

Development of High Performance Hematite-based Nanostructured Photoanodes for Efficient Photoelectrochemical Water Splitting

A thesis submitted in the fulfilment of the requirements for the degree of Doctor of Philosophy

by

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This thesis includes 6 original papers published in peer reviewed journals. The core theme of the thesis is development of high performance hematite-based nanostructured photoanodes for efficient photoelectrochemical water splitting. The ideas, development and writing up of all the papers in the thesis were the principal responsibility of myself, the student, working within the Malaysia School of Engineering under the supervision of Assoc. Prof. Dr. Chong Meng Nan and Prof. Dr. Chan Eng Seng.

The inclusion of co-authors reflects the fact that the work came from active collaboration between researchers and acknowledges input into team-based research.

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I have renumbered sections of submitted or published papers in order to generate a consistent presentation within the thesis.

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The undersigned hereby certifies that the above declaration correctly reflects the nature and extent of the student's and co-authors' contributions to the work in this thesis. In the instances where I am not the responsible author, I have consulted with the responsible author to agree on the respective contributions of the <u>authors</u>.

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Date: 15 August 2017

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LIST OF PUBLICATIONS

Journals:

- Yi Wen Phuan, Meng Nan Chong, Kumar Egamparan, Byeong Kyu Lee, Tao Zhu, Eng Seng Chan (2016) Understanding the synergistic between optimum dopant loading and charge transfer kinetics in platinum-mediated nanostructured hematite thin films, *Journal of the Taiwan Institute of Chemical Engineers*, 66, 249-257.
- Yi Wen Phuan, Elyas Ibrahim, Meng Nan Chong, Tao Zhu, Byeong Kyu Lee, Joey D Ocon, Eng Seng Chan (2017) In situ Ni-doping during cathodic electrodeposition of hematite for excellent photoelectrochemical performance of nanostructured nickel oxide-hematite p-n junction photoanode, *Applied Surface Science*, 392, 144-152.
- 3. **Yi Wen Phuan**, Meng Nan Chong, Tao Zhu, Joey D Ocon, Eng Seng Chan (2017) Employing electrochemical reduced graphene oxide as a co-catalyst for synergistically improving the photoelectrochemical performance of nanostructured hematite thin films, *Journal of the Taiwan Institute of Chemical Engineers*, 71, 510-517.
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ABSTRACT

Rapid industrialisation in the past century has unarguably enhanced the quality of life for all living. However, this comes at an expense of energetic and environmental related problems. From the past-to-present, considerable efforts have been devoted to the technological advancements in order to resolve the water-energy problems. Recently, photoelectrochemical (PEC) process has received immense attention owing to its ability in sustainably producing solar hydrogen (H₂) from water splitting reaction. Various type of semiconductor photocatalyst materials have been used for the fabrication of photoelectrodes for application in PEC water splitting. Among all, hematite has emerged as a promising semiconductor photocatalyst material due to its abundance, stability and high absorption into the visible light spectrum. However, the PEC performance is limited by its low-electron mobility, short-hole diffusion length and required large overpotential for water oxidation. Recent studies have shown that by controlling the surface morphology and employing advanced surface modifications on hematite can significantly enhance the PEC performance.

Thus, the main aim of this study is to synthesize high-performance nanostructured hematite thin films on photoanode for application in PEC process. In the initial phase, the incorporation of metal dopants, such as platinum (Pt) and nickel (Ni) into hematite nanostructured photoanodes was achieved through the electrodeposition synthesis method. Both the 3 M% Pt-doped and 25 M% Ni-doped hematite nanostructured photoanodes exhibited 3-fold and 5-fold enhancements, respectively, in terms of measured photocurrent density as compared to the pristine hematite photoanode. Such enhancements are attributed to the increased electron donor density and thus, lowering the energetic barrier for water oxidation activity at the optimum Pt or Ni dopant concentration. Concurrently, the metal-doping in hematite has also lowered the photogenerated charge carrier transfer resistance as measured by using the electrochemical impedance spectroscopy (EIS).

In the subsequent phases of this study, hematite nanostructured photoanodes were modified by introducing carbon-based nanomaterials as an alternative to the metal dopants. Carbon-based nanomaterials such as electrochemically reduced graphene oxide (eRGO), fullerene (C_{60}) or both have been used to modify hematite nanostructured photoanodes in order to enhance the PEC performance. Importantly, the inclusion of both highly conducting eRGO and electron scavenging C_{60} has mitigated the high interfacial recombination rate of hematite and led to a superior enhancement in PEC performance. Upon light irradiation, the photocurrent density was observed to be enhanced by 4.5-fold, 1.5-fold and 5-fold on the eRGO/hematite, C_{60} /hematite and eRGO/ C_{60} /hematite nanostructured photoanodes, respectively, relative to pristine hematite

photoanode. Through the EIS measurements, it was found that the introduction of C_{60} and eRGO onto hematite photoanode improved electron transfer and collection, reduced charge-carrier recombination efficiency and enhanced PEC activity.

Finally, the optimised Ni-dopant and nanocarbon of eRGO were employed on hematite nanostructured photoanode to form a ternary heterostructure. The design, fabrication, characterisation and PEC properties of the novel ternary eRGO/NiO/hematite nanostructured photoanode were presented. This unique ternary structure of eRGO/NiO/hematite showed a 9-fold improvement in terms of photocurrent density relative to pristine hematite photoanode. Based on the EIS measurement, the charge transfer resistance of ternary eRGO/NiO/hematite nanostructured photoanode was the lowest among all the as-synthesized photoanodes. This has demonstrated the combinatorial effects of excellent conductivity eRGO and p-n heterojunction effect of NiO have remarkably improved the electron mobility of hematite nanostructured photoanode by impeding the recombination process of photogenerated charge carriers and resulting in superior PEC performance.

KEYWORDS

Hematite, photoelectrochemical, water splitting, hydrogen, photocatalyst, photoanode, electrodeposition, electrochemically synthesised, dopant, carbon-based nanomaterials, platinum, nickel, nickel oxide, fullerene, graphene oxide, reduced graphene oxide, electrochemical reduced graphene oxide, surface modification, heterojunction, nanocomposite, ternary heterostructure, charge carrier, electron-hole pairs.

CHAPTER 1

INTRODUCTION

1.1. The Principle of PEC Water Splitting

The building of a sustainable society will necessitate reduction in the amount of environmental pollution and dependency on fossil fuels. At present, over 80% of the world's energy demand are derived from fossil fuels which will eventually lead to their foreseeable depletion [1]. The vast consumption of fossil fuels will cause global climate change and environmental deterioration. All these issues have become the main drivers in accelerating the transition from the utilisation of exhaustible fossil fuels to clean and renewable energy sources toward achieving sustainability without compromising the environment. Recently, the utilisation of solar energy has gained a lot of attention since it is the largest renewable energy source on Earth. If the energy from the Sun can be efficiently harvested, it will provide adequate power for all future energy requirements [2]. Amid the wide availability of various solar energy conversion options, PEC water splitting process is considered to be one of the most promising options in mimicking the natural photosynthesis process in plants that rearranges electrons in water (H₂O) and carbon dioxide (CO₂) to store solar energy in the form of carbohydrates [3]. It captures solar energy and converts the electromagnetic energy directly into chemical energy in the form of molecular bonds, such as H₂. H₂ is regarded as a clean and renewable energy fuel as well as an important future energy carrier, where the oxidation of H₂ produces energy with water as the only by-product.

In view of these, PEC process is an attractive and excellent technological solution to resolve the present energy- and environmental-related issues encountered by the contemporary society. In a typical PEC reactor (Figure 1), it usually consists of a working semiconductor-based photoanode that absorbs light photons to produce photogenerated electron-hole pairs. The photogenerated electron-hole pairs will further diffuse to the external photoanode surface in enabling: : (1) valence band holes react with water molecules to produce protons and oxygen (O₂) gas, and (2) conduction band electrons transfer to cathode through an external circuit and eventually reduce protons at cathode to produce H₂ gas [4]. In comparison, the PEC process is more preferable than the conventional photocatalytic process utilising semiconductor colloidal suspension, as the former allows the electrochemical separation of photogenerated charge carriers that effectively prevents the recombination of electron-hole pairs [5]. Thus, the PEC process is the ideal and promising technological solution in solving the world's increasing energy demand.

At present, however, the PEC process still exhibit a low photoconversion efficiency in solar H_2 production and high activation energy requirement of semiconductors by light irradiation. In order to achieve a higher photoconversion efficiency for PEC process, there are a number of key technical challenges that need to be addressed. For instances, the development of visible-active

semiconductor photoanodes that could absorb light photons into the visible light spectrum and yielding a higher solar-to-hydrogen (STH) conversion efficiency are crucial. The high PEC performance of a semiconductor photoanode is the key to achieve an efficient solar H_2 production. The important requirements that must be fulfilled by the chosen semiconductor photocatalyst for H_2 production are [5]:

- I. Semiconductor with narrow band gap energy for feasible absorption into solar spectrum.
- II. Both the conduction and valance band energy levels should overlap with the water oxidation and reduction potentials.
- III. High photoconversion efficiency of photogenerated carriers to H_2 and O_2 .
- IV. Stability in aqueous environment and extreme pH condition.
- V. Low cost and highly abundant material on earth.



Figure 1.1. Schematic diagram of a typical PEC process.

To date, there is not a single semiconductor material that can fulfil all the enlisted requirements [3]. Titanium dioxide (TiO₂) is the most popular semiconductor photoanode material for PEC process due to its high durability, low cost and non-toxicity [6]. Previously, TiO₂ has been widely used in degrading organic pollutants in both aqueous and gaseous phases, as well as H₂ gas production from the water splitting reaction. However, the major limitation of TiO₂ is that it only absorbs into the UV-visible light spectrum with $\lambda \leq 380$ nm owing to its large band gap of 3.2 eV [7]. Zinc oxide (ZnO) is the second most commonly used semiconductor after TiO₂. Since ZnO also possesses a large band gap of 3.37 eV, thus it was reported to behave similarly to TiO₂ in terms of the photocatalytic and photoconversion efficiency [8]. Though ZnO is known to be unstable in aqueous environment, where it is only functional under narrow pH range and may cause some photocorrosion effects in the solid-liquid phase [9]. Alternatively, tungsten trioxide

(WO₃) is a stable and inexpensive semiconductor metal oxide that can be used as photoanode material in the PEC process. However, the lower edge of WO₃ conduction band is not favourable for the reduction of water to generate H₂. In order to overcome the energy barrier for photogenerated electrons to reduce water and generate H₂, an external bias has to be applied to complete the PEC process. Owing to the relatively large WO₃ band gap of 2.8 eV, a maximum STH efficiency of achieving 8% is only plausible [10]. Other semiconductors such as cadmium sulphide (CdS), cuprous oxide (Cu₂O), bismuth vanadium oxide (BiVO₄) and iron oxide (Fe₂O₃) have also gained impetus recently owing to their much favourable band gap energy level. To date, CdS is the most extensively investigated Type II-IV semiconductor due to its narrow band gap of 2.4 eV [11]. However, the low conduction band of CdS has caused it to suffer from photocorrosion due to the photogenerated holes [12]. Whilst Cu₂O is a p-type semiconductor with a direct band gap of 2.0 eV [13]. The semiconductor Cu₂O has many characteristics that include non-toxicity, catalytically active, low cost and widely abundant material. However, the instability of Cu₂O in aqueous solution has limited its widespread application as photoanode material. Moreover, the upper edge of Cu₂O valance band is not favourable for water oxidation and will result in photocorrosion [14]. Meanwhile, BiVO₄ has a low band gap of 2.4 eV that is capable to absorb into the visible part of solar spectrum [15]. Most often, however, BiVO₄ is being used as the additive to enhance the visible light absorption as it is limited by the high electron-hole pairs recombination rate and low photocurrent generated [12]. Among the various semiconductor metal oxides, hematite (α -Fe₂O₃), the most thermodynamically stable and common form of Fe₂O₃, appears to be a potential candidate for PEC photoanode material in consideration of the aforementioned requirements. With a narrow band gap energy between 1.9 eV and 2.2 eV, it can absorb up to 40% of incident solar light [5]. The maximum theoretical STH efficiency for hematite was estimated to be 16.8 %, which has considerably high potential to convert water into H₂ and O₂ molecules among the discussed plausible semiconductor materials for PEC water splitting [16]. Additionally, iron is the most abundant metal on Earth where the pure form of iron is readily oxidised in the presence of moist air to form Fe₂O₃, which is also known as rust [17]. Thus, hematite possesses numerous advantages, including ubiquitous, excellent stability under most of the aqueous environment, environmental compatibility and low-cost [18].

1.2. Problem Statements

Since the first inception report on PEC water splitting into H2 and O2 in 1972 by Fujishima and Honda using TiO₂ photocatalyst [19], many scientific studies have been devoted on the development of new semiconductor materials for photoelectrodes used in PEC process. In 1976, Hardee and Bard constructed Fe₂O₃ photoanode via chemical vapor deposition (CVD) method [20] and over the next decade, numerous articles were published on the fabrication of Fe₂O₃ by different synthesis methods. Recently, the PEC process has received a lot of attention owing to its ability to simultaneous resolve the water and energy shortages. Among the semiconductor materials, hematite is a unique and excellent candidate for application as photoanode in the PEC process owing to its abundance, low cost, good stability as well as favourable band gap energy. Nevertheless, the practical applications of hematite are still hindered by several challenges and drawbacks that need to be addressed. Hematite has a very short diffusion length of minority carriers (i.e. 2-4 nm) as compared to the light absorption depth (i.e. 400-500nm), and poor majority carriers conductivity (i.e. 10^{-2} cm² V⁻¹ s⁻¹) [2]. These disadvantages result in a rapid recombination rate of charge carriers and significantly limit the charge transfer process, causing poor PEC activity for solar H₂ evolution. To date, researchers have attempted to improve the PEC performance of hematite via various approaches such as controlling surface morphology [21-28], elemental doping [29-31], surface treatment [32-34], coupling with other semiconductors [35-37] and others.

Thus, this research work focused on the design and modification of high performance hematitebased photoanodes for PEC water splitting via the incorporation of metal dopants and carbonbased nanomaterials for efficient charge transfer and separation by using electrodeposition synthesis method. Electrodeposition is a viable method in synthesizing hematite thin films due to its simplicity, inexpensive, low operating temperature and pressure, scalability and the ability to control the surface morphology, film thickness and nanoparticles size by tuning the electrodeposition synthesis conditions [38, 39].

1.3. Research Objectives

The main aim of this research is to synthesize high performance hematite-based nanostructured photoanodes for solar H_2 energy conversion. The main objectives of this research are listed as below:

- i. To synthesize metal-doped hematite nanostructured photoanodes with enhanced electron donor properties and recombination centres.
 - Optimum loadings of Pt and Ni dopants on hematite.
 - Study the fundamental mechanisms of Pt and Ni in enhancing the PEC activity.
- ii. To fabricate nanocarbon-based hematite nanostructured photoanodes with improved photogenerated charge transfer and separation.
 - Preparation of graphene oxide (GO) via Improved Hummers' method.
 - Modification of hematite by electrodepositing with C₆₀, eRGO or both for effective charge transfer and separation.
 - Optimum loadings of eRGO nanocarbon on hematite.
- iii. To develop a ternary hematite-based nanostructured photoanode with excellent PEC performance consisting of both metal dopant and nanocarbon.
 - Examine the coupled effects of both Ni-dopant and eRGO on hematite.
 - Understand the synergistic effects between Ni-dopant and eRGO on hematite.
- iv. To study the properties of as-synthesized hematite-based nanostructured photoanodes developed from objectives (i-iii) using various analytical instruments.
 - Study the surface morphology, functional groups, chemical composition and chemical status of each element.
 - Investigate the band gap energy and photoresponse.
 - Determine the charge carriers collection and separation efficiency.

1.4. Organisation of Thesis

Chapter 1 introduces a brief overview of the research project and the principle of PEC water splitting in potentially resolving the present energy- and environmental-related issues encountered by the contemporary society. The utilisation of semiconductor photocatalyst materials for PEC process and the essential requirements that must be fulfilled for effective solar H_2 production are also included. Then, the recent development of semiconductor materials is discussed with the emphasis on the PEC water splitting applications. In this regard, hematite is considered as a potential photoanode material due to its beneficial characteristics which have satisfied nearly all the desirable requirements. Following that, the problem statement as well as the research objectives of this study are presented.

Chapter 2 provides a literature review on the state-of-the-art advancement in the electrochemically synthesised hematite photoanodes for enhancing its PEC performance. The fundamental aspects and mechanisms of hematite photoanodes synthesized by the anodic electrodeposition, metal anodisation, cathodic electrodeposition and potential cycling/pulsed electrodeposition methods for PEC water splitting are explained. Next, the Chapter focuses on the key electrodeposition parameters controlling the surface morphology of pristine hematite photoanodes. This is followed by the surface modifications of hematite photoanodes for instances; elemental doping, surface treatment and heterojunctions to improve the charge collection and separation of hematite. Lastly, the Chapter concludes with a summary and outlook on the challenges and future prospects of hematite-based photoanode in PEC water splitting.

Chapter 3 emphasizes on the synthesis and evaluation of metal-doped hematite nanostructured photoanodes. Herein, a comprehensive study on the incorporation of metal dopants, such as Pt and Ni into hematite nanostructured photoanodes via the electrodeposition synthesis method are investigated. The Pt- and Ni-doped hematite photoanodes are characterised using FESEM, EDX, XRD, XPS, UV-Vis and EIS. Besides, the metal dopants loadings are systematically optimised and their synergistic roles in enhancing PEC performance are discussed. The PEC performance of the as-synthesized Pt- and Ni-doped hematite photoanodes are evaluated by investigating the photoresponse at ambient temperature and atmospheric pressure using a Philip 100 W halogen lamp. Through the optimisation study, it was found the 3 M% Pt-doped and 25 M% Ni-doped hematite nanostructured photoanodes exhibited 3-fold and 5-fold enhancements, respectively, in terms of measured photocurrent density as compared to pristine hematite photoanode. The enhancement mechanisms underlying the charge transfer and separation of the electron-hole pairs in the Pt- and Ni-doped hematite nanostructured photoanodes are proposed.

Chapter 4 presents the fabrication, assessment and comparison of nanocarbon-based hematite nanostructured photoanodes. As an alternative to the metal dopants presented in previous Chapter, the inclusion of electron donor-acceptor composites based nanocarbons such as C₆₀ and eRGO in enhancing the PEC performance of hematite nanostructured photoanodes are studied. Since both C₆₀ and eRGO can act as potential electron reservoirs to prolong the recombination of photogenerated electron-hole pairs, the combinatorial use of C₆₀ and eRGO on hematite photoanodes are synthesized for the first time via electrodeposition synthesis route to improve the low PEC efficiency in hematite. The effects of surface impedance on photogenerated charge carrier recombination are investigated through a series of comparison study among pristine hematite, C₆₀/hematite, eRGO/hematite and eRGO/C₆₀/hematite nanostructured photoanodes. The hematite nanocomposites photoanodes of C₆₀/hematite, eRGO/hematite and eRGO/C₆₀/hematite demonstrated increase in current densities by 1.5-fold, 4.5-fold and 5-fold, respectively when benchmarked against the current density of pristine hematite photoanode. Compared with eRGO, C₆₀ exhibits minor improvement in PEC efficiency of hematite photoanodes and thus only a series of eRGO/hematite nanostructured photoanodes are developed. It is worth noting that this is the first report in integrating eRGO with hematite via a facile and environmental benign two-step electrodeposition synthesis method. The as synthesized eRGO/hematite nanocomposites photoanode showed an intimate contact between the eRGO and hematite interfaces that increase PEC active surface area of hematite, improve charge transfer and as a result leads to high PEC performance. Lastly, a postulated mechanism for the PEC process associated with eRGO/hematite nanocomposites photoanode is presented.

Chapter 5 describes the design, fabrication, characterisation and PEC properties of a novel ternary eRGO/NiO/hematite nanostructured photoanode for PEC water splitting. In this Chapter, the combinatorial effects of both metal dopant of Ni (i.e. Chapter 3) and nanocarbon of eRGO (i.e. Chapter 4) on hematite nanostructured photoanode are examined. The surface morphology, phase structure, chemical composition, optical property and electronic band structures of the ternary eRGO/NiO/hematite nanostructured photoanode are systematically characterised. This unique ternary structure of eRGO/NiO/hematite showed a 9-fold improvement in terms of photocurrent density relative to bare hematite photoanode. This superior enhancement is attributed to the eRGO sheets that efficiently transfer the electrons in the p-n heterojunction without causing substantial bulk recombination, while forming an internal electrical field in the ternary hematite nanostructured photoanode. The internal electrostatic field could facilitate the efficient separation of the photogenerated charge carriers and thus, improving the PEC performance.

Chapter 7 summarises the overall research conclusion and major findings of this project. Future research for hematite-based photoanode in this emerging field of PEC water splitting to achieve the theoretical STH efficiency of 16.8 % is also discussed.

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CHAPTER 2

LITERATURE REVIEW

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Prospects of Electrochemically Synthesized Hematite Photoanodes for Photoelectrochemical Water Splitting: A Review



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ABSTRACT

Hematite (α -Fe₂O₃) is found to be one of the most promising photoanode materials used for the application in photoelectrochemical (PEC) water splitting due to its narrow band gap energy of 2.1 eV, which is capable to harness approximately 40 % of the incident solar light. This paper critically reviews the state-of-the-art progress of the electrochemically synthesized pristine hematite photoanodes for PEC water splitting. The fundamental principles and mechanisms of anodic electrodeposition, metal anodization, cathodic electrodeposition and potential cycling/pulsed electrodeposition are elucidated in detail. Besides, the influence of electroleposition and potential treatment conditions are systematically reviewed; for examples, electrolyte precursor composition, temperature and pH, electrode substrate, applied potential, deposition time as well as annealing temperature, duration and atmosphere. Furthermore, the surface and interfacial modifications of hematite-based nanostructured photoanodes, including elemental doping, surface treatment and heterojunctions are elaborated and appraised. This review paper is concluded with a summary and some future prospects on the challenges and research direction in this cutting-edge research hotspot. It is anticipated that the present review can act as a guiding blueprint and providing design principles to the scientists and engineers on the advancement of hematite photoanodes in PEC water splitting to resolve the current energy- and environmental-related concerns.

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Chapter 2 | Literature Review



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1. Introduction

The building of a sustainable society will necessitate reduction in the amount of environmental pollution and dependency on fossil fuels.

At present, over 80 % of the world's energy demand is derived from fossil fuels which will eventually lead to their foreseeable depletion [1]. The vast consumption of fossil fuels will cause global climate change and environmental deterioration. All these issues have become the main drivers in accelerating the transition from the utilization of exhaustible fossil fuels to clean and renewable energy sources toward achieving sustainability without compromising the environmental. Recently, the utilization of solar energy has gained a lot of attention since it is the largest renewable energy source on Earth. If the energy from the sun can be efficiently harvested, it will provide adequate power for all future energy requirements [2]. Amid the wide availability of various solar energy conversion options, photoelectrochemical (PEC) water splitting process is considered to be one of the most promising options in mimicking the natural photosynthesis process in plants that reorganizes electrons in water (H₂O) and carbon dioxide (CO₂) to store solar energy in the form of carbohydrates [3]. Notably, it uses the inexhaustible solar energy and converts the electromagnetic energy directly into chemical energy in the form of molecular bonds, such as hydrogen (H₂). H₂ is regarded as a clean and renewable energy fuel as well as an important future energy carrier where the oxidation of H₂ produces energy with water as the only by-product. In view of this, PEC process is an attractive and excellent technological solution to surmount the present energy- and environmental-related issues encountered by the contemporary society.

The PEC effect was first discovered by the French scientist Edmond Becquerel in 1839 [4]. In the 1960s, Russian and Japanese research groups began to study zinc oxide (ZnO) and titanium dioxide (TiO2) for heterogeneous photooxidation [5]. Later on, interests were reignited after the pioneering studies by two Japanese researchers, Fujishima and Honda on photocatalytic water splitting using TiO2 under nearultraviolet (UV) light in 1972 [6]. Four years after, Hardee and Bard constructed iron oxide (Fe₂O₃) photoanode via chemical vapor deposition (CVD) method [7] and over the next decade, numerous articles were published on the fabrication of Fe_2O_3 by different synthesis methods. Since then, a large array of semiconductor photocatalysts including TiO₂ [8-13], ZnO [14-16], Fe₂O₃ [17-20], CdS [21-23], WO₃ [24-28], Cu₂O [29-31], BiVO₄ [32-35], g-C₃N₄ [36, 37] and combinations thereof have been extensively investigated. To date, however, no single semiconductor photocatalyst can fulfil the essential and desirable requirements in achieving remarkable PEC performance, such as narrow band gap energy for wider spectral range of light absorption, conduction band (CB) and valance band (VB) energies that straddle the water redox potentials, high solar-to-hydrogen (STH) efficiency, high stability and durability in aqueous environment as well as affordability [3].

Among the various semiconductor photocatalysts, TiO₂ is the most widely used and well-known photoanode material for PEC application. Nevertheless, the major drawback of TiO₂ is that it only absorbs the UV light spectrum with $\lambda \leq 380$ nm owing to its relatively wide band gap of 3.2 eV. On the contrary, hematite (α -Fe₂O₃) is ideally suited to be applied as the photoanode material in consideration of the aforementioned requirements. With a narrow band gap energy of 2.1 eV, it is capable to absorb up to 40 % of the incident solar light and it has a high potential to convert water into H₂ and O₂ molecules due to its highly estimated theoretical STH efficiency of 16.8 % during PEC water splitting [38]. In comparison to other plausible semiconductor photocatalysts, hematite possesses numerous advantages, including excellent stability under most of the aqueous environment, ubiquitous, environmental compatibility and low-cost.

Various concerted efforts have been devoted to synthesize nanostructured hematite thin films; for instance sol-gel [39-41], hydrothermal [42-44], drop casting [45-47], spin coating [48-50], spray pyrolysis [51-53], atomic layer deposition (ALD) [54-56], CVD [57-59], electron beam evaporation [60-62], magnetron sputtering [63-65] and electrodeposition [66-69] methods. Albeit the synthesis methods

are able to develop highly-efficient nanostructured hematite photoanodes, most of the aforementioned synthesis methods are not suitable for large-scale fabrication of hematite thin films. Among all, electrodeposition is a viable method in synthesizing hematite thin films due to its simplicity, inexpensive, low operating temperature and pressure, scalability and the ability to control the surface morphology, film thickness and nanoparticles size by tuning the electrodeposition conditions [70, 71].

Over the past few decades, numerous approaches have been explored to improve the PEC performance of hematite photoanodes from the viewpoint of controlling surface morphology to surface chemistry and catalysis [54, 72-93]. To date, there are several review articles on hematite-based nanomaterials that emphasize the overview properties, synthesis methods, characterization, promising applications, and so forth [2, 38, 94, 95]. Recently, Tamirat and co-workers highlighted the current progress and challenges in utilizing hematite for application in PEC water splitting [96]. Shen et al. also provided another review focusing on hematite heterostructures, from rational materials design to charge carrier dynamics [97]. To the best of our knowledge, however, there is no review article that thoroughly discusses on the electrochemically synthesized hematite for PEC water splitting application as well as its surface modifications in elevating the PEC efficiency. In turn, this motivates us to critically review and elucidate a full picture of the concept on the electrochemically synthesized hematite and its surface modification for PEC technology.

In this review, we have critically reviewed the state-of-the-art development in the electrochemically synthesized hematite photoanodes for improving its PEC performance. The fundamental principles and mechanisms of hematite photoanodes synthesized by the anodic electrodeposition, metal anodization, cathodic electrodeposition and potential cycling/pulsed electrodeposition methods for PEC water splitting are elucidated in Section 2. The key electrodeposition parameters controlling the surface morphology of pristine hematite photoanodes are systematically reviewed, including the effect of electrolyte precursor, electrode substrate, applied potential, and annealing treatment. This is followed by the surface modifications of bare hematite photoanodes, such as elemental doping of hematite, surface treatment and heterojunctions to prolong the charge recombination process in hematite. Finally, a summary and outlook on the major challenges, opportunities and prospects are presented for future research in this emerging frontier of PEC water splitting. It is anticipated that the present review will open up new vistas in materials research toward electrochemically synthesized hematite photoanodes for the application in solar energy conversion.

2. Fundamental principles and mechanisms of electrochemically synthesized pristine hematite

Electrochemical synthesis is an efficient and environmental-friendly synthesis method, which is used to fabricate nanostructured hematite at ambient temperature and pressure conditions from an electrolyte precursor [98]. Previously, it has been demonstrated as a feasible synthesis method to prepare a plethora of nanoarchitectures hematite, such as nanoparticles [67, 98-111], nanospheres [69], nanorods [66, 112, 113], nanotubes [69, 70, 112, 114-118], honeycombs [119], nanodendrites [120, 121], nanocorals [68], nanoflakes [20], nanopetals [122], nanoplates [123], nanoporous [120, 124, 125] and nanowires [126]. The formation of diversified surface morphologies strongly depends on the electrochemical synthesis and annealing treatment conditions. It is evident that the electrodeposition synthesis parameters, including electrolyte precursor composition, temperature and pH, electrode substrate, applied potential, deposition time, annealing temperature, duration and atmosphere, could affect the PEC activity of the eventual nanostructured hematite formed [100]. Generally, the electrochemical synthesis method can be performed anodically, cathodically or both whereby the as-synthesized amorphous iron (Fe) film will undergo annealing treatment for crystallization

to produce nanostructured hematite [67].

2.1. Anodic electrodeposition/metal anodization

Anodic electrodeposition is performed at an applied positive potential in an electrolyte precursor containing Fe ions by using a three-electrode electrochemical setup consisting of working, counter and reference electrodes (Fig. 1a). The process involves the oxidation of Fe^{2+} to Fe^{3+} ions, followed by precipitation of Fe^{3+} ions as iron oxyhydroxide (FeOOH) films on the conductive electrode substrate (e.g. fluorine tin oxide (FTO) glass and indium tin oxide (ITO) glass) due to the limited solubility of Fe^{3+} ions in the liquid electrolyte precursor [127]. The reactions can be expressed as follow:

$$Fe^{2+} \rightarrow Fe^{3+} + e^{-} \tag{1}$$

$$Fe^{3+} + 2H_2O \rightarrow FeOOH + 3H^+$$
 (2)

With a global reaction

$$Fe^{2+} + 2H_2O \rightarrow FeOOH + 3H^+ + e^-$$
 (3)

Typically, the Fe²⁺ ions are barely dissolved in the electrolyte precursor and thus, complexing agents (e.g. ammonium fluoride (NH₄F) and ammonium sulfate ((NH₄)₂SO₄)) are added to stabilize Fe²⁺ ions in the solutions [99].



Fig. 1. Electrodeposition methods for synthesizing nanostructured hematite (a) anodic electrodeposition, (b) metal anodization and (c) cathodic electrodeposition.

In a similar manner, metal anodization is also carried out at an applied positive potential but using the conventional two-electrode electrochemical setup where metal and platinum (Pt) act as the anode and cathode, respectively (Fig. 1b). The induced voltage forms a thick compact oxide layer over the metal surface, where this enhances the corrosion resistance of the hematite surface [120]. Typically, the formation of metal oxide through metal anodization is carried out via two competing reactions, namely: (1) the applied potential causes oxidation of Fe metal substrate to form metal oxide, and (2) chemical dissolution of oxide due to the presence of highly complexing F^{-} ions, which can be substantially improved by the presence of H⁺ ions [115]. The reactions can be defined as below:

$$2Fe + 3H_2O \rightarrow Fe_2O_3 + 6H^+$$
(4)

$$Fe_2O_3 + 12F^- + 6H^+ \rightarrow 2[FeF_6]^{3-} + 3H_2O$$
 (5)

The formation of metal oxide continues to take place until reaching an equilibrium between the two competing reactions. Following that, this ceases the development of nanostructured metal oxide [69].

Table 1 summarizes the important studies on electrochemically synthesized nanostructured hematite. In particular, Spray and Choi prepared hematite films with various thicknesses by means of anodic electrodeposition to investigate the effect of film thickness on photon absorption and photocurrent generation [99]. Interestingly, the photocurrent of hematite films was improved as the film thickness increased to 400-500 nm. The photocurrent enhancement was attributed to the enhancement of photon absorption and the active surface area of the hematite films. Nonetheless, as the film thickness exceeded 400-500 nm, hematite nanoparticles agglomerated severely at the semiconductor-liquid junction (SCLJ), leading to an overall reduction in the

PEC performance. In another work, Jiao et al. employed anodic electrodeposition to construct morphology-dependent a-FeOOH films (e.g. rhombohedral rods, six-fold snowflakes, platelets, square rods and hexagonal particles) by controlling the electrolyte precursor compositions as depicted in Fig. 2 [123]. It was demonstrated that the α -FeOOH films could be transformed into hematite nanostructures with the identical morphologies upon annealing treatment. The photoresponse revealed that the hematite film exhibited the ntype behavior with remarkably high stability, implying that the film was resistant to photocorrosion. In a recent study by Fu and co-workers, the crystalline hematite nanorods (EG-α-Fe₂O₃) were synthesized by utilizing a modified electrochemical anodization on the FTO glass in the presence of ethylene glycol (EG) (C₂H₆O₂) in the electrolyte precursor [66]. In this instance, EG served as an assistant reactant to induce one-dimensional (1D) growth during the electrodeposition process. When EG was added, the morphology of hematite changed from nanoparticles to short nanorods with an average diameter and length of 20 and 120 nm, respectively. Both the optical and PEC analyses confirmed that the EG- $\alpha\text{-}\text{Fe}_2\text{O}_3$ nanorods showed an improvement in photoabsorption and photoresponse as compared to the original hematite. This was ascribed to the incompact nanorod architectures, which provided more photoactive area for efficient light harvesting, decreased the hole diffusion length for superior charge transfer, and enlarged the interfacial contact for rapid charge collection. Under the illumination of

simulated sunlight, the EG- α -Fe₂O₃ nanorods synthesized at the optimum condition produced a photocurrent density of 0.24 mA cm⁻² at 1.4 V_{RHE} in KOH (1 M).



Fig. 2. SEM images of different α -FeOOH morphologies: (a) rhombohedral rods, (b) six-fold snowflakes, (c) platelets, (d) square rods and (e) hexagonal particles prepared by anodic electrodeposition method. Reproduced with permission from ref. [123]. Copyright 2010, American Chemical Society.

Table 1

Summary of various electrochemically synthesized pristine hematite. *

Electrode	Electrolyte precursor	Applied	Deposition	Annealing	Morphology	Photocurrent density	Year/	
substrate		potential	time				Ref.	
Anodic Electrodeposition								
FTO glass	FeCl _{2.5} H ₂ O (0.02 M) (pH 4.1)	1.2 V _{Ag/AgCl}	8 min	520 °C for 30 min (2 °C min ⁻¹)	Nanoparticles	$0.52\ mA\ cm^{-2}$ in $C_{16}H_{36}IN$ (0.5 M), I_2 (0.04 M) under 3 W cm^{-2} from backside illumination	2009/ [46]	
ITO glass	(NH ₄) ₂ Fe(SO ₄) ₂ , CH ₃ COOK	$0.65 \ V_{SCE}$	1 h	400 °C for 1 h	Platelets	0.075 mA cm ⁻²	2010/ [70]	
α-Fe ₂ O ₃ / FTO glass	KOH (1 M)	0.6 V _{Ag/AgCl}	2 h	Dry in air	-	-	2011/ [75]	
FTO glass	(NH ₄) ₂ Fe(SO ₄) ₂ .6H ₂ O (0.05 M), Na ₂ SO ₄ (0.05 M), C ₂ H ₃ NaO ₂ .3H ₂ O (0.02 M)	$1.2 \; V_{\text{Ag/AgCl}}$	40 min	600 ℃ for 5 h, then 820 ℃ for 10 min (2 ℃ min ⁻¹)	Hexagonals	0.67 mA cm ⁻² at 1.23 V _{RHE} in NaOH (1 M) under 100 mW cm ⁻²	2012/ [76]	
FTO glass	NH ₄ Cl (3 M), FeCl ₂ .4H ₂ O (0.02 M) (pH 7.52)	0.45 V _{Ag/AgCl}	40 min	700 °C for 4 h	Nanoparticles	0.488 mA cm 2 at 0.4 $V_{Ag/AgCl}$ in NaOH (1 M) under 150 W Xe lamp	2012/ [47]	
α-Fe ₂ O ₃ / FTO glass	KOH (1 M)	0, 0.2, 0.6 V _{Ag/AgCl}	24 h	-	-	-	2012/ [77]	
FTO glass	FeCl ₂ , C ₂ H ₆ O ₂ (pH 4.1)	1.2 V _{Ag/AgCl}	20 min	600 °C for 20 min	Nanorods	0.24 mA cm ⁻² at 1.4 V _{RHE} in KOH (1 M) under 100 mW cm ⁻²	2014/ [32]	
ITO glass	FeCl ₂ (0.05 M), C ₂ H ₃ NaO ₂ (0.2 M)	$1.2 \; V_{\text{Ag/AgCl}}$	8 min	520 °C for 30 min	Nanoparticles	23.6 $\mu A~cm^{-2}$ at 1.23 V_{NHE} in NaOH (1 M) under 100 mW cm^{-2}	2015/ [45]	
α-Fe ₂ O ₃ / FTO glass	KOH (1 M) (pH 13.8)	0.7 V _{Ag/AgCl}	1, 10, 900 min	Dry in air	Nanoparticles	-	2016/ [49]	
Metal Anodizati	ion							
AAO template	FeCl ₃ .6H ₂ O, (NH ₄) ₂ C ₂ O ₄ .H ₂ O	15 V	10 min	600 °C for 2 h	Nanowires	-	2004/ [73]	
Fe foil	HNO ₃ , HF, NH ₄ F, C ₃ H ₈ O ₃	90 V (CE: Pt)	30 min	400 °C for 30 min (10 °C min ⁻¹)	Nanoporous	0.51 mA cm ⁻² at 0.6 V _{Ag/AgCl} in H ₂ O ₂ (0.5 M), NaOH (1 M) under 100 mW cm ⁻²	2006/ [71]	
Fe foil	NH4F, C2H6O2	50 V (CE: Pt)	3 min	400 ℃ for 30 min (5 ℃ min ⁻¹)	Nanotubes	-	2009/ [62]	
Fe foil	NH4F, Na5P3O10, C2H6O2	20 V + 50 V	10 + 15 min	550 °C for 10 min	Nanodendrites/Na noporous	0.74 mA cm ⁻² at 0.2 V _{Ag/AgCl} in KOH (1 M) under AM 1.5 illumination	2009/ [67]	

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Electrode substrate	Electrolyte precursor	Applied potential	Deposition time	Annealing	Morphology	Photocurrent density	Year/ Ref.
Fe foil	NH4F, C2H6O2	50 V (CE: Pt)	5 + 5 min	400 °C for 1 h (2 °C min ⁻¹)	Nanotubes	$0.352~mA~cm^{-2}$ at 0.6 $V_{Ag/AgCl}$ under 100 mW cm^{-2}	2010/ [61]
C foil	H ₃ PO ₄ (0.5 M), NH ₄ F (0.05 M)	20 V (CE: Pt)	15 min	350 °C for 1 h (5 °C min ⁻¹)	Nanoporous	0.8 mA cm ⁻² at 0.4 $V_{Ag/AgCl}$ in KOH (1 M) under 100 mW cm ⁻²	2010/ [72]
Fe foil	NH ₄ F, C ₂ H ₆ O ₂	60 V (CE: Pt)	30 + 3 min	550 °C for 2 h	Honeycombs	0.24 mA cm ⁻² at 1.23 V _{RHE} in NaOH (1 M) under AM 1.5 illumination	2012/ [66]
Fe foil	NH ₄ F, C ₂ H ₆ O ₂	50 V	1 min	400 °C for 1 h	Nanotubulars	0.25 mA cm ⁻² at 1.4 V _{RHE} in KOH (1 M) under 100 mW cm ⁻²	2014/ [36]
Fe foil	NH ₄ F, C ₂ H ₆ O ₂	50 V (CE: Pt)	3 min	500 °C for 3 h	Nanotubes	0.17 mA cm ⁻² at -0.185 V _{RHE} in NaOH (1 M) under 25 mW cm ⁻²	2014/ [63]
C steel	NH4F, C2H6O2	50 V (CE: Ti)	5 min	450 °C for 4 h (2 °C min ⁻¹)	Nanotubes	3.622 $\mu A~cm^{-2}$ in NaCl under 140 mW cm^{-2}	2015/ [64]
Fe foil/ FTO glass	NH ₄ F, C ₂ H ₆ O ₂	20 V (CE: Pt)	2 min	550 ℃ for 2 h (10 ℃ min ⁻¹)	-	0.59 mA cm ⁻² at 0.6 V _{SCE} under 100 mW cm ⁻²	2016/ [78]
FTO glass	γ -Fe ₂ O ₃ , C ₅ H ₅ N	50 V (CE: FTO)	0-160 s	450 °C for 30 min	Nanoparticles	-	2016/ [48]
Fe rod	NH4F, C2H6O2	50 V (CE: Pt)	15 min	500 °C for 30 min (15 °C min ⁻¹)	Nanospheres/ Nanoturbulars	0.143 mA cm ⁻² at 1.54 V _{RHE} in KOH (1 M) under 100 mW cm ⁻²	2016/ [35]
Cathodic Electr	rodeposition						
Graphite	α-Fe ₂ O ₃ , NaOH (18 M)	-1.25 V _{SHE}	-	-	Nanoparticles		2007/ [50]
AAO template	FeSO4, C6H8O6, H3BO3, H2NSO3H	-0.5 $V_{Ag/AgCl}$	15 min	500 °C for 6 h	Nanorods	$8~mA~cm^{-2}$ at 0.6 $V_{Ag/AgC1}$ in NaOH (1 M) under 100 mW cm^{-2}	2010/ [60]
AAO template	FeSO4.7H2O, C6H8O6, H3BO3, H2NSO3H	-1.5 V _{Ag/AgCI}	-	500 °C for 6 h	Nanorods/ Nanotubes	Nanorods: 0.59 mA cm ⁻² , Nanotubes: 2.18 mA cm ⁻² at 0.43 $V_{Ag/AgCI}$ in NaOH (1 M) under 100 mW cm ⁻²	2011/ [59]
ITO glass	FeSO ₄ (0.05 M), Na ₂ SO ₄ (0.1 M) (pH 4)	-0.4 V _{Ag/AgCl}	30 min	500 °C for 3 h (2 °C min ⁻¹)	Dendritics	43 $\mu A~cm^{-2}$ at 0.6 $V_{Ag/AgCl}$ in NaOH (1 M) under 100 mW cm^{-2}	2012/ [68]
Polystyrene/ FTO glass	FeSO4.7H2O, C6H8O6, H3BO3, H2NSO3H	-	9 min	400 °C for 6 h	Macroporous	3.1 mA cm ⁻² at 0.5 $V_{Ag/AgCI}$ in NaOH (1 M) under 100 mW cm ⁻²	2013/ [79]
β-FeOOH/ C cloth	LiCl (3 M)	-1.2 V _{Ag/AgCl}	100 s	550 °C for 1 h	Nanoflakes	0.38 mA cm ⁻² at 0.2 V _{Ag/AgCl} in NaOH (1 M) under 100 mW cm ⁻²	2015/ [14]
FTO glass	FeCl ₃ (0.025 M), KF (0.1 M), H ₂ O ₂ (1 M), KCl (0.1 M)	-0.25 V _{SCE}	10 min	625 °C for 12 h	Nanoparticles	$0.354~mA~cm^2$ at 0.557 V_{SCE} in KOH (1 M) under 100 $mW~cm^2$	2015/ [51]
ITO glass	FeCl ₂ .4H ₂ O, FeCl ₃ .6H ₂ O	1-10 mA cm ⁻ 2	0-200s	Dry in air	Hexagonal	-	2016/ [80]
ITO glass	C ₂ H ₃ NaO ₂ (0.1 M), GA (1 mM), (NH ₄) ₂ Fe(SO ₄) ₂ .6H ₂ O (0.02 M)	-1.2 V _{Ag/AgCl}	-	600 °C for 1 h (2 °C min ⁻¹)	Nanoparticles	-	2016/ [33]
FTO glass	NaNO ₃ (0.1 M)	-1.5 V _{SCE}	20 s	-	Nanoparticles	0.13 mA cm ⁻² at 0.75 V _{SCE} in NaNO ₃ (0.1 M) under 100 mW cm ⁻²	2017/ [52]
Potential Cyclin	ng/Pulsed Electrodeposition						
FTO glass	FeCl ₃ (5 mM), KF (5 mM), H ₂ O ₂ (1 M), KCl (0.1 M)	-0.9 to 0 V _{SMSE} , 0.02 mV s ⁻¹	50 cycles	500 °C for 20 min	Nanoparticles	-	2006/ [53]

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Electrode	Electrolyte precursor	Applied	Deposition	Annealing	Morphology	Photocurrent density	Year/
substrate		potential	time				Ref.
FTO glass	FeCl ₃ (5 mM), KF (5 mM), H ₂ O ₂ (1 M), KCl (0.1 M)	0 to -0.9 V _{SMSE} , 0.02 V s ⁻¹	50 cycles	500 °C for 20 min	-	0.26 mA cm ⁻² at 0.2 V _{SMSE} in NaOH (0.1 M) and KI (0.05 M) under 75 W Xe lamp	2007/ [81]
FTO glass	FeCl ₃ (10 mM), KF (10 mM), H ₂ O ₂ (1 M), KCl (0.1 M)	-0.9 to 0-0.5 V _{SMSE} , 0.02 V s ⁻¹	PC: 50 cycles, PP: 1300 cycles	520 °C for 20 min	Nanoparticles	PC: 0.05 mA cm ⁻² , PP: 0.36 mA cm ⁻² at 0.2 V _{SMSE} in NaOH (0.1 M) and KI (0.05 M) under 10 mW cm ⁻²	2010/ [54]
FTO glass	FeSO4, C6H8O6, H3BO3, H2NSO3H	6 to -4 V _{Ag/AgCl}	-	500 °C for 10 min	Nanopetals	0.75 mA cm ⁻² at 0.65 V _{Ag/AgCl} in NaOH (1 M) under 100 mW cm ⁻²	2012/ [69]
FTO glass	FeCl ₃ (0.01 M), LiCl (0.1 M), C ₂ H ₆ OS	0 to -1.5 V _{Ag/AgCl} , 0.05 V s ⁻¹	15 cycles	700 °C for 30 min	Nanoparticles	33 $\mu A~cm^2$ at 1.23 V_{RHE} in NaOH (0.1 M) under 6.5 mW cm^2	2014/ [55]
Fe foil	NH4F, C2H6O2	30 to 60 V (CE: Pt), 2.5 V s ⁻¹	21 min	600 °C for 2 h	Nanotubes	$1.4~mA~cm^{-2}$ at 1.23 V_{RHE} in KOH (1 M) under 100 mW cm^{-2}	2015/ [65]
FTO glass	FeCl _{3.6} H ₂ O (5 mM), KF (5 mM), H ₂ O ₂ (1 M), KCl (0.1 M)	0 to -0.2 V _{SCE} , 0.02 V s ⁻¹	40 cycles	450 °C for 1 h (5 °C min ⁻¹)	Nanoparticles	$4.5~\mu A~cm^{-2}$ at 0.2 V_{SCE} in NaOH (1 M)	2015/ [56]
FTO glass	FeSO ₄ , C ₆ H ₈ O ₆ , H ₃ BO ₃ , H ₂ NSO ₃ H (pH 5.71)	-6 to 4 V _{Ag/AgCl}	45 s	550 °C for 4 h + 800 °C for 15 min	Nanoparticles	0.504 mA cm ⁻² at 1.23 V _{RHE} in NaOH (1 M) under 100 mW cm ⁻²	2015/ [57]
Fe foil	C ₆ H ₈ O ₆ , H ₃ BO ₃ , H ₂ NSO ₃ H	-6 to 4 V _{Ag/AgCl}	5 min	Dry in N ₂	Nanocorals	0.813 mA cm ⁻² at 1.23 V _{RHE} in NaOH (1 M) under 100 mW cm ⁻²	2015/ [34]
FTO glass	FeCl ₃ (5 mM), NaF (5 mM), H ₂ O ₂ (1 M), KCl (0.1 M)	-0.5 to 0 V _{Ag/AgCl} , 0.1 V s ⁻¹	100 cycles	600 °C for 4 h	Nanoparticles	1.6 mA cm^{-2} at $0.6 \text{ V}_{Ag/AgC1}$ in NaOH (1 M) under 100 W halogen lamp	2015/ [58]

* FTO = fluorine tin oxide; ITO = indium tin oxide; AAO = anodized aluminum oxide; Fe = iron; C = carbon; CE = counter electrode; Pt = platinum; Ti = titanium; Ag/AgCl = silver/silver chloride; SCE = saturated calomel electrode; RHE = reversible hydrogen electrode; NHE = normal hydrogen electrode; SHE = standard hydrogen electrode; SMSE = saturated mercury/mercury sulfate electrode; I₂ = iodine; KI = potassium iodide; C₁₆H₃₆IN = tetrabutylammonium iodide; FeCl₂ = iron(II) chloride; FeCl₂.4H₂O = iron(II) chloride tetrahydrate; FeCl₃ = iron(II) chloride; FeCl₃ = iron(II) chloride; FeCl₃ = iron(II) chloride; FeCl₃ = iron(II) chloride; (NH₄)₂Fe(SO₄)₂ = ammonium iron(II) sulfate; FeSO₄ = iron(II) sulfate heptahydrate; NH₄F = ammonium fluoride; NH₄Cl = ammonium chloride; (NH₄)₂Fe(SO₄)₂ = ammonium iron(II) sulfate; (NH₄)₂Fe(SO₄)₂.6H₂O = ammonium iron(II) sulfate; C₁₃NaO₂ = sodium acetate; C₂H₃NaO₂.3H₂O = sodium acetate trihydrate; Na₄SP₃O₁ = sodium tripolyhosphate; CH₃COOK = potassium acetate; C₃H₅N = pyridine; C₂H₆OS = dimethyl sulfoxide; C₂H₆O₂ = ethylene glycol; C₃H₈O₃ = glycerol; KOH = potassium hydroide; NaO₃ = sodium nitrate; HNO₃ = nitric acid; HF = hydrofluoric acid; H₃PO₄ = phosphoric acid; C₆H₈O₆ = ascoribic acid; H₃BO₃ = boric acid; H₂NSO₃H = amidosulfonic acid; GA = γ -glucuronic acid.

For the metal anodization method, Prakasam et al. first reported the synthesis of self-aligned nanoporous hematite on Fe foil using an electrolyte consisting of nitric acid (HNO3), hydrogen fluoride (HF), ammonium fluoride (NH₄F) and glycerol ($C_3H_8O_3$) followed by annealing treatment at 400 °C [124]. The ranges of pore diameter and length were 50-250 nm and 300-600 nm, respectively. It is noted that the pore size largely depends on the anodization conditions, including the electrolyte compositions and applied potential. Under AM 1.5 illumination, the photocurrent density reached 0.51 mA cm⁻² at 0.6 V_{RHE} in an electrolyte containing hydrogen peroxide (H₂O₂) (0.5 M) and sodium hydroxide (NaOH) (1 M). On the other hand, selfassembly organized hematite nanotube arrays fabricated on Fe foil by a facile two-step anodization method were reported by Zhang et al. [114]. By employing this synthesis approach, hematite nanotubes exemplified a pore diameter of 40 nm, a length of 2 µm and a wall thickness of at least 10 nm, generating a photocurrent density of 0.352 mA cm⁻² at 0.6 $V_{Ag/AgCl}$ under AM 1.5 illumination. Both the PEC and photocatalytic activities of the hematite nanotubes were assessed by the degradation of methylene blue (MB) under AM 1.5 simulated solar light. Interestingly, the hematite nanotubes showed a high photostability with no significant loss of activity after five cycles continuous runs for the degradation of MB. In another study, Jun et al. reported well-ordered honeycomb hematite films synthesized by a two-step anodization method of Fe foil [119]. The obtained honeycomb nanostructure was found to be more efficient in generating a larger area film with uniform pore distribution than the nanotubes synthesized by a typical one-step anodization method. The

highest photocurrent density achievable for the honeycomb hematite film was 0.24 mA cm⁻² at 1.23 V_{RHE} in NaOH (1 M) under AM 1.5 illumination conditions. Importantly, the well-ordered honeycomb nanostructure allowed for a better interaction with the electrolyte precursor and therefore, significantly reduced the hole diffusion length. Recently, a new iron oxide bilayered nanostructure composed of top nanosphere and bottom nanoturbular layers was constructed on an Fe rod following a similar approach [69]. By integrating the individual distinctive properties of nanospheres and nanoturbular, the new bi-layered nanostructure demonstrated a better photocatalytic performance and a superior charge transfer behavior [120]. However, the highest photocurrent density achievable for such a nanostructure was relatively low, which was 0.143 mA cm⁻² at 1.54 V_{RHE} in potassium hydroxide (KOH) (1 M) under AM 1.5 simulated sunlight.

2.2. Cathodic electrodeposition

On the other hand, cathodic electrodeposition is carried out at a negative applied potential in a three-electrode electrochemical cell as shown in Fig. 1c. The most common cathodic electrodeposition method involves the reduction of H_2O_2 to hydroxide (OH⁻) ions in an electrolyte containing Fe^{3+} ions. As a result, the pH level near the working electrodes increases while the solubility of Fe^{3+} ions in the electrolyte decreases causing the precipitation of Fe^{3+} ions to form FeOOH films [134]. The reactions can be described as follow:

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(6)

 $\mathrm{H_2O_2} + 2\mathrm{e^-} \rightarrow 2\mathrm{OH^-}$

$$FeF^{2+} + 30H^- \rightarrow FeOOH + 2F^- + H_2O \tag{7}$$

With an overall reaction

$$3H_2O_2 + 2FeF^{2+} + 6e^- \rightarrow 2FeOOH + 2F^- + 2H_2O$$
 (8)

In order to improve the stability of Fe³⁺ ions in the electrolyte, complexing agents such as sodium fluoride (NaF) and potassium fluoride (KF) are used to form FeF²⁺ complex. The formation of FeF²⁺ complex ensures the potential for the reduction of Fe³⁺ to Fe²⁺ ions to be more cathodic than the reduction of H₂O₂ to OH⁻ ions [106]. The resulting amorphous FeOOH films can be converted into hematite films upon annealing treatment.

Mao et al. investigated two different routes to fabricate vertically aligned hematite nanorods and nanotubes (Fig. 3a) on anodized aluminum oxide (AAO) template by the cathodic electrodeposition method [112]. It is interesting to note that hematite nanotubes possess a higher PEC performance than the hematite nanorods, leading to an enhanced photoresponse, a more cathodic onset potential, an improved photon absorption and better electron transport properties. These are attributed to the uniform and well-aligned nanotubes that exhibit a higher effective surface area adjoining with the electrolyte and thus, allowing the diffusion transfer of the minority carriers to oxidize the species at the SCLJ. The highest photocurrent density achievable was approximately 2.2 mA cm⁻² at 0.43 VAg/AgCl in NaOH (1 M) under AM 1.5 solar irradiation from a 10 µm long hematite nanotubes that was almost 4 times higher than that of the hematite nanorods. In another study, dendritic Fe wire arrays were grown on the ITO glass substrates (Fig. 3b) and they were transformed into hematite by annealing treatment without changing the dendritic nanoarchitecture [121]. In spite of the distinctive morphology of dendritic hematite wire, the measured photocurrent density was considerably low as compared to those reported for hematite nanowires and nanotubes [112, 113, 135]. A plausible reason for this was that the dendritic hematite wire was too long (30 µm) to efficiently absorb light photons and extract the photogenerated electrons, leading to a poor photogenerated electron-hole pairs separation.



Fig. 3. FESEM images of hematite (a) nanorods and (b) nanotubes prepared by cathodic electrodeposition synthesis method. Reproduced with permission from ref. [112]. Copyright 2011, American Chemical Society. (c) Low magnification and (d) high magnification of SEM images of Fe dendritic wire on ITO glass substrates: The ends of dendritic wires grew both parallel and perpendicularly. Reproduced with permission from ref. [121]. Copyright 2012, Royal Society of Chemistry.

Additionally, Liu et al. discovered that the two-dimensional (2D) ultrathin hematite nanoflakes could be fabricated from the parent 1D hematite nanorods through cathodic electrodeposition synthesis [20]. Under optimized synthesis conditions, the hematite nanoflakes were found to have an average diameter of 100 nm and an average thickness of 10 nm. In comparison to the 1D nanorods, hematite nanoflakes have a larger surface area and a lower charge transfer resistance, in which the photocurrent density was found to be 0.38 mA cm⁻² at 0.2 V_{Ag/AgCl} in NaOH (1 M) under AM 1.5 illumination. The significant reduction in charge transfer resistance of hematite nanoflakes was resulted from its ultrathin thickness and hence, promoting a higher charge mobility in the 2D nanostructures in contrast to the 1D nanomaterials. In a more recent work published in 2016, Wang and co-workers reported the enhancement of PEC activity of α-Fe₂O₃/FTO via an electrochemical reduction synthesis method [105]. By electrochemical reducing α-Fe₂O₃/FTO, magnetite (Fe₃O₄) was generated at the α-Fe₂O₃/FTO interface and thus, forming a hydroxide ionmodified hematite surface as delineated in Fig. 4. The photoresponse of the partial electrochemically reduced α-Fe₂O₃/FTO was significantly enhanced by 25 times, producing a layer of more conductive Fe₃O₄ at the interface between hematite and FTO glass. As a result, the as-formed Fe₃O₄ layer was observed to favor the charge transfer and collection process at the SCLJ upon light irradiation and thus, impeding the recombination of photogenerated electronhole pairs.

2.3. Potential cycling/pulsed electrodeposition

In comparison to the anodic and cathodic electrodeposition synthesis methods as discussed in Sections 2.1 and 2.2, the potential cycling/pulsed electrodeposition synthesis method utilizes both anodic (E_A) and cathodic (E_C) limit of potentials that are maintained at constant (Fig. 5) [107]. During the potential cycling electrodeposition synthesis process, the potential varies between anodic and cathodic limit potentials with a sweep rate and different number of cycles. On the contrary, the potential pulsed electrodeposition comprises of an anodic pulse (t_A) when an anodic potential is applied, and a cathodic pulse (t_C) when a cathodic potential is applied. In this instance, the number of pulse cycles is fixed where each pulse cycle consists of an anodic pulse and a cathodic pulse. The mechanism of potential cycling/pulsed electrodeposition is based on the redox reaction at the SCLJ [110]. The nucleation and growth of the as-deposited films are directly governed by the adsorption and desorption processes, which can be systematically controlled by tuning the electrodeposition synthesis parameters.



Fig. 4. (a) Schematic of enhanced photocurrent density of α -Fe₂O₃/FTO after electrochemical reduction. (b) Photocurrent density vs potential curves for α -Fe₂O₃/FTO films reduced in NaNO₃ (0.1 M) under AM 1.5 light illumination. Reproduced with permission from ref. [105]. Copyright 2016, American Chemical Society.

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Fig. 5. Potential waveforms for (a) potential cycling electrodeposition and (b) potential pulsed electrodeposition.

Previously, Riveros et al. employed dimethyl sulfoxide (DMSO) (C2H6OS), a non-aqueous based solution to fabricate hematite thin films via a potential cycling electrodeposition synthesis method [108]. It was found that the hematite films grown by potential cycling were adherent and uniform. After optimizing the applied potential, electrolyte temperature and annealing temperature, the hematite film attained a photocurrent density of 33 µA cm⁻² at 1.23 V_{RHE} in NaOH (0.1 M) under 6.5 mW cm⁻² white light illumination. In a more recent study by Shinde et al., they prepared high quality hematite photoanodes by utilizing pulse reverse electrodeposition (PRED) synthesis method where the potential was switched between -6 V (E_c) and +4 V (E_A) [110]. It was observed that the PRED synthesis parameters facilitated the passivation of surface trapping states and therefore, markedly reduced the overpotential requirement for water oxidation reactions. The granular and compact hematite films were measured to have a thickness of 200 nm and achieved a photocurrent density of 0.504 mA cm⁻² at 1.23 V_{RHE} in NaOH (1 M) under AM 1.5 illumination. This enhancement was attributed to the increase in the donor density based on the Mott-Schottky analysis. As a continuation of the previous research, it is worth highlighting that the same research group obtained the highest photocurrent density (0.813 mA cm⁻² at 1.23 V_{RHE}) thus far for the pristine hematite photoanode synthesized from the Fe foil via the PRED synthesis method [68]. In their study, nanoflakes and nanocorals hematite were fabricated via two different growth conditions (Fig. 6a). The nanoflakes hematite was synthesized by annealing a Fe foil being exposed to air environment, whereas the nanocorals hematite was fabricated by treating the Fe foil with PRED prior to annealing treatment. The assynthesized nanocorals hematite exhibited a stable interface and high-index [104] facet sites and thus, considerably prolonging the recombination of electron-hole pairs and further enhancing the water oxidation reaction. Fig. 6b depicts the schematic of charge transfer behaviors in both nanoflakes and nanocorals hematite photoanodes. The nanoflakes hematite was measured up a length of 3-4 µm, whereby the photogenerated charge carriers required a longer electron transfer pathway to travel before the water oxidation reaction could take place. Owing to a larger diffusion distance in the hematite flakeshaped morphology, this actually increased the probability of recombination of electron-hole pairs. In contrary, nanocorals hematite was made up of 100-200 nm thin layer which would be beneficial for suppressing the recombination losses. This work has demonstrated a new strategy in engineering the structuredependent hematite photoanodes with excellent PEC performance which can be further improved.

3. Parameters controlling the morphology of pristine hematite

3.1. Electrolyte precursor

As a matter of fact, it is widely reported that electrolyte precursor composition, temperature and pH are the predominant electrodeposition synthesis parameters that influence on the structural, morphology, optical and electronic properties of the pristine hematite. Prakasam et al. prepared a nanoporous hematite with different concentrations of NH₄F. When the NH₄F concentration doubled at the precursor temperature of 4 $^{\circ}$ C, a well-defined nanoporous hematite was developed as a result of the increase in the rate of oxidation of Fe metal and the chemical dissolution of oxide layer [124].



Fig. 6. (a) Schematic illustrating the formation of nanoflakes and nanocorals hematite via different synthesis conditions (Path 1 and Path 2). (b) Diagram of the charge transfer mechanism in (i) nanoflakes and (ii) nanocorals hematite for the water oxidation reaction. Reproduced with permission from ref. [68]. Copyright 2015, Royal Society of Chemistry.

Additionally, it was noticed that the HF and HNO₃ concentrations had a direct effect on the overall thickness of the hematite film. As the concentration of HNO₃ (0.1 M) increased from 0.05 to 0.2 %, the overall thickness of hematite films also increased from 400 nm to 1 µm. In another similar work, LaTempa et al. studied the influence of precursor temperature and NH₄F concentration on the morphological structure of hematite [115]. Surprisingly, nanoporous hematite was fully transformed to nanotubes hematite when the precursor temperature reached 55 °C. With increasing precursor temperature, both the length and diameter of nanopores/nanotubes were gradually increased until reaching maturation at 50 °C when the formation of nanotubes occurred. This phenomenon could be elucidated by the fact that at a low precursor temperature, F ions mobility was restrained and thus, restricting the rate of chemical dissolution [136]. Although chemical dissolution is imperative for the formation of nanotubes, both the rate of oxidation and chemical dissolution will accelerate with the increase in precursor temperature, giving rise to a longer length and larger diameter of nanoporous/nanotubes [137]. Upon light irradiation, a substantial increase of the photocurrent density was observed with elevating precursor temperature. Meanwhile, the wall thickness was found to be directly dependent on the NH4F concentration. A higher concentration of NH₄F resulted in a thinner nanotubes hematite, in which the precursor temperature was necessarily tuned at the respective NH₄F concentration in order to obtain the desired nanotubes hematite. Recently, Huang et al. investigated the influence of precursor temperature on the PEC performance of hematite films prepared by anodizing sputtered Fe film on the FTO glass [131]. It was found that the thickness of the films and the size of nanoparticles were closely associated with the precursor temperature. This observation was attributed to the high etching rate of oxides, and nucleation occurred at the high precursor temperature [138]. It was noted that the nanostructured hematite transformed from films to nanorods as the precursor temperature increased. Importantly, this morphological transformation had gradually improved the photocurrent density up to 0.59 mA cm⁻² at 0.6 V_{SCE} under AM 1.5 illumination, which was approximately 5.3-fold higher than the hematite films.

Moreover, the influence of electrolyte precursor pH on the compositions and morphologies of hematite fabricated by an anodic electrodeposition synthesis method was explored by Spray and Choi [99]. Notably, the film prepared from the neutral pH medium (pH 7.5) was two times thicker and rougher than that from the acidic medium (pH 4.1) despite containing a
comparable amount of hematite. Nevertheless, the pH 7.5 film generated a lower photocurrent density by a factor of 2 than the pH 4.1 film. This was ensued from the higher surface area attained by the pH 7.5 film with a significant increase in the film thickness, which led to a reduction in both the surface area and hematite loading per unit thickness. As a consequence, the average distance for the photogenerated electrons to be collected became larger. Thus, the recombination losses were markedly increased owing to the low electron mobility and conductivity of the pH 7.5 hematite film. This is in accordance with another study by Yilmaz and Unal that examined the effects of electrolyte precursor concentration and pH on the structural characteristic of hematite films [98]. From their work, both acidic and neutral electrolyte precursors were used for the deposition of hematite, whereby the acidic and neutral solution composed of iron (II) chloride (FeCl₂) (0.02 M) (pH 3.8), and FeCl₂ (0.02 M) and sodium acetate (C₂H₃NaO₂) (0.08 M) (pH 6.2-6.8), respectively. For the former, the hematite film was constituted of spherical nanoparticles with diameters in the range of 300-400 nm (Fig. 7a). Whilst for the latter, the formation of spherical nanoparticles with reduced diameters of 50-100 nm was obtained (Fig. 7b). When the concentration of FeCl2 increased from 0.02 to 0.05 M, small nanoparticles (~50 nm) as well as large aggregated particles of varying sizes were observed (Fig. 7c). Upon increasing the concentrations of both FeCl2 and C2H3NaO2, nanoparticles with diameters of ~100 nm and the formation of micrometer-sized agglomerates were observed (Fig. 7d). Interestingly, the photocurrent densities of all these hematite samples exhibited an n-type semiconductor behavior with no sign of photocorrosion. Among all the samples, the better performance of hematite films was recorded at a higher pH with the highest photocurrent density of 23.6 µA cm⁻² at 1.23 V_{NHE} in NaOH (1 M) under AM 1.5 illumination.



Fig. 7. FESEM images of hematite films synthesized at different electrolyte precursor concentrations and pH (a) FeCl₂ (0.02 M) (pH 3.8), (b) FeCl₂ (0.02 M) and $C_2H_3NaO_2$ (0.08 M) (pH ~6.4), (c) FeCl₂ (0.05 M) (pH 3.8) and (d) FeCl₂ (0.05 M) and $C_2H_3NaO_2$ (0.2 M) (pH ~6.4). Reproduced with permission from ref. [98]. Copyright 2015, Royal Society of Chemistry.

3.2. Electrode substrate

Another key electrodeposition synthesis parameter that significantly affects the structural properties of nanostructured hematite is the selection of electrode substrates. By and large, the most commonly employed electrode substrate for the metal anodization is Fe substrates. In fact, there is a wide range of Fe substrates (e.g. Fe foil and Fe rod) being used in the reported literature up to date [69, 70, 114, 120], in which the chosen electrode substrate casts an absolute impact on the nanostructured hematite formation as well as its PEC water splitting performance. In 2014, Lee et al. utilized different purities of Fe substrates for the formation of hematite photoanodes [70]. Two Fe substrates with purities of 99.5 % and 99.99 % were investigated in their work. Upon electrodeposition, the most apparent differences between these two Fe substrates were the film thickness and the quality of nanotubes formed. A thin porous film of thickness \leq 750 nm was obtained for the 99.5 % Fe

substrate, whereas a well-defined nanoturbular morphology with a length of about 1.7 µm was formed for the 99.99 % Fe substrate. Furthermore, it was evidently observed that the onset potential and photocurrent density attained when using the 99.99 % Fe substrate were significantly better than that of the 99.5 % Fe substrate. It was deduced that the 99.5 % Fe substrate contained a higher manganese (Mn) impurity concentration, which could facilitate the dissolution of the oxide formed and led to a significant reduction in the photocurrent density. This study had proven that the purity of electrode substrate undeniably plays a pivotal role in the PEC water splitting performance. On the other hand, Schrebler et al. investigated the effect of Fe substrate (bare and pretreated Fe foils) on the surface morphology of the nanostructured hematite [116]. It was found that the hematite can be transformed from 1D nanoporous film (using a bare Fe foil) to a self-organized nanotube array (using a pretreated Fe foil by cathodic polarization). The PEC studies unveiled that the hematite grown on the pretreated Fe foil demonstrated a higher incident photon-to-current efficiency (IPCE) value (45 % at 375 nm) than that of being anodized on the bare Fe foil. In another research, Qiu and co-workers prepared 1D Fe wires on the copper (Cu) substrate followed by thermal oxidation to convert the Fe wires into hematite [139]. However, the stumbling block of using the Cu substrate was that it was not optically transparent and can be readily oxidized by the induced potential during water splitting process. In view of the bottleneck, a subsequent work on the development of dendritic hematite wires on the ITO and Cu/ITO glass substrates through the cathodic electrodeposition method has been conducted by the same group of researchers [121]. It was noteworthy that the density of Fe wires grown on the ITO and Cu/ITO substrates was comparatively lower than that on the Cu substrate. Evidently, a wide gap on the ITO and Cu/ITO substrates uncovered by the Fe wires was easily characterized and measured. This was attributed to the different surface roughness that presents on the electrode substrates.

Apart from that, AAO template was widely used to fabricate hematite nanorods through the cathodic electrodeposition synthesis method [113]. A schematic showing the synthesis process is depicted in Fig. 8a. Prior to the electrodeposition process, gold (Au) was sputtered on one side of the AAO template which served as a conductive electrode. Next the Fe ions were electrodeposited onto the Au nanorods within the AAO template and subsequently, annealed at 500 °C to transform them into hematite nanorods. Then the AAO template was removed by dissolving it in NaOH (0.5 M). The resulting hematite nanorods were well-aligned and perpendicularly grown on the substrate with high surface area. Consequently, the inverse opal structured hematite photoanodes constructed on the polystyrene (PS) template have also been reported by another research group of Park et al. as illustrated in Fig. 8b [132]. In this study, the effect of template size to fabricate hematite photoanodes for the PEC process was taken into consideration. It was noted that the photocurrent density gradually decreased, as the template size increased. It was possible that the inverse opal with a replicated shell covering the uniform face-centered-cubic (FCC) structure provided large specific surface area and porosity, which resulted in improved PEC performance [140]. In other words, a small size PS template would have higher specific surface area than a large size PS template. By removing the small size PS template, more disclosed areas of the inverse opal structure would be formed which were favorable to the enhanced photoresponse.



Fig. 8. Schematic of the synthesis processes to develop nanostructured hematite grown on the (a) AAO template and (b) PS template. Reproduced with permission from ref. [113, 132]. Copyright 2010 and 2013, Royal Society of Chemistry.

3.3. Applied potential

The applied potential is a requisite parameter in the electrochemically synthesis method that can significantly affect the formation of different FeOOH phases. Martinez et al. demonstrated that in the applied potential ranging from -0.4 to 1.0 $V_{Ag/AgCl}$, the formation of the phases followed the sequential order of magnetite (Fe₃O₄), goethite (α-FeOOH) and lepidocrocite (γ -FeOOH) when the potential was anodically shifted [127]. They proposed a phase diagram (Fig. 9), elucidating the effect of applied potential on the different FeOOH phases formed. The as-deposited films were adherent and uniform, where the colors of magnetite, goethite and lepidocrocite films were black, yellowish-brown and reddish-brown, respectively. At the applied potential of -0.34 VAg/AgCl, a magnetite phase was formed with a dense and regular film having a thickness of 1.1 µm, which composed of well-faceted polyhedral crystallites. Meanwhile, a film of goethite was obtained at the applied potential of -0.1 $V_{Ag/AgCl}$ where the film's thickness was found to be 3.6 µm, comprising vertically grown aggregated rhomboidal columns with some narrow voids among them. When the applied potential was further increased to 0.6 $V_{Ag/AgCl}$, a lepidocrocite film (thickness of 8.2 µm) with lathlike and elongated crystals was grown perpendicularly onto the electrode substrate. In short, different FeOOH phases can be successfully achieved by varying the applied potential despite using the same electrolyte precursor.



Fig. 9. (a) Scheme of different FeOOH phases formed as a function of applied potential. SEM images of (b) magnetite (Fe₃O₄), (c) goethite (α -FeOOH) and (d) lepidocrocite (γ -FeOOH) captured at different applied potentials. Reproduced with permission from ref. [127]. Copyright 2007, Electrochemical Society.

On another aspect, Tamboli et al. found that as the applied potential increased from -0.2 to 0.45 $V_{Ag/AgCl}$, the size of the nanoparticles progressively enlarged with the formation of elongated dumbbell nanoparticles [100]. At the applied potential higher than 0.45 $V_{Ag/AgCl}$, the nanoparticles transformed from the elongated dumbbell to granular structure. This phenomenon could be ascribed to the fact that at a low applied potential, the rates of oxides etching and nucleation were low and thus, requiring more time for the cluster formation and resulting in a larger particle formation. Whereas at a high applied potential, the high etching rate of oxides and nucleation enhanced the production rate of nuclei, causing them to grow individually and generate smaller particle sizes. It was also ascertained that the deposition time had a substantial effect on the film thickness as well as the photocurrent density of the resultant film. The increase in deposition time from 10 to 40 min was found to correlate with the increase in film thickness from 600 to 1120 nm. A similar increasing trend was also observed for the photocurrent density with deposition time, being increased from 0.253 to 0.488 mA cm⁻² at 0.4 $V_{Ag/AgCl}$ in NaOH (1 M) under 150 W Xe lamp. In another study, Bennett et al. had also reported the relationship between deposition time and film thickness [101]. The study revealed that film thickness was asymptotic dependent on the deposition time with the applied potential and electrolyte concentration being unchanged. At a shorter deposition time, the deposition rate was almost linear with respect to the film thickness. Nonetheless, a plateau was observed in the thicknessdeposition time curves at a longer deposition time. This was owing to a reduction in the strength of electric field at the film surface, and a depletion of electrolyte concentration when the deposition time further increased [141].

Recently, nanostructured hematite constructed by anodic ($0.4 V_{Ag/AgCl}$) and cathodic (-1.2 $V_{Ag/AgCl}$) electrodeposition methods was explored by Kimmich and co-workers [67]. Hematite films synthesized from both methods showed aggregated nanocrystallites (Fig. 10). However, the cathodically electrodeposited hematite film was composed of larger and agglomerated secondary nanoparticles originating from the primary nanocrystallites. The aggregated spherical nanoparticles of the cathodically electrodeposited hematite film resulted in a higher scattering efficiency, which was a central property in enhancing the PEC performance. Additionally, Rangaraju et al. prepared an ordered nanoporous hematite grown on the carbon (C) steel surface by using the anodization process at different applied potentials [125]. The size of the nanopores electrodeposited at 20 V and 40 V was found to be

in the range of 20-30 nm and 45-60 nm, respectively. The hematite nanoporous

was homogeneous and ordered on the ferrite grains.



Fig. 10. SEM images of nanostructured hematite synthesized by (a, b) anodic (0.4 $V_{Ag/AgCl}$) and (c, d) cathodic (-1.2 $V_{Ag/AgCl}$) electrodeposition methods. Reproduced with permission from ref. [67]. Copyright 2016, Elsevier.

Schrebler and co-workers compared two dissimilar electrodeposition methods (i.e. potential cycling and potential pulsed) in synthesizing hematite thin films [107]. In their work, the E_C (-0.9 V_{SCE}) was remained constant, while the E_A was varied between 0 and 0.5 V_{SCE} during the electrodeposition process. It was apparent that as the E_A shifted anodically, the obtained flat band potential became more positive with reduced donor density. By comparing the potential cycling and potential pulsed electrodeposition methods, it was interesting to note that the hematite film prepared by the former presented higher donor and surface states densities. Conversely, both the donor and surface states densities of the potential pulsed electrodeposited hematite film were diminished. In fact, the potential pulsed electrodeposited hematite film attained a photocurrent density of 10 times larger than the potential cycling electrodeposited hematite film. The significant improvement in photocurrent density was due to the fact that the potential pulsed electrodeposited hematite film comprised small and densely packed nanoparticles, leading to a shorter diffusion hole distance upon light absorption. The minority carriers were then rapidly transferred to the SCLJ to perform water oxidation reactions, prolonging the recombination of photogenerated electron-hole pairs. In another study by Mushove et al., single layer, multilayer and wave-like hematite nanotube arrays were successfully synthesized via anodic electrodeposition synthesis method [118]. The single layer nanotubes were fabricated by anodizing Fe foil at 40 V for 8 min. In contrary, the multilayer nanotubes were synthesized by potential pulsed between 45 and 20 V for 72 and 60 s, respectively, with a total of 5 pulse cycles. On the other hand, the wave-like nanotubes were electrodeposited by cycling potential from 30 to 60 V for 21 min. All these nanotubes films were converted into hematite upon calcination. SEM images (Fig. 11a-f) showed that the single layer and multilayer nanotubes were circular with uniform cross sections, whereas the wave-like nanotubes were circular with a wavy cross section. Due to the higher active surface area possessed by the wave-like nanotubes, this resulted in a

higher photocurrent density and IPCE values as compared to both the single layer and multilayers nanotubes (Fig. 11g-h).



Fig. 11. SEM images of (a, d) single layer, (b, e) multilayer and (c, f) wave-like hematite nanotubes. (g) IPCE and (h) photocurrent vs potential curves of single layer, multilayer and wave-like hematite nanotubes in KOH (1 M). Reproduced with permission from ref. [118]. Copyright 2015, American Chemical Society.

3.4. Annealing treatment

After the electrodeposition synthesis process, annealing treatment is of utmost importance to transform amorphous hematite into crystalline hematite that can be used as photoelectrode in the PEC water splitting application. Previous study had revealed that the crystallinity of film increased with annealing temperature [142]. Tamboli et al. investigated the effect of annealing temperature on PEC properties of hematite thin film [100]. Apart from the film crystallinity, the grain size increased while the voids within the film decreased with the increase in annealing temperature. The increment in grain size has effectively reduced the grain boundaries and thus, hindering the recombination of photogenerated electron-hole pairs. This in turn resulted in the enhancement of photocurrent density with annealing temperature. Similarly, the photocurrent density increased as the duration of annealing treatment was prolonged. The same group of researchers later synthesized nanostructured hematite by two times heat treatment [129]. Initially, the films were annealed at 600 $\,$ °C for 5 h and then subjected to a second heat treatment at 750 or 800 $\,$ °C for 10 min to acquire a highly activated nanostructured hematite. The second heat treatment has caused the particle size to increase from approximately 30 to 90 nm and thus, cracking the surface of the films. The film annealed for one time showed insignificant level of photocurrent density generation. However, the photocurrent density was significantly increased upon second heat treatment at 750 or 800 °C with photocurrent densities of 0.40 and 0.67 mA cm⁻², respectively, at 1.23 V_{RHE} in NaOH (1 M) under AM 1.5 simulated sunlight. This was attributed to the unintended diffusion of tin (Sn) from the FTO glass at high annealing temperatures that facilitated the improvement in the conductivity of the film.

Additionally, the influence of annealing atmosphere on the PEC performance of nanostructured hematite was examined by Rangaraju and coworkers [120]. There were two different annealing environments, namely: (1) 500 $^{\circ}$ for 1 h in hydrogen + argon gas mixture, and (2) 550 $^{\circ}$ for 10 min in acetylene + hydrogen + argon gas mixture. It was envisaged that thermal heating under a reducing environment can incorporate oxygen vacancies in the nanostructured hematite and thus, enhancing the film conductivity [143]. Interestingly, the films annealed under both atmospheres have introduced carbon element within the hematite structure, which could markedly enhance the conductivity of the films. In comparison, the film annealed in the environment (2) endowed a higher photocurrent density than that in the environment (1). However, the reason behind the increase in the photocurrent density was unclear. Therefore, there is a need for more detailed explanations on such phenomenon in the future research.

In 2016, Lucas-Granados et al. studied the annealing parameters for determining the optimal annealing conditions in synthesizing nanostructured hematite [69]. This encompassed (1) annealing temperatures of 300, 400 and 500 °C, (2) heating rates of 2, 5 and 15 °C min⁻¹ and without gradually heating, and (3) annealing atmospheres in air and argon. On the account of annealing temperature, the crystallinity of the nanostructures was significantly increased with annealing temperature. In this instance, the film annealed at 500 $\,^\circ\mathrm{C}$ exhibited the highest crystallinity with a rhombohedral structure [144]. Moreover, the film calcined at 500 $\,\,{}^\circ\!\!{\rm C}$ was found to comprise of both hematite and magnetite phases. By taking advantage on the co-existence of both phases in the film, this significantly enhanced the PEC performance with improved electron transfer rate. Also the high conductivity and lower band gap energy of magnetite promoted the water oxidation reaction [145]. Whilst for heating rate, the film that was annealed without gradually heating showed an uneven and irregular nanostructure, resulting in a negligible photocurrent density. Meanwhile, the film annealed at 15 °C min⁻¹ attained a higher photocurrent density, which was ascribed to the fact that the nanostructure crystallized more rapidly at a higher heating rate and incorporated the lattice structural defects (e.g. oxygen vacancies). In this regard, the defects served as donor states that could reduce surface recombination centers and thereby, improving charge transport behavior. On the other hand, the films annealed in the argon atmosphere generated a higher photocurrent density than that in the air environment. This improvement was due to the formation of magnetite and the incorporation of lattice structural defects upon annealing in the argon atmosphere, which remarkably enhance the film conductivity [146]. In overall, it can be seen that both electrochemically synthesis and annealing treatment parameters play an indispensable role not only in modulating the structural, textural and morphologies of hematite, but also in tuning the electronics properties of hematite. It is envisioned that a systematic understanding on the electrochemical synthesis parameters will give insightful perspectives towards rational design and engineering of pristine hematite photoanodes for application in PEC water splitting.

4. Modifications of hematite photoanodes

4.1. Elemental doping

The introduction of various elements (i.e. Ti, Sn, Zn, Al, Zr, W, Ta, Nb, Cd, Au and so forth) as impurity dopants into the hematite photoanode has been widely investigated in an attempt to tune the characteristics of doped hematite film into a *p*-type or an *n*-type semiconductor [79, 147-158]. For example, an *n*-type Sn-doped hematite photoanode was electrochemically deposited on the FTO glass [159]. After the incorporation of Sn doping, a conversion efficiency of 0.24 % with a remarkable high photocurrent density of 2.8 mA cm⁻² at 1.24 V_{RHE} was achieved. The enhancement was attributed to the increased donor density and conductivity by the Sn doping, whereby this indirectly promoted a favorable charge migration and separation for enhanced PEC performance. This study was in agreement with a previous study by Shinde and co-workers, which investigated the diffusion of Sn from the FTO glass upon annealing treatment that favored the photocurrent response of hematite photoanode [19]. In another study, Qi et al. developed a simple anodic electrochemical method to synthesize a unique *p*-type Zn-doped hematite nanotube array for PEC water splitting [160]. Based on the architecture design of photoanode, the nanotube arrays promoted the light absorption and effective charge collection. These resulted in a drop in potential due to the reduction in charge transport in bulk hematite, and also the corresponding recombination rate was decreased. This could be underpinned by a cathodic photocurrent density (40.4 μ A cm⁻² at 0.5 V_{RHE}) and a positive onset potential of photoresponse (i.e. 1.3 VRHE). This study casts a new research doorway for indepth investigations on the smart construction of p-n junction photoanodes and tandem devices for PEC water splitting.

As a proof of concept, Ti doping has been regarded as one of the common dopants that could improve both the photocurrent density and conductivity [161-163]. In 2016, Kalamaras and co-workers demonstrated the development of electrochemically deposited Ti-doped hematite photoanodes followed by a high temperature annealing process [164]. In their work, the possibility of hematite photoanodes beyond water splitting was investigated by introducing organic sacrificial agents for H_2 evolution. They observed a significant increase in the H_2 evolution rate, which was nearly doubled with the addition of ethanol in the PEC water splitting system.

Codoping between two dissimilar impurity dopants is also another key approach to significantly enhance the overall PEC performance [165-167]. Owing to the properties of both Zn and Ti dopants, Ferapontova's group explored the incorporation of these Ti and Zn dopants in the hematite matrix with the target of achieving an enhanced PEC performance in terms of high photocurrent density and low onset potential during the water splitting reaction [168]. The Ti/Zn-modified hematite photoanode attained a photocurrent density of 1.5 mA cm⁻² at 1.23 V_{RHE}, which was about 2.5-fold higher than the bare hematite photoanode. Additionally, the onset potential of the Ti/Zn codoped hematite photoanode was reduced by 63 mV. In order to further understand the individual contributing effects of Ti and Zn doping, the authors have explored the mono-doping of Ti and Zn. Surprisingly, the Ti-doped hematite shown a significantly enhanced photocurrent density on account of improved electrical conductivity and concentration of photogenerated charge carriers. Meanwhile, for the Zn-doped hematite, a reduction in the onset potential was owing to the Zn contribution for accelerating the kinetics of charge transfer, rendering Zn-doped hematite as the actual water oxidation catalyst (despite a less profound enhancement in the photocurrent density as compared to Ti-doped hematite). Hence, by leveraging on the unprecedented attributes of both Ti- and Zn-doping, the overall PEC activity of Ti/Zn modified hematite photoanode was improved with enhanced conductivity, charge carrier dynamics and decreased onset potential.

To date, most of the current studies focus on the incorporation of dopants into the hematite structure during the growth of hematite process, by which a certain extent of control over the doping is necessitated to prevent the issue of unintentional change in material growth [169]. On the contrary, post-growth doping strategies are relatively new and have not been explored thoroughly. The advantage of post-growth doping is that it is a facile and complementary doping strategy without much dependency on any synthesis methods of hematite photoanode. Therefore, this post-growth doping strategy can be applied to all undoped hematite nanomaterials for enhancement in PEC activity. Franking et al. performed a post-growth doping of hematite photoanodes by depositing Ti precursor followed by annealing under air environment [162]. Upon the introduction of Ti doping, the donor concentration of hematite was noticeably increased by 10 times as well as the carrier transport and collection were readily facilitated for an enhanced PEC efficiency. It was worth noting that Ti dopants markedly altered the electronic structure of hematite by passivating the surface trap states as a result of noticeable shifts in the flat-band potential. As such, smart engineering of surface trap states and efficient passivation approaches during the nanostructured hematite photoanodes are of fundamental and importance for practical benefits in the PEC activity.

Doping of hematite with the noble metal Pt has been evidently corroborated by numerous research groups for the enhancement of PEC efficiency [170]. Hu et al. performed an electrochemical process to develop the photoanode of Pt-doped hematite for PEC water splitting [171]. This work primarily demonstrated the possibility of introducing Pt into hematite via a coelectrodeposition synthesis approach. It was noted that 5 % Pt-doped hematite resulted in the highest PEC activity with a photocurrent density of 1.43 mA cm⁻² relative to the bare hematite (0.69 mA cm⁻²) at 0.4 V_{Ag/AgCI}. By means of the substitution of Fe³⁺ by Pt⁴⁺ within the lattice structure of hematite, Pt was functionalized in the role of an electron donor that increased the concentration of donor in the *n*-type photoanode for greater electrical conductivity and electrical charge over the space charge layer. Consequently, these enhanced the charge separation efficiency that prolonged the recombination rate of electron-hole pairs. Nonetheless, the presence of Pt doping in high concentration would cast an adverse effect on the width of space charge layer and thus, leading to the formation of highly-dense recombination centers and severely negated on the PEC activity. Hence, it is noteworthy that an optimum metal doping plays a predominant role as an effective electron donor in the PEC process.

Meanwhile, another group of researchers has vertically grown Pt-doped hematite nanorod arrays on Au substrate via a facile electrochemical codeposition method with the aid of AAO as a synthesis template [172]. Apparently, AAO has been extensively employed as a cost-effective nanotemplate synthesis for the fabrication of large arrays of nanorods due to its intriguing features such as good thermal stability, tunable pore size and high mechanical strength [173]. Herein, the 1D hematite nanorod arrays demonstrated high surface area, excellent solar light harvesting and improved conductivity with similar observation as reported by Hu et al. [171]. Pt could serve as an electron storage reservoir as well as facilitating the interfacial transfer of electrons, in which Pt-doped hematite photoanode showed a remarkable STH conversion efficiency of ca. 5 % under sunlight illumination. This study is in a good agreement with our recent study to synergistically understand the kinetics of charge migration in Pt-mediated hematite photoanodes [174]. In our work, the flat-band potential of hematite was found to be shifted by 30 mV to a less positive potential, which concurred well with the shift in the photocurrent onset potential.

Apart from the typical metal doping strategy on alleviating the low PEC activity bottlenecks in pure hematite, there are other works related to the modification of hematite with non-metal elements such as carbon [78, 175]. Surface coating of hematite with a carbon layer has been regarded as an alternative strategy to achieve a much improved PEC performance [176]. Previously, Wang and co-workers employed a facile electrodeposition synthesis method to develop carbon-coated hematite photoanodes via the addition of citric acid as the carbon source in the electrolyte [177]. In this study, citric acid used as the carbon source can easily bind to the porous surface of hematite due to its high affinity [178]. Owing to the strong interaction, the surface-bound citric acid would be transformed to a carbon layer upon annealing treatment. The carbon-coated hematite photoanodes generated a high photocurrent density of 2.1 mA cm⁻² at 0.4 V_{SCE} , which was about 7 times higher when compared to the unmodified hematite film. Such an improvement in the photocurrent density was attributed to the passivation effect of the surface-coated carbon layer. However, the main drawback was that the oxidation of surface-coated carbon layer could in turn reduce the hematite surface to FeOOH, significantly diminishing the photocurrent density by an order of magnitude. Therefore, future work on developing a "good" surface carbon-coating layer is of vital importance for improved PEC stability. Other than that, another related work on the synthesis of carbon-coated hematite via a facile pyrolysis synthesis method of ferrocene was investigated by Deng et al. [176]. In addition to carbon coating, oxygen vacancies were also created within the hematite lattice structure that was accountable for the high photocurrent density of 2.1 mA cm⁻² at 1.23 V_{RHE} in comparison to the carbonfree hematite (0.5 mA cm^{-2}).

Besides, the introduction of electrical conductive scaffolds such as carbon nanotubes, fullerene, carbon nanodots and graphene could also significantly improve the charge transfer dynamics of a semiconductor toward enhanced solar energy conversion [37, 179-183]. Recently, the utilization of 2D graphene in the graphene-based hybrid nanocomposites has become a cutting-edge research hotspot in global science specifically in the realm of energy production [184-186]. Until now, there has been a huge quest in increasing the PEC activity of hematite via the hybridization with graphene as efficient electrocatalysts [187]. The various benefits of 2D graphene include good flexibility and moderate van der Waals forces, rendering uniform distribution of graphene over the metal oxide photoanodes [188]. Not only that, graphene could function as a charge transfer scaffold and active catalytic sites for oxygen evolution reaction [189, 190]. In another most recent work by our research group, electrochemical reduced graphene oxide (eRGO)-hematite hybrid nanomaterials were synthesized by means of a two-step electrodeposition

synthesis method for enhanced PEC water splitting [191]. The hybrid nanocomposites demonstrated a significant 8-fold improvement in the photocurrent density relative to the bare hematite, which was attributed to the optimum controlled eRGO nanosheets that could enlarge the active surface area of hematite, improve absorption of solar light, act as a surface passivation layer as well as accelerate the transfer of photoexcited electrons from hematite into eRGO to prolong the lifetime of charge carriers (Fig. 12a). Similar phenomena on the use of graphene as an electron transporting bridge and channel for light-driven catalytic reactions have also been extensively reported by a number of researchers [192-196].



Fig. 12. (a) Illustration of charge transfer and separation in the eRGO-hematite for PEC water splitting. Reproduced with permission from ref. [191]. Copyright 2017, Elsevier. (b) Fabrication process of C_{60} /hematite, eRGO/hematite and eRGO/C₆₀/hematite photoanodes via electrodeposition. Reproduced with permission from ref. [197]. Copyright 2017, John Wiley & Sons, Inc.

As a continuation of our previous research in the area of carbonaceous nanomaterials [191], our group has further engineered a novel ternary hematite nanocomposite photoanode consisting of 2D eRGO and zero-dimensional (0D) fullerene (C₆₀) that could function as remarkable surface passivators [197]. Interestingly, the hybridization of highly conducting eRGO and electron scavenging C₆₀ evidently increased the absorption of visible light and near infrared. Based on the PEC water splitting performance, the binary eRGO/hematite and ternary nanocomposite photoanodes demonstrated 13.3 and 16.8 times greater in photocurrent density, respectively, when compared to the pristine hematite photoanode. A similar trend has also been observed from the EIS results for the reduction in charge transfer resistance for the resultant ternary eRGO/C₆₀/hematite photoanode. As such, rapid transfer of photoinduced electron-hole pairs and inhibition of charge recombination were the underlying factors, which accounted for significant improvement of PEC water splitting performance in the hematite-based photoanodes.

4.2. Surface treatment

Apart from elemental doping, numerous efforts have been investigated on surface modification of hematite to improve the oxygen evolution reaction (OER) kinetics by reducing the overpotential [38]. In this instance, various surface catalysts have been treated on the hematite surface via the electrodeposition synthesis method for efficient PEC water splitting. For example, the amorphous cobalt-phosphate (Co-Pi) catalyst has been extensively studied since the first article reported by Kanan and Nocera in 2008 [198]. A Co-Pi catalyst electrodeposited onto hematite photoanodes resulted in a 5-fold enhancement in the photocurrent density while the OER kinetics was observed at 1 V_{RHE} [199]. This result revealed that the incorporation of Co-Pi catalyst has considerably reduced the external power requirement for driving OER at 1 mA cm⁻² by more than 0.5 V under AM 1.5 simulated sunlight. A similar study has also been published by Zong et al. for hybridizing Co-Pi catalyst on hematite films to improve surface water oxidation kinetics and PEC performance [71]. It was found that the deposition of Co-Pi has evidently lowered the onset potential for water oxidation and increased the photocurrent density by over 20 % in comparison to pristine hematite. This was attributed to the formation of an inorganic heterojunction and improved charge transport behavior by introducing Co-Pi catalyst and hence, promoting the lifetime of photogenerated minority carriers in the hematite [200]. This study was in agreement with another previous study by Zandi et al., whereby the electrodeposited hematite films treated with Co-Pi catalyst achieved nearunity hole collection performance and the highest photocurrent density for the reported planar electrodes [201]. Additionally, Peerakiatkhajohn and coworkers developed Co-Pi/Ag/Fe2O3 nanosheets photoanodes via the electrodeposition synthesis method, and measured a remarkable photocurrent density of 4.68 mA $\rm cm^{\text{-2}}$ at 1.23 V_{RHE} in NaOH (1 M) under AM 1.5 solar illumination [202]. The improved PEC performance was ascribed to the introduction of both water oxidation Co-Pi catalyst and low-cost plasmonic Ag nanoparticles that potentially stabilized electrode surface, improved light absorption, promoted charge transfer, and hindered photogenerated electronhole pairs recombination (Fig. 13). This finding opens a new avenue towards a low-cost, high performance and stable PEC process for sustainable solar energy conversion.



Fig. 13. Schematic of Co-Pi/Ag/Fe₂O₃ nanosheets photoanode for the application in PEC water splitting. Reproduced with permission from ref. [202]. Copyright 2016, John Wiley & Sons, Inc.

A previous work by Zhang and co-workers reported the loading of Earthabundant metal complex, cobalt-oxo cubenes, as the surface catalyst for water oxidation on electrochemically synthesized hematite photoanodes [203]. This was the first report on the combinatorial use of a noble metal-free molecular catalyst and an inorganic semiconductor to perform water oxidation. Surprisingly, the modification of cobalt-oxo cubenes on hematite exhibited a higher photocurrent density and the onset potential for water oxidation was cathodically shifted by 0.4 V as compared to the bare hematite. Other than that, Herrera et al. prepared porphyrin-sensitized hematite thin films by using 5, 10, 15, 20-tetrakis (4-carboxyphenyl) porphyrin (TCPP) as the sensitizer and a complex for the Fe^{2+} ions (surface states) [204]. After surface modification, the porphyrin-sensitized hematite thin film exhibited an n-type semiconductor and produced 70 % higher photocurrent response in reference to the unmodified hematite. As such, the incorporation of TCPP has shifted the surface states energy levels to more cathodic potential values and thus, lowering the recombination process of photogenerated electron-hole pairs and resulting in an enhanced photocurrent response.

As critically reviewed in Section 4.1, literature studies have highlighted that Al and Sn dopants could distinctly improve the electrical conductivity and thus, enhance the PEC performance [19, 159, 205, 206]. Spay et al. fabricated α -Fe₂O₃-Al₂O₃ and α -Fe₂O₃-SnO₂ electrodes, which showed significantly enhanced photoresponse as well as negatively shifted open-circuit potential [207]. In this instance, the formation of surface coating layers consisting of Al3+ and Sn4+ ions eliminated the surface states and/or reverse reactions prompted by electrons leaking at the SCLJ and was accountable for the overall photocurrent density enhancement. In another similar study by Yin et al., Fe₂O₃-Au-Al₂O₃ thin films were fabricated and further demonstrated a 1.78fold enhancement in the photocurrent density relative to pristine hematite at 0.4 VAg/AgCl [208]. This was due to the combined factors of localized surface plasmon resonance (LSPR) of Au nanoparticles, surface passivation of Al₂O₃ coatings and the rapid charge transport owing to the Schottky junctions at the metal and semiconductor interface. By applying the similar approach with dissimilar surface catalyst, MnO-integrated hematite nanorods were synthesized by Gurudayal and co-workers [209]. Interestingly, the MnOtreated hematite showed a better photocurrent density than the bare hematite as well as the Co-Pi-treated hematite photoanodes. Based on the EIS analysis, both MnO- and Co-Pi-treated hematite possessed similar interface states capacitance values and these inferred an equivalent allocation of states to promote the charge transmission. The charge transfer resistance of MnOtreated hematite was the lowest, implying improved charge injection between the intermediate states and the electrolyte as compared to Co-Pi-treated hematite. Kleiman-Shwarsctein et al. demonstrated the electrodeposition synthesis of NiFe oxide catalyst from Ni(II)-Fe(III) precursor on the Ti-doped hematite to enhance the OER kinetics [210]. Both the photocurrent density and IPCE of the hybrid photoelectrode were significantly enhanced by 4.5 and 5 folds for water oxidation rates, respectively, in comparison to the control hematite sample.

Recently, surface modification by using FeOOH has been studied by a few research groups on BiVO₄ photoanodes [211, 212]. Since Fe is the most abundant metal element on earth [213] and highly stable in water oxidation reaction in neutral and alkaline conditions, it has been applied as a surface catalyst and demonstrated an enhanced photoresponse and the onset potential [214]. Based on this concept, Yu and co-workers modified hematite photoanode with nanostructured FeOOH by means of the photoelectrodeposition synthesis method [215]. From the study, it was found that the nanostructured FeOOH exhibited large surface area and high electrocatalytic activity and thus, facilitating the involvement of photogenerated minority carries in water oxidation reaction and expediting the water oxidation kinetics. This was underpinned by a 4-fold enhancement at $1.23 V_{RHE}$ in the photocurrent density and an obvious cathodic shift by 140 mV in the onset potential. Not only that, the Fe₂O₃/FeOOH photoanodes showed long-term stability with no noticeable decay in the PEC performance. All in all, it is expected that a greater PEC activity of the pristine hematite will be attained by treating its surface with catalysts for reducing the charge recombination rate in the PEC process. Capitalizing on the present stage forward, it is envisaged that the development of hematite photoanodes as described earlier can shed new light on the design of advanced hybrid nanocomposites toward achieving highly efficient hematite photoanodes for the PEC water splitting in the years to come.

4.3. Heterojunctions

By and large, it is apparent that the bare hematite nanomaterials typically encountered several intrinsic shortcomings in meeting the essential requirements (e.g. rapid charge migration and excellent solar light absorption) for a remarkable PEC performance [82, 216]. Apart from the modifications as outlined in Sections 4.1 and 4.2, another promising strategy to overcome these shortcomings is to develop well-defined heterojunction interfaces between hematite and other semiconductors with proper alignment of VB and CB edges [217]. Essentially, the formation of nanoscale heterojunction structure leads to a number of benefits, including: (1) enhanced transportation and separation of charge carriers, (2) improved absorption of visible light, and (3) prolonged the lifetime of electron-hole pairs [11, 218-222]. In this instance, the efficiency of water redox processes for H_2 and O_2 evolution could be considerably enhanced.

As a matter of fact, the charge transfer mechanisms depend largely on the development of band structures between hematite and the second semiconductor (for binary PEC system) and the third semiconductor (for ternary PEC system). Owing to that, the selection of second and/or third semiconductor that exhibits p-type or n-type characteristics is worthy of investigation for the effective interfacial transfer of charge carriers in the designed PEC system. As such, this will profoundly influence the band bending at the heterointerface of semiconductor-semiconductor, semiconductor-electrolyte and semiconductor-substrate in the hybrid heterojunction nanocomposites. To date, a large library of hematite-based heterojunction nanocomposite photoelectrodes has been engineered with an aim to significantly improving the PEC activity. This encompasses the hybridization of hematite with TiO2, ZnO, Cu2O, WO3, CdS, ZnFe2O4, g-C3N4 and many other semiconductors [97, 223-228]. In this section, recent progress on the hematite-based heterojunction structures with appropriate band alignment will be reviewed.

To date, nanoscale-architecturing of TiO_2/α -Fe₂O₃ photoanodes via a multitude of synthesis processes has been broadly examined by a number of research groups for PEC water splitting [227, 229, 230]. In 2008, Mohapatra and co-workers developed Fe₂O₃ nanorods inside a TiO₂ nanotubular array template through a facile pulsed electrodeposition (Fig. 14) [231]. It was found that the diameters and lengths of hematite nanorods were 80-90 and ca. 550 nm, respectively. In another related study, the Ti foils were firstly anodized to form TiO2 nanotube arrays followed by electrodepositing the hematite nanoparticles on the TiO₂ nanotube [232]. Interestingly, hematite nanoparticles were formed only on the mouth surface of TiO_2 nanotube when the pre-contact duration of Fe³⁺ aqueous was relatively short (1 h). In comparison with the precontact time of 1 h, the hematite nanoparticles filled the entire TiO₂ nanotube and even fully covered the top surface of TiO₂ nanotube when the pre-contact time was prolonged to 24 h. Furthermore, Tsui and Zangari electrodeposited hematite on the TiO2 nanotubes and the hybrid nanocomposites demonstrated extended visible light absorption due to the narrow band gap of hematite and achieved an IPCE of up to 2 % [227]. This phenomenon was attributed to the band offset of the heterojunction interface to realize effective charge transfer and separation. Collectively, all these works provide a facile synthetic protocol for the smart engineering of TiO_2/α -Fe₂O₃ photoanodes that could be a blueprint for the construction of diversified branched nanoarrays to further uncover their novel functionalities in the PEC activity.



Fig. 14. Schematic of developing Fe_2O_3 nanorods inside the arrays of TiO_2 nanotube via a pulsed electrodeposition method. Initially, Fe filled the nanochannels of TiO_2 nanotubes and subsequently, oxidation of Fe nanorods took place to form a spherical top end due to overgrowth of the Fe deposition. Reproduced with permission from ref. [231]. Copyright 2008, IOP Science.

Apart from the incorporation of wide band gap TiO2 which is only capable of absorbing UV irradiation, visible-light absorbing nanomaterials, namely WO₃ and g-C₃N₄ have recently become a hot topic in forming hybridized photoanodes with hematite. Among all, visible-light responsive WO3 has been widely employed in the design of hematite heterostructure due to its high photostability and cost-effectiveness [233, 234]. For example, Mao et al. successfully prepared nanostructured hematite/WO3 films for PEC water oxidation, in which the spherical WO3 nanoparticles were initially anchored on the FTO substrate via a surfactant-aided sol-gel process followed by electrochemical deposition of hematite onto the WO3 film forming an intact heterojunction interface [235]. In this hybrid heterojunction system, the photoanode possessed 9 times higher photocurrent response with a STH conversion efficiency of 0.5 % when compared to the unmodified WO₃. The improvement was due to the increased light absorption by expanding the spectral range, and the rapid separation of charge carriers across the heterojunction interface between WO3 and hematite.

As a matter of course, the *p*-type NiO possesses a strong oxygen evolution activity that could be easily developed from Ni to form a solid solution in common oxide [236]. Most recently, our research group has successfully demonstrated a nanostructured *p*-*n* junction NiO/hematite photoanode, which was constructed from an *in-situ* Ni-doping via cathodic electrodeposition of hematite [17]. In comparison to the pristine hematite, the optimized 25 molar % of NiO showed the highest photocurrent density with a 7-fold improvement. Such an improvement was attributed to the reduction in the overpotential of oxygen generation and the increased number of electron donor via the *p*-*n* junction and thereby, decreasing the activation energy barrier for water splitting process. Additionally, the charge transfer resistance was significantly reduced in the hybrid photoanode system, which benefitted from the presence of NiO/hematite heterojunction in facilitating the charge carrier diffusion and electron-hole migration in the opposite direction.

As discussed in Section 4.1, doping of Ti substitutes the Fe atoms in the crystal lattice structure and contributes to the increased in conductivity of hematite [152, 237]. In a study published by Qiu et al., they developed Timodified hematite photoanode through a facile Fe plating on the FTO glass followed by thermal calcination in air environment [238]. Relative to the bare hematite, the photoanode achieved two-fold higher in photocurrent density and exhibited superior stability under the AM1.5G irradiation. The profound enhancement in the PEC activity was due to the formation of crystalline Fe₂TiO₅ phase upon calcination, which then hybridized with hematite to develop a well-contacted Fe₂O₃/Fe₂TiO₅ heterojunction primarily improved the efficiency of charge separation to suppress the electron-hole recombination rate despite a marginally enhanced light-harvesting ability.

Apart from that, Ikram and co-workers sensitized CdSe quantum dots on the electrodeposited hematite (Fig. 15a) [224]. In this work, sensitization of CdSe quantum dots remarkably improved the photocurrent density, which was evidenced by the highest photocurrent density of 1.14 mA cm^2 at 0.8 V_{SCE} with a corresponding maximum solar-to-H₂ conversion efficiency of 0.53 %. The significantly enhanced PEC performance in the CdSe sensitized hematite thin film was emerged from the appropriate band edge alignment between hematite and CdSe quantum dots, more negative flat band potential, reduced charge transfer resistance as well as increased number of donor density compared to the pristine hematite.



Fig. 15. Band edge alignment of (a) CdSe quantum dots sensitized hematite and (b) ZnO quantum dots over hematite/electrolyte interface for PEC water splitting. Reproduced with permission from ref. [223, 224]. Copyright 2014 and 2015, Elsevier.

Due to the fact that Cd is environmentally hazardous and toxic, searching for environmentally safe quantum dots is of paramount importance for practical benefits. As a continuation of the previous research work, the same group of authors examined ZnO quantum dots sensitized electrodeposited hematite for photoelectrochemical H₂ evolution [223]. Interestingly, the photocurrent density of the optimal 24 h sensitization of hematite with ZnO quantum dots recorded as high as 2.84 mA cm⁻² at the potential of 0.75 V_{SCE} . This was a 5.5-fold enhancement in photocurrent density when compared to that of bare Fe₂O₃. Moreover, the maximum applied bias photon-to-current efficiency reached a value of 1.67 % that was related to the synergistic contribution of catalytic behavior of ZnO as well as ameliorated charge separation and transportation at the heterojunction, thus revealing the prominent role of ZnO quantum dots in boosting the injection of hole into the electrolyte (Fig. 15b). Importantly, the optimal sample successfully evolved 6 mL H_2 h⁻¹ cm⁻² at 0.75 V_{SCE}. As a whole, the innovative fabrication of hematite heterojunction nanostructures sensitized with quantum dots with intimate interfacial contacts is of technological importance in enhancing the photoconversion efficiency of water splitting process. Both studies pave new inroads into the utilization of quantum dots hybridized with hematite for boosted charge migration and transfer.

Recently, the development of metal-free visible-light active graphitic carbon nitride (g-C₃N₄) photocatalyst has attracted a considerable research upsurge owing to its nature of environmental benign, earth-abundant, relatively ease of preparation and appealing band edge potentials [36, 218, 239-242]. In 2014, Liu and her colleagues presented morphology-controllable g-C₃N₄-coated Fe₂O₃ heterojunction photoanodes that were synthesized via electrodeposition followed by chemical vapor deposition synthesis methods [243]. It was evident that the surface morphology of the hybrid could be altered from 2D nanosheets to porous cross-linked nanoarchitectures by tuning the filling degrees of g-C₃N₄ precursor (i.e. melamine) upon thermal calcination treatment. Extraordinarily, the PEC water splitting activity of g-C₃N₄/Fe₂O₃ was 70 times greater than that of the pristine Fe₂O₃. This was attributed to the appropriate band energy alignment, and also intimate well-contacted heterointerfaces between g-C₃N₄ and Fe₂O₃ that resulted in efficient electronhole transportation and separation.

To further improve the PEC activity of hematite, hematite-based ternary heterojunction comprising three components of semiconductors has been recently engineered. It is anticipated that the ternary heterojunction photoanode can dramatically improve the PEC performance by accelerating the transfer of photogenerated electron-hole pairs, increasing the solar light absorption and reducing the charge recombination rate [244]. Most recently, Wang et al. deposited hematite nanoparticles and graphene quantum dots



Fig. 16. (a) Schematic of the fabrication steps of Fe₂O₃/NF-TiO₂ and Fe₂O₃-GQDs/NF-TiO₂ photoanodes. (b) Photocurrent response of the studied Fe₂O₃-based photoanodes under chopped visible light irradiation ($\lambda > 420$ nm). (c) Charge transfer and separation mechanism of the Fe₂O₃-GQDs/NF-TiO₂ in the presence of GQDs as an electron accelerator for the inhibition of charge recombination. Reproduced with permission from ref. **[245]**. Copyright 2017, Elsevier.

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(GQDs) onto the N and F co-doped TiO2 (NF-TiO2) via a series of electrodeposition and electrooxidation synthesis method (Fig. 16a) [245]. Owing to the well-known properties of GQDs [246-248], GQDs were produced and anchored on the hematite/NF-TiO2 surface by merely employing a graphite sheet rather than the typical Pt as the anode during the electrodeposition stage. Interestingly, the photocurrent density of Fe2O3-GQDs/NF-TiO2 photoanodes exhibited a substantial 4.2-fold increment with respect to that of the Fe₂O₃/TiO₂-nanotube (Fig. 16b). The combined positive contributions from (1) excellent roles of GQDs as an electron mediator or accelerator, (2) improved visible-light absorption of hematite and NF-TiO2 as well as (3) the effective charge separation across the heterojunction interfaces simultaneously enhanced the overall PEC performance (Fig. 16c). Therefore, it is anticipated that the rational development of nanoscale-architecturing of hematite-based ternary heterojunction photoanodes would be promising towards the PEC performance in energy and environmental-related applications.

5. Future challenges and prospects

In short, we have critically reviewed the electrochemically synthesized hematite in the field of PEC water splitting for energy conversion. To some extents, the structural, morphological, composition, crystallinity, optoelectronic and PEC properties of pristine hematite were known to be influenced by a myriad of predominant factors. These encompass the electrodeposition and annealing conditions, namely electrolyte precursor composition, temperature and pH, electrode substrate, applied potential, deposition time as well as annealing temperature, duration and atmosphere. However, the PEC performance of pristine hematite is still hampered and precluded for niche applications due to its relatively poor electron conductivity, short hole diffusion length, small absorption coefficient and rapid recombination of photogenerated charge carriers [17]. Over the past decades, various efforts have been devoted to overcome these "Achilles' heels" and further enhance the PEC efficiency of hematite.



Fig. 17. Interrelationship of predominant factors in electrochemically synthesized and modifications of hematite photoanodes for advanced PEC solar water splitting towards achieving sustainability.

In this review, we have highlighted the state-of-the-art development in the modifications of hematite photoanodes that could be clustered into three main categories. First and foremost, the incorporation of various elemental dopants on hematite photoanodes has been proven as a prudent strategy to improve the electrical conductivity, increase the concentration of charge carriers and thus, prolong photogenerated electron-hole pairs recombination. Secondly, treating hematite photoanodes with surface catalysts are a promising means to minimize the overpotential required for the OER kinetics and subsequently, reduce the charge carriers recombination at the surface states. Lastly, developing an effective heterojunction interface between hematite and other semiconductors with well-matched band alignment has been demonstrated to enhance transportation and separation of charge carriers at the heterointerfaces of the hybrid PEC system. As a whole, the key connection of the predominant factors in electrochemically synthesized and the modifications of hematite (i.e. elemental doping, surface treatment and heterojunctions) can be pictorially illustrated in Fig. 17 as an overall mind map to the research community for the state-of-the-art progress in the hematite-based photoanodes.

In spite of numerous promising results reported thus far, the highest PEC water splitting efficiency achieved by the hematite photoanode was still significantly lower than the theoretical maximum photocurrent of 12.6 mA cm⁻² [38]. The record-breaking performance of 4.32 mA cm⁻² at 1.23 V_{RHE} under AM 1.5 illumination was attained by a Pt/Co-Pi/hematite wormlike photoanode via an all-solution method by Kin and co-workers [249]. This momentous breakthrough was attributed to the improved charge transfer behavior, and modification of hematite surface properties by introducing Pt dopants and Co-Pi surface catalysts. In this regard, the Pt/Co-Pi/hematite photoanode demonstrated high stability and durability with the production of stoichiometric H₂ and O₂ gases. In light of this, it can be clearly seen that the integration of different modification strategies in synthesizing hematite photoanodes is effective and promising for further enhancement in the PEC performance and thus, warrants potential research investigations on this energy field.

Another exciting approach to dramatically increase the PEC water splitting performance is to develop a tandem PEC cell by combining two or more light absorbing materials with well-matched absorption characteristics. This viable strategy enables greater light harvesting properties and better stability, since the semiconductors involved in both anode and cathode can be optimized individually [250]. As a matter of course, the band gap of hematite is considerably small (2.1 eV) compared to other semiconductors and therefore, engineering a tandem PEC cell with hematite photoanode and another photocathode will be favorable towards attaining high PEC performance. For instance, Jang et al. for the first time proposed an unassisted solar water splitting by using hematite photoanode and TiO₂/Pt/Si photocathode [251]. Although the reported photocurrent efficiency for the unassisted solar water splitting was 0.91 % which was indeed modest, it is projected that by systematic optimization, the PEC water splitting efficiency can be readily enhanced. Additionally, an alternative tandem cell configuration would be by merging a photoelectrode with a photovoltaic device [252-254], which combines solar H₂ generation and storage for achieving sustainability in the near future. Recently, Moon and co-workers constructed a tandem solar cell consisting of a dye-sensitized solar cell (DSSC) and a CuInGaSe₂ thin film solar cell with a remarkable achievement in the solar cell efficiency of 13 % [255].

Apart from the innovative materials design, it is of vital importance to explicate the fundamental enhancement of modified hematite photoanodes through the investigation of charge transfer dynamics, optical absorption, electronic band structure and interfacial charge transfer for the PEC performance. Hence, *in-situ* electrical conductivity measurements, transient absorption spectroscopy, *in-situ* attenuated total reflection surface-enhanced infrared absorption spectroscopy, X-ray absorption fine spectroscopy and theoretical calculations are powerful tools to gain deeper understandings into the mechanistic features and to offer scientific guidance for the modification of hematite photoanodes [256-259]. In addition to experimental findings, first-principles density functional theory (DFT) calculation is imperative to comprehend the structural and electronic properties of hematite photoanodes

as well as the PEC reaction mechanism. It offers a systematic approach in screening and designing photoanode materials in terms of band gap and stability [256]. In response to this, the synergy of both experimental verification and computational simulation is mandatory for further advancing the knowledge of hematite photoanodes in the arena of materials science, technology and engineering.

Looking to the future, there are still infinite opportunities and challenges present for the hematite-based photoanode materials. Thus, with the continuous research explorations by the scientific community, it is ultimately believed that the aim of achieving the theoretical STH efficiency of 16.8 % by the hematite-based photoanodes is not knotty and impossible, instead turning dreams into reality toward commercialization and practical benefits. Noteworthy, this necessitates the synergy collaboration from all disciplines of people including academia and industry in order to enrich the solar energy application in a more practical means to open an era of renewable energy. We are certain that this critical review will provide a good guidance in the research area of electrochemically synthesized hematite photoanodes for the advancement of PEC water splitting now and future.

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CHAPTER 3

SYNTHESIS AND CHARACTERISATION OF METAL-DOPED HEMATITE NANOSTRUCTURED PHOTOANODES

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Understanding the synergistic between optimum dopant loading and charge transfer kinetics in platinum-mediated nanostructured hematite thin films





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ABSTRACT

Photoelectrochemical (PEC) water splitting process has received immense attention owing to its ability in sustainably producing solar hydrogen from water. The main aim of this study was to systematically optimise the Platinum (Pt) dopant loadings and understand its synergistic role in enhancing the photoactivity in nanostructured hematite (α -Fe₂O₃) thin films. Through the optimisation study, it was found the 3 mol% Pt-doped nanostructured hematite thin film exhibited the highest photocurrent density of 0.91 mA/cm² at 0.7 V vs Ag/AgCl in 1 M NaOH. In comparison with the bare hematite film, this was a 3-fold enhancement in terms of measured photocurrent density. Such an enhancement in the measured photocurrent density was attributed to the increased donor density caused due to the incorporation of optimum Pt dopant. Further EIS analysis revealed that the flat-band potential of hematite was shifted to a more negative potential by 30 mV while the charge transfer resistance was considerably reduced through the incorporation of Pt dopant. All these suggested that the successful doping of optimum Pt loading will lead to a visible active, lower charge transfer resistance and an enhanced separation efficiency of the photogenerated charge carriers in nanostructured hematite thin films.

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1. Introduction

In recent years, it was reported that over 80% of the energy consumed in the world are derived from conventional fossil energy sources that are facing potential issues with depletion in the coming decades and being non-environmental benign in nature [1]. In order to overcome these issues, many researches have been devoted to search for renewable and sustainable energy sources. Hydrogen (H₂) is an attractive renewable and sustainable energy but its wider utilisation is hindered by the production methods and associated costs. Of late, photoelectrochemical (PEC) water splitting process has received immense attention owing to its ability in sustainably producing solar H₂ fuel from using water as the feedstock [2,3]. When compare to the H₂ fuels produced either directly or indirectly from using fossil energy sources, solar H₂ fuel produced via the PEC water splitting process has no carbon footprint. Thus,

* Corresponding author at: School of Engineering, Chemical Engineering Discipline, Monash University Malaysia, Jalan Lagoon Selatan, Bandar Sunway, Selangor DE 47500, Malaysia. Tel.: +60 3 5514 5680; fax: +60 3 5514 6207. solar H_2 fuel is well-regarded as the perfect and alternative energy fuel for future utilisations [4,5]. However, the performance of the PEC water splitting process is highly dependent on the materials used for either photoanode or photocathode.

To date, various types of semiconductor metal oxides materials have been used for the fabrication of efficient photoelectrodes for PEC water splitting application such as titanium dioxide (TiO_2) [6-8], zinc oxide (ZnO) [9-11], tungsten trioxide (WO₃) [12-14], cuprous oxide (Cu₂O) [15,16] and others. In comparison, hematite $(\alpha$ -Fe₂O₃) appears to be an attractive photoanode material for PEC application due to its Earth-abundant, high stability, environmental compatibility and low-cost. Furthermore, it possesses narrow band gap energy of 2.2 eV that is capable to absorb up to 40% of incident solar irradiation [17.18]. However, the practical application of hematite is limited by its low electron mobility, short-hole diffusion length and short lifetime of photogenerated electronhole pairs and thus, resulting in low PEC performance [19,20]. Thus, the effective separation of photogenerated electron-hole pairs and their migration to the semiconductor-liquid junction plays an important role in ensuring high PEC performance of the semiconductor hematite-based photoanode. Numerous

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material science and engineering efforts such as the addition of metal or non-metal dopants, co-catalysts and heterojunction structures have been attempted to enhance the PEC performance of semiconductor hematite-based photoanode [21].

Previously, the incorporation of metal dopants such as titanium (Ti) [22], iridium (Ir) [21], chromium (Cr) [23], molybdenum (Mo) [23], nickel (Ni) [24,25], zirconium (Zr) [26], aluminum (Al) [27] and platinum (Pt) [28] into semiconductor photoelectrodes have been successfully demonstrated to improve the PEC performance. In this instance, for hematite, the incorporation of metal (M) dopants will act as electron donors due to the substitution of Fe^{3+} with M^{4+} in the lattice structure [29]. Therefore, the metal dopants can prolong the recombination of electron-hole pairs by trapping the photogenerated conduction band electrons [30]. Chen et al. [31] reported on the synthesis of Pt-doped nanostructured hematite thin films but without systematically optimising the dopant loadings and its synergistic role in enhancing the PEC performance. On the other hand, the nanostructuring of surface morphology of semiconductor photoelectrodes is also known to enhance the photocurrent yield by minimising the diffusion length of minority carriers before reaching the solid semiconductor-liquid interface [32]. Nanostructured semiconductor metal oxides thin films exhibit a large solid semiconductor-liquid interface in which, the redox reaction can take place to facilitate the efficient charge separation [17].

Thus, the main aim of this study was to systematically optimise the Pt dopant loadings and understand its synergistic role in enhancing the photoactivity in nanostructured hematite thin films produced via the facile electrodeposition method. Prior to the study on the effects of Pt dopant, the morphological features of nanostructured hematite photoanodes were finely tailored by different electrodeposition processing conditions (i.e. deposition cycles and annealing temperatures). Different Pt: Fe mol% of 1-10 were also investigated and optimised for their PEC performance. These were followed by advanced characterisation of the Ptdoped nanostructured hematite thin films by using field emissionscanning electron microscopy (FE-SEM), energy dispersive X-ray (EDX) analysis, X-ray diffraction (XRD) analysis, UV-visible spectroscopy, PEC measurements and electrochemical impedance spectroscopy (EIS) analysis. This work constitutes a more fundamental approach toward understanding the impact of Pt loadings on prolonging the recombination of electron-hole pairs by trapping the photogenerated conduction band electrons, as well as improving the flat-band potential and charge transfer resistance of hematite photoanodes.

2. Experimental

2.1. Materials

Iron (III) chloride (FeCl₃) was purchased from Sigma-Aldrich. Hexachloroplatinic (IV) acid hexahydrate ($H_2PtCl_6 \cdot 6H_2O$) (40% Pt) was purchased from Merck. All these analytical grade chemicals were used without further purification. Fluorine-doped tin oxide (FTO) glass was also purchased from ChemSoln, USA. The FTO glass was further cut into 38 mm × 8 mm per piece. The smaller FTO pieces were cleaned with acetone and ethanol, followed by rinsing with deionised water for subsequent use in the synthesis of nanostructured hematite thin films.

2.2. Synthesis of bare and Pt-doped nanostructured hematite thin films

Cathodic electrodeposition experiment was performed using a three-electrode electrochemical cell containing Pt rod, silver/silver (I) chloride (Ag/AgCl) saturated by 3 M KCl and FTO glass piece

as the counter, reference and working electrodes, respectively. The precursor solution used for electrodeposition of nanostructured hematite films consists of 5.0 mM FeCl₃. Electrodeposition was performed using an Autolab potentiostat (PGSTAT 204, Netherlands) by cyclic voltammetry (CV) process from -0.2 V to 0 V at a potential sweep rate of 0.05 V/s for various potential cycles. After electrodeposition, the hematite films were washed with deionised water for several times, followed by annealing at different temperature ranging from 400 °C to 700 °C at 100 °C per increment and a dwell time of 4 h. For the Pt-doped hematite thin films, H₂PtCl₆·6H₂O was added into the hematite precursor solution with varying Pt molar ratio of 1%, 3%, 4%, 5% and 10% with respect to the total Pt and Fe contents.

2.3. Structural characterisation

Surface morphology and elemental composition analysis were carried out by using FE-SEM coupled with an EDX spectroscopy (SU8010 model, Hitachi). Whilst the polycrystalline hematite structures were analysed using XRD (Bruker D8 Discover) employing Cu K α radiation with 40 kV and 100 mA at 0.02° scan rate. X-ray photoelectron spectroscopy (XPS) analyses were performed using a scanning X-ray microprobe PHI Quantera II (Ulvac-PHI, INC.) with monochromatic Al-K α ($h\nu$ =1486.6 eV) X-ray source to study the chemical state of the elements. The optical properties were recorded using the UV-vis spectrophotometer (Agilent Technologies Cary Series), where a bare FTO glass slide was used as the baseline measurement.

2.4. PEC characterisation

PEC measurements were performed in the three-electrode electrochemical cell, where Pt-doped nanostructured hematite thin films, Pt rod and Ag/AgCl saturated by 3 M KCl were used as the working, counter and reference electrodes, respectively. The effective surface area of photoanodes was measured prior to the photocurrent measurements. The electrolyte solution used during the photocurrent measurements was 1 M NaOH. The photoanodes were irradiated by 100 W Philips halogen lamp at a lamp-to-sample distance of 10 cm. For the photocurrent-potential (J-V) curve, the photoanodes were scanned from 0 V to 1 V vs Ag/AgCl at a scan rate of 0.05 V/s for both dark and illuminated conditions.

EIS analysis was performed using the similar setup of threeelectrode electrochemical cell connected to the Autolab potentiostat. For the Mott–Schottky plots, AC impedance measurements were carried out in the dark condition at 1000 Hz to 10 Hz in a 1 M NaOH solution by scanning the potential range from -0.1 V to 0 V with a scan rate of 0.05 V/s. Whilst for the Nyquist plots, AC impedance measurements were carried out in a 1 M NaOH solution with a frequency range of 100 kHz to 0.1 Hz and an amplitude of 10 mV in dark and illuminated conditions.

3. Results and discussion

3.1. Effect of electrodeposition synthesis conditions

The electrodeposition synthesis conditions were optimised before the synthesis of Pt-doped nanostructured hematite thin films. Firstly, the CV deposition cycles were varied in the range of -0.2 V and 0 V between 50 and 200 cycles, followed by annealing treatment at 600 °C for 4 h. Generally, it was known that the number of CV deposition cycles imposed during the electrodeposition synthesis will have a direct influence on the thickness of hematite thin films formed. Since the number of CV deposition cycles determine the hematite film thickness, it would lower the photon penetration above certain film thickness and thus, reduce Y.W. Phuan et al./Journal of the Taiwan Institute of Chemical Engineers 66 (2016) 249-257



Fig. 1. XRD spectra of nanostructured hematite films annealed at different temperature (* symbol indicates the background peaks from FTO substrate). (For interpretation of the references to colour in this figure, the reader is referred to the web version of this article.)

the transfer of minority carriers to the semiconductor-liquid junction to perform one half of the water splitting reaction [33]. From this study, it was found that the CV deposition cycles above 50 cycles have no significant effect on the J-V curves (Fig. S1 in Supplementary material) of the eventual hematite thin films formed.

Secondly, the annealing treatment on the amorphous FeOOH thin films was varied between 400 °C and 600 °C. The complete conversion of FeOOH to hematite can be observed by the colour change on the amorphous thin films from yellow to dark red. FESEM images of the annealed hematite thin films at varying temperature depicted that the size of densely packed hexagonalshaped nanostructured hematite crystallites increased from 65 nm to 95 nm (Fig. S2 in Supplementary material). The growth of the hematite crystallites size was attributed to the migration of surface atoms that helps the incorporation of iron and oxygen into the lattice sites [9]. The effect of annealing treatment on the hematite crystallites structure was analysed by using XRD and as shown in Fig. 1. The XRD spectra showed weak hematite diffraction patterns that superimposed on a strong FTO background. XRD analysis confirmed that the synthesized hematite thin films displayed the same diffraction peaks of which only hematite crystalline phase $(2\theta = 24.14^{\circ} (012), 33.15^{\circ} (104), 35.61^{\circ} (110), 39.28^{\circ}$ (006), 40.86° (113), 43.52° (202), 49.48° (024), 54.09° (116), 56.15° (211), 57.59° (018), 62.45° (214), 63.99° (300) and 66.10° (128)) is present [4]. It was observed that the peak intensity of hematite increased when the annealing temperature increased. Besides, the crystallinity of the annealed hematite thin films was observed to increase from 71.9% to 79.3% with increasing annealing temperature from 400 °C to 600 °C. This was owing to the conversion from amorphous to crystalline structure with accompanying crystals growth size at increasing annealing temperature. The crystallinity of the hematite thin films will affect the amount of light being absorbed. Nanostructured hematite thin films with higher crystallinity will have a higher visible light absorption [34,35]. Thus, increasing the annealing temperature will enhance the crystallinity and improve the PEC performance of the films. Based on the above results, all the eventual Pt-doped hematite thin films were synthesized via the cathodic electrodeposition method for 50 CV deposition cycles followed by annealing treatment at 600 °C.

3.2. Characterisation of Pt-doped nanostructured hematite thin films

In order to confirm the existence of Pt atoms in the Pt-doped hematite thin films, FE-SEM, EDX and XRD analyses were performed. The surface morphology and characteristics of Pt-doped hematite thin films were explained by the FESEM images as shown in Fig. 2. The changes in surface morphology before and after Pt-doping were markedly. Bare hematite thin film showed a vertically-grown separated island of nanostructures built from small nanoparticles. In this study, it is important to note that the amount of Pt dopants used were referenced to the molar ratio of Pt over the total contents of Pt and Fe in the electrolyte. From the FE-SEM images, it was observed that the 1% Pt-doped hematite thin film did not show any significant difference as compared to the bare hematite thin film. However, the 3% Pt-doped hematite thin film appeared to have a higher surface uniformity and denser than the bare hematite thin film. Meanwhile, the FE-SEM image for the 4% Pt-doped hematite thin film showed a similar but less prominent effect as compared to the 3% Pt-doped hematite thin film. When the amount of Pt dopant was increased further (i.e. 5% and 10%), it was evident that the larger Pt atoms and/or agglomerates were exerting distortion over the normal growth mechanism of the hematite nanoparticles during the electrodeposition synthesis process. As a result, the size and morphology of the nanostructured hematite thin films were strongly affected. Whilst the elemental analysis of the Pt-doped hematite thin films was performed using EDX. All the thin film samples were analysed to contain C, Si, O and Sn elements that were originated from the FTO glass substrates, while the Fe and O elements were due to the hematite nanoparticles. The characteristic Pt peaks had confirmed the presence of Pt dopant in the Pt-doped nanostructured hematite thin films (Fig. S3 in Supplementary material).

The successful inclusion of Pt dopants was further validated by XRD analysis as illustrated in Fig. 3. All the XRD peaks were well indexed to the crystalline phases of hematite characteristic peaks according to the JCPDS 33-0664 [4].The observed peak at 46.28° for the Pt-doped hematite thin films was corresponded to the (200) Pt facet [30,36]. By comparing the bare and Pt-doped hematite thin films, the diffraction peaks of the Pt-doped hematite thin films were slightly different in terms of intensity. The most intense hematite diffractions for all the Pt-doped hematite thin films

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Fig. 2. FE-SEM images of bare and Pt-doped hematite thin films on FTO glass substrate: (a) bare (*i.e.* undoped), (b) 1% Pt, (c) 3% Pt, (d) 4% Pt, (e) 5% Pt and (f) 10% Pt dopant.



Fig. 3. XRD spectra of bare and Pt-doped hematite thin films (* symbol indicates the background peaks from FTO substrate).

were the (006) and (202) peaks, but the intensities of these peaks were lower than the same peaks found in bare hematite thin film. This was due to the incorporation of Pt atoms into the lattice structure of hematite [20]. The lattice structure of hematite was contracted when the Pt dopant was incorporated. As a result, the conductivity of Pt-doped hematite thin films was improved, where this was due to the dopant was not constricted by the spin forbidden electron transport [37].

The electronic states of component elements of Pt-doped hematite thin film were investigated by performing XPS analysis. Only the peaks due to Fe, O and Pt elements were detected for the Pt-doped hematite thin film. The high resolution Fe 2p spectrum in Fig. 4a showed two characteristic $2p_{3/2}$ and $2p_{1/2}$ bands of Fe³⁺ at 711 eV and 724 eV, respectively, which have been typically observed in α -Fe₂O₃ [38]. As displayed in Fig. 4b, the O 1s XPS proved the existence of the surface O²⁻ in the hematite lattice at 530 eV, the OH bond at higher binding energy of 533 eV as well as the contribution from PtO_x species at 531 eV [39]. Furthermore, the XPS analysis provided a valuable information on the Pt chemical state as depicted in Fig. 4c. From the Pt 4f spectrum, Pt was presented in the form of Pt⁴⁺ as evidenced by the characteristic 4f_{7/2}

and $4f_{5/2}$ bands at 74 eV and 78 eV, respectively [29]. This indicated that Pt was successfully introduced into the hematite lattice via the electrodeposition process followed by the annealing treatment.

UV-visible spectroscopic measurements were performed to investigate the optical response of bare and Pt-doped hematite thin films as illustrated in Fig. 5. All the samples exhibited a broad absorption in the measurement range with two bands at ${\sim}450\,\text{nm}$ and \sim 550 nm. This observation was consistent with the transitions reported in previous study by Marusak et al. [40]. They attributed the absorption peaks by $6t_{lu}\!\downarrow\!\to\!2t_{2g}\!\downarrow$ and $2t_{2g}\!\uparrow\!\to\!2t_{2g}\!\downarrow$ ligand field transitions for interlevel transitions for lower energy peaks, as well as high energy absorption. The strong characteristics of hematite in the UV and visible regions of the optical spectrum that allow transitions were attributed to the spin flip or the charge transfer in origin [40]. The small differences in the observed optical densities may be due to the thickness variation in the Pt-doped nanostructured thin films. In this instance, the onset wavelength of the bare hematite thin film was measured around 600 nm (orange), which was in accordance with the band gap of hematite of 2.15 eV [41]. It can be seen from the UV-visible spectra that the Pt-doped hematite thin films showed an obvious red shift in the

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Fig. 4. XPS spectra of (a) Fe 2p, (b) O 1s and (c) Pt 4f for 3% Pt-doped hematite thin film.



Fig. 5. UV-visible diffuse reflectance spectra of bare and Pt-doped hematite thin films. (For interpretation of the references to colour in this figure, the reader is referred to the web version of this article.

Table 1

Estimated band gap energies of bare and Pt-doped nanostructured hematite thin films.

Sample	Band gap (eV)	
	Indirect	Direct
Bare hematite	1.90	2.15
1% Pt-doped hematite	1.22	1.95
2% Pt-doped hematite	1.00	1.85
3% Pt-doped hematite	1.02	1.86
4% Pt-doped hematite	1.30	1.86
5% Pt-doped hematite	1.40	2.00
10% Pt-doped hematite	1.15	1.85

band gap transition with an onset wavelength of approximately 700 nm.

Subsequently, the UV–visible spectra were used to estimate for the optical band gap (E_g) of the Pt-doped nanostructured hematite thin films. The relationship between absorption coefficient (α) and incident photon energy ($h\nu$) of semiconductor is given by the following Eq. (1) [37]:

$$(\alpha h \nu)^n = A(h \nu - E_g) \tag{1}$$

where *A* is a constant and *n* is either 0.5 or 2 for indirect or direct transition semiconductor, respectively. Tauc plots for both indirect and direct band gap transitions with band gap energies are shown in Fig. 6a and b, respectively, while the estimated band gap energies are tabulated in Table 1. The direct band gap of the bare hematite thin film was estimated to be 2.15 eV, which is consistent with the previous study [42]. However, the optical absorption of

the hematite thin films is mostly credited to the indirect band gap transition that relies on the degree of crystallinity and preparation methods [23]. In this instance, the doping of Pt has reduced both the indirect and direct band gap energies. When the Pt dopant loading increased, both the indirect and direct band gaps energies decreased from 1.9 eV to 1.15 eV and from 2.15 eV to 1.85 eV, respectively. These were evidenced from the conduction band edge of hematite slightly affected by the incorporation of Pt dopant in the lattice structure [29]. In this instance, the Pt dopant introduced extra energy levels that are more positive than the conduction band of hematite. These will expedite electrons to be photoexcited from valance band to conduction band [43]. Thus, the incorporation of Pt dopant into hematite thin film had resulted in a better absorption in the visible region.

3.3. PEC performance of Pt-doped nanostructured hematite thin films

PEC performance of the Pt-doped nanostructured hematite thin films was studied using the three-electrode electrochemical cell connected to an Autolab potentiostat with a halogen lamp as the illumination source. Fig. 7a shows the *J*–*V* curve of bare and Pt-doped nanostructured hematite thin films under both dark and illuminated conditions. Whilst Fig. 7b illustrates the measured photocurrent densities at the constant potentials of 0.60 V, 0.65 V and 0.70 V against the Ag/AgCl reference electrode. For the bare hematite thin film, the photocurrent was onset at 0.62 V and reached 0.34 mA/cm² at 0.7 V (*vs* Ag/AgCl reference electrode).

As for the Pt-doped nanostructured hematite thin films, they attained higher photocurrent densities than the bare hematite thin film. In this instance, the Pt is acting as an electron donor where

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Fig. 6. (a) Indirect transition $(\alpha h v)^{0.5} vs h v$ and (b) direct transition $(\alpha h v)^2 vs h v$ of bare and Pt-doped nanostructured hematite thin films.



Fig. 7. Photocurrent density measurements of bare and Pt-doped nanostructured hematite thin films, where (a) *J*-*V* curve and (b) photocurrent densities at specific potentials (*i.e.* 0.60 V, 0.65 V and 0. 70 V vs Ag/AgCl).

Pt⁴⁺ will substitute Fe³⁺ within the lattice structure of hematite. Hu et al. [29] reported that the increase in donor concentration will enhance the conductivity and increase the charge transfer while reducing the electron hole pairs recombination rate. Besides, the increase in donor concentration will increase the electric field across the space charge layer resulting in a lower electron hole pairs recombination rate. However, increasing the donor concentration will reduce the space charge layer width and Pt⁴⁺ will have defect recombination property that would negate the increased separation efficiency at higher Pt concentration [26]. Similar effects can be observed in Fig. 7b, where the photocurrent density increased with the increase in the molar percentage of Pt-dopant from 1% to 3%, while it started to drop after 4%. Thus, the 3% Pt-doped nanostructured hematite thin film exhibited the highest PEC performance among the Pt-doped samples with a photocurrent density of 0.44 mA/cm² at 0.65 V and reached 0.91 mA/cm² at 0.7 V. This value is almost three-fold of the photocurrent density measured in bare hematite thin film. The increase in photocurrent was attributed to the optimum amount of Pt-dopant that increased the overall and effective surface area of the Pt-doped hematite thin films. Besides, the photocurrent onset potential was cathodically shifted from 0.62 V for bare hematite to 0.59 V for the 3% Pt-doped hematite. This indicated that the overpotential required for water oxidation is reduced in the 3% Pt-doped hematite thin film and thus, the surface of 3% Pt-doped hematite thin film become more catalytic for oxygen evolution than the bare hematite film [20].

3.4. EIS analysis of Pt-doped nanostructured hematite thin films

The change in electrical properties through the doping of Pt on nanostructured hematite thin films are shown by EIS measurements. The Mott–Schottky plot was obtained by measuring the semiconductor space charge layer capacitance (C_{sc}) for varying applied potential (*E*). From Fig. 8, it can be observed that both the

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Fig. 8. Mott-Schottky plots of bare and 3% Pt-doped hematite thin films at frequency of 1 kHz in 1 M NaOH (inset shows the calculated flat band potentials and carrier densities).



Fig. 9. Nyquist plots of (a) bare and (b) 3% Pt-doped hematite thin films at 0.6 V vs Ag/AgCl under dark and illuminated conditions, where the solid lines represent the fitted plot. (c) A diagram of the equivalent circuit model used to fit the impedance data.

bare and Pt-doped hematite thin films exhibited positive slopes and these indicated that they are the n-type semiconductor. The flat band potential (E_{fb}) and carrier density (N_d) of the thin films samples can be calculated from the intercept and slope, respectively from the Mott–Schottky plot by using the following Eq. (2) [3]:

$$\frac{1}{C_{sc}^2} = \frac{2}{e\varepsilon\varepsilon_o N_d A_s^2} \left(E - E_{fb} - \frac{kT}{e} \right)$$
(2)

where *e* is the electron charge, ε is the dielectric constant of the semiconductor, ε_o is the permittivity of the vacuum, A_s is the working electrode surface area, *k* is Boltzmann's constant and *T* is the temperature. The flat band potentials obtained were -0.81 V and -0.84 V for the bare and Pt-doped hematite thin films, respectively, which are in good agreement with the previously reported values [27]. The positive shift of the flat band potential to a more negative potential is consistence with the observation in the photocurrent onset potential shift. All the samples have flat band

potentials more negative than the photocurrent onset potentials where this suggests a high electron-hole pairs recombination rate and kinetic hindrance on the hematite surface that would benefit from a surface catalyst [4,37]. From the Mott–Schottky plot, the calculated carrier density of bare hematite was 2.37×10^{19} cm⁻³ which is consistent with the previous study [24]. Whilst the calculated carrier density of 3% Pt-doped hematite thin film was 6.61×10^{19} cm⁻³, which is almost 2-fold higher than the bare hematite thin film. The increase of the carrier density has proven that Pt dopants were successfully incorporated into the hematite lattice, by serving as efficient electron donors and synergistically enhancing the photoactivity of hematite nanoparticles [20].

In addition, the water oxidation kinetics at the semiconductorliquid junction was investigated by plotting a Nyquist plot for the bare and 3% Pt-doped hematite thin films at 0.6 V under both dark and illuminated conditions. From Fig. 9a and b, the Nyquist plot for both bare and 3% Pt-doped hematite thin films shows a similar semicircle shape but with different radii due to the charge

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transfer process. A smaller semicircle radius denotes a lower electron transport resistance and higher photogenerated electron-hole pairs separation efficiency [43]. The equivalent circuit as depicted in Fig. 9c was used to fit the Nyquist plot, where R_s is the solution resistance, R_{ct} is the charge transfer resistance and CPE_{ct} is the corresponding constant phase element. The equivalent circuit consists of two R_{ct} and CPE_{ct} in series, where they were accounted for the semiconductor and surface processes, respectively. For the bare hematite thin film, the fitted total R_{ct} values were 3832 Ω $(CPE_{ct} = 475 \text{ S})$ in dark and 3480 Ω $(CPE_{ct} = 520 \text{ S})$ under illuminated conditions. In this instance, the reduction in the R_{ct} value under illuminated condition was due to the current flow through the semiconductor-liquid junction for water oxidation. This indicated that the photo-induced had increased the conductivity of the Pt-doped nanostructured hematite thin films [4]. Whilst for the 3% Pt-doped hematite thin films, the corresponding fitted total R_{ct} value was 3950 Ω ($CPE_{ct} = 1175$ S) in dark and was further reduced to 2718 Ω (*CPE*_{ct} = 1245 S) under illuminated condition. The R_{ct} value of Pt-doped hematite thin film became smaller than the bare hematite thin film under irradiation, where this suggested that the inclusion of Pt dopant had reduced the charge transfer resistance and enhance the separation efficiency of the photogenerated electron-hole pairs. It is obvious that the fitted CPE_{ct} values of the Pt-doped hematite thin films were approximately 2-fold than that of the bare hematite thin film and these results coincided well with the Mott-Schottky analysis.

4. Conclusion

In this study, the Pt-doped nanostructured hematite thin films were successfully synthesized via the cathodic electrodeposition approach. The Pt dopant loadings were systematically optimised, while its synergistic role in enhancing the photoactivity in nanostructured hematite thin films were examined through various characterisation studies. By varying the electrolyte composition, the concentration of the Pt dopant in the nanostructured hematite thin films can be controlled. The PEC performance of the hematite films was found to improve quite substantially by the inclusion of Pt dopant. The highest photocurrent density obtained from nanostructured hematite thin film doped with 3 mol% Pt was 0.44 mA/cm^2 at 0.65 V vs Ag/AgCl and reached 0.91 mA/cm^2 at 0.7 V vs Ag/AgCl in 1 M NaOH. These photocurrent densities were enhanced by 3-fold than that measured in bare hematite thin film. The increase in photocurrent density was attributed to the optimum amount of Pt dopant that also increased the effective surface area of nanostructured hematite thin films. Pt dopant plays a vital role in facilitating charge transfer and separation, as well as improving the conductivity of hematite. With this, the Pt-doped nanostructured hematite thin films provide potential applications in the field of PEC water splitting for solar H₂ production.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.jtice.2016.06.031.

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In situ Ni-doping during cathodic electrodeposition of hematite for excellent photoelectrochemical performance of nanostructured nickel oxide-hematite p-n junction photoanode



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ABSTRACT

Nanostructured nickel oxide-hematite $(NiO/\alpha-Fe_2O_3)$ p-n junction photoanodes synthesized from in situ doping of nickel (Ni) during cathodic electrodeposition of hematite were successfully demonstrated. A postulation model was proposed to explain the fundamental mechanism of Ni²⁺ ions involved, and the eventual formation of NiO on the subsurface region of hematite that enhanced the potential photoelectrochemical water oxidation process. Through this study, it was found that the measured photocurrent densities of the Ni-doped hematite photoanodes were highly dependent on the concentrations of Ni dopant used. The optimum Ni dopant at 25 M% demonstrated an excellent photoelectrochemical performance of 7-folds enhancement as compared to bare hematite photoanode. This was attributed to the increased electron donor density through the p-n junction and thus lowering the energetic barrier for water oxidation activity at the optimum Ni dopant concentration. Concurrently, the in situ Ni-doping of hematite has also lowered the photogenerated charge carrier transfer resistance as measured using the electrochemical impedance spectroscopy. It is expected that the fundamental understanding gained through this study is helpful for the rational design and construction of highly efficient photoanodes for application in photoelectrochemical process.

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1. Introduction

Photoelectrochemical process by harnessing the abundance of solar energy is a good example of artificial photosynthesis, where it is a promising and sustainable solution to resolve the potential fossil fuel depletion in the near future [1]. Generally, the photoelectrochemical water splitting process involves the absorption of ample sunlight using a semiconductor electrode where

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http://dx.doi.org/10.1016/j.apsusc.2016.09.046 0169-4332/© 2016 Elsevier B.V. All rights reserved. electron-hole pairs are generated to drive the redox reactions namely oxidation and reduction of water to produce oxygen gas and hydrogen fuel [2]. Thus, it is vital to apply semiconductor electrode with good light absorption property in a photoelectrochemical cell, as this can determine the eventual solar energy conversion efficiency from the water splitting process. Recently, substantial efforts have been devoted in searching for semiconductor materials that combine the essential requirements of: (1) absorption into the wider light spectrum, (2) effective separation and transfer of photogenerated charge carriers, (3) favourable conduction and valance band energies for oxygen and hydrogen evolution reactions, (4) high stability in aqueous environment as well as (5) potential to be fabricated cost effectively into photoanodes [3]. Among the semiconductor materials being studied. hematite (α -Fe₂O₃) is an attractive and highly promising material in light of these requirements. With an ideal band gap energy of 1.9-2.2 eV that has the potential to absorb ca. 40% of the incom-

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ing sunlight, it has been extensively investigated for application in photoelectrochemical water splitting [4]. It possesses a maximum theoretical photocurrent density of 12 mA cm^{-2} at 1.23 Vvs reversible hydrogen electrode (RHE), and a solar-to-hydrogen (STH) conversion efficiency of 16.8% under the AM 1.5G simulated sunlight (100 mW cm^{-2}) [5].

Previously, hematite was found to demonstrate excellent stability and performance for application in photoelectrochemical water splitting. However, its conduction band was reported to be low (~0.35 V vs normal hydrogen electrode (NHE)) for water reduction where this can be overcome through the application of an external bias via a photovoltaic device, or by pairing with a photocathode in tandem [6]. In addition, hematite has a very short diffusion length for the minority carriers (i.e. 2–4 nm) as compared to the light absorption depth (i.e. 400–500 nm) and poor majority carriers conductivity (i.e. 10^{-2} cm² V⁻¹ s⁻¹) [7]. These drawbacks result in a rapid recombination rate for the charge carriers and significantly limit the charge transfer process, causing a poor photoelectrochemical performance in bare hematite photoanodes.

Nanostructuring synthesis techniques have been widely used to resolve some of these drawbacks associated with the short hole diffusion length and poor light absorptivity of typical hematite photoanodes [8-11]. These include atomic layer deposition [12,13], solution-based colloidal [14,15], spray pyrolysis [16-18], hydrothermal [19,20] and atmospheric pressure chemical vapour deposition [21,22]. Among all, electrodeposition is a promising method in synthesising nanostructured hematite photoanodes. It is inexpensive can be operated at room temperature. Additionally, the process is simple and scalable which will be beneficial for the fabrication of nanostructured hematite photoanodes used in photoelectrochemical water splitting [23]. Besides, it allows proper control of the size, thickness and surface morphology of hematite nanostructures by modulating the synthesis parameters and the ease of incorporating foreign dopants into the lattice structure [24]. Specifically, the poor majority carriers conductivity of hematite can be overcome by introducing foreign dopants in order to increase the ionised donor concentration and the conductivity [25-29].

Previously, the Ni-doping of hematite has not been widely investigated where Ni can act as an electron donor owing to the Ni²⁺ for Fe³⁺ ionic substitution. Liu and her colleagues [30] investigated the photoelectrochemical properties of Ni-doped hematite and found that the Ni²⁺ for Fe³⁺ ionic substitution was higher at the surface than in the bulk of hematite. By mean of different impregnation approaches, Cheng et al. [25] synthesized a highly active $Ni_xFe_{2-x}O_3$ overlayer on the surface of hematite nanotube which demonstrated a remarkably high enhancement (~280%) of the photoconversion efficiency. Due to the fact that Ni can readily form a solid solution in common oxide, and nickel oxide (NiO) exhibits an excellent oxygen evolution reactivity [31], NiO has been used as a promising semiconductor material in multilayer photoelectrode assemblies [32–34]. NiO is a p-type semiconductor with a direct band gap of 3.6 eV, and it is commonly employed as a water oxidation catalyst to decrease the overpotential for water oxidation process [35].

Therefore, it is of our interest to study the in situ Ni-doping via cathodic electrodeposition of hematite to produce NiO-hematite p-n junction photoanodes. In this study, the fundamental mechanism of Ni²⁺ ions involved was elucidated as well as the resultant surface morphology, chemical and elemental analysis, photoelectrochemical and dielectric properties. Different molarities of Ni dopant were attempted in order to understand the systemic correlation with the resultant photocurrent density and more importantly, the photoelectrochemical properties. It is expected that the fundamental understanding gained through this study is helpful for the rational design and construction of highly efficient

photoanodes for application in photoelectrochemical water splitting.

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2. Experimental

2.1. Material

Iron (III) chloride (FeCl₃) was purchased from Sigma-Aldrich and nickel (II) nitrate (Ni(NO₃)₂) was purchased from Merck, Malaysia. All these reagent grade chemicals were used without further treatment. Fluorine-doped tin oxide (FTO) glass electrodes were purchased from ChemSoln, USA. The FTO glass electrodes were slice into 8×38 mm pieces and sonicated successively in acetone, ethanol and deionised water prior to experimental use.

2.2. Synthesis of in situ Ni-doped hematite photoanodes

The bare hematite thin films were electrodeposited onto FTO working electrodes using an Autolab potentiostat PGSTAT204 model (Metrohm, Netherlands) cycling from -0.2 to 0V at $0.05 V s^{-1}$ for a total of 50 cycles from a precursor solution containing 5 mM FeCl₃. As for the in situ doping procedures of Ni²⁺ ions on hematite, the FTO electrodes were immersed in the hematite precursor solution containing Ni(NO₃)₂, of varying Ni molar ratios of 1-40%. Platinum (Pt) rod and silver/silver chloride (Ag/AgCl) saturated in 3 M potassium chloride (KCl) were used as the counter and reference electrodes, respectively. The as-electrodeposited films were rinsed with water and annealed at 600 °C under air environment with a dwell time of 4 h.

2.3. Materials characterisation

The surface morphology, chemical and elemental composition analyses were characterised by using a field emission-scanning electron microscopy (FE-SEM) (Hitachi SU8010) equipped with an energy dispersive X-ray (EDX) (Oxford-Horiba Inca XMax50). X-ray diffraction (XRD) analyses were performed with an X-ray diffractometer (Bruker D8) employing Cu-K α radiation (λ = 0.15406 nm) with 40 kV and 100 mA at a scan rate of 0.02° s⁻¹ in order to verify the crystalline structures. X-ray photoelectron spectroscopy (XPS) analyses were carried out using an Omicron Nanotechnology, Germany DAR400 to study the chemical state of the elements. Whilst the optical properties were recorded using an UV–vis spectrophotometer (Agilent, Cary 100), by further subtracting the UV spectrum of a blank FTO electrode. Photoluminescence (PL) measurements were carried out with a fluorescence spectrophotometer (LS 55, Perkin Elmer) using 320 nm as the excitation wavelength.

2.4. Photoelectrochemical and electrochemical analyses

The photoelectrochemical analyses were performed in a 1M NaOH (pH=13.6) electrolyte using the Autolab potentiostat PGSTAT302N (Metrohm, Netherlands) with a Pt rod counter electrode and Ag/AgCl saturated in 3 M KCl reference electrode. Cyclic voltammetry (CV) curves were scanned from -0.5 to 0.7 V with a scan rate of 0.05 V s^{-1} . Photocurrent-voltage (*J*-*V*) curves were scanned from 0 to 1 V vs Ag/AgCl with a sweep rate of 0.02 V s^{-1} . The curves were obtained at both dark and under front illumination with a 100 W Philips halogen lamp. The Mott-Schottky curves were measured at 1000 Hz to 10 Hz in dark sweeping between -0.1 V and 0 V vs Ag/AgCl with a scan rate of 0.05 V s⁻¹ in order to determine the donor density (N_d) and flat band potential (E_{fb}) . For the Nyquist curves, the AC impedance measurements were carried out with a frequency range of 100 kHz-0.1 Hz and amplitude of 10 mV under dark and illumination conditions. The resulting electrochemical impedance data were fitted using an electrochemical equivalent 146

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Fig. 1. Photocurrent density measurements of bare and in situ Ni-doped nanostructured hematite photoanodes, where (a) photocurrent density vs potential curves, and (b) photocurrent density at specific potentials of 0.60 V, 0.65 V and 0.70 V vs Ag/AgCl (3 M KCl).



Fig. 2. FE-SEM images of bare and in situ Ni-doped hematite photoanodes: (a) bare, (b) 5 M% Ni, (c) 25 M% Ni and, (d) 30 M% Ni.

circuit model to determine the charge transfer resistance (R) and the corresponding constant phase element (CPE_{ct}).

3. Results and discussion

The electrochemical behaviour of the Ni-doped hematite photoanodes was investigated from the CV curves (Supplementary materials Fig. S1). The bounded area of the CV curve indicates the real active surface area of the photoanode [36]. The Ni-doped hematite photoanode shows a larger area and a higher current density than the bare hematite photoanode. In order to further study the photoelectrochemical performance of the in situ Nidoped hematite photoanodes, photocurrent density measurements were performed as depicted in Fig. 1a. The modified photoanodes showed significant enhancements in terms of the measured photocurrent densities as compared to the bare hematite photoanode. Based on Fig. 1b, it can be observed that the measured photocurrent densities for the Ni-doped hematite photoanodes exhibited optimality in the different molar% of Ni dopant concentration attempted. At the initial 1 M% of Ni dopant used, the modified hematite photoanode showed improved majority carriers conductivity and enhanced photogenerated charge carriers transfer, thus reducing the electron-hole pairs recombination rate. Further increase in the molar% of Ni dopant used resulted in increased electron donor density, which would increase the electric field Y.W. Phuan et al. / Applied Surface Science 392 (2017) 144-152



Fig. 3. EDX characterisation of in situ 25 M% Ni-doped hematite photoanode.

across space charge layer up to the optimal point. After the optimal 25 M% of Ni dopant used, any further increase in the molarity of Ni dopant used would lower the space charge layer width. Whilst the Ni dopant would affect recombination properties that would negate the separation efficiency [37]. Thus, it could be concluded that the 25 M% Ni dopant was the optimal doping level found in this study. The measured photocurrent density for the 25 M% Ni-doped hematite photoanode was 2.3 mA cm^{-2} at a bias potential of 0.7 V, which was approximately 7-folds enhancement in the photoelectrochemical performance than that of bare hematite photoanode. Intuitively, the optimal point phenomenon could be due to the balanced off between the competing effects from improved conductivity and lowered space charge width. After the incorporation of Ni dopant, the onset potential was shifted from 0.62 to 0.50 V vs Ag/AgCl. The negative shift in the photocurrent onset potential might be due to the incorporation of Ni dopant that resulted in forming the p-n junction and subsequently, facilitated the extraction of accumulated holes and electronic structure of hematite.

The surface morphology and microstructure of the bare and Ni-doped hematite photoanodes were characterised by FE-SEM. Through FE-SEM imaging, it was observed that the bare hematite photoanode was composed of fine and well-aligned nanoparticles with a diameter of around 90.5 nm, grown in the direction perpendicular to the FTO substrate (Fig. 2a) [38]. After the in situ Ni-doping, the diameters of the hematite nanoparticles increased to approximately 116.5, 117.4 and 117.6 nm for the 5, 25 and 30 M% Ni-doped hematite photoanodes, respectively as depicted in Fig. 2b–d. The increase in the size of hematite nanoparticles was due to the sintering effect during annealing treatment. The FE-SEM images for both bare and in situ Ni-doped hematite photoanodes showed similar surface morphologies, while the latter has a larger nanoparticle size as well as appears to be more compact and denser nanostructures rather than the highly porous nature in bare hematite photoanode.

In order to prove the existence of Ni dopant, EDX characterisation as shown in Fig. 3 was performed on the in situ Ni-doped hematite photoanode. In overall, the C, Si and Sn elements were originated from the FTO electrode with mass percentages of 2.16, 2.69 and 49.02%, respectively, while the Fe and part of the O elements were from the hematite nanoparticles with mass percentages of 5.57 and 40.2%, respectively. The EDX analysis confirmed the presence of Ni element in the Ni-doped hematite photoanode. Owing to the small amount of the Ni-doping, the mass percentage of the Ni detected was 0.36%. Additionally, the polycrystalline structures of the bare and Ni-doped hematite photoanodes were studied by conducting XRD analysis (Fig. 4). All the XRD peaks were well indexed to the hematite characteristic peaks at $2\theta = 35.61^{\circ}$ (110), 39.28° (006), 43.52° (202), 57.59° (018) and 63.99° (300) according to the JCPDS No. 33-0664 [39]. In addition, the characteristic peaks observed for the Ni-doped hematite photoanodes at $2\theta = 43.1^{\circ}$ and 62.5° are corresponding to the (200) and (220) reflections of NiO (JCPDS No. 65-2901) [40]. This evidenced that the doping of Ni



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Fig. 4. XRD spectra of bare and in situ Ni-doped hematite photoanodes.

ions on hematite photoanodes had resulted to the formation of NiO-hematite p-n junction photoanode. The similar XRD patterns of bare and Ni-doped hematite photoanodes indicated that the polycrystalline structures underwent slight change after the incorporation of Ni dopant. As shown in the XRD spectra, a clear shift in the peaks position towards lower angles was observed when contrasted against the bare hematite photoanode. The peaks shift was due to the uneven strains distribution within the lattice structure of hematite attributed to the substitution nature of Ni-doping [41].

XPS analysis was performed to confirm the incorporation of Ni into hematite in the Ni-doped hematite photoanode, where the survey spectrum is shown in Fig. S2. There are only Fe and O elements peaks being detected for the bare hematite photoanode (Fig. 5a), while an additional Ni peak was found for the Ni-doped hematite photoanode (Fig. 5b). The high resolution Fe 2p spectra show two obvious peaks with binding energies at around 711 eV for Fe $2p_{3/2}$ and 725 eV for Fe $2p_{1/2}$. These values are typically observed for Fe_2O_3 [4,42]. In comparison, Fe $2p_{3/2}$ peak is narrower, stronger and has a greater area than the Fe $2p_{1/2}$ peak. This is due to the fact that $2p_{3/2}$ and $2p_{1/2}$ have four states and two states, respectively in spin-orbit (j-j) coupling [43]. The shakeup satellite peaks appeared in the Fe 2p spectra at about 719 eV prove the presence of Fe³⁺ ions in Fe₂O₃ [44]. On the other hand, the O 1s XPS spectra show an individual peak located at 530 eV with a shoulder on higher binding energy. The surface O²⁻ possessed in the oxides can be evidenced by the observed peaks at 530 eV, while the shoulder at higher binding energy was ascribed to the C-O and/or OH bond [45]. In the Ni 2p XPS spectrum, the Ni peak located at around 855.5 eV corresponded to Ni 2p_{3/2}. This particular peak is the characteristic value for NiO and it proves that the Ni dopant exists in the form of divalent [46]. The XPS results ratified that the Fe exists as Fe³⁺ and Ni as Ni²⁺ in the synthesized photoanodes.

The optical absorption properties of the bare and Ni-doped hematite photoanodes were measured by using UV-vis spectroscopy and (Fig. 6a). All the measured samples showed a typical absorption which is consistent with the transitions seen in hematite [47]. From the UV-vis spectra, no obvious correlation between the absorbance and the Ni molar% was obtained. Small differences in the observed absorbance values may attribute to the variations in the thickness and morphologically dependent scattering of the deposited films [39]. A slight shift of absorption edges towards longer wavelengths was observed for the Ni-doped hematite photoanodes when compared to the bare hematite photoanode. The absorption edges of both bare and Ni-doped hematite photoanodes were around 590 and 620 nm into the visible light region,

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Fig. 5. XPS spectra for (a) bare hematite and (b) 25 M% Ni-doped hematite photoanode.

respectively. The corresponding band gap energy were calculated following the Eq. (1) [28]:

$$\alpha h \nu = A \left(h \nu - E_g \right)^n \tag{1}$$

where, α is the absorption coefficient, $h\nu$ is the incident photon energy of semiconductor, A is a constant, E_g is the band gap energy, and n is 0.5 and 2.0 for direct and indirect transitions, respectively. The Tauc plots for direct band gaps are illustrated in Fig. 6b–e with inset band gap energies. The band gap energies for bare and Nidoped hematite photoanodes were extrapolated to be 2.10 and 1.95 eV, respectively. The incorporation of Ni dopant resulted in a slight reduction in band gap energies. These changes suggest that the conduction band edge of n-type hematite is slightly affected by the incorporation of Ni dopant in the lattice structure.

PL analysis was conducted in order to understand the charge transfer, migration, trapping and the recombination process of the charge carriers in the semiconductor material [48]. The intensity of the PL spectrum is a direct measurement of the recombination rate of photoexcited electron-hole pairs. A strong PL intensity implies a rapid electron-hole pairs recombination rate and conversely, a weak PL intensity indicates more excited electrons being trapped and transferred through the interface. Therefore, PL spectra of the bare and Ni-doped hematite photoanodes were used to understand the nature and state of the eventual photogenerated charge carriers in the fabricated photoanodes, and these are shown in Fig. 7a. When comparing to the bare hematite photoanode, the remarkably reduced PL emission intensity of the Ni-doped hematite photoanodes indicated a lower recombination rate of the photoexcited electron-hole pairs and with more efficient interfacial charge transfer. In this instance, Ni dopant acts as an electron donor, facilitating efficient charge separation in the Ni-doped hematite photoanodes.

Meanwhile, the other photoelectrochemical properties of the bare and Ni-doped hematite photoanodes were achieved through the Mott-Schottky analysis under dark condition as shown in Fig. 7b. Both the N_D and E_{fb} were estimated from the relationship of Mott-Schottky by using Eq. (2) [49]:

$$\frac{1}{C_{sc}^{2}} = \frac{2}{e\varepsilon\varepsilon_{o}N_{D}A_{s}^{2}} \left(E - E_{fb} - \frac{kT}{e} \right)$$
(2)

where, e is the electron charge, ε is the dielectric constant of semiconductor, ε_0 is the permittivity of vacuum, A_s is the surface area of working electrode, k is the Boltzmann's constant, and *T* is the temperature. The positive slopes indicated that both the bare and Ni-doped hematite photoanodes to be of the n-type semiconductor material. The calculated donor density increased from $2.37\times10^{19}\,cm^{-3}$ for bare hematite photoanode to $1.03\times10^{20}\,cm^{-3}$ for the Ni-doped hematite photoanode. This was approximately 4.5 times higher than bare hematite photoanode, and this has confirmed that the Ni dopant actually enhanced the donor density of the typical hematite nanostructures. Subsequently the enhanced donor density in Ni-doped hematite photoanodes has led to improved majority carrier conductivity via the lattice substitution of Fe³⁺ by Ni²⁺ in hematite and eventually resulting in a higher separation efficiency of the photogenerated charge carriers [30]. By taking the x-intercept of linear fit to the Mott-Schottky plots, the estimated flat band potential was found to be shifted from -0.81 V vs Ag/AgCl for bare hematite photoanode to -0.91 V vs Ag/AgCl for the Ni-doped hematite photoanodes. Such a negative shift in potential indicated a better ability of the photoanodes to promote the charge separation during photoelectrochemical water splitting activity [4].

The Nyquist plots for the bare and in situ Ni-doped hematite photoanodes are shown in Fig. 7c to reveal their corresponding dielectric properties. Both the charge transfer resistances (R_s and R_{ct}) and separation efficiency of photogenerated charge carriers are important factors to be examined for the application in photoelectrochemical water splitting [50]. The charge transfer resistance is equivalent to the semicircle diameter, which denotes the resistance of interface layer arising at the surface of the photoanode. Whilst the smaller semicircle radius indicates a higher separation Y.W. Phuan et al. / Applied Surface Science 392 (2017) 144-152



Fig. 6. (a) UV-vis spectra of bare and in situ Ni-doped hematite photoanodes. Tauc plots for (b) bare, (c) 5 M% Ni-doped, (d) 25 M% Ni-doped and (e) 40 M% Ni-doped hematite photoanodes.

efficiency of the photogenerated charge carriers [51]. An equivalent circuit as depicted in Fig. 7d, which consisted of two R_{ct}CPEct elements in series, was used to fit the Nyquist plots of bare and in situ Ni-doped hematite photoanodes. Typically, the charge transfer in bulk is faster than the charge transfer in semiconductor liquid interface. Thus, R_s is the charge transfer resistance in the bulk and R_{ct} is the charge transfer resistance in the semiconductor liquid interface, where *CPE_{ct}* is the accompanying constant phase element. The fitted values of the equivalent circuit parameters are given in Table 1. The impedance measurements were performed under dark and illumination conditions. Both the bare and Ni-doped hematite photoanodes present single semicircles. In this regard, the semicircles for the bare and Ni-doped hematite photoanodes were smaller under illumination condition, implying a reduction in the charge transfer resistance. Moreover, the resistance values of the Ni-doped hematite photoanodes were lower than that of the bare hematite

 Table 1

 The fitted values of the equivalent circuit parameters for bare and in situ Ni-doped hematite photoanodes.

Sample	$R_{s}(\Omega)$	$R_{ct}\left(\Omega\right)$	CPE_{ct} (µS)
Bare hematite (dark)	48.5	3832	475
Bare hematite (light)	51.9	3480	520
Ni-doped hematite (dark)	28.8	2463	1306
Ni-doped hematite (light)	26.6	1825	539

photoanode under dark and illumination conditions. As such, this proves the role of Ni dopant in facilitating the charge transfer in bulk and semiconductor liquid interface where the Ni dopant is associated with diffusion of Ni into the hematite subsurface region, forming a p-n junction that effectively extracts holes, improves the separation efficiency of photogenerated charge carriers, leading to enhanced photocurrent density.

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Fig. 7. (a) PL spectra of the bare and in situ Ni-doped hematite photoanodes. (b) Mott-Schottky plots of bare and in situ Ni-doped hematite photoanodes at frequency of 1 kHz, (b) Nyquist plots of the bare and in situ Ni-doped hematite photoanodes at 0.6 V vs Ag/AgCl under dark and light conditions, and (c) equivalent circuit model fitting the impedance data.



Fig. 8. Schematic illustrating the charge transfer and the separation of the electronhole pairs in the NiO-hematite p-n junction photoanode.

Accordingly, the energy band structure and photogenerated electron-hole pairs separation in the p-n junction between NiO and hematite could be depicted in Fig. 8. When the p-type NiO and n-type hematite are interacted, a p-n junction is created at the heterojunction because of the diffusion of charge carriers, generating a built-in electrical potential, thus allowing the transfer of electrons and holes in the opposite direction [52,53]. When the p-n junction is illuminated by solar light, the photoexcited electron-hole pairs will rapidly separate, in which the electrons relocate to

the conduction band of the hematite, whereas the holes extract to the valence band of NiO. Therefore, the NiO-hematite p-n junction photoanode can markedly separate photogenerated electron-hole pairs, enhance charge transfer, resulting in the improvement of the photoelectrochemical properties.

4. Conclusions

A simple technique of cathodic electrodeposition followed by annealing treatment was used to synthesize in situ Ni-doped hematite p-n junction photoanodes. A series of characterisations confirmed that the enhanced photoelectrochemical performance of the in situ Ni-doped hematite p-n junction photoanode is attributed by the improved charge carrier transport and conductivity through the incorporation of Ni-dopant. Ni-doping is combined with diffusion of Ni into the subsurface region of hematite, forming NiO surface overlayer. NiO acts as a hole extractor that promotes the separation of photoexcited electron-hole pairs, resulting in improved photoelectrochemical activity of water oxidation. Doped Ni atoms are shown to occupy the lattice positions of Fe atoms and their incorporation led to 4.5-folds increase in donor density in hematite. The apparent optimum at 25 M% Ni-doping exhibited a great photoelectrochemical performance of 7-folds enhancement when compared to bare hematite photoanode. Ultimately, the in situ Ni-doped hematite photoanode showed an enormous improvement in photoelectrochemical performance than the bare hematite photoanode, which is in consistent with the enhancement of the dielectric properties of the photoanodes after introducing Ni-dopant. This work provides useful information to the future development of a well photoelectrochemical performed hematite photoanode.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.apsusc.2016.09. 046.

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CHAPTER 4

SYNTHESIS AND CHARACTERISATION OF NANOCARBON-BASED HEMATITE NANOSTRUCTURED PHOTOANODES
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air to form iron oxide, which is also known

as rust. Among all, hematite $(\alpha$ -Fe₂O₃) is the most thermodynamically stable and

common form of iron oxides.^[2] Previously,

hematite has been extensively studied as

a semiconductor photoanode material for

photoelectrochemical (PEC) process.^[3] In

comparison to other semiconductor photocatalysts, for instance TiO₂,^[4] WO₃,^[5]

ZnO,^[6] Cu₂O,^[7] and BiVO₄,^[8] hematite

appears to be a very promising semi-

conductor photoanode material used for

the PEC process. Hematite possesses a

favorable band gap energy of 1.9-2.2 eV

that absorbs incident light for up to 40% into the visible light region.^[9] Neverthe-

less, the practical solar-to-hydrogen (STH)

conversion efficiency reported to date is

considerably lower than the theoretical

STH value of 12.9%.^[10] Such a discrep-

ancy between the ideal and practical STH

conversion efficiency is due to the low minority carrier mobility that resulted in

Synthesis and Characterization of a Novel Ternary Hematite Nanocomposites Structure with Fullerene and 2D-Electrochemical Reduced Graphene Oxide for Superior Photoelectrochemical Performance

Yi Wen Phuan, Meng Nan Chong,* Oodaye Satokhee, Andrew Brian De Souza, Tao Zhu, and Eng Seng Chan

In this study, a novel ternary hematite nanocomposites photoanode structure with superior photoelectrochemical (PEC) performance consisting of fullerene (C₆₀) and 2D-electrochemical reduced graphene oxide (eRGO) used as the effective surface passivators is developed. The introduction of both the electron scavenging C₆₀ and highly conducting eRGO has mitigated the high interfacial recombination rate of hematite and led to the superior enhancement in PEC performance. UV-vis analysis reveals that the incorporation of C₆₀ and eRGO can provide a stronger light absorption at the visible light (400 nm $< \lambda <$ 700 nm) and near infrared (IR) region (λ > 700 nm). Through the electrochemical impedance spectroscopy measurements, it can be concluded that the introduction of C₆₀ and eRGO onto hematite photoanode improves electron transfer and collection, reduces charge-carrier recombination efficiency, and enhances PEC activity. The resultant ternary hematite photoanode structure exhibits 16.8-fold enhancement in photocurrent density and 0.8-fold reduction in charge transfer resistance when compared to the bare hematite structure only. This study has shown that the application of C₆₀, 2D-eRGO, or in combination as a ternary structure provides the plasmonic effect that can enhance the PEC performance in hematite photoanode structure.

1. Introduction

Iron is the most abundant metal on earth, where it comprises \approx 5% of the earth's crust and up to 80% of the earth's core.^[1] The pure form of iron is readily oxidized in the presence of moist

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short hole collection length, poor majority carrier conductivity, relatively small absorption coefficient, and ultrafast recombination of photogenerated electron-hole pairs.^[11]

In order to address these drawbacks and further improve the STH conversion efficiency, numerous material engineering efforts have been attempted on hematite. Recent studies include optimizing the morphology of hematite at nanometer scale for example nanorod,^[12] nanotube,^[3b,13] nanoflake,^[14] and honeycomb^[15] had demonstrated improvements in PEC performance. These improvements from the morphology control in hematite are attributed to the larger area of contact between the electrolyte and semiconductor photocatalysts and thus, facilitate the separation of photogenerated charge carrier. Other efforts for improving the low STH efficiency in hematite for PEC water oxidation include various surface treatments^[16] to decrease the overpotential required, which in turn, enhances the oxygen evolution reaction. Additionally, the introduction of foreign dopant species into the lattice structure of hematite including Pt,^[17] Zn,^[18] Ti,^[19] Zr,^[20] and Sn^[21] has also been attempted to elevate its poor PEC performance through alterations to the intrinsic

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Chapter 6 | P cpqectdqp/Dcugf Hematite Nanostructured Photoanodes

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electronic properties and charge transfer resistance. Recently, the reinforcement of hematite with electron donor–acceptor composites based nanocarbons is gaining popularity as an effective strategy to improve the PEC performance of hematite as they can ameliorate photogenerated charge carrier transfer and separation.

The electron donor-acceptor composites based nanocarbons, such as fullerene (C₆₀), graphene, and other carbonaceous materials are recent subjects of interests in the fabrication of PEC photoelectrode assemblies. Fullerene (C₆₀) was first reported in 1985 by Kroto and Smalley et al.,^[22] and is a 0D soccer-ball-like nanocarbon. Previous studies had reported that the incorporation of C₆₀ is able to enhance the PEC performance of semiconductor photocatalysts, such as TiO2,^[23] CdSe,^[24] CdTe,^[25] and ZnO.^[26] The enhancement was ascribed to the electron-collector properties, electrical transfer features, and strong UV light absorption by C₆₀.^[27] Apart from C₆₀, reduced graphene oxide (RGO) has also attracted remarkable research interest owing to its unique 2D honeycomb lattice of six-membered rings and electron donor-acceptor properties.^[28] RGO offers an excellent electrical conductivity (2×10^5 cm² V⁻¹ s⁻¹) and can serve as an efficient electron transporting bridge.^[29] Recently, RGO-based semiconductor nanocomposites have garnered considerable attention due to its highly enhanced PEC performance.^[30] Both C₆₀ and RGO can act as potential electron reservoirs to prolong the recombination of photogenerated electron-hole pairs.^[23] To date, however, there is a knowledge gap in the literature that reported on the combinatorial use of C₆₀ and RGO to synergistically improve the low STH efficiency in hematite through the synthesis of ternary nanocomposites structure.

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Thus, the main aim of this study was to develop a novel ternary hematite nanocomposites photoanode structure with superior PEC performance consisting of C_{60} and 2D-electrochemical reduced graphene oxide (eRGO) used as the effective surface passivators. The resultant ternary hematite nanocomposites structure was characterized using current versus potential (I-V) curves, electrochemical impedance spectroscopy (EIS), X-ray diffractometer (XRD), field emission-scanning electron microscopy (FE-SEM), Raman spectroscopy, and ultraviolet-visible (UV-vis) spectroscopy. Additionally, the effects of surface impedance on photogenerated charge carrier recombination were investigated through a series of comparison studies among bare hematite, C₆₀/hematite, eRGO/hematite, and eRGO/C₆₀/hematite nanocomposites photoanode structures. This study provides an in-depth understanding of the potential use of two carbonaceous materials of C₆₀ and eRGO to enhance the PEC performance in hematite through effective electron shuttling at the surface molecular level.

2. Results and Discussion

The electrodeposition synthesis process of hematite nanocomposites photoanodes is depicted in **Figure 1**. All the photoanodes were prepared using the similar method, except for the different materials used. The C_{60} /hematite was prepared by electrodepositing C_{60} on hematite photoanode. While the eRGO/ hematite was synthesized by the electrochemical reduction of GO into eRGO on hematite photoanode. Lastly, the C_{60} /eRGO/ hematite was fabricated by simultaneously electrodepositing



Figure 1. Schematic illustrating the electrodeposition synthesis process of hematite nanocomposites photoanodes.



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Figure 2. a) Current density measured at different bias potentials for bare and hematite nanocomposites photoanode structures. b) Nyquist plots of bare and hematite nanocomposites photoanode structures. The inset is the equivalent circuit model used to fit the EIS data.

 C_{60} and followed by eRGO onto hematite photoanode. The nanocomposites built from hematite, C_{60} , and eRGO have been well designed and synthesized, where various characterizations were carried out to investigate the PEC performance.

In order to assess the effects of C₆₀ and eRGO in synergistically improving the PEC performance of hematite, the PEC properties of bare hematite and hematite nanocomposites photoanode structures were evaluated and illustrated in Figure 2a. For the bare hematite photoanode, the onset potential under illumination was measured to be ≈0.60 V (see Figure S1, Supporting Information). At 0.60 V, the hematite nanocomposites photoanode structures of C₆₀/hematite, eRGO/hematite, and eRGO/C₆₀/hematite demonstrated significant increase in current densities by 1.2-fold, 13.3-fold, and 16.8-fold, respectively, when benchmarked against the current density of bare hematite photoanode. From Figure 2a, it can be observed that the current density was significantly enhanced by purely introducing C₆₀ and eRGO onto hematite photoanode. The enhanced current densities are attributed to the excellent charge transfer properties of C₆₀ and eRGO, where the photogenerated charge carriers are trapped and thus impede the recombination of electronhole pairs. Furthermore, the ternary hematite nanocomposites structure of eRGO/C₆₀/hematite exhibited more enhancement in the PEC performance, where the photocurrent density was increased by almost 7.1-fold and 0.3-fold when compared to the C_{60} /hematite and eRGO/hematite nanocomposites structures. This is owing to the synergistic effects of both C_{60} and eRGO by increasing the surface contact area between the hematite and carbonaceous nanocomposites.^[31]

To further elucidate the improved PEC performance of hematite through the inclusion of nanocarbons, EIS analysis was conducted and the resulting Nyquist plots are depicted in Figure 2b. In Figure 2b, the symbols represent the experimental values, while the continuous lines represent the fitted electrochemical impedance responses according to the equivalent circuit model (inset of Figure 2b). The semicircle arcs in the Nyquist plots indicate the occurrence of charge transfer process and are correlated to the resistances of photoanodes.^[32] The larger semicircle arc implies that the charge transfer is a limiting process and can be ascribed to the charge transfer resistance at the semiconductor-liquid junction.^[23] Typically, smaller semicircle arc radii implie better charge transfer capability.^[33] By comparing both Figure 2a and 2b, the reduction in semicircle arc radii of the Nyquist plots coincides well with the measured current densities. The fitted values to the equivalent circuit model are tabulated in Table 1, where $R_{\rm s}$ is the contact resistance of base fluorine-doped tin oxide (FTO) glass used, R_{ct} is the charge transfer resistance at the semiconductor-liquid junction, and CPE is the parallel constant phase element. Results showed that the surface

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Table 1. EIS fitting values of the equivalent circuit model parameters for bare and hematite nanocomposites photoanode structures.

R [Ω]	R _s	R _{ct1}	R _{ct2}
CPE [μS]		CPE ₁	CPE ₂
Bare hematite	40.70	1231.90	895.15
		204	1450
C ₆₀ /hematite	37.60	1021.80	664.17
		135	1154
eRGO/hematite	36.74	1013.90	640.31
		3980	817
eRGO/C ₆₀ /hematite	23.77	1173.80	206.23
		1233	929

modification of hematite by nanocarbons leads to an overall reduction in the resistances and thus, facilitate the electron transfer and charge separation processes. The decrease in R_s value indicates that the hematite nanocomposites photoanode structures have smaller contact resistance and greater intrinsic conductivity when compared to bare hematite. The most challenging reaction on the photoanode occurs at the semiconductor-liquid junction and thus, the charge transfer resistance is generally much higher than the contact resistance.^[30a] In comparison to the bare hematite, the R_{ct2} values for hematite nanocomposites photoanode structures of C₆₀/hematite, eRGO/hematite, and eRGO/C60/hematite photoanodes have been reduced by 0.26-fold, 0.28-fold, and 0.77-fold, respectively. These infer that the inclusion of nanocarbons during the synthesis of hematite nanocomposites photoanodes provides electron transporting bridges for more efficient charge transfer between the hematite and electrolyte interface and results in a lower electron-hole pairs recombination rate. The resultant ternary hematite structure of eRGO/C₆₀/hematite exhibited the lowest charge transfer resistance with almost 0.8-fold reduction when compared to bare hematite. This was due to the substantial increase in the contact area between the hematite and carbonaceous nanocomposites and thus, ensued the highest photocurrent density.

Furthermore, Mott-Schottky analyses were performed to investigate the effect of nanocarbons on the flat band potential ($E_{\rm fb}$, [V]) and donor density ($N_{\rm d}$, [cm⁻³]) of the hematite. The positive slopes of the Mott-Schottky plots (**Figure 3**) indicate that all hematite photoanodes are *n*-type semiconductor. Both the $E_{\rm fb}$ and $N_{\rm d}$ were determined using the following Mott-Schottky equation^[34]

$$\frac{1}{C_{\rm sc}^2} = \frac{2}{\epsilon \epsilon \epsilon_{\rm o} N_{\rm d} A_{\rm s}^2} \left(E - E_{\rm fb} - \frac{kT}{e} \right) \tag{1}$$

where $C_{\rm sc}$ is the semiconductor space charge layer capacitance [cm³], *e* is the electron charge [C], ε is the dielectric constant of the semiconductor, $\varepsilon_{\rm o}$ is the permittivity of the vacuum [F cm⁻¹], $A_{\rm s}$ is the working electrode surface area [cm²], *E* is the applied potential [V], k is the Boltzmann's constant, and T is the temperature [K]. The estimated $E_{\rm fb}$ of bare hematite, C_{60} /hematite, eRGO/ hematite, and $eRGO/C_{60}$ /hematite are -0.90, -0.80, -0.72 and -0.79 V, respectively. Obviously, the $E_{\rm fb}$ of the hematite nanocomposites photoanodes are positively shifted as compared to that of bare hematite. This phenomenon may be attributed to the electronic interaction between nanocarbons and hematite in the nanocomposites photoanode structure.^[35] From the inset of Figure 3, the calculated $N_{\rm d}$ for hematite nanocomposites photoanode structures of C₆₀/hematite, eRGO/hematite, and eRGO/ C_{60} /hematite photoanodes have been enhanced by 0.2-fold, 2.6fold, and 3.1-fold, respectively, when compared to the bare hematite photoanode. The increase in N_d through the incorporation of nanocarbons supports the aforementioned observation regarding effective charge carriers seperation and transfer and thus, restrain the electron-hole pairs recombination that results in a superior PEC performance.

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The XRD analyses were performed to ratify the phase formation of hematite photoanodes before and after the inclusion of nanocarbons (Figure 4). All the diffraction peaks of hematite nanocomposites photoanode structures are in consistency with the reference hematite patterns (JCPDS no. 34-0664). No characteristic peaks of C₆₀ and eRGO were measured by XRD for the hematite nanocomposites photoanode structures. This might be due to the low concentration of nanocarbons included in the hematite nanocomposites photoanode structures. Hence, Raman spectroscopy was used to further validate the successful inclusion of C₆₀ and eRGO in the hematite nanocomposites photoanode structures. The surface morphology of the hematite nanocomposites photoanode structures was further analyzed by using FE-SEM as shown in Figure 5. The surface morphology of bare hematite photoanode was composed of fine hematite nanoparticles and had a strong tendency to aggregate during the electrodeposition and annealing processes (Figure 5a). Looking at the C₆₀/hematite photoanode depicted in Figure 5b, there is no obvious effect of introducing C₆₀ on the morphology and particle size of the hematite nanoparticles. However, the surface aggregation of C₆₀ nanoparticles was noticeably observed in the eRGO/C₆₀/hematite nanocomposites



Figure 3. Mott-Schottky plots of bare and hematite nanocomposites photoanode structures at the frequency of 10 kHz in NaOH (1 $_{\rm M}$). The inset is the calculated donor densities.





Figure 4. XRD diffraction patterns of bare hematite and hematite nanocomposites photoanodes. The H symbols indicate the characteristic peaks for hematite according to the JCPDS no. 33-0664, and the remaining peaks are from the FTO glass.

photoanode structure. Whilst the as-synthesized eRGO/hematite and eRGO/ C_{60} /hematite nanocomposites photoanode structures revealed crumpled texture of 2D-eRGO sheets, demonstrating the corrugation and flexibility nature of the 2D-eRGO sheets. The 2D-eRGO sheets had increased the interfacial area and provided an intimate interaction between hematite and eRGO and thus, promoted an efficient charge transfer process leading to a better PEC performance.

In order to further validate the presence of C_{60} and eRGO, Raman spectroscopy was used as an instant and non-destructive method to characterize the electronic and lattice structures of nanocarbons used.^[36] **Figure 6** shows the Raman spectra for GO, bare hematite, and hematite nanocomposites photoanodes. The sharp peak at 1317 cm⁻¹ comes from the two photon scatterings of bare hematite photoanode.^[37] The Raman spectra of GO present two distinct peaks at 1354 and 1596 cm⁻¹, while the eRGO/hematite and eRGO/C₆₀/hematite nanocomposites photoanodes show two obvious peaks at 1323 and 1605 cm⁻¹ that correspond to the D-band and G-band, respectively. The



Figure 5. FE-SEM images of a) bare hematite, b) C_{60} /hematite, c) eRGO/ hematite, and d) eRGO/ C_{60} /hematite nanocomposites photoanodes.

D-band (sp3 carbon) is attributed to the existence of structural defects in the honeycomb graphitic lattice that were introduced during the electrochemical reduction process of GO to eRGO.^[38] Whilst the G-band (sp2 carbon) is related to the Eg² photon close to the Brillouin zone center.^[30b] Previously, it was known that an increase in the intensity of D-band indicates a higher density of disorder carbon structures,[30b] but this effect cannot be observed in Figure 6 due to the overlapping of eRGO with the hematite peak. The peak at 1467 cm⁻¹ observed in C₆₀/hematite and eRGO/C60/hematite nanocomposites photoanodes was corresponded to the pentagonal pinch mode Ag(2) of C60 single crystal.^[32] These results affirmed that both C60 and eRGO were successfully incorporated onto the hematite photoanodes.

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Figure 7a shows the UV–vis absorption spectra of the bare hematite and hematite nanocomposites photoanodes. For the bare

hematite photoanode, an absorption edge at 650 nm that conformed to the band gap energy of 2.05 eV (Figure 7b) was observed. The absorption band in the range of 400-600 nm is ascribed to the excitation of the Fe³⁺ 3d-3d spin forbidden.^[39] By comparing the bare hematite and hematite nanocomposites photoanodes, all the spectra showed identical absorption peak values. However, it can be clearly observed that the reinforcement by nanocarbons had induced a stronger absorption at wavelength greater than 600 nm that enhanced light absorption into the visible light and near IR regions. This is attributed to the electronic interactions between the nanocarbons and hematite molecules. Based on the Tauc plot (Figure 7b), the extrapolated band gap energies for C₆₀/hematite, eRGO/ hematite, and eRGO/C₆₀/hematite nanocomposites photoanodes are 1.97, 1.92, and 1.89 eV, respectively.^[9] Therefore, it can be concluded that the incorporation of nanocarbons into hematite photoanodes is able to enhance the light absorption and thus, elevate the PEC performance.

These results suggest that the PEC performance of hematite photoanodes has significantly been improved through the incorporation of C₆₀ and eRGO. The incorporation of nanocarbons leads to different structural morphology, synergistic interaction between hematite and nanocarbons, and thus, PEC performance. Overall, the eRGO/C₆₀/hematite nanocomposites photoanode exhibited a synergistic improvement in the PEC performance when compared to solely incorporate C60 or 2D-eRGO only. The synergistic improvement is due to that the combination of nanocarbons has greatly increased the charge transfer property by providing a direct conduction path through both the electron scavenging C₆₀ and highly conducting 2D-eRGO sheets.^[40] Moreover, the significant reduction in surface charge transfer resistances was due to the increased surface area through the intercalation of C₆₀ nanoparticles and 2D-eRGO sheets. Zhang et al. proposed that more contact between two materials leads to a lower charge transfer resistance and thus, increase in electrical conductivity that favours the PEC process.^[38] However, more research efforts are needed



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Figure 6. Raman spectra of bare hematite and hematite nanocomposites photoanodes. The inset represents the Raman spectrum of GO.

Wavenumber [cm⁻¹]

to completely understand the fundamental role and mechanism of C_{60} nanoparticles and 2D-eRGO sheets in influencing the PEC performance of semiconductor photocatalysts.



Figure 7. a) UV-vis absorption spectra and b) Tauc-plots of bare hematite and hematite nanocomposites photoanodes.

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3. Conclusion

In conclusion, ternary hematite photoanode modified with C₆₀ nanoparticles and 2D-eRGO sheets were successfully fabricated through the facile electrodeposition method. The PEC performance of the synthesized hematite nanocomposites photoanodes was investigated. Results showed that the photocurrent densities of C60/hematite, eRGO/ hematite, and eRGO/C₆₀/hematite nanocomposites photoanodes were enhanced by 1.2-fold, 13.3-fold, and 16.8-fold, respectively. Whilst the EIS results demonstrated that the corresponding charge transfer resistances have substantially been reduced. This is attributed to the outstanding electron conducting nature of C₆₀ nanoparticles and 2D-eRGO that can ameliorate photogenerated charge transfer and separation. On the other hand, it was confirmed that the incorporation of nanocarbons has minor influence on the crystal phase, nanoparticle size, and surface morphology of hematite photoanodes. The introduction of nanocarbons has extended

the light absorption ability into the visible light and near IR regions. This study provides an in-depth understanding of the potential use of two carbonaceous materials of C_{60} and eRGO to enhance the PEC performance in hematite through effective electron shuttling at the surface molecular level.

4. Experimental Section

Materials: Iron (III) chloride (FeCl₃, 97%) (Sigma Aldrich, USA), potassium chloride (KCl) (R&M, UK), acetone, acetonitrile, ethanol, graphite powder, sodium hydroxide (NaOH), toluene (Merck, Germany), FTO glass, and C₆₀ (ChemSoln, USA) were used. The FTO glasses were sonicated in acetone for 20 min, and ethanol for 20 min in an ultrasonic bath, followed by rinsing in water and drying in ambient air condition. All chemicals were reagent grade quality and used without further purification.

Preparation of $C_{60}/eRGO/Hematite$ Nanocomposites Photoanode: An Autolab potentiostat (Metrohm, PGSTAT204) with three-electrode electrochemical cell consisting of FTO glass, platinum (Pt) rod, and silver/silver chloride (Ag/AgCl) saturated in KCl (3 ${\mbox{\scriptsize M}})$ as the working, counter, and reference electrodes, respectively, was used during the synthesis process. Nanostructured hematite films were synthesized on FTO glass by electrodepositing in a FeCl₃ (5 \times 10⁻³ M) electrolyte precursor solution. Electrodeposition was carried out by cyclic voltammetry between -0.2 and 0 V with a scan rate of 0.05 Vs⁻¹ for 50 cycles. The air dried amorphous hematite (FeOOH) films were annealed at 600 °C for 4 h. Prior to the synthesis of eRGO/hematite nanocomposites photoanode, GO powder was synthesized from graphite powder via the Improved Hummers' method.^[41] The eRGO/hematite nanocomposites photoanode was prepared by electrochemical reduction of GO onto the nanostructured hematite films. The electrodeposition solution was prepared by dispersing GO powder (100 mg) in KCl (50 mL, 0.1 M). Next, the solution was ultrasonicated for 30 min and the pH of the solution was maintained at pH 7.3 throughout the synthesis process. Using the hematite films as the working electrode, the cyclic voltammetric reduction was performed from -1.5 to 0.5 V for ten cycles at 0.05 V s⁻¹ sweep rate. The obtained eRGO/hematite nanocomposites Chapter 6 | P cpqectdqp/Dcugf Hematite Nanostructured Photoanodes



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photoanode was dried at 60 °C for 1 h. On the other hand, the C₆₀/ hematite nanocomposites photoanode was prepared by adding C₆₀ (0.2 mg mL⁻¹) to a mixture of acetonitrile and toluene in a 3:1 ratio. The electrolyte suspension was then ultrasonicated for 30 min to obtain a homogeneous C₆₀ dispersion. The electrodeposition was conducted using chrono amperometry at a potential of 0.15 V for 4 min, where hematite films act as the working electrode. The resultant C₆₀/hematite nanocomposites photoanode was dried at 80 °C. Lastly, the C₆₀/eRGO/ hematite nanocomposites photoanode was prepared by using the same methods mentioned above, where C₆₀ was first electrodeposited onto the hematite followed by 2D-eRGO sheets.

Characterisation: The UV-vis absorption spectra were obtained by using an UV-vis spectrometer (Agilent Cary 100). The optical band gap energy (E_g) of photoanodes was estimated following the equation: $(\alpha h\nu)^n = A(h\nu - E_g)$, where α is the absorption coefficient, $h\nu$ is the incident photon energy, n is a constant value of 2 for indirect transition semiconductor, and A is the absorption coefficient.^[42] The surface morphologies were observed by using a FE-SEM (Hitachi SU8010). The crystal structures were characterized using an XRD (Bruker D&) employing Cu-K α radiation with 40 kV and 100 mA at 0.02° s⁻¹ scan rate. The Raman spectra were acquired from a Raman spectrometer (Horiba Scientific) with a solid state laser operating at an excitation source of 514 nm.

PEC Measurements: PEC measurements were carried out in NaOH (1 M, pH 13.6) electrolyte solution using a three-electrode electrochemical cell, where the hematite nanocomposites photoanodes was made as the working electrodes. The photoanodes were illuminated by a 100 W halogen lamp (Philips) with a fixed lamp-to-photoanode distance of 10 cm. The current density versus potential (*I–V*) curves and Nyquist plots were attained by using the Autolab potentiostat PGSTAT204 and PGSTAT302N (Metrohm), respectively. EIS was conducted with a frequency range of 100 kHz–0.1 Hz at –0.6 V bias voltage. Mott-Schottky analyses were performed at 10 kHz by scanning the potential range from –1 to 0 V at 0.05 V s⁻¹ sweep rate.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Employing electrochemical reduced graphene oxide as a co-catalyst for synergistically improving the photoelectrochemical performance of nanostructured hematite thin films



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ABSTRACT

In this study, a series of electrochemical reduced graphene oxide (eRGO)-hematite nanocomposites were developed through a facile and environmental benign two-step electrodeposition method with high photoelectrochemical (PEC) performance. The resulting nanocomposites formed an intimate contact between the eRGO and hematite interface as supported by the field emission-scanning electron microscopy (FE-SEM) analysis. A remarkable 8-fold enhancement in the photocurrent density was observed on the eRGO-hematite-4 nanocomposite (using 2.0 mg/ml GO precursor) relative to the bare hematite under light irradiation. This improvement is ascribed to the finely controlled eRGO sheets that enhance the light absorption, increase PEC active surface area of hematite, improve efficient transfer of the photoinduced electrons from the conduction band of hematite to eRGO sheets and as a result leads to a minimised electronhole pairs recombination rate. This was further evidenced with impedance characteristics, where the obtained surface charge resistance values of eRGO-hematite-4 nanocomposite are much lower than the bare hematite, revealing an efficient charge transfer step to impede the charge recombination. Lastly, a postulated mechanism for the PEC process associated with eRGO-hematite nanocomposite was presented.

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1. Introduction

Photoelectrochemical (PEC) process based on earth-abundant semiconductor materials is a promising technology to harness the solar energy directly [1]. By efficiently utilising the solar energy, PEC process may potentially supply the world's energy demand with minimal environmental impact and carbon-neutral energy carrier [2]. Since the first report for the photoelectrolysis of water over titanium dioxide (TiO₂) by Fujishima and Honda in 1972, numerous semiconductor materials have been extensively studied for this purpose [3]. In order to achieve higher photoconversion efficiency for PEC process, there are a number of key technical challenges that need to be addressed. For instance, the development of visible-active photoanode that possesses the ability to absorb light photons in the visible light spectrum and yield high solarto-hydrogen (STH) conversion efficiency [4]. Note that photoanode

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is the oxygen evolution electrode while hydrogen is evolved at the counter cathode in a PEC cell.

Recently, hematite (α -Fe₂O₃) with narrow band gap energy of 2.0-2.2 eV has attracted considerable attention due to its capability in absorbing a large fraction of solar light [5,6]. Hematite is the most thermodynamically stable and common iron oxide, and it is ubiquitous, nontoxic as well as inexpensive [7,8]. These desirable properties make hematite a promising material as a photoanode for PEC process. However, the poor electron mobility $(<1 \text{ cm}^2/\text{Vs})$ and short hole diffusion length (2-4 nm) which resulted in the rapid recombination rate of photoexcited electron-hole pairs have limited the PEC performance of hematite photoanode [9,10]. Generally, most photogenerated electron-hole pairs have the tendency to go through fast recombination process before carrying out the chemical reactions [11]. Therefore, it is of vital importance to develop new strategies for a more efficient hematite photoanode which could enhance the conductivity and promote charge transfer process of photogenerated electron-hole pairs by hindering the recombination process.

A strategy to enhance the charge transfer property of semiconductor materials is to introduce conductive materials, for example,

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carbon nanotube (CNT) [12-14], fullerene [15-17] and the new class of carbonaceous material, graphene or reduced graphene oxide (RGO) as co-catalysts [18-20]. Graphene comprises of an atomically thick sp² hybrid carbon atoms arranged in a honeycomb structure has attracted tremendous interest from researchers owing to its intriguing characteristics [21]. In particular, graphene offers excellent electrical conductivity, acting as a superior electron transport matrix and thus favouring the transfer process of photogenerated charge carriers, as well as prolonging the lifetime of photogenerated electron-hole pairs [22]. Therefore, semiconductor materials modified with graphene or RGO are believed to provide a new route to develop high performance PEC electrode. Recently, several RGO-hematite composite photoanodes have been demonstrated via different synthesis techniques for PEC process. For instance, Ren et al. developed hierarchical superparamagnetic iron oxide/graphene with a superb water dispersibility and strong photoluminescence by a one-step hydrothermal method [23]. Besides, Wu et al. synthesised ultrathin hematite RGO films using a separated two-phase hydrolysis-solvothermal reaction followed by spin-coating of GO colloidal solution and sintering process [24]. It was found that graphene could be used as an alternative co-catalyst to improve PEC process of ultrathin hematite film. Similarly, a three dimensional urchin-like hematite nanostructure prepared via a solution-based method followed by annealing treatment, and ultra-thin RGO sheets spin-coated on hematite followed by thermal treatment have recently been presented by Tamirat et al. [25]. The dual effect of RGO as surface passivation layer and electron transporting bridge were proven by the charge separation and injection efficiencies of the RGO-hematite nanocomposite.

Generally, graphene or RGO sheets on hematite electrodes have been obtained by drop-casting, spin coating and dip coating. Although these methods can directly deposit graphene or RGO on large surface substrate, the thickness and uniformity of the sheets are difficult to control [26]. On the other hand, the electrodeposition technique is a promising, well-developed and economical method that has been previously used for the deposition of carbonaceous materials [16,27,28]. In particular, electrochemical reduction of graphene oxide (GO) to electrochemical reduced graphene oxide (eRGO) has numerous advantages over the earlier mentioned methods, for instance low-cost, low temperature, simplicity and environmentally friendly [29]. Hence, inspired by previous works, we show a facile and environmental benign two-step electrodeposition process to synthesis eRGO-hematite nanocomposite with improved PEC performance, in which limited research has been accomplished in the past. Furthermore, we reveal the synthesis mechanism by analysing the feasibility of GO electrodeposition in aqueous solutions with various concentrations and optimised the relative mass of eRGO on hematite to attain the maximum PEC efficiency.

2. Experimental

2.1. Materials and reagents

All the reagents were analytical grade and were used as received without additional treatment. Iron (III) chloride (FeCl₃) was purchased from Sigma-Aldrich, Malaysia. Potassium chloride (KCl) was purchased from ChemSoln, USA. Hydrogen peroxide (H_2O_2) (30 wt%), graphite flakes, sulphuric acid (H_2SO_4) (96 wt%), phosphoric acid (H_3PO_4) (75 wt%), potassium permanganate (KMnO₄), hydrochloric acid (HCl) (30 wt%), sodium hydroxide (NaOH) and graphite powder were purchased from Merck, Malaysia. Fluorinedoped tin oxide (FTO) glass was purchased from ChemSoln, USA.

2.2. Synthesis of GO

GO was synthesised from natural graphite powder via the Improved Hummers' method [30]. Briefly, graphite powder (1.5 g) and KMnO₄ (9 g) were added in a mixture of concentrated H₂SO₄ (180 ml) and H₃PO₄ (20 ml) in a 9:1 ratio. The exothermic reaction produced heat and thus, the mixture was kept below 20 °C by using ice bath. The resultant mixture was heated to 65 °C and stirred at 250 rpm for 3 day. After cooling to room temperature, ice (200 ml) and 30% H₂O₂ (1.5 ml) were poured into the mixture. The resulting black precipitate was obtained by centrifugation at 4000 rpm for 4 h and washed in sequence with 120 ml of deionised water, 120 ml of 30% HCl, 120 ml of ethanol, 120 ml of deionised water. The remaining solid materials after the thorough multiple wash process were coagulated by adding 100 ml of ether and then drying overnight at room temperature to obtain the GO product.

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2.3. Synthesis of eRGO-hematite nanocomposites

The eRGO-hematite nanocomposite was synthesised using a facile two-step process; electrodeposition of hematite onto the FTO glass followed by electrochemical reduction of GO onto the nanostructured hematite. The synthesis of nanostructured hematite was carried out according to our previous work [31]. Electrodeposition was performed in a 5.0 mM FeCl₃ precursor solution on an Autolab potentiostat (Metrohm PGSTAT204, Netherlands) using a three-electrode electrochemical system where platinum (Pt) rod, silver/silver chloride (Ag/AgCl) saturated by 3 M KCl and FTO acted as the counter, reference and working electrodes, respectively. Nanostructured hematite was prepared by cyclic voltammetry process at a potential scan rate of 0.05 V/s, from -0.2 to 0 V vs. Ag/AgCl for 50 cycles. The as-deposited amorphous hematite (FeOOH) thin films were washed with deionised water and was further annealed at 600 °C for 4 h

To synthesise the eRGO-hematite nanocomposite, GO powder was first dispersed in a solution of 0.1 M KCl with vigorous stirring. Then, the GO solution was sonicated for 1 h to obtain a homogeneous GO dispersion (0.5, 1.0, 1.5 2.0 and 2.5 mg/ml). The cyclic electrochemical reduction of GO was performed in the GO precursor solution on the Autolab potentiostat with a three-electrode electrochemical system where Pt rod, Ag/AgCl saturated by 3 M KCl and nanostructured hematite as the counter, reference and working electrodes, respectively. The electrochemical reduction was carried out between -1.5 to 0.5 V vs. Ag/AgCl at a scan rate of 0.05 V/s for 10 cycles. The obtained eRGO-hematite nanocomposite was washed with deionised water, after that drying at $60 \,^{\circ}$ C for 1 h The resulting eRGO-hematite nanocomposite products were abbreviated as eRGO-hematite-i (i = 1-5) which are in accordance to 0.5, 1.0, 1.5 2.0 and 2.5 mg/ml GO dispersion used.

2.4. Characterisation

The functional groups of synthesised GO were identified by using a Fourier transform infrared (FTIR) spectrometer (Thermo Scientific Nicolet iS10). Field emission-scanning electron microscopy (FE-SEM) (Hitachi SU8010) was used to examine the surface morphology of eRGO-hematite nanocomposite. Raman spectra were acquired from a Raman spectrometer (Horiba Scientific) with a solid state laser operating at an excitation source of 514 nm. XRD patterns were obtained by using an X-ray diffractometer (Bruker D8) employing Cu-K α radiation with 40 kV and 100 mA at 0.02°/s scan rate. Materials composition and oxidation states of iron and carbon atoms in the eRGO-hematite nanocomposites were analysed using an X-ray photoelectron spectrometer (XPS) (Omicron Nanotechnology DAR400). Optical absorption measurements were obtained

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Fig. 1. FTIR spectrum of synthesised GO.

using an ultraviolet-visible (UV-vis) spectrometer (Agilent Cary 100). The band gap energies of the samples were estimated from the extrapolation of the Tauc plot. PL measurements were performed with fluorescence spectrometer (Perkin Elmer LS 55) using 320 nm as the excitation wavelength.

2.5. PEC analyses

The PEC characterisations were performed on an Autolab potentiostat (Metrohm PGSTAT302N, Netherlands) with three-electrode electrochemical system. The reference and counter electrodes were Ag/AgCl saturated in 3 M KCl and Pt rod, respectively. All the PEC measurements were performed in a 1 M NaOH electrolyte solution. Photocurrent–voltage (I–V) curves were scanned from 0 to 1 V vs. Ag/AgCl at a sweep rate of 0.02 V/s. The photoanodes were illuminated using a 100 W halogen lamp (Philips) with a fixed lampto-sample distance of 10 cm. The illumination area was measured prior to the PEC measurements. Electrochemical impedance spectroscopy (EIS) was performed with a frequency range of 100 kHz– 0.1 Hz at the potential of 0.6 V vs. Ag/AgCl.

3. Results and discussion

3.1. Electrochemical reduction of GO

Prior to the electrochemical reduction of GO, the chemical property of the synthesised GO was characterised by using FTIR. From the FTIR spectra as shown in Fig. 1, the GO functional groups were identified, for instances, C–O vibrations (1250 cm^{-1}) , C–C from unoxidised sp² C–C bonds $(1590-1620 \text{ cm}^{-1})$, C–O stretch-



Fig. 3. FE-SEM images of (A) bare hematite, (B) eRGO-hematite-1 nanocomposite, (C) eRGO-hematite-4 nanocomposite, and (D) eRGO-hematite-5 nanocomposite.

ing vibrations $(1720-1740 \text{ cm}^{-1})$ and O–H stretching vibrations (3420 cm^{-1}) [30].

The cyclic voltammograms of electrochemical reduction of GO on hematite are shown in Fig. 2, where during the electrochemical reduction of GO, one anodic and two cathodic peaks were observed. Both the anodic and the cathodic peak (I) are attributed to the redox pair of surface oxygenated species on the GO plane, while the cathodic peak (II) is ascribed to the irreversible eRGO formation [29]. The continual increase of the peaks currents from the 1st to 6th cycle indicates that the deposition of GO on hematite was successfully achieved. Starting from the 7th cycle, the reduction in the current for the cathodic peak (II) was observed and it disappeared at 10th cycle where this showed that the electrochemical reduction of GO could be reduced electrochemically to form eRGO [33].

3.2. Structural and chemical characterisations

The surface morphology and microstructure of the bare hematite and eRGO-hematite were characterised by field emissionscanning electron microscopy (FE-SEM) and the images are as shown in Fig. 3. The morphology of bare hematite in Fig. 3(A)



Fig. 2. Cyclic voltammograms of electrochemical reduction of GO.

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Fig. 4. XRD patterns of (A) bare hematite and (B–E) eRGO-hematite-i (i = 1-4) nanocomposites (* indicating the FTO peaks).



Fig. 5. Raman spectra of (A) bare hematite, (B–F) eRGO-hematite-i (i = 1-5) nanocomposites and (G) GO.

has typically the characteristic of uniform and densely packed nanostructures with open porosity of Fe_2O_3 . Fig. 3(B)–(D) revealed that the eRGO-hematite nanocomposites consist of many hematite nanoparticles and eRGO sheets with compact and ample interfacial contacts. The eRGO sheets appeared a wrinkled texture that was associated with the existence of flexible and ultrathin eRGO sheets. The cross sectional FE-SEM image of eRGO-hematite-4 nanocomposite revealed the thickness of thin film of 360 nm (Fig. S1 in Supplementary material). In the eRGO-hematite-1 and 4 nanocomposites, the hematite nanoparticles were clearly observed underneath the thin and semi-transparent eRGO sheets (Fig. 3(B) and (C)). As for the eRGO-hematite-5 nanocomposite (Fig. 3(D)), the hematite nanoparticles cannot be clearly seen due to the restacking phenomenon during the electrochemical reduction of GO (2.5 mg/ml) to eRGO that resulted in crumpled-like eRGO sheets.

The X-ray diffraction (XRD) patterns of the bare hematite and eRGO-hematite-i nanocomposites are illustrated in Fig. 4. Interestingly, no characteristic peak of graphene ($2\theta = 24.5^{\circ}$) was observed in all the eRGO-hematite-i nanocomposites where this was due to the low loading amount and comparatively weak diffraction intensity of graphene [25]. The electrochemical reduction of GO to eRGO was further confirmed by Raman spectra, as discussed later. On the other hand, most of the diffraction peaks for eRGO-hematitei nanocomposites were well indexed to the hematite phase with distinct peaks corresponding to {104}, {110}, {006}, {202}, {116}, {211} and {300} planes according to the JCPDS 33–0664 [34]. These indicate that the phase purity of hematite was not altered after the formation of nanocomposite between hematite and eRGO. Although most of the eRGO-hematite-i nanocomposites showed similar diffraction peaks with the bare hematite, the intensity of the diffraction peaks for the nanocomposites decreased with increasing GO concentration [35].

Further information on the electrochemical reduction of GO to eRGO was characterised by using Raman spectroscopy as illustrated in Fig. 5. The Raman spectrum of bare hematite showed all the characteristic peaks of a well-crystallised hematite [36]. The eRGOhematite-i nanocomposites revealed the characteristic features of hematite, which is compatible with the XRD observation. Both GO and eRGO-hematite-i nanocomposites appeared to have a D-band around 1354 cm⁻¹ and a G-band around 1596 cm⁻¹. The D-band is attributed to the breathing modes of sp² atoms in aromatic rings while the G-band is originated from the bond stretching in both chains and rings of all pairs of sp² atoms [37]. The D/G intensity ratio (I_D/I_G) is a measure of the disorder in graphene where the increase in I_D/I_G indicates that the GO or eRGO contains more defects [38]. However, the I_D/I_G ratio cannot be calculated due to the overlapping of eRGO D-band with the hematite peak at 1324 cm⁻¹. In the empiricist view, all eRGO-hematite-i nanocomposites have a higher D-band than G-band. On the contrary, GO has a higher Gband than D-band. This might be owing to the higher density of disorder carbon structures formed during the electrochemical reduction of GO to eRGO, where the defects were due to the formation of smaller size eRGO sheets [39].

The chemical composition and status of the elements in the eRGO-hematite nanocomposite was further characterised by performing X-ray photoelectron spectroscopy (XPS). The XPS survey spectrum in Fig. 6(A) depicted that the nanocomposite was constituted of Fe, O and C elements. The Fe 2p spectrum in Fig. 6(B) showed two distinct peaks with binding energies of approximately 710 and 724 eV for Fe $2p_{3/2}$ and Fe $2p_{1/2}$, respectively, and are the characteristic peaks for Fe³⁺ ions in hematite [40]. High resolution C 1s spectrum in Fig. 6(C) exhibits only the binding energy attributing to the C–C bond (286.8 eV) [41]. Since the

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Fig. 6. XPS spectra of (A) survey, (B) Fe 2p, (C) C 1s and (D) O 1s for eRGO-hematite-4 nanocomposite.



Fig. 7. (A) UV-vis spectra and (B) Tauc plot for the bare hematite and eRGO-hematite-i nanocomposites.

intensity of C–O bond is very low, this indicated that the oxygenated functional groups in GO are mostly being reduced to eRGO during the electrochemical reduction process. This is concordant with the observation in Raman spectra (Fig. 5) where the removal of oxygenated functional groups during the electrochemical reduction process has caused the number of disorder to increase and the size of graphitic domains to decrease [42]. For the O 1s spectrum in Fig. 6(D), the peak at 530.9 eV is attributed to the presence of oxygen groups within the lattice structure of hematite, whereas the peak at 532.5 eV is a result of the oxygen groups bonded to the carbon atoms in eRGO.

Ultraviolet-visible (UV-vis) absorption spectroscopic measurements were conducted in order to examine the optical response of eRGO-hematite nanocomposites. Both the bare hematite and eRGO-hematite-i nanocomposites exhibited an intense absorption in the visible region of the UV-vis spectra (Fig. 7(A)), which corresponded to the intrinsic band gap absorption of hematite as a result of the transfer of electrons from the valance band to the conduction band [43]. This indicated that the eRGO sheets in the eRGO-hematite-i nanocomposites served as an electron reservoir for the hematite photoanodes. By extrapolating the linear region of the Tauc plot in Fig. 7(B), the band gap energy of bare hematite was approximated to be around 2 eV. Additionally, a slight red shift was noticed for the eRGO-hematite-i nanocomposites where this was associated with a slight reduction of the band gap energy to about 1.85 eV. This slight decrease in the band gap energy was due to the presence of eRGO in the nanocomposites which favours the light absorption. This phenomenon has also been elucidated in other RGO-based semiconductor materials [22,44].

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Fig. 8. (A) Photocurrent versus potential (I–V) curves, (B) photocurrent measured at various potentials, (C) PL spectra and (D) Nyquist plots of the bare hematite and eRGO-hematite-i nanocomposites.

3.3. PEC performance

The PEC behaviours for both bare hematite and eRGO-hematitei nanocomposites were examined in order to understand the influence in controlling the GO concentration during the electrochemical reduction process. From Fig. 8(A), it can be seen that the electrodeposition of eRGO sheets onto hematite had significantly impacted on the PEC performance of hematite photoanodes. All the eRGO-hematite-i nanocomposites showed improved photocurrent densities and lower onset potentials when compared with bare hematite. Among the eRGO-hematite-i nanocomposites, the eRGO-hematite-4 exhibited the highest photocurrent density of 1.26 mA/cm² at 0.7 V vs. Ag/AgCl that is approximately 8-fold enhancement. Additionally, the onset potential was cathodic shifted for 90 mV relative to bare hematite as illustrated in Fig. 8(B). Further increase in the GO concentration for electrochemical reduction process had led to reduction of photocurrent density to 0.98 mA/cm^2 . This might be due to the crumpled-like structure or restacking of eRGO sheets in the eRGO-hematite-5 nanocomposite as evidence from the FESEM image, (Fig. 3(D)) that resulted in the decrease of PEC active surface area for hematite. Besides, the photoresponse of bare hematite and eRGO-hematite-4 nanocomposites was confirmed by measuring the transient photocurrent response for several on-off cycles of intermittent irradiation (Fig. S2 in Supplementary material). Without irradiation, the photocurrent drops abruptly to close to zero while it yields a steady-state photocurrent upon irradiation that is the characteristic for several onoff cycles. Furthermore, the onset potential of the eRGO-hematite-i nanocomposites was observed to be slight cathodic shifted, implying that the kinetic energy barrier for the transfer of charge at the semiconductor-liquid junction was lowered in comparison to bare hematite. As a result, the overpotential needed for water oxidation was reduced. The results obtained in this work are in accordance with the previous literatures [25,45,46]. The enhanced PEC performance due to the synergistic effects of eRGO was further illustrated with impedance responses of the photoanodes in the later section.

Based on Fig. 8(C), a noticeable photoluminescence (PL) quenching effects was observed when the hematite was modified with eRGO. The PL spectrum intensity is a direct measurement of the recombination rate of photogenerated electron-hole pairs, where the higher intensity implies higher recombination rate of charge carriers and as a result the PEC performance of the semiconductor materials is unfavourable [47]. The eRGO-hematite-4 nanocomposite showed the lowest PL intensity. This was owing to the optimum amount of depositing eRGO sheets on the hematite which has efficiently inhibited the recombination of photogenerated electronhole pairs where eRGO possesses the ability to effectively migrate the photogenerated charge carriers. The observation from PL spectra was well aligned to the photocurrent results in Fig. 8(A) and (B). On top of that, the EIS was further investigated in order to understand the surface charge resistances of the eRGO-hematite-4 nanocomposite. The Nyquist plots of bare hematite and eRGOhematite-4 nanocomposite are depicted in Fig. 8(D) where they were fitted with an equivalent circuit model to determine the electrochemical parameters. R_s is the series resistance in the interface

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Fig. 9. Schematic of charge transfer in the eRGO-hematite nanocomposite for oxidation and reduction of water molecules.

 Table 1

 The fitted values of equivalent circuit model for bare hematite and eRGO-hematite-4 nanocomposite.

Sample	$R_s(\Omega)$	$R_{ct} (\Omega)$	CPE (μ Mho)
Bare hematite	52	3480	520
eRGO-hematite-4	37	2283	839

between FTO and hematite, R_{ct} is the charge transfer resistance in the semiconductor liquid junction, and *CPE* is the corresponding constant phase element [48]. The fitted values of equivalent circuit model are listed in Table 1. It is well acknowledged that both R_s and R_{ct} are important parameters of total series resistance of the photoanode, where these values are inversely proportional to the electrochemical performance of the photoanode [24]. The obtained R_s and R_{ct} values of eRGO-hematite-4 nanocomposite are 37 Ω and 2283 Ω , respectively, which are much lower than those of bare hematite ($R_s = 52 \Omega$ and $R_{ct} = 3480 \Omega$), manifesting the more efficient of charge transfer and hinder the charge recombination process. The enhancement in the separation efficiency of photogenerated charge carriers is consistent with the higher photocurrent density of eRGO-hematite-4 nanocomposite where this was owing to the incorporation of highly conductive eRGO sheets.

Based on the collective characterisations and analyses, the PEC performance of nanostructured hematite can be synergistically improved by employing eRGO as a co-catalyst where its mechanism is postulated in Fig. 9. The possible electron transfer mechanisms upon light irradiation are shown as below:

hematite + eRGO
$$\xrightarrow{h\nu}$$
 hematite (h^+) + eRGO (e^-) (1)

$$2h^+ + 20H^- \rightarrow H_20 + 1/20_2$$
 (2)

$$2e^{-} + 2H_2O \rightarrow H_2 + 2OH^{-}$$
 (3)

Upon light irradiation, hematite with band gap energy of 2 eV was excited where electrons can make transition from the valence band to the conduction band, leaving mobile holes in the valence band. Since eRGO sheets offer an excellent electrical conductivity and act as a superior electron transport matrix [22], the photogenerated electrons from the conduction band of hematite

were migrated to the eRGO sheets. Therefore, the successful transfer of photogenerated electrons had remarkably supressed the recombination of photogenerated electron-hole pairs. The photoinduced holes on the valence band of hematite reacted with water molecules to generate oxygen gas and protons. Meanwhile, the accumulated electrons on the eRGO sheets transferred to the Pt electrode via an external circuit and reduced protons to yield hydrogen gas. It can be concluded that eRGO acts as an efficient co-catalyst for the surface charge modification of nanostructured hematite. In this instance, the eRGO sheets favour the transfer process of photogenerated charge carriers and thus lead to improved PEC performance of eRGO-hematite nanocomposites.

4. Conclusion

In conclusion, the eRGO-hematite nanocomposites were successfully developed by using a facile and environmental benign two-step electrodeposition technique. Nanostructured hematite thin films modified with eRGO sheets showed an enhanced photo current density of 1.26 mA/cm^2 at 0.7 V (vs. Ag/AgCl), which is around 8 times higher than the bare hematite. The enhancement was associated with the synergistic interactions between hematite and eRGO, resulting in a higher photogenerated electron-hole pairs separation efficiency to retard the charge recombination as supported by XPS, PL and EIS studies. This is because eRGO functions as both surface passivation layer and electron transporting bridge that favours the transport process of photogenerated charge carriers. Overall, our work highlights the significance of the heterojunction interface between semiconductor and conductive eRGO, which can be synthesised by a simple two-step electrodeposition method. It is anticipated that our current work will provide new possibilities in the fabrication of eRGO-based semiconductor and various multicomponent nanocomposites by using electrodeposition technique with improved PEC performance for environmental and energy-related applications.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.jtice.2016.12.017.

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CHAPTER 5

DEVELOPMENT OF A NOVEL TERNARY ELECTROCHEMICAL REDUCED GRAPHENE OXIDE/NICKEL OXIDE/HEMATITE NANOSTRUCTURED PHOTOANODE FOR PEC WATER SPLITTING

Chapter 5 | Ternary eRGO/NiO/Hematite Nanostructured Photoanodes

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A novel ternary nanostructured carbonaceous-metal-semiconductor eRGO/ NiO/α -Fe₂O₃ heterojunction photoanode with enhanced charge transfer properties for photoelectrochemical water splitting



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ABSTRACT

A novel ternary hematite (α -Fe₂O₂)-based nanostructured photoanode with excellent photoelectrochemical (PEC) performance consisting of 2D-electrochemical reduced graphene oxide (eRGO) and nickel oxide (NiO) was successfully developed through electrodeposition synthesis method. Surface morphology studies showed that the flexible eRGO sheets provided intimate and coherent interfaces between α -Fe₂O₃, NiO, and eRGO that enhanced charge transfer properties and thus, lowering the recombination rate of photogenerated electron-hole pairs. The incorporation of eRGO and NiO has also endowed α -Fe₂O₃ nanostructured photoanode with a wider spectral absorption range, where the light absorption intensities in the visible light and near infrared regions were improved. Electrochemical impedance spectroscopy analysis further confirmed that the ternary eRGO/NiO/ α -Fe₂O₃ nanostructured photoanode possessed the lowest charge transfer resistance among all as-synthesized photoanodes. This indicates that the combinatorial effects of eRGO and NiO could improve the electron mobility and prolong the recombination process of photogenerated charge carriers that result in enhanced PEC performance. In this instance, the eRGO sheets act as surface passivation layer and electron transporting bridge that increase the electrons transfer at the semiconductor/liquid junction. Whilst NiO serves as hole scavenger that also effectively hinders the recombination of photogenerated electron-hole pairs, and provides electron donor centres that accelerate the interfacial charge transfer. Finally, the hydrogen evolution rate from the ternary eRGO/NiO/ α -Fe₂O₃ nanostructured photoanode was measured to be 92 μ mol h⁻¹ cm⁻², which was about 3-fold higher than bare α -Fe₂O₃ nanostructured photoanode. It is expected that the fundamental understanding gained through this study is helpful for the rational design and construction of highly efficient ternary nanostructured heterojunction photoanodes for application in PEC water splitting.

1. Introduction

Hematite iron oxide (α -Fe₂O₃) has been extensively used as a semiconductor photoanode material in photoelectrochemical (PEC) process owing to its high physical and chemical stability, environmental compatibility, non-toxicity, Earth-abundant and low unit cost. Besides, α -Fe₂O₃ is an *n*-type semiconductor material that possesses a narrow band gap of ~2.0–2.2 eV that allows ~16% of theoretical solar-to-hydrogen (STH) conversion efficiency at AM 1.5 G solar irradiation [1]. Thus, it has been considered as one of the most promising semiconductor materials for application in PEC water splitting. However, the practical PEC performance of α -Fe₂O₃ is limited by its intrinsic defects,

such as relatively large overpotential for water oxidation, extremely poor majority carrier conductivity ($\sim\!10^{-2}\,{\rm cm}^2\,{\rm V}^{-1}\,{\rm s}^{-1}$), and short diffusion length ($\sim\!2\text{-}4\,{\rm nm}$) of minority carriers that significantly inhibit the charge separation and collection efficiency [2]. These limitations of $\alpha\text{-Fe}_2O_3$ have resulted in a much lower practical STH conversion efficiency as compared to the theoretical estimation value.

Owing to these limitations, a plethora of researches have concentrated on fabricating α -Fe₂O₃ heterostructures by introducing a second semiconductor material to enhance surface catalysis for accelerated water oxidation reaction, charge transfer and collection for prolonging the recombination rate of photogenerated charge carriers. Furthermore, the role of the second semiconductor material in α -Fe₂O₃ heterostructures are constructed by the role of the second semiconductor material in α -Fe₂O₃ heterostructures are constructed by the role of the second semiconductor material in α -Fe₂O₃ heterostructures are constructed by the role of the second semiconductor material in α -Fe₂O₃ heterostructures are constructed by the role of the second semiconductor material in α -Fe₂O₃ heterostructures are constructed by the role of the second semiconductor material in α -Fe₂O₃ heterostructures are constructed by the role of the second semiconductor material in α -Fe₂O₃ heterostructed by the role of the second semiconductor material in α -Fe₂O₃ heterostructed by the role of the second semiconductor material in α -Fe₂O₃ heterostructed by the role of the second semiconductor material in α -Fe₂O₃ heterostructed by the role of the second semiconductor material to the role of the role of the role of the

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ture is to improve the light absorption ability of α -Fe₂O₃ [3]. The second semiconductor material could either be an *n*-type or a *p*-type semiconductor prior to the consideration of its band structure [4]. Nevertheless, the rational design of α -Fe₂O₃ heterostructures with direct contact of n-type and p-type semiconductors have gained enormous attention due to the high gradient of potentials that facilitates effective separation of photogenerated charge carriers at the p-n junction [3]. Recently, Ahmed et al. had developed a nanostructured α -Fe₂O₃ *p*-CaFe₂O₄/*n*-Fe₂O₃ heterojunction structure with 100% photocurrent improvement than the bare α -Fe₂O₃ structure. The enhancement was attributed to the enhanced charge separation and reduced charge transfer resistance at the semiconductor/liquid junction [5]. Similarly, Sharma et al. had fabricated a *p*-*n* heterojunction of Ti-Fe₂O₃/Cu₂O with superior PEC performance by using the spray pyrolysis synthesis method. They attributed the improvement to the internal electric field at the *p*-*n* junction that impeded the recombination of photogenerated charge carriers, as well as the proper band edge alignment of both semiconductors that improved the light absorption ability [6]. Among the p-type semiconductors, nickel oxide (NiO) is highly active where it acts as a hole extractor in the water splitting reaction [7,8]. In our previous communication, we had demonstrated the in-situ doping of Ni on α -Fe₂O₃ that led to the formation of NiO/ α - $Fe_2O_3 p$ -*n* heterojunction photoanode. The α -Fe₂O₃ heterostructure was characterised to have a lower transfer resistance of photogenerated charge carriers that subsequently enhanced the PEC performance [9]. However, there is still additional room at the bottom-up electrodeposition synthesis method to further improve the PEC performance of α -Fe₂O₃ heterostructures by introducing other active catalytic materials.

Electron donor-acceptor composites based nanocarbons, for instance, carbon nanotube [10-13], graphene [14-17] and other carbonaceous materials [18-20] are recent subjects of interests in enhancing the PEC performance. In view of this, graphene and reduced graphene oxide (RGO) are two-dimensional (2D) sp²-hybridised carbon sheets that have attracted enormous research attention due to their unique properties, such as high electrical conductivity, excellent electron mobility and large specific surface area [21,22]. Graphene can serve as an electron mediator for transporting electrons to prolong the lifetime of photogenerated electron-hole pairs [23]. These intriguing characteristics of graphene can be harnessed to form graphene-hybridised materials for improving the PEC performance. To date, there are several previous studies reported on graphene/a-Fe₂O₃ or RGO/a-Fe₂O₃ heterostructures fabricated via different synthesis methods. For instance, Carminati et al. fabricated the RGO/α-Fe2O3 heterostructure via a two-step doctor-blade and drop-cast synthesis method. They found that the incorporation of RGO in α -Fe₂O₃ resulted in a positive effect in lowering the electron-hole pairs recombination rate [24]. In another study, Kim et al. developed graphene-carbon nanotube composite as a conducting scaffold for α -Fe₂O₃ through spray coating followed by electron beam evaporation synthesis methods. The α -Fe₂O₃-composite showed an enhanced water oxidation activity where this was brought upon by the synergistic effects of graphene-carbon nanotube composite [25]. To the best of our knowledge, previously there is no study on the fabrication of ternary nanostructured electrochemical reduced graphene oxide (eRGO) modified NiO/ α -Fe₂O₃ heterojunction photoanode for the application in PEC water splitting.

In this work, we present the design, fabrication, characterisation and application in PEC water splitting of a novel ternary nanostructured carbonaceous-metal-semiconductor eRGO/NiO/ α -Fe₂O₃ heterojunction photoanode. For the photoanode design, the NiO/ α -Fe₂O₃ heterostructure was synthesized by electrodeposition-annealing synthesis method. Thereafter, a thin layer of eRGO was coated by electrochemical reduction of graphene oxide (GO) directly on top of the NiO/ α -Fe₂O₃ heterostructure. The ternary nanostructured eRGO/NiO/ α -Fe₂O₃ heterostruction photoanode was constructed, where the step-by-step synthesis process is illustrated in Fig. 1. The main aim of this study was to understand the synergistic effects of NiO and eRGO on the PEC performance of $\alpha\text{-Fe}_2O_3$ nanostructured photoanodes. The structural, morphology, optical and PEC properties of the $\alpha\text{-Fe}_2O_3$ nanostructured photoanodes were examined. It is anticipated that the finding from this study may inspire the future development of various ternary nanostructured heterojunction photoanodes and their application in electrocatalysis and photoelectrocatalysis.

2. Experimental sections

2.1. Materials

All the reagents were of analytical grade and used without further purification. Iron(III) chloride (FeCl₃) was purchased from Sigma-Aldrich, USA. Potassium chloride (KCl) and sodium fluoride (NaF) were purchased from ChemSoln, USA. Hydrogen peroxide (H₂O₂) (30 wt%), graphite powder, nickel(II) nitrate (Ni(NO₃)₂·6(H₂O)) and sodium hydroxide (NaOH) were purchased from Merck, Malaysia.

2.2. Photoanode synthesis

α-Fe₂O₃ nanostructured photoanodes were synthesized via a facile electrodeposition synthesis method. Specifically, 5 mM FeCl₃ was dissolved in a mixed solution containing 0.1 M KCl, 1 M H₂O₂ and 5 mM NaF under vigorous magnetic stirring. The mixture was transferred to a three-electrode electrochemical cell, where fluorine-doped tin oxide (FTO) glass (1 cm×3 cm), Ag/AgCl saturated in 3 M KCl and Pt rod served as the working, reference and counter electrodes, respectively. Electrodeposition was performed by cyclic voltammetry between -0.2 V and 0 V at a sweep rate of 0.05 V s⁻¹ for 50 cycles using an Autolab Potentiostat (Metrohm PGSTAT204, The Netherlands). After electrodeposition, the resulting photoanodes were rinsed with deionised water followed by annealing in air at 600 °C with a dwell time of 4 h for better crystallisation. For the fabrication of NiO/ α -Fe₂O₃ nanostructured photoanodes, 24.2 mg of Ni(NO₃)₂·6(H₂O) was mixed with the precursor solution (50 mL). The electrodeposition was conducted using the same three-electrode electrochemical system and scanned from -0.5 V to 0 V for 100 cycles at a potential scan rate of 0.05 V s^{-1} . The as-synthesized photoanodes were washed with deionised water and calcined in air at 600 °C for 4 h.

Prior to the electrochemical reduction of GO to eRGO sheets, GO powder was synthesized from graphite powder based on the reported Improved Hummers' method [26]. In the preparation of GO dispersion, 0.1 g of GO powder was added into 0.1 M KCl solution (50 mL) under magnetic stirring and subsequently ultrasonicated for 1 h. The pH value of the GO dispersion was adjusted to 7.5 via the addition of a diluted NaOH solution. By using α -Fe₂O₃ or NiO/ α -Fe₂O₃ photoanode as the working electrode, the electrochemical reduction was carried out for a whole of 10 cycles from -1.5 V to 0.5 V at 0.05 V s⁻¹ scan rate. The photoanodes were dried at 60 °C for 1 h resulting in the formation of the eRGO/ α -Fe₂O₃ and ternary nanostructured eRGO/NiO/ α -Fe₂O₃ heterojunction photoanodes.

2.3. Characterisations

X-ray diffraction (XRD) measurements were carried out on a Bruker D8 Discover diffractometer equipped with Ni-filtered Cu-K α radiation operated at 40 kV and 40 mA with a scan rate of 0.02° s⁻¹ to obtain the crystalline phase composition of the samples. Raman spectra were collected using a Horiba Scientific spectrometer (λ =514 nm). X-ray photoelectron spectroscopy (XPS) analysis was performed using an Omicron Nanotechnology DAR400 system to measure the elements of the sample. Ultraviolet-visible (UV–vis) diffuse reflectance spectra were recorded with an Agilent Cary 100 spectrometer. Field emission-scanning electron microscope with an accelerating voltage of 3 kV. Elemental mapping images were acquired using an Oxford-Horiba



Fig. 1. Step-by-step illustration of the synthesis process of ternary nanostructured $eRGO/NiO/\alpha$ -Fe₂O₃ heterojunction photoanode.

Inca XMax50 energy dispersive X-ray (EDX) spectroscopy. High-resolution transmission electron microscopy (HRTEM) and selected area electron diffraction (SAED) measurements were performed on a Tecnai G2 F20 electron microscope operated at 200 kV. Photoluminescence (PL) emission spectra were characterised using a Perkin Elmer LS55 spectrometer at an excitation wavelength of 325 nm.

2.4. PEC measurements

The PEC measurements of the samples were carried out in a PEC setup using 1 M NaOH solution with a three-electrode electrochemical system where the as-synthesized photoanodes were used as the working electrode, Ag/AgCl saturated in 3 M KCl served as the reference electrode and Pt rod used as the counter electrode. Cyclic voltammograms (*CV*) and current density versus potential (*J-V*) curves were measured by applying an external bias using a Metrohm PGSTAT204 potentiostat at a scan rate of 0.02 V s^{-1} under 100 W Philips halogen lamp. Electrochemical impedance spectroscopy (EIS) measurements were carried out by using a Metrohm PGSTAT302N potentiostat with a frequency range of 100 kHz to 0.1 Hz at 0.6 V.

3. Results and discussion

XRD analysis (Fig. 2A) was carried out to investigate the crystal phase structures of α -Fe₂O₃, eRGO/ α -Fe₂O₃, NiO/ α -Fe₂O₃ and ternary nanostructured eRGO/NiO/a-Fe2O3 heterojunction photoanodes. All the XRD patterns were indexed to the characteristic peaks of reference α -Fe₂O₃ phase (JCPDS no. 34-0664), corresponding to crystal planes of (104), (110), (202), (116), (211), (018), (214) and (300). The analysis results indicated that the phase purity of α -Fe₂O₃ was not affected by the incorporation of NiO, eRGO or both onto the α -Fe₂O₃ nanostructured photoanodes. The incorporation of NiO on NiO/ α -Fe₂O₃ and eRGO/NiO/a-Fe₂O₃ nanostructured photoanodes was evidenced from the two additional peaks at 2θ values of 43.3° and 62.8° that linked to the crystal planes of (200) and (220) in NiO (JCPDS no. 47-1049). Raman spectroscopy analysis (Fig. 2B) was carried out to confirm the presence of eRGO on eRGO/α-Fe₂O₃ and ternary nanostructured eRGO/NiO/a-Fe₂O₃ heterojunction photoanodes. Whilst the Raman spectra in the 100–3000 cm^{-1} frequency range was depicted in Fig. S1. Both the as-synthesized α -Fe₂O₃ and NiO/ α -Fe₂O₃ nanostructured photoanodes showed an obvious peak at 1317 cm⁻¹ that ascribed to the two photon scattering of α -Fe₂O₃ [27]. Meanwhile, the Raman spectrum of GO showed two distinct peaks at 1354 and 1596 cm⁻¹, whereas the eRGO/α-Fe₂O₃ and ternary nanostructured eRGO/NiO/α-Fe₂O₃ heterojunction photoanodes showed two prominent peaks at 1330 cm^{-1} and 1600 cm^{-1} that corresponded to the disordered (D) and graphitic (G) bands of the eRGO sheets, respectively [28]. The intense peak at 1317 cm $^{-1}$ of $\alpha\text{-Fe}_2\text{O}_3$ was shifted to about 1330 cm $^{-1}$ in both eRGO/ α -Fe₂O₃ and ternary nanostructured eRGO/NiO/ α -Fe₂O₃ heterojunction photoanodes. This may due to the overlapping of the D band (around 1350 cm⁻¹) in the eRGO and the formation of a new peak



Fig. 2. (A) XRD diffraction patterns and (B) Raman spectra of (a) α -Fe₂O₃, (b) eRGO/ α -Fe₂O₃, (c) NiO/ α -Fe₂O₃ and (d) ternary nanostructured eRGO/NiO/ α -Fe₂O₃ heterojunction photoanodes. The inset in (B) represents the Raman spectrum of GO.

at 1330 cm⁻¹ [29]. This observation has proven that eRGO sheets were successfully electrodeposited onto eRGO/ α -Fe₂O₃ and ternary eRGO/NiO/ α -Fe₂O₃ nanostructured photoanodes.

The chemical composition and electronic state of the elements in the



Fig. 3. XPS spectra of (A) Fe 2p, (B) Ni 2p, (C) C 1s and (D) O 1s of ternary nanostructured eRGO/NiO/ α -Fe₂O₃ heterojunction photoanode.

ternary nanostructured eRGO/NiO/ α -Fe₂O₃ heterojunction photoanode was characterised by using XPS, where the results are shown in Fig. 3. The XPS survey spectrum in Fig. S2 demonstrated that the ternary nanostructured eRGO/NiO/ α -Fe₂O₃ photoanode was constituted of Fe, Ni, C and O elements with atomic percentages of 13.27%, 0.75%, 15.56% and 70.41%, respectively. In the observed Fe 2p spectrum

(Fig. 3A), Fe element was in the +3 oxidation state of Fe₂O₃ with Fe $2p_{3/2}$ and Fe $2p_{1/2}$ peaks at 711.1 eV and 724.3 eV, respectively [30]. The Ni $2p_{3/2}$ and Ni $2p_{1/2}$ peaks that appeared at 855.1 eV and 872.2 eV indicated the +2 oxidation state of NiO [31]. This further evidenced that Ni exists in the form of divalent in the ternary nanostructured $eRGO/NiO/\alpha$ -Fe₂O₃ heterojunction photoanode. The high resolution XPS spectrum of C 1s was deconvoluted into four components, the C-C (284.6 eV), C-O (285.8 eV), C=O (288.3 eV) and O-C=O (289.1 eV) bonds [32]. The C-C bond has the highest peak intensity, which indicated the most oxygenated species on GO sheets was being removed during the electrochemical reduction process of GO into eRGO. This observation coincided well with the previous studies on the synthesis of RGO [33,34]. For O 1s spectrum, the peak at 529.8 eV corresponded to the oxygen groups in the metal oxides Fe₂O₃ and NiO [35]. Whilst the peak at 531.3 eV was attributed to the oxygenated functional groups bonded with carbon atoms in the eRGO sheets [24].

The light absorption of the photoanode is one of the most vital aspects for examining the PEC performance. Thus, UV-vis diffuse reflectance spectra of α -Fe₂O₃, eRGO/ α -Fe₂O₃, NiO/ α -Fe₂O₃ and ternary nanostructured eRGO/NiO/a-Fe2O3 photoanodes were evaluated as shown in Fig. 4. The incorporation of NiO has endowed α-Fe₂O₃ nanostructured photoanode with a wider spectral absorption range, where the light absorption intensities in the whole region have been improved. The difference in the observed optical densities may be also due to the thickness variation when NiO was incorporated on α -Fe₂O₃ heterostructure. Previously. a similar phenomenon was observed in the α -Fe₂O₃/Mn₃O₄ photoanode [36]. Conversely, eRGO sheets have slightly expanded the light absorption after 600 nm at the visible light and near infrared regions. The little contribution on light absorption enhancement was due to the zero-bandgap of eRGO sheets [37]. By extrapolating the linear region of the Tauc plot in Fig. S3, the band gap energies of α -Fe₂O₃, eRGO/ α -Fe₂O₃, NiO/ α -Fe₂O₃ and ternary nanostructured eRGO/NiO/a-Fe₂O₃ photoanodes were approximated to about 2, 1.95, 2.57 and 2.55 eV, respectively. The obvious increment of NiO/α-Fe₂O₃ and ternary nanostructured eRGO/NiO/α-Fe₂O₃ photoanodes band gap energies may be ascribed to the formation of new energy level in the band structure of α -Fe₂O₃ since chemical bonds between NiO and α -Fe₂O₃ may have been formed.

Fig. 5 shows the FE-SEM images of the fabricated nanostructured photoanodes. The α -Fe₂O₃ nanostructured photoanode was composed of finely and densely packed spherical nanoparticles. After the incorporation of NiO, the *p*-*n* heterojunction photoanode showed aggregation of NiO and α -Fe₂O₃ nanoparticles where the surface became thicker and rougher than the pristine α -Fe₂O₃ nanostructured photoanode. A similar phenomenon has also been observed in the ternary



Fig. 4. UV-vis diffuse reflectance spectra of α -Fe₂O₃, eRGO/ α -Fe₂O₃, NiO/ α -Fe₂O₃ and ternary nanostructured eRGO/NiO/ α -Fe₂O₃ heterojunction photoanodes.



Fig. 5. FE-SEM images of (A) α -Fe₂O₃, (B) eRGO/ α -Fe₂O₃, (C) NiO/ α -Fe₂O₃ and (D) ternary nanostructured eRGO/NiO/ α -Fe₂O₃ heterojunction photoanodes.



 $\label{eq:Fig. 6.} \ \text{(A) SAED pattern and (B-D) HRTEM images of ternary nanostructured eRGO/NiO/α-Fe_2O_3 heterojunction photoanode.}$

nanostructured $eRGO/NiO/\alpha$ -Fe₂O₃ heterojunction photoanode. From Fig. 5B and D, it can be clearly observed that the surfaces of α -Fe₂O₃ and NiO/ α -Fe₂O₃ were covered with wrinkled and thin layered eRGO sheets where the nanoparticles underneath were still visible. Interestingly, the interconnected nanostructures among α -Fe₂O₃, NiO and eRGO sheets led to an increase in the active surface area available. This actually promotes the diffusion of species, and the migration of photogenerated charge carriers at the semiconductor/liquid junction. In overall, the alignment of α -Fe₂O₃ was not significantly influence by the incorporation of NiO, eRGO or both. Besides, EDX mapping images revealed the homogeneous distribution of C, O, Fe, Ni and Si elements throughout the whole matrix (Fig. S4). The surface morphology and structure of the ternary nanostructured eRGO/NiO/a-Fe₂O₃ heterojunction photoanode was further investigated by HRTEM and SAED as shown in Fig. 6. The SAED pattern showed the polycrystalline nature of the nanostructured photoanode. From Fig. 6B-D, it can be observed that the flexible eRGO sheets provide intimate and coherent interfaces between α-Fe₂O₃, NiO and eRGO. Fig. S5 further revealed that a few layers of eRGO membranes were observed near its edge. This excellent

interaction among the materials is favourable to promote charge transfer over their interfaces, where further measurements on the interfacial charge transfer from EIS are discussed in the later section [38]. Fig. 6C and D show the clear lattice fringes spacing of 0.25, 0.34 and 0.24 nm which coincides well with the reflections from (110) plane of α -Fe₂O₃ [39], (002) plane of eRGO [40] and (200) plane of NiO [3]. This result was in agreement with the XRD diffraction patterns and thus, it has further proven that α -Fe₂O₃ has been decorated with eRGO and NiO. Thus, it can be concluded that the ternary nanostructured eRGO/NiO/ α -Fe₂O₃ heterojunction photoanode was successfully developed using the electrodeposition-annealing synthesis method.

In order to demonstrate the enhanced PEC performance of the ternary nanostructured eRGO/NiO/ α -Fe₂O₃ heterojunction photoanode, both *CV* and *J*-*V* curves of all the as-synthesized photoanodes were investigated (Fig. 7). The *CV* curves were scanned in the potential range of -0.4–0.7 V with a scan rate of 0.05 V s⁻¹. Generally, the bounded region of the CV curves is directly proportional to the active surface area available in the photoanode [41]. From Fig. 7A, the ternary nanostructured eRGO/NiO/ α -Fe₂O₃ heterojunction photoanode shows

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Fig. 7. (A) CV curves, (B) J-V curves and (C) current density measured at various applied potentials of α -Fe₂O₃, eRGO/ α -Fe₂O₃, NiO/ α -Fe₂O₃ and ternary nanostructured eRGO/NiO/ α -Fe₂O₃ heterojunction photoanodes.

a larger bounded area and a higher current response than those of α -Fe₂O₃, eRGO/ α -Fe₂O₃, NiO/ α -Fe₂O₃ photoanodes under the same experimental condition. The larger bounded area observed for the ternary nanostructured photoanode indicated that the real active surface area of the photoanode was increased via the introduction of both eRGO and NiO, which is consistent with the observation in FESEM image. The *J*-V curves in Fig. 7B provide a direct evidence for the enhancement in PEC performance for the decoration of eRGO and NiO on α -Fe₂O₃ nanostructured photoanode. For the pristine α -Fe₂O₃ nanostructured photoanode, the onset potential was approximately 0.65 V that was considerably high for water oxidation reaction. For eRGO/ α -Fe₂O₃, NiO/ α -Fe₂O₃ and ternary nanostructured eRGO/NiO/ α -Fe₂O₃ heterojunction photoanodes, the onset potentials were negatively shifted to 0.60 V, 0.56 V and 0.50 V, respectively. This indicated that the incorporation of eRGO, NiO or both has reduced the recombi-

nation rate of photogenerated electron-hole pairs. Fig. 7C presents the current density obtained at various applied potentials. At 0.70 V, the current densities of α -Fe₂O₃, eRGO/ α -Fe₂O₃ and NiO/ α -Fe₂O₃ nanostructured photoanodes were 0.48 mA cm^{-2} , 1.01 mA cm^{-2} and 1.45 mA cm⁻², respectively. The enhanced current density of eRGO/ α -Fe₂O₂ photoanode can be ascribed to the fact that eRGO sheets act as electron mediator that migrate electrons to prolong the lifetime of photogenerated electron-hole pairs at both surface and interface areas. This is because the electrons extracted by eRGO sheets can easily transfer to the cathode through an external electrical circuit, while the remaining holes can effectively perform water oxidation at the semiconductor/liquid junction. On the other hand, the NiO/ α -Fe₂O₃ photoanode attained a higher current density than the α -Fe₂O₃ nanostructured photoanode is because of three aspects: (i) NiO can improve the light absorption ability, (ii) NiO serves as a catalyst to lower the overpotential for oxygen evolution, and (iii) p-n heterojunction possesses the ability to separate photogenerated charge carriers [7]. The ternary nanostructured eRGO/NiO/a-Fe2O3 heterojunction photoanode attained the highest current density of 2.46 mA cm⁻² at 0.70 V, which was almost 8 times greater than that of pristine α -Fe₂O₃ nanostructured photoanode. This additional enhancement is attributed to the eRGO sheets that efficiently transfer the electrons in the p-n heterojunction without causing substantial bulk recombination, while forming an internal electrical field in the ternary nanostructured photoanode. The internal electrostatic field could facilitate the effective separation of photogenerated charge carriers so more holes could participate in water oxidation reaction instead of recombination.

From the PL emission spectra shown in Fig. 8, it can be observed that the PL intensity was greatly influenced by the introduction of eRGO, NiO or both into α -Fe₂O₃ nanostructured photoanode. Generally, PL emission is resulting from the recombination of photogenerated electron-hole pairs and it has been used to determine the efficiency of charge carrier trapping and transfer in the semiconductor materials [42]. Hence, lower PL intensity indicates higher separation efficiency of the photogenerated electron-hole pairs and better quantum efficiency [43,44]. Based on the PL emission spectra, the PL intensity was following the order of α -Fe₂O₃>eRGO/ α -Fe₂O₃>NiO/ α -Fe₂O₃>eRGO/NiO/ α -Fe₂O₃, providing an order of increase in prohibiting the recombination of photogenerated charge carriers. Thus, promoting the charge transfer at the interface of semiconductor/liquid junction, leading to higher quantum efficiency and PEC performance [45]. This result agrees well with the observation in the *J*-*V* curves.

In order to gain an in-depth understanding into the charge transfer properties for the ternary nanostructured eRGO/NiO/ α -Fe₂O₃ heterojunction photoanode, the Nyquist plots derived from EIS measurements



Fig. 8. PL emission spectra of α -Fe₂O₃, eRGO/ α -Fe₂O₃, NiO/ α -Fe₂O₃ and ternary nanostructured eRGO/NiO/ α -Fe₂O₃ heterojunction photoanodes.



Fig. 9. Nyquist plots (A) in dark and (B) under light irradiation of α -Fe₂O₃, eRGO/ α -Fe₂O₃, NiO/ α -Fe₂O₃ and ternary nanostructured eRGO/NiO/ α -Fe₂O₃ heterojunction photoanodes at the frequency of 10 kHz.

of α -Fe₂O₃, eRGO/ α -Fe₂O₃, NiO/ α -Fe₂O₃ and ternary nanostructured $eRGO/NiO/\alpha$ -Fe₂O₃ heterojunction photoanodes are compared (Fig. 9). Fig. S6 illustrates the equivalent circuit model used to fit the EIS data. The smaller arc radius observed in Nyquist plots suggested that the charge transfer resistance controlling the surface kinetics at the semiconductor/liquid junction were lower [46]. In this instance, the arc radius of all as-synthesized photoanodes under light irradiation were smaller than in dark. This is due to the increase in electron conductivity under light irradiation. Upon light irradiation, the arc radius reduced dramatically when α -Fe₂O₃ were loaded with eRGO, NiO or both. This indicated that the modified α -Fe₂O₃ nanostructured photoanodes showed better surface kinetics than pristine a-Fe₂O₃ nanostructured photoanode, as reflected by the smaller arc radius (i.e. lower charge transfer resistances). As mentioned earlier, eRGO sheets act as surface passivation layer and electron transporting bridge that increase the electrons transfer at the semiconductor/liquid junction. Whilst NiO serves as hole scavenger that effectively hinders the recombination of photogenerated electron-hole pairs and accelerates the interfacial charge transfer. Therefore, the ternary nanostructured eRGO/NiO/a-Fe2O3 heterojunction photoanode exhibited the combined effects of excellent conductivity of eRGO and high potentials gradient of p-n heterojunction with NiO that have considerably improved the electron mobility and resulting in an enhanced PEC performance.

Finally, the PEC water splitting activity towards hydrogen (H₂) evolution was evaluated for both pristine α -Fe₂O₃ and ternary eRGO/NiO/ α -Fe₂O₃ nanostructured photoanodes. As presented in Fig. 10, the H₂ evolution for pristine α -Fe₂O₃ photoanode was 35 µmol h⁻¹ cm⁻² and 92 µmol h⁻¹ cm⁻² for the ternary nanostructured eRGO/NiO/ α -Fe₂O₃ heterojunction photoanode. This enhancement emphasizes the important roles played by the respective eRGO and NiO that promote

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Fig. 10. H_2 evolution from pristine $\alpha\text{-}Fe_2O_3$ and ternary nanostructured eRGO/NiO/ $\alpha\text{-}Fe_2O_3$ heterojunction photoanodes.

the effective charge transfer and trapping, and prolong the charge recombination. By comparing with the record-breaking performance achieved up to date on a Pt/Co-Pi/ α -Fe₂O₃ wormlike photoanode by Kin and co-workers [47], the H₂ evolution efficiency exhibited by the ternary nanostructured eRGO/NiO/ α -Fe₂O₃ heterojunction photoanode is considerably low. However, this is the first time in the combinatorial used of NiO and eRGO to improve the PEC efficiency of α -Fe₂O₃ nanostructured photoanode.

Based on the results, we proposed a mechanism of electrons transfer in the ternary nanostructured eRGO/NiO/α-Fe2O3 heterojunction photoanode for PEC water splitting (Fig. 11). Under light irradiation, the photogenerated electrons and holes separate and appear in the conduction and valence band edges of *n*-type α -Fe₂O₃ and *p*-type NiO, respectively. Since eRGO does not have an energy band, it does not donate any photogenerated charge carriers. The eRGO sheets work as an electron conducting bridge that facilitate the effective separation of electron-hole pairs. At the p-n heterojunction, eRGO can easily assist the transfer of electrons from the conduction band of NiO to the conduction band α -Fe₂O₃ and to the FTO glass substrate. Then, the electrons transfer to Pt counter electrode through an external circuit and eventually reduce H⁺ ions to produce H₂ molecules. Concurrently, holes extracted from the valence band of α -Fe₂O₃ to the valence band of NiO react with O^{2-} ions to generate oxygen (O_2) molecules. Therefore, the photogenerated electron-hole pairs are remarkably being separated, leading to the enhancement in the PEC water splitting activity.

4. Conclusion

In summary, a novel ternary nanostructured eRGO/NiO/a-Fe₂O₃ heterojunction photoanode was successfully fabricated and its characteristics as a photoanode for PEC water splitting was investigated. The incorporation of both NiO and eRGO onto α -Fe₂O₃ nanostructured photoanode has improved light-harvesting efficiency, impeded photogenerated charge carriers recombination and accelerated the interfacial charge transfer that contributes to the enhanced PEC water splitting activity. This is attributed to the eRGO sheets that substantially favour the transfer process of photogenerated charge carriers at the p-nheterojunction and form an internal electrical field in the ternary nanostructured eRGO/NiO/a-Fe2O3 heterojunction photoanode. Moreover, the H₂ evolution rate further confirmed the excellent performance of ternary nanostructured eRGO/NiO/a-Fe₂O₃ heterojunction photoanode. Therefore, this study offers an alternative strategy to design and construct high efficiency heterostructure nanostructured photoanodes for practical PEC water splitting application.

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Fig. 11. Schematic of electron transfer mechanism in ternary nanostructured eRGO/NiO/α-Fe₂O₃ heterojunction photoanode for PEC water splitting.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.solmat.2017.05.028.

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Chapter 5 | Ternary eRGO/NiO/Hematite Nanostructured Photoanodes

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CHAPTER 6

CONCLUSIONS AND FUTURE RECOMMENDATIONS

6.1 Overall Conclusions

In this research project, the design and development of high performance hematite-based nanostructured photoanodes and their applications in the PEC water splitting were examined. In this study, hematite was the main focus of semiconductor photocatalyst used for the PEC process due to its Earth-abundant, low-cost, high stability and environmentally benign nature. However, the PEC performance of pristine hematite is still limited by its low electrical conductivity, short hole diffusion length and fast photogenerated electron-hole pairs recombination. Therefore, numerous modifications have been systematically employed in this project to improve the PEC performance.

In the first stage of the project, Pt and Ni dopants were successfully incorporated into hematite nanostructured photoanodes with enhanced PEC performance. The Pt and Ni dopant loadings were systematically optimised, while its synergistic role in enhancing the photoactivity in hematite nanostructured photoanodes were investigated through various characterisation studies. The Pt and Ni dopants acted as electron donor via the lattice substitution of Fe³⁺ by Pt⁴⁺ and Ni²⁺, respectively in hematite and eventually resulting in a higher separation efficiency of photogenerated charge carriers. In addition to Ni dopant, Ni-doping was combined with diffusion of Ni into the subsurface region of hematite, forming a p-n junction that effectively extracts holes and further enhanced the PEC performance. The apparent optimum at 3M% Pt- and 25M% Ni-doping exhibited a high PEC performance of 3-fold and 5-fold enhancement, respectively, when compared to pristine hematite photoanode.

As an alternative to the metal dopants, the reinforcement of hematite with electron-donoracceptor composites based nanocarbons is gaining popularity as an effective strategy to improve the PEC performance of hematite. In the following stage of this project, hematite nanostructured photoanodes were modified by coupling with eRGO, C_{60} or both. It was evidenced that the incorporation of nanocarbons has minor influence on the crystals phase, nanoparticle size and surface morphology of hematite photoanodes. The photocurrent densities of C_{60} /hematite, eRGO/hematite and eRGO/ C_{60} /hematite nanocomposites photoanodes were enhanced by 1.5-fold, 4.5-fold and 5-fold, respectively. This is attributed to the outstanding electron conducting nature of both C_{60} and eRGO. By comparing C_{60} /hematite and eRGO/hematite, the enhancement achieved by eRGO/hematite was much higher where this is due to the synergistic interactions between hematite and eRGO, resulting in a higher photogenerated electron-hole pairs separation efficiency to retard the charge recombination. Additionally, this is because eRGO functions as both surface passivation layer and electron transporting bridge that favors the transport process of photogenerated charge carriers.

Chapter 6 | Conclusions and Future Recommendations

From the previous work, Ni-doped hematite that led to the formation of NiO/hematite p-n heterojunction photoanode was demonstrated. Nevertheless, there is still additional room at the bottom-up electrodeposition synthesis method to further improve the PEC performance of hematite by combining with electron-donor-acceptor composites based nanocarbon. In this study, the design, fabrication, characterization and application in PEC water splitting of a novel ternary nanostructured carbonaceous-metal-semiconductor eRGO/NiO/hematite heterojunction photoanode was presented. The incorporation of both NiO and eRGO onto hematite nanostructured photoanode has improved light-harvesting efficiency, impeded photogenerated charge carriers recombination and accelerated the interfacial charge transfer that contributes to the enhanced PEC water splitting activity. This is attributed to the eRGO sheets that substantially favor the transfer process of photogenerated charge carriers at the p-n heterojunction and form an internal electrical field in the ternary nanostructured eRGO/NiO/hematite heterojunction photoanode. Moreover, the H₂ evolution rate further confirmed the excellent performance of ternary nanostructured eRGO/NiO/hematite heterojunction photoanode.

Figure 6.1 summarises all the types of hematite-based nanostructured photoanodes developed from this research work for the application in PEC water splitting. Among all the studies, eRGO/NiO/hematite revealed the highest photocurrent density of 2.46 mA cm⁻² at 0.70 $V_{Ag/AgCl}$, which is almost 9 times greater than that of pristine hematite nanostructured photoanode. This research work provides new possibilities in the design of novel carbonaceous-metal-semiconductor heterojunction photoanode with high efficiency for practical PEC water splitting application.



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Figure 6.1 Photocurrent density obtained at 0.7 $V_{Ag/AgCl}$ in 1 M NaOH for all the types of hematitebased photoanodes developed in this research work.

6.2 **Recommendations for Future Work**

In spite of numerous promising results reported thus far, the highest PEC water splitting efficiency achieved by the hematite photoanode was still significantly lower than the theoretical maximum photocurrent of 12.6 mA cm⁻² [1]. The record-breaking performance of 4.32 mA cm⁻² at 1.23 V_{RHE} under AM 1.5 illumination was attained by a Pt/Co-Pi/hematite wormlike photoanode via an all-solution method by Kin and co-workers [2]. This momentous breakthrough was attributed to the improved charge transfer behavior, and modification of hematite surface properties by introducing Pt dopants and Co-Pi surface catalysts. In this regard, the Pt/Co-Pi/hematite photoanode demonstrated high stability and durability with the production of stoichiometric H₂ and O₂ gases. In light of this, it can be clearly seen that the integration of different modification strategies in synthesizing hematite photoanodes is effective and promising for further enhancement in the PEC performance and thus, warrants potential research investigations on this energy field.

Another exciting approach to dramatically increase the PEC water splitting performance is to develop a tandem PEC cell by combining two or more light absorbing materials with well-matched absorption characteristics. This viable strategy enables greater light harvesting properties and better stability, since the semiconductors involved in both anode and cathode can be optimised individually [3]. As a matter of course, the band gap of hematite is considerably small (2.1 eV) compared to other semiconductors and therefore, engineering a tandem PEC cell with hematite photoanode and another photocathode will be favorable towards attaining high PEC performance. For instance, Jang et al. for the first time proposed an unassisted solar water splitting by using hematite photoanode and TiO₂/Pt/Si photocathode [4]. Although the reported photocurrent efficiency for the unassisted solar water splitting was 0.91 % which was indeed modest, it is projected that by systematic optimisation, the PEC water splitting efficiency can be readily

Chapter 6 | Conclusions and Future Recommendations

enhanced. Additionally, an alternative tandem cell configuration would be by merging a photoelectrode with a photovoltaic device [5-7], which combines solar H₂ generation and storage for achieving sustainability in the near future. Recently, Moon and co-workers constructed a tandem solar cell consisting of a dye-sensitised solar cell (DSSC) and a CuInGaSe₂ thin film solar cell with a remarkable achievement in the solar cell efficiency of 13 % [8].

Apart from the innovative materials design, it is of vital importance to explicate the fundamental enhancement of modified hematite photoanodes through the investigation of charge transfer dynamics, optical absorption, electronic band structure and interfacial charge transfer for the PEC performance. Hence, *in-situ* electrical conductivity measurements, transient absorption spectroscopy, *in-situ* attenuated total reflection surface-enhanced infrared absorption spectroscopy, X-ray absorption fine spectroscopy and theoretical calculations are powerful tools to gain deeper understandings into the mechanistic features and to offer scientific guidance for the modification of hematite photoanodes [9-12]. In addition to experimental findings, first-principles density functional theory (DFT) calculation is imperative to comprehend the structural and electronic properties of hematite photoanodes as well as the PEC reaction mechanism. It offers a systematic approach in screening and designing photoanode materials in terms of band gap and stability [9]. In response to this, the synergy of both experimental verification and computational simulation is mandatory for further advancing the knowledge of hematite photoanodes in the arena of materials science, technology and engineering.

Looking to the future, there are still infinite opportunities and challenges present for the hematite-based photoanode materials. Thus, with the continuous research explorations by the scientific community, it is ultimately believed that the aim of achieving the theoretical STH efficiency of 16.8 % by the hematite-based photoanodes is not knotty and impossible, instead turning dreams into reality toward commercialisation and practical benefits. Noteworthy, this necessitates the synergy collaboration from all disciplines of people including academia and

industry in order to enrich the solar energy application in a more practical means to open an era of renewable energy.

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Appendices

APPENDICES

A1 Additional Information for Chapter 3 – Section 3.1

Supplementary Material



Fig. S1. Effects of CV deposition cycles on J-V curves of nanostructured hematite thin films in dark and under irradiation.



Fig. S2. FESEM images of hematite thin films annealed at different temperatures where (a) 400°C, (b) 500°C and (c) 600°C.



Fig. S3. (a) FESEM image and (b) EDX characterization of 3% Pt-doped nanostructured hematite thin films.

A2 Additional Information for Chapter 3 – Section 3.2



Supplementary Materials

Fig. S1. CV curves of bare and in situ Ni-doped hematite photoanodes at a scan rate of 0.05 V s⁻¹.
A3 Additional Information for Chapter 4 – Section 4.1



Supporting Information

Fig. S1. Current density versus potential curves of bare and hematite nanocomposites photoanode structures. The inset is the photograph of the (a) bare hematite, (b) C60/hematite,(c) eRGO/hematite and (d) eRGO/C60/hematite photoanodes.

Supplementary Material



Fig. S1. Cross sectional FE-SEM image of the eRGO-hematite-4 nanocomposite.



Fig. S2. Transient photocurrent response of the bare hematite and eRGO-hematite-4 nanocomposite at 0.55 V vs Ag/AgCl. The arrows specify when light was turned on and off.

A5 Additional Information for Chapter 5

Supporting Information



Fig. S1. Raman spectra of (a) α -Fe₂O₃, (b) eRGO/ α -Fe₂O₃, (c) NiO/ α -Fe₂O₃ and (d) ternary nanostructured eRGO/NiO/ α -Fe₂O₃ heterojunction photoanodes in the 100-3000 cm⁻¹ frequency range.



Fig. S2. XPS survey scan of ternary eRGO/NiO/α-Fe₂O₃ nanostructured photoanode.

Appendices



Fig. S3. Tauc plots of α -Fe₂O₃, eRGO/ α -Fe₂O₃, NiO/ α -Fe₂O₃ and ternary nanostructured eRGO/NiO/ α -Fe₂O₃ heterojunction photoanodes.



Fig. S4. Elemental mapping images of ternary nanostructured $eRGO/NiO/\alpha$ -Fe₂O₃ heterojunction photoanode.



Fig. S5. HRTEM image of a few layers of eRGO membranes near its edge.



Fig. S6. Equivalent circuit model used to fit the EIS data where R_s is the contact resistance, R_{ct} is the charge transfer resistance and *CPE* is the parallel constant phase element.