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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 electron–hole 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.

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 (TiO_2) 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 solar-to-hydrogen (STH) conversion efficiency [4]. Note that photoanode is the oxygen evolution electrode while hydrogen is evolved at the counter cathode in a PEC cell.

Recently, hematite (α-Fe_2O_3) 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 ($<1\ cm^2/Vs$) 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 sp^2 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 ($FeCl_3$) 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 ($KMnO_4$), hydrochloric acid (HCl) (30 wt%), sodium hydroxide (NaOH) and graphite powder were purchased from Merck, Malaysia. Fluorine-doped 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 $KMnO_4$ (9 g) were added in a mixture of concentrated H_2SO_4 (180 ml) and H_3PO_4 (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% H_2O_2 (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, 120 ml of ethanol and 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.

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 $FeCl_3$ 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 °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-Kα 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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