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Economic synthesis of Co_3S_4 ultrathin nanosheet/reduced graphene oxide composites and their application as an efficient counter electrode for dye-sensitized solar cells

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ABSTRACT

Despite cobalt sulfide nanosheets gain great attention for their excellent electrochemical performance, the lack of economic and scalable synthesis method limits their applications. Herein, a simple and cost-effective noninjection hydrothermal process is proposed to synthesize Co_3S_4 ultrathin nanosheets on the surface of reduced graphene oxide (rGO) by controlling the polarity of the reaction solution and introducing NH_3. Experimental and theory results reveal that the obtained Co_3S_4 nanosheets have higher electrochemical properties for the reduction of I_3^- than bulk due to their larger density of electron states in the nearby of Fermi level facilitating fast electron-transfer and providing highly active sites for catalytic reaction. With the synergistic effect of rGO, electrocatalytic performances of Co_3S_4 nanosheets can be further optimized. The dye-sensitized solar cell (DSSC) device with Co_3S_4 nanosheet/rGO as counter electrode (CE) material exhibits a power conversion efficiency (PCE) of up to 8.08%, which is superior to that of Co_3S_4 nanosheet (7.13%) and Pt (7.62%) at the same measurement condition. Moreover, Co_3S_4 nanosheet/rGO composites show enhanced cycling stability, indicating the great possibility of them for replacing Pt as an advanced CE in DSSCs.

1. Introduction

The rapidly increasing utilization for global energy has significantly promoted the development of photovoltaic technologies, which can convert clean and renewable solar energy into electrical energy [1–3]. Dye-sensitized solar cells (DSSCs) with pollution-free nature, low consumption and simple manufacturing procedures have received increasing attention as an alternative to current commercial silicon-based solar cells [4–6]. Generally, a typical DSSC system consists of photoanode, photosensitive dye, redox couple and counter electrode (CE, usually Pt) [7,8]. Among them, CE is a key component governing the electrochemical performance. It not only collects the electrons from the external circuit to electrolyte, but also catalyzes the reduction of electrolyte [6]. In liquid-junction DSSCs, iodide/triiodide (I^-/I_3^-)-based electrolyte was usually used as hole-transporting medium to achieve high efficiencies [9]. For its excellent catalytic reduction ability of I_3^-, noble metal Pt is usually chosen as CE material. However, the high cost and rarity of Pt inspire the exploration for stable and economic alternatives [10]. In recent report, metal chalcogenides [10–12], metal oxides [13–15] (M_xN_y, where M = Mo, W, Co or Ni and N = S or O) have been studied and tried to replace Pt for their large abundance, good stability and excellent electrocatalytic ability [16]. Our previous report has indicated that 2D porous Co_3O_4 nanoflakes show relatively low power conversion efficiency (PCE) of only about 1.20%, which is supposed to be ascribed to their poor conductivity hindering charge migration during the electrocatalytic process [13]. Co_3S_4 nanostructures, with attractive metallic nature and intrinsic activities, have showed excellent performance in oxygen evolution reaction and supercapacitor [17,18]. Based on these, Co_3S_4 nanostructures are expected to show improved electrochemical performance when working as CEs. In order to further enhance the PCE of Co_3S_4-based DSSC, there are still a few issues to be addressed: (1)

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the controllable preparation of two dimensional (2D) atomically thin Co_3S_4 nanosheets. 2D Co_3S_4 nanosheets are believed to possess high surface area, fast interfacial charge transfer and more highly active sites for catalytic reaction [19–21]. For anisotropic layered transition metal dichalcogenides (TMDs) including WS_2 and MoS_2, 2D nanostructures can be efficiently exfoliated via mechanical exfoliation, CVD growth and chemical exfoliation [16,20]. However, for non-layer compounds, like Co_3S_4, limited by the lack of intrinsic anisotropic growth driving force or the strong in-plane bonds [20], common methods are invalid. Recently, it was reported that Co_3S_4 nanostructures with shape of sheets could be prepared via the two-step anion exchange reaction of $Co(OH)_2$ and phase transformation from Co_3O_4 [20,22]. However, the obtained sheet-like nanostructures possessed thickness of a few nanometers, showing unsatisfied electrochemical activation. In addition, these two preparation methods are involved with polystep reactions, limiting the further development. Thereafter, it is still highly demanded to propose an efficient, economic, and scalable synthesis method for the preparation of ultrathin Co_3S_4 nanosheets [23]. (2) The protection of Co_3S_4 nanosheets from agglomeration. During the practical usage process, Co_3S_4 nanosheets are liable to agglomerate due to its 2D feature, which will reduce the exposure of active sites and result in the stability reduction. (3) The diffusion length reduction of the electrolyte to a maximum extent. The formation of open 2D permeable channels will be of favor to the electrolyte diffusion, which needs the formation of composite with other laminar nanostructures of large specific surfaces. (4) The further increase of conductivity. The couple of Co_3S_4 nanosheets and conductive material can further reduce the charge transfer resistance (R_{ct}) at the counter electrode/electrolyte interface, improving the catalytic ability of the CE for the reduction of I_3^- to I^-. Graphene featuring high electron mobility (~15 000 $cm^2/(V\,s)$) at room temperature [1], excellent flexibility [24], has been proved to be a superior auxiliary CE material for constructing TMDs/graphene composite [23,25]. Its large specific surface and flexibility can ensure the formation of open permeable channels and the protection from agglomeration of Co_3S_4 nanosheet. In addition, the synergistic effects between graphene and Co_3S_4 nanosheets are expected to provide more highly active sites [26,27].

Herein, with tuning reaction solution polarity and introducing NH_3, ultrathin Co_3S_4 nanosheets were prepared on a large scale via a mild one-pot synthesis method for the first time. Both theoretical calculation and experiment results show that our Co_3S_4 nanosheets exhibit intriguing charge mobility. With introducing graphene oxide (GO) in the reaction solution, Co_3S_4 nanosheets were synthesized on the surface of GO via electrostatic interaction and GO nanosheets were reduced at the same time, forming Co_3S_4/reduced graphene oxide (rGO) nanocomposites, which exhibit higher catalytic activity toward I_3^- and faster charge transfer ability than Co_3S_4 nanosheets and rGO. Using Co_3S_4/rGO composites as CE materials, the assembled DSSC shows PCE of 8.08%, higher than that of the DSSC with Pt (7.62%). Considering its cost, good stability and the improved PCE, the Co_3S_4/rGO composite is a promising candidate to replace metal Pt as the CE of DSSC.

2. Experimental

2.1. Materials

Cobalt chloride hexahydrate ($CoCl_2 \cdot 6H_2O$, ≥99%), Thioacetamide (C_2H_5NS, 99%), Ammonium hydroxide ($NH_3 \cdot H_2O$, AR, 25–28%), Hydrochloric acid (HCl, AR, 36–38%), Hydrogen peroxide (H_2O_2, AR, ≥30%), Phosphoric acid (H_3PO_4, AR, ≥85%), Potassium permanganate ($KMnO_4$, ≥99.5%) and ethanol (C_2H_6O, 99.7%) were purchased from Sinopharm Chemical Reagent Co., Ltd.

2.2. Synthesis of the ultrathin Co_3S_4 nanosheets

In a typical synthesis, 300 mg of $CoCl_2$ was dissolved in 80 mL of mixture solution with ethanol and distilled water (1:1). After vigorous stirring for half an hour, 4.8 mL of NH_4OH was slowly introduced. Then 189 mg of thioacetamide (TAA) was added followed by stirring for another 1 h. The mixture was transferred into a 100 mL Teflon-lined autoclave, to be sealed and heated at 180 °C for 24 h. After being naturally cooled to room temperature, the obtained product was collected by centrifuging, and washed with water and ethanol for a few times in turn. Finally, the precipitation was freeze-dried for further use.

2.3. Synthesis of GO nanosheet

Graphene oxide nanosheets were synthesized by modified Hummers method [28]. Firstly, 180 mL of H_2SO_4 (98%) and 20 mL of H_3PO_4 (85%) were mixed, followed by adding 1.5 g of graphite powder. Secondly, the mixture solution was transferred to 50 °C water bath. Then, 9 g of $KMnO_4$ was slowly added, keeping the solution temperature at 50 °C. After that, the mixture was stirred for 6 h at the same condition. Thirdly, 200 mL of diluted H_2O_2 was slowly introduced into the mixture until the color of solution changed from black, purple to bright yellow. With another 3 h stirring, the solution was cooled to room temperature and the product was separated by centrifugation and washed with deionized water for several times until the supernatant tuned to neutral. The obtained GO was dried for further use.

2.4. Synthesis of Co_3S_4/RGO nanocomposite

50 mg of GO was dissolved in water and ethanol. Then, 300 mg of $CoCl_2$ was added to the mixture solution with vigorous stirring for half an hour. Next, 4.8 mL of NH_4OH was slowly added, followed by stirring for 10 min. Then 189 mg of TAA was added. After stirring for 1 h, the precursor was transferred into a 100 mL Teflon-lined autoclave, sealed and heated at 180 °C for 24 h. After being naturally cooled to room temperature, the obtained product was collected by centrifuging, and washed for further use.

2.5. Fabrication of CE

In a typical process, 40 mg of sample power and poly(ethylene glycol) powder (weight ratio of 4:1) were dispersed in 1 mL of ethanol solution. The mixture was grinded with a mortar to form an ink. Fluorine-doped tin oxide (FTO)-coated glass was masked by a 3 M Scotch tape with an exposed area of $0.5 \times 1\ cm^2$. Then, the ink was painted on FTO conductive glass with doctor-bladed method for fabricating CE film. After natural drying, CE was annealed at 400 °C for 60 min under the protection of argon atmosphere. Next, the CE was scraped into a film with an area of $0.5 \times 0.5\ cm^2$ using a blade for further use. A sandwich DSSC device was composed of TiO_2 photoanode sensitized by ethanol solution of 0.5 mM N719 dye for 24 h, the as-prepared CEs and the redox electrolyte [29].

2.6. First-principles calculation

The first principle calculation based on density functional theory (DFT) was carried out using Cambridge Serial Tatal Energy Package module (CASTEP) code in the program of Materials Studio 8.0 version. During the process of calculation, PBE-GGA was used as the exchange and correlation functionals. The energy cutoff was fixed to 330 eV. The k-point mesh was $4 \times 4 \times 4$.