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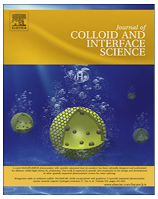

Regular Article

Sn-doped hematite modified by $CaMn_2O_4$ nanowire with high donor density and enhanced conductivity for photocatalytic water oxidation

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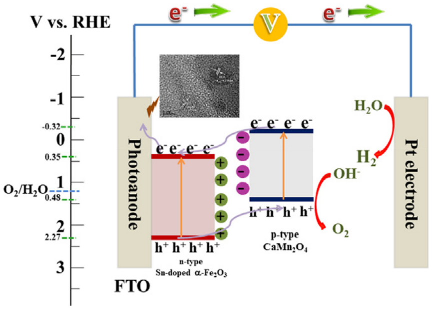
GRAPHICAL ABSTRACT



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ABSTRACT

Herein, we report a novel nanocomposite consisting of n-type Sn-doped hematite and p-type $CaMn_2O_4$ nanowire ($CaMn_2O_4/\alpha$-Fe_2O_3). The nanocomposite was characterized by X-ray diffraction (XRD), high resolution transmission electron microscopy (HRTEM), ultraviolet-visible absorption spectroscopy, X-ray photoelectron spectroscopy (XPS), which showed that nanospindle-like Sn-doped hematite and $CaMn_2O_4$ nanowire contact intimately in the nanocomposite, resulting in efficient charge transfer and separation. Photoelectrochemical results reveal that the nanocomposite possesses higher donor density, enhanced conductivity and lower overpotential for dioxygen evolution. In addition, the nanocomposite demonstrates high photocatalytic activity for water oxidation to produce oxygen in a photoelectrochemical cell. The amount of O_2 evolved from the optimized photoanode of the photoelectrochemical cell was 1.98 μmol in 2 h of simulated sunlight irradiation. This work demonstrates a facile synthesis of a novel nanocomposite as anode material for photocatalytic water oxidation to produce O_2.

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1. Introduction

Exploring clean and renewable energy to replace traditional fossil fuels for a sustainable society is an important issue and particular challenge [1–3]. Solar-driven water splitting to produce hydrogen and oxygen in photoelectrochemical (PEC) cells presents a promising method for supplying non-carbon clean energy [4–6]. In typical PEC water splitting reaction process, oxygen is produced on photoanode via water oxidation reaction while hydrogen is generated on photocathode via water reduction reaction [7].

Hematite is a promising photoanode material for solar water splitting due to its low cost, nontoxic nature, chemical stability both in solid or in basic liquid solutions, and easy preparation to an electrode [8,9]. Moreover, the band gap of hematite is approximately 2.0 eV, which enables it absorb light in the visible light range up to λ ~ 600 nm [10]. However, the poor conductivity, short lifetime and high recombination rate of photogenerated charge carriers, as well as high overpotential for water photooxidation

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of hematite limit its photocatalytic performance [11,12]. Hence, it is highly desirable to find a way to improve the photocatalytic activity of hematite. Lots of strategies can be considered, such as doping hematite to enrich its donor density, thus, enhancing its conductivity [13–15], nanotexturing or engineering its nanoarchitectures to improve light trapping [16,17], and modifying hematite with co-catalysts [18].

Up to now, $CaMn_2O_4$, which was first reported by Gaudefroy et al., who discovered the compound from naturally occurring marokite mineral [19], has been regarded as one of the most dense metal oxide with AB_2O_4 structure [20]. Many follow-up researches studied the structure and magnetism of the material [21,22]. However, few researches have studied its optical properties and its application as the component of a composite for improving photocatalysis.

In this paper, we report synthesis, characterization and photocatalysis of a novel catalyst composited of Sn-doped α-Fe_2O_3 nanospindle and $CaMn_2O_4$ nanowire. The composite was used for fabricating photoanode of a PEC cell for water splitting. The anode of the PEC cell exhibited much enhanced photocatalytic performance compared with the one prepared by pristine hematite. To our best knowledge, there have been no reports on the photoelectrochemical properties and photocatalytic water splitting abilities of this sub-100 nm nanocomposite prepared by modifying Sn-doped α-Fe_2O_3 nanospindle with $CaMn_2O_4$ nanowire.

2. Experimental

2.1. Materials

Iron (III) chloride hexahydrate ($FeCl_3{\cdot}6H_2O$, ≥99%), sodium dihydrogen phosphate dihydrate ($NaH_2PO_4{\cdot}2H_2O$, ≥99%), tin(IV) chloride pentahydrate ($SnCl_4{\cdot}5H_2O$, ≥99%), calcium chloride anhydrous ($CaCl_2$, ≥96%), manganese (II) chloride tetrahydrate ($MnCl_2{\cdot}4H_2O$, ≥99%), potassium permanganate ($KMnO_4$, ≥99.5%), sodium sulfate anhydrous (Na_2SO_4, ≥99%), sodium hydroxide (NaOH, ≥96%) and potassium hydroxide (KOH, ≥85%) were purchased in analytical grades from Sinopharm Chemical Reagent Company (Shanghai, China). All reagents were used without further purification.

2.2. Preparation of samples.

2.2.1. Synthesis of Sn-doped α-Fe_2O_3

Sn-doped α-Fe_2O_3 was synthesized by a simple hydrothermal method [23]. Typically, 2.0 mL (0.5 M) of $FeCl_3$ solution, 1.8 mL (0.02 M) of NaH_2PO_4 solution, and 1.5 mL (0.02 M) of $SnCl_4$ solution were added to 46 mL of deionized water under magnetic stirring. The mixture was transferred to a Teflon-lined stainless autoclave and was heated to 220 °C and maintained the temperature for 2 h. The solid product obtained by centrifugation was washed with deionized water and ethanol for several times and dried at 60 °C overnight. Finally, the powder was calcined at 400 °C for 3 h, resulting in Sn-doped α-Fe_2O_3. The samples were labeled as FS-x, where x stands for the molar ratio of Sn^{4+} in the sample. For comparison, pure α-Fe_2O_3 without doping was prepared according to the same procedure using $FeCl_3$ and NaH_2PO_4 as starting materials.

2.2.2. Synthesis of $CaMn_2O_4$

$CaMn_2O_4$ was synthesized using a modified hydrothermal method [24]. In a typical experiment, 0.11 g of $CaCl_2$ (1 mmol), 0.10 g of $KMnO_4$ (0.6 mmol) and 0.28 g $MnCl_2$ (1.4 mmol) were dissolved in 40 mL of deionized water under magnetic stirring, then 10 mL (7.8 M) of KOH solution was dropwise added to the above solution. The mixture was transferred to a Teflon-lined autoclave and heated at 180 °C for 72 h. The brown solid obtained by centrifugation was washed with distilled H_2O for several times and then was dried in a vacuum furnace at 60 °C overnight.

2.2.3. Synthesis of $CaMn_2O_4$ modified Sn-doped α-Fe_2O_3 composite

For the preparation of $CaMn_2O_4$ modified Sn-doped α-Fe_2O_3 composite, 0.05 g of FS-3 was dispersed in 10 mL of distilled water and the suspension was ultrasonic stirred for 10 min. Then, 2.5 mg of grinded $CaMn_2O_4$ was added to the suspension under ultrasonication and stirred continuously for 2 h. The solid obtained by filtration was dried in vacuum at 60 °C for 12 h, and then was calcined in Ar at 400 °C for 2 h, resulting in $CaMn_2O_4$ modified Sn-doped α-Fe_2O_3 nanocomposite. Changing the dosage of $CaMn_2O_4$, $CaMn_2O_4$ modified FS-3 composite in different composition can be prepared using the same procedure. The samples were labeled as FS-x/C-y, where y stands for the weight percent of $CaMn_2O_4$ in the sample. For comparison, the physical mixture of $CaMn_2O_4$ and FS-3 [labelled as FS-x/C-y (p)] was prepared without the calcination.

2.2.4. Preparation of photoanode

In a typical preparation, 20 mg of FS-3/C-10 were firstly dispersed in a 5 mL of the solution consisting of ethanol-ethylene glycol-polyvinyl pyrrolidone (4 mL:1 mL:1.5 mg), and then the suspension was spin-coated on the surface of a clean fluorine-doped tin-oxide (FTO) substrate. The FTO plate with the deposited sample was dried on a heating plate at 50 °C for 20 min and was then sintered in Ar at 400 °C for 0.5 h. The electrode coved $CaMn_2O_4$ modified Sn-doped α-Fe_2O_3 nanocomposite in different composition can be prepared in the same method.

2.3. Characterization

Crystal structure of the samples was analyzed by X-ray diffraction (XRD) (Japan, XD-3A) using Cu Kα radiation in the 2θ range of 20–80°. Transmission electron microscopy (TEM) was performed on a TECNAI-G20 electron microscope (JEOL JEM-2100, Japan) operated at an accelerating voltage of 200 kV. Energy dispersive diffraction spectrum (EDS) was taken on a Hitachi S-4700 microscope (Hitachi Corporation). The X-ray photoelectron spectroscopy (XPS) measurements were carried out with an AXIS Ultra DLD system (Kratos Analytical Inc). UV-vis absorption spectra of the as-prepared nanocomposites were recorded on a UV3600 Spectrophotometer.

2.4. Photoelectrochemical measurements

The PEC performance of the samples was measured in a three-electrode system composed of a working electrode, a saturated calomel electrode (SCE) as the reference electrode, and a platinum wire as the counter electrode. The electrodes were immersed in 0.2 M of Na_2SO_4 solution. The system was connected with a CHI 660D potentiostat/galvanostat electrochemical analyser. The working electrode was irradiated by a 150 W xenon lamp. The Nernst equation

$$R_{RHE} = E_{SCE} + 0.059\text{pH} + E^{o}_{SCE} \tag{1}$$

was used for converting the measured potential vs. SCE to the potential vs. reversible hydrogen electrode (RHE), where E_{RHE} is the potential vs. RHE, E_{SCE} is the measured potential vs. SCE, and E^{o}_{SCE} = 0.2415 V at 25 °C.

The flat band potential of the semiconductors can be calculated by the Mott-Schottky Eq. (2) and the electron density can be calculated from the Eq. (3):

$$\frac{1}{C^2} = \frac{2}{e_0\varepsilon\varepsilon_0 N_d} \times \left(E - E_{fb} - \frac{kT}{e_0}\right) \tag{2}$$

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