



Synthesis of carbonized-cellulose nanowhisker/FeS₂@reduced graphene oxide composite for highly efficient counter electrodes in dye-sensitized solar cells



Mengjuan Zhou^{a,b}, Jianxin He^{a,c,*}, Lidan Wang^{a,c}, Shuyuan Zhao^{a,c}, Qian Wang^{a,c}, Shizhong Cui^{a,c}, Xiaohong Qin^b, Rongwu Wang^{b,**}

^a Henan Provincial Key Laboratory of Functional Textile Materials, Zhongyuan University of Technology, Zhengzhou 450007, China

^b Key Laboratory of Textile Technology, Ministry of Education, College of Textiles, Donghua Science & University, Shanghai 201620, China

^c Collaborative Innovation Center of Textile and Garment Industry, Henan Province, Zhengzhou 450007, China

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ABSTRACT

Iron pyrite (FeS₂) is one of the most promising materials for solar energy technology owing to its abundance and optical properties. In this work, a carbonized-cellulose nanowhisker/FeS₂@reduced graphene oxide (C-CW/FeS₂@RGO) composite is synthesised through a facile hydrothermal method with CW as the bio-template. In this method, the carbon matrix formed by high-temperature carbonization of CW is coated with FeS₂ nanocrystals to form hollow, porous nanorods, which are randomly dispersed over the surface of the RGO sheets. The C-CW/FeS₂@RGO composite presents the following structural advantages for application as a counter electrode (CE) for dye-sensitized solar cells (DSSCs): its hollow and porous structure, the rod-like morphology inside the continuous carbon matrix, and the two-dimensional continuous conducting pathway created by the RGO sheets. According to the cyclic voltammetry, impedance spectroscopy, and Tafel polarization analyses, the electrocatalytic activity of the C-CW/FeS₂@RGO CE for the reduction of triiodide ions is higher than that of Pt CE. The DSSC assembled with the C-CW/FeS₂@RGO CE delivers a photoconversion efficiency ($\eta = 7.38\%$) higher than that of Pt CE ($\eta = 6.24\%$). Owing to its excellent performance, C-CW/FeS₂@RGO CE is expected to replace the expensive Pt electrode in DSSCs.

1. Introduction

Dye-sensitized solar cells (DSSCs) have attracted widespread attentions due to their low-cost, simple fabrication, relatively high energy conversion efficiency, and low environmental toxicity (Jeon et al., 2012). DSSCs generally present a sandwich-type structure consisting of a transparent conductive oxide layer, dye-coated TiO₂ as the photoanode, an electrolyte (traditionally containing I⁻/I₃⁻ as the redox couple), and a counter electrode (CE) Grätzel, 2005. The CE is a crucial component that directs electrons from an external circuit to the redox electrolyte and promotes the regeneration of I⁻ from I₃⁻, completing the cell circuit (Grätzel, 2003; Hagfeldt et al., 2010). Hence, an efficient CE should display good stability, high electrical conductivity, and superior electrocatalytic activity to minimise energy losses (Yao et al., 2013). Traditionally, the CEs of DSSCs are fabricated with the platinum, which exhibits high electrocatalytic properties, excellent electrical conductivity, and good stability. However, Pt is very expensive and

easily corroded by the electrolyte, which limits the large-scale production of DSSCs. Therefore, many alternative CE materials with relatively high catalytic activity have been investigated to replace Pt in DSSCs, such as conductive polymers (Bay et al., 2006; Saito et al., 2002, 2004), carbon-based materials (Roymayhew et al., 2010; Trancik et al., 2008; Joshi et al., 2010), and transition metal based inorganic materials (Gong et al., 2012; Li et al., 2011).

Among them, transition-metal sulphides have drawn widespread interest owing to their facile preparation and unique electrical and catalytic properties (Zhong et al., 2003; Zhou et al., 2014). As a typical binary multimetal sulphide, iron pyrite (FeS₂), with a narrow band gap of ~0.95 eV, has attracted great interest for photovoltaic applications in recent years owing to its inherent advantages, such as high absorption capacity, high electron mobility, and inexpensive, abundant, and non-toxic constituents (Qian et al., 2001; Ennaoui et al., 1993). Shukla et al. (2014) efficiently prepared catalytic FeS₂ films by a simple scalable spray pyrolysis technique. The photoconversion efficiency (PCE) of

* Corresponding author at: Key Laboratory of Textile Technology, Ministry of Education, College of Textiles, Donghua Science & University, Shanghai 201620, China.

** Corresponding author.

E-mail addresses: hejianxin771117@163.com (J. He), wrw@dhu.edu.cn (R. Wang).

a DSSC based on a FeS₂ CE was found to be 8.0% with an I⁻/I₃⁻ electrolyte. Song et al. (2016) synthesized high-purity FeS₂ powders by a hydrothermal method and investigated the effect of NaOH addition on the crystal size and electrocatalytic activity of FeS₂. The PCE was determined to be 5.78% and 4.76% for FeS₂ CEs with and without NaOH, respectively. Therefore, FeS₂ is a promising low-cost industrial material for DSSCs.

Graphene, an atom-thick planar sheet of sp²-bonded carbon atoms arranged in a hexagonal “honeycomb” lattice structure, has become an increasingly important material in nanotechnology research (Liu et al., 2012; Yun et al., 2011; Palma et al., 2016). Kilic et al. (2016) realised a novel CE with graphene/FeS₂ thin films by deep coating and hydrothermal methods. A DSSC based on graphene/FeS₂, in combination with a TiO₂ mesoporous photoanode and I⁻/I₃⁻ redox electrolyte, exhibited an energy conversion efficiency η of 7.43%, approximately 16.1% higher than that of Pt CE ($\eta = 6.40\%$).

In this paper, we fabricated cellulose nanowhisker (CW)/FeS₂ composite nanorods by a facial hydrothermal method using HCWs as a bio-template. Then chitosan-adsorbed CW/FeS₂ nanorods were uniformly assembled onto the surface of grapheme oxide (GO) sheets by electrostatic interactions. After thermal treatment, a carbonized-cellulose nanowhisker (C-CW)/FeS₂@RGO composite was obtained, in which C-CW/FeS₂ nanorods with a porous structure were uniformly distributed over the surface of RGO sheets. A DSSC constructed with the C-CW/FeS₂@RGO CE displayed enhanced catalytic performance, including a η up to 7.38%.

2. Experimental

2.1. Materials

Iron (II) chloride, tetrahydrate (FeCl₂·4H₂O, AR), thiourea (CH₄N₂S, AR), chitosan (BR), hydrochloric acid (HCl, AR), sodium hydroxide (NaOH), Carbon disulfide (CS₂, AR), sublimed sulfur (99.95%), and sodium chloroacetate (ClCH₂COONa) were purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). The N719 dye, TiO₂ paste, electrolyte (E23), and fluoride-doped tin oxide (FTO) glasses were purchased from Dyesol. All chemicals were used directly without further purification.

2.2. Fabrication of the C-CW/FeS₂@RGO composite

Cellulose nanowhisker (CNW) was extracted from absorbent cotton. A colloidal suspension of CNW (20 g) in water was prepared as described elsewhere (Dong et al., 1996; Lima et al., 2003; Samir et al., 2004) and poured into 100 mL of a 50 wt% NaOH solution in ethanol-water (85% volume fraction) for alkalization under ultrasonic stirring for 1 h. Then, ClCH₂COONa (5 g) powder was added to the above solution, and the mixture was kept under ultrasonic stirring at about 60 °C for 2 h. Finally, the obtained mixture was centrifuged to remove the supernatant, then the precipitate was moved into a beaker with deionized water under magnetic stirring for 20 min, which was repeated several times to remove the impurities. The homogeneous carboxylated whisker (HCW) solution was obtained.

To fabricate the C-CW/FeS₂@RGO composite, 1.17 g of FeCl₂·4H₂O powder was dispersed in 300 mL of the above HCW solution and stirred ultrasonically at ~35 °C for 30 min. Then, NaOH solution with deionized water was added into the mixture drop by drop to adjust PH to ~11 used the laboratory PH meter. Then, 0.9 g of CH₄N₂S powder was added to the solution, which was stirred for 3 h. Sulfur powder (0.075 g) was added to the mixture under electric stirring for 30 min, and the solution was sealed in a Teflon-lined stainless steel autoclave (filled at 80%) and heated at 200 °C for 20 h in an oven before being cooled down to room temperature. The product, CW/FeS₂, was collected by centrifugation and then stirred magnetically for 20 min with dilute HCl (1.4 M), CS₂, ethanol, and distilled water separately to

remove the excess sulfur and iron species. Pure FeS₂ particles were fabricated using the same method without HCW. The obtained CW/FeS₂ composite was poured into 100 g of a 0.3 wt% chitosan solution (deionized water as the solvent) and stirred ultrasonically for 30 min. Next, the product absorbed chitosan was washed in a centrifuge with distilled water to obtain a neutral composite.

The graphene oxide (GO) used in this work was prepared by the modified Hummers method (Hummers and Offeman, 1958). The above CW/FeS₂ composite absorbed chitosan was mixed with 20 mL of the GO solution at a concentration of 1.5 mg mL⁻¹ and stirred ultrasonically for 3 h. Finally, the product was dried at 60 °C in a vacuum oven and then carbonized at 800 °C for 2 h under argon atmosphere at a heating rate of 5 °C min⁻¹, the C-CW/FeS₂@RGO composite was obtained. A C-CW/FeS₂ sample was fabricated by the same method without RGO.

2.3. CE preparation

First, FTO plates were cleaned in an ultrasonic bath with deionized water and absolute ethanol for 30 min each. Pastes were prepared by dispersing the FeS₂, C-CW/FeS₂, or C-CW/FeS₂@RGO samples in a mixture of ethyl terpineol, tetraisopropyltitanate, acetylene black, and cellulose, and then ground in an agate mortar for 4 h. Each paste was coated onto a washed FTO plate by the doctor blade method to form a 4–6- μ m-thick layer, followed by drying at 80 °C under vacuum for 30 min and heating at 450 °C for 30 min under argon. For comparison, a Pt CE was prepared using the squeeze-printing method with the Pt paste on an FTO plate, followed by sintering at 450 °C for 30 min.

2.4. Cell fabrication

FTO plates were coated with a TiO₂ slurry, and sintered at 450 °C for 30 min, followed by immersing in an N719 dye solution in anhydrous ethanol overnight. Subsequently, the dye-sensitized TiO₂ photoanodes were washed with anhydrous ethanol and dried under moisture-free air. The dye-adsorbed TiO₂ electrodes were assembled and sealed with as-prepared CEs by a thermoplastic sealant (Surlyn® 1702) to fabricate sandwich-structured cells with an active area of 0.36 cm². The electrolyte (E23) was injected into the solar cell through a hole drilled in the CE.

2.5. Characterization

The crystalline structure of the prepared composites was studied by wide-angle X-ray diffraction (XRD, D8 ADVANCE, Germany Bruker) with Cu-K α radiation operated at 36 kV and 25 mA ($\lambda = 1.5418 \text{ \AA}$). The morphology and detailed structure of samples were investigated by field-emission scanning electron microscopy (FE-SEM, Hitachi, S-4800) and transmission electron microscopy (TEM, JSM-2010) at 200 kV. X-ray photoelectron spectroscopy (XPS) was carried out to analyze the surface of samples using a Thermo ESCALAB 250 (USA) with an Al K α source. Laser Confocal Micro-Raman Spectroscopy (Raman, LabRAM HR800, France Horiba) was used to evaluate the composition of the samples at an excitation wavelength of 532 nm. Brunauer–Emmett–Teller (BET) nitrogen absorption–desorption measurement (Autosorb-Iq, USA) was used to investigate the specific surface area and pore-size distribution of samples.

2.6. Photovoltaic and electrochemical properties

Photovoltaic performance of the DSSCs was measured under 100 mW cm⁻² irradiation (1 sun calibrated beforehand by a standard silicon solar cell) with AM 1.5 illumination (Beijing ZOLIX INSTRUMENTS CO., LTD, China). The electrochemical performance of the prepared CEs was evaluated using an electrochemical workstation (Model: CHI600E). Cyclic voltammetry (CV) measurement was performed in a three-electrode system (the prepared CEs served as the working

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