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Double laminated reduced graphene/Cu_2S/reduced graphene/graphene oxide nanofilms and their photoelectrochemical properties

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ABSTRACT

In this work, an efficient photocatalytic material was prepared directly on Indium tin oxide (ITO) glass substrates by fabricating Cu_2S and graphene oxide onto graphene for photoelectrochemical (PEC) water splitting. The double laminated reduced graphene/Cu_2S/reduced graphene/graphene oxide (RG/Cu_2S/RG/GO) nanofilms were characterized, and an enhanced photoelectrochemical response in the visible region was discovered. The photocurrent density of the nanofilms for PEC water splitting was measured to be up to 1.98 mA/cm^2, which could be ascribed to the followings: (i) a higher efficiency of light-harvesting because of GO coupling with Cu_2S that could broaden the absorbing solar spectrum and enhance the light utilization efficiency; (ii) a stepwise structure of band-edge levels in the Cu_2S/GO electrode was constructed; (iii) double laminated electron accelerator (RG) was used in the Cu_2S/GO materials to get better electron-injecting efficiency.

1. Introduction

Photoelectrochemical (PEC) splitting of water into hydrogen and oxygen by means of semiconductor nanomaterials has been considered as an ideal solution for environment and energy crisis [1,2], because it can convert and store solar energy efficiently. Since Fujishima and Honda demonstrated to produce the hydrogen using PEC water splitting in 1972 [3], numerous active semiconductor materials (such as TiO_2 [4]) have been proven to be able to serve as the photoelectrodes of PEC system. TiO_2 has been extensively investigated as an excellent photocatalyst, owing to its exceptional properties such as non-toxicity, low cost, and long-term stability against photo and chemical corrosion [4,5].

Nevertheless, the absorption of TiO_2 is limited to UV region because of the large band gap, which restricts their practical applications. Therefore, considerable efforts have been made to extend the absorption spectrum to the visible light region using different semiconductor materials. And the most efficient photocatalyst used by people is sulfide, such as CdS [6], $CuInS_2$ [7], $ZnIn_2S_4$ [8], $AgSbS_2$ [9], $AgInS_2$ [10,11], or quaternary sulfide [12]. Among all of the sulfide materials, copper sulphide (Cu_2S) is an important semiconductor nanocrystals, and it can be applied in water splitting to produce clean hydrogen energy [13,14]. Cu_2S belongs to I-VI group compound of semiconducting material. And it is widely used in solar cells because of its superior activity and stability. The band gap of Cu_2S (1.1 eV) is narrower than that of TiO_2 (3.2 eV), which has a high visible-light-driven photoactivity, and it makes Cu_2S a competitive candidate as a photocatalyst. Korgel et al. prepared Cu_2S nanorods, nanodiscs and nanoplatelets by solvent-less thermolysis of a copper-alkylthiolato precursor [15]. Meidan et al. prepared Cu_2S that was used in quantum dot-sensitized solar cells [16]. Furthermore, the Cu_2S possessed abundant pairs of available electrons states, which was beneficial to the photocatalytic activity [17]. Moreover, semiconductor quantum dots have attracted considerable attention in photocatalytic hydrogen production [18,19]. The higher photon conversion efficiencies and the larger specific surface area were all contribute to the hydrogen production. However, the high recombination rates of photogenerated electron–hole pairs and the reunite of Cu_2S significantly decreased the photocatalytic efficiency. Hence, great efforts should dedicate to reducing the recombination of the photo-induced electron–holes and further to improve the photocatalytic performance. It is generally accepted that coupling with GO could greatly improve the hydrogen evolution efficiency of photocatalysts from water in the presence of sacrificial reagents. GO synthesized through the graphite oxide powders are shown that GO is suitable for both the reduction and the oxidation of water by the electrochemical analysis along with the MottSchottky equation. And it has an ideal band gap to couple with Cu_2S, which makes GO to be an effective choice of material for coupling with Cu_2S. An electron accelerator can be used in the Cu_2S/GO materials to get better electron-injecting efficiency.

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Reduced graphene (RG), which offers an excellent electron transport property and possesses an extremely high specific surface area [20,21], is highly recognized as an ideal high-performance photocatalyst carrier or promoter. Recently, it has been shown that combining semiconductor materials with RG can enhance their electronic [22], optoelectronic [23], electrocatalytic [24], and photocatalytic properties [25].

In this work, for the first time, the double laminated RG/Cu_2S/RG/GO nanofilms on ITO glass substrates were synthesized, which can be used as electrode for efficient PEC water splitting. The thickness of the double laminated RG/Cu_2S/RG/GO nanofilms can be controlled by the SILAR technique to gain the maximum hydrogen production efficiency. And a conformal coating can be achieved through a dip-coating method. Among these materials, Cu_2S presents relatively high electrocatalytic activity in polysulfide redox system (S^{2-}/S_x^{2-}) [23]. A stepwise structure of band-edge levels in the RG/Cu_2S/RG/GO electrode was constructed. On the basis of a stepwise structure of RG/Cu_2S/RG/GO, the best photoelectrochemical performance with relatively high photocurrent density of 1.98 mA/cm^2 was obtained, which is due to the improved absorption and appropriate energy gap structure, implying a potential application for PEC water splitting.

2. Experimental

2.1. The synthesis of reduced graphene

The synthesis of RG involved the oxidation of the graphite and the reduction of GO. An improved Hummers method for the preparation of GO was described. GO nanosheets were directly reduced through the cyclic voltammetric reduction to get RG. It was a simple, low-cost, efficient and environmental friendly electrochemical method to produce RG films. In addition, by combining the electrochemical technique with a dip-coating method, the synthesis of large-area RG films could be achieved on ITO glass.

2.2. Fabrication of double laminated RG/Cu_2S/RG/GO nanofilms

By combining the SILAR technique with a dip-coating method, the double laminated RG/Cu_2S/RG/GO nanofilmes could be obtained. It started with cleaning ITO glass substrates ultrasonically. The ultrasonic treatment was 0.5 h in acetone, iso-propyl alcohol and absolute ethanol in sequence. A GO layer was then deposited onto an ITO glass by dip-coating method. The thickness of GO could be increased by repeating the dip-coating cycles and the GO layers were dried in the open air.

The Cu_2S layer was coated with the GO by the SILAR technique. Typically, the ITO glasses with GO layers were successively immersed in two different aqueous solutions for 20 s respectively, one containing Cu^+ cations (50 mM CuCl) and the other containing S^{2-} anions (50 mM $Na_2S{\bullet}9H_2O$). Between each immersion step, the samples were rinsed with deionized water for several times to remove excess ions that were weakly bound to the GO surfaces. The incorporated amount of Cu_2S could be increased by repeating the SILAR cycle and the samples were dried by drying oven. After that, another GO layer was deposited onto the ITO glass by dip-coating method. The GO/Cu_2S/GO samples were directly reduced through the cyclic voltammetric reduction to get RG/Cu_2S/RG nanosheets. At last, the double laminated RG/Cu_2S/RG/GO nanofilmes could be obtained by depositing GO layer onto the ITO glass, and were dried in the drying oven for 0.3 h at 60 °C.

2.3. Characterization of samples

The morphologies of the samples were characterized by SEM (HITACHI S-4800I field-emission SEM at an accelerating voltage of 100 kV) at different magnifications. Powder X-ray diffraction (XRD) patterns were performed on a Rigaku D/max-2500 using Cu $K\alpha$ radiation ($\lambda = 0.154059$ nm). Optical absorbance spectra of photoanodes films were examined by DU-8B UV–vis double-beam spectrophotometer. A photocurrent density–voltage (J–V) curve was measured using an electrochemical workstation (LK2005A, Tianjin, China), a three-electrode configuration, with graphene-based films on ITO as the working photoelectrode, saturated Ag/AgCl as reference electrode, and a platinum foil as counter electrode, respectively. The electrolyte was 0.1 M Na_2S aqueous solution without additive. Meanwhile, photocurrents were tested under the illumination of a xenon lamp (CHF-XM500, 100 mW/cm^2).

3. Results and discussion

3.1. Synthesis process and mechanism of double laminated RG/Cu_2S/RG/GO nanofilmes

The synthetic route for double laminated RG/Cu_2S/RG/GO nanofilms is schematically illustrated in Fig. S1. Firstly, the GO sheets were glued on ITO substrates by a dip-coating method as shown in Fig. S1(b). The Cu_2S thin films were composed of many Cu_2S nanorods as shown in Fig. S1(c). The sulfidation reaction could take place to produce Cu_2S during the process:

$$2Cu^+ + S^{2-} \rightarrow Cu_2S \text{ (nanorods)} \quad (1)$$

The samples were dried at about 60 °C to make Cu_2S nanofilms grow stronger on ITO glass. Different thicknesses of Cu_2S nanofilms could be obtained by repeating the SILAR cycles. In Fig. S1(d), the double laminated GO/Cu_2S/GO was obtained on the surface of the ITO glass after the second-dip-coating cycles and was directly reduced through the cyclic voltammetric reduction to get RG/Cu_2S/RG nanosheets. At last, the GO layer were deposited onto the ITO glass by dip-coating method and dried in the drying oven.

3.2. Morphology and properties of RG/Cu_2S nanofilms

As we can see in Fig. 1(a), SEM images of RG/Cu_2S with 10 SILAR cycles of Cu_2S are not continuous and uniform. They show a typical layered structure of RG. The structure of the RG sheet tends to shrink and the appearance of wrinkling regions is observed in detail. It was also clearly shown that the RG/Cu_2S film consists of Cu_2S nanorods and the average nanorod length is not uniform. They are not evenly distributed and the quantity is very small. In Fig. 1(b), SEM image of RG/Cu_2S with 15 SILAR cycles of Cu_2S can be observed. It shows a typical layered structure of RG, and the average nanorod length is more uniform than that in Fig. 1(a). The Cu_2S nanorods are more evenly distributed than that in Fig. 1(a). Fig. 1(c) exhibits the SEM of RG/Cu_2S with 20 SILAR cycles of Cu_2S. Fig. 1(c) clearly shows that the RG/Cu_2S consists of Cu_2S nanorods and the RG with a layered structure. There are many Cu_2S nanorods evenly distributed and the average nanorod length is uniform. The RG/Cu_2S with 20 SILAR cycles of Cu_2S have the best distribution of Cu_2S on the surface of RG nanosheets.

As shown in Fig. 2(a), it can be seen that blank-Cu_2S film consists of Cu_2S particles and the average diameter of Cu_2S particles is less than 200 nm. The as-deposited Cu_2S membranes are uniform. Fig. 2(b) clearly shows that the resultant RG/Cu_2S consists of Cu_2S nanorods and the wrinkling RG with a layered structure. The Cu_2S nanorods covered the RG films. We can see the clear shape of Cu_2S in the picture inset of Fig. 2(b). In contrast, the morphology of RG/Cu_2S nanofilm is obviously different from that of blank-Cu_2S nanofilms. The size of Cu_2S in RG/Cu_2S is bigger than that in blank-Cu_2S film. Fig. 2(c) clearly shows that the RG/Cu_2S/RG/GO

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