Bulk and surface chemical modification of hematite photoanode for solar water splitting

Gurudayal

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NANYANG
TECHNOLOGICAL
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**BULK AND SURFACE CHEMICAL MODIFICATION OF
HEMATITE PHOTOANODE FOR SOLAR WATER SPLITTING**

GURUDAYAL

SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

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OF HEMATITE PHOTOANODE FOR SOLAR WATER
SPLITTING**

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ENGINEERING**

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Abstract

Due to increasing demand of energy and the limited supply of the main energy sources (coal, oil, uranium etc.), scientists are looking for the alternative energy sources which are renewable, low cost, easy to manufacture, abundant, light weight and efficient. Photoelectrochemical (PEC) cell has the potential to convert and store solar energy into chemical bonds through the splitting of water into molecular oxygen and hydrogen. Hematite (α -Fe₂O₃) is a promising photoanode material due to its chemical stability in aqueous mediums, suitable energy band gap for light harvesting, low cost and environment friendliness. However, its performance for water oxidation is limited by low carrier concentration and poor electronic properties that lead to high overpotential for water oxidation and low solar to hydrogen conversion (STH) efficiency. Nanostructuring, elemental doping, surface passivation layers and deposition of co-catalyst layers are the possible ways to improve the performance of hematite.

Here, I report a comprehensive approach (nanostructuring, doping and surface passivation) to improve the performance of hematite photoanode. A substantial improvement in the photoelectrochemical (PEC) performance of hematite (α -Fe₂O₃) has been observed by doping with manganese (Mn). Fe₂O₃ nanorods sample with 5% Mn treatment show a photocurrent density of 1.6 mAcm⁻², (75% higher than that of pristine Fe₂O₃) at 1.23 V vs. RHE and a plateau photocurrent density of 3.2 mAcm⁻² at 1.8 V vs. RHE in 1M NaOH electrolyte solution (pH 13.6). Consequently, we established a simple method to passivate the surface defects of hematite photoanode for water splitting with a core-shell hematite (α -Fe₂O₃) nanorods system. Electrochemical impedance spectroscopy (EIS) characterization reveals passivation of the surface defects by the highly crystalline hematite shell layer, which enhances the charge injection. In pristine hematite, more holes are accumulated on the surface and the charge transfer to the electrolyte occurs through surface states, whereas in core-shell hematite photoanode, the majority of hole transfer process occurs through the valence band. As a result, the photoactivity of the core-shell nanorods: 1.2 mAcm⁻², at 1.23 V vs. RHE, is twice that of pristine hematite nanorods. After establishing the Mn doped and core-shell

hematite systems, we employed intensity modulated photocurrent spectroscopy (IMPS) to understand their charge dynamics for PEC water splitting. The information about the photogenerated holes transfer at the electrode/electrolyte interface for water oxidation and losses due to electron-hole recombination via surface states will help to understand the limiting factors in hematite photoanodes. We observed a two-fold increase in charge transfer rate upon Mn doping, and more than one order reduction in charge recombination rate in core-shell hematite as compared to the pristine hematite photoanode. These results indicate that both Mn doped and core shell hematite photoanodes enhance the PEC performance, although the reasons behind the enhancement are different. Single hematite photoanode even after modifications has remained elusive for overall unassisted water splitting due to stringent overpotential, photovoltage, electronic and thermodynamic requirements. A tandem cell, wherein the total photovoltage is generated by complementary optical absorption across different semiconducting electrodes, is a possible pathway to unassisted overall light induced water splitting. Here, we demonstrate a single solution processed organic-inorganic halide perovskite ($\text{CH}_3\text{NH}_3\text{PbI}_3$) solar cell in tandem with a core-shell/Mn doped Fe_2O_3 photoanode can achieve overall unassisted water splitting with a solar to hydrogen conversion efficiency of 2.4%. It was observed that the overall STH efficiency was limited by the hematite's onset potential and photocurrent. To understand these limitations, we have calculated the intrinsic solar to chemical conversion efficiency of the Fe_2O_3 photoanodes. The total photo-potential generated by our tandem system (1.87 V) exceeds both the thermodynamic and kinetic requirements (1.6V), for overall unassisted water splitting.

The work presented here focused on enhancing the performance of hematite based PEC device by bulk and surface modifications and also through coupling it with perovskite based PV to provide additional voltage. These implementations resulted in improved performance; however, the reported efficiency could be further improved. Based on the observed limitation in this work, I propose strategies for improving the efficiency of hematite.

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Abbreviations

PEC:	Photoelectrochemical Cell
FTO:	Fluorine Doped Tin Oxide
WE:	Working Electrode
RE:	Reference Electrode
CE:	Counter Electrode
RHE:	Reversible Hydrogen Electrode
Ec:	Conduction Band Edge of a Semiconductor
Ev:	Valence Band Edge of a Semiconductor
EIS:	Electrochemical Impedance Spectroscopy
XPS:	X-Ray Photoelectron Spectroscopy
FESEM:	Field Emission Scanning Electron Microscopy
HRTEM:	High Resolution Transmission Electron Microscopy
IPCE:	Incident Photon to Current Efficiency
APCE:	Absorb Photon to Current Efficiency
STH:	Solar to Hydrogen Conversion Efficiency
IMPS:	Intensity Modulated Photocurrent Spectroscopy
ISTC:	Intrinsic Solar To Chemical Conversion Efficiency
OER:	Oxygen Evolution Reaction
V _{OC} :	Open Circuit Voltage
J _{SC} :	Short Circuit Current
FF:	Fill Factor
J _{OP} :	Operating Current Density

Chapter 1

Introduction

In this chapter, the motivation behind the research on photoelectrochemical cells is described. The increasing demand for energy and the negative impacts of global warming across the globe is urging us to discover alternative renewables and ecofriendly solutions. Solar energy, which has the potential to meet the world's energy demand, will be highlighted in the thesis.

1.1 Energy Crisis and Climate Change

Rapid economic and demographic changes are continuing to increase the energy dependency on fossil fuels. The industrial revolution, great increase in urbanization and population are alarming factors for future energy crisis. The world population of ~ 7 billion people are consuming nearly 15 TW of power now, and the expected population will reach 8.7 billion by 2035,[1, 2] therefore the power need will get rise to 28 TW .[2, 3] Presently, more than 85% of our energy usage is coming from fossil fuels, i.e. oil, coal and natural gases.[2-4] However, these sources of energy are limited, and we are diminishing them rapidly. Power generation, transport and industrialization, are expected to account for a surge in share of fossil fuel (coal, gas and oil) consumption. [2-4] Here are the estimated duration to diminish the reserve fossil fuels, if their usage continues at the current rate; oil - 35 years, natural gas - 37 years and coal - 107 years.[5] Although, the usage is constantly changing, so the above numbers have to be corrected every year. Finally, these numbers are doubtable as uncertainty in the prediction of future demand and available energy sources. The developing countries are likely to consume more energy, especially with the rising energy demand. Apart from this, finite energy production from fossil fuels results in by-products of combustion, or harmful emissions. These emissions affect our environment and cause climate change. Fossil fuels continue to meet more than 80% of the total primary energy demand and over 90% of greenhouse gas emissions (CO_2), methane (CH_4) and nitrous oxide (N_2O).[2-4] Methane emissions originate from oil and gas extraction, whereas nitrous oxide emissions from energy transformation industry, transport and buildings.[4] The current atmospheric CO_2 level is more than 400 ppm which is the highest in comparison of past decades.[6, 7] The average annual rate of CO_2 emission has increased to 2.11 parts per million (ppm) for the last ten years (2005 - 2014), which is more than double the increase in the 1960s (Figure 1.1).[6] The CO_2 emission rate is ~35 GT per year which expected to increase. Although, the CO_2 concentration in the atmosphere is depends on the sources

and sinks of CO₂. This will have severe and irreversible impacts across the world. The international commitment to keep the increase in long-term average temperatures to below two degrees Celsius (2 °C), relative to pre-industrial levels, will require substantial and sustained reductions in global emissions.[8]

Figure 1.1. Trend of CO₂ level present in atmosphere.[6]

International energy agency (IEA) analysis has repeatedly shown that the cost and difficulty of mitigating greenhouse-gas emissions increases every year, and it is clear that the energy sector must play a critical role to reduce the greenhouse gas emissions. In recent years, progress has been made in developing cleaner, more efficient energy technologies.

As the energy generation and usage account for more than two thirds of the world's greenhouse gas emissions, a constraint need to apply on growth in oil and coal consumption while further boosting renewable energy sources. The energy context in which climate goals are being set is changing rapidly, as the cost and performance of many low carbon technologies improves and many countries start to look into the low carbon emission technologies. The strategy set out to keep the 2 °C climate goal within reach in the near-term, but goals beyond 2025 need to be strengthened in due course.[2, 3, 8] The awareness of climate change is getting more attention worldwide. Recently in December 2015, an international conference and energy summit on climate change held

in Paris, where more than 190 countries and 140 world leaders have participated.[8] In Paris energy summit, individual countries have signed an agreement to adopt a low carbon emission route, while transparency to enhance co-operation. In this serious scenario, we need to look in to renewables to address sustainable energy solutions.[8]

1.2 Possible Solutions for Sustainable Energy

Development of new technologies is necessary in order to meet energy demands without generating any greenhouse gases. Solar, wind, biomass, hydroelectric power, geothermal and hydrogen fuel cells are the key renewable energy sources (figure 1.2).[2, 9] Among all, wind and solar technologies have played a pivotal role in driving down costs and accomplishing large scale deployment. Solar energy has the potential to meet our energy demand, if we can harness it properly, because Sun provides 120,000 Terawatts of energy every day at the Earth's surface.[1] This energy far exceeds the consumption of global population i.e., 15 TW. It has been estimated that covering 0.16 % of earth's area with solar cells of 10% efficiency could meet around twice the required global energy consumption.[10] However, the challenge is to convert and store solar energy by efficient and cost effective methods on a large scale. In contrast, renewable energy resources, as the name implies, are constantly replenished naturally and will never be exhausted. Their use generally has a much lower environmental impact than that of conventional fuels.

Figure 1.2. Possible renewable energy sources data with years.[2]

Storing solar energy in the form of fuels have been proven advantageous and environment friendly.[9, 11-13] Hydrogen can be generated by splitting of water and used as an efficient fuel or converted to the electricity in fuel cells.[14-18] The production of hydrogen does not emit any greenhouse gases and requires only 237 kJ/mol of energy, which can easily be provided by solar energy.[19-24] Hydrogen has high gravimetric energy density, which is nearly three times the energy density of gasoline.[25] Hydrogen generation from photoelectrochemical (PEC) cell is a well-established route.[13, 21, 26-34] However, the main challenge is to improve the efficiency of PEC water splitting cells.[35-45]

1.3 Photoelectrochemical (PEC) Water Splitting

Photoelectrochemical (PEC) water splitting is inspired from the natural photosynthesis process in plants, where solar energy is captured and converted into hydrocarbons, glucose and oxygen.[11, 30, 46] In a PEC cell, water molecules are broken into hydrogen at the cathode and oxygen at the surface of a semiconductor photoanode. Photon absorption by semiconductor photoanode leads to the formation of charge carriers as electrons and holes in the conduction and valence bands respectively (Figure 1.3 (a) and Appendix A Figure A1).[12, 14, 18, 28, 47, 48, 49] When a semiconducting photo-electrode is immersed in an electrolyte solution, a charge transfer reaction occurs between the semiconducting electrode and the electrolyte until the equilibrium condition is achieved (Appendix A Figure A2). The upward band bending happens at the surface of electrode to bring the Fermi level of the semiconductor and the redox level of the electrolyte to the same position. Due to this, the concentration of electrons get depleted, this region is known as the depletion layer or the space charge layer.[18, 50, 51] A space charge layer results in an electric field, which is advantageous for the separation of photo-generated electron and hole pairs. Figure 1.3 (b) shows the energy levels of an isolated and submerged n-type semiconducting photo-electrode and the redox potentials of the redox species in the electrolyte. There has been a significant development to make an efficient device for hydrogen production by water splitting using PEC cells, although

there is a big gap between the achieved and theoretically predicted efficiencies of PEC cells.[35, 37, 39, 52] The overall water splitting reaction, water reduction and oxidation driven by photo-generated electron and holes are represented by the following reaction schematic;[12, 53-56]

The water splitting half reaction potentials reported in equation (b) and (c) are at pH 0 condition. The redox potential of water splitting half reactions are strongly pH dependent and the redox potential change per pH can be derived from the well-known Nernst equation.

Figure 1.3. (a) The isolated band diagram of the n-type semiconductor and the electrolyte, and (b) The equilibrated band diagram and the formation of space charge layer in n-type semiconductor when it is immersed in to the electrolyte.

1.4 Materials for PEC Water Splitting

It remains a challenge to find a material or a system as efficient as a natural leaf.[57, 58] In short, such materials must have good aqueous stability, appropriate band levels with respect to water redox levels, high absorption in visible range, good thermodynamic and chemical stability and good conductivity.[54, 59, 60] A material which can possess above all qualities is a holy grail of this field. Many semiconducting materials for solar water splitting have been discovered in past, but the position of conduction and valance band are not favorable for both water reduction and oxidation potential simultaneously.(Figure 1.4).[14, 53] Metal oxides are relevant for PEC water splitting, mainly due to their semiconducting properties, stability in aqueous solutions and reasonably low cost.[53, 54, 60] However, most of metal oxides have wide energy band gap and poor semiconducting properties in comparison with traditional III-V semiconductors and Silicon.[53, 60]

For large scale applications, a PEC device should cost less than US\$ 160 per m^2 with a STH efficiency of 10%.[61] To achieve this target, a PEC cell must be composed of abundant environment friendly materials combined with facile, cost-effective and scalable fabrication techniques to meet the high throughputs required of the PEC device. [21, 61-63]

Among all semiconductor oxides, TiO_2 has attracted much attention owing to its band levels, but high energy band gap and inefficient absorption of sunlight spectrum has limited its performance.[15, 64, 65] To tackle this problem, dyes, with high visible light absorption capability, were used quite frequently in devices like dye sensitized solar cell (DSSC).[41, 66-68] The photovoltage generated by DSSC is used to drive water splitting reaction, however this system was still not efficient in splitting water due to inadequate photovoltage, two reactor system i.e a solar cell integrated with electrolyzer cell, and inability to find suitable dyes.[44] Bismuth vanadate is another material explored for PEC water splitting. However, this has reached 90% of its theoretically predicted STH efficiency, but mainly suffering from the stability problem.[36, 43, 69-71]

Another material, InP which has a smaller band gap of ~ 1.3 eV could also not be used due to its poor aqueous stability as well as its cost.[72] Another inexpensive stable oxide, WO_3 has been recognized as a photoanode material that can be integrated with DSSC in a tandem device.[40, 42, 44, 70, 73-76] This system showed water splitting photocurrent density of $\sim 2.5 \text{ mAcm}^{-2}$ at 1.23 V vs RHE but exhibited low solar-to-hydrogen (STH) efficiency due to its large energy band gap, high kinetic losses and low stability.[44] There have been major developments in the preparation of oxynitride materials, which have an optimum energy band gap and can undergo both water oxidation and reduction but the reported quantum efficiency ($\sim 5\text{-}6\%$) is still low.[32, 77, 78] Out of all these candidates, the most promising photocurrent reported to date was achieved using Iron (III) oxide i.e. Fe_2O_3 or hematite.[37, 55, 56, 79-88] Iron (III) oxide shows largely favorable properties for water splitting. Although it has an unfavorable conduction band level to reduce water, yet it is most commonly used in photoelectrochemical cells that split water by application of an external bias.[55, 56] The conduction band minima position of hematite could be changed with an applied bias or by having a tandem configuration with a proper energy band gap material. In the following subsection, we will discuss about the establishment of iron oxide as a photoanode for solar water splitting.

Figure 1.4. The band edge positions of different photoelectrodes with water oxidation/reduction potential. Reprinted with the permission of Royal Society of Chemistry, copyright@2009. [53]

1.5 Hypothesis

Hematite is a promising photoanode material for PEC water splitting because of its abundance, stability, promising energy band gap and an appropriate valence band position with respect to water oxidation level. However, the performance of hematite is limited by short minority carrier diffusion length (5-10 nm), low carrier conductivity, slow water oxidation kinetics, and small photopotential.[33, 55] Hematite has an attractive optical band gap of ~ 2.0 eV, which provides a theoretical maximum solar to hydrogen (STH) conversion efficiency of 15%.[55] Although, the highest reported STH efficiency so far is only 2.4%.[37] Undoubtedly, there is a big room for improvement in order to achieve the highest performance from hematite. In practice, hematite requires high overpotential to initiate the water oxidation.[50, 51] We hypothesized several strategies to realize efficient PEC water splitting with hematite.

a. Hypothesis 1: Manganese doping will improve the carrier conductivity which in turn would enhance the PEC performance of hematite

Efficient transport of charge carriers in hematite is essential for water oxidation, which is limited by poor electrical conductivity.[55, 80, 83] It has been reported that the electrical conductivity can be improved by adding impurities to act as electronic dopants.[63, 83] We hypothesize that the manganese doping will improve the carrier conductivity of hematite because Mn^{4+} ions will be substituted in place of Fe^{3+} and create more electrons. In addition, manganese has multivalent oxidation states, good Oxygen evolution reaction (OER) properties and Mn^{4+} (67 pm) has a similar ionic radii with respect to Fe^{3+} (69 pm).[89-91]

b. Hypothesis 2: A highly crystalline thin overlayer of Fe_2O_3 on hydrothermally grown hematite nanorods would passivate the surface defects

Surface recombinations of holes with conduction band electrons or surface defects suppress the photocurrent in hematite photoanodes.[33, 51, 55] Surface coatings (overlayers) with high energy band gap metal oxides and

electrocatalysts have been demonstrated to passivate the surface recombinations or enhance the charge injection at the electrode/ electrolyte interface.[50, 55, 92] The surface states (dangling bonds) at the surface of hematite can easily trap the holes and reduced the performance of hematite. We have proposed a spray deposited highly crystalline thin overlayer of Fe_2O_3 on hydrothermally grown hematite nanorods to passivate these surface states and improve the charge transport at hematite electrode/electrolyte interface.

- c. **Hypothesis 3: Mn doped hematite sample could have a better hole transfer rate as compared to the pristine, whereas core-shell hematite would show a lower hole recombination rate than pristine hematite at the electrode/electrolyte interface**

The photo-generated holes in hematite photoanodes can either recombine with the electrons from the conduction band via surface states, or transfer to the electrolyte to oxidize water because of their slow oxygen evolution kinetics. Understanding of the dynamics of hole transfer and recombinations at electrode/electrolyte interface will provide further insights to tackle the limiting factors in hematite photoanodes. Our third hypothesis is to study the behavior of hole transfer and recombinations rate constants at Mn doped and core-shell hematite/electrolyte interfaces with the help of intensity modulated photocurrent spectroscopy (IMPS) would provide the better understanding of each modification for PEC water splitting.

- d. **Hypothesis 4: A tandem cell with core-shell/Mn doped hematite photoanode and a single perovskite solar cell would generate enough photovoltage to drive solar assisted water splitting**

Based on the free energy change required to split one molecule of H_2O to H_2 and $\frac{1}{2} \text{O}_2$ under standard conditions, 1.23 eV (237.2 kJ/mol) energy is required.[45, 55] However in practice, taking into account the kinetic barriers associated with oxygen and hydrogen evolution reactions, about 1.8 - 2.0 V of

solar generated photopotential is necessary to realize efficient water splitting.[36, 37, 44, 52] A single photoabsorber including hematite cannot generate this much photopotential, consequently multiple photoabsorbers with complimentary absorption spectrums need to connect in series for unassisted overall water splitting.[37, 44] We hypothesized that the required photopotential (1.8 -2.0 V) can be generated by fabricating a tandem cell with core-shell/Mn doped hematite photoanode ($E_g = 2.05$ eV) and a single perovskite solar cell ($E_g = 1.55$ eV) in series.

1.6 Thesis Objective and Scope

The objective of this thesis is to investigate the effect of doping and surface modification on hematite photoanode and to study the charge dynamics of these materials in PEC cells for water oxidation. To fulfill the objective, the scope of the thesis is as follows:

a. Investigation of the role of Manganese doping in hematite nanorods

photoanode

Pristine and Mn doped hematite photoanodes have been fabricated through a cost effective and environment friendly solution processed hydrothermal method. The effect of Mn doping in hematite nanorods has been analyzed through a series of structural, photoelectrochemical and opto-electrical measurements. Mn doping in hematite is found to improve the charge carrier concentration, which is one of the main constraint of hematite photoanodes. The transient, electrochemical impedance spectroscopy, and intensity modulated photocurrent spectroscopy (IMPS) measurements have been carried out to study the effect of manganese doping in bulk and surface of hematite.

b. Introduction of a Core-shell structured hematite photoanode for efficient charge transport at the electrode/electrolyte interface

Surface recombinations are the main limiting factors in photoelectrodes for water splitting cells; those can easily be identified from their high transient behavior in chopped photocurrent-voltage measurements. This limitation can be overcome by depositing an oxygen evolution catalyst or wide energy band gap metal oxide on the surface of hematite. Here, we discovered an inexpensive

method to passivate surface defects by spraying a highly crystalline layer of hematite onto the pristine hydrothermally-grown hematite nanorods, thus combining the nanostructuring effect with the surface passivation. Core-shell hematite photoanodes studied by electrochemical impedance spectroscopy (EIS) to elucidate the role of shell layer and the observed enhancement in the PEC performance. TEM study confirmed that the main reason underlying the different charge dynamics is the improved crystallinity due to the shell deposition. In order to understand the charge dynamics at the electrode/electrolyte interface, IMPS measurements have been performed. Whereas, these IMPS results again support the EIS study.

c. Investigation on the dynamics of hole transfer and recombination at hematite/electrolyte interface

Better understanding of the kinetics at photoelectrode/electrolyte interface is necessary to develop the best photoelectrodes. Efficient hole transfer at electrode/electrolyte interface is the main bottleneck in hematite photoanodes. Here, we study the surface carrier dynamics of pristine, Mn doped and core-shell hematite photoanodes with the help of intensity modulated photocurrent spectroscopy (IMPS). The IMPS study revealed the role of Mn doping and core-shell structure, Mn doping results in a three-fold increase in the hole transfer rate constant, whereas the core-shell architecture does not affect the hole transfer rate constant; it instead reduces the surface recombination rate constant by a factor of ~5.

d. Demonstration of a hematite-perovskite cell for overall unassisted water splitting

We have synthesized high performing core-shell/Mn doped hematite nanorods sample via hydrothermal and spray pyrolysis techniques and then photoelectrodeposited an OER CoPi catalyst on it to improve the onset potential. A systematic opto-electrical and photoelectrochemical analysis have been conducted and found that hematite photoanode generates insufficient photovoltage for unassisted water splitting. In order to achieve unassisted water splitting, we have utilized a solution processed perovskite solar cell in series

with hematite photoanode. This tandem system generates sufficient photovoltage to achieve overall unassisted water splitting. Systematic PEC, UV-vis, and transient measurements have been conducted to find out the limiting factors of tandem system.

1.7 Thesis Organization

The thesis consists of 7 chapters. Chapter 1 introduces the motivation of solar water splitting i.e., the energy crisis and global warming. This chapter presents the basics of photoelectrochemical (PEC) water splitting and background of the potential as photoanodes materials for PEC water splitting followed by the objective and scope of thesis.

Chapter 2 shows the literature review of Hematite (Fe_2O_3) as a photoanode for PEC water splitting. This chapter shows the different possible solutions for tackling the various limitations in hematite photoanode and concludes with a tandem cell approach for overall unassisted water splitting cell.

Chapter 3 exhibits the methodology and preparation of hematite photoanodes by using various techniques like hydrothermal and spray pyrolysis. This chapter also discusses the co-catalyst loading (CoPi) on the surface of hematite photoanode by photo-electro deposition method. Finally, it demonstrates the details of material characterization including photoelectrochemical characterization to observe the performance of hematite photoanode.

Chapter 4 presents the results of pristine and Mn doped hematite photoanodes for solar water splitting. This chapter discusses the role of Mn doping in hematite photoanode and possible aspects of improvement in PEC performance. Finally, electrochemical impedance spectroscopy has been used to calculate the carrier concentration in pristine and Mn doped hematite photoanodes.

Chapter 5 exhibits core-shell Fe_2O_3 nanorods for efficient PEC water splitting. This chapter discusses the role of shell layer for PEC water splitting via electrochemical impedance spectroscopy in dark and under 1 Sun illumination. A hole scavenger (H_2O_2) has been employed to estimate the surface catalyst and charge injection efficiencies. Finally, we conclude in this chapter that the

Fe₂O₃ shell layer on Fe₂O₃ nanorods partially passivates the surface states and improves the PEC performance.

Chapter 6 employs an intensity modulated photocurrent spectroscopy (IMPS) technique to understand the performance of pristine, Mn doped and core-shell hematite photoanodes for water oxidation. IMPS analysis shows that the Mn doping improves the rate of hole transfer by nearly two times than pristine hematite, while core-shell hematite demonstrates a reduction in charge recombination rate at the electrode/electrolyte interface.

Chapter 7 displays a perovskite-hematite tandem cell approach for unassisted overall water splitting. This chapter discusses the overall photovoltage requirement for unassisted water splitting and solar to hydrogen conversion (STH) efficiency deliver by our perovskite-hematite tandem cell.

Chapter 8 concludes the beneficial effect of manganese doping and core-shell structure with a bias free tandem cell for solar water splitting. This chapter also recommends the future directions to work on hematite photoanodes for photoelectrochemical water splitting.

1.8 Thesis Contribution

The original contributions of thesis are as follows:

1. The role of manganese doping in hematite photoanode is studied for PEC cell. The manganese doping is found *for the first time* to improve the PEC performance more than two times as compared to pristine hematite photoanode. The Mn doping improve the bulk conductivity of hematite and also enhance the hole injection rate at electrode/electrolyte interface.
2. A high quality core-shell hematite photoanode for PEC water splitting is demonstrated for the first time. A systematic EIS study reveals the impact of Fe₂O₃ shell layer on Fe₂O₃ nanorods in minimizing surface recombination, which is the main limiting factor in pristine hematite photoanodes.
3. A comprehensive intensity modulated photocurrent spectroscopy (IMPS) study revealed the reason for the improvement in the performance of Mn doped and core-shell hematite photoanodes to the pristine ones. The Mn doping

enhance the hole transfer rate constant, while core-shell structure reduce the charge recombination rate at the hematite/electrolyte interface.

4. A successful demonstration of the state-of-the-art tandem cell for overall unassisted water splitting based on Fe_2O_3 photoanode and single solution processed organic-inorganic halide perovskite ($\text{CH}_3\text{NH}_3\text{PbI}_3$) solar cell. For the first time, we have reported the highest STH efficiency based on single junction solar cell and hematite photoanode i.e., 2.4%

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Chapter 2.

Literature Review

This chapter presents various characteristics of hematite photoanodes for solar water splitting. I will discuss the advantage and disadvantage of hematite as a photoanode for solar water splitting followed by different approach to address the well described limitations of hematite. Section 2.1 covers the crystal structure, advantages and limitations of hematite as one of the most appropriate candidates for PEC water splitting. The main limitations of hematite photoanodes are poor charge carrier conductivity, low minority carrier diffusion length, high absorption depth, slow OER kinetics and surface recombinations. Section 2.1.1 shows the crystal structure of hematite. Section 2.1.2 suggests the different nanostructuring methods to resolve the minority carrier diffusion length and high absorption depth issues. Section 2.1.3 exhibits the different elemental doping strategies of tackling the poor carrier conductivity. Section 2.1.4 and 2.1.5 display the different possible solution of surface treatments by wide band gap metal oxides or co-catalysts to passivate the surface defects or enhance the reaction rate. Section 2.2 introduces a tandem approach to efficiently utilize the solar spectrum by employing more than one absorber in series and generate enough photovoltage for unassisted overall water splitting. Whereas section 2.3 describes different efficiencies of photoelectrodes and PEC water splitting cell.

2.1 Hematite as a Photoanode for PEC Water Splitting

Hematite, a form of iron ore is the fourth most abundant element in earth's crust (6.3 % by weight).[1, 2] It is a low cost, nontoxic and stable material in aqueous solution which makes it a promising photocatalyst for solar water splitting.[3-5] Gratzel's team demonstrated Fe_2O_3 for solar water oxidation with an external applied bias.[6-10] Fe_2O_3 is a n-type semiconductor, with a band gap of 2.0 - 2.2 eV that covers a wide range of solar spectrum absorption and has an appropriate valence band for water oxidation.[11, 12] One major drawback of Fe_2O_3 is the tradeoff between its low minority carrier diffusion length (2-10 nm) and high absorption depth.[13-15] To ensure optimum light absorption, ~120 nm thick Fe_2O_3 (at wavelength 550 nm) is needed at the expense of charge recombinations, which reduces the overall charge transport efficiency.[16] Figure 2.1 shows the typical J-V curve of a hematite photoanode.[17] A good photoanode should have a high plateau current and a low onset potential.. It has been discussed that to increase the plateau current, advancements in nanostructures and doping are required, while to lower down the onset potential, the surface properties of semiconducting active layer needs to be improved.[17] This could be done by employing a co-catalysts on the surface of the photoanode.[9, 17] In recent times, there has been tremendous advancement in the morphologies of hematite thin films to improve yield of photoelectrochemical efficiencies.[11, 18, 19] Different nanostructures (nanorods, dendritic nanowires, cauliflower-type, nanoflowers etc.,) of hematite photoanodes have been reported by various groups.[18, 20-26] Xi et al utilized hydrothermally grown Sn doped hematite nanorods and reported enhanced photocurrent density from 1.24 mAcm^{-2} of pristine hematite to 2.25 mAcm^{-2} of doped hematite.[21] Recently, the high photocurrent of 4.5 mAcm^{-2} for CoPi treated Pt doped hematite wormlike structures have been reported.[24] There has been good progress in the hematite performance over past decades, however the reported performance is still far off from the theoretically predicted values. In the next section, a brief overview of the crystal structures of Fe_2O_3 and its optoelectronic properties are presented.

Figure 2.1. Theoretically predicted performance for hematite photoanode (blue) compared with present hematite photoanode (black); possible parameters in enhancing the performance marked with arrows.

2.1.1 Crystal Structure

Hematite is the most common form of crystalline iron oxide and utmost thermodynamically stable form of iron oxide in ambient environments.[1] The iron and oxygen atoms in hematite organize in a corundum structure, which is trigonal-hexagonal, with space group $R\bar{3}c$, lattice parameters $a = 5.0356 \text{ \AA}$, $c = 13.7489 \text{ \AA}$, and six formula units per unit cell.[27-29] The Fe^{3+} cations occupy the octahedral interstices in the (001) basal planes and O^{2-} anions are accommodated in a hexagonal closed packed lattice along the [001] direction (Figure 2.2).[27, 30, 31]

Figure 2.2 (a). The unit cell of hematite and **(b)** The FeO₆ octahedral face-sharing along the c direction.

2.1.2 Nanostructuring

There has been much improvement in surface morphologies of hematite thin films by introducing different nanostructures to improve the charge dynamics.[7, 18, 32-35] The best performing cauliflower-type nanostructured hematite photoanode was synthesized by APCVD,[10] while others by solution growth techniques (hydrothermal[11, 18], spray pyrolysis[36], electrodeposition[26, 37] and template assisted synthesis[38, 39]) are also studied widely. Kay et al showed cauliflower type of nanostructures, which decreased recombination effects drastically owing to its smaller feature size.[40] Earlier, ALD grown ultra-thin films of Fe₂O₃ on TiS₂ nanonets was

shown with an enhanced performance in terms of photocurrent and efficiency.[41] Sn-doped hematite nanostructures were also synthesized by hydrothermal treatment and was claimed to enhance carrier density and hence, appreciable photocurrent density of 1.86 mAcm^{-2} was achieved at 1.23V vs RHE.[42] A major development in increasing the surface area and efficiency of hematite for light induced water splitting, was introduced by inexpensive solution based hydrothermally prepared Fe_2O_3 nanorods.[11, 18, 43] Due to its perpendicular alignment with respect to FTO substrate and high surface area, Fe_2O_3 nanorods yielded a good photocurrent with excellent photoelectrochemical efficiency.[33, 44] Hematite nanorod arrays allow higher conductivity along [110] direction and the small diameter of nanorods allow the holes to reach electrolyte for water oxidation before being neutralized by recombination.[22] This has taken the photocurrent values to another level reaching 0.72 mAcm^{-2} pristine and 1.6 mAcm^{-2} in Mn doped photoanodes[18] and as high as 4.3 mAcm^{-2} for CoPi/ SnO_x treated hematite nanorods.[Under Consideration]

2.1.3 Elemental Doping strategies

Low electrical conductivity of hematite photoanodes again limit its PEC performance.[9] The process of doping is well established and has been proven to be beneficial to many semiconductor systems in enhancing the bulk carrier concentration and hence the conductivity.[45-48] Pure hematite has very low electrical conductivity ($10\text{-}14 \text{ }\Omega^{-1}\text{cm}^{-1}$),[49-52] electron concentration of 10^{18} cm^{-3} and electron mobility of $10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. [49, 53] Since the conductivity of a material is given by $\sigma = ne\mu_e + pe\mu_p$, increasing carrier concentration (i.e. n or p) by doping, is often used to compensate for the low electron (μ_e) and hole mobilities (μ_p). Hematite is an n-type semiconductor due to naturally occurring oxygen vacancies in the bulk. When divalent dopants, such as Mg, Cu and Ni, replace the Fe^{3+} cations in the lattice, hole carriers are formed and hematite becomes p-type.[51, 54-56] When tetravalent dopants, such as Ti, Zr, Sn, Mn and Si, replace Fe^{3+} , extra electrons will be generated and hematite will remain as n-type with increased electron concentration.[7, 16, 18, 42, 55, 57-60]

The photoactivity in hematite nanorods was improved by Sn^{4+} doping and the carrier concentration was found to increase from 7×10^{19} to $2.45 \times 10^{20} \text{ cm}^{-3}$. [21] These Sn^{4+} ions either diffused into the Fe_2O_3 nanostructures from the FTO substrate during high temperature annealing, or was added intentionally. [19, 42] Gratzel et al reported Si doped hematite cauliflower with high donor density of 10^{20} cm^{-3} , which could play a major role in the enhancement of PEC performance. [16]

The donor concentrations of the pure and Ti doped Fe_2O_3 thin films were calculated by Mott–Schottky plot as $2.0 \times 10^{19} \text{ cm}^{-3}$ and $1.2 \times 10^{20} \text{ cm}^{-3}$, respectively. [61] Ti doped hematite nanostructures show an urchin-like morphology, which enhanced the effective surface area compared to undoped nanostructures. [62] A remarkable plateau photocurrent density value of 3.76 mAcm^{-2} was observed for Ti doped nanostructures under AM 1.5G in 1M NaOH electrolyte, which is 2.5 times higher than that for undoped nanostructures (1.48 mAcm^{-2}). [62]

A theoretical study on Cu and Ti doped hematite was done by Meng et al. [55] They showed that the conduction band maxima (CBM) of Cu doped hematite crossed the hydrogen production level by first principle calculations density function theory (DFT) method, and thus the oxygen and hydrogen productions all lie between the region of VBM and CBM. [55] They proposed that the Cu doped hematite could yield the production of hydrogen spontaneously under visible light irradiation without voltage bias. Electronic conductivity was improved after Ti doping in hematite as the Ti dopant created shallow donor levels, which changed the band gap slightly, and encouraged Fermi level to enter into the conduction band of hematite. [55]

Platinum and CoPi surface treated hematite photoanode illustrated a stable and record breaking performance of 4.32 mAcm^{-2} photo current at 1.23 V vs. RHE under simulated 1 sun (100 mWcm^{-2}). [24] The hematite nanorods formed by two step annealing process at 550°C and 800°C , had a unique “wormlike” morphology. Platinum doping was used to improve the charge transfer characteristics in the bulk of hematite and an oxygen evolution co-catalyst

(CoPi) on the surface of hematite. Platinum doping resulted in an improvement in the electrical conductivity of hematite by increasing its donor density $3.27 \times 10^{17} \text{ cm}^{-3}$, $2.77 \times 10^{18} \text{ cm}^{-3}$, and $3.91 \times 10^{18} \text{ cm}^{-3}$ for bare Fe_2O_3 , Pt doped Fe_2O_3 , and Pt doped $\text{Fe}_2\text{O}_3/\text{CoPi}$, respectively.[24] Also, the efficacy with which doping could be achieved through solution processing is questionable as it can be seen from literature that hematite required high temperature post annealing (750-800°C) to allow diffusion of Sn from FTO to the hematite lattice even after elemental doping through solution processed methods.[21, 58, 62, 63] However, intentionally tin doping is also found useful by reducing the annealing temperature and enhancing conductivity of hematite photoanode.[42] The table 1 below shows the differently doped hematite photoanode reported with their performance. Charge carrier recombination is the main loss mechanism in the photoelectrodes. Photogenerated charge carriers recombine through radiative and non-radiative processes in the bulk of semiconductors, in the depletion region, and at defects on the surface of photoelectrodes (Figure 2.3). These recombination processes reduce the rates of water splitting. Surface and interfacial recombination rates can be reduced due to their larger specific surface area by nanostructuring.[64-66] Surface treatment with co-catalysts is also an alternative way to reduce the charge recombination at electrode/electrolyte interface.[22, 23]

2.1.4 Surface treatment

Another important drawback of hematite is the need of over-potential which is attributed to: i) the position of the conduction band of hematite, which is 0.4 - 0.5V too positive to allow water reduction to hydrogen and ii) the sluggish hole transport at the semiconductor/water interface.[9, 80, 81]

The sluggish hole transport can be improved by surface treatment of wide band gap metal oxides, which either causes surface passivation or acts as co-catalysts.[82] These two phenomena have fundamentally different mechanism in assisting hole transport. Surface passivation implies passivation of the hematite surface defects, which reduces the recombination of holes at the hematite surface, while co-catalysts implies the oxidation of the metallic

element within the catalysts, which enhances the rate of hole transport from hematite to the electrolyte.[82, 83] It should be noted that the mechanism of surface treatment by using cobalt, iridium, and iron-nickel based materials is still a topic of debate, because there is no conclusive experimental evidence which can clearly determine whether they act as surface passivation or co-catalysts.[66, 84, 85]

Figure 2.3. Charge recombination and transfer pathways for photoexcited carriers in a semiconductor/electrolyte system.

Table 2.1. Hematite photoanodes doped with different elements and their PEC performance.

Dopant	Photocurrent Density (mAcm ⁻²)	Potential vs. RHE	Electrolyte	References
Mn	1.60	1.23	1M NaOH	[18]
Sn	1.86	1.23	1M NaOH	[42]
Sn	1.63	1.40	1M NaOH	[67]
Sn	1.60	1.60	1M NaOH	[68]
Sn	2.25	1.23	1M NaOH	[21]
Sn	3.10	1.23	1M NaOH	[U.C.]
Si	2.30	1.4	1M NaOH	[16]
Si	2.40	1.23	1M NaOH	[69]
Si	2.20	1.23	1M NaOH	[40]
Si	1.45	1.23	1M NaOH	[70]
Pt	1.43	1.42	1M NaOH	[24]
Ti	1.20	1.60	1M NaOH	[71]
Ti	1.64	1.23	1M NaOH	[72]
Ti	1.91	1.23	1M NaOH	[73]
Ti	2.28	1.23	1M NaOH	[74]
Zr	2.10	1.66	1M NaOH	[75]
Mo	1.50	1.32	1M NaOH	[37]
Al	1.10	1.32	1M NaOH	[76]
Nb	0.65	1.56	1M NaOH	[12]
Ta	0.45	1.6	0.5M Na ₂ SO ₄	[77]
Cu	0.07	1.66	1M NaOH	[55]
Cr	0.70	1.32	1M NaOH	[78]
Ni	1.50	1.67	1M NaOH	[79]
Mg	0.45	1.23	1M NaOH	[54]

*U.C. – Under Consideration

A few surface passivation strategies such as CoF_3 , [86] Al_2O_3 , [82] Ga_2O_3 , [87] NiO_x , [88, 89] and SnO_x [21] have been reported so far. Hu et al showed the flat band shift in Ti doped iron oxide thin films after surface modification with CoF_3 aqueous solution for improved PEC performance. [86] The photogenerated electrons, due to this flat band shift, were able to reduce protons and generate hydrogen without any applied bias, emphasizing the importance of surface modification in shifting band level positioning. Formal et al were able to reduce overpotential by 100 mV by using an ultra-thin coating of Al_2O_3 deposited by Atomic Layer Deposition technique on hematite photoanodes. [82] This alumina overlayer enhanced photocurrent to a record value of 0.42 mAcm^{-2} at 0.9 V vs RHE. Through electrochemical and optical spectroscopy, its role was confirmed as the surface passivation layer reduced surface recombination due to high density of traps present on nanostructured hematite. [82] Hisatomi et al showed a negative shift of 200mV in overpotential using Al_2O_3 and Ga_2O_3 overlayers. [87]

2.1.5 Photoanode/co-catalyst systems

In the previous section, we discussed about advancements and progress in tackling surface recombination with the addition of surface overlayers of oxides. A common pattern among all the reported surface overlayers strategies can be perceived as the recombination is reduced because of either release in lattice strain or due to passivation of surface defects. But there are some materials, which can act as catalysts to improve charge transfer kinetics. These materials have been used to reduce the overpotential of hematite by some extent.

Various oxygen evolution catalysts like CoPi , [90-92] IrO_2 , [66] CoO_x [84] and FeNiO_x [88] etc. have also been used with hematite photoanodes because of their fast kinetics exhibit better charge transfer for water oxidation. A co-catalyst at the photoelectrode/electrolyte interface act as a mediator to ease hole transfer from surface owing to its less kinetic barrier and then could oxidize water which eventually decreases the overpotential. [91] Tilley et al showed surface modification of nanostructured hematite photoanode by IrO_2

nanoparticles, which resulted in an overpotential shift of 0.2 V and a photocurrent as high as 3.75 mAcm^{-2} . [66] One of the best co-catalyst in terms of overpotential, IrO_2 nanoparticles on the surface catalyzed the photogenerated hole transfer to lower down the overpotential of hematite. Nocera et al reported cobalt-phosphate (CoPi), a novel oxygen evolving catalyst, (CoPi OEC) which can be deposited and coupled with a photoanode by electrodeposition. [83, 92] Since the development of CoPi, it has gained a lot of interest because of a low overpotential of only 0.41 V required to oxidize water at pH=7 with a current density of 1 mAcm^{-2} . [92] Zhong et al reported a 350 mV cathodic shift in overpotential for CoPi/ $\alpha\text{-Fe}_2\text{O}_3$ composite photoanode. [90] McDonald et al showed photochemically deposited CoPi OEC on electrodeposited iron oxide films. [96] These results demonstrated an enhancement in photocurrent, which implied an improvement in O_2 evolution kinetics as well. Recently, Carlos et al has demonstrated a transparent FeNiO_x co-catalyst loaded hematite for tandem overall unassisted water splitting with a nearly 250 mV cathodic shift in onset potential. [88] Table 2.2 below shows the different overlayers and co-catalysts employed with hematite for solar water splitting.

Table 2.2. Hematite photoanode with various surface co-catalysts/overlayers for water oxidation.

Surface Overlayer/ Co-catalyst	Photocurrent Density (mAcm^{-2})	Potential vs. RHE	Cathodic Shift in Onset Potential	Electrolyte	References
Al_2O_3	2.3	1.23	100 mV	1M NaOH	[82]
TiO_2	1.2	1.23	190 mV	1M NaOH	[93]
SnO_x	2.25	1.23	62 mV	1M NaOH	[21]
ZnO	1.08	1.23	170 mV	1M NaOH	[94]
Ga_2O_3	0.25	1.02	200 mV	1M NaOH	[87]
Co_3O_4	1.20	1.23	40 mV	1M NaOH	[22]
CoO_x	0.45	1.23	100 mV	0.1M NaOH	[84]
CoF_3	0.15	1.00	200 mV	1M NaOH	[86]
CoPi	0.3	1.23	230 mV	0.1M KPi	[91]
CoPi	3.1	1.23	200 mV	1M NaOH	[11]
CoPi	2.8	1.23	170 mV	1M NaOH	[90]
IrO_2	3.0	1.23	200 mV	1M NaOH	[66]
$\text{Ni(OH)}_2/\text{IrO}_2$ Conjugated	1.6	1.23	200 mV	1M NaOH	[95]
FeNiO_x	2.75	1.23	200 mV	1M KOH	[88]
$\text{Ni}_x\text{Fe}_{2-x}\text{O}_3$	1.0	1.23	60 mV	1M KOH	[79]
NiFeO_x	1.2	1.23	550 mV	0.5M Phosphate Buffer	[85]

2.2 Tandem Cell

Semiconducting photoelectrodes have received much attention for solar water splitting.[97, 98] As discussed above, a single photoelectrode is not efficient for overall, unassisted water due to both the thermodynamic requirements of the reaction and the overpotentials. The multiple light absorber tandem PEC systems (photoanode-photocathode, PEC-PV, and PV-EC tandem) can easily harvest a significant portion of the solar spectrum and generate enough voltage to overcome the overpotential and thermodynamical potential for water splitting (Appendix A Figure A3). However, a tandem cell configuration (PEC-PV), wherein the total photovoltage is produced by complementary optical absorption by two or more photoabsorbers connected in series to split water efficiently.[6, 11, 99-105] Still, the photovoltage outputs of the sub-cells are crucial, especially the photovoltage generated by traditional solar cells i.e., silicon, CIGS and DSSC is not enough to drive water splitting reaction.[106-108] In this context, the relatively large open circuit voltages of the halide perovskites have made them attractive candidates as the photovoltaic components of solar fuel devices.[109-115]

Figure 2.4. Reported solar to hydrogen conversion efficiency (STH) with years and arranged by number of absorbers. The references of these reports can be seen in above text.

Tandem approaches for solar to hydrogen conversion have been reviewed recently.[102, 104, 116-118] There are a number of demonstrations of overall water splitting tandem cell with decent solar to hydrogen conversion efficiency reported from different groups (Figure 2.4).[11, 100, 102-105, 107, 108, 118-125]

2.3 Efficiencies of Solar Water Splitting

Herein, we show the various efficiency values those explain the PEC performance of different materials and PEC cell. PEC materials characterization and efficiency protocols are necessary to adopt in a way that allows for direct comparison. There are four standard efficiencies, which facilitate the performance of standard photoelectrodes as solar to hydrogen conversion efficiency (STH), applied bias to current efficiency (ABPE), incident photon-to-current efficiency (IPCE), and absorbed photon-to-current efficiency (APCE).[126-128]

2.3.1 Solar to hydrogen conversion efficiency (STH)

STH efficiency is the most important water splitting efficiency because it gives the overall efficiency of a PEC water splitting cell without any additional bias between the working electrode and counter electrode under 1 Sun illumination. Most importantly, the working electrode and counter electrode should be short circuited (2 electrode system) and immersed in the same pH solution. Moreover, electrolyte solution should not contain any sacrificial reagents because the redox reactions will no longer reproduce the accurate water splitting. STH efficiency is defined as incident solar energy converted into chemical energy and explained as below;[126, 128]

$$\eta_{STH} = \left(\frac{J_{sc} \times 1.23 \times \eta_F}{P_{Solar}} \right) \quad (2.1)$$

Where J_{sc} is the short-circuit current density (mAcm^{-2}), 1.23 eV is the energy equivalent of Gibbs free energy for water disassociation, η_F is the Faradaic efficiency and P_{Solar} is the irradiance intensity of 100 mWcm^{-2} (AM1.5G).

2.3.2 Applied bias to current conversion efficiency (ABPE)

A bias between the working and counter electrodes under illumination provide the information for material development. The ABPE is explained as below;[126, 128]

$$\eta = I_{ph} \left(\frac{1.23 - V}{P_{Solar}} \right) \quad (2.2)$$

where V is the applied Voltage vs. RHE, I_{ph} is the photocurrent density at the particular voltage, and P_{Solar} is the irradiance intensity of 100 mWcm⁻² (AM1.5G). If applied bias is equivalent or exceeded the thermodynamic water splitting potential (1.23 V) than this efficiency is questionable. However, this efficiency describes the early onset potential of a material before the thermodynamic water splitting potential. This efficiency should also be measured in a two-electrode configuration. However, most of the reports shows ABPE measured in a three electrode configuration, where a bias is applied versus a reference electrode and not with the counter electrode. It results in a half reaction measurement and not a complete device measurement because a bias versus a reference electrode excludes the second half reaction occurring at the counter electrode.

2.3.3 Incident photon-to-current conversion efficiency (IPCE)

The IPCE is the most powerful analytical efficiency for a PEC cell as it illustrates the photocurrent generated per incident photon as a function of illumination wavelength. One can estimate the photocurrent by integration of IPCE data over the solar spectrum. STH efficiency could be easily calculated by measuring the IPCE in a two electrode configuration with zero applied bias. IPCE accounts for three fundamental processes: electron-hole pair generation per incident photon absorption, charge separation, and interfacial charge transfer.[126]

$$IPCE = EQE = \eta_{(e^- - h^+)} + \eta_{separation} + \eta_{transport} \quad (2.3)$$

The IPCE calculated, corresponds to the ratio of the photocurrent with the rate of incident photons as a function of wavelength;[126, 127]

$$\text{IPCE (\%)} = \left(\frac{1240 \times I_{\text{ph}}}{\lambda \times J_{\text{Light}}} \right) \times 100 \quad (2.4)$$

where 1240 (V nm) represents a multiplication of h (Planck's constant) and c (the speed of light), I_{ph} (mAcm^{-2}) is the measured photocurrent density at a particular wavelength, λ (nm) is the wavelength of incident light, and J_{Light} (mWcm^{-2}) is the measured irradiance at a specific wavelength.

2.3.4 Absorbed photon-to-current efficiency (APCE)

In IPCE measurement, we assume that all the incident photon are absorbed and the reflected and transmitted losses are not taken into account. To understand the intrinsic performance of a material, it is necessary to subtract these optical losses and measure the efficiency only corresponding to the absorbed photons. The APCE can be calculated from IPCE by dividing the absorptance of the material as shown below;[18, 126]

$$\text{APCE (\%)} = \left(\frac{1240 \times I_{\text{ph}}}{\lambda \times J_{\text{Light}} \times 1 - 10^{-A}} \right) \times 100 \quad (2.5)$$

where 1240 (V nm) represents a multiplication of h (Planck's constant) and c (the speed of light), I_{ph} (mAcm^{-2}) is the measured photocurrent density at a particular wavelength, λ (nm) is the wavelength of incident light, and J_{light} (mWcm^{-2}) is the measured irradiance at a specific wavelength.

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Chapter 3

Experimental procedures and Characterization

This chapter discusses step by step processes for fabrication of nanostructured photoanode and solar cell for photoelectrochemical (PEC) water splitting. It will explain the various synthesis methods, those utilized to fabricate pristine, Mn doped, core-shell hematite nanorods and synthesis route of perovskite solar cell. We have synthesized pristine, Mn doped, core-shell and core-shell/Mn doped hematite nanorods samples via an environmental friendly and economically viable solution processed hydrothermal and spray pyrolysis methods. Hydrothermal synthesis method has the potential to fabricate different nanostructure and ease to tune the size and morphology of nanomaterials. An oxygen evolution catalyst CoPi has been photoelectrodeposited on hematite nanorods samples to further improve their PEC performance. We have also fabricated perovskite solar cell via a solution processed spin coating method, which is again economically viable simple method. Finally we have described different characterization tools to understand the performance of our photoanodes and solar cell separately and in tandem configuration.

** Published subsequently as Gurudayal et al., [1-3]*

3.1 Preparation of clean FTO Substrates

Most of the chemicals, from Sigma Aldrich (unless specified), were used without any modification. Transparent fluorine doped tin oxide (FTO) substrates, (Nippon Sheet Glass Co Ltd, 400 nm thick FTO on 2.2 mm glass substrate with 14 Ohm/square), were used as the base electrode for thin film fabrication. Before depositing thin films, the FTO substrates were ultrasonically cleaned thoroughly with soap solution, DI water, ethanol and eventually with isopropanol. They were subsequently dried using a stream of N₂.

3.2 Hydrothermal Synthesis of Pristine and Mn Doped Hematite

Nanorods

The pristine and Mn treated hematite nanorod arrays were grown on a fluorine treated tin oxide (FTO, Nippon Sheet Glass Co Ltd, 14 ohm/sq, 1×2.5 cm) substrate. FTO coated glass substrates were cleaned by the above explained procedure. In brief, a 10 mL aqueous solution containing 1.5 mmol FeCl₃•6H₂O (Sigma-Aldrich) and 1.5 mmol urea (Sigma-Aldrich) was transferred into a 20 mL Teflon lined autoclave and the substrates were placed with FTO side facing the wall of the autoclave at an angle. The Mn treated hematite nanorods were prepared in a similar method as the pristine hematite with 1 %, 2 %, 5% and 10 % (by mole percent) of MnCl₂•4H₂O (Sigma-Aldrich) added to the precursor solutions. After 10 hrs of reaction at 100 °C, a uniform layer of FeOOH film was formed on the FTO substrate. The substrates were thoroughly rinsed with DI water and annealed at 550 °C for 2 hrs to convert FeOOH to Fe₂O₃ nanorods. For photoelectrochemical (PEC) measurements, these samples were further annealed at 750 °C for 20 min.[1]

Figure 3.1 Schematics of synthesis of Fe₂O₃ nanorods by hydrothermal technique.

3.3 Hydro-Spray Synthesis of Core-Shell Hematite Nanorods

The pristine and core-shell hematite nanorod arrays were grown on fluorine doped tin oxide (FTO, Nippon Sheet Glass Co Ltd, 14 ohm/sq, 1×2.5 cm) substrate. The hematite nanorods were prepared by a procedure modified from our previous method. The core-shell hematite nanorods were synthesized by two step process. Firstly, we have used a 10 mL aqueous solution containing 1.5 mmol FeCl₃•6H₂O (Sigma-Aldrich) and 1.5 mmol NH₂CONH₂ (Sigma-Aldrich) was transferred into a 23 mL teflon lined autoclave and the substrates were placed with FTO side facing the wall of the autoclave at an angle of about 45 degrees. After 6 hrs of hydrothermal reaction at 100 °C, uniform FeOOH nanorods were formed on the FTO substrate. The FeOOH coated FTO substrates were thoroughly rinsed with DI water. Secondly, a 0.1 M Fe(AcAc)₃ precursor in absolute ethanol was sprayed on to the cleaned FeOOH nanorods with 4 cycles (15 sec on-off) on hot plate at 525°C for core-shell sample and finally annealed at 550 °C for 2 hrs to convert FeOOH to a hematite film. For photoelectrochemical (PEC) measurements, pristine and core-shell samples were further annealed at 750 °C for 20 min.[2]

Figure 3.2 Schematics of synthesis of core-shell Fe_2O_3 nanorods by hydro-spray technique.

3.4 Combined approach to synthesis core-shell/Mn doped hematite

photoanode

For tandem cell measurements, we have synthesized the core-shell/Mn doped hematite photoanode by combining the above mentioned strategies. First, we have synthesized the Mn doped hematite photoanode via hydrothermal synthesis method. For this, a 10 mL aqueous solution containing 1.5 mmol $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (Sigma-Aldrich), 5% (by mole percent) of $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ (Sigma-Aldrich), and 1.5 mmol urea (Sigma-Aldrich) have been transferred to autoclave. The FTO coated glass substrate were also placed in the autoclave at an angle of about 45 degrees. The hydrothermal synthesis was carried out for 6 hrs. After 6 hrs of reaction at 100 °C, a uniform layer of Mn doped FeOOH film was formed on the FTO substrate. Secondly, a 0.1 M $\text{Fe}(\text{AcAc})_3$ precursor in absolute ethanol was sprayed on to the cleaned FeOOH nanorods with 2 cycles (15

sec on-off) on hot plate at 525°C for core-shell sample and finally annealed at 550 °C for 2 hrs and 750 °C for 20 min.[3]

3.5 Photoelectro-deposition of Cobalt-Phosphate (CoPi) on Hematite

An oxygen evolution catalyst CoPi has been deposited on 750 °C for 20 min annealed hematite samples via photoelectro-deposition method. A 0.5 mM cobalt nitrate hexahydrate (Sigma-Aldrich) dissolved in 1M KPi solution under vigorous stirring for 15 min and then transferred to electrodeposition bath for deposition. For photoelectrodeposition a three electrode setup (hematite as working electrode, platinum coil counter electrode, and an Ag/AgCl reference electrode) has been used and deposition occurs under 1 Sun (100 mWcm^{-2}) illumination. Finally, CoPi has been deposited on hematite at 0.4 V vs. Ag/AgCl for 15 sec.[3]

3.6 Fabrication of Single Solution Processed Organic–Inorganic Halide

Perovskite ($\text{CH}_3\text{NH}_3\text{PbI}_3$) solar cell for Tandem Overall Water

Splitting

A 2.2 mm thick, Pilkington FTO coated glass substrates, with a sheet resistance of <14 ohm/square were used for the fabrication of the perovskite solar cell. The desired pattern was laser etched and cleaned by ultra-sonication in decon soap solution followed by subsequent rinsing with DI water and ethanol. The substrates were further ultrasonicated in ethanol for 15 min and then dried by using nitrogen gas. A thin (80-100 nm) and compact TiO_2 blocking layer was deposited on these cleaned and etched FTO by aerosol spray pyrolysis of a diluted solution of titanium diisopropoxide bis (acetylacetonate) (75 wt. % in isopropanol (IPA)) using ambient air as carrier gas. The titanium diisopropoxide bis (acetylacetonate) solution was diluted with absolute ethanol in the 1: 9 ratio by volume. These substrates were then immersed in 0.1 M titanium tetra chloride (TiCl_4) solution at 70 °C for 1 h followed by annealing at 500 °C for 1 h. Then 1.5 x 2 cm of these substrates were masked with tape on either sides partly covering the laser etched area and the FTO. On the

exposed area, diluted TiO₂ paste (DSL 30 NRD, Dyesol, 1:3.5 by weight in absolute ethanol) was spin coated at 4000 rpm for 30s followed by annealing at 120 °C for 10 min and 500 °C for 15 min. The TiO₂ films were subjected to 20 mM TiCl₄ solution at 70 °C for 30 min followed by rinsing with DI water and ethanol. 1 M of lead iodide (PbI₂) solution in N,N-dimethyl formamide (DMF) was spin coated at 6000 rpm for 5 s inside the glove box followed by immersion in methyl ammonium iodide (CH₃NH₃I) solution (8 mg/mL in isopropanol (IPA)) for 20 min in dry box (relative humidity < 15 %) for the formation of perovskite layer on the mesoporous films. The perovskite loaded films were then spin coated at 4000 rpm and dried at 100 °C for 30 min. The widely used hole transporting material (HTM) namely spiro-OMeTAD (2, 2', 7, 7'-tetrakis-(N, N-di-p-methoxyphenylamine) 9, 9'-spirobifluorene) was used in chlorobenzene (100 mg/mL) with additives like Li (CF₃SO₂)₂N (520 mg/mL in acetonitrile), tert-butylpyridine (48 µL) and FK102 dopant (10 mol% in acetonitrile (ACN)). The HTM was spin coated at 4500 rpm for 30 s inside the dry box and finally the gold (Au) contacts were deposited by thermal evaporation yielding an active area of 0.2 cm². [3]

3.7 Morphological and Structural Characterization of Hematite

nanorods

The morphology of pristine, Mn doped and core-shell hematite nanorod samples was observed with Field Emission Scanning Electron Microscopy (FESEM, JEOL, JSM-7600F). These samples were coated with platinum to avoid charging problems. For further structural characterization, HRTEM Analysis (JEOL 2010) was done by using thin film samples scratched from FTO substrates, dispersed in ethanol, ultrasonicated for 15 sec and eventually loaded onto the copper grip. The crystal structure of hematite films was determined using thin film X-ray diffraction (XRD) which were conducted with a Shimadzu LabX-XRD-6000 using Cu K α radiation ($\lambda=1.5418\text{\AA}$) for a 2θ range of 20 to 60 degree at a scanning rate of 2 degree/min. Ultraviolet-visible (UV-Vis) absorption spectra of the hematite samples were obtained using a

Perkin Elmer UV-Vis spectrophotometer. X-ray Photoelectron Spectroscopy (XPS) measurements were carried with VG Escalab 220i XL. The binding energies were calibrated with respect to the residual C (1s) peak at 285.0 eV.

3.8 Photoelectrochemical (PEC) Characterization of Hematite Photoanodes

PEC measurements were performed with a CHI 660D working station (CH Instruments, Inc.) using a three-electrode electrochemical system comprising of hematite working electrode, a platinum wire as counter electrode and Ag/AgCl reference electrode with 1M NaOH (pH=13.6) electrolyte. The image of the setup used for PEC measurements is shown in Figure A1. The active area of hematite photoanode was 0.12 cm². Simulated sunlight from a 150 W xenon solar simulator (96000, Newport Corp.) through a solar filter (KG3) with intensity equivalent to standard AM1.5 sunlight (100 mWcm⁻²) was irradiated on the hematite samples. The electrolyte i.e. the aqueous solution of 1 M NaOH (pH 13.6) was degassed by purging N₂ gas for 10 min before PEC measurement. The hematite photoanodes were scanned -0.6 V and 1.0 V vs. Ag/AgCl under 1 sun illumination. For measurements under the influence of hole scavenger, 1M NaOH + 0.5M H₂O₂ electrolyte was used with other conditions kept same as mentioned above.

To calculate applied bias with respect to Reversible Hydrogen Electrode, (V vs RHE) potential, Nernst equation was used as follows:

$$V_{RHE} = V_{Ag/AgCl} + .0059 \times pH + V_{0Ag/AgCl} \quad (3.1)$$

where $V_{Ag/AgCl}$ is the applied voltage with respect to Ag/AgCl reference electrode, and $V_{0Ag/AgCl}$ is the standard potential of Ag/AgCl at room temperature, which is equal to 0.197 V.

Figure 3.3. Schematic of Photoelectrochemical (PEC) cell, which is containing hematite nanorods sample as working electrode, platinum counter electrode and an Ag/AgCl reference electrode.

Incident Photon to Current Efficiency (IPCE) was measured using a xenon light source (MAX5303, Asahi Spectra Co. Ltd.) and a monochromator (CMS5100, Asahi Spectra Co. Ltd.). Electrochemical impedance spectroscopy (EIS) measurements were carried out using an automated potentiostat (Metrohm Autolab) in a three-electrode electrochemical system. Counter electrode, reference electrode and electrolyte were same as that used for PEC measurements. Measurements for Nyquist plots were performed both in dark and light conditions at 1.23V vs. RHE from 10 KHz to 0.1 Hz. Mott Schottky plots were extracted for a potential scan of 0.6 V to 2.0 V vs. RHE in dark at 1 KHz.

3.9 Intensity Modulated Photocurrent Spectroscopy (IMPS)

Characterizations

IMPS measurements of pristine, Mn doped and core-shell hematite photoanodes were conducted using a (Princeton 283) potentiostat in a three electrode configuration with an Ag/AgCl reference electrode, and a platinum wire counter electrode. The electrolyte was 1 M NaOH. Modulated illumination was provided by a light-emitting diode (LED: 455 nm) controlled by a (Thor Lab DC 2100) LED driver that allowed superimposition of sinusoidal modulation (typically less than 10%) on a dc illumination level. The sine wave signal was provided by a Solartron 1250 frequency response analyzer.

Upon illumination of a semiconductor-electrolyte junction, the semiconducting photoelectrode absorbs photons and generates photo-excited carriers (electrons in the conduction band and holes in the valence band). If the generation occurs within the depletion layer, these electrons and holes will be separated due to the presence of built-in electric field. For an n-type semiconductor, such as hematite, electrons will move to the back contact. On the other hand, holes will be drifted to the semiconductor/electrolyte interface. Combined with the holes generated in the bulk that are within its diffusion length, this constitutes the hole current (J_{hole}), i.e., the total number of holes that arrive at the semiconductor/electrolyte interface.[4-5] The processes at the semiconductor/electrolyte interface is described and illustrated in chapter 6. The photo-generated holes can either recombine with the electrons from the conduction band via surface states, or transfer to the electrolyte to oxidize water.[6] The most common photoelectrochemical method used to probe these interface processes is transient photocurrent measurement. The sample is subjected to chopped illumination at a constant potential, and the resulting photocurrent is monitored. In a transient photocurrent spectrum, the instantaneous photocurrent is the measured displacement current directly upon illumination. This is simply the number of holes that arrive at the interface (J_{hole}). At longer times, recombination process starts to occur, and the

photocurrent decays to the steady-state photocurrent (J_{ss}). This corresponds to the amount of holes transferred to the electrolyte after recombination. The resulting hole transfer efficiency at the semiconductor/electrolyte interface is therefore the ratio of the steady state photocurrent (J_{ss}) to the instantaneous photocurrent (J_{hole}). Unfortunately, in transient photocurrent measurement, we may be limited by the convolution of additional processes, other than hole transfer and surface recombination. This is related to the big difference between dark and illuminated conditions, which may cause changes in band bending and/or significant population or depopulation of states. In the end, these may also affect the rate constants, and complicate the analysis of the data. In contrast, this is not (or less of) a problem in intensity modulated photocurrent spectroscopy (IMPS). This is because we apply a small amplitude (~10-20%) sinusoidal modulation of light intensity on top of a constant dc value. This modulation results in a change in phase and amplitude (i.e., real and imaginary component) of the photocurrent. This photocurrent response of intensity modulated illumination as a function of frequency results in semicircles in the complex plane, as shown in Figure 6.1 chapter 6. In our particular case, this complex normalized photocurrent (J_{photo}/J_{hole}) is obtained by normalizing our frequency response analyzer reading so that the real-axis intercept is equal to unity.[6]

The lower quadrant semicircle represents the attenuation by the total series resistance of the photoelectrochemical cell and the capacitances of the sample, typically referred to as the RC time constant of the cell. Of more particular interest to us, is the upper quadrant semicircle, also referred to as the recombination semicircle. The first order rate constants k_{tr} and k_{rec} can be obtained by analyzing this semicircle. The high and low frequency intercepts in the complex plane are comparable to the steady state and instantaneous photocurrents in the transient photocurrent measurement. The ratio of the low and high frequency intercept therefore corresponds to the hole transfer efficiency. The maximum of the semicircle occurs at a radial frequency that is equal to the sum k_{tr} and k_{rec} , i.e., the characteristic relaxation constant of the

system. Based on these values, both k_{tr} and k_{rec} can be calculated.[4-6] Further details on IMPS theory can be found in chapter 6.

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Chapter 4

Pristine and Mn Doped Hematite Nanorods for PEC Water Splitting

Pristine and manganese (Mn) doped hematite nanorods were grown on FTO substrate by hydrothermal. Systematic structural and optoelectrical analysis were performed to investigate the presence of Mn in hematite sample. Hematite nanorods sample with 5 mol% Mn treatment shows a photocurrent density of 1.6 mAcm^{-2} , (75% higher than that of pristine hematite) at 1.23 V vs. RHE and a plateau photocurrent density of 3.2 mAcm^{-2} at 1.8 V vs. RHE in 1M NaOH electrolyte solution (pH 13.6). This increase in photocurrent density of Mn doped hematite nanorods is attributed to enhancement in donor density, which is confirmed by Mott-Schottky measurement. Manganese doping also suppress the transient current, which indicate a better charge injection in Mn doped hematite sample.

These results have been published in ACS Appl. Mater. Interfaces, 2014, 6 (8), pp 5852–5859

4.1 Introduction

Hematite ($\alpha\text{-Fe}_2\text{O}_3$) has emerged as one of the most promising candidate for solar water splitting due to its favorable energy band gap (2.0 to 2.2 eV), good stability in aqueous solutions, nontoxicity, abundance and economic viability.[1-6] However, the low carrier conductivity, short lifetime of photogenerated charge carriers (<10 ps), short hole diffusion length (2–4 nm), slow oxygen evolution reaction kinetics, and low flat band potential limit the performance of hematite.[1, 7-10] To address the above-mentioned drawbacks, nanostructuring, surface modification and doping of hematite have been explored to improve the electronic and optical properties.[5, 11-14] Morphological control of these nanostructures for improved performance can be accomplished by employing a solution based hydrothermal synthesis routes to synthesize nanorods arrays on conducting substrates (FTO).[15-17] Here, we describe a strategy to enhance the PEC performance of hematite by doping with manganese. The Mn doping was also expected to generate energy states within the band gap of Fe_2O_3 and therefore could be beneficial in modulating the electrical conductivity. We synthesize Mn doped Fe_2O_3 nanorods using a hydrothermal method. Systematic structural and opto-electrical characterizations of pristine and Mn doped hematite photoanodes have been carried out to understand their PEC performance.

4.2 Results and Discussion

The XRD patterns of pristine hematite and Mn-doped hematite nanorods can be indexed to the characteristic peaks of Fe_2O_3 (JCPDS no. 003-0440), (Figure 4.1(a)). A prominent diffraction peak at $2\theta = 35.8^\circ$ implies that hematite nanorods grow preferentially in the [110] direction as reported previously.[13] This is a preferred direction for charge transport because the conductivity in this basal plane (001) is four orders of magnitude higher than the orthogonal plane; which improve the photo-oxidation process.[13] Whereas no additional peak observed in XRD pattern after adding the manganese precursor in Mn doped hematite sample. Impressively, there is no peak shift or broadening of XRD peaks observed, which is commonly associated with doping.[18] To

clarify the presence of Mn into hematite lattice, XPS and UPS measurements were performed. The obtained XPS data is shown in Appendix B, Figure B1. The presence of manganese was not detected from the wide survey scan, which could be explained as the actual amount of doping (~ 1 at %) in the final sample is less than the amount added during the synthesis (5 % by mol ratio) which is lower than the detection limit of XPS characterization. Therefore, a more sensitive SIMS measurement was carried out on pristine and Mn doped samples to confirm the manganese presence (Figures 4.1(b)). As the counts for Mn was relatively low, we examined closely the pristine and two differently doped hematite samples near the Mn mass (Figure 4.1(c)).

Figure 4.1. (a) XRD patterns of pristine and Mn doped hematite nanorod on FTO. The * denotes $\alpha\text{-Fe}_2\text{O}_3$ (JCPDS 33-0664) and # denotes SnO_2 (JCPDS 46-1088), respectively. (b) SIMS depth profile of both pristine and 5% Mn doped hematite, (c) Intensity profile of secondary ions with mass near Mn. Shaded area increase with increasing doping. (d) UV-Vis absorption spectra of pristine and 5% Mn doped hematite, inset shows band gap extracted using Tauc's analysis. Reprinted with the permission from [19]. Copyright 2015 American Chemical Society.

The presence of Mn is ~ 1 at%, however it shows significant changes in the electronic properties.[20, 21] To examine the electronic properties, work function measurements of the pristine and Mn doped hematite were performed by using ultraviolet photoelectron spectroscopy (UPS). The work function of pristine hematite was 5.09 eV while the Mn doped hematite shows a smaller work function i.e., 4.79 eV, results a shift in the Fermi level (See Appendix, Figure B2).[22] This Fermi level shift towards the conduction band facilitates the charge separation at electrode/electrolyte interface, increase the degree of upward band bending at the hematite surface.[22, 23] UV-vis spectra of pristine hematite and Mn doped hematite are shown in Figure 4.1(d). The absorption curves and the energy band gaps calculated from Tauc's analysis are nearly same for both samples (Figure 4.1(d)). The similar energy band gap (2.05 and 2.07 eV) show that the Mn doping doesn't change the crystal structure of hematite. Surface view field emission scanning electron microscopy (FESEM) images of pristine and Mn doped hematite exhibit a nanorods like structure and doping does not affect the growth of hematite nanorods (Figure 4.2). The thickness (400 nm) and diameter ranges (50–60 nm) of pristine and Mn doped hematite samples remains same (Figure 4.3). Photocurrent-voltage measurements were performed for pristine and Mn doped hematite nanorods in 1 M NaOH electrolyte (pH = 13.6), under simulated sunlight illumination at AM 1.5G 100 mWcm⁻² (Figure 4.4 (a)). All PEC measurements were carried out in three-electrode electrochemical configuration, using an Ag/AgCl reference electrode and a Pt wire as the counter electrode. Mn doped hematite photoanode was found to give higher performance compared to pristine hematite (Figure 4.4 (a)).

Figure 4.2. Top view FESEM images of (a) pristine hematite after annealing at 550°C, (b) 5 % Mn doped hematite after annealing at 550°C, (c) pristine hematite after annealing at 750°C and (d) 5% Mn doped hematite after annealing at 750°C. Reprinted with the permission from [19]. Copyright 2015 American Chemical Society.

Figure 4.3. Cross section images of (a) pristine and (b) Mn doped hematite nanorods after annealing at 750°C for 20 min. Reprinted with the permission from [19]. Copyright 2015 American Chemical Society.

Although higher Mn (10%) doped hematite shows lower PEC performance, (Appendix Figure B3) and 1-2% initial Mn doping did not show any change in photocurrent (data not shown). The 5% initial Mn doping shows the beneficial

effect in PEC performance so we are comparing the pristine and 5% manganese precursor treated samples. The pristine and Mn doped hematite photoanodes deliver photocurrent density of 0.45 mAcm^{-2} and 1.40 mAcm^{-2} at 1.23 V vs. RHE respectively.

Figure 4.4. (a) Photocurrent-potential curve of pristine and Mn doped hematite measure under AM 1.5G 100 mWcm^{-2} in 1 M NaOH electrolyte solution, (b) IPCE action spectrum of pristine and Mn doped hematite measured at 1.23 V vs. RHE, inset shows APCE, (c) Integrated photocurrent calculated from electron flux, (d) Mott Schottky plots of pristine (inset) and Mn doped hematite extracted from electrochemical impedance data measured at 1 KHz in the dark. Donor densities (N_d) and flat band potential (V_o) extracted are shown in the figure. Reprinted with the permission from [19]. Copyright 2015 American Chemical Society.

A plateau photocurrent density of 2.4 mAcm^{-2} for pristine hematite and 3.2 mAcm^{-2} for Mn doped hematite from 1.6 to 1.8 V vs. RHE was observed, before the dark current rises. To understand the tradeoff between the photoactivity and the light absorption of hematite photoanodes, we measured

their photoactivity as a function of wavelength of the incident light. Incident photon to current conversion efficiency (IPCE) is a powerful method to characterize the photo-conversion efficiency of photoelectrodes because it is independent from the light sources and filters used in the measurement. IPCE measurements were performed on pristine and Mn doped hematite photoanodes at 1.23 V vs. RHE (Figure 4.4 (b)). IPCE can be expressed using the following equation:[24]

$$IPCE (\%) = \left(\frac{1240 \times I_{Ph}}{\lambda \times J_{Light}} \right) \times 100 \quad (4.1)$$

Where I_{Ph} is the measured photocurrent density at a particular wavelength, λ is the wavelength of incident light, and J_{Light} is the measured irradiance at a specific wavelength. Mn doped hematite shows higher photoactivity than the pristine hematite over the entire UV-visible region. The IPCE drops to zero at wavelengths higher than 610 nm, which is consistent with the energetics of the hematite photoanode. is shown in the inset of Figure 4.4 (b) and was found that the Mn doped hematite demonstrating higher absorbed photon to current conversion (APCE) efficiency, which reflects better collection and charge separation capability as compared to pristine hematite.

The integrated photocurrent density was estimated from the IPCE spectra with a standard AM 1.5G (100 mWcm^{-2}) solar spectrum using the following equation:[24, 25]

$$I_{Ph} = \int_{350}^{610} \frac{\lambda IPCE(\lambda) E(\lambda) d(\lambda)}{1240} \quad (4.2)$$

Where $E(\lambda)$ is the solar spectral irradiance at a particular wavelength (λ) and $IPCE(\lambda)$ is the obtained IPCE at 1.23 V vs. RHE. The integrated photocurrents are 0.41 mAcm^{-2} and 1.4 mAcm^{-2} for pristine and Mn doped samples respectively, (Figure 4.4 (c)) and suitably match with the measured photocurrent densities at 1.23 V vs. RHE. In order to understand the reason behind the photocurrent improvement by Mn doping, electrochemical impedance spectroscopy (EIS) was performed under dark conditions (1 kHz).

The flat band potential and donor densities of these samples were calculated from the slopes of Mott Schottky plots using the equations:[10, 26, 27]

$$\frac{1}{C^2} = \left[\frac{2}{e\epsilon\epsilon_0 N_D} \right] \left[V_A - V_{Flat} - \frac{K_B T}{e} \right] \quad (4.3)$$

$$N_D = \left(\frac{2}{e\epsilon\epsilon_0} \right) \left[\frac{d(1/C^2)}{dV} \right]^{-1} \quad (4.4)$$

Where e is the electron charge, ϵ is the dielectric constant of hematite ($\epsilon=80$)[28], ϵ_0 the permittivity of vacuum, N_d is the donor density, and V_A is the applied bias at the electrode. Both samples show a positive slope in the Mott Schottky plots, which is expected from a n-type semiconductor (Figure 4.4 (d)).[29] The calculated flat band potential and donor densities of the pristine hematite and 5% Mn doped hematite nanorods were 0.45 V vs. RHE, $2.66 \times 10^{17} \text{ cm}^{-3}$ and 0.42 V vs. RHE, $3.02 \times 10^{19} \text{ cm}^{-3}$, respectively. However, the Mott Schottky is derived from a flat electrode model and may have errors in determining the absolute value of donor density from nanostructured photoanodes.[28, 30] Enhanced donor density is possibly shift the Fermi level of hematite towards the conduction band, which is in good agreement with the UPS results (Appendix Figure B2). The increase in the photocurrent density of the Mn doped hematite sample can be attributed to the increase in the charge carrier concentration (Appendix B Figure B3).

The photoresponse with increasing bias voltage of both pristine and Mn doped hematite was measured with chopped illumination at 0.02 Hz under AM 1.5 solar irradiance, shown in Figure 4.5 (a). At lower voltages, a mixture of both transient and faradic currents was observed for the Mn doped sample under illumination, while pristine sample clearly demonstrated transient behavior. This difference is attributed to the accumulation of holes at semiconductor-electrolyte interface as commonly observed in pristine hematite samples.[31] This implies that for Mn doped hematite sample, most of the holes generated upon illumination contribute to water oxidation and indicate suppression of electron-hole recombination.[31, 32] Moreover such a suppression in current

transient behavior was not usually observed when a redox reagent or hole scavengers were employed in the electrolyte solution.[32, 33]

Apparently the preparation method for making nanostructured hematite has a direct effect in reduction of the transient behavior as observed in previous studies and is further reflected in the Mn doped samples investigated in this work.[32] When the light is switched off, a transient behavior is again observed for pristine hematite. This is due to recombination of the excited electrons in the conduction band with the holes which are accumulated at the semiconductor-electrolyte interface.[32] This effect was reduced after Mn doping possibly because the multivalent oxidation states of manganese leads to a low (O-Mn-O) energy barrier for hole transport.[34] This is also reflected in the APCE measurements (Figure 4.4 (b), inset) where the collection efficiency of the photo-excited charges increases by 100 % (at $\lambda = 350$ nm) for the Mn doped samples. Oxygen evolution experiments were also conducted to confirm that the photocurrent generated is translated to O₂. It can be seen in Figure 4.5 (b), that the rate of oxygen generation with 5% Mn doped hematite photoanode was significantly greater than that of the pristine hematite. Based on the calculated Faradaic efficiencies of 70.03% and 73.64% for 5% Mn doped and pristine hematite respectively, the amount of O₂ evolved was less than the expected values. This is probably in part due to gas leakage during the sampling and manual injection into the GC. Nevertheless, most of the photogenerated holes were consumed for oxygen production in our PEC system.

Finally, Manganese doping helps to improve the carrier concentration, which is the main cause of better PEC performance. However, we were not able to detect the exact oxidation state of Mn, but EIS analysis proved n-type of doping, which is only possible when Mn is in 4+ state.

Figure 4.5. (a) Chopped photocurrent-potential curve of pristine hematite photoanode and 5 %Mn doped. (b) Time progression of light induced oxygen evolution of 5% Mn doped hematite and pristine hematite photoanodes at an applied potential of 1.23 V vs. RHE. Both sets of measurements were conducted under AM 1.5G 100 mWcm⁻² illumination in 1M NaOH electrolyte solution. Reprinted with the permission from [19]. Copyright 2015 American Chemical Society.

4.3 Conclusion

In this chapter, we have successfully demonstrated a simple and cost effective solution processed hydrothermal method to synthesize pristine and Mn doped hematite for photoelectrochemical water splitting. Systematic structural and electrical studies were carried out to investigate the presence of manganese in hematite nanorods sample. 5 mol % Mn precursor doped hematite photoanode enhance the photocurrent densities by 3 times at 1.23 V vs. RHE and also in reducing the onset potential by 30 mV compared to the pristine hematite. The reason of enhance in PEC performance was ascribed to increase in charge carrier densities as estimated by Mott-Schottky analysis. Chronoamperometry studies reveals that the transient currents reduced for Mn treated sample compared to pristine hematite, showing the favourable effects of Mn doping. A reduction in transient photocurrent may occur due to the suppression in recombination at the electrode/electrolyte interface. This study clearly indicates the beneficial effect of Mn doping in hematite photoanode for PEC water splitting.

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Chapter 5

Core-Shell Hematite Photoanode for Photoelectrochemical Water Splitting

In this chapter, we discuss a simple method by combining spray pyrolysis and hydrothermal synthesis to produce a stable core-shell hematite ($\alpha\text{-Fe}_2\text{O}_3$) photoanode for solar water splitting. The core-shell hematite nanorods sample provides a photocurrent density of 1.2 mAcm^{-2} , at 1.23 V vs. RHE, which is nearly twice than that of pristine hematite sample. A systematic electrochemical impedance spectroscopy (EIS) study revealed that the different charge dynamics of both samples. Pristine hematite sample demonstrate a charge transfer behavior from surface states to the electrolyte, whereas in the core-shell hematite photoanode the majority of hole transfer through the valence band. This indicates a partial passivation of the surface states by the shell layer deposition, which results in an increase of the charge injection through the hematite.

These results have been published in ACS Appl. Mater. Interfaces, 2015, 7 (12), pp 6852–6859.

5.1 Introduction

Photoelectrochemical (PEC) cells are advantageous to convert and store solar energy into chemical fuels by splitting water into molecular hydrogen and oxygen. Hematite has been used as a potential photoanode in PEC cells to perform water splitting half reaction (OER) because of its favorable energy band gap (2.0 – 2.2 eV) and aqueous stability.[1-3] However, the main drawbacks of hematite are the requirement for an overpotential, which occurs due to the slow oxygen evolving reaction (OER) kinetics and the surface trap states.[4-9] Surface modification with oxygen evolution catalysts (OEC) have been used to overcome the OER kinetic issue, while surface passivation by different wide band gap metal oxides have been reported to reduce the surface traps.[10-23] In this chapter, we investigate the role of surface states on hydrothermal grown hematite nanorods and demonstrate an inexpensive spray pyrolysis method to passivate those defects. To accomplish this we have used spray deposition technique to coat a very thin hematite overlayer on the surface of hydrothermally grown FeOOH nanorods. Electrochemical Impedance Spectroscopy (EIS) has been employed to study the pristine and core-shell hematite photoanodes surface properties. Pristine hematite sample shows the charge transfer through the surface states to the electrolyte, while core-shell hematite photoanodes exhibit a charge transfer process through the valence band. TEM is also used to investigate the atomic arrangements of the nanostructures, which support that the reason behind different charge dynamics is defects present in the samples.

5.2 Results and Discussion

The XRD patterns of the pristine and core-shell hematite photoanodes can be indexed to the characteristic peaks of Fe₂O₃ (JCPDS no. 003-0440), (Figure 5.1(a)). These XRD results clearly indicate that the sprayed deposited thin hematite overlayer on pristine hematite nanorods does not generate any additional peak, peak shift or a broadening of XRD peaks. Strong (110) diffraction peak at $2\theta = 35.8^\circ$ implies that hematite nanorods grow preferentially in the [110] direction, as previously reported.[24] This is a

preferred direction for charge transport because the conductivity in this basal plane (001) is four orders of magnitude higher than the orthogonal plane, which enhances the PEC performance.[25] UV-vis spectra of pristine and core-shell hematite samples shows that the shape of the absorption curves and the energy band gaps (2.01 and 2.04 eV for pristine and core-shell respectively), extracted from Tauc's analysis are nearly the same (Figure 5.1(b)). The similar energy band gap results are consistent with the XRD data of both samples, which indicates no structural change occurs of pristine hematite after spraying the hematite shell. The thickness of pristine and core-shell hematite photoanodes are 350 nm and 370 nm respectively (Figure 5.2). Surface view images from field emission scanning electron microscopy (FESEM) show that, pristine and core-shell hematite nanostructures exhibit nanorods structure, which remain unchanged after the deposition of the thin shell layer (Figures 5.2 (a) and (b)). The length and diameter (50 – 60 nm and the length is ~ 350 nm) of pristine hematite nanorods slightly increase after shell layer deposition (70 -80 nm and the length becomes 370-380 nm) followed by annealing at 550 °C for 2 h and 750°C for 20 min, (Figure 5.2 (a) and (b)).

Figure 5.1. (a) XRD patterns of pristine and core-shell hematite on FTO coated glass substrate after annealing at 550 °C for 2 h. The * denotes α-Fe₂O₃ (JCPDS 33-0664) and # denotes SnO₂ (JCPDS 46-1088), respectively. (b) UV-Vis absorption spectra of pristine and core-shell hematite, inset shows band gap extracted using Tauc's plot. Reprinted with the permission from [26]. Copyright 2015 American Chemical Society.

The compositional analysis was carried out by EDX line scan measurements along the interface of core and shell (See Appendix C Figure C1 and C2) and observed signals for Fe and O concurred well with hematite for both pristine and core-shell hematite samples. TEM image of the pristine hematite nanorods shows that these are about 50 nm and 350 nm in diameter and length (figure 5.2 (c)). Figure 5.2 (d) clearly shows a conformal surface overlayer with a thickness of about 20 nm on hematite nanorod in core-shell hematite sample. These TEM results of pristine and the core-shell hematite nanorods are consistent with the FESEM observations. Photocurrent–voltage curves of core-shell hematite shows better performance compared to pristine hematite photoanode (Figure 5.3(a)). The photocurrent density is 0.45 mAcm^{-2} at 1.23 V vs. RHE for the pristine hematite and 1.20 mAcm^{-2} at 1.23 V vs. RHE for core-shell hematite. A plateau photocurrent of about 0.7 mAcm^{-2} and 2.6 mAcm^{-2} from 1.6 to 1.7 V vs. RHE observed for the pristine and core-shell hematite respectively. This photocurrent enhancement for the core-shell hematite photoanode at 1.23 V vs. RHE is comparable with hydrothermally grown 5% Mn treated hematite photoanode.[24] Photocurrent transient measurements were performed in order to observe the role of surface states at the pristine and core-shell hematite-electrolyte interface. The photoresponse with increasing bias voltage of pristine and core-shell hematite photoanodes were measured under chopped illumination at 0.02 Hz (Figure 5.3(b)).

The positive photocurrent transient just after the illumination can be arise from the photogenerated holes accumulation at the photoanode surface because of the slow OER kinetics and defects on the photoanode surface. Likewise, negative photocurrent transients are observed upon switching the light off, which reveal the photo-induced electrons recombine with the accumulated holes. These current transients disappear at high potentials, indicating that the injection barrier does not obstruct the transfer of holes from the photoanode surface to the electrolyte and consequently all holes those arrive at the surface contribute in the water oxidation reaction.

Figure 5.2. Top view FESEM images of (a) pristine hematite, (b) Core-shell hematite, (c) TEM image of pristine hematite nanorod, and (d) TEM image of core-shell hematite. Reprinted with the permission from [26]. Copyright 2015 American Chemical Society.

A small reduction in transients at lower bias voltages is observed for the core-shell hematite photoanode, while pristine hematite clearly shows high transient behavior. This transient difference is attributed to the accumulation of holes at photoanode/electrolyte interface as normally detected in pristine hematite samples. The enhancement in photocurrent in core-shell hematite cannot be explained by an enhancement in the catalytic activity, but it is convincing to assume that the density of trap states at the surface of pristine hematite photoanodes partially passivated by the deposition of a thin overlayer of Fe_2O_3 .

To understand the relationship between the photoactivity and light absorption of pristine and core-shell hematite photoanodes, we measured their

performance as a function of wavelength of the incident light. IPCE was obtained from pristine and core-shell hematite nanorods at 1.23 V vs. RHE (Figure 5.3(c)). IPCE can be expressed using the following equation:[27]

$$IPCE (\%) = \left(\frac{1240 \times I_{ph}}{\lambda \times J_{Light}} \right) \times 100 \quad (5.1)$$

Where I_{ph} is the measured photocurrent density at a particular wavelength, λ is the wavelength of incident light, and J_{Light} is the measured irradiance at a specific wavelength. Core-shell hematite photoanode show higher IPCE value over the entire spectral region than the pristine hematite. The IPCE drops to zero at wavelengths longer than 610 nm, which is consistent with the energetics of the hematite band gap.

Absorbed photon to current conversion (APCE) efficiency found to be higher for core-shell hematite photoanode, which demonstrate better injection and charge separation capability (See Appendix C Figure C3). The photocurrent density was calculated by integrating the IPCE spectra with a standard AM 1.5G (100 mWcm⁻²) solar spectrum using the following equation:[24, 27]

$$I_{ph} = \int_{350}^{650} \frac{\lambda IPCE(\lambda) J(\lambda) d(\lambda)}{1240} \quad (5.2)$$

Where $J(\lambda)$ is the solar spectral irradiance at a particular wavelength (λ) and $IPCE(\lambda)$ is the obtained IPCE as a function of wavelengths (λ) at 1.23 V vs. RHE. The calculated integrated photocurrents are 0.40 mAcm⁻² and 0.9 mAcm⁻² for pristine and core-shell hematite photoanodes respectively (Figure 5.3(d)), which is consistent with the measured photocurrent densities at 1.23 V vs. RHE. The analogous optical absorption of both pristine and core-shell hematite photoanodes (figure 5.1(b)) excludes optical absorption as the reason behind the improved PEC performance. The charge injection and collection efficiency of the pristine and core-shell hematite photoanodes were further examined by utilizing a hole scavenger (0.5M H₂O₂) along with the 1M NaOH electrolyte solution. This measurement relies on the hole scavenger eliminating surface

recombination, thus allowing bulk recombination phenomena to be estimated.[28]

Figure 5.3. (a) Photocurrent-potential curve of pristine and core-shell hematite photoanodes measure under AM 1.5G 100 mWcm⁻² in 1M NaOH electrolyte solution, (b) Chopped photocurrent-potential curve of pristine hematite and core-shell hematite photoanodes, (c) IPCE action spectrum of pristine and core-shell hematite photoanodes collected at 1.23 V vs. RHE, inset shows the extrapolated IPCE from wavelength 450 to 650 nm, and (d) Integrated photocurrent based on the IPCE data (300 nm to 650 nm) collected at 1.23 V vs. RHE, solar photon flux is shown as a reference. Reprinted with the permission from [26]. Copyright 2015 American Chemical Society.

By comparing the photocurrents with H₂O₂, H₂O and the theoretical photocurrent, the surface recombination can also be estimated (see Appendix C). The analysis yields (i) charge separation efficiency which is the yield of photogenerated holes arriving on the hematite surface, as well as (ii) surface catalysis efficiency which estimates the hole injection into the electrolyte. Due to the facile oxidation of the hole scavenger, current transients under chopped illumination disappear and pure Faradaic photocurrents are observed in the

complete potential range for both hematite samples (see Appendix C Figure C4). To understand the efficiency of hole injection at the hematite/electrolyte interface, the J-V curves of pristine and core-shell hematite photoanodes were measured with and without 0.5 M H₂O₂ under 1 Sun (AM 1.5G) illumination. The photocurrent is found to double after adding 0.5M H₂O₂ in 1M NaOH electrolyte (Figure 5.4 (a) and (b)). The charge separation and surface catalysis efficiency of pristine and core-shell samples are calculated (Figure 5.4(c) and 4(d)) by following a previous method reported by Dotan et al.^[28] The charge separation efficiency starts to rise at an anodic potential than the flat band potential and reached 15% for pristine hematite and 30% for core-shell hematite at 1.23 V vs RHE (Figure 5.4(c)). The charge separation efficiency increases with the applied voltage because of the widening of the space charge layer. The higher charge separation efficiency of the core-shell hematite than the pristine nanorods shows that the large number of holes arriving at the surface of the core-shell hematite than the pristine hematite. Therefore, the surface catalysis efficiency increases from 16% to 31% for core-shell hematite photoanode at 1.23 V vs RHE by employing a H₂O₂ hole scavenger (Figure 5.4(d)). This study shows that in the core-shell sample more holes are being injected to the electrolyte. Both of the observations (better hole transport and injection) show that the deposition of shell improves the quality of the pristine hematite photoanode. To further understand the reason behind this enhancement in the PEC performance, electrochemical impedance spectroscopy (EIS) study was performed. Capacitance measurements of the pristine core-shell hematite photoanodes at a frequency of 1 and 10 kHz were performed under dark conditions. The flat band potential and donor densities of these samples were calculated from the Mott Schottky plots using the equations:[29, 30]

$$\frac{1}{C^2} = \left[\frac{2}{e\epsilon\epsilon_0 N_d} \right] \left[V_A - V_{fb} - \frac{K_B T}{e} \right] \quad (5.3)$$

Where C is the space charge layer capacitance, e is the electron charge, ϵ is the relative permittivity of hematite ($\epsilon = 80$)[30], ϵ_0 the permittivity of vacuum, N_d

is the donor density, V_{fb} is the flat band potential and V_A is the applied bias at the electrode.

Figure 5.4. (a) Photocurrent-potential curve of pristine hematite photoanode measure under AM 1.5G in 1 M NaOH and 1 M NaOH with 0.5M H₂O₂ electrolyte solution, (b) Photocurrent-potential curve of core-shell hematite photoanode measure under the same conditions, (c) Charge separation efficiency of pristine and core-shell hematite photoanodes for water oxidation, and (d) Surface catalysis efficiency of pristine and core-shell hematite for water oxidation. Reprinted with the permission from [26]. Copyright 2015 American Chemical Society.

Pristine and core-shell hematite samples show a positive slope in the Mott Schottky plots, which is expected from a n-type semiconductor (Figure 5.5 (a)). The calculated donor densities are $8.19 \times 10^{17} \text{ cm}^{-3}$ and $1.39 \times 10^{18} \text{ cm}^{-3}$ and flat band potential 0.35 V vs RHE and 0.34 V vs. RHE for pristine and core-shell hematite photoanode respectively.

To understand the fundamental differences of the working mechanisms of the pristine and core-shell hematite photoanodes, electrochemical impedance spectroscopy (EIS) measurements were executed at different DC potentials under 1 Sun AM 1.5G illumination. Similar Nyquist plot patterns were obtained for both pristine and core-shell samples (Figure 5.5 (b) and Appendix Figure C5), however the fitted data revealed different processes leading the performance of both types of samples. The pristine hematite sample exhibit a charge transfer through surface states (where R_s represents the series resistance from the substrate and wires, $R_{trapping}$ is the resistance to fill the surface states, $R_{ct,trap}$ is the resistance to inject the charge from the surface states to the electrolyte, whereas C_{bulk} and C_{trap} are the capacitances of the bulk and surface states respectively, (See equivalent circuit in Appendix C Figure C6). These results are in good agreement with previously reported studies on the same kind of samples.[16] The characteristic pattern of this behavior is a peak of C_{trap} and a simultaneous valley of $R_{ct,trap}$ due to the filling of the surface states when the current is increasing, as shown in Figure 5.5 (c). However, a different pattern is obtained for core-shell hematite. The fitting of the EIS results to the surface state charge transfer model does not show the characteristics peak, which indicates passivation of the surface states. In this condition, the charge transfer occurs mainly through the valence band, and the fitted equivalent circuit is different ($R_{ct,trap}$ is simplified and a new resistance accounting for the valence band charge transfer, $R_{ct,VB}$, is introduced in parallel to C_{bulk} see Appendix B). The difference in the performance can be explained when the total resistance for the respective charge transfers ($R_s + R_{trapping} + R_{ct, trap}$ in the pristine case and $R_s + R_{ct,VB}$ in the core-shell case) are plotted (figure 5.5 (d)).

The different charge injection processes are in line with the HRTEM structural characterization. Electrochemical devices are very sensitive to surface modifications even crystallographically identical constituents can favorably alter the structure (surface as well as bulk) so that an improved electrochemical performance can be achieved.

Figure 5.5. (a) Mott Schottky plots of pristine and core-shell hematite extracted from EIS data measured at 1 kHz in the dark. Donor densities (N_d) and flat band potential (V_{fb}) extracted are shown in the figure. (b) Nyquist plots of pristine and core-shell hematite measured at pH 13.6 at 1.23 V vs RHE under 1 sun illumination. (c) Plots of equivalent circuit parameter $R_{ct, trap}$ obtained from fitting of EIS data under the illumination of 1 sun light, and (d) R_{tot} values determined by the EIS fitting, where resistances associated with charge transfer. Reprinted with the permission from [26]. Copyright 2015 American Chemical Society.

The HRTEM image of the core-shell hematite photoanode (Figure 5.6 (b)) displays fewer defects and better crystallinity in comparison to the pristine hematite nanorods (Figure 5.6 (a)), whereas pristine hematite clearly exhibits line defects and vacancies in the lattice. The SAED pattern (inset of figure 5.6 (b)) of the core-shell hematite sample revealed that the nanorods are crystalline with a [110] preferred orientation. The polycrystalline nature of the pristine sample with certain orientation masks its SAED pattern (See Appendix C

Figure C7). The improvement in the crystallinity stems from diffusion of the Fe^{3+} ions from shell to the core of hematite during high temperature fabrication process of the shell (525 °C), which saturates the surface and bulk traps sites as well (i.e. dislocations). Therefore, it is conclusive that the presence of the thin hematite shell not only provides the surface uniformity to the core-shell architecture but also improves the crystallinity and passivates the surface and bulk sites. As a result, it modifies the charge transfer dynamics and enhances the photo catalytic activity.

Figure 5.6. (a) HRTEM image of pristine nanorod showing the line defects by arrows and inset image showing the diffraction pattern and (b) HRTEM image of core-shell hematite showing the good crystallinity without any line defects and inset image showing the inserted SAED pattern taken from [001] zone axis. Reprinted with the permission from [26]. Copyright 2015 American Chemical Society.

5.3 Conclusion

To summarize, we have established a solution processed method to synthesize of pristine and core-shell hematite nanorods samples. The core-shell structure shows an improvement in the PEC water splitting activity compared to the pristine hematite nanorods. Core-shell hematite photoanode can enhance the photocurrent densities by 2.5 times at 1.23 V vs. RHE compared to the pristine hematite. EIS and TEM measurements of the core-shell hematite samples compared to pristine ones indicate the beneficial effects of surface layer (shell), which seems to originate from the passivation of surface states and consequent charge injection through the valence band rather than through the surface energetic defects. This study confirms that hematite shell enhances the charge carriers and partially passivates the surface states and emphasizes that this treatment results in better PEC performance of Fe_2O_3 nanostructured photoanodes.

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Chapter 6

Revealing the Charge Dynamic Behaviors of Doping and Surface Treatment in Hematite Photoanodes

Intensity modulated photocurrent spectroscopy (IMPS) is used to examine the rate of charge transfer and recombinations of different photoelectrodes. Here, we study the role of manganese (Mn) doping and core-shell structure on the surface charge carrier dynamics of hematite photoanodes with the help of IMPS. We reveal that the doping of Mn into hematite enhance the charge transfer rate constant and decreases the surface recombination rate constant, however it being considered as a bulk donor-type dopant. Whereas, the core-shell hematite sample shows a reduction in surface recombination rate and no change has been detected in charge transfer rate constant.

6.1 Introduction

Photoelectrochemical (PEC) water splitting is an attractive way to overcome the intermittency of sunlight, by storing solar energy in the form of chemical fuels.[1-5] However, the progress in obtaining highly-efficient PEC performance has been limited by the availability of photoanode materials for water oxidation half reaction.[6-9] Most reports, however, showed that the obtained water splitting efficiency is still far from the theoretical efficiency. Some of the main limiting factors are poor electronic transport and low hole injection efficiency, leading to high required overpotentials.[10-13] This is especially true in the case of hematite (Fe_2O_3). Despite being an economically viable, aqueous stable semiconductor with a suitable bandgap energy for catalysing the visible-light induced oxygen evolution reaction,[13-16] the short hole diffusion lengths and sluggish kinetics of hole injection limit the performance of hematite. In particular, the short hole diffusion length, combined with the fact that hematite's optical penetration depth is larger than the depletion layer width,[17, 18] means that a big portion of the photogenerated charge carriers does not reach the surface and instead recombines in the bulk. Additionally, photogenerated holes that arrive at the hematite/electrolyte interface are injected with a very low efficiency, despite the valence band of hematite being thermodynamically favorable (i.e., ~ 1.2 V more positive than the oxygen evolution potential).[19] This indicates that the kinetics of hole transfer for oxygen evolution is rather slow in hematite.

The problems mentioned above have, however, been overcome to a certain extent through various efforts. The mismatch of optical penetration and carrier transport has been addressed by nanostructuring, thereby increasing the probability of holes reaching the electrode/electrolyte interface. Significant improvements in the performance of hematite photoanodes have also been achieved by improving its conductivity through doping (e.g., with Mn, Sn, Ti, Si).[20-23] Finally, kinetics issues were resolved by depositing co-catalyst onto the surface of hematite (e.g., CoO_x , SnO_x , TiO_x , CoPi and IrO_2).[15, 24-28] These efforts are often combined in order to obtain an improved performance

in hematite photoanode. For example, in our previous manuscripts, we synthesized a Mn doped, core-shell, and nanorod-structured hematite in order to overcome the low conductivity, the sluggish kinetics, and the short hole diffusion length, respectively.[20, 24, 29] As a result, we obtained a factor of three improvements as compared to a bare thin film hematite. Despite the improvements observed, the exact mechanism of improvement behind all of the above-mentioned modifications is not clear. Understanding this will arguably bring us closer in achieving the theoretically predicted maximum solar-to-hydrogen conversion efficiency of hematite of 15%, assuming that all photons in the AM 1.5G solar spectrum that have energy larger than the energy bandgap of hematite can be collected and converted to the photocurrent.[30, 31]

6.1.1 IMPS theory

Intensity modulated photocurrent spectroscopy (IMPS) is a useful tool to study the surface kinetics of a photoelectrode by extracting the rate constants of charge transfer and recombination at the illuminated photoelectrode/electrolyte interface (Figure 6.1(a)). Semiconducting photoelectrodes generate electron-hole pairs under the illumination and those can easily be separated by built-in electric field within the depletion layer. Consequently, the photogenerated minority carriers move to the semiconductor/electrolyte interface, while the majority carriers transfer to the back contact. The photocurrent response of a semiconducting photoelectrode to a square pulse illumination is a combined effect of hole transfer and surface recombination (Figure 6.1(b)). In case of hematite, transient photocurrent is observed due to the sluggish water oxidation kinetics. Due to this sluggish kinetics, the holes accumulate significantly at the interface until they are eliminated by either charge transfer or surface recombination. The transient current is resulted from electron and hole contributions. The positive transients represent the accumulation of holes at the electrode/electrolyte interface without injection into the electrolyte. Similarly, negative transients in photocurrent were observed upon turning the light off which reflects the back reaction of conduction band electrons recombining with

the accumulated holes. In transient photocurrent spectra, the instantaneous photocurrent (J_{hole}) is the measured current just after the illumination which occurs due to the absolute value of photogenerated holes before recombination and the steady-state photocurrent (J_{ss}) corresponds to the amount of holes transferred to the electrolyte after recombination. The resulting hole transfer efficiency at photoelectrode/electrolyte interface is the ratio of steady state photocurrent (J_{ss}) to the instantaneous photocurrent (J_{hole}). We speculate that hole transfer and recombination reaction rates are pseudo first order rate constants, however the hole transfer efficiency can also be expressed in terms of the hole transfer (K_{tr}) and recombination (K_{rec}) rates

$$\eta_{tr} = \frac{k_{tr}}{k_{tr} + k_{rec}} \quad (6.1)$$

In IMPS technique, a small amplitude (10%) sinusoidal modulation of the light intensity about a DC value results in a change in phase and amplitude of the photocurrent. This photocurrent response of intensity modulated illumination as a function of frequency gives a semicircle in the complex plane as shown in figure 6.1(c). The first order rate constants K_{tr} and K_{rec} can be obtained by analysing the low frequency upper semicircle. The high and low frequency intercepts in the complex plane correspond to the steady state and instantaneous photocurrents. The high frequency intercept occurs at unity because the measured current is equal to the instantaneous current. The maxima of the semicircle give the radial frequency which is equal to the sum K_{tr} and K_{rec} , represent the exponential decay constant $(K_{\text{tr}} + K_{\text{rec}})^{-1}$ of the transient photocurrent. The high frequency response of IMPS (first quadrant) is attenuated by a RC time constant of the PEC cell, which arises from the series resistance of the FTO and the bulk of hematite nanorods. Further detailed explanations on the model and interpretation of IMPS measurements can be found in the literature.[32-34]

Figure 6.1. (a) Schematic of competition between charge transfer and recombination. k_{tr} and k_{rec} are the first order rate constants for charge transfer and surface recombination respectively. (b) Photocurrent transients measured under AM 1.5G 1 Sun illumination. (c) IMPS response shows a semicircle in upper quadrant which corresponds to the competition between charge transfer and recombination and semicircle in the lower quadrant due to the RC attenuation time constant of the hematite photoanode.

6.2 Results and Discussions

As mentioned above, we are interested in the improvement mechanism behind the photocurrent increase in hematite photoanodes. Specifically, Mn doping and the deposition of highly crystalline shell layer, which we have shown to significantly improve the photocurrent of our hematite nanorods,[20] are investigated. Figure 6.2 illustrates these improvements in the AM1.5 photocurrent-voltage characteristics. While our pristine hematite shows an AM1.5 photocurrent density of $\sim 0.5 \text{ mAcm}^{-2}$ at 1.23 V vs RHE and an onset potential of ~ 1.0 V vs RHE typical for an undoped hematite, either Mn doping

or core-shell modification similarly show twice as high photocurrent and cathodic shift of onset potential by ~200 mV.

Figure 6.2. Photocurrent-potential curve of pristine, Mn doped and core-shell hematite photoanodes measure under AM 1.5G (100 mWcm^{-2}) in 1M NaOH electrolyte solution.

We first characterize the structural properties of our samples with x-ray diffractometry (XRD) and scanning electron microscopy (SEM). The XRD patterns of the hydrothermally grown pristine, Mn doped and core-shell hematite photoanodes (Figure 6.3) have no significant difference and they can be indexed to the characteristic peaks of $\alpha\text{-Fe}_2\text{O}_3$ (JCPDS no. 003-0440).

Top and cross section view SEM images of all samples (Figure 6.4) show that the nanorods geometry is maintained, and the core-shell hematite has slightly larger nanorods radius, as expected.

Figure 6.3. XRD patterns of Pristine, Mn doped, and Core-shell hematite samples on FTO. The * denotes hematite (JCPDS 33-0664) and # denotes (FTO) SnO₂ (JCPDS 46-1088), respectively.

Figure 6.4. Top view of FESEM images (a) Pristine hematite, (b) Mn doped hematite and (c) Core-shell hematite photoanode.

Figure 6.5 (a) shows the UV-vis absorption spectra of pristine, Mn doped and core-shell hematite photoanodes, indicating that no distinct features can be observed between these samples. The optical indirect band gaps of all samples, extracted from Tauc's analysis (Figure 6.5 (b)), show a consistent value of 2.05 ± 0.02 eV. Overall, we observed no significant difference of structural and optical properties between the pristine, Mn doped and core-shell hematite photoanodes consistent with our previous reports,[20, 29] thereby ruling out

structural or optical effects as the cause of the observed photocurrent improvement.

Figure 6.5 (a). UV-Vis absorption spectra of pristine, Mn doped, and Core-shell hematite, (b) Indirect band gap energy extracted of pristine, Mn doped, and Core-shell hematite by using Tauc's analysis.

Photocurrent transient measurements were performed in order to observe the role of surface carrier dynamics at the pristine, Mn doped and core-shell hematite-electrolyte interface under 455 nm blue LED illumination (Figure 6.6). The applied potential was kept constant at 1.2 V vs RHE. The normalized photocurrent transient reduces for the Mn doped and core-shell hematite photoanodes as compared to the pristine sample, which indicates better charge injection efficiency to the electrolyte. Based on this data, it is, however, not possible to identify whether the enhancement for each samples come from the reduction of surface recombination, the improvement of charge transfer, or both. To understand the interplay between the photoactive charge transfer and surface recombination processes in these hematite samples, we measured their intensity modulated photocurrent spectroscopy (IMPS) response over a potential range of 0.6 V to 1.3 V vs. RHE. Here, we used blue LED ($\lambda = 455$ nm) as the light source with a 10% modulation amplitude. Figure 6.7 (a) shows the complex photocurrent spectra of pristine (black) and core-shell (red) hematite, taken at 1.0 V vs RHE.

Figure 6.6. Chopped normalized photocurrent-potential curve of pristine, Mn doped and core-shell hematite photoanode measure under blue LED illumination in 1 M NaOH electrolyte.

As explained above in the theory section, the low-frequency semicircle (upper quadrant) can be used to de-convolute the charge transfer and surface recombination rate constant. The smaller radius of the semicircle for the core-shell hematite as compared to the pristine one is consistent with the photocurrent improvement that we observed in the photocurrent-voltage curves (Figure 6.2).

We then calculated the charge transfer (K_{tr}) and surface recombination (K_{rec}) rate constants for the pristine and core-shell hematite at different potentials, as shown in Figure 6.7 (b) and (c). While both samples show relatively similar K_{tr} , the core-shell hematite has ~ 1 order of magnitude lower K_{rec} as compared to the pristine sample for the entire potential range. This observation indicates that the core-shell architecture is effective in improving the photocurrent by suppressing surface recombination, instead of increasing charge transfer. The surface of the pristine hematite consists of large number of surface states, which

act as recombination centers. Upon the deposition of highly-crystalline shell layer, these surface states are passivated, which in turn reduces the amount of surface recombination and improves the photocurrent. This is also consistent with our previous electrochemical impedance spectroscopy (EIS) results, where the core-shell hematite was shown to have a lower charge transfer resistance than the pristine hematite.[29] We proposed that charge transfer occurs via surface trap state for the pristine hematite and directly from the valence band for the core-shell hematite. This is again in agreement with our IMPS results, therefore validating our analysis and surface kinetics model.

We now turn our attention to the Mn doped hematite sample. The IMPS spectrum obtained at 1.0 V vs RHE for the Mn doped hematite is shown in Figure 6.7 (a) (blue). Similar to the core-shell hematite, the radius of the low-frequency semicircle (upper quadrant) of the Mn doped hematite is also decreased as compared to the pristine hematite. Based on the complex IMPS spectra, the potential dependent rate constants, K_{tr} and K_{rec} , for the Mn doped hematite were calculated (Figure 6.7 (b) & (c), blue). Figure 6.7 (b) shows that the Mn doped hematite shows higher 2-fold improvement of K_{tr} as compared to either pristine or core-shell hematite. This means that by introducing Mn into hematite, its surface hole transfer kinetics is improved. While this is rather unexpected, similar observation has also been reported in the case of Sn doped hematite.[35] In that report, Dunn et al. showed Sn-enrichment at the surface, which in turn improved the catalytic properties at the surface. To confirm if this is also the case in our Mn doped hematite, we performed Mn-depth profile measurement using secondary ion mass spectroscopy (SIMS), as shown in Figure 6.8 which shows the presence of Mn in the surface and bulk of hematite. We believe that this is the main reason behind the enhancement of hole transfer rate constant. The multivalent oxidation states of manganese possibly leads to a low (O-Mn-O) energy barrier for hole transfer, and improves the OER activity of hematite photoanode.[36]

Figure 6.7. (a) IMPS spectra of pristine, Mn doped and core-shell hematite samples observe at 1.0 V vs. RHE under blue LED ($\lambda = 455$ nm) illumination in 1M NaOH electrolyte solution. (b) Charge transfer rate constant K_{tr} of pristine, Mn doped and core-shell hematite samples as a function of potential. (c) Charge recombinations rate constant K_{rec} of pristine, Mn doped and core-shell hematite samples as a function of potential. (d) Transfer efficiency of pristine, Mn doped and core-shell hematite samples as a function of potential. The dashed lines in (b), (c) and (d) are intended to guide the eye.

In addition to the increased K_{tr} , the Mn doped hematite also shows lower K_{rec} as compared to the pristine hematite (Figure 6.7 (c)), despite still being higher than the core-shell hematite. We believe that this is simply a result of increased carrier concentration in Mn doped hematite, which shifts the Fermi level closer to the conduction band.[20] Upon contact with electrolyte, this results in a larger potential drop in the depletion layer. The distance between the Fermi level and the conduction band at the surface is therefore larger for a Mn doped

hematite, as compared to a pristine one. This corresponds to lower surface majority carrier concentration, which in turn decreases the recombination rate constant. Indeed, our ΔOCP measurement reveals a ~ 25 mV higher value for the Mn doped hematite, as compared to the pristine hematite. This value corresponds to a factor of ~ 2.5 -3 lower surface majority carrier concentration, which agrees well with the reduction of k_{rec} shown in Figure 6.7 (c). Figure 6.7 (d) shows the charge transfer efficiency ($K_{\text{tr}}/K_{\text{tr}}+K_{\text{rec}}$) as a function of potential for all the hematite samples: pristine, core-shell and Mn doped. Although the exact improvement mechanisms (i.e., the K_{tr} and K_{rec} values) for core-shell and Mn doped hematite are different, the overall charge transfer efficiencies are similarly improved as compared to the pristine hematite. This improvement is also consistent with the photocurrent improvement shown in the photocurrent-voltage curve (Figure 6.2), which further validates our IMPS measurement and analysis.

Finally, we note that the charge transfer efficiencies shown in Figure 6.7 (d) have reached a value of close to unity despite at high potential. However, at these potentials, the photocurrent is still much lower than the theoretical maximum. This means that the bulk properties of hematite are also limiting the performance for water oxidation. Future efforts on hematite, if one chooses to work on it, should focus on bulk modification and not only directed to the surface modifications.

Figure 6.8. Depth intensity (counts) profile of Mn (as a function of time) in the Mn doped hematite measured with Secondary Ion Mass Spectroscopy (SIMS).

6.3 Conclusions

In conclusion, we have analyzed the effect of Mn doping and core-shell architecture on the surface carrier dynamics of hematite. Surprisingly, doping with Mn results in a three-fold increase in the hole transfer rate constant. Despite doping being considered a bulk modification, the higher concentration of Mn at the surface of our hematite (as shown by SIMS measurement) also increases the catalytic activity. This observation has also been shown for Sn doping in hematite.[35] In contrast, the core-shell architecture does not affect the hole transfer rate constant; it instead reduces the surface recombination rate constant by a factor of ~ 5 . These different enhancements are the main reason for the observed increased AM1.5 photocurrent. Finally, we have demonstrated the capability of IMPS to analyze and provide insights into the surface carrier dynamics of photoelectrode materials for solar water oxidation.

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Chapter 7

Hematite-Perovskite Tandem Cells for Efficient Overall Solar Driven Water Splitting

Thermodynamically a photovoltage of 1.23 V is required to split water in to molecular hydrogen and oxygen, however, in practice an additional photovoltage of (0.4 to 0.6 V) is required to overcome the kinetics losses. It's a holy grail to extract this much photopotential from a single photoelectrode, so a tandem approach has been utilized whereas more than one photoabsorbers together provide the required photovoltage to split water without any external bias. In this chapter, we demonstrate a tandem cell containing hematite photoanode and a single solution processed organic-inorganic halide perovskite ($\text{CH}_3\text{NH}_3\text{PbI}_3$) solar cell, which can achieve overall unassisted water splitting with a solar to hydrogen conversion efficiency (STH) of 2.4%. Systematic electro optical studies were performed to investigate the performance of tandem device.

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7.1 Introduction

The growing demand for sustainable clean energy to combat the substantial use of fossil fuels has motivated the scientific community to find alternative ways of harnessing solar energy.[1] Photoelectrochemical (PEC) cells are attractive for storing solar energy in chemical bonds through cleaving of water into oxygen and hydrogen.[2, 3] The free energy change required to split one molecule of H_2O to H_2 and $\frac{1}{2} \text{O}_2$ under standard conditions (1.23 eV) as well as the kinetic barriers associated with oxygen and hydrogen evolution reactions, about 1.8 - 2.0V of solar generated photovoltage is necessary.[4-7] In general, this potential requirement could be attained from a semiconductor photoelectrode with appropriate valence and conduction bands illuminated by visible light. This approach involves a single semiconductor which absorbs two photons (S2) to generate a molecule of H_2 . Although, designing an S2 system which generates high photovoltage, while possessing appropriate energy levels to drive the water splitting reaction is challenging.[8] To generate higher photovoltage by increasing the bandgap of a semiconductor results in poor solar absorption and low photocurrents. These energetic limitations beside with the aqueous stability problem have not been efficiently met by a single semiconductor photoabsorber material.[8, 9] A more flexible approach comprises more than one absorber system which utilizes a total of 4 photons (D4) to realize solar water splitting. Such a tandem PEC system can consist of a photoanode/photocathode, photoelectrode/photovoltaic (PV) or photovoltaic (PV)/electrocatalyst design.[10-16] Due to the low operational voltages of conventional photovoltaic systems (Si, CuInGaS/Se), many of the D4 designs have required the series integration of several solar cells to generate the photopotential required for splitting water.[17-19] These complicated approaches require a careful balance of the optical absorption and photocurrent generation within each solar cell to drive the overall reaction efficiently.[20-22]

While designing a D4 system for efficient water splitting, the choice of the photoelectrode is critical. Hematite is an economically viable, aqueous stable

semiconductor with a suitable bandgap for catalyzing the oxygen evolution reaction using visible light.[23-26] The maximum solar-to-hydrogen conversion efficiency of hematite is predicted to be 15%.[26-28] However the short hole diffusion lengths and sluggish kinetics of hole injection, limit the performance of hematite.[5, 29] More critically, the position of its conduction band is not favorable for H_2 reduction; require an external bias to drive the complete water splitting reaction.[30, 31] A solar cell that can produce significant photovoltage and sufficient spectral mismatch with hematite is required to drive unassisted water splitting. Since Fe_2O_3 has a bandgap of 2.1 eV, the semiconductor utilized in the solar cell should possess a smaller bandgap for absorption in the red end of the solar spectrum and still be able to generate sufficient photovoltage.

In this chapter, we demonstrate a tandem cell comprises hematite photoanode and single organic-inorganic halide perovskite ($CH_3NH_3PbI_3$) solar cell for unassisted overall photoelectrochemical water splitting. Impressively, the open circuit voltages noted in these solar cells have been close to 1V (approaching its bandgap of 1.55eV), pointing to its excellent charge transport properties and low recombination rates.[32-34] Therefore an ideal way of performing unassisted water splitting using hematite photoanode can be realized by stacking the photoelectrode with a perovskite solar cell which has an extended optical absorption up to ~800 nm. The high open circuit voltage of perovskite solar cells can be exploited to drive water splitting by connecting hematite photoanode and perovskite solar cell in series. Here, we show a tandem device containing a single perovskite solar cell and core-shell/Mn doped hematite photoanode with a STH efficiency of 2.4%. We have employed cost effective solution processable fabrication methods (spin coating, hydrothermal method) to fabricate perovskite solar cells and nanostructured Mn doped hematite photoanodes. Mn doped hematite photoanode provides a higher photovoltage (0.85 V) which in series with the photovoltage of the perovskite solar cell (1.1 V) enables light driven water splitting in the absence of an external potential

bias. To the best of our knowledge, this is the highest efficiency achieved in a system incorporating a single solar cell and a Fe_2O_3 photoanode.

7.1.1 ISTC calculation:

The electric power generated by hematite photoanodes is further reduced by the conversion efficiency of the chemical reaction rate by the following equation;[35]

$$\eta_{cl} = \frac{1.23V_{RHE} \times \eta_F}{U_{Dark}} \quad (7.1)$$

Where η_F is Faradaic efficiency, which is nearly 100% for hematite photoanode and U_{Dark} is the potential applied in dark to reach the same current density as observed in light. The chemical reaction rate is 64 % and 60 % at the observed current density where $U_{dark} = 1.9$ and 2.07 V vs. RHE. Thus, the light-induced contribution to the chemical power produced by the photoanode is $64\% \times 0.82(\text{mWcm}^{-2}) = 0.52 \text{ mWcm}^{-2}$ for pristine hematite and $60\% \times 3(\text{mWcm}^{-2}) = 1.80 \text{ mWcm}^{-2}$ for core-shell/Mn doped hematite, which correspond to an ISTC efficiency of 0.52% and 1.80 % for pristine and Mn doped hematite respectively.

7.2 Results and discussion

Figure 7.1. (a) Schematic of the dual junction perovskite solar cell/ hematite photoanode tandem cell, (b) Current-Voltage curve of a perovskite solar cell-hematite photoanode tandem devices together under standard AM 1.5G irradiation, (c) I-t curve of tandem cell (TS2) in 1 M NaOH electrolyte under 1 Sun AM1.5G (100mWcm^{-2}) up to 120 sec and that of core-shell/Mn doped hematite photoanode measured at 1 V vs RHE (d) IPCE spectra of hematite photoanodes (pristine and core-shell/Mn doped) and perovskite solar cell at 1.1 V vs RHE and at short circuit condition respectively. Reprinted with the permission from [36]. Copyright 2015 American Chemical Society.

Figure 7.1(a) shows the schematic diagram of the tandem device, in which hematite photoanode connected externally in series with perovskite solar cell. We employed a mesoporous perovskite solar cell (See Appendix D, Figure D1) fabricated through double step procedure ($J_{\text{SC}}=17.72 \text{ mAcm}^{-2}$, $V_{\text{OC}}=1.11\text{V}$; $\text{FF}=0.53$; $\text{PCE}=10.5\%$) for tandem device. We synthesis pristine and core-shell/Mn doped hematite photoanodes (See Appendix D, Figure D2 and D3) of optimized thicknesses (pristine hematite $\sim 350 \text{ nm}$ and core-shell/Mn doped

hematite ~ 300 nm) for two tandem devices (TS1 and TS2), wherein they are coupled with the perovskite solar cell. An oxygen evolution catalyst (Co-Pi) was photoelectro-deposited on the hematite photoanodes to improve onset potential. The operating current density (J_{op}) of the tandem cells perovskite/pristine hematite (TS1) and perovskite/core-shell-Mn doped hematite (TS2) were calculated by the intersection point of the photocurrent densities of hematite photoanodes and perovskite solar cell with an active area of 0.12 cm^2 . [37] For accuracy in operating current density estimation, the J-V curves of perovskite solar cell were measured by placing the hematite photoanode in front of the solar cell to account for optical absorption by the hematite photoanodes as shown in Figure 7.1(a).

The operating current densities of the distinct constituents and together in tandem have been calculated by the intersection point of two photocurrent densities curves. The estimated operating current density value in detached component measurements are 1.33 mA cm^{-2} and 2.33 mA cm^{-2} for perovskite/pristine hematite and perovskite/core-shell-Mn doped hematite respectively (Appendix D, Figure D4), whereas in tandem configuration the operating current densities are 1.21 mA cm^{-2} and 1.93 mA cm^{-2} for perovskite/pristine hematite (TS1) and perovskite/core-shell-Mn doped hematite (TS2) respectively (Figure 7.1(b)). The trivial inconsistency between these two measurements can be attributed to the losses inside the PEC cell and electrolyte. The fill factor of the perovskite solar cell in the tandem structure increases from 0.55 to 0.62 and 0.68 for TS1 and TS2 devices respectively. The PEC performance of the tandem devices and hematite photoanodes were tested in 1M NaOH electrolyte without any external bias in the two electrode configuration (Figure 7.1(c)) under chopped illumination (AM 1.5G 100 mW cm^{-2}). The current density nearly matches J_{op} extracted from Figure 7.1(b).

The solar to hydrogen conversion efficiency has been calculated using the equation; [27]

$$\eta_{STH} = \left(\frac{J_{op} \times 1.23 \times \eta_F}{P_{Solar}} \right) \quad (7.2)$$

where J_{op} is the operating current density (mAcm^{-2}), η_F is the Faradaic efficiency (preliminarily assumed to be 100%) and P_{Solar} is the irradiance intensity of 100 mWcm^{-2} (AM1.5G). The solar to hydrogen efficiencies (STH) were calculated to be 1.5% and 2.4% for pristine hematite/perovskite solar cell (TS1) and core-shell-Mn doped hematite/perovskite solar cell (TS2) respectively.

To figure out the opto-electrical limitations in tandem devices, transmittance of hematite photoanodes has been measured to examine the remaining spectrum available for perovskite solar cell. The spectral response of pristine and core-shell/Mn doped hematite photoanodes were suitably matched with the reported hematite energy band gap ($\sim 2 \text{ eV}$). Incident photon to current conversion efficiency (IPCE) of every component in tandem cell plays an important role in understanding the opto-electrical limitations and device performance. IPCE of hematite photoanodes were measured at 1.1 V vs RHE and at short circuit condition for perovskite solar cell (Figure 7.1(d)). IPCE can be expressed using the following equation:[4, 38]

$$IPCE (\%) = \left(\frac{1240 \times I_{Ph}}{\lambda \times J_{Light}} \right) \times 100 \quad (7.3)$$

Where I_{Ph} is the measured photocurrent density at a particular wavelength, λ is the wavelength of incident light, and J_{Light} is the measured irradiance at a specific wavelength. The incident solar spectrum on the perovskite solar cell can be determined by multiplying the standard solar photon flux with the measured transmittance of hematite photoanodes (Figure 7.2).

Figure 7.2.(a) Standard solar AM 1.5 G photon flux and incident photon flux for solar cell calculated by multiplying the standard photon flux by the transmittance of the hematite. The shaded areas are electron flux from pristine hematite and Perovskite solar cell used to calculate the integrated photocurrent density of hematite photoanodes. (b) Standard solar AM 1.5 G photon flux and incident photon flux for solar cell calculated by multiplying the standard photon flux by the transmittance of the core-shell/Mn doped hematite. The shaded areas are electron flux from core-shell/Mn doped hematite and Perovskite solar cell used to calculate the integrated photocurrent density of hematite photoanodes. Reprinted with the permission from [36]. Copyright 2015 American Chemical Society.

Electron flux of each light absorber can be calculated by multiplying the incident spectral response with its measured IPCE value. The integrated current density values of the individual pristine hematite/Perovskite and core-shell-Mn doped hematite/Perovskite device configurations are 1.40 mAcm^{-2} / 4.56 mAcm^{-2} and 1.95 mAcm^{-2} / 8.13 mAcm^{-2} respectively. These results shows that the optical absorption in hematite photoanode does not constrain the photocurrent generated by the perovskite solar cell, however there is an overlap in the optical absorption of hematite and perovskite solar cell in the tandem device. Additionally, the lower optimized thickness of the core-shell-Mn doped hematite further diminishes the constraints on the photocurrent of perovskite solar cell. In order to calculate the Faradaic efficiency of the tandem device, gas evolution experiment was carried out in a twin PEC reactor under 1 Sun AM 1.5 G (100 mW cm^{-2}) illumination. This gas evolution experiments confirm that the photocurrent generated is converted to O_2 and H_2 at respective electrodes. We have measured the evolved gases from the tandem cell (TS2)

continuously up to 8 hrs. The amount of evolved H_2 and O_2 with time is shown in Figure 7.3 while the inset shows the measured photocurrent during the gas evolution measurement. The theoretical amounts of evolved gases has been calculated by integrating the photocurrent with time while considering that the O_2 and H_2 evolution reactions are four and two electron reactions respectively (straight lines in Figure 7.3). The measured amount of gases suitably matched with the theoretical predicted values with a small deviation of 5 and 7% for O_2 and H_2 respectively. The Faradaic efficiency is nearly 100 % for our tandem device based on the evolved gases, which matches previous reports.[20, 39] The gas evolution experiment was performed in air (with high humidity 60~80% based on Singapore weather) upto 8 hrs, therefore the performance of perovskite cell decay and the photocurrent of tandem cell dropped by 25%.

Figure 7.3. Faradaic efficiency measurement for tandem device TS1. Red and black symbols correspond to the O_2 and H_2 gases measured by gas chromatography while the black and red lines correspond to the integration of the photocurrent with respect to time. Inset shows the photocurrent measured during the gas evolution. Reprinted with the permission from [36]. Copyright 2015 American Chemical Society.

The poor stability of perovskite solar cell is well known. However, the stability can be improved by proper lamination and also improved by hematite control. Perovskite solar cell is just an external voltage source here that can be replaced

by another type of solar cell like GaAS or multijunction Si solar cells. The only advantage of perovskite is high open circuit voltage. Finally, hematite is the most stable photoanode and can survive at any environment. Our results clearly indicate that the hematite/perovskite solar cell tandem devices are able to perform light induced water splitting without any external applied bias. An unassisted water splitting system requires a total voltage of about ~1.8 to 2.0 V for efficient water splitting. However, the perovskite solar cell generates about 1.1 V of photovoltage, while the remaining photovoltage providing from the hematite photoanode. To evaluate the performance of our hematite photoanodes, the intrinsic solar to chemical conversion efficiency (ISTC) has been calculated based on a previous report.[35] In order to calculate ISTC of hematite photoanode, current-potential measurement has performed in three-electrode configuration with 1M NaOH electrolyte solution (pH 13.6) under dark and illumination. The photocurrent is calculated by the difference between light and dark currents i.e., $J_{\text{photo}} = J_{\text{L}} - J_{\text{D}}$ and the photovoltage is simply the potential difference between the light current and the dark current, as shown by the arrows in Figure 7.4. The photocurrent density is 1.7 mAcm^{-2} at 1.23 V vs. RHE for pristine hematite photoanode and 3.5 mAcm^{-2} for core-shell/Mn doped hematite. To obtain the intrinsic power to chemical conversion efficiency of pristine hematite and core-shell/Mn doped hematite photoanodes, the intrinsic photovoltaic power of the hematite photoanodes were derived by the product of their photocurrent and photovoltage and multiplied by the chemical conversion rate (See the calculation above). The intrinsic photovoltaic power density reaches a maximum of 0.82 mWcm^{-2} at a potential of 1.22 V vs. RHE for pristine hematite and 3.0 mWcm^{-2} at a potential of 1.3 V vs. RHE for Mn doped hematite (Figure 7.5 (a) and (b)). This corresponds to the electrical power conversion efficiency. However, the photoanode performs chemical work by splitting water in order to produce oxygen and electrons at the back contact for hydrogen generation. Thus the total power to chemical conversion efficiency or intrinsic solar to chemical conversion efficiency (ISTC) of hematite photoanode can be calculated by using the following equation;[35]

$$ISTC = \frac{1.23(V_{RHE})}{V_{dark}(V_{RHE})} \left[\frac{J_{photo}(mAcm^{-2}) \times V_{photo}(V)}{100(mWcm^{-2})} \right]_{AM1.5G} \quad (7.4)$$

where J_{photo} and V_{photo} are the photocurrent and photovoltage, while V_{dark} is the potential that need to be applied on the photoanode to reach the respective current.

Figure 7.4. Photocurrent – voltage curve of hematite photoanodes (pristine and Mn doped) in 1M NaOH electrolyte (pH 13.6) under 1 sun irradiation AM 1.5G (100 mWcm^{-2}). Reprinted with the permission from [36]. Copyright 2015 American Chemical Society.

We have examined the Faradaic efficiency of hematite photoanodes from gas evolution experiment, which is nearly 100% for both pristine hematite and Mn doped hematite photoanodes. The ISTC efficiency of the individual photoanode reaches a maximum of 0.52% at a photocurrent density of 1.62 mAcm^{-2} (at 1.22 V vs. RHE) for pristine hematite and 1.80% at a photocurrent density of 3.82 mAcm^{-2} (at 1.3 V vs. RHE) for core-shell/Mn doped hematite photoanode (Figure 7.5 (c) and 7.5 (d)). Meanwhile, the onset potentials of the hematite photoanodes are not favorable, consequently the operating point of our tandem system does not coincide with the ISTC maxima.

By examining the photocurrent-potential curves (Figure 7.4(a)), it is possible to extract the photovoltage generated by hematite. In the dark condition, hematite anodes would have to be biased to a higher potential of 1.92 V vs. RHE and 2.07 V vs RHE to produce the same photocurrent as at 1.22 V vs RHE for pristine hematite and 1.29 V vs RHE for core-shell/Mn doped hematite. This clearly shows that illumination generates a photovoltage of 0.7 V (1.92-1.22V) in the pristine hematite photoanode and 0.77 V (2.07-1.3V) in the core-shell/Mn doped hematite photoanode. These photovoltages in series with the photopotential generated by the perovskite solar cell (1.1V) leads to efficient unassisted water splitting. We have shown the role of Mn doping with hematite photoanode in previous chapter.

Figure 7.5. (a) The intrinsic power characteristics of pristine hematite photoanode, (b) The intrinsic power characteristics of core-shell/Mn doped hematite photoanode, (c) Intrinsic solar to chemical conversion efficiency (ISTC) of pristine hematite photoanode, and (d) Intrinsic power to chemical conversion efficiency of core-shell/Mn doped hematite photoanode. Reprinted with the permission from [36]. Copyright 2015 American Chemical Society.

7.3 Conclusion

We have demonstrated an efficient, stable, cost effective and simple water splitting D4 tandem PEC-PV cell with a STH efficiency of 2.4% by connecting core-shell/Mn doped hematite photoanode ($E_g = 2.05$ eV) and a single perovskite solar cell ($E_g = 1.55$ eV) in series. Systematic electro optical studies were performed to investigate the performance of tandem device. The photovoltage, internal photovoltaic power characteristics and the intrinsic solar to chemical conversion efficiency of hematite photoanodes have been extracted by linear scanning voltammetry curves under dark and illumination. The high open circuit voltages (1.1 V) generated by the perovskite solar cell in series with an efficient hematite photoanode resulted in unassisted light induced water splitting. Currently, the performance of the tandem system is limited by the low photocurrents and high onset potential generated by hematite photoanode.

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Chapter 8

Conclusion and Future Outlook

This chapter provides an overview of my research outcomes. A cost effective and ecofriendly path has been adopted to synthesize highly performing hematite photoanodes for photoelectrochemical water splitting. I have addressed the low conductivity issue of hematite by manganese doping and surface recombinations by core-shell structure. Finally, I have combined both of these strategies together and fabricated an efficient core-shell/Mn doped hematite photoanode. I demonstrated unassisted overall water splitting from hematite based tandem system with a solar to hydrogen conversion efficiency of 2.4%; first of its kind in literature. Finally, this chapter also delivers further insights to future work on hematite photoanodes.

In chapter 4, I have fabricated the pristine and Mn doped hematite nanorods by using a solution processed hydrothermal method. 5 mol % Mn precursor doping was found to be optimum quantity to enhance the photocurrent density by 3 times at 1.23 V vs. RHE and also in reducing the onset potential by 30 mV compared to the pristine hematite. A decrease in PEC performance was observed for 10% Mn whereas no effect was observed with 1% and 2% Mn. The enhancement in current density was attributed to increase in charge carrier density as estimated by Mott-Schottky analysis. Although, Mott-Schottky measurement is applicable on flat surface samples but a relative comparison can be made for nanostructured samples. Chronoamperometry studies also showed that a decrease in transient current for Mn doped samples as compared to pristine hematite. These results indicated the beneficial effects of Mn doping which is responsible for the suppression in electron-hole recombination and reduction in energy barrier for hole transport.

The surface passivation of hematite photoanode was performed by developing a core-shell structure discussed in chapter 5. The core-shell hematite photoanode delivered a photocurrent density of 1.2 mAcm^{-2} , at 1.23 V vs. RHE, which is nearly 2 times higher as compared to pristine hematite. In order to determine the charge separation and surface catalytic efficiency, a hole scavenger (0.5 M H_2O_2) was employed. The core-shell hematite demonstrated a two fold increase in both charge separation and surface catalytic efficiency. Finally, EIS measurements revealed the beneficial effects of surface layer (shell), in particular the passivation of surface states and consequent charge injection through the valence band rather than through the surface states. Even though Mn doped and core-shell hematite samples delivered nearly similar photocurrent density enhancement, IMPS results demonstrate that the reason of this enhancement is different for both samples. IMPS study showed a threefold increase in the rate of hole-transfer in Mn doped hematite, whereas a fivefold decrease in charge recombination rate was observed in core-shell hematite photoanode, as compared to pristine hematite.

Finally, we further optimized and combined both strategies (Mn doping and core-shell) together to understand the contribution of each strategy. The core-shell/Mn doped hematite sample shows superior PEC activities in comparison of only Mn doped or core-shell structure hematite photoanodes. The core-shell/Mn doped hematite demonstrated a high photocurrent density of 1.65 mAcm⁻² at 1.23 V vs RHE, which is higher than the Mn doped hematite (1.45 mAcm⁻² at 1.23 V vs RHE) and core-shell hematite photoanode (1.15 mAcm⁻² at 1.23 V vs RHE) (Figure 8.1).

Figure 8.1. Photocurrent-potential curve of pristine, Mn doped, core-shell and Mn doped/core-shell hematite photoanodes measure under AM 1.5G 100 mWcm⁻² in 1M NaOH electrolyte solution.

The electrochemical impedance spectroscopy study of pristine, Mn doped, core-shell and core-shell/Mn doped hematite photoanodes were carried out to understand their charge transfer dynamics. The Nyquist plots of core-shell/Mn doped hematite obtained at 1.23 V vs RHE, clearly show the smallest semicircle as compared to Mn doped and core-shell hematite photoanodes (Figure 8.2 (a)). The Nyquist plots obtained (Figure 8.2 (a)) indicate different charge transfer mechanism for pristine, Mn doped and core-shell and core-shell/Mn doped hematite samples (Figure 8.2 (a)). As we have discussed earlier in chapter 5, the fitted data revealed different processes governing the performance of pristine and core-shell systems. The equivalent circuits employed for the fitting are presented in Appendix C. The pristine and Mn doped samples follow the trend corresponding to a charge transfer through surface states, whereas core-shell and core-shell/ Mn doped hematite samples exhibit a charge transfer through the valence band. The difference in the performance can be explained when the total resistance for the respective charge transfers ($R_s + R_{trapping} + R_{ct, trap}$ for pristine and Mn doped hematite and $R_s + R_{ct, VB}$ for core-shell and core-shell/Mn doped) are plotted (Figure 8.2(b)). The lower total charge transfer resistance results in a higher photocurrent. Therefore, we conclude that the charge transfer process in the core-shell and core-shell/Mn doped hematite samples is predominantly occurring through the valence band, which is most likely due to the passivation of the surface states. The higher charge transfer capacitance value of Mn doped hematite clearly indicates that more holes are reaching to the surface as compared to the pristine hematite photoanode (Figure 8.2 (c)). Therefore, Mn doped sample exhibit a higher photocurrent than the pristine hematite. The core-shell/Mn doped hematite sample showed better charge transport at electrode/electrolyte interface in comparison with Mn doped and core-shell hematite photoanodes because of the combined effect of bulk as well as surface modification.

Figure 8.2. (a) Nyquist plots of pristine, Mn doped, core-shell and core-shell/Mn doped hematite photoanodes measured at 1.23 V vs RHE in 1M NaOH electrolyte solution, (b) Plots of equivalent circuit parameters $R_{ct, trap}$ and C_{trap} obtained from fitting of EIS data under the illumination of 1 sun light, and (c) R_{total} values determined by the EIS fitting, where resistances associated with charge transfer.

The charge injection and surface catalysis efficiency of the pristine, Mn doped, core-shell and core-shell/Mn doped hematite photoanodes were further examined by utilizing a hole scavenger (0.5M H₂O₂) along with the 1M NaOH electrolyte solution. As we have discussed in chapter 5, this measurement relies on the hole scavenger eliminating surface recombination, thus allowing bulk recombination phenomena to be evaluated. By comparing the photocurrents with H₂O₂, H₂O and the theoretical photocurrent, the surface recombination can also be estimated (see Appendix C). The analysis yields (i) charge separation efficiency which is the yield of photogenerated holes arriving on the hematite surface, as well as (ii) surface catalysis efficiency which estimates the hole injection into the electrolyte. Due to the facile oxidation of the hole scavenger, photocurrent transients under chopped illumination disappear and pure Faradaic photocurrents are observed in the complete potential range for all hematite samples (See Appendix C, Figure C4) The charge separation and surface catalysis efficiency of pristine, Mn doped, core-shell and core-shell/Mn doped hematite samples were calculated (Figure 8.3 (a) and (b)). The charge separation efficiency rise from a potential anodic to the flat band potential reaching 22%, 41%, 72%, and 81% at 1.23 V vs RHE for pristine, core-shell,

Mn doped, and core-shell/Mn doped hematite, respectively (Figure 8.3 (a)). This increase with applied voltage is because of the widening of the space charge layer. The higher charge separation efficiency of Mn doped and core-shell/Mn doped hematite photoanodes with respect to the pristine ones indicate that a larger fraction of photo-generated holes reach the surface of the treated nanorods indicating better charge transport/ lower bulk recombination. This is a clear evidence that Mn improves the bulk transport properties, which may arise because Mn doping donates electron to the hematite. Concurrently, the surface catalysis efficiency is 41%, 66%, 56% and 72% at 1.23 V vs RHE for pristine, core-shell, Mn doped, and core-shell/Mn doped hematite respectively (Figure 8.3(b)) indicating that a larger fraction of holes are injected into the electrolyte for core-shell structured samples. Both observations (better hole transport and injection) show that the Mn doping improves the bulk properties and core-shell structure passivate the surface defects which eventually improves the overall quality of the hematite photoanode.

In chapter 7, a solution processed perovskite solar cell in tandem with CoPi treated core-shell/Mn doped hematite was utilized for unassisted overall water splitting. I have successfully demonstrated a stable and cost effective water splitting tandem PEC-PV cell with a STH efficiency of 2.4%. The high open circuit voltages (1.1 V) generated by the perovskite solar cell in series with an efficient hematite photoanode resulted in unassisted light induced water splitting. Currently, the performance of the tandem system is limited by the low photocurrents and high onset potential produced by hematite photoanode. This will provide a scope for further enhancement in the STH efficiency.

Figure 8.3. (a) Charge separation efficiency of pristine, core-shell, Mn doped, and core-shell/Mn doped hematite photoanodes for water oxidation, and (b) Surface catalysis efficiency of pristine, core-shell, Mn doped, and core-shell/Mn doped hematite for water oxidation.

Future work on hematite photoanodes

In this report, I have mentioned the two techniques to tackle bulk and surface recombination in hematite which are the main limiting factors for the performance. Although an appreciable performance was achieved using Mn doping and core-shell structural modification, the efficiency could still be increased further to its theoretical maximum. This could be achieved by persistent efforts in tackling the recombination mechanisms through multi-pronged approach in synthesis procedures. Hereby, I propose a few approaches which comprise of modifying the intrinsic properties of hematite and coupling it with materials with suitable band alignment, which could enhance the charge separation and transport efficiency.

1. Bulk conductivity of hematite photoanode

Hematite performance for PEC water splitting has been limited by poor carrier conductivity although different doping elements have been used in literature to overcome the conductivity issues.[1-6] We have successfully demonstrated the beneficial effect of Mn doping in hematite nanorods. The incorporation of Mn^{4+}

seemed to increase the carrier density of hematite and improve its bulk transport properties. This increase in carrier density can potentially shift the Fermi level towards the conduction band and increase the band bending at the semiconductor/electrolyte interface, which could enhance the charge separation. Mn doping further reduce the energy losses due to the internal resistance of bulk hematite. However, after Mn doping, we still need high temperature annealing to attain the better PEC performance from hematite photoanode. This high temperature annealing is used to incorporate the Sn into hematite lattice from FTO substrate. Based on this research, I would recommend applying the solution processed Mn doping for different photoanode materials because of its beneficial OER activity and stability. The doping concentration need to be controlled precisely to reduce the bulk defects and obtain the decent PEC performance, so one can also try more controlled synthesis processes like; pulsed laser deposition (PLD) and atomic layer deposition (ALD). The gradient doping would also be beneficial to built-in voltage at the surface of electrode which will help in charge separation.

I would also recommend to working on n-type of dopants (especially Sn^{4+}), with similar ionic radius with hematite to enhance the optical and electrical properties while avoiding defects associated with lattice strains or phase separations. I would recommend to employ the Sn^{4+} dopant because the size of Sn^{4+} (0.69 Å) cation is similar to Fe^{3+} (0.65 Å) cation. The incorporation of Sn^{4+} ions can also enhance the electrical as well as optical properties.

2. Surface Passivation strategies

After improving the carrier conductivity by manganese doping, I have focused on surface dynamics of hematite photoanode. The slow kinetics is one of the main limiting factors in hematite photoanodes. A major part of the photogenerated holes recombine with the surface states or electrons present in conduction band, instead of performing water oxidation reaction at electrode/electrolyte interface. These surface states can be passivated with

highly crystalline overlayers, while the kinetics of hole transfer can be improved by integrating an oxygen evolution catalyst on the surface of hematite. We have demonstrated a highly crystalline Fe_2O_3 overlayer on hematite photoanode, which can passivate the surface defects and enhance the PEC performance. However, the precise control on overlayer thickness and conformity is crucial in spray pyrolysis technique because of manual operation. For the future work on surface passivation layers, I would recommend to use a more controlled technique such as atomic layer deposition (ALD), which can control the conformity, thickness and crystallinity of overlayer. These overlayers would not restrict the light absorption of hematite photoanode and also help in surface states passivation. The overlayer thickness, crystallinity and conformity are the main important factors, so one should optimize all of these parameters to obtain the best performance.

3. Further scope in synthesis procedure:

The annealing temperature plays a crucial role in the performance of hematite because it enhances electrical conductivity and crystallinity. As we have discussed earlier, the low carrier conductivity problem in hematite can be tackled by elemental doping. But even after elemental doping in hematite, we need high temperature annealing to get a decent PEC performance. Hematite nanostructures grown on Fluorine doped tin oxide (FTO) glass requires high-temperature post annealing at 750-800°C to allow Sn^{4+} incorporation from FTO to hematite electrodes to perform water splitting efficiently. However, this is accompanied by deformation/brittleness of the substrate, increased series resistance and coarsening of nanostructures. On the other hand, lower post annealing temperature allows the sheet resistance of FTO to remain low (84.0 Ωcm^{-2} for 650°C annealing; 685.8 Ωcm^{-2} for 800°C annealing, Figure 8.4). The lowered resistances of the hematite bulk and FTO together enable more of the applied external voltage to drop across the semiconductor-electrolyte interface. This additional voltage increases the depletion layer width, collects more photogenerated holes and improves water-splitting performance. The effect of

the reduced resistance is also observed in the cathodic shift of dark current onset potential (Figure 8.4(b)) There are few reports of intentionally added Sn into hematite to reduce the sintering temperature, although the value of sintering temperature was still high i.e 650°C.[1, 7]

Figure 8.4 (a) Nyquist plots and (b) J-V curves of hematite samples annealed at 650 °C (red), 750 °C (blue), and 800 °C (black), measured in 1 M NaOH electrolyte solution. Samples annealed at 650 °C, 750 °C and 800 °C; show series resistance values 84.0 Ωcm^{-2} , 160.1 Ωcm^{-2} and 685.8 Ωcm^{-2} respectively.

This annealing temperature can be further reduced by employing underlayer and overlayer of SnO_2 because during the sintering process, these layer can easily diffuse from both side into hematite lattice and enhance the conductivity of hematite. Another approach is to synthesize high quality in-situ Sn doped hematite for better photoelectrochemical water splitting.

4. Band overlap:

Moreover, the unsuitable conduction band minima of hematite with respect to water redox level is again hurdle for overall water splitting, which cause high onset potential. We seriously need to look some alternative iron based materials like Fe_2TiO_5 , Fe_2SnO_5 etc., which should also be robust, highly stable, good carrier conductors and highly efficient for water splitting. Although our group has published a series of papers on Fe_2TiO_5 . [8, 9] More importantly, the energy band gap should not be more than 2.2 eV because again it limits the maximum solar to hydrogen conversion efficiency. Further, these materials with higher

conduction band could be coupled with hematite to facilitate better charge separation and transport. Such heterojunctions with complementary properties could lead us to efficient PEC devices.

5. Limitations in the hematite/perovskite tandem cell

The late onset potential of hematite photoanode requires additional bias to achieve the maximum photocurrent, which generally occurs due to its slow kinetics. To perform overall unassisted water splitting, a photovoltage of 1.6-1.8 V is required. Perovskite solar cell generates decent open circuit voltage (1.1 V), which is sufficient for a series connected tandem cell with hematite (0.6-0.7 V) photoanode. However, the perovskite solar cell suffers from the stability issue because of moisture. The PV-PEC tandem cell configuration has been studied widely but the performance of this configuration is limited because of low photovoltage/photocurrent generated by photoelectrodes. Finally, one needs to synthesize an efficient electrocatalyst for OER/HER, which can produce higher current with lower overpotential and connect them in series with multi-junction solar cell. Most importantly, a tandem cell should generate minimum 10% solar to hydrogen conversion (STH) efficiency for economically viable hydrogen economy.

6. Scale up of hematite photoanode

We have discussed earlier that the hematite grown on Fluorine doped tin oxide (FTO) glass substrate requires high-temperature post annealing at 750-800°C to allow Sn^{4+} incorporation from FTO to hematite electrodes even after elemental doping to perform water splitting efficiently. This is accompanied by a high series resistance at the back contact which could inhibit the transport of electrons to the contact point. Since large area hematite samples introduce more resistance in the path of electrons, the multiple contacts on FTO in series and parallel are one way to resolve this problem to some extent. I would also recommend using metal foil (especially iron foil) to grow hematite nanostructures. By using this method, one can completely remove the additional resistance which occurs due to the annealing as well as from large area samples.

I hope above mentioned future outlooks will provide a new direction to work on hematite photoanodes.

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Appendix A: Introduction

Figure A1. Photoelectrochemical (PEC) cell contains Fe_2O_3 working electrode, platinum counter electrode and an Ag/AgCl reference electrode with 1 M NaOH electrolyte solution.

Figure A2. Schematics of water redox reactions on n-type and p-type photoelectrode in Photoelectrochemical cells.

Figure A3. Schematics of tandem cells configurations for overall unassisted water splitting, (a) Photocathode-photanode tandem cell, (b) PEC-PV tandem cell and (c) EC-PV tandem configuration.

Appendix B: Pristine and Mn Doped Hematite

Nanorods for PEC Water Splitting

Figure B1. XPS survey scan of pristine and Mn-doped hematite nanorods grown on FTO.

Figure B2. UPS data of pristine hematite (inset) and Mn doped hematite taken at -10V bias. Work function was obtained by subtracting the width of secondary cut off to the expected Fermi level. Charging was checked by referencing C 1s of carbon using XPS. Note: The E_F is not the indicated line as shown.

Figure B3. Photocurrent-potential curve of pristine hematite photoanode, 5% and 10% Mn treated hematite measure under AM 1.5G (100 mWcm^{-2}) in 1M NaOH electrolyte solution

Figure B4. Band diagram and charge transfer schematics of (a) pristine, (b) Mn doped hematite.

Appendix C: A Systematic Charge Kinetics Study of Core-Shell Hematite Photoanode for Photoelectrochemical Water Splitting

1. Charge separation and surface catalysis efficiency calculation:

To understand the charge dynamic of pristine and core-shell hematite photoanode a hole scavenger (0.5 M H_2O_2) has been employed with 1 M NaOH electrolyte. The overall water splitting photocurrent can be described by the following equations;

$$J_{\text{H}_2\text{O}} = J_{\text{absorption}} \times \eta_{\text{Charge Separation}} \times \eta_{\text{Surface Catalysis}} \quad (1)$$

Where $J_{\text{absorption}}$ is the photocurrent density corresponding to rate of photon absorption, $\eta_{\text{separation}}$ is the charge carrier separation efficiency and $\eta_{\text{surface catalysis}}$ is water oxidation efficiency at photoanode surface. $J_{\text{absorption}}$ has been calculated by multiplying the absorption spectrum with AM 1.5 G standard spectrums, followed by integration over visible wavelength region as described in equation below.

$$J_{\text{absorption}} = \int_{\lambda_2}^{\lambda_1} \text{Absorption spectrum} \times \text{AM 1.5G spectrum} \quad (2)$$

When a hole scavenger (H_2O_2) was added in electrolyte, as a result all holes which reach the electrode/electrolyte interface participate in water oxidation ($\eta_{\text{Surface Catalysis}} = 1$) consequently the fraction of photocurrent that participates in water oxidation followed the equation below;

$$J_{\text{H}_2\text{O}_2} = J_{\text{absorption}} \times \eta_{\text{charge separation}} \quad (3)$$

Thus, we can easily calculate the charge separation efficiency and surface catalysis efficiency based on equations 1,2,3 as equations below;

$$\eta_{\text{charge separation}} = \frac{J_{\text{H}_2\text{O}_2}}{J_{\text{absorption}}} \quad (4)$$

$$\eta_{\text{surface catalysis}} = \frac{J_{\text{H}_2\text{O}}}{J_{\text{H}_2\text{O}_2}} \quad (5)$$

Figure C1. EDX line scan measured at the interface of nanorods (core) and shell hematite sample, inset is showing the core-shell nanorods with a line scan.

Figure C2. EDX line scan of the pristine hematite nanorods sample along the diameter, inset is shows the pristine hematite nanorods with the location of the EDX line scan.

Figure C3. APCE action spectrum of pristine hematite and core-shell hematite calculated from IPCE.

Figure C4. Chopped photocurrent-potential curve of pristine hematite photoanode and core-shell hematite photoanode in 0.1 M H₂O₂ and 1M NaOH electrolyte under 1 sun illumination (100mW cm⁻²) Include arrow to show light on and off

Figure C5. Nyquist plots of pristine and core-shell hematite measured at pH 13.6 at 1.5 V vs RHE under 1 sun illumination.

Figure C6. (a) Equivalent circuit for charge dynamics of pristine hematite sample, showing the charge transfer from surface states to the electrolyte. (b) Equivalent circuit for charge dynamics of core-shell hematite sample, showing the charge transfer from valance band to the electrolyte. Band energy schematics of the charge transfer from the hematite to the electrolyte for the case of (c) pristine hematite and (d) core-shell hematite.

Figure C7. The SAED pattern of pristine hematite has been taken from [001] zone axis.

Appendix D: Hematite-Perovskite Tandem Cells for Efficient Overall Solar Driven Water Splitting

Figure D1. Cross-sectional image of perovskite solar cell (SC) employed in this study.

Figure D2 (a) FESEM surface morphology of pristine hematite photoanode and (b) FESEM surface morphology of Mn doped hematite photoanode.

Figure D3. Image of Mn doped sample and pristine sample.

Figure D4. Current-Voltage curve of a perovskite solar cell and hematite photoanodes measured separately under standard AM 1.5G irradiation.

List of Publications

- **Gurudayal**, Sing Yang Chiam, Mulmudi Hemant Kumar, Prince Saurabh Bassi, Hwee Leng Seng, James Barber and Lydia Helena Wong; “Improving the efficiency of hematite nanorods for photoelectrochemical water splitting by doping with manganese”; ACS Appl. Mater. Interfaces, 2014, 6 (8), pp 5852–5859
- **Gurudayal**, Chee, P. M., Boix, P. P., Ge, H., Yanan, F., Barber, J., Wong, L. H., “Core–Shell Hematite Nanorods: A Simple Method To Improve the Charge Transfer in the Photoanode for Photoelectrochemical Water Splitting”, ACS Appl. Mater. Interfaces 2015, 7 (12), 6852-6859.
- **Gurudayal**, Sabba, D., Kumar, M. H., Wong, L. H., Barber, J., Grätzel, M., Mathews, N., “Perovskite–Hematite Tandem Cells for Efficient Overall Solar Driven Water Splitting”, Nano Lett. 2015, 15 (6), 3833-3839
- Prince Saurabh Bassi, **Gurudayal**, Lydia Helena Wong and James Barber; “Iron based photoanodes for solar fuel production”; *Phys. Chem. Chem. Phys.*, 2014, 16, 11834-11842
- Prince Saurabh Bassi, Sing Yang Chiam, **Gurudayal**, James Barber and Lydia Helena Wong; “Hydrothermal Grown Nanoporous Iron Based Titanate, Fe₂TiO₅ for Light Driven Water Splitting”; ACS Appl. Mater. Interfaces, 2014, 6 (24), pp 22490–22495
- **Gurudayal**, Donghyuk Jeong, Kyoungsuk Jin, Hyo-Yong Ahn, Pablo P Boix, Fatwa F. Abdi, Nripan Mathews, Ki Tae Nam, and Lydia Helena Wong.,

Highly Active MnO Catalysts Integrated onto Fe₂O₃ Nanorods for Efficient Water Splitting. DOI: 10.1002/admi.201600176.

- Danping Wang, Prince Saurabh Bassi, Huan Qi, Xin Zhao, **Gurudayal**, Lydia Helena Wong, Rong Xu, Thirumany Sritharan, Zhong Chen., Improved Charge Separation in WO₃/CuWO₄ Composite Photoanodes for Photoelectrochemical Water Oxidation, *Materials* 2016, 9(5), 348.

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- **Gurudayal** , Rohit Abraham John, Pablo P Boix, Chenyi Yi, Chen Shi, Sjoerd A. Veldhuis, S. M. Zakeeruddin, Lydia Helena Wong , Michael Grätzel , and Nripan Mathews., Atomically Altered Hematite for Highly Efficient PEC Water Splitting Tandem Cell. Submitted to *Nature Energy*.
- **Gurudayal**, Laurence M. Peter, Roel van de krol, Lydia Helena Wong and Fatwa F. Abdi. Revealing the Influence of Doping and Surface Treatment to the Surface Carrier Dynamics in Hematite Photoanodes, Submitted to *JACS*.

Conferences

- **Gurudayal** and Lydia Helena Wong, "Mn doped Hematite for Efficient PEC Water Splitting " International conference on materials and advanced techniques (ICMAT-2013), Materials research society Singapore (MRS-S)-Singapore, 20/6/2013- 05/07/2013 (**Poster**)

- **Gurudayal** and Lydia Helena Wong, “Iron Based Photoanodes for Solar water Splitting” International Workshop on Solar energy Organized by NTU Singapore, 2014 (**Poster**).
- **Gurudayal** and Lydia Helena Wong, "Role of Doping in Hematite Photoanodes for Efficient Solar Water Splitting "20th International conference on Photochemical Conversion and storage of Solar Energy (IPS-20),Berlin, Germany, 27/7/2014- 01/08/2014 (**Talk**)
- **Gurudayal** and Lydia Helena Wong, “Hematite-Perovskite Tandem Cell for Unassisted Water Splitting” International conference on materials and advanced techniques (ICMAT-2015), Materials research society Singapore (MRS-S)-Singapore, 28/6/2015- 03/07/2015 (**Talk**)
- **Gurudayal** and Lydia Helena Wong, “Challenges and Possible Solutions of Hematite Based Water Splitting” Monthly Meet, Organized by HZB Berlin Singapore, 2015 (**Talk**).
- **Gurudayal**, James Barber, Michael Graetzel, Nripan Mathews and Lydia Helena Wong* “Perovskite- Hematite Tandem Cells for Efficient Bias-Free Solar Driven Water Splitting”, 4th International Workshop on on “Solar Energy for Sustainability: “Photosynthesis and Bioenergetics” Organized by NTU Singapore, 2016 (**Best Poster Award**).