concentration used as the dopant. The samples were synthesized using a total spray time of 100 s and at 390°C and 395°C.

D. The Effect of Copper Concentration

In Fig. 3.15, it can be seen that the photocurrent was low when Cu$^{2+}$ dopant concentration was low (around 0.099 M [Cu$^{2+}$]) and then increased to a maximum when the [Cu$^{2+}$] was 0.01155 M. After 0.01155 M [Cu$^{2+}$], there was a slow, but steady decline in photocurrent. With a lowering of the temperature by 5°C, the maximum shifted to a higher Cu$^{2+}$ concentration of 0.01265 M and the photocurrent density at the maximum point decreased. The maximum photocurrent density, $j_p$, for the samples prepared using the substrate temperature above and below 395°C did not match the photocurrent density observed for the samples prepared using this temperature for the substrate at the lower concentration of 0.01155 M.

E. Reproducibility of Photocurrent Density

An important aspect of the synthesis of thin films is the reproducibility of photoresponse when samples are spray pyrolytically synthesized using identical conditions. To test the reproducibility
of photoresponse for copper-doped p-Fe$_2$O$_3$ thin films, three samples were synthesized at an optimum temperature of 395°C, total spray time of 100 s using a spray solution of 0.11 M FeCl$_3$·6H$_2$O and 0.01155 M Cu(NO$_3$)$_2$ in ethanol. Photocurrents of these samples were measured in 0.5 M H$_2$SO$_4$ electrolyte using a light intensity of 40.0 mW/cm$^2$. These three samples were found to have an electrode potential of $+0.70 \pm 0.04$ V/SCE at open circuit conditions. Figure 3.16 shows the photocurrent density, $j_p$, versus measured potential, $E_{\text{meas}}$ (V/SCE). All three samples exhibit almost equal values of photocurrent densities at all measured potentials. At $+0.0$ V/SCE, the samples showed fairly consistent values for maximum photocurrent density. An average photocurrent density of 0.844 mA/cm$^2$ was found at $+0.0$ V/SCE for these samples. These data points correspond to a standard deviation ($\sigma$) of $\pm 0.019$ mA/cm$^2$. These results of photocurrent densities show excellent reproducibility for the synthesis of copper-doped p-Fe$_2$O$_3$ by spray pyrolytic deposition (SPD).

![Figure 3.16](image_url)

**Figure 3.16.** Photocurrent density, $j_p$ at copper-doped p-Fe$_2$O$_3$ thin film electrode at an illumination intensity of 40 mW/cm$^2$ versus the measured potential, $E_{\text{meas}}$ (V/SCE) of three p-Fe$_2$O$_3$ films synthesized by SPD to demonstrate the reproducibility for the synthesis of p-Fe$_2$O$_3$ by copper doping using a spray time of 100 s and a substrate temperature of 395°C. All samples had an electrode potential of $E_{\text{aoc}} = 0.70 \pm 0.04$ V/SCE at open circuit conditions under illumination of 40 mW/cm$^2$. 0.5 M H$_2$SO$_4$ was used as the electrolyte.
F. Photoconversion Efficiency

Figure 3.17 shows the percent photoconversion efficiency versus $E_{\text{app}}$ (vs $E_{\text{aoc}}$) for copper-doped p-Fe$_2$O$_3$ films. At a measured potential of 0.0 V/SCE at which the applied potential becomes $E_{\text{app}} = +0.7$ V, a maximum photoconversion efficiency of 1.26% was observed.

Figure 3.18 shows the total conversion efficiency ($\%\epsilon_{\text{total}}$) versus $E_{\text{app}}$ (vs $E_{\text{aoc}}$) for copper-doped p-Fe$_2$O$_3$ thin films under a 150 W xenon arc lamp using a light intensity of 40.0 mW/cm$^2$. The results indicate a maximum total efficiency of 2.9% for copper-doped p-Fe$_2$O$_3$, which is more than ten times higher than those reported earlier for magnesium-doped p-Fe$_2$O$_3$ thin film electrodes.$^{30,108,111,116}$

![Photoconversion Efficiency](image)

**Figure 3.17.** Maximum photoconversion efficiency ($\%\epsilon_{\text{photo}}$) at copper-doped p-Fe$_2$O$_3$ thin film electrode at light intensity of 40.0 mW/cm$^2$ as a function of applied potential, $E_{\text{app}}$ (V vs $E_{\text{aoc}}$, $E_{\text{aoc}} = + 0.7$ V/SCE) for samples prepared at a substrate temperature of 395°C with a total spray time of 100 s at 0.01155 M of Cu$^{2+}$ dopant.

G. Uv-vis Spectroscopic Results

Figure 3.19 shows the uv-vis spectroscopic data for a copper-doped p-type Fe$_2$O$_3$ semiconductor. The absorption spectrum shows a broad absorption in the ultraviolet (UV) to
visible region with a tail extending to 550 nm. The threshold of absorption at 550 nm (2.25 eV) is in close agreement with a band gap value of 2.2 eV for n-Fe₂O₃. This sample was synthesized using an optimum substrate temperature of 395°C, 100 s total spray time, spray solution of 0.11 M FeCl₃ and 0.01155 M of Cu(NO₃)₂.

Figure 3.18. Total conversion efficiency, \( \varepsilon_{\text{total}} \), at copper-doped p-Fe₂O₃ thin film electrode at light intensity of 40.0 mW/cm² as a function of applied potential, \( |E_{\text{app}}| \) (V vs. \( E_{\text{aoc}} \), \( E_{\text{aoc}} = +0.7 \) V/SCE) for samples prepared at a substrate temperature of 395°C. 95% CL error bars are shown for a total spray time of 100 s at 0.01155 M of Cu²⁺ dopant.

**H. X-Ray Diffraction (XRD) Results**

Figure 3.20 shows X-ray diffraction (XRD) plots of p-type iron(III) oxide (p-Fe₂O₃) thin film electrodes. The peaks on the plots were identified as \( \alpha \)-Fe₂O₃ (a), In₂O₃ (b), and copper(II) iron(III) oxide, CuFe₂O₄ (c). Figure 3.20 indicates that \( \alpha \)-Fe₂O₃ is the only form of iron oxide present in the thin films. Indium oxide (peaks labeled as b) from the indium-doped tin oxide substrate was identified. Analysis of XRD confirms that copper dopant did not exist as solid copper or copper oxide. All copper was identified in the form of CuFe₂O₄. These peaks
indicate that spray pyrolytically synthesized p-Fe$_2$O$_3$ has mixed structures of α-iron(III) oxide and copper(II) iron(III) oxide (CuFe$_2$O$_4$). Pure Fe$_2$O$_3$ lacks adequate conductivity to be an effective semiconductor; whereas, the presence of copper in the form of CuFe$_2$O$_4$ was found to show improved magnetic and conductive properties$^{163}$ making it a suitable match for Fe$_2$O$_3$, when introduced in optimum ratios. Pure α-state iron(III) oxide was found to be unstable in acidic solution.$^{104}$ On the other hand, these Cu-doped iron oxide electrodes showed signs of deterioration in an acidic solution over time, making copper doping an unfavorable process. Pure α-state iron(III) oxide semiconductors have very poor conductivity and have shown almost zero photocurrent,$^{104}$ hence, mixed structures of spray pyrolytically synthesized p-Fe$_2$O$_3$ samples were responsible for improved photocurrents compared to earlier results.$^{30,108,111,116}$

The average crystal size was 5.73 nm for α-Fe$_2$O$_3$ and for CuFe$_2$O$_4$, it was indeterminate because the peaks for CuFe$_2$O$_4$ were not defined or large enough to do a Scherer calculation, thus the crystal size is approaching 0.10 nm or 1Å. With the low amount of copper precursor added to the spray solution, there is a low amount of material available for crystal formation, thus the crystals are more than a factor of fifty times smaller than the Fe$_2$O$_3$ crystals.

![Figure 3.19. Uv-vis reflectance data for copper-doped p-Fe$_2$O$_3$ thin film electrodes.](image-url)
I. XPS Results

The X-ray photoelectron spectroscopic (XPS) data showed a 0.2 atomic % of copper in the copper-doped p-Fe$_2$O$_3$ thin films prepared by use of an optimum dopant concentration of 0.01155 M [Cu$^{2+}$] in the spray solution.

![XPS spectrum](image)

**Figure 3.20.** X-ray diffraction (XRD) plots of copper-doped p-type iron(III) oxide (p-Fe$_2$O$_3$) thin film electrodes. The peaks on the plots were identified as $\alpha$-Fe$_2$O$_3$ (a), In$_2$O$_3$ (b), and copper(II) iron(III) oxide, CuFe$_2$O$_4$ (c).

J. Flatband Potentials and Acceptor Density determined from Mott-Schottky Plots

**Figure 3.21** illustrates a Mott-Schottky plot for a copper-doped p-Fe$_2$O$_3$ thin film measured at various ac frequencies (250 Hz and 791 Hz) under dark conditions with the following conditions: electrolyte solution, 0.01 M H$_2$SO$_4$; ac amplitude, 10 mV; spray solution concentration, 0.11 M FeCl$_3$ in 100% ethanol; spray time, 80 s; copper doping, 0.01265 M; substrate temperature, 395°C; the reference saturated calomel electrode (SCE) and a platinum gauze counter electrode. For both
ac frequencies, an intercept at +0.1 V/SCE was observed. Hence, after subtraction of the thermal contribution, kT/e₀, with T=296 K, a flat band potential of +0.08 V/SCE was found, which is 0.32 V/SCE more negative than the onset potential at +0.4 V/SCE (see Figure 3.12). This value for the flatband potential is consistent with results reported earlier for Fe₂O₃ semiconductors.²,⁸,¹⁰⁶,¹¹⁹

![Figure 3.21](image-url)

**Figure 3.21.** Mott-Schottky (1/C² vs measured potential, E_meas, where C is the capacitance) plot for a copper-doped p-Fe₂O₃ film measured at various ac frequencies under dark conditions: electrolyte solution, 0.01 M H₂SO₄; ac amplitude, 10 mV; spray solution concentration, 0.11 M FeCl₃ in 100% ethanol; spray time, 100 s; copper doping, 0.01265 M; substrate temperature, 395°C.

From the slopes of the Mott-Schottky plots we find the acceptor density, N_d = 4.41 x 10¹⁷ cm⁻³ and 5.57 x 10¹⁷ cm⁻³ at ac frequencies of 791 Hz and 250 Hz, respectively. To calculate these results a dielectric constant of 12 was used for Fe₂O₃.² These results are three orders of magnitude lower than for self-doped n-Fe₂O₃ results reported earlier.² These lower acceptor densities may be responsible for the lower efficiencies of copper-doped p-Fe₂O₃ compared to n-Fe₂O₃.² The
acceptor density is found to be higher for the lower frequency which is consistent with the fact that surface states contribute at lower frequencies.

K. Onset Potential

Figure 3.16 shows the dependence of photocurrent density, $j_p$, with respect to the measured potential ($E_{\text{meas}}$) for copper-doped p-Fe$_2$O$_3$ thin films. The photocurrent is found to start at +0.4 V/SCE, which is 0.3 V/SCE more negative than the electrode potential at the open circuit condition, $E_{\text{aoc}} = +0.7$ V/SCE. This behavior was found to be common for copper-doped p-Fe$_2$O$_3$ thin films made using various spray times. This onset potential, however, was observed only in acidic (0.5 M H$_2$SO$_4$) conditions at pH = 0.0. The onset potential, $E_{\text{onset}}$, of +0.4 V/SCE and the flatband potential, $E_{\text{fb}}$, of +0.08 V/SCE did not match in this case because of charge transfer interference at semiconductor-solution interface. This is because unlike a Schottky junction in the solid state, the charge transfer can occur via tunneling through the interfacial barrier prior to 0.32 V and preceding the band flattening out at the flat band potential.
3.3. Photoresponse of p-Type Zinc-doped Iron(III) Oxide Thin Films

A. Photocurrent Density

Figure 3.22 shows the dependence of cathodic photocurrent density, $j_p$ (mA/cm$^2$), on measured potential ($E_{meas}$, V/SCE) for p-Fe$_2$O$_3$ samples. The highest photocurrent density of 1.24 mA/cm$^2$ at 0.0 V/SCE at a light intensity of 40 mW/cm$^2$ was observed for a p-Fe$_2$O$_3$ thin film electrode synthesized using a spray time of 80 s and a substrate temperature of 663 K. All the samples used in the figure were synthesized using a spray solution of 0.0088 M zinc nitrate and 0.11 M iron(III) chloride in 100% absolute ethanol. These p-Fe$_2$O$_3$ thin film electrodes showed electrode potentials at open circuits from +0.82 to +0.90 V/SCE. The dark currents for these samples are also shown and found to be identical for all these samples. The photocurrent density at the measured potential of 0.0 V/SCE as a function of spray times is given in Figure 3.23. The highest photocurrent density is observed for the sample prepared using a spray time of 70 s.

The p-Fe$_2$O$_3$ thin film synthesized in this work by zinc doping showed higher photoresponses compared to those presented in prior works, where p-Fe$_2$O$_3$ electrodes were prepared by pellet pressing methods. For example, in a prior work the maximum photocurrent density of $\sim$0.48 mA/cm$^2$ was observed compared to 1.13 mA/cm$^2$ observed in this study under the same illumination conditions. The difference in the photocurrent density to prior works can be attributed to better quality uniform thin films generated by spray pyrolysis versus pellet pressing methods employed earlier to fabricate p-Fe$_2$O$_3$ electrodes. Furthermore, use of single crystals would be quite expensive for mass production, whereas spray pyrolysis provides a convenient and inexpensive method for mass production of p-Fe$_2$O$_3$ thin film semiconductors.

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Figure 3.22. Photocurrent density, \( j_P \) (mA/cm\(^2\)), under an illumination intensity of 40 mW/cm\(^2\) versus the measured potential, \( E_{meas} \) (V/SCE), for zinc-doped p-Fe\(_2\)O\(_3\) samples synthesized at various spray times at a substrate temperature of 663 K. 0.0088 M zinc doping in 0.11M iron(III) chloride spray solution in pure ethanol was used for the synthesis of p-Fe\(_2\)O\(_3\). The dark current for the samples is shown and was found to be identical for all samples. The open circuit potential was 0.832 ± 0.05 mA/cm\(^2\).

Figure 3.23. Dependence of maximum photocurrent density (\( j_p \), mA/cm\(^2\)) at \( E_{meas} = 0.0 \) V/SCE on the spray time during the spray pyrolytic synthesis of zinc-doped p-Fe\(_2\)O\(_3\) thin film electrodes. The spray conditions include: spray solution concentration of 0.11 M FeCl\(_3\) with 0.0088 M zinc nitrate in 100% ethanol; substrate temperature of 663 K; light intensity of 150 W Xe lamp, 40 mW/cm\(^2\); electrolyte solution, 0.5 M H\(_2\)SO\(_4\).
Figure 3.24 shows the highest current density of 1.1 mA/cm² under an illumination intensity of 40 mW/cm² for optimized zinc-doped p-Fe₂O₃ thin films when a two-electrode system involving a platinum counter electrode was used. This value is close to the highest photocurrent density of 1.13 mA/cm² in a three-electrode system. The increase in photocurrent density with an increase of cathodic bias indicates the p-type conductivity of zinc-doped Fe₂O₃ thin films. Beyond a cathodic bias of –0.8 V/Pt, the dark current density and the current density under illumination were found to be identical due to reduction of Fe₂O₃ at higher cathodic potentials beyond -0.8 V/Pt. Hence, no limiting region was observed for zinc-doped p-Fe₂O₃ thin films.

**Figure 3.24.** Cathodic current density at zinc-doped p-Fe₂O₃ under illumination with a light intensity of 40 mW/cm² from a 150 W xenon arc lamp vs a platinum electrode in a two electrode configuration. Measurements were done in 0.5 M H₂SO₄ solution. The open circuit potential was found to be -0.25 V/Pt.

**B. Reproducibility of Photocurrent Density**

An important aspect for the synthesis of thin films is the reproducibility of photocurrent when they are made by SPD using identical conditions. To test the reproducibility of photocurrent for zinc-doped p-Fe₂O₃ thin films, three samples were synthesized at the optimum temperature of...
390°C for a total spray time of 70 s using a spray solution of 0.11 M FeCl\textsubscript{3}·6H\textsubscript{2}O and 0.0088 M Zn(NO\textsubscript{3})\textsubscript{2} in ethanol. The photocurrent density, \(j_p\), vs measured potential, \(E_{\text{meas}}\) (V/SCE), are shown in Figure 3.25. Photocurrents of these samples were measured in 0.5 M H\textsubscript{2}SO\textsubscript{4} electrolyte solution using a light intensity of 40.0 mW/cm\textsuperscript{2}. All three samples exhibit almost identical values of photocurrent density at each of the measured potentials. At +0.0 V/SCE, the samples showed fairly consistent values for maximum photocurrent density. An average photocurrent density of 1.179 mA/cm\textsuperscript{2} (1.114, 1.184, and 1.240 mA/cm\textsuperscript{2}) was found at +0.0 V/SCE. These data points correspond to a standard deviation (\(\sigma\)) of ±0.052 mA/cm\textsuperscript{2}. These photoresponse results show excellent reproducibility for the synthesis of zinc-doped p-Fe\textsubscript{2}O\textsubscript{3} by SPD.

![Figure 3.25](image-url)

**Figure 3.25.** Reproducibility test of spray pyrolytic synthesis of p-Fe\textsubscript{2}O\textsubscript{3} thin film electrodes. The average results of photocurrent density versus the electrode potential for three p-Fe\textsubscript{2}O\textsubscript{3} films synthesized by SPD were plotted.

**C. Dependence on Zinc Dopant Concentration**

It can be seen in Figure 3.26 that the photocurrent density increased with an increase of the zinc dopant concentration from 0.0077 to 0.0088 M. After 0.0088 M, there was a steady decline in photocurrent density up to 0.011 M. The plateau region (between 0.0088 and 0.011 M) was
seen only when all other parameters were kept fixed to optimized values. However, changing the optimum temperature of the substrate from 390 to 395°C removed this plateau region. The lowering of the photocurrent beginning at 0.011 M zinc dopant concentration can be attributed to enhanced recombination of photogenerated carriers in the presence of excess zinc dopant.

Figure 3.26. The dependence of photocurrent density on zinc dopant concentration (M) in 0.11 M FeCl₃·6H₂O spray solution at measured potential, E_{meas} = 0.0 V/SCE. All samples were synthesized using a total spray time of 70 s.

D. Quantum Efficiency

The results of quantum efficiency versus the wavelength of light were plotted in Figure 3.27. The zinc-doped p-Fe₂O₃ using 0.0088 M zinc dopant showed a maximum quantum efficiency of 21.1% at 325 nm and the threshold was observed at 590 nm, which corresponds to a band gap of 2.1 eV. However, in an earlier study, a magnesium-doped p-Fe₂O₃ electrode showed a maximum quantum efficiency of 3.0% at 380 nm and a threshold was observed at ~515 nm. A maximum quantum efficiency of 10.97% was observed at wavelength 325 nm. Quantum efficiencies for zinc doping at 0.0088, 0.0099, and 0.01155 M are shown in Figure 3.27. As is
shown the quantum efficiency at these two dopant concentrations is considerably lower than the quantum efficiency at the optimum zinc concentration. At lower wavelengths from 300 to 425 nm, the quantum efficiency difference is a difference of 10 percentage points, and at higher wavelengths, the difference is lowered to around 5 and <5 percentage points. Undoped n-Fe$_2$O$_3$ is also shown in Figure 3.27. As can be seen, the quantum efficiency is low and matches that of the 0.0099 and 0.01155 M zinc-doped p-Fe$_2$O$_3$ samples.

![Quantum efficiency graph](image)

**Figure 3.27.** Quantum efficiency, $\eta(\lambda)$, versus the wavelength, $\lambda$, of light for zinc-doped p-Fe$_2$O$_3$ synthesized using 0.0088, 0.0099, and 0.01155 M (Zn(NO$_3$)$_2$) and undoped n-Fe$_2$O$_3$, measured at a potential of +0.2 V/SCE (+0.5 V/SCE for n-Fe$_2$O$_3$) using a Kratos model GM 100 monochromator with a 1.4 mm slit width. 0.5 M H$_2$SO$_4$ was the electrolyte solution, and a total light intensity of 40 mW/cm$^2$. The spray conditions include: spray solution concentration of 0.11 M FeCl$_3$ with various zinc nitrate concentrations given above in 100% ethanol and a substrate temperature of 390°C.

**E. Band gaps**

**Figure 3.28** shows plots of $(\eta h \nu)^{1/2}$ (for indirect band gap) and $(\eta h \nu)^{2}$ (for direct band gap) versus light energy, $h \nu$, for zinc-doped p-Fe$_2$O$_3$. $\eta$ is the light frequency ($\nu$) dependent quantum
efficiency. The linear fit near the threshold quantum efficiency suggests that zinc-doped p-Fe$_2$O$_3$ is a direct band gap semiconductor having a band gap of 2.2 eV. The zinc-doped p-Fe$_2$O$_3$ was found to be a direct band gap semiconductor having a band gap of 2.2 eV, which is in agreement with the known indirect band gap of Fe$_2$O$_3$. Thus, zinc converted the indirect band gap of Fe$_2$O$_3$ to a direct band gap semiconductor due to formation of ZnFe$_2$O$_4$.\textsuperscript{64,66}

The band gaps were also determined from uv-vis data. Figure 3.29 shows uv-vis spectra for the p-Fe$_2$O$_3$ synthesized using the optimum conditions that include: spray solution concentration, 0.11 M FeCl$_3$ in 100% ethanol; spray time, 80 s; zinc doping, 0.00935 M; substrate temperature, 663 K; electrolyte solution, 0.5 M H$_2$SO$_4$.\textsuperscript{15,69,105} A band gap 2.19 eV at the adsorption edge of wavelength 566 nm was found. This result is in the expected range of values of band gap for a Fe$_2$O$_3$ semiconductor (2.0 to 2.2 eV) and is in agreement with the results of 2.2 eV obtained from monochromatic photocurrent density data.

F. X-ray Diffraction (XRD) and X-ray Photoelectron Spectroscopy (XPS) Results

X-ray photoelectron spectrum (XPS) results confirm a Fe$_2$O$_3$Zn$_{0.08}$ structure or 4.05% zinc-doping through the entire film thickness. Figure 3.30 shows an X-ray diffraction (XRD) plot of zinc-doped p-Fe$_2$O$_3$. XRD data indicates that $\alpha$-Fe$_2$O$_3$ is the only form of iron oxide present in the thin films. Indium oxide from the indium-doped tin oxide substrate was identified. Analysis of XRD confirms that zinc dopant did not exist as solid zinc or zinc oxide. All zinc was identified in the form of ZnFe$_2$O$_4$.\textsuperscript{61,164-166} These peaks indicate that spray pyrolytically synthesized p-Fe$_2$O$_3$ has mixed structures of $\alpha$-iron(III) oxide and zinc(II) iron(III) oxide (ZnFe$_2$O$_4$). Pure Fe$_2$O$_3$ lacks adequate conductivity to be an effective semiconductor; whereas, the presence of zinc in the form of ZnFe$_2$O$_4$ was found to show improved magnetic and conductive properties\textsuperscript{61,64,127,128} making it a suitable match for Fe$_2$O$_3$, when introduced in optimum ratios (concentration). Pure $\alpha$-state
iron(III) oxide was found to be unstable in acidic solution. On the other hand, these zinc-doped iron oxide electrodes showed no obvious signs of deterioration in an acidic solution; however, extended runs to specifically examine the stability of these electrodes were not performed to ascertain their longevity.

The average crystal size was 6.80 nm for $\alpha$-Fe$_2$O$_3$ and 0.59 nm for ZnFe$_2$O$_4$. With the low amount of zinc precursor added to the spray solution, there is a low amount of material available for crystal formation, thus the crystals are a factor of ten times smaller than the Fe$_2$O$_3$ crystals.

![Figure 3.28](image).

**Figure 3.28.** Plots $(\eta h\nu)^{1/2}$ (for indirect band gap) and $(\eta h\nu)^2$ (for direct band gap) versus light energy, $h\nu$, for zinc-doped p-Fe$_2$O$_3$. $\eta$ is the light frequency ($\nu$) dependent quantum efficiency. The linear fit near the threshold quantum efficiency suggests that zinc-doped p-Fe$_2$O$_3$ is a direct band gap semiconductor having a band gap of 2.2 eV.

G. Flatband Potentials Determined from Mott-Schottky Plots

**Figure 3.31** illustrates a Mott-Schottky plot for a p-Fe$_2$O$_3$ thin film measured at an ac frequency of 2500 Hz in the dark for the sample prepared at the optimum conditions given as: electrolyte solution of 0.01 M H$_2$SO$_4$; ac amplitude of 10 mV; dielectric constant of Fe$_2$O$_3$ of 12; for a sample prepared using a spray solution concentration of 0.11 M FeCl$_3$ in 100% ethanol; zinc doping concentration of 0.0088 M with a substrate temperature of 663 K and a spray time of 70 s.
using a SCE reference electrode. The ac frequency has an intercept at 0.0 V/SCE. These flatband potentials are similar to those p-Fe₂O₃ reported earlier.⁸,¹⁰⁶,¹¹⁹ An acceptor concentration of $4.4 \times 10^{18}$ cm⁻³ was found at 2500 Hz from the slope of the straight line.

![Figure 3.29](image_url)

**Figure 3.29.** UV-vis absorbance data (a.u. = arbitrary units) of zinc-doped p-Fe₂O₃ thin film electrodes. This is for a sample synthesized using a spray solution having 0.11 M FeCl₃ and 0.0088 M Zn(NO₃)₂·6 H₂O in 100% ethanol; total spray time of 70 s; substrate temperature of 663 K; and an electrolyte solution of 0.5 M H₂SO₄. A band gap of 2.19 eV at the adsorption edge of wavelength 566 nm was found. This result is in the expected range of values of the band gap for a Fe₂O₃ semiconductor (2.0 to 2.2 eV).
Figure 3.30. X-ray diffraction (XRD) plots of zinc-doped p-type iron(III) oxide (p-Fe₃O₅) thin films synthesized using 0.11 M Fe³⁺ and 0.0088 M Zn²⁺ solution as a dopant. The peaks in the plots were identified as α-Fe₂O₃ (a), cubic In₂O₃ (b), and zinc(II) iron(III) oxide, ZnFe₂O₄ (z).

Figure 3.31. Mott-Schottky (1/C² vs measured potential, Eₘₑₐₛ (V/SCE), where C is the capacitance) plot for zinc-doped p-Fe₂O₃ films measured at an ac frequency of 2500 Hz under dark conditions using an electrolyte solution of 0.01 M H₂SO₄ and an ac amplitude of 10 mV. The dielectric constant of Fe₂O₃ was used as 12. The reference electrode was SCE. An acceptor concentration of 4.4 × 10¹⁸ cm⁻³ was found from the slope of the plot at 2500 Hz.
H. Photoconversion Efficiency

Non-self-driven photovoltaic cells (PEC), such as the one presented here, cannot generate enough photovoltage to overcome the reversible potential for the reaction ($E^{\circ}_{\text{rev}}$). Therefore, an applied potential ($E_{\text{app}}$) has to be administered for the reaction to proceed forward, thereby overcoming the $E^{\circ}_{\text{rev}}$ thermodynamic barrier. Consequently, the efficiency equation for a non-self-driven PEC utilizes the power output as $j_P(E^{\circ}_{\text{rev}} - |E_{\text{app}}|)$, where $E_{\text{app}} = E_{\text{meas}} - E_{aoc}$ and $E_{aoc}$ is the electrode potential measured at the same illumination conditions using the same reference electrode as shown in Figure 3.32. For a self-driven PEC, it is $j_P(E^{\circ}_{\text{rev}})$ as is shown in Figure 3.34.

![Photoconversion Efficiency](image)

**Figure 3.32.** Photoconversion efficiency ($\% \varepsilon_{\text{photo}}$) under an illumination intensity of 40 mW/cm$^2$ from a 150 W Xe arc lamp versus $E_{\text{app}}$ vs $E_{aoc}$ ($E_{aoc}$ at +0.864 V/SCE). The spray conditions include: spray solution concentration, 0.11 M FeCl$_3$ with 0.0088 M zinc nitrate in 100% ethanol; substrate temperature, 663 K; electrolyte solution, 0.5 M H$_2$SO$_4$.

The maximum photoconversion efficiencies versus spray time are shown in Figure 3.33. The maximum photoconversion efficiency of zinc-doped p-Fe$_2$O$_3$ thin films was found to be 1.25% at an applied potential of -0.66 V vs $E_{aoc}$ ($E_{aoc} = 0.78$ V/SCE) for the sample synthesized using a
The spray time of 70 s, which is considerably higher than those reported earlier.\textsuperscript{109-111,116} The photoconversion efficiency of n-Fe\textsubscript{2}O\textsubscript{3} thin films were reported at 1.84\% in a prior work.\textsuperscript{8} Therefore, a p-type Fe\textsubscript{2}O\textsubscript{3} thin film of 1.25\% efficiency is of considerable interest, since n-type is the preferred state of Fe\textsubscript{2}O\textsubscript{3}. Figure 3.34 shows the total conversion efficiency for the two-electrode configuration. As was mentioned above, the total conversion efficiency neglects any effect from the applied voltage to the semiconductor during illumination.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure3.33.png}
\caption{Dependence of maximum photoconversion efficiency ($\varepsilon_{\text{photo}}$) ($E_{\text{meas}}$ at +0.0 V/SCE) on spray time during the spray pyrolytic synthesis of zinc-doped p-Fe\textsubscript{2}O\textsubscript{3} thin film electrodes. The spray conditions include: spray solution concentration, 0.11 M FeCl\textsubscript{3} with 0.0088 M zinc nitrate in 100\% ethanol; substrate temperature of 390\,°C. The light intensity of Xe lamp was 40 mW/cm\textsuperscript{2} and the electrolyte solution was 0.5 M H\textsubscript{2}SO\textsubscript{4}.}
\end{figure}

I. Three Dimensional Plots

A plot of three parameters at once gives us the ability to get a clearer picture to trends that may be occurring during the fabrication of these thin films. In Figure 3.35, a plot of photocurrent density, $j_p$ (mA/cm\textsuperscript{2}), vs the measure voltage ($E_{\text{meas}}$, V/SCE) vs the zinc dopant solution concentration is shown. All the data follows a similar trend; however, the points show a steady
increase and a maximum photocurrent at 0.0088 M zinc dopant solution concentration. If the dopant concentration is held constant at 0.0088 M and the spray time is varied, then we get Figure 3.36, which shows photocurrent density, $j_p$ (mA/cm$^2$), vs the measure voltage ($E_{\text{meas}}$, V/SCE) vs spray time. In this figure, the maximum photocurrent is observed at 90 s spray time and at $E_{\text{meas}}$ of 0.0 V/SCE.

![Graph showing dependence of photoconversion efficiency on applied potential](image)

**Figure 3.34.** Dependence of photoconversion efficiency ($\%\epsilon_{\text{photo}}$) on applied potential, $E_{\text{app}}$, vs $E_{\text{aoc}}$ (open circuit voltage) based on a two-electrode system with platinum as the counter electrode. Measurements were done in 0.5 M H$_2$SO$_4$ solution. The open circuit potential was found to be -0.25 V/Pt.
J. Energy Dispersive Analysis by X-rays (EDAX) and Scanning Electron Microscopy (SEM) Analysis

Figure 3.37 shows the EDAX spectra for optimized zinc-doped p-Fe\textsubscript{2}O\textsubscript{3} thin films. The silicon, tin, and indium peaks are from indium-doped tin oxide glass substrate. The computer analysis of the thin film was unable to identify the zinc, which is visible as a side arm to the silicon peak to the left side. The peaks were too close to each other to be adequately resolved in data analysis.

![Figure 3.35. 3D plot of photocurrent density, \(j_p\) (mA/cm\(^2\)), vs the measure voltage (E\textsubscript{meas}, V/SCE) vs the zinc dopant concentration added to the ethanolic iron(III) chloride spray solution. A maximum photocurrent plateau is seen between 0.0099 and 0.0088 M zinc dopant solution concentration.](image)
Figure 3.36. 3D plot of photocurrent density, $j_P$ (mA/cm$^2$), vs the measure voltage ($E_{\text{meas}}$, V/SCE) vs spray time amount added to the ethanolic iron(II) chloride spray solution. A maximum photocurrent is seen with 90 s total spray time at $E_{\text{meas}} = 0.0$ V/SCE.

Figures 3.38a and 3.38b show SEM images for 0.0088 M zinc dopant with 0.11 M iron chloride concentration at 390°C. Both films show various areas of differing chemical composition. The dispersion of the spots is even, and is reproducible on films made under the same conditions at different times as is shown in each figure.
Figure 3.37. Energy dispersive analysis by X-rays (EDAX) plot of a zinc-doped p-Fe$_2$O$_3$ thin film electrode with 0.0088 M zinc doping.

Figures 3.38a and 3.38b. Scanning electron micrographs of zinc-doped p-Fe$_2$O$_3$ at 0.0088 M zinc doping with 0.11 M FeCl$_3$·6H$_2$O at 390°C.
3.4. Photoresponse of Indium-doped n-Type Iron(III) Oxide Thin Films Towards Water Splitting Reaction

A. Photocurrent Density and Photoconversion Efficiency

Figure 3.39 shows the photocurrent density (j_p, mA/cm^2) versus the measured potential (E_{meas}) for indium-doped n-Fe_2O_3 samples as well as undoped samples. The dark current was also shown. Photocurrent only appears in the dark after +0.6 V/SCE. This sample was made using a total spray time of 60 s with an optimized concentration of 0.11 M iron chloride and at a substrate temperature of 415°C. A maximum photocurrent density of 3.61 mA/cm^2 at +0.6 V/SCE was observed with 0.0044 M indium dopant added to iron chloride solution at an illumination intensity of 40 mW/cm^2. This result was found to be much higher than the results published previously for undoped n-type Fe_2O_3. Figure 3.40 shows the maximum photocurrent density of various dopant concentrations. There is a clear trend showing 0.0044 M indium doping as optimum with a decrease in photocurrent density with a decrease or increase in indium dopant concentration. These electrodes showed electrode potentials from -0.37 to -0.47 V/SCE at open circuit conditions under an illumination intensity of 40 mW/cm^2. The dark current for these samples is also shown and was identical for all samples presented; occurring only after +0.6 V/SCE.

Photoconversion efficiencies versus applied potential, E_{app} (vs E_{aoc}) versus the indium concentration are shown in Figure 3.41. The maximum photoconversion efficiency of indium-doped n-Fe_2O_3 thin films was found to be 3.73% at an applied potential of +0.67 V vs E_{aoc} (E_{aoc} = -0.37 V/SCE) at total spray time of 60 s, which is higher than those reported previously for undoped n-type Fe_2O_3 semiconductors.  

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Figure 3.39. Photocurrent density, \( j_P \) (mA/cm\(^2\)), for an indium-doped n-Fe\(_2\)O\(_3\) at an illumination intensity of 40 mW/cm\(^2\) from a 150 W xenon arc lamp versus measured potential (\( E_{\text{meas}} \)) for n-Fe\(_2\)O\(_3\) samples synthesized at an optimum total spray time of 60 s at a substrate temperature of 688 K. 1M NaOH (pH=13) was the electrolyte solution. Various indium dopant concentrations from 0.0022 to 0.0055 M were used. The electrode potential at open circuit conditions was found to vary from -0.372 V/SCE at 0.0022 M dopant conc. to -0.470 V/SCE at 0.0055 M dopant conc. The dark current for all samples started to appear only after +0.6 V/SCE to higher potential values, as evidenced by the lowering of photocurrent in the plots shown. The results are compared to undoped Fe\(_2\)O\(_3\) (Akikusa et. al.\(^8\)) and are also normalized to 40 mW/cm\(^2\), which is the intensity these results are reported at. These thin films were the same thickness as the one presented here.

i. Effect of Substrate Temperature

Figure 3.42 shows the photocurrent density (\( j_P \), mA/cm\(^2\)) versus the measured potential (\( E_{\text{meas}} \), V/SCE) for indium-doped n-Fe\(_2\)O\(_3\) samples that were synthesized using substrate temperatures from 683 to 698 K. All samples were made with a total spray time of 60 s. These samples were all made with 0.0044 M indium chloride dopant and 0.11 M iron chloride concentrations, both optimized in the previous section. A maximum photocurrent density of 3.61 mA/cm\(^2\) at +0.6 V/SCE was observed with 0.0044 M indium chloride dopant added to 0.11 M iron chloride solution. The electrodes had open circuits that varied from -0.37 to -0.49 V/SCE.
Figure 3.40. The photocurrent density maximums vs indium dopant solution concentration at an applied voltage of +0.6 V/SCE in 1M NaOH electrolyte solution.

Figure 3.41. Photoconversion efficiency versus applied potential ($E_{app}$) for indium-doped n-Fe$_2$O$_3$ samples synthesized at an optimum total spray time of 60 s at a substrate temperature of 415°C in 1M NaOH electrolyte solution. Various indium doping concentrations were utilized from 0.0022 to 0.0055 M, with an optimum photocurrent at 0.0044 M indium doping in 0.11M iron(III) chloride spray solution in pure ethanol was used for the synthesis of n-Fe$_2$O$_3$. The electrode potential at open circuit condition was found to vary from -0.372 to -0.568 V/SCE.

Figure 3.43 shows the maximum photoconversion efficiency for samples prepared at various substrate temperatures. The most efficient samples were found to be the ones synthesized at a substrate temperature of 415°C.
ii. Spray Time Dependence

**Figure 3.44** shows the photocurrent density ($j_p$, mA/cm$^2$) versus the measured potential ($E_{\text{meas}}$, V/SCE) for the indium-doped n-Fe$_2$O$_3$ samples prepared using different spray times. All of these samples were synthesized using optimum concentrations of 0.0044 M indium chloride dopant and 0.11 M iron chloride at an optimum substrate temperature of 415°C. An optimum amount of photocurrent density is observed for the samples prepared at spray times of 60 s at +0.6 V/SCE. However, for the spray time beyond 60 s, the quality of the film degrades due to too many layers (i.e., the film is too thick) that generate recombination centers.

![Figure 3.44](image)

**Figure 3.44.** Photocurrent density, $j_p$ (mA/cm$^2$), versus measured potential ($E_{\text{meas}}$, V/SCE) for indium-doped n-Fe$_2$O$_3$ samples produced at a total spray time of 60 s at various substrate temperatures from 410 to 420°C with an indium dopant concentration of 0.0044 M and a 0.11 M iron(III) chloride spray solution in pure ethanol for the synthesis of n-Fe$_2$O$_3$. 1 M NaOH was used as the electrolyte solution. The electrode potential at open circuit condition was found to vary from -0.385 to -0.495 V/SCE. The dark current for all samples appeared only after +0.6 V/SCE, as evidenced by the lowering of photocurrent, where the dark current was subtracted.

**Figure 3.45** shows the corresponding photoconversion efficiencies of samples prepared at different spray times of 50 to 70 s and shows a maximum photoconversion efficiency of 3.07% for the sample prepared using 60 s total spray time. The photoconversion efficiencies and
consequently lower photocurrent densities are observed and depend on electrode potentials at open circuit conditions. The reason for this is that at lower spray times, the thickness of the film is smaller and cannot absorb enough light and consequently lower photocurrents are observed. The electrode potentials at open circuit condition, $E_{aoc}$, were found to be -0.363, -0.372, and -0.438 V/SCE at 50, 60, and 70 s respectively at an illumination intensity of 40 mW/cm$^2$. It is better to have more positive open circuit, $E_{aoc}$, if the onset potential, $E_{onset}$, for the photocurrent density is close to $E_{aoc}$. However, these samples do not show an $E_{onset}$ close to $E_{aoc}$.

![Graph showing photoconversion efficiency maximums versus temperature for indium-doped n-Fe$_2$O$_3$ samples produced at a total spray time of 60 s at various substrate temperatures from 410 to 425°C with an indium dopant concentration of 0.0044 M and a 0.11 M iron(III) chloride spray solution in absolute ethanol for the synthesis of n-Fe$_2$O$_3$. 1 M NaOH was used as the electrolyte solution. The electrode potential at open circuit condition was found to vary from -0.385 to -0.495 V/SCE.]

Figure 3.43. Photoconversion efficiency maximums versus temperature for indium-doped n-Fe$_2$O$_3$ samples produced at a total spray time of 60 s at various substrate temperatures from 410 to 425°C with an indium dopant concentration of 0.0044 M and a 0.11 M iron(III) chloride spray solution in absolute ethanol for the synthesis of n-Fe$_2$O$_3$. 1 M NaOH was used as the electrolyte solution. The electrode potential at open circuit condition was found to vary from -0.385 to -0.495 V/SCE.

**B. Total Conversion Efficiency**

The maximum total conversion efficiencies versus applied potential, $E_{app}$ (vs $E_{aoc}$) with respect to spray time are shown in **Figure 3.46** for the optimum samples made with 0.0033 and 0.0044 M indium dopant and 0.11 M iron chloride at 415°C with a total spray time of 60 s for each sample.
The maximum total conversion efficiency of indium-doped n-Fe₂O₃ thin films was found to be 11.65% at an applied potential of +0.60 V/SCE vs E_{aoc} (E_{aoc} = -0.37 V/SCE) at 0.0033 M indium dopant concentration and 9.65% at an applied potential of +0.60 V/SCE vs E_{aoc} (E_{aoc} = -0.38 V/SCE) at 0.0044 M indium dopant concentration. A large or a small open circuit is no longer affecting the potential in the numerator. As well as the applied potential to the system in the form of E_{meas} is neglected.

![Graph](image)

**Figure 3.44.** Photocurrent density, j_P (mA/cm²), maximum vs spray time for n-Fe₂O₃ samples produced at various total spray times of 50, 60, and 70 s at a substrate temperature of 415°C with an indium dopant concentration of 0.0044 M and a 0.11 M iron(III) chloride spray solution in absolute ethanol for the synthesis of n-Fe₂O₃. The electrolyte solution is 1 M NaOH. The electrode potential at open circuit condition was found to vary from -0.372 to -0.589 V/SCE. The dark current for all samples appeared only after +0.6 V/SCE, as evidenced by the lowering of photocurrent, where the dark current was subtracted.

**C. Quantum Efficiency**

The results for quantum efficiency as a function of wavelength are shown in **Figure 3.47**. A maximum quantum efficiency of 26.05% was observed at a wavelength of 295 nm for the indium-doped n-Fe₂O₃ synthesized under optimum conditions. The quantum efficiency showed a zeroing around 565 nm, which corresponds to a band gap energy of 2.19 eV. Quantum efficiency
remained relatively high at 320 nm at 23.65% and shows 14% at 400 nm. The quantum efficiency is low in the visible region indicating a low absorption coefficient of light in this region. It is notable that the quantum efficiency of indium-doped n-Fe$_2$O$_3$ is similar to that presented for pure n-Fe$_2$O$_3$ (i.e., no dopant materials were added). These quantum yields are low and still need to be improved by minimizing the recombination of photogenerated holes and also improving the absorption coefficient of visible light.

**Figure 3.45.** Photoconversion efficiency maximums versus spray time for indium-doped n-Fe$_2$O$_3$ samples produced at various total spray times from 50, 60, and 70 s in 1 M NaOH electrolyte solution at a substrate temperature of 415°C with an indium dopant concentration of 0.0044 M and a 0.11 M iron(III) chloride spray solution in absolute ethanol for the synthesis of n-Fe$_2$O$_3$. The electrode potential at open circuit condition was found to vary from -0.372 to -0.589 V/SCE.

**D. Band Gap Determination**

**Figure 3.48** shows a plot of $(\eta \nu)^{1/2}$ versus $\nu$ (eV) for direct allowed transitions and $(\eta \nu)^2$ versus $\nu$ (eV) for indirect allowed transitions. The straight line near the threshold was observed for indirect allowed transitions which shows an intercept at 2.1 eV, which corresponds to the known band gap energy of n-Fe$_2$O$_3$ thin films. The correlation of the indirect allowed transitions was 0.9957. All the band gap transitions were measured at an applied potential of +0.6 V/SCE.
Direct allowed transitions (n=1/2) gave a non-linear response at all points and direct forbidden transitions (n=3/2) were also non-linear as would be expected mathematically, if n=1/2 is non-linear (not shown). These results confirmed that indium-doped n-Fe$_2$O$_3$ is an indirect allowed transitions semiconductor.

![Graph](image)

**Figure 3.46.** Percent total photoconversion efficiency versus $E_{\text{app}}$ (vs $E_{\text{aoc}}$) of n-type iron oxide via spray pyrolysis at 415°C at 20 PSI in denatured ethanol at 0.11M FeCl$_3$ with 0.00330 M and 0.00440 M InCl$_3$ with a total of 60 s spray time. The open circuit for the sample was -0.385 V/SCE for 0.0033 M and -0.372 V/SCE for 0.0044 M indium doping. The samples were illuminated with a xenon bulb at 40 mW/cm$^2$. The samples were tested in 1.0 M NaOH solution using platinum gauze as a counter electrode and SCE as the reference electrode.

**Figure 3.49** shows uv-vis spectra of the same sample. The sample shows photoresponse to approximately 550 nm, which corresponds to a band gap of 2.25 eV.

**E. Flatband Potentials Determined from Mott-Schottky Plots**

**Figure 3.50** illustrates a Mott-Schottky plot for an indium-doped n-Fe$_2$O$_3$ thin film measured at an ac frequency of 1000 Hz in the dark with the following conditions: electrolyte solution of 1.0 M NaOH; ac amplitude of 10 mV; dielectric constant of Fe$_2$O$_3$ was 12; spray solution concentration of 0.11 M FeCl$_3$ in absolute ethanol; spray time of 80 s; indium doping of 0.00935
M; substrate temperature of 390°C. The reference electrode was SCE. The ac frequency of 1000 Hz had an intercept range of -0.62 V/SCE, which is similar to that of pure n-Fe$_2$O$_3$.\(^8\) From the slopes of the Mott-Schottky plot, the donor density ($N_d$) can be calculated. At 1000 Hz, the donor density was calculated as $7.37 \times 10^{20}$ 1/cm$^3$. These results are similar to those of pure n-Fe$_2$O$_3$ results reported earlier.\(^8\) The donor density is found to be higher for lower frequencies, which is consistent with the fact that the surface states contribute at lower frequencies.

![Graph](image)

**Figure 3.47.** Quantum efficiency ($\eta$) versus wavelength (nm) for indium-doped n-Fe$_2$O$_3$ thin film electrodes synthesized at the following spray conditions: spray solution concentration, 0.11 M FeCl$_3$ with 0.00440 M indium chloride in absolute ethanol; substrate temperature of 415°C; total light intensity of xenon lamp at 40 mW/cm$^2$; electrolyte solution of 1.0 M NaOH; and applied potential of +0.50 V/SCE using a Kratos model GM 100 monochromator with a 1.4 mm slit width. The intersection with the x-axis is at 565 nm, which corresponds to a band gap of 2.1 eV for indium-doped n-Fe$_2$O$_3$.

### F. Results of XRD, XPS, EDAX, and SEM

The presence of indium and indium iron(III) oxide was confirmed by sputtering X-ray photoelectron spectrum (XPS), X-ray diffraction (XRD), and energy dispersive by X-rays (EDAX) analysis. **Figure 3.51** shows XRD plots for optimized thin films of indium-doped n-
Fe$_2$O$_3$ made with 0.0033 to 0.0077 M indium dopant with 0.11 M iron chloride. From the XRD plots, three compounds were identified as Fe$_2$O$_3$, In$_2$O$_3$, and InFeO$_3$. The indium oxide was confirmed to be coming from the indium-doped tin oxide substrate. The thin films thus were a combination of iron(III) oxide and indium iron(III) oxide. As the indium dopant concentration was increased, it should be noted that the intensity of the InFeO$_3$ peaks increased.

The average crystal size was 0.87 nm for $\alpha$-Fe$_2$O$_3$ and 0.39 nm for InFeO$_3$. With the low amount of indium precursor added to the spray solution, there is a low amount of material available for crystal formation, thus the crystals are twice as small as the Fe$_2$O$_3$ crystals. However, the crystal sizes are much closer than the p-type Fe$_2$O$_3$ films.

![Figure 3.48](image)

**Figure 3.48.** Band gap determination of indium-doped p-Fe$_2$O$_3$. The linear fit of the indirect band gap data near the band-edge confirms that indium-doped p-Fe$_2$O$_3$ is an indirect band gap semiconductor with a band gap value of 2.1 eV, which is in agreement with the known band gap of Fe$_2$O$_3$. This was found to conform to uv-vis data having a value of 2.2 eV.

XPS results confirm 1.5% indium-doping relative to the other elements present. The results translate into an overall thin film make-up of Fe$_2$In$_{0.3}$O$_{2.7}$. The XPS of the optimized indium-doped n-Fe$_2$O$_3$ thin film is presented in **Figure 3.52**.
Figure 3.49. UV-vis reflectance data for indium-doped n-Fe$_2$O$_3$ thin film electrodes of a sample at the optimized state of conditions that include: spray solution concentration of 0.11 M FeCl$_3$ in absolute ethanol; spray time of 60 s; indium doping of 0.0044 M; and a substrate temperature of 415°C.

Figure 3.50. Mott-Schottky ($1/C^2$ vs measured potential ($E_{\text{meas}}$, V/SCE), where C is the capacitance) plot for n-Fe$_2$O$_3$ films measured at 1000 Hz ac frequency under dark conditions: electrolyte solution of 1.0 M NaOH; ac amplitude of 10 mV; dielectric constant of Fe$_2$O$_3$, 12; spray solution concentration of 0.11 M FeCl$_3$ in absolute ethanol; spray time of 110 s; indium dopant conc. of 0.00440 M; substrate temperature of 415°C; reference electrode, SCE. Mott-Schottky data showed a flatband potential of -0.62 V/SCE for an ac frequency of 1000 Hz. The donor density was calculated from the slope of the Mott-Schottky plot of 7.4×10$^{20}$ cm$^{-3}$ at an ac frequency 1000 Hz.
Figure 3.51. X-ray diffraction (XRD) plots of indium-doped n-type iron(III) oxide (n-Fe$_2$O$_3$) thin film electrodes at 0.0033, 0.0044, 0.0055, 0.0066, and 0.0077 M indium doping. The peaks on the plots were identified as follows $\alpha$-Fe$_2$O$_3$ (▲), cubic In$_2$O$_3$ (●), and iron(III) indium oxide, FeInO$_3$ (■).
Figure 3.52. XPS spectrum of indium-doped n-Fe₂O₃ thin film electrode on indium-doped tin oxide substrate on Pyrex glass. The sample was optimized using conditions that include: spray solution concentration of 0.11 M FeCl₃ in absolute ethanol; spray time of 80 s; indium doping of 0.00440 M; substrate temperature of 415°C; electrolyte solution of 1.0 M NaOH. From the atomic percentages, neglecting contributions from the glass substrate, the formula for the indium iron(III) oxide would be Fe₂In₀.₁₃₅O₃.₅.
Figure 3.53 shows the EDAX spectra for optimized indium-doped n-Fe$_2$O$_3$ thin films with 0.0044 indium doping present. The silicon peak is from glass substrate. The tin peak is from the indium-doped tin oxide which was applied to the glass substrate to provide the conductive surface to which the indium-doped n-Fe$_2$O$_3$ thin film was applied. Indium dopant was a harder compound to separate in data analysis, especially with data from EDAX since indium was present in the conductive film and is present in the film we are fabricating, thus in depth analysis was not possible.
3.5. Photoresponse of Iodine-Doped n-Type Iron(III) Oxide Thin Films in Water Splitting Reaction

A. Photocurrent Density and Photoconversion Efficiency

i. Iodine Concentration Dependence

Figure 3.54a shows the photocurrent density ($j_p$, mA/cm$^2$) versus the measured potential ($E_{\text{meas}}$) for iodine-doped n-Fe$_2$O$_3$ samples. In this figure, we see the optimum iodine dopant concentrations of 0.00935 and 0.0100 M added in the form of pure iodine. Figure 3.54a also shows the undoped Fe$_2$O$_3$ data from works of Khan and Akikusa. The addition of I$_2$ is very different from most studies in that most dopants are commonly added as oxides or as compounds that form oxides when deposited onto a hot substrate surface.

All samples were made with a total spray time of 90 s. These samples were all made with 0.11 M iron chloride concentration and at a substrate temperature of 415°C. A maximum photocurrent density of 3.07 mA/cm$^2$ at +0.6 V/SCE was observed with 0.0100 M iodine dopant added to 0.11 M iron chloride solution. Figure 3.54b shows the maxima for each dopant concentration at the optimized substrate temperature of 415°C and for 405°C, which shows a similar trend at lower photocurrents at almost all spray times. At both temperatures, there is a clear trend to a maxima at 0.100 M iodine dopant and lowering of photocurrent after 0.100 M iodine dopant. The electrodes had open circuits that varied from -0.33 to -0.56 V/SCE. The dark current for these samples is also shown and was identical for all samples presented. Current density was observed in the dark only after +0.6 V/SCE.

Photoconversion efficiencies versus applied potential, $E_{\text{app}}$ vs $E_{\text{aoc}}$ for samples prepared having iodine concentrations of 0.0935, 0.0100, and 0.0121 M are shown in Figure 3.55. The maximum photoconversion efficiency of iodine-doped n-Fe$_2$O$_3$ thin films was found to be 3.06% at an
applied potential of +0.73 V/SCE vs \( E_{\text{aoc}} \) (\( E_{\text{aoc}} = -0.33 \) V/SCE) at total spray time of 90 s, which is higher than previously studied n-type Fe\(_2\)O\(_3\) semiconductors,\(^8,9,70,121,167\) except for n-type Fe\(_2\)O\(_3\) thin film semiconductors incorporating indium dopant.\(^29\)

**Figures 3.54a and 3.54b.** (a.) Photocurrent density, \( j_P \) (mA/cm\(^2\)), at an illumination intensity of 40 mW/cm\(^2\) from a 150 W xenon arc lamp versus measured potential (\( E_{\text{meas}} \), V/SCE) for iodine-doped n-Fe\(_2\)O\(_3\) samples produced at an optimum spray time of 90 s at a substrate temperature of 415\(^\circ\)C. 1 M NaOH was the electrolyte solution. Various iodine dopant concentrations from 0.00825 to 0.01210 M were used. (b.) Photocurrent density versus \([I_2]\) (M) at +0.6 V/SCE for two samples synthesized at substrate temperatures of 405 and 415\(^\circ\)C.

**Figure 3.55.** Photoconversion efficiency versus applied potential (\( E_{\text{app}} \)) for iodine-doped n-Fe\(_2\)O\(_3\) samples produced at an optimum spray time of 90 s having 10 s spray periods at a substrate temperature of 415\(^\circ\)C. 1 M NaOH was the electrolyte solution and light intensity of 40 mW/cm\(^2\) from a 150 W Xe arc lamp. The electrode potential at open circuit condition was found to vary from -0.328 to -0.532 V/SCE.
Figures 3.56. Photocurrent density, $j_p$ (mA/cm$^2$), versus measured potential ($E_{\text{meas}}$) for iodine-doped n-Fe$_2$O$_3$ samples produced at a spray time of 90 s at substrate temperatures of 415, 420, and 425°C with an iodine dopant concentration of 0.0100 M and a 0.11 M iron(III) chloride spray solution in absolute ethanol for the synthesis of iodine-doped n-Fe$_2$O$_3$. 1 M NaOH was the electrolyte solution and light intensity of 40 mW/cm$^2$ from a 150 W Xe arc lamp.

ii. Substrate Temperature Dependence

Figure 3.56 shows the photocurrent density ($j_p$, mA/cm$^2$) versus the measured potential ($E_{\text{meas}}$) for iodine-doped n-Fe$_2$O$_3$ samples prepared using substrate temperatures of 415, 420, and 425°C on the indium-doped tin oxide glass substrate. These temperatures were maintained to an accuracy of ±1 °C. All samples were made with a total spray time of 90 s. These samples were all made with optimized 0.0100 M iodine dopant and 0.11 M iron chloride concentrations. A maximum photocurrent density of 3.07 mA/cm$^2$ at +0.6 V/SCE was observed for samples synthesized with 0.0100 M iodine dopant added to iron chloride solution. The electrodes had open circuits that varied from -0.33 to -0.57 V/SCE.

Figure 3.57 shows the maximum photoconversion efficiency for samples at various temperatures from 405 to 425°C. A similar trend as that for photocurrent is seen with a clear maximum at 415°C. From this plot it can be seen that the photoconversion efficiency at +0.3 V/SCE is ~33% higher than all other temperatures. It is clear that iodine dopant concentration,
iron chloride concentration, and substrate temperature all play critical roles in producing optimized iodine-doped iron(III) oxide. The most dominant property in the optimization of iodine-doped n-Fe$_2$O$_3$ thin films was the substrate temperature.

**Figures 3.57.** Photoconversion efficiency maximum versus substrate temperature ($^\circ$C) used for synthesizing iodine-doped n-Fe$_2$O$_3$ samples synthesized using a spray time of 90 s at various substrate temperatures from 405 to 425$^\circ$C with an iodine dopant concentration of 0.0100 M and a 0.11 M iron(III) chloride spray solution in absolute ethanol for the synthesis of iodine-doped n-Fe$_2$O$_3$. The electrode potential at open circuit condition was found to vary from -0.328 to -0.567 V/SCE.

**Figure 3.58.** Photocurrent density, $j_P$ (mA/cm$^2$), versus spray time for iodine-doped n-Fe$_2$O$_3$ samples produced at various spray times from 70 to 120 s at an optimized substrate temperature of 415$^\circ$C with an iodine dopant concentration of 0.0100 M and a 0.11 M iron(III) chloride spray solution in absolute ethanol for the synthesis of iodine-doped n-Fe$_2$O$_3$. The dark current for all samples appeared only after +0.6 V/SCE. The electrolyte solution was 1 M NaOH.
iii. Spray Time Dependence

Figure 3.58 shows the photocurrent density ($j_p$, mA/cm$^2$) versus spray time for iodine-doped n-Fe$_2$O$_3$ samples on the indium-doped conductive tin oxide glass substrate from 70 to 120 s. All of these samples were made using the optimized conditions of 0.0100 M iodine dopant and 0.110 M iron chloride concentrations at a substrate temperature of 415°C. With respect to photocurrent density measurements, the spray time was found to have a pointed influence on the outcome over a rather broad range from 70 to 120 s as shown in Figure 3.58. A 90 s spray time is found to be the optimum spray time at a spray temperature of 415°C.

Figure 3.59. Photoconversion efficiency versus spray time (s) for iodine-doped n-Fe$_2$O$_3$ samples synthesized using various spray times from 70 to 120 s at a substrate temperature of 415°C with an iodine dopant concentration of 0.0100 M and a 0.11 M iron(III) chloride spray solution in absolute ethanol. The electrode potential at open circuit condition was found to vary from -0.328 to -0.532 V/SCE.

Figure 3.59 shows the maximum photoconversion efficiencies for spray times from 70 to 120 s. The maximum photoconversion efficiency is found at 90 s total spray time with a value of 3.06% at +0.728 V/SCE vs $E_{aoc}$. There is a distinct maximum at 90 s with all the other spray time falling to a lower level of ~1.75% photoconversion efficiency. The open circuits of the electrodes
were found to range from -0.328 to -0.526 V/SCE for samples synthesized from 70 to 120 s at an illumination intensity of 40 mW/cm² from a 150 W xenon arc lamp.

Figure 3.60. The effectiveness of placing two electrodes at a 60° angle to each other. The two electrodes that were used were an iodine-doped n-Fe₂O₃ with 0.0100 M iodine dopant and 0.11 M FeCl₃ at 415°C and an undoped Fe₂O₃ prepared at optimum conditions which were evaluated earlier.

iv. Photocurrent for Two Photoelectrodes Run in Serial Connection

The effect of iodine-doped n-Fe₂O₃ needs to be compared to ascertain how effective adding a dopant to the thin film will be. In Figure 3.60, the maximum photocurrent as shown in the previous sections is displayed as well as the maximized photocurrent of undoped n-Fe₂O₃, which was produced using the same parameters as were published earlier. As can be seen, there is a slight improvement in the photocurrent with the addition of iodine to thin films of Fe₂O₃.

Additionally, the effect of running an iodine-doped n-Fe₂O₃ thin film electrode and an undoped n-Fe₂O₃ thin film electrode in tandem was ascertained. Because of the dark coloration of the thin film with the addition of iodine dopant, it was decided that running the electrodes at 60° to each other would be the best way to maximize photocurrent, while keeping the total area the same. Placing the electrodes at a 60° angle to each other also allowed for multiple reflections off of the
two electrodes. It was determined from our own studies that with undoped n-Fe₂O₃ that only 
~60% of the light made it from the back of the first substrate to the second substrate when the 
electrodes were stacked with undoped Fe₂O₃ electrodes. However, only ~40% of the light made it 
from the first substrate to the second as while using iodine-doped n-Fe₂O₃, thus making stacking 
iodine-doped Fe₂O₃ an impractical set-up.

**B. Total Conversion Efficiency**

The maximum total conversion efficiency (see **Equation 1.9**) versus applied potential, $E_{\text{app}}$ (vs 
$E_{\text{aoc}}$) is shown in **Figure 3.61** for a sample optimized at 0.0100 M iodine dopant and 0.11 M iron 
chloride at 415°C with a spray time of 90 s. The maximum total conversion efficiency of iodine-
doped n-Fe₂O₃ thin films was found to be 9.43% at an applied potential of +0.60 V/SCE vs $E_{\text{aoc}}$ 
($E_{\text{aoc}} = -0.328$ V/SCE). The total conversion efficiency of iodine-doped n-Fe₂O₃ thin films is 
lower than that of indium-doped n-Fe₂O₃ thin films which showed a maximum photoconversion 
efficiency of 11.65%. However, the total photoconversion efficiency of iodine-doped Fe₂O₃ thin 
film electrodes is still higher than the total photoconversion efficiency of undoped n-Fe₂O₃ thin 
film electrodes that was found to be 4.92%.²
Figure 3.61. Total photoconversion efficiency (see Equation 1.9) versus $E_{\text{app}}$ (vs $E_{\text{aoc}}$) of iodine-doped n-type iron oxide via spray pyrolysis at 415°C at 138 kPa in absolute ethanol at 0.11M FeCl$_3$ with 0.0100 M I$_2$ with a 90 s spray time. The open circuit for the sample was -0.328 V/SCE. The samples were illuminated with a 150 W xenon lamp at 40 mW/cm$^2$. The samples were tested in 1.0 M NaOH solution using platinum gauze as a counter electrode and SCE as the reference electrode.

C. Reproducibility Results of Spray Pyrolysis

The reproducibility was tested for thin films of iodine-doped n-Fe$_2$O$_3$ produced with 0.0100 M iodine dopant and 0.11 M iron chloride concentrations at 415°C at a spray time of 90 s. Three samples were produced at these conditions and there individual photocurrents are shown in Figure 3.62. Photocurrents of these samples were measured in 1.0 M NaOH electrolyte using a light intensity of 40.0 mW/cm$^2$ using a 150 W xenon arc lamp. All three samples exhibit almost equal values for photocurrent density at all of the measured potentials.
Figures 3.62. Reproducibility test of SPD of iodine-doped n-Fe$_2$O$_3$ thin film electrodes, which shows the photocurrent density versus the measured potential ($E_{\text{meas}}$) of three iodine-doped n-Fe$_2$O$_3$ films. The spray conditions for the three samples included: spray time of 90 s; spray solution concentration of 0.11 M FeCl$_3$ with 0.0100 M I$_2$ in absolute ethanol; substrate temperature of 415°C; electrolyte solution of 1.0 M NaOH; light intensity of 40.0 mW/cm$^2$. All samples have open circuits ranging from +0.52 ± 0.01 V/SCE.

At +0.3 V/SCE, which is where the photoconversion efficiency of the thin films is maximized, the samples showed fairly consistent values for photocurrent density. An average photocurrent density of 1.626 mA/cm$^2$ was found at +0.3 V/SCE for these samples. These data points correspond to a standard deviation ($\sigma$) of ±0.101 mA/cm$^2$. All three samples had an open circuit value of +0.521 ±0.009 V/SCE. The reproducibility of the samples is within acceptable limits.

One of the factors that affected the results is the quality of the iron chloride used for the synthesis of these thin films. The iron oxide was bought at 99.95% purity from several sources and it was found that each sample of iron chloride was producing different photocurrent results. It was later determined that moisture content was dictating the concentration of iron present during SPD.
D. Quantum Efficiency

The results for quantum efficiency as a function of wavelength were are shown in Figure 3.63. A maximum quantum efficiency of 30.88% was observed at wavelength 330 nm as shown in Figure 3.63. This was observed for samples prepared at the maximized conditions of 415°C with 0.0100 M iodine dopant with 0.11 M FeCl₃. The quantum efficiency plot showed an intersection around 560 nm, which corresponds with a band gap energy of 2.21 eV. The quantum efficiency of iodine-doped n-Fe₂O₃ is higher than that for indium-doped or pure n-Fe₂O₃ (i.e., no dopant materials were added) as was presented earlier. These quantum yields are low and still need to be improved, because recombination of photogenerated holes on the film surface leads to the absence of hydrogen and oxygen gas production.

Figures 3.63. Quantum efficiency (η) versus wavelength (nm) for an iodine-doped n-Fe₂O₃ thin film electrode synthesized at the following spray conditions: spray solution concentration of 0.11 M FeCl₃ with 0.0100 M iodine in absolute ethanol; substrate temperature of 415°C; light intensity of 150 W Xe lamp, 40 mW/cm²; electrolyte solution of 1.0 M NaOH; applied potential, +0.40 V/SCE. The intersection with the x-axis is at 560 nm, which corresponds to a band gap of 2.21 eV for iodine-doped n-Fe₂O₃.
E. Band gap Determination

*Figure 3.64* shows the indirect and direct band gap determination of iodine-doped n-Fe$_2$O$_3$ thin films from plots of $(\eta h \nu)^{1/2}$ versus $h \nu$ (eV) for allowed indirect transitions and $(\eta h \nu)^2$ versus $h \nu$ (eV) for direct allowed transitions. A linear response was observed for indirect allowed transitions with an intercept at 2.1 eV, which corresponds to the known band gap energy of n-Fe$_2$O$_3$ thin films. The correlation of the indirect allowed transitions was 0.9929. All the band gap transitions were measured at measured potential of +0.6 V/SCE. Direct allowed transitions ($n = 1/2$) gave a non-linear response at almost all points. Both of these plots confirmed that iodine-doped n-Fe$_2$O$_3$ is an indirect allowed transitions semiconductor.

![Figure 3.64](image.png)

*Figure 3.64.* Band gap determination of iodine-doped p-Fe$_2$O$_3$. The linear fit of the indirect band gap data near the band-edge confirms that iodine-doped p-Fe$_2$O$_3$ is an indirect band gap semiconductor with a band gap value of 2.1 eV, which is in agreement with the known band gap of Fe$_2$O$_3$ semiconductors. The sample conditions were 0.11 M FeCl$_3$ in absolute ethanol, a spray time of 90 s with iodine doping at 0.0100 M at a substrate temperature of 415°C.
Figure 3.65. UV-vis reflectance data for iodine-doped n-Fe$_2$O$_3$ thin film electrodes at the optimized state of conditions that include: spray solution concentration of 0.11 M FeCl$_3$ in absolute ethanol; spray time of 90 s; indium doping of 0.0100 M; substrate temperature of 415°C.

Therefore, the next step involves examining the band gaps determined from uv-vis data. Figure 3.65 shows uv-vis spectra of the same sample. The sample shows photoresponse to approximately 560 nm, which corresponds to a band gap of 2.25 eV.$^{15,69,105,121}$

F. Flatband Potential determined from Mott-Schottky Plot

Figure 3.66 illustrates a Mott-Schottky plot for an iodine-doped n-Fe$_2$O$_3$ thin film measured at an ac frequency of 1000 Hz in the dark with the following conditions: electrolyte solution of 1.0 M NaOH; ac amplitude of 10 mV; dielectric constant of Fe$_2$O$_3$ was 12; spray solution concentration of 0.11 M FeCl$_3$ in absolute ethanol; spray time of 90 s; iodine dopant concentration of 0.0100 M; substrate temperature of 415°C. The reference electrode was SCE. Linear data points are observed for most of the data points with a correlation of 0.9911. The ac frequency had an intercept point at -1.0 V/SCE, which is similar to that of indium-doped or pure n-Fe$_2$O$_3$. From the slope of the Mott-Schottky plot, the donor density ($N_d$) can be calculated. At 1000 Hz, the slope was 4.678×10$^{10}$ m$^4$/CF, which corresponds to a donor density of 2.51×10$^{20}$ 1/cm$^3$. These results are similar to those of indium-doped and pure (undoped) n-Fe$_2$O$_3$ results reported earlier.$^8$
The donor density is found to be lower for higher frequencies (i.e., at 2320 Hz; a donor density of $1.92 \times 10^{20}$ 1/cm$^3$ and at 5000 Hz, a donor density of $1.18 \times 10^{20}$ 1/cm$^3$), which is consistent with the fact that the surface states contribute at lower frequencies.

![Graph](image)

**Figure 3.66.** Mott-Schottky ($1/C^2$ vs measured potential, where $C$ is the capacitance) plot for iodine-doped n-Fe$_2$O$_3$ films measured at an ac frequency of 1000 Hz under dark conditions: electrolyte solution of 1.0 M NaOH; ac amplitude of 10 mV; dielectric constant of Fe$_2$O$_3$ of 12; spray solution concentration of 0.11 M FeCl$_3$ in absolute ethanol; spray time of 90 s; iodine doping of 0.0100 M; substrate temperature of 415°C; reference electrode, SCE.

**G. X-ray Diffraction (XRD) Analysis of Thin Films**

The presence of iodine has been confirmed by sputtering X-ray diffraction (XRD). **Figure 3.67** shows XRD plots for optimized thin films of iodine-doped n-Fe$_2$O$_3$ made with 0.0077 to 0.0121 M iodine dopant with 0.11 M iron chloride. From the XRD plots, three compounds were identified $\alpha$-Fe$_2$O$_3$, I$_2$, and In$_2$O$_3$. The indium oxide was confirmed to be coming from the indium-doped tin oxide substrate. The thin films thus were a combination of $\alpha$-iron(III) oxide and iodine as the dopant within the thin films. As the iodine dopant concentration was increased, there were only small changes in the iodine peaks. These changes were small due to the low concentrations of iodine present in the thin films.
Figure 3.67. X-ray diffraction (XRD) plots of iodine-doped n-type iron(III) oxide (n-Fe$_2$O$_3$) thin film electrodes at 0.00770, 0.00825, 0.00880, 0.00935, 0.01000, and 0.01210 M iodine-doping. The peaks on the plots were identified as follows $\alpha$-Fe$_2$O$_3$ (a), cubic In$_2$O$_3$ (b), and iodine, I$_2$ (c).

Figures 3.68a and 3.68b. Scanning electron micrographs of iodine-doped n-Fe$_2$O$_3$ at (A) 0.00825 M iodine doping with 0.11 M FeCl$_3$·6H$_2$O at 410°C and at (B) 0.0100 M iodine doping with 0.11 M FeCl$_3$·6H$_2$O at 415°C.
The average crystal size was 1.10 nm for $\alpha$-Fe$_2$O$_3$ and 0.43 nm for I$_2$. With the low amount of iodine precursor added to the spray solution, there is a low amount of material available for crystal formation, thus the crystals are three times as small as the Fe$_2$O$_3$ crystals. However, the crystal sizes are much closer than the p-type Fe$_2$O$_3$ films. There is a general trend forming that the p-Fe$_2$O$_3$ films have much larger Fe$_2$O$_3$ crystals than the n-Fe$_2$O$_3$ films.

H. Scanning Electron Microscopy (SEM) Analysis of Thin Films

Figure 3.68a shows a SEM image for 0.00825 M iodine dopant with 0.11 M iron chloride concentration at 410°C and for 0.0100 M iodine dopant with 0.11 M iron chloride concentration at 415°C in Figure 3.68b. Both films show a very ordered and even structure. No large scale defects were seen on the films. There were a certain amount of defects present on other films made with indium, zinc, or copper as dopants.

![Figure 3.69](image)

**Figure 3.69.** Comparison of an iodine-doped Fe$_2$O$_3$ thin film electrode run under three- and two-electrode conditions. The electrode was prepared at 0.0100 M iodine-doping with 0.11 M FeCl$_3$ at 415°C at a spray time of 90 s.
I. Comparison of Photocurrent from Two- and Three-Electrode Configurations

In Figure 3.69, the optimized iodine-doped n-Fe$_2$O$_3$ thin film made with 0.0100 M iodine dopant with 0.11 M FeCl$_3$ at 415°C with a spray time of 90 s was run in two- and three-electrode configurations. The three-electrode configuration is the same result shown in earlier plots. The three-electrode configuration consisted of the iodine-doped n-Fe$_2$O$_3$ as a working electrode, platinum gauze as the counter electrode, and SCE as the reference electrode. The two-electrode system has the iodine-doped n-Fe$_2$O$_3$ as the working electrode and platinum gauze as the counter electrode with the absence of the reference electrode. The reference electrode is compared to the counter electrode. The three-electrode results are slightly lower than the results reported in earlier plots due to continued testing with electrode. However, the two-electrode system that was run back to back on the same day with the three-electrode run shows a lower output. For example, at the optimum efficiency voltage of $+0.3$ V, the photocurrent with three-electrodes was 1.51 mA/cm$^2$ and with two-electrodes, the photocurrent was 0.90 mA/cm$^2$. This is because in the two electrode system, p-Fe$_2$O$_3$ is acting as a reference electrode and hence the working electrode (n-Fe$_2$O$_3$) is not getting the same bias that it receives when the reference electrode is platinum.
3.6. Photoresponse of Manganese and Calcium-Doped n-Type Iron(III) Oxide Thin Films

A. Photocurrent-Potential Dependence

Figure 3.70 shows the dependence of photocurrent density \( (j_p, \text{mA/cm}^2) \) as a function of measured potential \( (E_{\text{meas}}, \text{V/SCE}) \) for the samples prepared by various spray times (80, 90, 100, 110, 120, and 130 s) for calcium-doped \( \text{Fe}_2\text{O}_3 \). These samples were made at a temperature of 415°C. The highest photocurrent density (at maximum efficiency) of 1.203 mA/cm\(^2\) at +0.2 V/SCE at a light intensity of 40 mW/cm\(^2\) was observed at the n-\( \text{Fe}_2\text{O}_3 \) thin film electrode synthesized using a spray time of 90 s. The results show an upward trend for the samples prepared using a spray times up to 90 s, and the photocurrent was constant till 130 s, and then a sharp decline in photocurrent was observed for the sample prepared using a spray time of 130 s. This behavior can be attributed to the fact that at lower spray times, the thickness of the film was not enough to absorb enough light. However, at higher spray times beyond 130 s, recombination becomes the dominant process as the field drop is reduced with further modification of the thin film to lengthen the time for the hole to react at the solution interface and electron migration time becomes too great to overcome and thus energy is lost to recombination.

Figure 3.71 shows the dependence of photocurrent density \( (j_p, \text{V/SCE}) \) as a function of measured potential \( (E_{\text{meas}}, \text{V/SCE}) \) for the samples prepared by various spray times (80, 90, 100, 120, and 130 s) for manganese-doped \( \text{Fe}_2\text{O}_3 \). These samples were made at a substrate temperature of 415°C. The highest photocurrent density (at maximum efficiency) of 0.655 mA/cm\(^2\) at +0.3 V/SCE at a light intensity of 40 mW/cm\(^2\) was observed at the n-\( \text{Fe}_2\text{O}_3 \) thin film electrodes synthesized using a spray time of 130 s. The results show an upward trend for the samples prepared using a total spray time of 130 s. This behavior can be attributed to the fact that at lower spray times, the thickness of the film is not enough to absorb enough light. However, at higher
spray times beyond 130 s, recombination becomes the dominant process as was seen above with calcium-doping.

**Figure 3.70.** Photocurrent density ($j_p$, mA/cm$^2$) versus measured potential ($E_{\text{meas}}$) for n-Fe$_2$O$_3$ samples produced at various spray times at a substrate temperature of 415°C. 0.0121 M calcium doping in 0.11M iron(III) chloride spray solution in absolute ethanol was used for the production of n-Fe$_2$O$_3$. The open circuit potentials varied from +0.39 to +0.55 V/SCE. Dark current measurements are shown and were the same for all samples, appearing only after +0.6 V/SCE.

**Figure 3.71.** Photocurrent density ($j_p$, mA/cm$^2$) versus measured potential ($E_{\text{meas}}$) for n-Fe$_2$O$_3$ samples produced at various spray times at a substrate temperature of 415°C. 0.0121 M manganese doping in 0.11M iron(III) chloride spray solution in absolute ethanol was used for the production of n-Fe$_2$O$_3$. The open circuit potentials varied from -0.32 to -0.39 V/SCE. Dark current measurements are shown and were the same for all samples, appearing only after +0.6 V/SCE.
Figure 3.72. Photocurrent, $j_P$ (mA/cm$^2$) & photoconversion efficiency ($\%\varepsilon_{\text{photo}}$) vs total time of spray prepared at 10 s spray intervals at 415°C for calcium-doped Fe$_2$O$_3$.

The photocurrent ($j_p$, mA/cm$^2$) and percent photoconversion efficiency ($\%\varepsilon_{\text{photo}}$; for $j_p$ at $E_{\text{meas}} = +0.2$ V/SCE) as a function of total spray time for different substrate temperatures are shown in Figures 3.72, 3.73, and 3.74 for calcium-doped Fe$_2$O$_3$ and manganese-doped (from manganese(II) nitrate and manganese(II) acetate) Fe$_2$O$_3$ samples, respectively.

Table 3.2. Percent photoconversion and total conversion efficiencies for calcium and manganese-doped p-Fe$_2$O$_3$ samples prepared using 10 spray periods for a total of 90 s spray time for calcium doping and 130 s for manganese doping at 415°C.

<table>
<thead>
<tr>
<th>Dopant</th>
<th>$E_{\text{aoc}}$ vs SCE (Volt)$^\dagger$</th>
<th>$%\varepsilon_{\text{photo}}$</th>
<th>$%$ Total Conversion Efficiency$^\dagger$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaCl$_2$</td>
<td>-0.512 Volt</td>
<td>1.56%</td>
<td>5.82%</td>
</tr>
<tr>
<td>Mn(NO$_3$)$_2$</td>
<td>-0.390 Volt</td>
<td>0.88%</td>
<td>2.91%</td>
</tr>
<tr>
<td>Mn(C$_2$H$_3$O$_2$)$_2$</td>
<td>-0.288 Volt</td>
<td>0.36%</td>
<td>1.06%</td>
</tr>
</tbody>
</table>

$^\dagger$ Note: $E_{\text{aoc}}$ equals $E_{\text{app}}$ where $E_{\text{meas}} = +0.3$ V/SCE

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Under the same conditions for production of all the thin film electrodes, calcium-doped Fe$_2$O$_3$ semiconductors have almost twice the photocurrent and photoconversion efficiency as that of manganese-doped semiconductors. One more property of note is that of the selection of the initial dopant material to be utilized in the Fe$_2$O$_3$ thin film to produce the needed dopant effect, which needs to be adequately close in parameters for a good thin film electrode to be formed. By examining Figures 3.73 and 3.74, we can see that the photocurrent and photoconversion efficiency are almost double when we used manganese(II) nitrate tetrahydrate over manganese(II) acetate tetrahydrate.

Figure 3.73. Photocurrent density, $j_p$ (mA/cm$^2$) and photoconversion efficiency ($\% \varepsilon_{\text{photo}}$) vs total time of spray prepared at 10 s spray intervals at 415°C for manganese-doped Fe$_2$O$_3$. (Note: Manganese(II) nitrate tetrahydrate was used in this set of data.)

**B. Reproducibility of Photoresponse of Spray Pyrolytically Synthesized of n-Fe$_2$O$_3$ Thin Films**

An important hallmark to thin film production is the reproducibility of any given semiconductor including magnesium-doped n-Fe$_2$O$_3$ thin films being studied herein. To test the
reproducibility of calcium-doped n-Fe₂O₃ thin films, three samples were synthesized at the optimum conditions of 415°C for 90 s spray time using a spray solution of 0.11 M FeCl₃ and 0.0121 M calcium chloride (CuCl₂) in absolute ethanol. Photocurrents of these samples were measured in 1.0 M NaOH electrolyte using a light intensity of 40.0 mW/cm². These samples were found to have an open circuits ranging of +0.52 ± 0.01 V/SCE.

**Figure 3.74.** Photocurrent density, $j_P$ (mA/cm²) and photoconversion efficiency (%$\varepsilon_{\text{photo}}$) vs total time of spray prepared at 10 s spray intervals at 415°C for manganese-doped Fe₂O₃. (Note: Manganese(II) acetate tetrahydrate was used in this set of data.)

**Figure 3.75** shows the photocurrent density ($j_P$, mA/cm²) versus measure potential ($E_{\text{meas}}$, V/SCE). All three samples had a constant set of values at all potential values. At +0.3 V/SCE, the samples had a fairly constant value of photocurrent, which represented also the maximum efficiency point. An average photocurrent density of 1.364 mA/cm² (1.419, 1.386, and 1.288 mA/cm²) was found at +0.3 V/SCE for these samples. These data points correspond to a standard
deviation (σ) of ±0.05568 mA/cm². This indicates a good reproducibility by spray pyrolytically synthesized n-Fe₂O₃ thin films in the present work.

Figure 3.75. Reproducibility test of spray pyrolysis synthesis of calcium-doped n-Fe₂O₃ thin film electrodes. The photocurrent density (j_p, mA/cm²) versus the measured potential (E_{meas}, V/SCE) of three calcium-doped n-Fe₂O₃ films synthesized by SPD. The conditions used on the three samples were 90 s total spray time, 0.11 M FeCl₃ and 0.0121 M CaCl₂ in absolute ethanol, pyrolysis temperature of 415°C, electrolyte solution of 1.0 M NaOH, and a light intensity of 150 W Xe lamp of 40.0 mW/cm². All samples have open circuits ranging from +0.52 ± 0.01 V/SCE.

C. Uv-vis Spectroscopic Results

Figure 3.76 shows the uv-vis spectroscopic data for calcium and manganese-doped n-type Fe₂O₃ semiconductors. The absorption spectrum exhibits a broad absorption in the visible region, which extends into the uv region, with a tail extending to 580 nm. The threshold of absorption at 580 nm (2.14 eV) is in approximate agreement with the band gap value of 2.2 eV for undoped Fe₂O₃. This sample was synthesized using the optimum conditions which include 90 s (Mn) and 100 s (Ca) spray time, 0.11 M FeCl₃ and 0.0121 M CaCl₂ and 0.0121 M Mn(NO₃)₂ in absolute ethanol and pyrolysis temperature of 415°C.
Figure 3.76. UV-vis reflectance data for calcium and manganese-doped Fe$_2$O$_3$. The samples show intersections with the x-axis at 580 nm for both, which corresponds to a band gap of 2.14. The calcium-doped sample exhibited a higher amount of photon absorption in the visible region of the solar spectrum than the manganese-doped sample.

Figure 3.77. X-Ray diffraction plots of manganese (top line) and calcium (bottom line)-doped n-type iron(III) oxide. The peaks on the plots were identified as $\alpha$-Fe$_2$O$_3$ (A), In$_2$O$_3$ (B), Fe$_2$MnO$_4$ (C), and Fe$_2$CaO$_4$ (D).
D. X-Ray Diffraction Results

Figure 3.77 shows X-ray diffraction (XRD) plots of n-type iron(III) oxide (p-Fe$_2$O$_3$) thin film electrodes with manganese doping (top line) and calcium doping (bottom line.) The peaks on the plots were identified as $\alpha$-Fe$_2$O$_3$ (A), In$_2$O$_3$ (B), and iron(III) manganese(II) oxide, Fe$_2$MnO$_4$ (C) and iron(III) calcium(II) oxide, Fe$_2$CaO$_4$ (D). The In$_2$O$_3$ was from the indium-doped tin oxide substrate on which the doped Fe$_2$O$_3$ thin films were deposited. Many of the peaks of iron(III) calcium(II) oxide and iron(III) manganese(II) oxide were not as pronounced, because their amounts in the thin film are minimal. These peaks indicate that spray pyrolytically synthesized n-Fe$_2$O$_3$ have mixed structures of $\alpha$-iron(III) oxide and iron(III) manganese(II) oxide or iron(III) calcium(II) oxide.

It was reported earlier$^{68,94,111,118,120}$ that the best Fe$_2$O$_3$ semiconductors are of mixed states. These semiconductors are clearly of mixed states, $\alpha$-Fe$_2$O$_3$, Fe$_2$MnO$_4$, and Fe$_2$CaO$_4$. The presence of Fe$_2$MnO$_4$ and Fe$_2$CaO$_4$ in the XRD plots clearly shows the presence of manganese and calcium in their respective thin film semiconductors.

The average crystal size was 0.93 nm for $\alpha$-Fe$_2$O$_3$ with Mn-doping, 0.88 nm for $\alpha$-Fe$_2$O$_3$ with Ca-doping, 0.45 nm for Fe$_2$MnO$_4$, and 0.18 nm for Fe$_2$CaO$_4$. With the low amount of manganese and calcium precursor added to the spray solutions, there is a low amount of material available for crystal formation, thus the crystals are twice as small as the Fe$_2$O$_3$ crystals with manganese doping and five times smaller than the Fe$_2$O$_3$ crystals. However, the crystal sizes are much closer than the p-type Fe$_2$O$_3$ films. Thus this demonstrates why manganese and calcium doping showed n-type behavior rather than the expected p-type behavior.

However, these n-type electrodes did not improve the photocurrent of the n-type Fe$_2$O$_3$ electrodes with the addition of calcium or manganese. It was expected that these dopants would produce p-type Fe$_2$O$_3$ thin films, but when run in the opposite direction and in an acidic media, the
electrodes showed none or almost no photocurrent. When these electrodes are run in basic media for n-type scanning, the electrodes did not show significant photocurrent results. In fact, the results were on the order of 3 to 4 times lower than those for undoped Fe$_2$O$_3$ thin films made by spray pyrolysis.$^8$
3.7. Photoelectrochemical Water Splitting by a Carbon Modified CM-n-TiO₂⁵

A. X-ray diffraction and SEM results

The X-ray diffraction (XRD) of the CM-n-TiO₂ film showed mainly rutile structure (Figure 3.78a). However, the reference n-TiO₂ film shows a mixture of rutile and anatase crystalline forms (Figure 3.78a). The scanning electron microscopic (SEM) results indicate that CM-n-TiO₂ is more porous (represented by more dark spots) compared to a reference n-TiO₂ sample (Figures 3.78, b and c). X-ray photoelectron spectroscopic (XPS) data indicate an average composition of CM-n-TiO₂ to be n-TiO₂₋ₓCₓ where x is ~ 0.15. The presence of CO₂, a combustion product in the natural gas flame at 850°C, facilitated the incorporation of carbon in the n-TiO₂ films. The presence of steam (H₂O) in the flame is expected to enhance the rate of titanium oxide film formation.¹⁶⁹ The XPS analysis also showed the absence of nitrogen and hydrogen in both CM-n-TiO₂ and the reference n-TiO₂ films. Scherer’s calculations show an average crystal size of 0.75 nm.

B. Uv-vis results

The optical absorption spectra (Figure 3.79) show that CM-n-TiO₂ films absorb appreciably at wavelengths less than 535 nm (which corresponds to a band gap energy of 2.32 eV) whereas the reference n-TiO₂ samples did not. The CM-n-TiO₂ films show two optical absorption thresholds at 535 and 440 nm (Figure 3.79) in the visible range, whereas the reference n-TiO₂ shows only one at 414 nm which corresponds to a band gap energy of 3.0 eV (Figure 3.79). These two

adsorption thresholds indicate two possible compositions of carbon modified titanium oxide, n-TiO$_{2-x}$C$_x$.

C. Photocurrent Density and Photoconversion Efficiency

The photoresponse of CM-n-TiO$_2$ films was evaluated by measuring the rate of water-splitting reaction to hydrogen and oxygen which is proportional to photocurrent density, $j_p$. We verified that H$_2$ and O$_2$ are the photoproducts by gas chromatographic (GC) analysis using a SRI 8610 chromatograph equipped with a thermal conductivity detector (TCD). Also, CO and CO$_2$ were not found in the photoproducts by GC analysis using Perkin Elmer 8500 chromatograph equipped with TCD. Furthermore, we collected gaseous photoproducts and observed exactly 2 to 1 volume ratio of H$_2$ and O$_2$ which further confirmed water splitting.

Figure 3.78. (a) X-ray diffraction (XRD) pattern for a CM-n-TiO$_2$ (flame made) and the reference n-TiO$_2$ (electric tube furnace or oven made) photoelectrodes where Ti represents titanium metal, A = Anatase and R = Rutile peaks, respectively; Scanning electron micrograph (SEM) of (b) CM-n-TiO$_2$ (flame made) and (c) reference n-TiO$_2$ (electric tube furnace or oven made) samples.
Photocurrents were measured using a 0.2 cm$^2$ area CM-n-TiO$_2$ sample under illumination from a 150 W xenon arc lamp (Hanovia) fitted with an infrared light filter. This xenon arc lamp can generate maximum half of the power density (50 mW/cm$^2$) of air mass 1.5.$^{53}$ The electrical contact was made with Ti metal substrate by using silver epoxy connected to a copper wire. A conventional three electrode configuration in a single compartment cell was used with CM-n-TiO$_2$ film, platinum foil and a saturated calomel electrode (SCE) as the working, counter and reference electrodes, respectively. Photocurrent density as a function of electrode potential were measured with an EG&G 362 scanning potentiostat and recorded using an X-Y recorder, Houston, model RE0092. The intensity of the light source (in mW/cm$^2$) was measured by a radiometer (International Light Co., model IL 1350). The electrolyte, 5 M KOH, was freshly prepared using double deionized water having resistivity of 18 MΩ/cm. All solutions were prepared from analytical grade reagents.

**Figure 3.79.** The uv-vis spectra of CM-n-TiO$_2$ (flame made) and reference n-TiO$_2$ (electrical tube furnace or oven made). The Flame made sample shows threshold wavelength of 535 nm (band gap of 2.32 eV) and 440 nm (band gap of 2.82 eV); electric tube furnace or oven made sample shows 414 nm (band gap of 3.0 eV).
Photocurrent densities, \( j_p \) (which correspond to rates of production of hydrogen and oxygen) from the water-splitting reaction at CM-n-TiO\(_2\) as a function of applied potential, \( E_{\text{app}} \) under illumination of light of power density 40 mW/cm\(^2\) from a 150 W xenon lamp are shown in Figure 3.80. The observed dark current densities were found to be negligible (Figure 3.80).

The maximum photoconversion efficiency, \( \%\varepsilon_{\text{photo}} \) of 8.35\% (which corresponds to a total conversion efficiency of 11.0\%) was observed at a minimal applied potential of 0.30 V with a photocurrent density of 3.60 mA/cm\(^2\) (Figure 3.80). For CM-n-TiO\(_2\) electrode \( E_{\text{aoc}} = -1.0 \) V/SCE was observed at illumination intensity of 40 mW/cm\(^2\) in 5 M KOH solution. Note that the total conversion efficiency of light and electrical energy to chemical energy, \( \varepsilon_{\text{total}} \) was calculated by neglecting \( E_{\text{app}} \). However, under similar conditions of illumination the maximum photoconversion efficiency of 1.08\% was observed at a higher applied potential of 0.60 V for the reference n-TiO\(_2\) samples under 150 W xenon lamp illumination (Figure 3.81). These results confirm that flame pyrolysis carbon modified n-TiO\(_2\) and lowered its band gap energy to a minimum value of 2.32 eV to absorb visible light. The lowering of the band gap energy did not affect the stability of CM-n-TiO\(_2\), because photoconversion efficiency did not reduce during its successive uses under 40 mW/cm\(^2\) illumination intensity in the last six months.

**D. Water Splitting in the Presence of Methanol**

There was also an interest in the methanol and ethanol chemistry with CM-n-TiO\(_2\). To better understand what is taking place to make this chemistry favorable, we need to look at the reactions involved in these hydrogen production processes.

The reaction for the solar production of hydrogen at the photocatalyst (CM-n-TiO\(_2\)) electrode from methanol/water is the following:
Hydrogen from methanol and water (6 electron-hole transfer reaction):

\[
\text{CH}_3\text{OH} + \text{H}_2\text{O} + \text{CM-nTiO}_2 \text{ (photocatalyst)} + \text{sunlight} \rightarrow 3\text{H}_2 + \text{CO}_2 \tag{3.1}
\]

It is important to note that a **three-fold** increase in hydrogen (H\(_2\)) production is expected when one mole of methanol in presence of one mole of water is oxidized (**Reaction 3.1**) as compared to that from photo-splitting of water itself (**Reaction 1.5**). However, it is notable that only one mole of carbon dioxide is generated during methanol/water oxidation compared to that obtained by combustion of high carbon content fuel. Very small amounts of carbon dioxide could be easily collected at the photoanode for sequestration. Our results of water splitting in the presence of methanol in aqueous acidic electrolyte (0.5 M H\(_2\)SO\(_4\)) at a CM-n-TiO\(_2\) electrode shows much higher rate (photocurrent density) of photochemical generation of hydrogen as compared to that from photosplitting of water itself in the same electrolyte (**Figure 3.82**).

There is also a considerable improvement in efficiency by the addition of methanol to an acidic solution. **Figure 3.83** show a plot of photoconversion efficiency versus applied potential (E\(_{\text{app}}\) vs E\(_{\text{aoe}}\)). The efficiency goes from 6.9\% at +0.46 V to 8.9\% at +0.28 V. This equates to almost a 25\% gain in photoconversion efficiency by the addition of methanol to the solution.
Figure 3.80. Photocurrent density, $j_p$ (mA cm$^{-2}$) as a function of applied potential, $E_{app}$ (V) at CM-n-TiO$_2$ (flame made) and the reference n-TiO$_2$ (electric tube furnace or oven made) photoelectrodes under xenon lamp illumination at an intensity of 40 mW/cm$^2$. Also the dark current densities at CM-n-TiO$_2$ (flame made) as a function of applied potential are given.

Figure 3.81. Photoconversion efficiency ($\%\varepsilon_{\text{photo}}$) as a function of applied potential, $E_{app}$ (V) at CM-n-TiO$_2$ (flame made) and the reference n-TiO$_2$ (electric tube furnace or oven made) photoelectrodes under xenon lamp illumination at an intensity of 40 mW/cm$^2$. 
Figure 3.82. Photocurrent density, $j_p$ (mA/cm$^2$) as a function of measured potential, $E_{\text{meas}}$ (V/SCE) at a CM-n-TiO$_2$ (flame made) photoelectrodes under xenon lamp illumination at an intensity of 40 mW cm$^{-2}$. It shows that at lower applied potential the rate of photochemical hydrogen generation (photocurrent density, $j_p$) is much higher from methanol/water system and water itself in 0.5M H$_2$SO$_4$ solution.

Figure 3.83. Photoconversion efficiency, ($\%e_{\text{photo}}$) as a function of applied potential, $E_{\text{app}}$ (V) vs $E_{\text{aoc}}$ (where $E_{\text{aoc}}$ is the electrode potential at open circuit under illumination which was found –1.0 V/SCE) at a CM-n-TiO$_2$ (flame made) photoelectrodes under xenon lamp illumination at an intensity of 40 mW/cm$^2$. 
E. Longevity Study

We also tested in the stability of CM-n-TiO$_2$ semiconductors. Figure 3.84 shows the photocurrent data for a highly efficient CM-n-TiO$_2$ run in various experiments over a two year period. This figure shows the initial photocurrent data for the sample and photocurrent data for the sample that was recorded two years later. No noticeable change in photocurrent was observed. The observed negligible change is within experimental error.

![Photocurrent data for CM-n-TiO$_2$ that was run intermittently over a two year period. The photocurrent data from the initial photocurrent scan and a scan done 2 years later are presented. The illumination intensity was 40 mW/cm$^2$ from a 150 W xenon lamp.](image)

F. A Study on Samples Prepared by Pittsburgh Plate Glass (PPG) Corporation

After the publication of our work on carbon-modified (CM) n-TiO$_2$ by flame oxidation, we received samples prepared by Pittsburgh Plate Glass (PPG) Corporation. These samples were much larger than samples that we normally synthesized in our lab. While preparation of larger size samples will be the eventual goal of the research, these samples lacked uniformity, and thus
were cut down into regions and samples from distinct regions were measured. The samples labeled PPGA, PPGB, and PPGC were from one sample, which exhibited the best photocurrent response. These samples most closely resembled the samples prepared in our lab. These results along with the results of our two samples (#s 11 and 50) were tabulated. The corresponding plot of current density under 40 mW/cm² from a 150 W xenon arc lamp are shown in Figure 3.85 and the photoconversion efficiencies are plotted in Figure 3.86. These results clearly show that PPG could closely reproduce the results that we obtained in our laboratory and reported earlier. In Table 3.3, these results are summarized for the PPG samples and also for samples (#11 and #50) prepared in our laboratory.

Table 3.3. Results of % photoconversion efficiency and % total conversion efficiency of CM-n-TiO₂ synthesized by flame oxidation prepared by Pittsburgh Plate Glass (PPG) Corp (PPGA, B, and C) and samples 11 and 50 were made in our laboratory.

<table>
<thead>
<tr>
<th>Sample #</th>
<th>Electrode Area (cm²)</th>
<th>i_p (Max.) (mA/cm²)</th>
<th>% Photoconversion Eff.</th>
<th>%ε_eff (Max.)</th>
<th>E meas (V/SCE)</th>
<th>E_aoc (V/SCE)</th>
<th>E_app (V) vs E_aoc</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPGA</td>
<td>0.257</td>
<td>3.7</td>
<td>6.81</td>
<td>-0.6</td>
<td>-1.093</td>
<td>0.493</td>
<td></td>
</tr>
<tr>
<td>PPGB</td>
<td>0.214</td>
<td>3.53</td>
<td>7.86</td>
<td>-0.6</td>
<td>-0.939</td>
<td>0.339</td>
<td></td>
</tr>
<tr>
<td>PPGC</td>
<td>0.291</td>
<td>3.64</td>
<td>7.7</td>
<td>-0.7</td>
<td>-1.085</td>
<td>0.385</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>0.178</td>
<td>4.08</td>
<td>8.23</td>
<td>-0.6</td>
<td>-1.023</td>
<td>-1.023</td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>0.132</td>
<td>4.47</td>
<td>8.55</td>
<td>-0.6</td>
<td>-1.065</td>
<td>-1.065</td>
<td></td>
</tr>
</tbody>
</table>
Figure 3.85. Photocurrent density, $j_p$, at xenon arc lamp light intensity of 40.0 mW/cm² versus measured potential ($E_{meas}$) for CM-n-TiO₂ samples supplied by PPG.

Figure 3.86. Photoconversion efficiency, $\% \varepsilon_{\text{photo}}$, at 150 W xenon arc lamp light intensity of 40.0 mW/cm² versus applied potential ($E_{app}$ vs $E_{aoc}$, $E_{aoc} = -1.0$ V/SCE) for CM-n-TiO₂ samples from PPG produced from the better quality sample.
3.8. Photoresponse of Metal Islet Deposited n-Fe₂O₃ Thin Films

A. Gold Photoelectrodeposition

Electrodeposition was carried out using the method outlined earlier. Various metals islets were deposited galv昂statically at a various current densities. The samples were illuminated with the 150 W xenon lamp at an intensity of 100 mW/cm² during electrodeposition.

![Gold Deposition @ -0.1 mA/cm²](image)

**Figure 3.87.** Gold deposition at -0.1 mA/cm² on n-Fe₂O₃ for 1, 2, & 3 s. The fabrication conditions include: temperature of 415°C; spray time of 90 s; spray solvent of absolute ethanol; and electrolyte solution of 1.0 M NaOH.

All samples used had electrode potentials at open circuit conditions that had an average value of +0.4 ± 0.1 V/SCE. **Figure 3.87** shows gold deposition for 1, 2, & 3 s with gold electrodeposition done under -0.1 mA/cm² at an illumination intensity of 100 mW/cm² during electrodeposition. **Figure 3.88** shows gold deposition for 1, 2, 3 & 4 s with gold electrodeposition done under -0.2 mA/cm² at an illumination intensity of 100 mW/cm² during electrodeposition. **Figure 3.89** is for gold deposition done at -0.3 mA/cm². All samples used had electrode potentials.
at open circuit conditions that had an average value of $+0.4 \pm 0.1$ V/SCE. There was negligible catalytic activity from gold deposition on the surface of n-Fe$_2$O$_3$ thin films at -0.1 mA/cm$^2$, the gold deposition decreased the current density results. However, gold deposition using -0.2 mA/cm$^2$, there was a small increase in photocurrent density after 2 seconds of deposition. The photocurrent density increased most significantly between a measured potential of +0.3 and +0.4 V/SCE, which is where the photoconversion efficiency is maximized. The factor that would have made these electrocatalysts effective would have been their ability to shift the onset potential to a more negative potential. However, this was not observed for any gold deposition conditions, as well as for platinum deposition. Also, it should be noted that the photocurrent density for samples with no electrocatalyst present varied for each set of data. That is because all optimized samples used for the electrocatalyst deposition were not of identical quality.

Figure 3.88. Gold deposition at -0.2 mA/cm$^2$ on n-Fe$_2$O$_3$ for 1, 2, 3, & 4 s. The fabrication conditions include: temperature of 415°C; spray time of 90 s; spray solvent of absolute ethanol; and electrolyte solution of 1.0 M NaOH.
Gold Deposition @ -0.3 mA/cm²

0 s
1 s
2 s
3 s
4 s

Photocurrent Density $j_P$ (mA/cm²)

Emas (V/SCE)

Gold deposition at -0.3 mA/cm² on n-Fe₂O₃ for 1, 2, 3, & 4 s. The fabrication conditions include: temperature of 415°C; spray time of 90 s; spray solvent of absolute ethanol; and electrolyte solution of 1.0 M NaOH.

Pt Dep. @ -0.1 mA/cm²

0 s
1 s
2 s
3 s

Photocurrent Density $j_P$ (mA/cm²)

Emas (V/SCE)

Platinum deposition at -0.1 mA/cm² on n-Fe₂O₃ for 1, 2, & 3 s. The fabrication conditions include: temperature of 415°C; spray time of 90 s; spray solvent of absolute ethanol; and electrolyte solution of 1.0 M NaOH.
B. Platinum Photoelectrodeposition

Photoelectrodeposition of platinum was done on various n-Fe₂O₃ samples from -0.4 to -0.1 mA/cm². Electrocatalyst deposition done at -0.4 and -0.3 mA/cm² gave negative results (i.e., photocurrent density decreased). Figure 3.90 shows platinum deposition for 1, 2, & 3 s with platinum electrodeposition done under -0.1 mA/cm² at an illumination intensity of 100 mW/cm² during electrodeposition. Figure 3.91 is the same as Figure 3.90 but with platinum deposition done at -0.2 mA/cm². Electrocatalyst deposition at -0.1 and -0.2 mA/cm² with platinum showed improved photocurrent density at 1 and 2 s; however, as mentioned above the onset potential did not shift in the negative voltage range, thus no marked improvement was made. Electrodeposition at -0.3 mA/cm² may have blocked the surface of the semiconductor and reduced light absorption and consequently photocurrent density decreased considerably as shown in Figure 3.91. Note that platinum deposition improved the photoresponse of n-Fe₂O₃, but gold deposition reduced the photoresponse due to the fact that gold acted as a recombination center rather than a catalyst.

![Figure 3.90](image1.png)

**Figure 3.90.** Platinum deposition at -0.2 mA/cm² on n-Fe₂O₃ for 1, 2, & 3 s. The fabrication conditions include: temperature of 415°C; spray time of 90 s; spray solvent of absolute ethanol; and electrolyte solution of 1.0 M NaOH.
3.9. Comparison of Running Undoped n-Fe$_2$O$_3$ under 150 and 1000 W Light Sources

In this section, we give our research on two distinctly different light sources so as to compare the results. In Figure 3.92, the upper line shows results for an undoped Fe$_2$O$_3$ thin film run under a 150 W xenon lamp set at 165 mW/cm$^2$. This is the typical lamp that the research was performed under. The bottom line shows the same sample run under the 1000 W lamp at 200 mW/cm$^2$. Both scans were run consecutively the same day to avoid uncertainty in the results.

![Photocurrent Density vs. Measured Voltage](image)

**Figure 3.92.** Undoped n-Fe$_2$O$_3$ was run under illumination with a 150 W xenon lamp at 165 mW/cm$^2$ and with a 1000 W xenon lamp at 200 mW/cm$^2$.

So, the question that needs to be resolved is to why there is such a large difference between the photocurrent from each lamp. In Figure 3.93, we show the AM 1.5 solar standard with the output from a 150 W xenon lamp standardized to the solar standard and a 1000 W xenon lamp standardized to the same level. The key issues that are causing the large difference between the photocurrent measurements between the 150 W lamp results and the 1000 W lamp results from Figure 3.93 are quite unclear. It is observed that the loss in the uv region by the solar simulator is
over-compensated in the visible region. Hence, such an observation is difficult to explain for iron oxide, which can easily absorb light up to 620 nm. Also, since uv radiation is higher for the 150 W xenon arc lamp, the number of photons may not be high. This is because each uv photon is high in power. The absorption coefficient of uv light may be higher than that of visible light for Fe₂O₃. Also, the electron-hole pair generated by high energy uv light may undergo a lower rate of recombination than those generated by visible light. Hence, visible light photons cannot produce higher photocurrent density due to enhanced recombination of carriers generated visible light photons.

![Graph showing power vs. wavelength for different lamps](image)

**Figure 3.93.** Comparison of the AM 1.5 (Global) solar standard, and a 150 W xenon lamp and a 1000 W xenon lamp standardized to the solar standard. The recorded lamp data tails off, because the range of the detector used was reached.
3.10. **The Effect of Stacking Undoped n-Fe₂O₃ Thin Film Semiconductors**

After the significant amount of work that has been done to optimize doped and undoped films, there is an interest in the effect of running several electrodes in tandem, or in other words stacking electrodes. We can also place electrodes at 60° angles to each other and then multiple absorptions and reflections of light can occur to enhance the photocurrent density.

The optimized undoped n-Fe₂O₃ thin films are used in stacks and the results were given in Figure 3.94. It is observed that one, two, three, and four stacked layered electrodes generated photocurrent slightly higher than each other according to the expected trend. However, there is a decline in photocurrent density for five layered electrodes. This result is not according to the expected trend. It is possible that the contribution of photocurrent density is minimized from the fifth electrode and these photocurrents should have shown limiting behavior. But the observed decline for five layered electrodes is not clearly defined; however degradation of electrodes may be responsible for such behavior.

Another interesting phenomenon that needed to be explored was the difference between the stacking 2 electrodes and aligning them at a 60° angle from each other. In Figure 3.95, the photocurrent densities for two layered electrodes stacked back to back and also at a 60° angle (see Figure 3.96) are shown. This arrangement at a 60° angle relies on multiple reflections between two samples, as well as direct illumination. These samples were run under the 150 W Xe lamp. The results show that photocurrent density was slightly better, when the samples were illuminated at 60°, rather than stacked back to back as shown in Figure 3.95 and illustrated in Figure 3.96. The advantage to putting two samples at a 60° angle is that the net area being illuminated is equal to illuminating only one sample of two equal area electrodes as shown in Figure 3.97.
Figure 3.94. The effect of stacking electrodes back-to-back. The light passes from the front of one electrode and out the back of the first electrode and on to the front surface of the second electrode and continues to the fifth electrode. The electrodes being stacked are undoped n-Fe$_2$O$_3$. The electrode order was switched in several configurations with the same result. The 5 electrodes used here are all high quality and equal to the 1 layer results presented.

Figure 3.95. The light passes from the front of one electrode and out the back of the first electrode and onto the front surface of the second electrode. The electrodes being stacked are undoped n-Fe$_2$O$_3$. Two stacked electrodes run under a 150 W Xe lamp illumination. There are also results for two electrodes at a 60° angle facing each other, which relies on direct reflections on each sample. These were also run under a 150 W xenon arc lamp at 40 mW/cm$^2$.
Figure 3.96. Schematic diagram for the arrangement of 3 n-Fe$_2$O$_3$ electrodes back to back for photoelectrochemical illumination. The light passes through the first electrode and out the back of the substrate, where ~60% of the light remains to fall onto the surface of the second electrode. After going the second substrate and to the second ~45% of the light remains to pass onto the surface of the third electrode. The same is done up to five layers total.

Exposed Area = 1 cm$^2$

Figure 3.97. Overhead view of two equal area electrodes arranged in a 60° angle to each other. When arranged in this configuration the area at the front equals 1 cm$^2$, which is also the area of a single electrode.
3.11. Effect of Spray Solution Solvent on Photoresponse of Undoped n-Fe$_2$O$_3$

During the initial study of Fe$_2$O$_3$, the parameters of synthesis time of thin films of n-Fe$_2$O$_3$ were optimized, including the temperature of the substrate, the angle at which the spray solution was sprayed, the pressure of the carrier gas, and the solvent used to make iron chloride spray solution compound.

In Figure 3.98, the effect of the solvent of the spray solution used for spray pyrolysis was examined. For undoped Fe$_2$O$_3$, it was found that increasing the solvent molecular weight increased the photocurrent density and photoconversion efficiency. Another key is that the onset potential also moved to a more negative direction as the solvent molecular weight was increased also. This doubling of photocurrent density when the solvent was changed from ethanol to 1-pentanol may be due to incorporation of more carbon by more carbon containing solvent in the n-Fe$_2$O$_3$ structure that helped to increase the conductivity of iron(III) oxide.

![Figure 3.98. The effect of spray solution solvent used during SPD of undoped n-Fe$_2$O$_3$.](image)

Figure 3.98. The effect of spray solution solvent used during SPD of undoped n-Fe$_2$O$_3$. 
Figure 3.99. X-ray diffraction (XRD) plot of undoped n-type iron(III) oxide (n-Fe$_2$O$_3$) thin film electrodes made using 1-pentanol as the spray solution solvent. The peaks on the plots were identified as follows $\alpha$-Fe$_2$O$_3$ (a) and cubic In$_2$O$_3$ (b).

Figure 3.99 shows an X-ray diffraction (XRD) plot of undoped n-Fe$_2$O$_3$ synthesized using 1-pentanol as the spray solvent. XRD data indicates that $\alpha$-Fe$_2$O$_3$ is the only form of iron oxide present in the thin films. Indium oxide from the indium-doped tin oxide substrate was identified. The average crystal size was found to be 0.40 nm for $\alpha$-Fe$_2$O$_3$. 
3.12. A Self-Driven p/n-Fe$_2$O$_3$ Tandem Photoelectrochemical Cell (PEC) for Water Splitting

A. Photocurrent Density

We report here a self-driven p/n-Fe$_2$O$_3$ PEC for direct water photoelectrolysis. The set-up (Figure 3.100) of the electrode was such that the light was absorbed by the n-Fe$_2$O$_3$ thin film (counter electrode) and the transmitted light (~60%) that passed through the quartz substrate and the electrolyte solution was then absorbed by the p-Fe$_2$O$_3$ thin film (working electrode). This tandem arrangement of photoelectrodes was advantageous because the total surface area considering equal surface areas for both photoelectrodes was that of the front electrode (n-Fe$_2$O$_3$), which was directly exposed to the light source. A quartz substrate was purchased from Swift Glass Co. The inset of Figure 3.100 shows the individual electrode construction with an indium-doped tin oxide (ITO) coating deposited on the surface. The Fe$_2$O$_3$ thin films were fabricated on ITO coated quartz substrate by spray pyrolytic deposition (SPD). The details of zinc-doped p-Fe$_2$O$_3$ and undoped n-Fe$_2$O$_3$ thin film electrodes were reported earlier.$^{8,9,28,30,121}$ Note that the undoped n-Fe$_2$O$_3$ used in this PEC was synthesized using 1-pentanol as the solvent for making the 0.11 M FeCl$_3$·6H$_2$O spray solution. The photoresponse of this sample is given in Figure 3.101.

Figure 3.101 shows the cathodic current density versus voltage for a zinc-doped p-Fe$_2$O$_3$ thin film electrode run in a two-electrode configuration using Pt as the counter electrode in 0.5 M H$_2$SO$_4$ (curve 1). The key to this result is that Fe$_2$O$_3$ is naturally an n-type semiconductor; however, when a zinc-doped Fe$_2$O$_3$ thin film is run in an acidic solution in the anodic direction, there is zero photocurrent; however, when run in the cathodic direction, there is a notable photocurrent carrier. Curve 2 shows the current-voltage dependence of the p/n-Fe$_2$O$_3$ PEC with p-Fe$_2$O$_3$ as the working electrode and n-Fe$_2$O$_3$ as the counter electrode in 0.1 M H$_2$SO$_4$. These photoelectrodes were exposed to light of intensity of 100 mW/cm$^2$ (or 1 sun) from an Oriel (Model
91192) solar simulator with an AM 1.5 direct filter. To ascertain, if the photocurrent density is correct, the experiments were run without illumination, to get a dark current density measurement. There was negligible dark current density, which reinforced the fact that the photocurrent was observed for p- and n-type thin films put in tandem.

**Figure 3.100.** (Left) Schematic diagram of a two photoelectrodes (p- and n-type Fe\(_2\)O\(_3\)) back to back in tandem, where p-Fe\(_2\)O\(_3\) was used as the working electrode and n-Fe\(_2\)O\(_3\) as the counter electrode with which the reference electrode was connected, for water splitting PEC with an inset of an individual photoelectrode configuration. The p- and n-Fe\(_2\)O\(_3\) thin films were deposited on the indium-doped tin oxide (ITO) coated quartz substrate. (Right) An idealized schematic for a p/n-Fe\(_2\)O\(_3\) electrolyte interface.

**B. Self-Driven Current Density**

In a self-driven PEC in the absence of externally applied potential, photocurrent for H\(_2\) evolution must be observed at zero voltage or at any voltage in the positive direction at the photocathode (p-Fe\(_2\)O\(_3\)) when it is used as the working electrode and n-Fe\(_2\)O\(_3\) is used as the counter electrode.\(^{76}\) **Figure 3.102** shows the self-driven current density for the p/n-Fe\(_2\)O\(_3\) photoelectrochemical cell shown in **Figure 3.100.** The photoelectrode in the front (n-Fe\(_2\)O\(_3\)) was
exposed to illumination intensity of 100 mW/cm² from an Oriel solar simulator with an AM 1.5 direct filter (or 1 sun). This shows a short circuit current density, $I_{sc}$ of -0.091 mA/cm² and an open circuit potential, $V_{oc}$ of +0.5 V. A fill factor, $ff = \frac{I_{m}E_{m}}{I_{sc}V_{oc}}$, of 0.267 was found for at a measured photocurrent density, $I_{m}$, of -0.06 mA/cm², measured potential, $E_{m}$, of 0.2 V. As we mentioned earlier, it is advantageous to illuminate the two thin films back to back because the total area is used in calculations involving photocurrent and efficiency and running the two electrodes back to back reduces the total area by a factor of 2. The photoconversion efficiency is 0.11%.

![Figure 3.101. Current-voltage dependence for two electrode systems of p-Fe$_2$O$_3$/Pt (curve 1) and p-Fe$_2$O$_3$/n-Fe$_2$O$_3$ (curve 2) electrode systems in 0.5 M H$_2$SO$_4$ (curve 1) and 0.1 M H$_2$SO$_4$ (curve 2) under an illumination intensity of 100 mW/cm$^2$ from an Oriel solar simulator with an AM 1.5 direct filter. The open circuit potential was found to be -0.254 V for curve 1 and +0.5 V for curve 2. At and near zero current density, the dark current for each of the samples zero till -0.6 to -0.8 V. Both experiments showed almost zero current density in the measured voltage range.](image-url)
The major drawback of this p/n-Fe₂O₃ tandem PEC was its low photocurrent density and the consequent low efficiency for the self-driven water splitting in this initial study. Low photocurrent density is due to low photocatalytic activity and low electrical conductivity and hence high recombination of photogenerated electrons and holes. The conductivity was improved to some degree by incorporation of proper dopants.²⁸,³⁰,³¹,¹²¹ However, both p- and n-Fe₂O₃ thin films showed stability during repeated usage. The stability of the electrodes was verified during an extended test to see if the electrodes would produce stoichiometric amounts of hydrogen and oxygen in as a 2:1 ratio upon splitting water. After four hours of continuous running, enough gas was collected to make an adequate determination. The ratio was very close to 2:1 with around 2 mL of H₂ gas and 0.9 mL of O₂ gas produced at the end of the trial.

![Current-voltage characteristics for self-driven current of a p-Fe₂O₃/n-Fe₂O₃ PEC in 0.1 M H₂SO₄ under 1000 W solar simulator.](image)

**Figure 3.102.** Current-voltage characteristics for self-driven current of a p-Fe₂O₃/n-Fe₂O₃ PEC in 0.1 M H₂SO₄ under 1000 W solar simulator. Efficiency = 0.091 mA/cm² × 1.23 V × 100/100 mW/cm² = 0.11%. A fill factor of 0.267 was found.
C. Flatband Potentials

In Figure 3.103, the zinc-doped p-Fe$_2$O$_3$ shows a flatband potential of 0.0 V; whereas, the undoped n-Fe$_2$O$_3$ thin film show a flatband potential around -0.8 V, indicating that zinc-doped Fe$_2$O$_3$ acts as a p-type and the undoped n-Fe$_2$O$_3$ acts as a n-type semiconductor. It would be assumed that the p-type electrode should have a more positive flatband potential; however, the naturally-doped n-Fe$_2$O$_3$ is present in high enough concentration to affect the optical properties.

\[ E_{\text{meas}} \text{ (V vs. SCE)} \]

\[ 1/C^2 \text{ (10}^{10} \text{ F}^{-2} \text{ cm}^4) \]

\[ 0 \quad 5 \quad 10 \quad 15 \quad 20 \quad 25 \]

\[ -0.9 \quad -0.6 \quad -0.3 \quad 0 \quad 0.3 \quad 0.6 \]

\[ \text{n-type Fe}_2\text{O}_3 \]

\[ \text{p-type Fe}_2\text{O}_3 \]

**Figure 3.103.** Mott-Schottky ($1/C^2$ vs. measured potential, $E_{\text{meas}}$, where C is the capacitance) plot for p-type and n-type Fe$_2$O$_3$ films measured at various ac frequencies under dark conditions: electrolyte solution, 0.01 M H$_2$SO$_4$; AC amplitude, 10 mV; spray solution concentration, at an ac frequency of 791 Hz.

D. Quantum Efficiency

The quantum efficiencies of the two electrodes used in the p/n-Fe$_2$O$_3$ PEC show comparable results. (Figure 3.104) The absorption of the p-type Fe$_2$O$_3$ further into the visible spectrum is
expected by the presence of ZnFe$_2$O$_4$. However, both electrodes show comparable peak efficiency levels.

**Figure 3.104.** Quantum efficiency, $\eta(\lambda)$, versus the wavelength, $\lambda$, of light for p-Fe$_2$O$_3$ (curve 1) and n-Fe$_2$O$_3$ (curve 2) thin film electrodes, measured at a potential of +0.0 V/SCE (p-Fe$_2$O$_3$) and +0.5 V/SCE (n-Fe$_2$O$_3$) using Oriel model 77250 monochrometer with a 1.0 mm slit width and 1200 l/mm grating and a total light intensity of 100 mW/cm$^2$ from an Oriel solar simulator with a direct AM 1.5 filter.

A. Self-driven current density

We report here a direct water electrolysis system based on a dual photoelectrochemical cell (PEC) that uses p-GaInP$_2$ as the photocathode and CM-n-TiO$_2$ as the photoanode (Figure 3.105a). The set-up is rather simple and employs p-GaInP$_2$ obtained from the National Renewable Energy Laboratory (NREL)$^{77,172,173}$ and CM-n-TiO$_2$, synthesized in our laboratory,$^7$ that recently showed a photoconversion efficiency of 11.99%.$^{24}$ This p-GaInP$_2$ was used as a working electrode, where H$_2$ evolution occurs and CM-n-TiO$_2$ as the counter electrode, where O$_2$ evolution occurs, as shown in Figure 3.105a. Each electrode had an area of ~0.25 cm$^2$. Photoelectrochemical characteristics were measured with an EG&G Princeton Applied Research model 362 potentiostat. The electrolyte solution was 3.0 M H$_2$SO$_4$ and 0.01 M Triton-X was freshly prepared using deionized water having a resistivity of 18 MΩ/cm. The Triton-X is a surfactant used to promote the formation of smaller bubbles so as to leave the electrode surfaces faster, thus minimizing surface pitting of the electrodes. To reduce the overvoltage losses that have been associated with the noncatalytic surface of p-GaInP$_2$, a thin layer of platinum was electrochemically deposited on the surface of the semiconductor electrode using a 8.0% by weight hydrogen hexachloroplatinate(IV) in double de-ionized water. Photoassisted galvanostatic deposition was done at a cathodic current density of 1 mA/cm$^2$ with a platinum quantity corresponding to a charge of 10 mC/cm$^2$. Illumination of the electrodes was done using an Oriel xenon lamp solar simulator (model 91192) with an AM 1.5 direct filter. The intensity of the light was measured with an International Light (model IL 1350) radiometer. The measured light intensity was 200.0 ± 2.0 mW/cm$^2$ (or about 2 suns).
For this PEC configuration to be self-driven, the p-GaInP$_2$ must have sufficient conduction band edge matching with the level of H$_2$O/H$_2$ half of the redox reaction and the valence band of CM-n-TiO$_2$ electrode must match the valence band of the H$_2$O/O$_2$ half of the redox reaction. However, the band gap of CM-n-TiO$_2$ is sufficiently large enough to provide enough photopotential that is needed to split water (1.23 eV). Figure 3.105b shows an idealized diagram of the energetics involved with CM-n-TiO$_2$ and p-GaInP$_2$ and their interaction in the electrolyte.

Figure 3.106a shows the current density-voltage curves for platinum catalyzed p-GaInP$_2$ (Pt) vs CM-n-TiO$_2$ (curve 1) and p-GaInP$_2$ vs Pt (curve 2) electrodes measured in a two-electrode configuration. Figure 3.106b shows the current density plot for CM-n-TiO$_2$ vs Pt measured in a two-electrode configuration. Under illumination, the p-GaInP$_2$ (Pt) electrode exhibited a current density curve that was similar to that reported earlier.$^{76}$ The p-GaInP$_2$ vs Pt requires additional external voltage in order for the semiconductor to split water. The p-GaInP$_2$(Pt)/CM-n-TiO$_2$ electrode exhibited an open circuit voltage of +0.4 V, indicating extra photovoltage being generated by the CM-n-TiO$_2$ electrode. Evolution of H$_2$ started immediately after the open circuit voltage. The current density reached a limiting value of ~22 mA/cm$^2$ at ~-0.1V and remained constant with increasing negative bias potential. Figure 3.107 shows the self-driven current density for the dual p-GaInP$_2$ / CM-n-TiO$_2$ PEC system. There is a continual increase in current density as the bias potential moves in the negative direction with a maximum at ~20 mA/cm$^2$ at 0.0 V vs CM-n-TiO$_2$. 


Figures 3.105 a & b. (a) Schematic of a dual photoelectrode water splitting system with insets of the individual electrode configurations. Each electrode is illuminated directly from a 1000 W Oriel xenon lamp (model 91192) with an AM 1.5 direct filter at 200 mW/cm² (or 2 suns). (b) Idealized energy level diagram for a p-GaInP₂/CM-n-TiO₂ photo-electrolysis system with an electrolyte interface.

B. Stoichiometric Gas Production

A simple set-up was performed to examine H₂ and O₂ production. Each of the individual electrodes was placed up a separate test tube, and the gases were collected from each electrode separately. The ratio of gas production was 2:1 for H₂:O₂ as expected. The efficiency of the H₂ production was calculated by dividing the power out of the system by the total power put into the system. The power input was the 200 mW/cm² from the solar simulator. The power output at 0.0 V, which is the maximum current density for the self-driven system, is 20.25 mA/cm² and is multiplied by 1.23 eV (the water splitting voltage). Using these values, the H₂ gas production efficiency of this system was found to be 12.46% by using Equation 1.10. A current density of 20.54 mA/cm² was obtained by dividing the measured photocurrent by the sum of the areas of both photoelectrodes (p-GaInP₂ and CM-n-TiO₂).
Figures 3.106 a & b. (a) Current-voltage measurements for p-GaInP$_2$/n-TiO$_2$ (curve 1) and p-GaInP$_2$/Pt (curve 2) in 3.0 M H$_2$SO$_4$ and 0.01 M Triton-X under 1000 W solar simulator. Efficiency = \( \frac{20.254 \text{ mA/cm}^2 \times 1.23 \text{ V} \times 100}{200 \text{ mW/cm}^2} = 12.46\% \). (b) Current-voltage measurements for n-TiO$_2$/Pt in 5.0 M KOH under 1000 W solar simulator.

Figure 3.107. Current-voltage characteristics of self-sustaining current of p-GaInP$_2$/n-TiO$_2$ in 0.1 M H$_2$SO$_4$ under 1000 W solar simulator. A fill factor of 0.185 was found.
Figure 3.108. Quantum efficiency of CM-n-TiO$_2$ at an applied potential of 0.0 V under illumination from a 150 W xenon lamp.

C. Quantum Efficiency

The key to this dual photoelectrochemical cell is the CM-n-TiO$_2$. The quantum efficiency of the CM-n-TiO$_2$ is shown in Figure 3.108. From this efficiency profile, there are two areas of efficiency for the bulk n-TiO$_2$, the first is from 350 to 400 nm, which corresponds to a band gap of 3.1 eV. There is a second quantum efficiency peak that starts around 500 nm, and peaks around 720 nm, and then goes to zero at 750 nm, which corresponds to a band gap of 1.65 eV.

We present here a self-driven system based on a dual photoelectrochemical cell (PEC) in which p-Fe$_2$O$_3$ is used as the working electrode (photocathode) and carbon-modified (CM)-n-TiO$_2$ as the counter electrode (photoanode). The set-up is shown in Fig. 3.109a, where the p-Fe$_2$O$_3$ electrode was illuminated directly and the light passed through the backside of substrate and then the transmitted photons illuminated onto the surface of the CM-n-TiO$_2$ electrode. The percentage of light photons that made it through the front electrode (p-Fe$_2$O$_3$) to the back electrode (n-TiO$_2$) was $\sim 60\%$. Figure 3.109b shows an idealized diagram of the energetics involved in p-Fe$_2$O$_3$ and CM-n-TiO$_2$ and the energy states for the H$_2$O/H$_2$ and H$_2$O/O$_2$ are also given.

**Figure 3.109.** (a) Schematic of a dual photoelectrode water splitting system with insets of the individual electrode configurations. The p-Fe$_2$O$_3$ electrode is illuminated directly from a 1000 W Oriel xenon lamp (model 91192) with an AM 1.5 direct filter at 200 mW/cm$^2$ (or 2 suns), then the unutilized photons pass through the back of the electrode, through the electrolyte, and onto the surface of the CM-n-TiO$_2$ electrode. Approximately 60% of light photons were found to leave the back of the front electrode and fall on the CM-n-TiO$_2$ electrode. (b) Idealized energy level diagram for a p-Fe$_2$O$_3$/CM-n-TiO$_2$ photo-electrolysis system with an electrolyte interface.
A. Self-Driven Current Density

Figure 3.110 shows the self-driven current-voltage characteristics for a p-Fe$_2$O$_3$/CM-n-TiO$_2$ dual electrode system. For p-Fe$_2$O$_3$ when it acts as a working electrode to demonstrate self-driven current density for the H$_2$ reaction, there must be current density above 0.0 V vs CM-n-TiO$_2$ (in the positive direction). However, CM-n-TiO$_2$ in combination with p-Fe$_2$O$_3$ contributes enough photovoltage to split water without use of external voltage. The zinc-doped p-Fe$_2$O$_3$/CM-n-TiO$_2$ PEC exhibited an open circuit voltage ($V_{oc}$) of +0.6 V upon illumination.

![Graph of self-sustaining current-voltage measurements for p-Fe$_2$O$_3$/CM-n-TiO$_2$ in 0.5 M H$_2$SO$_4$ under 1000 W solar simulator, when p-Fe$_2$O$_3$ was used as the working electrode.](image)

**Figure 3.110.** Self-sustaining current-voltage measurements for p-Fe$_2$O$_3$/CM-n-TiO$_2$ in 0.5 M H$_2$SO$_4$ under 1000 W solar simulator, when p-Fe$_2$O$_3$ was used as the working electrode.

B. Quantum Efficiency

To see the overall work-function of the two semiconductors, we can look at their quantum efficiencies separately. In Figure 3.111, curve 1 is the quantum efficiency for zinc-doped p-Fe$_2$O$_3$ and curve 2 is for CM-n-TiO$_2$. As would be expected the overall quantum efficiency for p-Fe$_2$O$_3$ was lower than CM-n-TiO$_2$; however, its efficiency extended in the visible spectrum to around
600 nm. CM-n-TiO₂ had much higher quantum efficiency, up to ~80% between 350 and 375 nm; however, its efficiency dropped off to zero around 425 nm.

A key to this dual photoelectrochemical cell is the CM-n-TiO₂. The quantum efficiency of the CM-n-TiO₂ is shown in Figure 3.111. From this efficiency profile, there are two areas of efficiency on for bulk n-TiO₂ from 350 to 400 nm, which corresponds to a band gap of 3.1 eV. There is a second quantum efficiency peak that starts around 500 nm, peaks around 720 nm, and goes to zero at 750 nm, which corresponds to a band gap of 1.65 eV.

C. Stoichiometric Gas Production

A simple set-up was performed to examine the H₂ and O₂ production. Each of the individual electrodes was placed inside separate inverted test tubes, and the gases were collected from each electrode separately by displacement of electrolyte solution. The ratio of gas production was 2:1 for H₂:O₂ as expected; however, it takes several hours to produce measurable amounts of gas, due to the low rate of water-splitting by this self-driven PEC. The efficiency of the H₂ production was calculated by dividing the power output of the system by the total power input into the system. The power input was the 200 mW/cm² from the solar simulator. The power output at 0.0 V, which is the maximum current density for the self-driven system, is 0.0334 mA/cm² and is multiplied by 1.23 eV (the water splitting voltage). These power output values assume a 100% photocurrent electrolysis efficiency. Using these values, the H₂ gas production efficiency of this system reaches 0.021%. This system shows low current density output because of several factors, an important problem is the mismatch in the size of the two electrodes. The CM-n-TiO₂ exhibits a large amount of current density at negative voltages, but this efficiency is lowered by the area of the larger zinc-doped p-Fe₂O₃, which is at a minimum of 4× larger than the area of the CM-n-TiO₂ electrode.
Figure 3.111. Quantum efficiencies of CM-n-TiO$_2$ at an applied potential of -0.2 V (curve 1) and p-Fe$_2$O$_3$ at an applied potential of +0.1 V (curve 2) under illumination of 200 mW/cm$^2$ (AM 1.5 Direct Filter) from a 1000 W solar simulator.
4. Summary

The major contributions are summarized below:

1) Spray pyrolytic synthesis of p-type iron(III) oxide (p-Fe₂O₃) was possible by the addition of appropriate amounts of magnesium dopant. The optimal substrate temperature (e.g., 390°C) and magnesium dopant concentration (0.0132 M, Mg(NO₃)₂) were found to be the key factors in generating good quality p-Fe₂O₃. A peak photoconversion efficiency of 0.33% and a total conversion efficiency of 1.00% were achieved with the possibility of higher efficiencies with future thin film modifications using other dopants. X-ray diffraction (XRD) results showed that the magnesium-doped optimized thin films of p-Fe₂O₃ in the present study are of a mixed structure of α-Fe₂O₃ with Fe₂MgO₄.

2) Spray pyrolytic synthesis of p-type iron(III) oxide semiconductors (p-Fe₂O₃) was found to be possible by appropriate amounts of copper doping. A substrate temperature of 395°C, spray time of 100 s, and a copper dopant concentration of 0.01155 M (Cu(NO₃)₂) were found to be the optimum conditions to spray pyrolytically synthesize copper-doped p-Fe₂O₃. A peak photoconversion efficiency of 1.3% and a total conversion efficiency of 2.9% were achieved. X-ray diffraction (XRD) and XPS results showed that the copper-doped optimized thin films of p-Fe₂O₃ are of a mixed structure of α-Fe₂O₃ and CuFe₂O₄ incorporated with 0.2 atomic % of Cu doping into the Fe₂O₃ structure. While copper-doping provides a significant amount of photocurrent density compared to other p-type dopants, its stability was rather low, compared to zinc-doped p-Fe₂O₃.
3) Spray pyrolytic deposition (SPD) of p-type iron(III) oxide semiconductors (p-Fe$_2$O$_3$) was found to be possible by utilizing appropriate amounts of zinc doping. Zinc doping gives an order of magnitude higher rate for photoelectrolysis of water and also the photoconversion efficiency compared to magnesium doped electrodes.$^{30,111,117}$ The peak photoconversion efficiency of 1.3% was obtained for optimized zinc-doped p-Fe$_2$O$_3$. This was accomplished by addition of an optimum amount of zinc present (0.0088 M Zn(NO$_3$)$_2$) in the thin film electrodes, thereby improving conductivity of the iron(III) oxide. XRD results show the presence of Fe$_2$O$_3$ and ZnFe$_2$O$_4$. The optimal substrate temperature (e.g., 390°C) was found to be the key factor in synthesizing efficient zinc-doped p-Fe$_2$O$_3$. The results of this study indicate the possibility of using other dopants or combinations of those dopants to improve the photoresponse of p-Fe$_2$O$_3$ for use in combination with an n-Fe$_2$O$_3$ to fabricate a p/n-Fe$_2$O$_3$ solar cell and use it for efficient photoelectrochemical water splitting.

4) Spray-pyrolytic deposition (SPD) of indium doped n-type iron(III) oxide semiconductors (n-Fe$_2$O$_3$) was found to be possible by appropriate amounts of indium doping (0.0044 M InCl$_3$). Indium doping helped to improve the conductivity of the films thus increasing the photocurrent over pure (or naturally) doped n-Fe$_2$O$_3$ thin films. This was accomplished by addition of an optimum amount of indium iron(III) oxide present in the thin film iron(III) oxide electrodes. The optimal substrate temperature (e.g., 415°C) was found to be the key factor in generating good quality indium-doped p-Fe$_2$O$_3$. A peak photoconversion efficiency of 3.73% with a maximum photocurrent of 3.61 mA/cm$^2$ at 40 mW/cm$^2$ from a 150 W xenon arc lamp was achieved.

5) Spray-pyrolytic deposition (SPD) of iodine-doped n-type iron(III) oxide semiconductors (n-Fe$_2$O$_3$) was found to be possible by appropriate amounts of iodine doping (0.0100 M I$_2$). Iodine
doping improved the conductivity of the films thus increasing the photocurrent over pure or undoped n-Fe₂O₃ thin films. The optimal substrate temperature (e.g., 415°C) was found to be the key factor in generating good quality iodine-doped n-Fe₂O₃. A peak photoconversion efficiency of 3.06% with a maximum photocurrent of 3.07 mA/cm² at 40 mW/cm² was achieved. XRD results confirmed the presence of I₂ and Fe₂O₃.

6) Spray pyrolytic synthesis of n-type iron(III) oxide semiconductors (n-Fe₂O₃) was found to be possible by the appropriate addition of calcium and manganese dopants. A peak photoconversion efficiency of 1.25% for calcium doped samples and 0.88% for manganese doped samples were observed; however, photoresponse did not improve compared to those of indium and iodine-doped n-Fe₂O₃. X-ray diffraction (XRD) results showed that the calcium and magnesium-doped optimized thin films of n-Fe₂O₃ in the present study were of a mixed structure of α-Fe₂O₃ and Fe₂CaO₄, and α-Fe₂O₃ and Fe₂MnO₄, respectively.

7) A tandem p/n–Fe₂O₃ PEC using the thin films of zinc-doped p-Fe₂O₃ synthesized using ethanol as the spray solution and n-type Fe₂O₃ synthesized using 1-pentanol as spray solution solvent were fabricated. This PEC produced self-driven photocurrent for water splitting, which generated stoichiometric quantities of hydrogen and oxygen. Furthermore, though the efficiency of this p/n-Fe₂O₃ PEC is found to be low (0.11%), much more improvement will be possible by synthesizing p-Fe₂O₃ in 1-pentanol and using combinations of dopants.

8) The p-GaInP₂ / CM-n-TiO₂ PEC was found to be self-driven with a photoconversion efficiency of 12.4% for water splitting under AM 1.5 illumination. This PEC may be
commercially viable if p-GaInP₂ could be fabricated inexpensively (e.g., by electrodeposition) and could be made stable by depositing on its surface a transparent layer of carbon-doped CM-n-TiO₂ and indium-doped transparent tin oxide on its surface.

9) The p-Fe₂O₃ / CM-n-TiO₂ PEC generated self-driven photocurrent density. The present self-driven photoconversion efficiency for water splitting by this PEC was 0.021%, which is too low for any practical application. Further improvements of p-Fe₂O₃ are essential.

10) Photoelectrodeposition of various metal electrocatalyst did not improve the photoresponse of p-Fe₂O₃ or n-Fe₂O₃ for water splitting; except for a slight enhancement in photocurrent density when platinum was electrodeposited on the surface of the thin films.

11) Scherer’s calculations have shown that the average crystal size of Fe₂O₃ is approximately 5 to 6 times larger in p-type Fe₂O₃ versus the average crystal size of Fe₂O₃ in n-type Fe₂O₃ thin films. The crystals formed from the dopant materials are approximately the same size in p-type and n-type Fe₂O₃ thin films.
5. References


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