Photoelectrochemical Water Splitting for Hydrogen Production with Metal Oxide (Hematite and Cupric Oxide) Based Photocatalysts

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University of Denver

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PHOTOELECTROCHEMICAL WATER SPLITTING FOR HYDROGEN PRODUCTION WITH METAL OXIDE (HEMATITE AND CUPRIC OXIDE) BASED PHOTOCATALYSTS

A Dissertation

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the Faculty of Engineering and Computer Science

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by

Houwen Tang

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Advisor: Dr. Mohammad A. Matin
ABSTRACT

Solar hydrogen is one ideal energy source to replace fossil fuel, as it is sustainable and environmentally friendly. Solar hydrogen can be generated in a number of ways. Photoelectrochemical (PEC) water splitting is one of the most promising methods for solar-to-chemical energy conversion. In this research project, metal oxide-based photocatalysts, especially hematite (α-Fe₂O₃) and cupric oxide (CuO), were investigated for use as electrodes in PEC water splitting for solar hydrogen production.

In our research project of hematite-based electrodes, we started with the incorporation of transition metal, particularly titanium (Ti), in hematite thin films to modify the valence and conduction band edges of hematite. We found that Ti impurities improve the electron conductivity of hematite and consequently lead to significantly enhanced photocurrents. We further investigated the Ti and Mg co-alloyed hematite. In this case, Ti is the donor and Mg is the acceptor in hematite. The co-alloying approach enhanced the solubility of Mg and Ti, which led to reduced electron effective mass and therefore increased electron mobility. Also, co-alloying
tunes the carrier density and therefore allows the optimization of electrical conductivity. The densities of charged defects were found to be reduced, and therefore carrier recombinations were reduced. As a result, the Ti and Mg co-alloyed hematite thin films exhibited much improved performance in PEC water splitting as compared to pure hematite thin films.

For the study of cupric oxide-based electrodes, we first investigated the possibility of reducing the electrode corrosion of cupric oxide in aqueous solutions by incorporating Ti as an electrode corrosion inhibitor. We found that Ti alloying can enhance the stability of cupric oxide in base solutions at the cost of reducing its crystallinity and optical absorption, and consequently lowering its photon-to-electron conversion efficiency. In order to balance the stability and the generated photocurrent, we developed a two-layer structure in which a thin layer of Cu-Ti-O was deposited on bare CuO thin film as a protective layer. Our experimental results indicated that this two-layer structure has an ideal thickness for the protection layer and is suitable for high-performance and long-term application for PEC water splitting.
Acknowledgement

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# TABLE CONTENTS

Abstract .................................................................................................................. i

Acknowledgements .............................................................................................. iii

List of Figures ......................................................................................................... vi

List of Tables ......................................................................................................... ix

Chapter 1: Introduction
  1.1 Introduction ..................................................................................................... 1
  1.1.1 Research background ................................................................................ 1
  1.1.2 Problem Statement .................................................................................... 2
  1.1.3 Objective .................................................................................................. 3
  1.1.4 Scope of research work ............................................................................. 4
  1.1.5 Methodology ............................................................................................ 4
  1.2 Photoelectrochemical water splitting for hydrogen production .................. 5
    1.2.1 Photoelectrochemical water splitting .................................................. 5
  1.2.2 PEC cell criteria ....................................................................................... 7
  1.3 Hematite ........................................................................................................ 9
  1.4 Cupric oxide .................................................................................................. 10

Chapter 2: Synthesis and Characterization of Titanium and Magnesium Co-Alloyed Iron Oxide for PEC Water
  2.1 Synthesis and Characterization of pure hematite ....................................... 12
  2.2 Improved photocurrent and onset potential of Ti-alloyed hematite .......... 14
  2.3 P-type magnesium-alloyed hematite .......................................................... 33
  2.4 Improved PEC performance of Ti and Mg co-alloyed hematite .............. 50

Chapter 3: Synthesis and Characterization of CuO and Cu-Ti-O Coated Copper Oxide for PEC Water Splitting
  3.1 Synthesis and characterization of Ti-alloyed CuO ..................................... 63
  3.2 Synthesis and characterization of Ti-alloyed CuO ..................................... 66
  3.3 Synthesis and characterization of Ti-alloyed CuO ..................................... 75

Chapter 4: Conclusions and Future Work
  4.1 Conclusions ................................................................................................. 84
  4.2 Future Work ................................................................................................. 85
  4.3 Journal Publications ..................................................................................... 87
  4.3 Conference Publications ............................................................................. 88

References ............................................................................................................ 89
List of Figures

Figure 1 Photocatalysis of water: conduction band (CB), valence band (VB), bandgap (Eg), electron (e-), and hole (h+) ................................................................. 6

Figure 2 A typical photoelectrochemical cell used for PEC water splitting .................. 7

Figure 3 XRD patterns of pure hematite films deposited in Ar/O2 ambient with various conditions ................................................................. 14

Figure 4 Absorption patterns of pure hematite films deposited in Ar/O2 ambient with various conditions ................................................................. 15

Figure 5 Calculated electronic band structure of (a) pure α-Fe2O3; (b) α-Fe2O3:Ti (spin up); (c) α-Fe2O3:Ti (spin down) ................................................................. 16

Figure 6 XRD patterns of pure and Ti-alloyed hematite films deposited in Ar/O2 ambient (a) and pure and Ti-alloyed hematite films deposited in N2/O2 ambient (b) ...... 20

Figure 7 SEM images of (a) pure hematite and (b) 1.3%, (c) 3.9% (c), and (d) 10.5% Ti-alloyed hematite thin films deposited in Ar/O2 ambient ........................................... 22

Figure 8 SEM images of (a) pure hematite, (b) 0.4%, (c) 0.7%, and (d) 1.8% Ti-alloyed hematite thin films deposited in N2/O2 ambient ........................................... 23

Figure 9 Absorption patterns of pure and Ti-alloyed hematite films deposited in (a) Ar/O2 ambient and (b) N2/O2 ambient ......................................................... 25

Figure 10 Optical absorption co-efficient of pure and Ti-alloyed hematite films deposited in (a) Ar/O2 ambient and (b) N2/O2 ambient ......................................................... 27

Figure 11 Current-potential curves of pure and Ti-alloyed hematite films deposited in (a) Ar/O2 ambient and (b) N2/O2 ambient ......................................................... 29

Figure 12 Mott–Schottky plots of pure and Ti-alloyed hematite films deposited in (a) Ar/O2 ambient and (b) N2/O2 ambient ......................................................... 31

Figure 13 IPCE measured for pure hematite and Ti-alloyed hematite films deposited in (a) Ar/O2 ambient and (b) N2/O2 ambient ......................................................... 33

Figure 14 XRD patterns of pure and Mg-alloyed hematite films deposited in (a) Ar/O2 ambient and (b) N2/O2 ambient ......................................................... 38
Figure 15 SEM images of (a) pure hematite and (b) 4.9%, (c) 8.1%, and (d) 13.4% Mg-alloyed hematite thin films deposited in Ar/O$_2$ ambient.................................................40

Figure 16 SEM images of (a) pure hematite, (b) 0.7%, (c) 1.8%, and (d) 3.2% Mg-alloyed hematite thin films deposited in N$_2$/O$_2$ ambient..........................................................41

Figure 17 Absorption patterns of pure and Mg-alloyed hematite films deposited in (a) Ar/O$_2$ ambient and (b) N$_2$/O$_2$ ambient ..........................................................43

Figure 18 Optical absorption co-efficient of pure and Mg-alloyed hematite films deposited in (a) Ar/O$_2$ ambient and (b) N$_2$/O$_2$ ambient ..........................................................45

Figure 19 Current-potential curves of pure and Mg-alloyed hematite films deposited in (a) Ar/O$_2$ ambient and (b) N$_2$/O$_2$ ambient..........................................................47

Figure 20 Mott–Schottky plots of pure and Mg-alloyed hematite films deposited in (a) Ar/O$_2$ ambient and (b) N$_2$/O$_2$ ambient..........................................................49

Figure 21 XRD patterns of pure, Ti-alloyed, and Ti and Mg co-alloyed hematite thin films deposited in Ar/O$_2$ ambient ..........................................................53

Figure 22 SEM images of (a) pure hematite; (b) 10% Ti-alloyed hematite thin films; (c) (Fe$_{0.87}$Ti$_{0.10}$Mg$_{0.03}$)$_2$O$_3$; (d) (Fe$_{0.84}$Ti$_{0.09}$Mg$_{0.07}$)$_2$O$_3$; (e) (Fe$_{0.79}$Ti$_{0.09}$Mg$_{0.12}$)$_2$O$_3$ deposited in Ar/O$_2$ ambient..........................................................54

Figure 23 Absorption patterns of pure hematite, Ti-alloyed, and Ti and Mg co-alloyed hematite thin films ..........................................................55

Figure 24 Optical absorption co-efficient of pure hematite, Ti-alloyed, and Ti and Mg co-alloyed hematite thin films ..........................................................56

Figure 25 Current-potential curves of pure, Ti-alloyed, and Ti and Mg co-alloyed hematite thin films ..........................................................58

Figure 26 Mott–Schottky plots of pure, Ti-alloyed, and Ti and Mg co-alloyed hematite thin films ..........................................................59

Figure 27 IPCE measured for pure, Ti-alloyed, and Ti and Mg co-alloyed hematite thin films ..........................................................61

Figure 28 XRD patterns of pure CuO films deposited in Ar/O$_2$ ambient under various conditions ..........................................................65

Figure 29 Absorption patterns of pure CuO films deposited in Ar/O$_2$ ambient under various conditions ..........................................................66
Figure 30 XRD patterns of pure CuO and Ti-alloyed CuO films deposited in Ar/O<sub>2</sub>.....69

Figure 31 SEM images of (1) pure CuO and (b) 2.1%, (c) 5.6% (c), and (d) 9.7% Ti-alloyed CuO thin films...............................................................70

Figure 32 Absorption patterns of pure CuO and Ti-alloyed CuO films .........................71

Figure 33 Optical absorption co-efficient of a) direct bandgap of pure CuO and Ti-alloyed CuO and b) indirect bandgap of pure CuO and Ti-alloyed CuO samples ..........72

Figure 34 Dark current scan of pure CuO and 2.1%, 5.6%, and 9.7% Ti-alloyed CuO samples........................................................................................................73

Figure 35 Photocurrent of pure CuO (1) and 2.1% (2), 5.6% (3), and 9.7% (4) Ti-alloyed CuO films.........................................................................................74

Figure 36 Stability test of 5.6% Ti-alloyed and 9.7% Ti-alloyed CuO .........................75

Figure 37 SEM images of a typical Cu-Ti-O coated CuO sample with its mapping of the Cu L orbital and Ti K orbital .................................................................77

Figure 38 Absorption patterns of pure CuO and Cu-Ti-O coated CuO films..............78

Figure 39 Optical absorption co-efficient of pure CuO (1), Ti-alloyed CuO (2–4), and Cu-Ti-O coated CuO (5–7) samples .................................................................79

Figure 40 Dark scan of Cu-Ti-O coated CuO films..................................................80

Figure 41 Photocurrent of 50-nm Cu-Ti-O coated CuO (1), 80-nm Cu-Ti-O coated CuO (2), and 100-nm Cu-Ti-O coated CuO (3) films ..............................................81

Figure 42 Stability test of 80-nm Cu-Ti-O coated CuO (1) and 100-nm Cu-Ti-O coated CuO (2) films....................................................................................82

Figure 43 IPCE values of 100-nm Cu-Ti-O coated CuO (7) before and after stability test................................................................................................................83
List of Tables

Table I Thicknesses of pure hematite films deposited at various conditions .................13

Table II Thicknesses and Ti doping concentrations of pure and Ti-alloyed hematite films at various deposition conditions ..................................................................................17

Table III Thicknesses and Mg concentrations of pure and Mg-alloyed hematite films at various deposition conditions ..................................................................................36

Table IV Thicknesses and Mg concentrations of pure and Mg-alloyed hematite films at various deposition conditions ..................................................................................51

Table V Deposition conditions for CuO ...........................................................................64

Table VI Thicknesses, growth rate, Ti concentrations, and resistivity of pure and Ti-alloyed CuO films at various deposition conditions .........................................................68

Table VII Thicknesses of protective layer and resistivity of Cu-Ti-O coated CuO ........76
Chapter 1

1.1 Introduction

1.1.1 Research Background

World energy consumption has increased rapidly since the start of the industrial revolution 200 years ago. Today, most human activity relies on fossil fuel [1]. Unfortunately, fossil fuels are not renewable. The depletion of the world oil reserve is foreseen within the next 40 to 50 years [2]. Moreover, the combustion of fossil fuel produces exhaust gases, such as CO₂, NOₓ and SO₂ that directly contribute to global warming and acid rain [3]. Due to the energy shortage and climate change, scientists have been seeking for alternative clean and renewable energy resources to replace fossil fuel.

Hydrogen is a clean and environmentally friendly energy source, as the combustion of hydrogen produces water. It is considered to be an ideal energy source to replace fossil fuel. Hydrogen is also the most abundant element on earth, with the lightest weight and highest energy per unit mass. The heat energy of burning hydrogen is around 34 Kcal/g, which is much higher than that of fossil fuel, which is around 10 Kcal/g [4].

However, hydrogen does not occur in large amounts in nature. Hydrogen atoms are commonly found as part of larger molecules — for example, water. Usually, an external
energy needs to be supplied in order to split water into hydrogen and oxygen. If this external energy can be provided by a source of clean and renewable energy, such as sunlight, then solar hydrogen can be produced in a green and sustainable manner. Therefore, solar hydrogen is considered to be the most promising form of energy to replace fossil fuel and relieve the global energy shortage while at the same time keeping our environment green.

Currently, there are three solar hydrogen technologies for water splitting using semiconducting materials. In a micro-heterogeneous system, fine semiconductor particles are dispersed throughout an aqueous solution to absorb sunlight and split the water within the solution [5]. Photovoltaic-electrolysis systems use conventional photovoltaic solar cells to supply the energy for a separate water electrolysis system [6]. Photoelectrochemical systems use the Schottky junction at the interface between the semiconducting material and the aqueous solution to perform water splitting in the solution [7]. In this research, we examined the feasibility of photoelectrochemical solar hydrogen systems based on metal oxides, especially hematite (α-Fe2O3) and cupric oxide (CuO).

1.1.2 Problem Statement

During the past few decades, a significant effort has been paid to search for low cost and efficient PEC cells. An ideal PEC cell needs to have the optimum bandgap with right band positions for both of its conduction band and valence band. Also, it needs to be
abundant, non-toxic and stable in aqueous solutions. Moreover, this material has to have a high absorption and good photon-to-electron conversion efficiency. So far, no single material has been found that meets all the criteria for a cheap and efficient PEC cell. Most of the existing materials suffer from either stability issues or low photon-to-electron conversion efficiency. Several non-oxides such as GaP, CdS and CdSe possess sufficient potentials for water splitting and good absorption properties in the visible region, suffer from stability under irradiation because the materials decompose during oxidation of water. Other oxides such as TiO₂ and ZrO₂, have a potential for water splitting reaction under UV-light irradiation, but they cannot absorb visible light. Band engineering is considered to be the only solutions to improve the performance for the current available materials.

1.1.3 Objective

In this research project, metal oxide-based photocatalysts, especially hematite (α-Fe₂O₃) and cupric oxide (CuO), were investigated for use as electrodes in PEC water splitting for solar hydrogen production. We will demonstrate using different approaches to achieve the following goals:

I. Good band position of photocatalyst (sufficient potential for spontaneous water splitting and high visible light absorption)

II. Stability of the photocatalysts (photostability and insolubility in water)

III. Fine crystallinity of the photocatalysts (reduce the recombination between electrons and hole, and increase the surface charge transfer)
1.1.4 Scope of research work

At the beginning stage, a full investigation of the intrinsic material properties for hematite and cupric oxide as photocatalyst was carried, including the crystallinity, the morphology, the structure, the absorption, and PEC response. By addressing the shortcomings for each material, several possible solutions were carried out. All the possible solutions were tested using the characterization devices. The band engineered samples was then compared with the intrinsic ones to validate our assumptions.

1.1.5 Methodology

The composition of the sputtered films was analyzed by energy-dispersive x-ray spectroscopy (EDS). The amorphous nature of the synthesized films was characterized by x-ray diffraction (XRD), operated with a Cu radiation source at 44kV and 40mA. The scanning speed is 0.5 deg/min over a 2-theta range of 30° to 60°. The ultraviolet-visible absorption spectra of the samples were measured by and n&k analyzer 1280 (n&k Technology, Inc.). In the measurements, both transmittance and reflectance were collected separately. A correction for scattering and transmittance from the substrate glass was made to optimize the results.

The surface morphology was examined by scanning electron microscopy (SEM, Nova NanoSEM 630, FEI Inc.). Electrical properties were obtained from PEC measurement with a three-electrode cell with a flat borosilicate-glass window to facilitate
illumination of the photoelectrode surface. The sputter-deposited films the working electrodes with an active surface area of about 1 cm². Pt mesh and an Ag/AgCl electrode (with 3M KCL filling solution) electrode were used as counter and reference electrodes, respectively. The measurements were carried with a potentiostat (Solartron 1286) interfaced with a computer. Before the measurements, the electrode was first stabilized under a light intensity of approximately 0.5W/cm² (5 sun) for 2 minutes under open circuit conditions. A 250 W quartz tungsten lamp (model 66883, Newport Corporation) with a liquid filter (model 6123NS, Newport Corporation) was employed as the light source. All photoelectrochemical experiments were carried out at room temperature. Electrical properties of our samples were measured by Mott-Schottky analysis, obtained by alternating current (ac) impedance measurements. The IPCE measurements consisting of a 300 W Xe arc lamp (model 66902, Newport Corporation), a model 150 monochromator (Acton Research Corporation), and a Versastat4 (Princeton Applied Research). A 305 nm long-pass filter was used to eliminate second-order harmonics. During the measurements, the Ti-alloyed iron oxide electrode was held at 0.3 V and the photocurrent was measured at 10nm intervals. The lamp spectral output is examined by using a silicon cell which the quantum efficiency at each wavelength is known. The collected data was then compared with this reference cell to determine the IPCE.

1.2 Photoelectrochemical water splitting for hydrogen production

1.2.1 Photoelectrochemical water splitting

Photoelectrochemical (PEC) water splitting is a clean and efficient way to produce hydrogen from direct sunlight absorption [8, 9]. It utilizes a semiconducting photoanode
and a metal cathode immersed in an electrolyte to split water for hydrogen production. When a photon with energy equal to or above the bandgap of a semiconducting material impinges on a photocatalyst, an electron is excited from its valence band to the conduction band, leaving a hole.

![Diagram of photocatalysis](image)

**Figure 1. Photocatalysis of water: conduction band (CB), valence band (VB), bandgap (Eg), electron (e⁻), and hole (h⁺).**

Energetic holes and electrons (h⁺/e⁻) generated by photon absorption perform the oxidation/reduction reactions in the aqueous electrolyte:

\[ 2\text{H}_2\text{O} + 2\text{h}^+ = \frac{1}{2}\text{O}_2 + 2\text{H}^+ \] (at the n-type photoanode side)

\[ 2\text{H}^+ + 2\text{e}^- = \text{H}_2 \] (at the counter electrode side).
1.2.2 PEC cell criteria

PEC water splitting has attracted great attention since the demonstration of water splitting using a titanium oxide (TiO$_2$) photoanode illuminated with ultraviolet light almost forty years ago by Fujishima and Honda [10]. For spontaneous water splitting, the semiconductor has to meet several criteria.

First of all, the semiconductor needs to have an ideal bandgap of 1.7 eV~2.0 eV. The thermodynamic potential for the water-splitting reaction is 1.23 eV. However, in order to overcome the energy losses relating to reaction kinetics and charge transfer through the
electrical leads and electrolyte, i.e., the electrode overpotentials and Ohmic overpotentials [11], in reality, 1.7 eV~2.0 eV is needed.

For spontaneous water splitting under irradiation, the conduction band edge of a semiconductor photoelectrode should be above the reduction potential of water so that the electrons can be transferred to easily reduce water to hydrogen. Meanwhile, the valence band should be located below the oxidation potential, which allows the hole to be transferred to oxidize water to oxygen. However, in reality, many semiconductors have conduction band edges lower than the reduction potential of water. For these materials, spontaneous water splitting is impossible because an electron transfer barrier is created. To assist these semiconductors in water splitting, an external electrical bias or internal chemical bias is normally needed.

Ideally, the photoelectrode semiconductor should have a direct bandgap, where the two band edges occur at the same $k$-vector value. Based on the general rule in physics that momentum must be conserved, the transition will easily occur for a direct bandgap material between its conduction band and valence band. In an indirect bandgap transition, in order to get absorption, we must either absorb a phonon in addition to the photon, or emit another phonon after the absorption of the incoming photon.

Moreover, the photoelectrode should be abundant, economically available, non-toxic, and stable in aqueous solutions [12, 13]. An efficient PEC cell involves a p-n junction
with hydrogen evolved from the photocathode site and oxygen from the photoanode site. However, such a device has not been realized thus far.

1.3 Hematite

Hematite ($\alpha$-Fe$_2$O$_3$) has been considered a promising material that may potentially meet the above-mentioned criteria because of the following advantages [14, 15]: It is inexpensive, abundant, nontoxic, and stable in most alkaline electrolytes. It has a bandgap of 2.2 eV, which is capable of absorbing roughly 40% of the solar spectrum, leading to a maximum theoretical solar-to-hydrogen conversion efficiency of about 13% under AM1.5 illumination. However, despite these favorable characteristics, the maximum experimental solar-to-chemical efficiency reported in the literature for hematite is less than 3% [16]. The extremely low electrical conductivity and the indirect bandgap (weak optical absorption) are the two most critical factors that limit the PEC performance of hematite [17, 18].

The poor electrical conductivity of hematite is mainly due to the fact that the conduction band edge of hematite is extremely localized, leading to a very heavy electron effective mass and, therefore, very low electron mobility [19]. Both experimental and theoretical research has shown that incorporating 3$d$ transition metals can enhance the electron mobility and electrical conductivity and therefore lead to improved PEC
performance [20-24]. For example, the incorporation of titanium (Ti) and chromium (Cr) in hematite has led to significantly enhanced photocurrents [22, 24].

1.4 Cupric oxide

Copper oxide is also a potential semiconductor for PEC water splitting [25-28]. Copper oxide has two forms, Cu$_2$O (cuprous oxide) and CuO (cupric oxide). Both of them are cheap, abundant, and non-toxic p-type semiconductors. Cu$_2$O has a bandgap of around 2.2 eV with a cubic crystal structure [29-32], and CuO has a bandgap of around 1.4 eV with a monoclinic crystal structure [33]. Both of them are favorable for both PEC and photovoltaic (PV) applications because they are direct bandgap materials and have good absorption coefficients [34, 35]. Also, both of them exhibit good electric transport properties, which are great advantages for PEC application. However, it has been reported that Cu$_2$O is unstable in air and can readily convert to CuO in air at room temperature [36]. Also, even though that theoretical report predicted that Cu$_2$O can reach 12% absorption efficiency, no reports have shown success in experiments exceeding 2%. A mixed phase of Cu, CuO, and Cu$_2$O is generally obtained instead of pure Cu$_2$O for most of the Cu$_2$O studies [37, 38]. The un-avoided defects created during the fabrication process result in great energy loss, and the nature of its relatively large bandgap (ideal bandgap is 1.7 eV~ 2.1 eV) has limited its performance as a good p-type absorber. CuO is stable in air. It also shows a competitive absorption spectrum over a wide range from 400 nm~900 nm compared to Cu$_2$O [39]. One major drawback for CuO to become a good p-type absorber is that it is not stable in aqueous solutions. Also, due to its relatively small bandgap, photons absorbed by CuO are insufficient to support water splitting [40].
There are two main traditional approaches to prevent the surface photocorrosion; one is to incorporate impurities into the material, and the other is to add a protective layer on the top of the sample. Several elements have been studied as dopants to stabilize the surface of copper oxide in aqueous solutions, such as iron (Fe), Cr, and Ti. Among these, Ti has shown great success [41].
Chapter 2

Synthesis and Characterization of Titanium and Magnesium Co-Alloyed Iron Oxide for PEC Water Splitting

2.1 Synthesis and characterization of pure hematite

Our first step is to find an ideal deposition condition to deposit pure hematite by radio frequency (RF) magnetron sputtering of an iron oxide target. F-doped SnO$_2$ (FTO) (20–23 Ω/cm) coated transparent glass was used as the substrate. We chose Ar/O$_2$ as the reactive gas for our deposition, and we found that RF power and oxygen partial pressure are the two crucial factors that greatly affected the structure and crystallinity of the deposited film. We varied the O$_2$/\((O_2+Ar)\) ratio from 5% to 10% and the RF power on the iron oxide target from 50 W to 200 W in order to find an optimized RF power with an oxygen partial pressure suitable for a well-crystallized hematite film and a fairly good growth rate. The substrates were kept at room temperature during the deposition processes, and all the depositions were set to be 3 hours. We found that 50 W RF power is insufficient to sputter the iron oxide atoms from the target, and as a result, we were unable to get a thin film using this RF power. The thicknesses of the other deposited films were measured to be in the range of 150 nm to 700 nm by thickness stylus profilometry using an RF power of 100 W and above, and films deposited with 10% O$_2$
were found to be thinner than the films deposited with 5% O\textsubscript{2} using the sample RF power, which suggested that higher oxygen partial pressure leads to a lower deposition rate.

**Table I. Thicknesses of pure hematite films deposited at various conditions.**

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>RF power</th>
<th>O\textsubscript{2} partial pressure</th>
<th>Thickness</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>50 W</td>
<td>5%</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>100 W</td>
<td>5%</td>
<td>150 nm</td>
</tr>
<tr>
<td>3</td>
<td>150 W</td>
<td>5%</td>
<td>450 nm</td>
</tr>
<tr>
<td>4</td>
<td>200 W</td>
<td>5%</td>
<td>700 nm</td>
</tr>
<tr>
<td>5</td>
<td>50 W</td>
<td>10%</td>
<td>0</td>
</tr>
<tr>
<td>6</td>
<td>100 W</td>
<td>10%</td>
<td>100 nm</td>
</tr>
<tr>
<td>7</td>
<td>150 W</td>
<td>10%</td>
<td>350 nm</td>
</tr>
<tr>
<td>8</td>
<td>200 W</td>
<td>10%</td>
<td>600 nm</td>
</tr>
</tbody>
</table>


Figure 3 shows the x-ray diffraction (XRD) curves of pure hematite films grown at different RF powers in mixed Ar/O\textsubscript{2} ambient with 5% and 10% O\textsubscript{2} partial pressure. Dotted lines in the figure indicate peaks from substrate (FTO). Strong hematite peaks were registered in the pattern, as indicated by the solid lines. All the deposited hematite film displayed a polycrystalline nature with a main peak at 35.6° corresponding to the
[110] plane, indicating a preferred growth. Films deposited with 150 W and 200 W in 10% O₂ show slightly larger intensity, indicating that the crystallinity and morphology of these films could be slightly better than that of the rest.

Figure 3. XRD patterns of pure hematite films deposited in Ar/O₂ ambient with various conditions [45].

Figure 4 shows the optical absorption spectra of the pure hematite grown at different RF powers in Ar/O₂ ambient with different oxygen partial pressure. No obvious difference is found for these samples from 350 nm–550 nm except that the absorption tail of the hematite deposited using 100 W and 5% O₂ is slightly lower than the rest, indicating that this sample has fewer defects. However, we find that such sample has very slow growth rate (150 nm/3 hours). Generally, the ideal film thickness for PEC measurement should be around 500 nm to 1000 nm. Films with less than 500 nm might
be insufficient for photon absorption. Combining the growth rate and crystallinity of the deposited films, we decided to choose 150 W and 10% O\textsubscript{2} as the deposition condition for the Ti-alloyed hematite, because under this deposition condition, the film has a fairly good growth rate (350 nm/3 hours) and it shows a strong hematite (110) peak with less defects at the absorption tail.

![Absorption patterns of pure hematite films deposited in Ar/O\textsubscript{2} ambient with various conditions](image)

**Figure 4.** Absorption patterns of pure hematite films deposited in Ar/O\textsubscript{2} ambient with various conditions [45].

### 2.2 Improved photocurrent and onset potential of Ti-alloyed hematite

As we know that hematite has very poor electrical conductivity and a high non-radiative recombination rate, due to heavy carrier effective masses, both the conduction band minimum (CBM) and valence band maximum (VBM) are derived from the rather localized Fe 3\textit{d} states. Moreover, the CBM of hematite is lower than the H\textsubscript{2}/H\textsuperscript{+} reduction
half-reaction potential. Consequently, hematite requires an external bias to shift the Fermi level of the counter electrode above the hydrogen evolution potential.

Adding impurities can help improve hematite’s electronic properties by modifying its band structure. It has been proven both theoretically and experimentally that incorporating 3$d$ transition metals can improve hematite’s conductivity by reducing the effective mass of its electrons. Among all the 3$d$ transition metals, incorporating Ti is expected to exhibit the greatest increase in electrical conductivity due to the relatively more delocalized Ti 3$d$ orbital (Fig. 5).

Here, we report on our synthesis of Ti-alloyed hematite thin films by RF magnetron co-sputtering of iron oxide and titanium targets in two different working ambient: Ar/O$_2$ and N$_2$/O$_2$. The Ti concentration was controlled by applying different RF powers to the titanium target.

![Fig. 5. Calculated electronic band structure of (a) pure $\alpha$-Fe$_2$O$_3$; (b) $\alpha$-Fe$_2$O$_3$:Ti (spin up); (c) $\alpha$-Fe$_2$O$_3$:Ti (spin down).](image-url)
Ti-alloyed hematite thin films were deposited by reactive co-sputtering of iron oxide and titanium targets (Table II). We chose two different chamber ambient gases, Ar/O₂ or N₂/O₂, as the reactive gas to observe the effect of different working ambient on the materials’ quality. Also, our intention for using nitrogen is to see if nitrogen would help to modify the band structure as well as compensate for the charge imbalance caused by replacing Fe³⁺ with Ti⁴⁺. The mass flow rate ratios of O₂/ (O₂+Ar) or O₂/ (O₂+N) were 10%. All the films were annealed at 300°C for 3 hours after deposition. The RF power for the iron oxide target was fixed at 150 W, while the RF power for the titanium target varied from 50 W to 200 W.

**Table II. Thicknesses and Ti doping concentrations of pure and Ti-alloyed hematite films at various deposition conditions.**

<table>
<thead>
<tr>
<th>RF power on iron oxide target</th>
<th>RF power on titanium target</th>
<th>Film thickness</th>
<th>Ti concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>150 W</td>
<td>50 W</td>
<td>380 nm</td>
<td>1.3%</td>
</tr>
<tr>
<td>150 W</td>
<td>100 W</td>
<td>430 nm</td>
<td>3.9%</td>
</tr>
<tr>
<td>150 W</td>
<td>200 W</td>
<td>530 nm</td>
<td>10.5%</td>
</tr>
<tr>
<td>150 W</td>
<td></td>
<td>300 nm</td>
<td></td>
</tr>
<tr>
<td>150 W</td>
<td>50 W</td>
<td>320 nm</td>
<td>0.4%</td>
</tr>
<tr>
<td>150 W</td>
<td>100 W</td>
<td>350 nm</td>
<td>0.7%</td>
</tr>
<tr>
<td>150 W</td>
<td>200 W</td>
<td>400 nm</td>
<td>1.8%</td>
</tr>
</tbody>
</table>

Energy-dispersive x-ray spectroscopy (EDS) data indicate that Ti concentrations in the films deposited in Ar/O\(_2\) ambient with RF power of 50 W, 100 W, and 200 W on the titanium target were 1.3%, 3.9%, and 10.5%, respectively. However, the Ti concentrations in the films deposited in N\(_2\)/O\(_2\) ambient with RF power of 50 W, 100 W, and 200 W on the titanium target were much lower, only 0.4%, 0.7%, and 1.89%, respectively. At equivalent RF powers and deposition times, films deposited in N\(_2\)/O\(_2\) ambient were thinner than the films deposited in Ar/O\(_2\) ambient.

Figure 6 (a) shows the XRD curves of pure hematite and Ti-alloyed hematite films grown at different RF powers in mixed Ar/O\(_2\) ambient with O\(_2\) mass flow rate of [O\(_2\)/(Ar+O\(_2\))]=10%. Dotted lines in the figure indicate peaks from the substrate (FTO). Strong hematite peaks were registered in the pattern, as indicated by the solid lines. We found that the hematite structure was preserved after Ti was incorporated into hematite thin films by RF sputtering.

The pure hematite film and all of the Ti-alloyed hematite films displayed a polycrystalline nature with a main peak at 35.6° corresponding to the [110] plane, indicating a preferred growth. With an increase in Ti incorporation, we found that the intensity of the [104] peak increased. However, no TiO\(_2\) peaks were detected, possibly due to a lack of crystallinity and low TiO\(_2\) concentration. The crystallite size of pure hematite film deposited in Ar/O\(_2\) was calculated to be 32.2 nm from XRD patterns using the Scherrer equation. This agreed well with SEM observations.
With the incorporation of Ti, the particle sizes were found to increase. As estimated from the XRD patterns, the Ti-alloyed hematite particles possessed sizes of 35.7 nm, 52.5 nm, and 54.1 nm corresponding to RF power of 50 W, 100 W, and 200 W applied to the titanium target, respectively. Figure 6 (b) shows the XRD patterns of pure and Ti-alloyed hematite films grown at different RF powers in mixed N$_2$/O$_2$ ambient with O$_2$ mass flow rate of [O$_2$/N$_2$ + O$_2$]=10%. No observable difference was found in the spectra of the Ti-alloyed samples and pure hematite, indicating no evidence of new phases. However, films deposited in Ar/O$_2$ gas exhibit stronger XRD peak intensities for the [110] and [300] planes compared to the films deposited in N$_2$/O$_2$ ambient, suggesting that films deposited in mixed Ar/O$_2$ have better crystallinity. EDS analysis revealed that the better crystallinity is due to the higher Ti concentration.
Figure 6. XRD patterns of pure and Ti-alloyed hematite films deposited in Ar/O₂ ambient (a) and pure and Ti-alloyed hematite films deposited in N₂/O₂ ambient (b) [43].

Figures 7 (a), (b), (c), and (d) show the scanning electron microscope (SEM) images of the pure and 1.3%, 3.9%, and 10.5% Ti-alloyed samples grown under Ar/O₂
ambient, respectively. The insets are enlarged areas showing the details of grain morphologies. The features of large grains in Fig. 7 (a) are from the FTO grains on the substrates. The hematite grains are very small. However, it is still clear enough to see that the small hematite grains are grown on the large FTO grains. As the Ti concentration increases, the hematite grain size increases. The hematite grains exhibit triangle shapes with facets, which could be the consequence of orientation preferred grain growth as indicated by XRD plots.

Figures 8 (a), (b), (c), and (d) show the SEM images of the pure and 0.4%, 0.7%, and 1.8% Ti-alloyed samples grown under N₂/O₂ ambient, respectively. It is seen that as the Ti concentration increases, the hematite grain size becomes bigger. However, Ti-alloyed hematite films grown under N₂/O₂ ambient have much smaller grain sizes, due to the much lower Ti concentration. The grain shape and size shown in Fig. 7 (b) are similar to that shown in Fig. 8 (d) because these two films contain similar amounts of Ti: 1.3% in Fig. 7 (b) and 1.8% in Fig. 8 (d). These results indicate that the grain size and shape of hematite films grown by RF sputtering are affected by the incorporation of Ti.
Figure 7. SEM images of (a) pure hematite and (b) 1.3%, (c) 3.9% (c), and (d) 10.5% Ti-alloyed hematite thin films deposited in Ar/O$_2$ ambient [43].
Figure 8. SEM images of (a) pure hematite, (b) 0.4%, (c) 0.7%, and (d) 1.8% Ti-alloyed hematite thin films deposited in N$_2$/O$_2$ ambient [43].

Figure 9 (a) shows the optical absorption spectra of the hematite and Ti-alloyed hematite films grown at different RF powers in Ar/O$_2$ ambient. The absorption edge shifted slightly to the longer wavelength regions as the Ti doping concentration increased, indicating that Ti doping in hematite leads to a small bandgap reduction. It is known that Ti atoms occupying Fe sites in hematite are shallow donors. The high-concentration Ti (heavily alloyed) will create partial occupied bands. The lowest
unoccupied band forms a new CBM, which should be slightly lower in energy than the original CBM of hematite. The position of the new CBM depends on Ti concentration. Higher Ti concentration leads to lower new CBM position because of the band broadening effect. This explains why the measured bandgap narrows as the Ti concentration increases. Figure 9 (b) shows the optical absorption spectra of the hematite and Ti-alloyed hematite films grown at different RF powers in N$_2$/O$_2$ ambient. The absorption edges were almost the same for hematite thin films alloyed with 0.4% and 0.7% Ti, due to the low Ti concentration. The absorption edge for the hematite film alloyed with 1.8% Ti shifted slightly to the longer wavelength regions as compared with the unalloyed hematite thin film. The origin for this red shift is the same as that for those Ti-alloyed hematite films grown in Ar/O$_2$ ambient. Comparing the pure hematite thin films grown in Ar/O$_2$ and N$_2$/O$_2$ ambient finds no significant difference, suggesting that nitrogen might not be incorporated into the hematite films grown in N$_2$/O$_2$ ambient, which is consistent with EDS analysis.
Figure 9. Absorption patterns of pure and Ti-alloyed hematite films deposited in (a) Ar/O$_2$ ambient and (b) N$_2$/O$_2$ ambient [43].

We have determined both the direct and indirect bandgaps of pure and Ti-alloyed hematite films by extrapolating the linear portion of a Tauc plot created by taking both
transmittance and reflectance into account (Fig. 10). A correction for scattering and transmittance from the substrate glass was taken into consideration. We found that the indirect bandgap results are more consistent with the trend of the optical absorption spectra shown in Fig. 9. Therefore, the indirect bandgaps are considered in this paper. The indirect bandgap is found to be about 2.11 eV for pure hematite deposited in Ar/O\textsubscript{2} ambient and 2.07 eV for pure hematite film deposited in N\textsubscript{2}/O\textsubscript{2}. The small difference could be due to the different crystallinity of these two films. The latter contains more defects, which could lead to additional absorption. For the films deposited in Ar/O\textsubscript{2} ambient [Fig. 10 (a)], the bandgaps of unalloyed and 1.3%, 3.9%, and 10.5% Ti-alloyed hematite films are measured to be about 2.11 eV, 2.1 eV, 2.08 eV, and 2.06 eV, respectively. The bandgap decreases as the Ti concentration increases, which is consistent with the optical absorption spectra shown in Fig. 9 (a).

For the films deposited in N\textsubscript{2}/O\textsubscript{2} ambient [Fig. 10 (b)], the bandgaps of unalloyed and 0.4%, 0.7%, and 1.8% Ti-alloyed hematite films are measured to be about 2.07 eV, 2.06 eV, 2.04 eV, and 2.01 eV, respectively. Like the hematite films deposited in Ar/O\textsubscript{2} ambient, the bandgap decreases as the Ti concentration increases, which is consistent with the optical absorption spectra shown in Fig. 9 (b). The bandgaps of hematite films deposited in N\textsubscript{2}/O\textsubscript{2} ambient are generally narrower than those that of the films deposited in Ar/O\textsubscript{2} ambient. As explained earlier, this difference is caused by the different crystallinity, which is evident in XRD patterns and SEM images. It has been noticed that metal oxide films deposited at room temperature in N\textsubscript{2} containing ambient usually lead to poor crystallinity.
We have further tested the PEC performance of the pure hematite and Ti-alloyed hematite films grown in different ambient. Figures 11 (a) and (b) show the current-potential curves of both pure and Ti-alloyed hematite films grown in Ar/O₂ and N₂/O₂, respectively.
respectively, in 1 M NaOH solution over a potential range of -0.4 V to 0.5 V under light on/off illumination. The dark current under light-off conditions hardly changed across the potential range. This indicates that the deposited films are stable in the neutral solutions. Low photocurrent is registered for the pure hematite film, as we expected. The pure hematite film deposited in Ar/O₂ ambient exhibits a higher photocurrent than the one deposited in N₂/O₂ ambient. The photocurrent at 0.4 V vs. Ag/AgCl is 2µA cm⁻² for pure hematite film deposited in Ar/O₂, and it is 1µA cm⁻² for the pure hematite film grown in N₂/O₂ ambient. This could be related to the difference in crystallinity and film thickness. It is evident from Fig. 11 that Ti doping leads to two effects on the PEC performance of hematite thin films. First, Ti doping enhanced photocurrent magnitude. For hematite films deposited in both Ar/O₂ and N₂/O₂ ambient, Ti doping led to significant improvement in photocurrent. Higher Ti concentration resulted in higher PEC response. The hematite thin film alloyed with 10.5% Ti showed the highest photocurrent, as seen in Fig. 11. Secondly, Ti doping shifted the photocurrent onset potentials to more negative values for hematite thin films deposited in both Ar/O₂ and N₂/O₂ ambient. From the current-potential curves, we obtained onset potentials of 0.3 V, 0.0 V, -0.05 V, and -0.1 V (vs. Ag/AgCl) for pure hematite and 1.3%, 3.9%, and 10.5% Ti-alloyed hematite films deposited in Ar/O₂ ambient, respectively. For the hematite films deposited in N₂/O₂ ambient, we obtained onset potentials of 0.3 V, 0.25 V, 0.1 V, and 0.1 V for pure hematite and 0.4%, 0.7%, and 1.8% Ti-alloyed hematite films deposited in N₂/O₂ ambient. The first effect could be due to the enhancement of electrical conductivity caused by Ti doping. The second effect could be due to the change of hematite/electrolyte caused by the presence of Ti.
Figure 11. Current-potential curves of pure and Ti-alloyed hematite films deposited in (a) Ar/O\(_2\) ambient and (b) N\(_2\)/O\(_2\) ambient [43].
To understand what causes the improvement in the electrical conductivity of Ti-alloyed hematite thin films, we have measured Mott-Schottky plots (capacitance-potential) for the pure hematite and Ti-alloyed hematite films (Fig. 12). Based on the Mott-Schottky equation, the slope of the plots has an inverse relationship with the carrier density:

\[
\frac{1}{C^2} = \frac{2}{e_0 \varepsilon_0} \cdot \frac{1}{N_D} \cdot \frac{1}{\varepsilon} \cdot \frac{1}{e} \cdot \frac{1}{T}
\] (1)

where \( e_0 \) is the electron charge, and \( \varepsilon \) and \( \varepsilon_0 \) are relative and vacuum electric permittivities. With a value of 80 for hematite, our results indicate that the carrier densities are 1.76 \( 10^{14} \) cm\(^{-3} \), 7.06 \( 10^{14} \) cm\(^{-3} \), 8.83 \( 10^{14} \) cm\(^{-3} \), and 1.41 \( 10^{15} \) cm\(^{-3} \) for pure hematite and 1.3%, 3.9%, and 10.5% Ti-alloyed hematite thin films deposited in Ar/O\(_2\) ambient [Fig. 12 (a)]. Clearly the carrier concentration increases as the Ti concentration increases, confirming that Ti is a donor in hematite.

For hematite films deposited in N\(_2\)/O\(_2\) ambient, the carrier densities are 1.81 \( 10^{14} \) cm\(^{-3} \), 2.04 \( 10^{14} \) cm\(^{-3} \), 2.43 \( 10^{14} \) cm\(^{-3} \), and 9.56 \( 10^{14} \) cm\(^{-3} \) for pure hematite and 0.4%, 0.7%, and 1.8% Ti-alloyed hematite thin films. Obviously, the carrier densities of films deposited in N\(_2\)/O\(_2\) ambient were lower than those of the films deposited in Ar/O\(_2\) ambient, due to lower Ti doping concentration.

The flatband potential was determined by extrapolating the linear portion of the Mott-Schottky plots. The flatband potential was 0.19 V, 0.05 V, 0.04 V, and 0.035 V vs.
Ag/AgCl for the pure and 1.3%, 3.9%, and 10.5% Ti-alloyed hematite thin films deposited in Ar/O₂ ambient, respectively. For the films deposited in N₂/O₂ ambient, the flatband potential was 0.31 V, 0.3 V, 0.24 V, and 0.19 V vs. Ag/AgCl for unalloyed and 0.4%, 0.7%, and 1.8% Ti-alloyed hematite thin films.

Figure 12. Mott–Schottky plots of pure and Ti-alloyed hematite films deposited in (a) Ar/O₂ ambient and (b) N₂/O₂ ambient [43].
Incident-photon-to-current-efficiencies (IPCE) for pure hematite and Ti-alloyed hematite were measured at 0.3V vs. Ag/AgCl as a function of incident light wavelength (Fig. 13). The IPCE values for the pure hematite films are very low, below 3% for the film deposited in Ar/O\textsubscript{2} mixed ambient and below 1.8% for pure unalloyed hematite film due to the poor electrical conductivity and high non-radiative recombination rate. As Ti doping concentration increases, the IPCE values for Ti-alloyed hematite films increase. At 350 nm, the IPCE of the 10.5% Ti-alloyed film deposited in Ar/O\textsubscript{2} ambient is almost six times higher than that of the pure hematite film. This is direct evidence that the photoresponse has been improved by Ti doping. However, such a large improvement is not found in the films deposited in N\textsubscript{2}/O\textsubscript{2} ambient. At 350 nm, the IPCE of the 1.8% Ti-alloyed hematite is only 1.5 times that of the pure hematite film. This is mainly because of the low Ti concentration.

From Fig. 13 (a), the IPCE edge is 590 nm for the pure hematite film deposited in Ar/O\textsubscript{2}, corresponding to a bandgap of 2.1 eV. The edges are 610 nm, 630 nm and 630 nm for 1.3%, 3.9%, 10.5% Ti-alloyed films, corresponding to bandgaps of 2.03 eV, 1.97 eV and 1.97 eV, respectively. From Fig. 13 (b), the IPCE edge is 590 nm for the pure hematite film deposited in N\textsubscript{2}/O\textsubscript{2}, corresponding to a bandgap of 2.1 eV. The edges are 610 nm, 640 nm and 640 nm for 0.4%, 0.7%, and 1.8% Ti-alloyed films, corresponding to bandgaps of 2.03 eV, 1.93 eV and 1.93 eV, respectively. There is about 0.2 eV difference between the IPCE measured bandgaps and the indirect optical bandgaps. This difference is expected because the absorption at long wavelength regions shown in the
optical absorption spectra may contribute very low photocurrents, which may not show up in the IPCE curves. As a result, the bandgaps measured by IPCE are expected to be larger than those measured by optical absorption spectra.

Figure 13. IPCE measured for pure hematite and Ti-alloyed hematite films deposited in (a) Ar/O$_2$ ambient and (b) N$_2$/O$_2$ ambient [43].
2.3 P-type magnesium-alloyed hematite

It is known that the Fermi level position of a thin film depends on both the type of conductivity (n-type or p-type) and the carrier concentration. To explore the full potential of semiconductors for PEC water splitting, both n-type and p-type need be considered. Hematite thin films are naturally n-type semiconductors that exhibit several advantages for PEC hydrogen production. While improving the n-type conductivity of hematite has been intensively studied with different kinds of dopants, the p-type conductivity of hematite has studied much less. It has been suggested both theoretically and experimentally that incorporating magnesium (Mg) into hematite can improve the p-type activity of hematite. Here, we report on our synthesis of Mg-alloyed hematite thin films by RF magnetron co-sputtering of iron oxide and titanium targets in two different ambient conditions: Ar/O\textsubscript{2} and N\textsubscript{2}/O\textsubscript{2}. The Mg concentration was controlled by varying the amount of Mg source (Mg powder pressed disk) on the iron oxide target. Our results demonstrated that the type of conductivity and the bandgap of hematite can be modified by adjusting the amount of Mg impurities. The films deposited under N\textsubscript{2}/O\textsubscript{2} ambient exhibited poorer crystallinity than the ones deposited under Ar/O\textsubscript{2} ambient.

Table III shows the various conditions of deposition of the pure hematite and Mg-alloyed hematite films. It is known that the ambient gas can affect the morphology of the deposited films. Two different working ambients, Ar/O\textsubscript{2} and N\textsubscript{2}/O\textsubscript{2}, were used for both pure and Mg-alloyed hematite films. Meanwhile, an oxygen-rich environment was maintained to avoid the formation of Fe\textsuperscript{2+}. The RF power for the iron oxide target was fixed at 150 W. EDS data indicates that Mg concentrations in the films deposited in
Ar/O\textsubscript{2} ambient were 4.9\%, 8.1\%, and 13.4\%, corresponding to the MgO disks with diameters of 1 cm, 1.5 cm, and 2 cm, respectively. However, the Mg concentrations in the films deposited in N\textsubscript{2}/O\textsubscript{2} ambient were much lower, only 1.7\%, 2.8\%, and 4.2\%, corresponding to the MgO disks with diameters of 1 cm, 1.5 cm, and 2 cm, respectively. For all hematite films deposited in N\textsubscript{2}/O\textsubscript{2} ambient, no nitrogen was detected by EDS. At equivalent RF power deposition times, films deposited in N\textsubscript{2}/O\textsubscript{2} ambient were thinner than the films deposited in Ar/O\textsubscript{2} ambient.
Table III. Thicknesses and Mg concentrations of pure and Mg-alloyed hematite films at various deposition conditions.

<table>
<thead>
<tr>
<th>RF power on iron oxide target (W)</th>
<th>Diameter of Magnesium powder piece (cm)</th>
<th>Film thickness (nm)</th>
<th>Mg concentration (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>150</td>
<td>330</td>
<td>330</td>
<td></td>
</tr>
<tr>
<td>150</td>
<td>1</td>
<td>350</td>
<td>4.9</td>
</tr>
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<td>1.5</td>
<td>440</td>
<td>8.1</td>
</tr>
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<td>150</td>
<td>2</td>
<td>530</td>
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<td></td>
</tr>
<tr>
<td>150</td>
<td>1</td>
<td>330</td>
<td>0.7</td>
</tr>
<tr>
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<td>1.5</td>
<td>360</td>
<td>1.8</td>
</tr>
<tr>
<td>150</td>
<td>2</td>
<td>470</td>
<td>3.2</td>
</tr>
</tbody>
</table>


Figure 14 (a) shows the XRD curves of pure hematite and Mg-alloyed hematite films grown at an RF power of 150 W in mixed Ar:O₂ ambient with an O₂ mass flow rate of [O₂/(Ar+O₂)]=10%. Dotted lines in the XRD plots indicate substrate peaks (FTO). Strong hematite peaks are registered in the pattern obtained from pure hematite thin film, as indicated by the solid lines. We found that hematite structure was preserved after Mg
was incorporated into hematite thin films by RF sputtering. The pure hematite film and all of the Mg-alloyed hematite films displayed a polycrystalline structure with a main peak at 35.6° corresponding to a [110] plane, indicating a preferred growth. Small peaks of magnesium oxide (MgO) [200] were discovered at 44.5° for the films with the highest Mg concentration. The crystallite size of the pure hematite film deposited in Ar/O₂ was calculated to be 32.2 nm from XRD patterns using the Scherrer equation. This agreed well with SEM observations. With the incorporation of Mg, the particle sizes were found to increase. As estimated from the XRD patterns, the Mg-alloyed hematite particles possessed sizes of 39.8 nm, 44.1 nm, and 50.2 nm, corresponding to Mg concentration of 4.9%, 8.1%, and 13.4%, respectively. Figure 14 (b) shows the XRD patterns of pure hematite and Mg-alloyed hematite films grown at different RF powers in mixed N₂/O₂ ambient with O₂ mass flow rate of [O₂/(N₂ +O₂)]=10%. No MgO peaks were detected, possibly due to the much lower Mg concentration. The films deposited in Ar/O₂ gas exhibited stronger XRD peak intensities for the (110) plane and (300) planes compared to the films deposited in N₂/O₂ ambient, suggesting that films deposited in the mixed Ar/O₂ ambient have better crystallinity. The crystallite size of the pure hematite film deposited in N₂/O₂ was calculated to be 34.5 nm. The Mg-alloyed hematite particles possessed sizes of 36.7 nm, 38.4 nm, and 40.2 nm corresponding to Mg concentration of 0.7%, 1.8%, and 3.2%. EDS analysis revealed that the better crystallinity correlates with the higher Mg concentration.
Figure 14. XRD patterns of pure and Mg-alloyed hematite films deposited in (a) Ar/O$_2$ ambient and (b) N$_2$/O$_2$ ambient.
Figures 15 (a), (b), (c), and (d) show the SEM images of the pure and 4.9%, 8.1%, and 13.4% Mg-alloyed samples grown under Ar/O$_2$ ambient, respectively. The insets show the details of the grain morphologies. The features of large grains in Fig. 15 (a) are from the FTO grains on the substrates. The hematite grains are very small. However, it is still clear enough to see that the small hematite grains are grown on the large FTO grains. As the Mg concentration increases, the hematite grain size increases.

Figures 16 (a), (b), (c), and (d) show the SEM images of the pure and 0.7%, 1.8%, and 3.2% Mg-alloyed samples grown under N$_2$/O$_2$ ambient, respectively. It is seen that as the Mg concentration increases, the hematite grain size becomes bigger. However, Mg-alloyed hematite films grown under N$_2$/O$_2$ ambient have much smaller grain sizes, due to the much lower Mg concentration.
Figure 15. SEM images of (a) pure hematite and (b) 4.9%, (c) 8.1%, and (d) 13.4% Mg-alloyed hematite thin films deposited in Ar/O$_2$ ambient.
Figure 16. SEM images of (a) pure hematite, (b) 0.7%, (c) 1.8%, and (d) 3.2% Mg-alloyed hematite thin films deposited in N₂/O₂ ambient.

Figure 17 (a) shows the optical absorption spectra of pure hematite and Mg-alloyed hematite films grown at different RF powers in Ar/O₂ ambient. The absorption edge shifted slightly to the shorter wavelength regions as the Mg doping concentration increased, indicating that Mg alloying in hematite leads to larger bandgap. Figure 17 (b) shows the optical absorption spectra of the pure hematite and Mg-alloyed hematite films grown at different RF powers in N₂/O₂ ambient. The Mg-alloyed hematite film exhibits a
similar absorption pattern to that of the pure hematite films, which is probably due to the low Mg concentration. Comparing the pure hematite thin films grown in the Ar/O_2 and N_2/O_2 ambient finds no significant difference, suggesting that nitrogen might not be incorporated into the hematite films grown in N_2/O_2 ambient, which is consistent with EDS analysis.
Figure 17. Absorption patterns of pure and Mg-alloyed hematite films deposited in (a) Ar/O$_2$ ambient and (b) N$_2$/O$_2$ ambient [44].
We have determined both the direct and indirect bandgaps of pure and Mg-alloyed hematite films by extrapolating the linear portion of a Tauc plot created by taking both transmittance and reflectance into account (Fig. 18) as well as correcting for scattering and transmittance from the substrate glass. We found that the indirect bandgap results are more consistent with the trend of the optical absorption spectra shown in Fig. 17. Therefore, the indirect bandgaps are considered in this paper. The indirect bandgap is found to be about 2.11 eV for pure hematite deposited in Ar/O$_2$ ambient and 2.07 eV for pure hematite film deposited in N$_2$/O$_2$. The small difference could be due to the different crystallinity of these two films. The latter contains more defects, which could lead to additional absorption. For the films deposited in Ar/O$_2$ ambient [Fig. 18 (a)], the bandgaps of 4.9%, 8.1%, and 13.4% Mg-alloyed hematite films are measured to be about 2.14 eV, 2.15 eV, and 2.3 eV, respectively. The bandgap increases as the Mg concentration increases. This is consistent with the optical absorption spectra shown in Fig. 17 (a).

For the films deposited in N$_2$/O$_2$ ambient [Fig. 18 (b)], the bandgaps of 0.4%, 0.7%, and 1.8% Ti-alloyed hematite films are measured to be 2.08 eV, 2.09 eV, and 2.09 eV. The bandgap does not change much due to the low Mg concentration. This is consistent with the optical absorption spectra shown in Fig. 17 (b). The bandgaps of hematite films deposited in N$_2$/O$_2$ ambient are narrower than those of the films deposited in Ar/O$_2$ ambient. As explained earlier, this difference is caused by the different crystallinity, which is evident in XRD patterns and SEM images. It has been noticed that
metal oxide films deposited at room temperature in N₂-containing ambient usually lead to poor crystallinity.

Figure 18. Optical absorption co-efficient of pure and Mg-alloyed hematite films deposited in (a) Ar/O₂ ambient and (b) N₂/O₂ ambient [44].
We have further tested the PEC performance of the pure hematite and Mg-alloyed hematite films grown in different ambient. Figures 19 (a) and (b) show the current-potential curves of both pure and Mg-alloyed hematite films grown in Ar/O₂ and N₂/O₂, respectively, in 1 M Na₂SO₄ solution over a potential range of -0.2 V to 0.8 V under light/off illumination. The dark current under light-off conditions hardly changed across the potential range. Low photocurrent is registered for the pure hematite film, as we expected. The pure hematite film deposited in Ar/O₂ ambient exhibited n-type activity, while the Mg-alloyed hematite films mainly showed p-type activity. This indicates that most of the Mg atoms have been alloyed on the substitutional sites of iron oxide. The p-type activity increases as the Mg concentration increases for most of the films. However, for the 13.4% Mg-alloyed hematite film, no photoresponse is detected. This could be the result of phase separation, which has been observed in XRD patterns. The formation of MgO in hematite films would dramatically reduce the electrical conductivity of the thin film and therefore lead to very low current. From the current-potential curves, we estimated onset potentials around 0.4–0.5 V for pure and Mg-alloyed hematite films.
Figure 19. Current-potential curves of pure and Mg-alloyed hematite films deposited in (a) Ar/O\textsubscript{2} ambient and (b) N\textsubscript{2}/O\textsubscript{2} ambient [44].
We have further measured Mott-Schottky plots (capacitance-potential) for the pure hematite and Mg-alloyed hematite films (Fig. 20). Based on the Mott-Schottky equation, the slope of the plots has an inverse relationship with the carrier density:

\[
\frac{1}{\text{carrier density}}
\]

\[\text{carrier density} \propto \text{inverse of slope}
\]

where, \(e_0\) is the electron charge, and \(\varepsilon\) and \(\varepsilon_0\) are relative and vacuum electric permittivity. With a value of 80 for hematite, our results indicate that the carrier densities are 1.76 \(10^{14}\) cm\(^{-3}\) for pure hematite and 2.06 \(10^{14}\) cm\(^{-3}\) and 3.41 \(10^{15}\) cm\(^{-3}\) for 4.9\% and 8.1\% Mg-alloyed hematite thin films deposited in Ar/O\(_2\) ambient [Fig. 20 (a)]. Since no photoresponse can be detected for the 13.4\% Mg-alloyed hematite, the Mott-Schottky plot is not shown in the figure. The carrier concentration of Mg-alloyed hematite is almost the same as that of the pure hematite. However, their types of conductivity are different. The pure hematite thin films are n-type, but the Mg-alloyed hematite thin films are p-type.

For hematite films deposited in N\(_2\)/O\(_2\) ambient [Figure 20(b)], the carrier densities are 1.81 \(10^{14}\) cm\(^{-3}\) for pure hematite, and 2.04 \(10^{14}\) cm\(^{-3}\), 2.43 \(10^{14}\) cm\(^{-3}\), and 3.14 \(10^{14}\) cm\(^{-3}\) for 0.7\%, 1.8\%, and 3.2\% Mg-alloyed hematite thin films. The flatband potential was determined by extrapolating the linear portion of the Mott-Schottky plots. The flatband potentials were 0.57 V, 0.54 V, and 0.48 V vs. Ag/AgCl for the pure and 4.9\%, and 8.1\% Mg-alloyed hematite thin films deposited in Ar/O\(_2\) ambient, respectively. The
flatband potentials were 0.72 V, 0.59 V, 0.61 V, and 0.61 V vs. Ag/AgCl for the pure and 0.7%, 1.8%, and 3.2% Mg-alloyed hematite thin films deposited in N$_2$/O$_2$ ambient

![Mott–Schottky plots of pure and Mg-alloyed hematite films deposited in Ar/O$_2$ ambient and N$_2$/O$_2$ ambient.](image)

Figure 20. Mott–Schottky plots of pure and Mg-alloyed hematite films deposited in (a) Ar/O$_2$ ambient and (b) N$_2$/O$_2$ ambient [44].
2.4 Improved PEC performance of Ti and Mg co-alloyed hematite

The incorporation of $3d$ transition metals in hematite modifies the valence and conduction band edges of hematite. In particular, the incorporation of Ti reduces the electron effective mass, which would improve the electron conductivity of hematite and hence explains why the incorporation of Ti in hematite has led to significantly enhanced photocurrents. However, incorporating Ti into hematite has the following drawbacks: (1) The amount of Ti that can be incorporated into hematite is limited by the solubility of Ti in hematite; (2) The incorporated Ti introduces charged defects, which are effective non-radiative recombination centers; and (3) The incorporated Ti creates levels below the conduction band edge of hematite, which lower the energy of the photo excited electrons. We found that these problems can be overcome by a charge-compensated donor-acceptor co-alloying approach. We found that Ti and Mg co-alloying resulted in the following effects: (1) It enhanced the solubility of Mg and Ti, which led to reduced electron effective mass and therefore increased electron mobility; (2) It tuned the carrier density and therefore allowed the optimization of electrical conductivity; and (3) It reduced the density of charged defects and therefore reduced carrier recombination. As a result, the Ti and Mg co-alloyed hematite thin films exhibited improved performance in PEC water splitting as compared to pure hematite thin films. Our results suggest that charge-compensated co-alloying is a suitable approach for engineering hematite for the application of PEC water splitting.

Table IV shows the various deposition conditions of Ti-alloyed and Ti and Mg co-alloyed hematite thin films. An oxygen-rich environment was maintained to avoid the
formation of Fe\textsuperscript{2+}. The Ti-alloyed hematite films were deposited by cosputtering an iron oxide target and a titanium target. For deposition of Ti/Mg co-alloyed hematite thin films, MgO disks with different diameters were placed on the titanium target to serve as the Mg sources. The RF power applied to the iron oxide target was 150 W, and the RF power applied to the titanium target was 200 W. Our previous work has shown that these RF powers result in a Ti concentration around 10% and exhibit the best PEC performance. The compositions of the deposited hematite thin films were characterized by EDS. The data are listed in Table IV. For comparison, we have prepared five sets of samples. Set one is pure hematite thin film. Set two is Ti-alloyed hematite, which contains about 10% Ti. Sets three to five are Ti and Mg co-alloyed hematite thin films with MgO disks with diameters of 1 cm, 1.5 cm, and 2 cm. EDS results showed that these three set of samples have the compositions of (Fe\textsubscript{0.87}Ti\textsubscript{0.10}Mg\textsubscript{0.03})\textsubscript{2}O\textsubscript{3}, (Fe\textsubscript{0.84}Ti\textsubscript{0.09}Mg\textsubscript{0.07})\textsubscript{2}O\textsubscript{3}, and (Fe\textsubscript{0.79}Ti\textsubscript{0.09}Mg\textsubscript{0.12})\textsubscript{2}O\textsubscript{3}.

**Table IV. Thicknesses and Mg concentrations of pure and Mg-alloyed hematite films at various deposition conditions.**

<table>
<thead>
<tr>
<th>RF power on Fe\textsubscript{2}O\textsubscript{3} target</th>
<th>RF power on Ti target</th>
<th>MgO disk diameter</th>
<th>Final thickness</th>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>150 W</td>
<td>200 W</td>
<td>350 nm</td>
<td>Fe\textsubscript{2}O\textsubscript{3}</td>
<td></td>
</tr>
<tr>
<td>150 W</td>
<td>200 W</td>
<td>530 nm</td>
<td>(Fe\textsubscript{0.9}Ti\textsubscript{0.1})\textsubscript{2}O\textsubscript{3}</td>
<td></td>
</tr>
<tr>
<td>150 W</td>
<td>200 W</td>
<td>1 cm</td>
<td>530 nm</td>
<td>(Fe\textsubscript{0.87}Ti\textsubscript{0.10}Mg\textsubscript{0.03})\textsubscript{2}O\textsubscript{3}</td>
</tr>
<tr>
<td>150 W</td>
<td>200 W</td>
<td>1.5 cm</td>
<td>550 nm</td>
<td>(Fe\textsubscript{0.84}Ti\textsubscript{0.09}Mg\textsubscript{0.07})\textsubscript{2}O\textsubscript{3}</td>
</tr>
<tr>
<td>150 W</td>
<td>200 W</td>
<td>2 cm</td>
<td>540 nm</td>
<td>(Fe\textsubscript{0.79}Ti\textsubscript{0.09}Mg\textsubscript{0.12})\textsubscript{2}O\textsubscript{3}</td>
</tr>
</tbody>
</table>

Figure 21 shows the XRD curves obtained for the five sets of samples, pure hematite, Ti-alloyed hematite, and Ti and Mg co-alloyed hematite. Dotted lines in the figure indicate the peaks from substrate (FTO). Strong hematite peaks were registered in the pattern, as indicated by the solid lines. We found that hematite structure was preserved after Ti alloying and Ti and Mg co-alloying. The pure hematite film displayed a polycrystalline nature with a main peak at 35.6° corresponding to the (110) plane, indicating a preferred growth. The Ti-alloyed hematite film does not exhibit preferred grain growth, as both the [110] and [104] peaks are strong. No TiO$_2$ peaks were detected in the Ti-alloyed hematite film. The crystallite size of the pure hematite film was calculated to be about 32.2 nm from XRD patterns using the Scherrer equation. This agrees well with SEM observations. The particle size increased to 54.1 nm for Ti-alloyed hematite with 10% Ti. For Ti and Mg co-alloyed hematite films with the highest Ti:Mg atomic ratio, the films still exhibit (110) plane preferred growth. However, when the Ti:Mg ratio decreased, the preferred growth vanished. The crystallite size of the Ti and Mg co-alloyed hematite thin films was calculated to be 58.2 nm, 60.3 nm, and 40.5 nm, corresponding to the MgO disks with diameters of 1 cm, 1.5 cm, and 2 cm, respectively.
Figure 21. XRD patterns of pure, Ti-alloyed, and Ti and Mg co-alloyed hematite thin films deposited in Ar/O$_2$ ambient [43].

Figures 22 (a) and (b) show the SEM images of the pure and Ti-alloyed hematite samples grown under Ar/O$_2$ ambient. The inset shows the details of the grain morphologies. The features of large grains in Fig. 22 (a) are from the FTO grains on the substrates. The hematite grains are very small. However, it is still clear enough to see that the small hematite grains are grown on the large FTO grains. With the incorporation of Ti impurities, the hematite grain size increased. The hematite grains exhibited triangle shapes with facets, which could be the consequence of orientation-preferred grain growth, as indicated by XRD plots.

Figures 22 (c), (d), and (e) show the SEM images of Ti and Mg co-alloyed hematite thin films. It is seen that when the Ti:Mg increases, the grain morphology
changes dramatically. At high Ti:Mg ratios, the grains consist of triangles with a limited number of orientations, but at low Ti/Mg ratios, the grain morphology is no longer mainly triangular, and the orientation of the grains is random.

Figure 22. SEM images of (a) pure hematite; (b) 10% Ti-alloyed hematite thin films; (c) (Fe$_{0.87}$Ti$_{0.10}$Mg$_{0.03}$)$_2$O$_3$; (d) (Fe$_{0.84}$Ti$_{0.09}$Mg$_{0.07}$)$_2$O$_3$; (e) (Fe$_{0.79}$Ti$_{0.09}$Mg$_{0.12}$)$_2$O$_3$ deposited in Ar/O$_2$ ambient [43].
Figure 23 shows the optical absorption spectra of the pure hematite, Ti-alloyed, and Ti and Mg co-alloyed hematite thin films. The absorption edge shifted slightly to the longer wavelength regions for the 10% Ti-alloyed hematite film compared to the pure hematite, indicating that Ti alloying in hematite leads to a small bandgap reduction. It is known that Ti atoms occupying Fe sites in hematite are donors. The Ti alloying will create partial occupied bands below the CBM of hematite. The lowest unoccupied band forms a new CBM, which should be slightly lower in energy than the original CBM of hematite. The position of the new CBM depends on Ti concentration. Higher Ti concentration leads to lower new CBM position because of the band broadening effect. This explains why the Ti-alloyed hematite has a smaller bandgap than the pure hematite. For the Ti and Mg co-alloyed hematite with low Mg concentration, the absorption edge does not change significantly. However, for the Ti and Mg co-alloyed hematite with high Mg concentration, the absorption edge is shifted significantly to high energy.

Figure 23. Absorption patterns of pure hematite, Ti-alloyed, and Ti and Mg co-alloyed hematite thin films [43].
We have determined both the direct and indirect bandgaps of pure hematite, Ti-alloyed, and Ti and Mg co-alloyed hematite thin films by extrapolating the linear portion of a Tauc plot created by taking both transmittance and reflectance into account (Fig. 24). A correction for scattering and transmittance from the substrate glass was taken into consideration. We found that the indirect bandgap results are more consistent with the trend of the optical absorption spectra shown in Fig. 23. Therefore, the indirect bandgaps are considered in this paper. The indirect bandgap was found to be about 2.08 eV for the pure hematite and 2.01 eV for 10% Ti-alloyed hematite. For the Ti and Mg co-alloyed hematite thin films, the bandgaps were 2.05 eV, 2.06 eV, and 2.28 eV for the samples with compositions of \((\text{Fe}_{0.87}\text{Ti}_{0.10}\text{Mg}_{0.03})_2\text{O}_3\), \((\text{Fe}_{0.84}\text{Ti}_{0.09}\text{Mg}_{0.07})_2\text{O}_3\), and \((\text{Fe}_{0.79}\text{Ti}_{0.09}\text{Mg}_{0.12})_2\text{O}_3\), respectively. The dramatically increased bandgap for the Ti and Mg co-alloyed hematite film with the high Mg concentration, \((\text{Fe}_{0.79}\text{Ti}_{0.09}\text{Mg}_{0.12})_2\text{O}_3\), could be due to the precipitation of MgO. The XRD curve did not show the presence of MgO, indicating that the MgO precipitates could have very small grain sizes.

Figure 24. Optical absorption co-efficient of pure hematite, Ti-alloyed, and Ti and Mg co-alloyed hematite thin films [43].
We have tested the PEC performance of the pure hematite, Ti-alloyed, and Ti and Mg co-alloyed hematite thin films. Figure 25 shows the current-potential curves of these thin films in 1 M Na$_2$SO$_4$ solution over a potential range of 0 V to 1 V. The dark current under light-off conditions hardly changed across the potential range. Low photocurrent was registered for the pure hematite film, as we expected. Ti alloying led to two effects on the PEC performance of hematite thin films. First, Ti alloying enhanced photocurrent magnitude significantly. Secondly, Ti alloying shifted the photocurrent onset potentials to more negative values. From the current-potential curves, we obtained onset potentials of 0.6 V [vs. (Ag/AgCl)] for pure hematite, and 0.4 V [vs. (Ag/AgCl)] for 10% Ti-alloyed hematite film. The first effect could be due to the enhancement of electrical conductivity caused by Ti doping. The second effect could be due to the change of hematite/electrolyte caused by the presence of Ti.

We further found that Ti and Mg co-alloying can further improve the PEC performance of hematite thin films. It is seen from Fig. 25 that the hematite films with compositions of (Fe$_{0.84}$Ti$_{0.09}$Mg$_{0.07}$)$_2$O$_3$ and (Fe$_{0.87}$Ti$_{0.10}$Mg$_{0.03}$)$_2$O$_3$ exhibited much higher current than the pure and Ti-alloyed hematite films. The Ti:Mg ratio is expected to influence the PEC performance of Ti and Mg co-alloyed hematite films. From a theoretical point of view, the Ti:Mg ratio should be close to 1:1 because this results in the lowest density of charged defects, which are mostly non-radiative recombination centers. Indeed, Fig. 25 shows that the sample with a composition of (Fe$_{0.84}$Ti$_{0.09}$Mg$_{0.07}$)$_2$O$_3$ exhibited better current than the sample with a composition of (Fe$_{0.87}$Ti$_{0.10}$Mg$_{0.03}$)$_2$O$_3$, because 0.09:0.07 is closer to 1:1 than 0.10:0.03. If the Ti:Mg ratio is much smaller than
1:1, that could lead to the precipitation of MgO. In this case, the film will exhibit poor performance because MgO is very insulating. Indeed, the film with a composition of (Fe$_{0.79}$Ti$_{0.09}$Mg$_{0.12}$)$_2$O$_3$ exhibited very small current. Because Mg is an acceptor in hematite, when Ti:Mg is smaller than 1:1, the films should exhibit p-type behavior, which is clearly evident in Fig. 7.

![Image of current-potential curves](image)

**Figure 25.** Current-potential curves of pure, Ti-alloyed, and Ti and Mg co-alloyed hematite thin films [43].

We have further measured Mott-Schottky plots (capacitance-potential) for the pure hematite, Ti-alloyed, and Ti and Mg co-alloyed hematite thin films (Figure 26). Based on the Mott-Schottky equation, the slope of the plots has an inverse relationship with the carrier density:
where, $e_0$ is the electron charge, and $\varepsilon$ and $\varepsilon_0$ are relative and vacuum electric permittivities. With a value of 80 for hematite, our results indicate that the carrier densities are $1.76 \times 10^{14}$ cm$^{-3}$ for pure hematite and $1.41 \times 10^{15}$ cm$^{-3}$ for 10\% Ti$^{4+}$-alloyed hematite thin films. Clearly the carrier concentration increases as the Ti concentration increases, confirming that Ti is a donor in hematite. The carrier densities measured for Ti and Mg co-alloyed hematite thin films are about $2.94 \times 10^{15}$ cm$^{-3}$ for the film with a composition of $(Fe_{0.84}Ti_{0.09}Mg_{0.07})_2O_3$ and $4.23 \times 10^{15}$ cm$^{-3}$ for the film with a composition of $(Fe_{0.87}Ti_{0.09}Mg_{0.03})_2O_3$. The current-potential curve indicates that the sample with a composition of $(Fe_{0.79}Ti_{0.09}Mg_{0.12})_2O_3$ can be characterized as either n-type or p-type. In Fig.26 we treated it as an n-type material, and the calculated electron density is about $5.24 \times 10^{14}$ cm$^{-3}$.

$1/C^2 \propto \varepsilon_0 \varepsilon \varepsilon_0$  \hspace{1cm} (1)

![Figure 26. Mott-Schottky plots of pure, Ti-alloyed, and Ti and Mg co-alloyed hematite thin films [43].](image-url)
IPCE for pure hematite, Ti-alloyed, and Ti and Mg co-alloyed hematite thin films were measured at 0.6 V vs. Ag/AgCl as a function of incident light wavelength (Fig. 27). The IPCE values for the pure hematite films are very low, below 3% due to the poor electrical conductivity and high non-radiative recombination rate. The 10% Ti-alloyed hematite showed increased IPCE values. At 400 nm, the IPCE of the 10% Ti-alloyed film deposited in Ar/O₂ ambient is almost four times higher than that of the pure hematite film. This is direct evidence that the photoresponse has been improved by Ti doping. The IPCE values for Ti and Mg co-alloyed hematite films with compositions of (Fe₀.₈₄Ti₀.₀₉Mg₀.₀₇)₂O₃ and (Fe₀.₈₇Ti₀.₁₀Mg₀.₀₃)₂O₃ are even higher than that of the Ti-alloyed hematite. At 400 nm, the IPCE value of (Fe₀.₈₄Ti₀.₀₉Mg₀.₀₇)₂O₃ is almost twice as high as that of the Ti-alloyed hematite film. Due to the potential precipitation of MgO, the Ti and Mg co-alloyed hematite film with a composition of (Fe₀.₇₉Ti₀.₀₉Mg₀.₁₂)₂O₃, the IPCE data, the current-potential curves, and the optical absorption coefficient are consistent with our theoretical results.
Conclusion

We have studied the effects of Ti and Mg co-alloying of hematite thin films on PEC performance using density functional theory calculation and materials synthesis and characterization. We have found that Ti and Mg co-alloyed hematite thin films with Ti:Mg close to 1:1 can significantly enhance the PEC performance as compared to pure and solely Ti-alloyed hematite thin films. Our study has suggested that the charge-compensated donor-acceptor co-alloying can lead to the following effects: (1) It enhances the solubility of Mg and Ti, which leads to reduced electron effective mass and therefore increased electron mobility; (2) It tunes the carrier density and therefore allows the optimization of electrical conductivity; and (3) The donor-acceptor compensation reduces the density of charged defects and therefore reduces carrier recombination as compared to...
the noncompensated alloying. Our results suggest that charge-compensated co-alloying is a suitable approach for engineering hematite for the application of PEC water splitting.
Chapter 3

Synthesis and Characterization of CuO and Cu-Ti-O Coated Copper Oxide for PEC Water Splitting

3.1 Synthesis and characterization of Ti-alloyed CuO

First of all, we need to find an ideal deposition condition to deposit pure CuO film by radio frequency (RF) magnetron sputtering of a copper target. F-doped SnO₂ (FTO) (20–23 Ω/cm) coated transparent glass was used as the substrate. We chose Ar/O₂ as the reactive gas, and we found that RF power and oxygen partial pressure are the two crucial factors that greatly affected the structure and crystallinity of the deposited film. Therefore, we varied the O₂/(O₂+Ar) ratio from 5% to 10% and the RF power on the iron oxide target from 60 W to 100 W in order to find an optimized RF power with an oxygen partial pressure suitable for a well-crystallized hematite film with a fairly good growth rate. The substrates were kept at room temperature during all the deposition processes, and the growth rate was monitored by a crystal monitor installed near the substrate holder. A thickness of 500 nm was set as the final thickness for all the deposited film. We found that higher oxygen partial pressure reduced the growth rate of the film, and higher RF power led to a high deposition rate.
<table>
<thead>
<tr>
<th>RF power</th>
<th>O₂ partial pressure</th>
<th>Growth rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>60 W</td>
<td>5%</td>
<td>0.8 A/s</td>
</tr>
<tr>
<td>80 W</td>
<td>5%</td>
<td>1 A/s</td>
</tr>
<tr>
<td>100 W</td>
<td>5%</td>
<td>1.5 A/s</td>
</tr>
<tr>
<td>60 W</td>
<td>10%</td>
<td>0.2 A/s</td>
</tr>
<tr>
<td>80 W</td>
<td>10%</td>
<td>0.5 A/s</td>
</tr>
<tr>
<td>100 W</td>
<td>10%</td>
<td>0.8 A/s</td>
</tr>
</tbody>
</table>


Figure 28 shows the XRD curves of pure CuO films grown at different RF powers in mixed Ar/O₂ ambient with 5% and 10% O₂ partial pressure. Dotted lines in the figure indicate peaks from substrate (FTO). Strong Cu, CuO, and Cu₂O peaks were registered in the pattern, as indicated by the solid lines. Films deposited with 80 W and 100 W using 5% O₂ show both Cu₂O and Cu peaks, which suggests that 5% O₂ is insufficient to support enough oxygen to form CuO using these RF powers during the deposition process. Films deposited using 10% O₂ and the film deposited using 5% O₂ and 60 W show main peaks at CuO [111] and CuO [111] without showing any Cu₂O peaks.
Figure 28. XRD patterns of pure CuO films deposited in Ar/O\textsubscript{2} ambient under various conditions [46].

Figure 29 shows the optical absorption spectra of the pure CuO grown at different RF powers in Ar/O\textsubscript{2} ambient with different oxygen partial pressure. We find that the film deposited with 80 W and 10\% O\textsubscript{2} exhibited better absorption over the visible range wavelength, and its absorption tail is also lower than the others, indicating that this sample has fewer defects. Therefore, we chose to use 80 W and 10\% O\textsubscript{2} as our deposition condition for the Ti-alloyed CuO.
Figure 29. Absorption patterns of pure CuO films deposited in Ar/O\textsubscript{2} ambient under various conditions.

3.2 Synthesis and characterization of Ti-alloyed CuO

In order to address the stability problem of CuO, we first investigated incorporating Ti as impurities to stabilize the CuO film in aqueous solutions. We used a co-sputtering process using a copper target and a titanium target. Table VI shows the conditions used for the deposition of pure CuO and Ti-alloyed CuO thin films. As we have found the best deposition condition for pure CuO, we will keep using this condition for the Ti-alloyed CuO films. So the RF power on the copper target was set to be 80 W, with an oxygen partial pressure of 10% for all the depositions. For Ti-alloyed CuO thin films, we varied the RF power on the titanium target from 50 W to 150 W. EDS data indicates that Ti concentrations were 2.1%, 5.6%, and 9.7%, corresponding to the Ti RF power of 50 W, 100 W, and 150 W, respectively. For pure CuO and Ti-alloyed CuO thin
films, we controlled the film thickness to be around 500 nm. We tried to keep the thickness at the same level in order to eliminate the thickness effect from the PEC performance. The growth rate was read directly from the crystal monitor installed in the vacuum chamber next to the substrate holder. We found that the growth rate increased with increasing RF power on titanium target. We also measured the resistivity of the deposited films, and we found that the resistivity increased dramatically for Ti-alloyed CuO samples compared to the pure CuO sample, suggesting that the electric transportation properties became poor. This is probably due to the incorporated Ti impurities, which created defects and largely affected the crystallinity of the film.
Table VI. Thicknesses, growth rate, Ti concentrations, and resistivity of pure and Ti-alloyed CuO films at various deposition conditions.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>RF power on copper target</th>
<th>RF power on titanium target</th>
<th>Film thickness</th>
<th>Growth rate</th>
<th>Ti concentration</th>
<th>Resistivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>80 W</td>
<td>500 nm</td>
<td>0.5 A/s</td>
<td>500 nm</td>
<td>~400 Ω/ cm²</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>80 W</td>
<td>50 W</td>
<td>510 nm</td>
<td>0.7 A/s</td>
<td>2.1%</td>
<td>~1.1 kΩ/ cm²</td>
</tr>
<tr>
<td>3</td>
<td>80 W</td>
<td>100 W</td>
<td>490 nm</td>
<td>0.8 A/s</td>
<td>5.6%</td>
<td>~1.4 kΩ/ cm²</td>
</tr>
<tr>
<td>4</td>
<td>80 W</td>
<td>150 W</td>
<td>500 nm</td>
<td>1.0 A/s</td>
<td>9.7%</td>
<td>~5.3 kΩ/ cm²</td>
</tr>
</tbody>
</table>

Figure 30 shows the XRD curves of the pure CuO and Cu-Ti-O coated CuO samples. All the films were deposited by RF sputtering using an RF power of 80 W, and the O₂ mass flow rate was [O₂/(Ar+O₂)] = 10%. Dotted lines in the figure indicate peaks from substrate (FTO). Strong CuO peaks were registered in the pattern, as indicated by the solid lines. We found that pure CuO film exhibited a very strong peak at the CuO (111) plane (2θ=36.4°) and CuO (002) plane (2θ=38.8°), indicating that the single phase of CuO film was obtained. We found that the CuO structure was still preserved with 2.1%, 5.6%, and 9.7% incorporated Ti, and no TiO₂ peaks were detected. With the incorporation of Ti, the intensity of CuO (111) decreased. The same tendency was also observed on the CuO (002) and CuO (110) planes. This suggested that the crystallinity of Ti-alloyed CuO becomes poor as Ti impurities create defects that largely affect the structure of the films. The crystallite size of the pure CuO film was calculated to be 20.8 nm from XRD patterns using the Scherrer equation. The Ti-alloyed hematite particles
possessed sizes of 35.3 nm, 32.8 nm, and 37.6 nm corresponding to the RF power of 50 W, 100 W, and 150 W applied to the titanium target, respectively.

Figure 30. XRD patterns of pure CuO and Ti-alloyed CuO films deposited in Ar/O₂.

Figure 31 shows the top field emission scanning SEM images of the pure CuO (1) and 2.1%, 5.6%, and 9.7% Ti-alloyed CuO (2–4) samples. The insets are enlarged areas showing the details of the grain morphologies. The pure CuO sample (1) displays a highly dense and uniform film with triangle-shaped grains, which could be the consequence of orientation-preferred grain growth as indicated by XRD plots. All the Ti-alloyed CuO samples display larger grain sizes compared to the pure CuO. This matches their XRD results. 2.1% Ti-alloyed CuO (2) exhibits similar morphology to the pure CuO, except that the film is less uniform. This is probably due to low Ti concentration, while the higher-Ti-concentration samples (3 and 4) exhibited different morphologies.
These results indicate that the grain size and shape of CuO films grown by RF sputtering are affected by the incorporation of Ti.

Figure 31. SEM images of (1) pure CuO and (b) 2.1%, (c) 5.6% (c), and (d) 9.7% Ti-alloyed CuO thin films.
Absorption spectroscopy revealed high absorption for pure CuO. Figure 32 shows the optical absorption spectra of the pure CuO and Ti-alloyed CuO samples. The absorption edge of the Ti-alloyed CuO and Cu-Ti-O samples slightly shifted to longer wavelengths compared to the pure CuO sample, indicating that these samples have smaller bandgaps compared to the pure CuO. The conduction band of CuO mainly consists of the Cu S orbital. The energy level of the Ti S orbital is higher than that of Cu S, which means that Ti is a shallow donor in CuO. So the reduced bandgap could be caused only by the defect levels created below the CBM of CuO by introducing Ti. We also found that the absorption efficiencies of Ti-alloyed CuO are lower than that of the pure CuO, especially in the visible wavelength region. Meanwhile, Ti-alloyed CuO samples showed higher absorption at the tail, which is most likely created by defects.

![Figure 32. Absorption patterns of pure CuO and Ti-alloyed CuO films.](image)
CuO is acknowledged to be a direct bandgap semiconductor. However, Ti-alloyed CuO is very likely to change its band structure. Therefore, we analyzed both the direct and indirect bandgaps of pure CuO and Ti-alloyed CuO films by taking both transmittance and reflectance into account (Fig. 33). A correction for scattering and transmittance from the substrate glass was taken into consideration. We find that our pure CuO sample showed a direct bandgap of 1.45 eV, which is consistent with the data reported elsewhere. The Ti-alloyed CuO samples are found to be indirect bandgap materials with bandgaps of around 1.3 eV; the narrower bandgap might be caused by the defect level that was created below the CBM of CuO.

Figure 33. Optical absorption co-efficient of a) direct bandgap of pure CuO and Ti-alloyed CuO and b) indirect bandgap of pure CuO and Ti-alloyed CuO samples.
A major drawback of CuO when used as a photocathode for PEC water splitting is that it is not stable in aqueous solutions. Figure 34 shows the dark current of all samples scanned in 1 M Na₂SO₄-aqueous solution. As we expected, pure CuO shows great photooxidation with a main corrosion peak at around 0.3 V. We observed that the film color turned from black to brown, and part of the film was wiped off quickly in the solution after the dark current scan. XRD data proves that the film has been reduced to a mix of Cu, Cu₂O, and CuO. The same observation was obtained for the 2.1% Ti-alloyed CuO. However, no obvious photocorrosion was observed from the 5.6% or 9.7% Ti-alloyed CuO samples during the dark current scan.

![Figure 34. Dark current scan of pure CuO and 2.1%, 5.6%, and 9.7% Ti-alloyed CuO samples.](image-url)
We further tested the photocurrent of these samples under illumination with a light intensity of around 0.5 W/cm² (5 suns) (Fig. 35). At the cathodic potential region, all samples show negative photocurrents, which indicates that these samples are p-type semiconductors. Pure CuO shows good photocurrent: around 1.5 mA at -0.3 V bias (Fig. 35-1). We find that increasing Ti concentration in CuO film leads to a dramatic decrease of the photocurrent. 9.7% Ti-alloyed CuO only shows around 0.2 mA at -0.3 V bias (Fig. 35-4). This could be mainly ascribed to the defects created by the Ti-alloying, and as we concluded from the absorption spectrum, the absorption co-efficients of the Ti-alloyed CuO samples are much lower than that of the pure CuO sample.

Figure 35. Photocurrent of pure CuO (1) and 2.1% (2), 5.6% (3), and 9.7% (4) Ti-alloyed CuO films.
Even though the photocurrent decreased after incorporating Ti, the stability test shows that Ti-alloyed CuO does possess better stability in aqueous solution than the pure CuO sample (Fig. 36). After a 2-hour stability test, 5.6% Ti-alloyed CuO is found to be corroded during the test, while 9.7% Ti-alloyed CuO still shows no photocorrosion in a dark current scan. However, despite the fact that no evidence of photocorrosion of CuO is observed, the photocurrent still decreased with illumination time.

![Figure 36. Stability test of 5.6% Ti-alloyed and 9.7% Ti-alloyed CuO.](image)

3.3 Synthesis and characterization of Cu-Ti-O coated CuO

We found that 9.7% Ti-alloyed CuO showed no photocorrosion, but the photocurrent dropped, and the absorption also decreased compared to the pure CuO. In order to find a balance between the stability and the efficiency, we decided to try an
alternative method. We designed a double layer structure. First, a 500-nm layer of CuO was deposited on the FTO substrate. Then, a protective layer of Cu-Ti-O (9.7% Ti concentration) was deposited on top of the CuO films by co-sputtering of a copper target (80 W) and a titanium target (150 W). Our PEC measurement showed lower photocurrent response for the Ti-alloyed CuO samples compared to the pure CuO sample. Therefore, we varied the thickness of this Cu-Ti-O layer from 50 nm to 100 nm to find an optimized thickness in order to keep a balance between the stability and efficiency.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>RF power on copper target</th>
<th>RF power on titanium target</th>
<th>CuO film thickness</th>
<th>Cu-Ti-O protective layer thickness</th>
<th>Resistivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>80 W</td>
<td>150 W</td>
<td>500 nm</td>
<td>50 nm</td>
<td>~11.2 kΩ/cm²</td>
</tr>
<tr>
<td>6</td>
<td>80 W</td>
<td>150 W</td>
<td>500 nm</td>
<td>80 nm</td>
<td>~10.7 kΩ/cm²</td>
</tr>
<tr>
<td>7</td>
<td>80 W</td>
<td>150 W</td>
<td>500 nm</td>
<td>100 nm</td>
<td>~15.4 Ω/cm²</td>
</tr>
</tbody>
</table>

Table VII. Thicknesses of protective layer and resistivity of Cu-Ti-O coated CuO.

Figure 37 shows the typical SEM image for Cu-Ti-O coated CuO samples with a mapping of Cu L and Ti K from the top field scanning. All Cu-Ti-O coated CuO samples display similar morphologies. The grain sizes of these samples are generally larger than those of the Ti-alloyed CuO samples. From the top field mapping image, the coated layer shows uniform distribution of Cu and Ti atoms. This is direct evidence to show that a uniform protective layer was deposited on CuO.
Figure 37. SEM images of a typical Cu-Ti-O coated CuO sample with its mapping of the Cu L orbital and Ti K orbital.

Figure 38 shows the optical absorption spectra of the Cu-Ti-O coated CuO samples. The absorption edge of Cu-Ti-O coated CuO samples barely changes compared to that of the pure CuO sample, indicating that these samples have similar bandgaps to the pure CuO. The Cu-Ti-O coated CuO samples with 50-nm and 80-nm protective layers show similar absorption patterns compared to the pure CuO sample. However, the 100-nm coated sample exhibits a poor absorption coefficient in the visible region and higher absorption at the absorption tail, likely caused by the defects introduced by Ti impurities.
Figure 38. Absorption patterns of pure CuO and Cu-Ti-O coated CuO films.

We found that our deposited pure CuO is a direct bandgap semiconductor, while the Ti-alloyed CuO showed an indirect bandgap. Therefore, we analyzed both the direct and indirect bandgaps of pure CuO and Cu-Ti-O coated CuO (Fig. 39) films by taking both transmittance and reflectance into account. A correction for scattering and transmittance from the substrate glass was taken into consideration. We find that our pure CuO sample showed a direct bandgap of 1.46 eV. The Cu-Ti-O coated CuO samples are found to be indirect bandgap materials with bandgaps of around 1.48 eV, which is very close to the indirect bandgap that we measured for pure CuO.
Figure 39. Optical absorption co-efficient of pure CuO (1), Ti-alloyed CuO (2–4), and Cu-Ti-O coated CuO (5–7) samples.

Figure 40 shows the dark current of CuO and Cu-Ti-O coated samples scanned in 1 M Na$_2$SO$_4$-aqueous solution. We found that the thickness of the protective layer does have a great effect on the performance of the film. The 50-nm Cu-Ti-O coated sample still shows photocorrosion during the dark scan. However, no obvious photocorrosion was observed for the 80-nm and 100-nm Cu-Ti-O coated CuO samples.
Figure 40. Dark scan of Cu-Ti-O coated CuO films.

We further tested the photocurrent of these samples under illumination with a light intensity of around 0.5 W/cm$^2$ (5 suns) (Fig. 41). Cu-Ti-O coated CuO samples exhibited larger photocurrent compared to the Ti-alloyed CuO, and the 100-nm Cu-Ti-O coated CuO sample exhibits around 0.4 mA at -0.3 V bias.
Figure 41. Photocurrent of 50-nm Cu-Ti-O coated CuO (1), 80-nm Cu-Ti-O coated CuO (2), and 100-nm Cu-Ti-O coated CuO (3) films.

The 80-nm Cu-Ti-O coated CuO sample is found to be corroded during the stability test, while 100-nm coated CuO still shows no photocorrosion in a dark current scan after the stability test. However, despite the fact that no evidence of photocorrosion of CuO is observed, the photocurrent still decreased with illumination time.
Figure 42. Stability test of 80-nm Cu-Ti-O coated CuO (1) and 100-nm Cu-Ti-O coated CuO (2) films.

IPCE data was collected with an external potential of -0.3 V applied on the working electrode, and the photocurrent was measured at 10-nm intervals (Fig. 43). The collected data was then compared with this reference cell to determine the IPCE. 100-nm Cu-Ti-O coated CuO shows about 8% efficiency at a 400-nm wavelength, and its efficiency drops to 3% after a 2-hour stability test. This is directly related to its lowered photocurrent after the stability test, as we have observed. Even though no photocorrosion was observed during our measurement, there is no guarantee that the possibility of side reactions could occur and degrade the electrode with a longer timescale than used in this work.
Figure 43. IPCE values of 100-nm Cu-Ti-O coated CuO (7) before and after stability test.
Chapter 4
Conclusions and Future Work

4.1 Conclusion

We have studied the effects of Ti and Mg co-alloying of hematite thin films on PEC performance using density functional theory calculation and materials synthesis and characterization. We have found that Ti and Mg co-alloyed hematite thin films with Ti:Mg close to 1:1 can significantly enhance the PEC performance as compared to pure and solely Ti-alloyed hematite thin films. Our study has suggested that the charge-compensated donor-acceptor co-alloying can lead to the following effects: (1) It enhances the solubility of Mg and Ti, which leads to reduced electron effective mass and therefore increased electron mobility; (2) It tunes the carrier density and therefore allows the optimization of electrical conductivity; and (3) The donor-acceptor compensation reduces the density of charged defects and therefore reduces carrier recombination as compared to the noncompensated alloying. Our results suggest that charge-compensated co-alloying is a suitable approach for engineering hematite for the application of PEC water splitting.

We have synthesized and characterized pure CuO, Ti-alloyed CuO, and Cu-Ti-O coated CuO thin films on F-doped SnO₂ coated glass substrates by RF magnetron co-
sputtering of copper and titanium targets in mixed Ar/O\textsubscript{2} ambient. We find that the crystallinity and morphologies of CuO can be affected significantly by the Ti impurities. The CuO film exhibits good crystallinity with a favorable absorption coefficient. Ti-alloyed CuO shows less absorption in the visible region and larger grain sizes. Ti impurities barely change the bandgap; however, Ti-alloyed CuO shows an indirect bandgap while pure CuO has been proven to be a direct bandgap semiconductor. Incorporating Ti in CuO lowers its photocurrent, while at the same time increasing its stability in aqueous solutions. Our 10\% Ti-alloyed CuO shows the best stability with no photooxidation even after a 2-hour stability test. However, its photocurrent is lower than that of pure CuO by almost 80\%. In order to find a balance between photocurrent and photocorrosion, we designed a double-layer structure with CuO as the base layer and Cu-Ti-O on top of CuO as a protective layer. We varied the thickness of Cu-Ti-O protective layer to find an ideal thickness for better efficiency and stability. We find that our 100-nm Cu-Ti-O coated CuO sample shows good stability while keeping the photocurrent in a reasonable range. The efficiency of this sample is tested to be 8\% before the stability test and 3\% after the test, even though no photocorrosion was observed.

4.2 Future Work

We have studied the effects of Ti and Mg co-alloying of hematite thin films for the application of PEC water splitting, and we found that the charge-compensated donor-acceptor co-alloying can lead to following effects: (1) It enhances the solubility of Mg and Ti, which leads to reduced electron effective mass and therefore increased electron
mobility; (2) It tunes the carrier density and therefore allows the optimization of electrical conductivity; and (3) The donor-acceptor compensation reduces the density of charged defects and therefore reduces carrier recombination as compared to noncompensated alloying. Our results suggest that charge-compensated co-alloying is a suitable approach for engineering hematite for the application of PEC water splitting. Further research will focus on searching for other dopants for higher efficiency. Mg will be replaced by other p-type dopants, such as Ca. Since Mg has a smaller atom size compared to Fe, our Mg-alloyed hematite showed some n-type activity, which suggested that some of the Mg atoms had been alloyed in the interstitial site instead of the substitutional site, while Ca has a similar atom size compared to Fe. We expect higher efficiency from Ti and Ca co-alloyed hematite film.

We investigated the Ti-alloyed CuO and designed the double-layer structure to stabilize the surface of CuO. Even though we found that our 9.7% Ti-alloyed CuO showed no photocorrosion in the stability test and our 100-nm Cu-Ti-O coated CuO exhibited a fairly good photocurrent with good stability, the efficiency remains low (2% after stability test). We will look into the other form of copper oxide, Cu₂O, which has a larger bandgap and better absorption in visible-range wavelengths. Cu₂O might be easier for band engineering, as raising the CBM is almost impossible to achieve, as we have proven with CuO.
4.3 Journal publications


4.4. Conference presentations


References


