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Effects of annealing temperature on the physicochemical, optical and photoelectrochemical properties of nanostructured hematite thin films prepared via electrodeposition method

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ABSTRACT

Hematite (α-Fe_2O_3) is a promising photoanode material for hydrogen production from photo-electrochemical (PEC) water splitting due to its wide abundance, narrow band-gap energy, efficient light absorption and high chemical stability under aqueous environment. The key challenge to the wider utilisation of nanostructured hematite-based photoanode in PEC water splitting, however, is limited by its low photo-assisted water oxidation caused by large overpotential in the nominal range of 0.5–0.6 V. The main aim of this study was to enhance the performance of hematite for photo-assisted water oxidation by optimising the annealing temperature used during the synthesis of nanostructured hematite thin films on fluorine-doped tin oxide (FTO)-based photoanodes prepared via the cathodic electrodeposition method. The resultant nanostructured hematite thin films were characterised using field emission-scanning electron microscopy (FE-SEM) coupled with energy dispersive X-ray spectroscopy (EDX), X-ray diffraction (XRD), UV-visible spectroscopy and Fourier transform infrared spectroscopy (FTIR) for their elemental composition, average nanocrystallites size and morphology; phase and crystallinity; UV-absorptivity and band gap energy; and the functional groups, respectively. Results showed that the nanostructured hematite thin films possess good ordered nanocrystallites array and high crystallinity after annealing treatment at 400–600 °C. FE-SEM images illustrated an increase in the average hematite nanocrystallites size from 65 nm to 95 nm when the annealing temperature was varied from 400 °C to 600 °C. As the crystallites size increases, the grain boundaries reduce and this suppresses the recombination rate of electron–hole pairs on the nanostructured hematite thin films. As a result, the measured photocurrent densities of nanostructured hematite thin films also increased. The highest measured photocurrent density of 1.6 mA/cm^2 at 0.6 V vs Ag/AgCl in 1 M NaOH electrolyte was achieved for the nanostructured hematite thin film annealed at 600 °C. This study had confirmed that strong interdependencies exist between the average hematite nanocrystallites size and grain boundaries with annealing temperature on the eventual PEC water splitting performance of nanostructured hematite thin films. The annealed hematite thin films at a higher temperature will enhance the nanocrystals growth and thus, suppressing the electron–hole pairs recombination rate, lowering the grain boundary resistance and enabling higher photocurrent flow at the molecular level. As a result, the photocurrent density and thus, the overall PEC water splitting performance of the nanostructured hematite thin films are significantly enhanced.

1. Introduction

Recently, the photoelectrochemical (PEC) water splitting process has received increasing attention as an effective means to convert solar energy into chemical energy to resolve the potential energy crisis caused by rapid fossil fuels depletion. Hydrogen produced via the PEC approach is highly attractive owing to its environmental benign with zero carbon footprint, in addition

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to being an efficient chemical energy carrier with high energy density [1,2]. In a typical PEC cell, it consists of a semiconductor-based photoanode that absorbs light photons to induce the formation of photogenerated electron–hole pairs. The photogenerated electron–hole pairs will further diffuse to the external photoanode surface to enable: (1) valence band holes react with water molecules to produce protons and oxygen gas and (2) conduction band electrons transfer to cathode through an external circuit and eventually reduce protons at cathode to produce hydrogen gas [3]. At present, however, the PEC process still exhibits low photo-assisted water oxidation efficiency for hydrogen production due to the high band gap energy requirement of semiconductors [4].

In order to find a suitable photoanode material, various semiconductor metal oxide photocatalysts such as titanium dioxide (TiO_2) [5,6], zinc oxide (ZnO) [7], tungsten trioxide (WO_3) [8], bismuth vanadate ($BiVO_4$) [9], copper(I) oxide (Cu_2O) [10] and iron(III) oxide (Fe_2O_3) [11] have been widely investigated for PEC water splitting application. Among the various metal oxide semiconductors, hematite (α-Fe_2O_3) appears to be a potential photoanode material for PEC water splitting owing to its narrower band gap energy level that can absorb up to 40% of solar irradiation. In addition, hematite is abundant, low-cost, highly stable under most of the aqueous environment and has a high theoretical solar-to-hydrogen (STH) efficiency of 12.9% [12]. Despite the various advantages of hematite, the feasible application of hematite as the ideal photoanode material is still hindered by its low conductivity, short hole-diffusion length, fast electron–hole pairs recombination rate [13]. However, recent studies indicated that the nanostructured morphology is a solution to overcome these limitations and improve the overall PEC performance [14,15]. In this instance, nanostructured metal oxide photocatalysts offer a large semiconductor liquid junction wherein the redox reactions can occur to enable charge separation, in addition to minimise the diffusion length of minority carriers [16].

To date, a number of synthesis methods have been investigated for synthesising nanostructured hematite thin films such as colloidal method [17,18], hydrothermal method [19,20], spray pyrolysis method [21–24], atomic layer deposition (ALD) method [15,25], atmospheric pressure chemical vapor deposition (APCVD) method [26–28] and electrodeposition method [29–31]. Although, it is well-accepted from the open literatures that high performance nanostructured hematite thin films can be fabricated with almost all of the reported synthesis methods, most of them however are not suitable for large-scale fabrication due to the high production cost. Among all, the electrodeposition method is a promising and alternative method for the synthesis of nanostructured hematite thin films due to its simplicity, low-cost, ambient temperature and pressure processing conditions and the ability to control the crystallinity, phase composition as well as other physicochemical properties [30,32].

This study was concentrated on the fundamental understanding of nanostructured hematite thin films prepared by using the electrodeposition method. Previously, Tamboli et al. [33] found that the physical, chemical and PEC properties of nanostructured hematite thin films can be manipulated by simply tuning the electrodeposition synthesis condition. Thus, the aim of this work was to investigate the effects of annealing temperature on the physiochemical and PEC properties of nanostructured hematite thin films under visible light irradiation. The nanostructured hematite thin films were synthesised via cathodic electrodeposition approach followed by varying the annealing treatment in the range of 400–600 °C. The resultant nanostructured hematite thin films were characterised using field emission-scanning electron microscopy (FE-SEM) coupled with energy dispersive X-ray spectroscopy (EDX), X-ray diffraction (XRD), UV-visible spectroscopy and Fourier transform infrared spectroscopy (FTIR). This work constitutes a preliminary study on the more fundamental approach toward nanostructured hematite-based photoanode in improving the overall PEC water splitting performance on hydrogen production.

2. Experimental

2.1. Materials

Iron(III) chloride ($FeCl_3$), potassium chloride (KCl), sodium fluoride (NaF) and hydrogen peroxide 30 wt% (H_2O_2) were purchased from HmbG Chemicals (USA). All of these chemicals were used without further purification. Fluorine-doped tin oxide (FTO) glass slides were supplied by ChemSoln (USA). The FTO glass slides were further cut into smaller 10 mm × 25 mm pieces. The cut smaller FTO glass slides were cleaned with acetone and ethanol, followed by rinsing with deionised water for subsequent synthesis of nanostructured hematite thin films.

2.2. Synthesis of nanostructured hematite thin films

The cathodic electrodeposition method was employed to synthesise nanostructured hematite thin films onto the surface of FTO glass slides. The precursor solution was made up of 5.0 mM $FeCl_3$, 5.0 mM NaF, 0.1 M KCl and 1.0 M H_2O_2. Electrodeposition synthesis was performed using a conventional three-electrode electrochemical cell containing platinum (Pt) rod, Ag/AgCl saturated by 3 M KCl and FTO substrate as the counter, reference and working electrodes, respectively. The electrochemical cell was connected to an Autolab potentiostat that was used for regulating the electrodeposition synthesis conditions of nanostructured hematite thin films, as well as for other electrochemical-related measurements. The nanostructured hematite thin films were prepared by cyclic voltammetry process at a potential sweep rate of 0.1 V/s, from −0.5 V to 0 V for 100 cycles. During the electrodeposition process, the temperature of precursor solution was set constant at 21 °C (room temperature). After the electrodeposition synthesis, the as-deposited amorphous iron oxy-hydroxide (FeOOH) thin films were washed with deionised water for several times, followed by annealing treatment at 400 °C, 500 °C and 600 °C with a dwell time of 4 h.

2.3. Structural characterisations

The polycrystalline structures of nanostructured hematite thin films samples were analysed by using XRD analysis with an X-ray powder diffractometer (Bruker D8 Discover) employing Cu Kα radiation with 40 kV and 100 mA at 0.02°/s scan rate. FE-SEM coupling with EDX (SU8010 model, Hitachi) was used to estimate the average hematite nanocrystallites size, as well as to examine the surface morphologies and chemical elemental compositions of the nanostructured hematite thin films, respectively. The FTIR-spectra of nanostructured hematite thin films samples were recorded using the Thermo Scientific Nicolet iS10 spectrophotometer. The optical properties of nanostructured hematite thin films were characterised by using the UV-visible spectrophotometer (Agilent Technologies Cary Series 100).

2.4. Photoelectrochemical characterisations

The PEC characterisations of nanostructured hematite thin films on FTO (working electrode) were performed by using the same Autolab potentiostat setup with three-electrode electrochemical cell containing Pt rod and Ag/AgCl saturated by 3 M KCl as the counter and reference electrodes, respectively. The active