



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,

solar H₂ 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 (TiO₂) [6–8], zinc oxide (ZnO) [9–11], tungsten trioxide (WO₃) [12–14], cuprous oxide (Cu₂O) [15,16] and others. In comparison, hematite (α -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 electron-hole 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 Pt-doped nanostructured hematite thin films by using field emission-scanning 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 (FeCl_3) was purchased from Sigma-Aldrich. Hexachloroplatinic (IV) acid hexahydrate ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$) (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 $38\text{ mm} \times 8\text{ mm}$ 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 FeCl_3 . 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 $400\text{ }^\circ\text{C}$ to $700\text{ }^\circ\text{C}$ at $100\text{ }^\circ\text{C}$ per increment and a dwell time of 4 h. For the Pt-doped hematite thin films, $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ 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 $\text{Cu K}\alpha$ 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 $\text{Al-K}\alpha$ ($h\nu = 1486.6\text{ eV}$) 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 three-electrode 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 $600\text{ }^\circ\text{C}$ 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

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