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In-situ growth of Cu_2ZnSnS_4 nanoparticles on thiol reduce graphene oxide for Cu_2ZnSnS_4-sensitized solar cells

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ABSTRACT

Cu_2ZnSnS_4 (CZTS) as a narrow band gap semiconductor had been used to couple with TiO_2 for enhancing the utilization of solar energy. In this article, the TiO_2-thiol reduce grapheme oxide (TrGO)-CZTS heterostructure is constructed via a facile in-situ solvothermal method. The in-situ solvothermal method could acquire the uniform particles sizes and no aggregation of CZTS by adjusting the sulfur source and reactant solvent. The formation mechanism of TiO_2-TrGO-CZTS structure and the combination behavior of TrGO and CZTS were proposed. The thiol groups in TrGO give the site for CZTS to grow and form the chemical bond which could stabilize the connection of CZTS and TrGO. The in-situ reaction CZTS composite electrode exhibited a better photoelectrochemical performance than the self-assemble CZTS.

1. Introduction

Titanium dioxide (TiO_2) has been widely applied to the areas of photocatalysis and photovoltaics owing to its remarkable photocatalytic activity, fantastic chemical stability, environmentally friendly and low cost [1–5]. While the applications of TiO_2 are hindered ascribed from the wide band gap (anatase ca. 3.2 eV, rutile ca. 3.0 eV) leading to the low utilization of solar energy. To solve these issues, some narrow band gap semiconductors, such as CdS [6,7], CdSe [8,9] and $CuInS_2$ [10,11], have been developed to couple with TiO_2. However, those toxic and rare elements limit the large scale applications.

Cu_2ZnSnS_4 (CZTS), which has attracted much attention because of its abundant and low toxic of the composition elements, possessing a characteristic of a direct band gap and high optical absorption coefficient [12]. Several methods have been proposed to synthesize CZTS thin films, such as direct current/radio-frequency magnetron sputtering deposition [13], thermal evaporation [14], pulsed laser deposition [15], spray pyrolysis deposition [16], electron beam evaporation [17], nanoparticle-based method [18], photochemical deposition [19], sol-gel deposition [20], screen-printing [21], and electrodeposition [22]. Especially, solvothermal method can control the composition and crystal-phase of CZTS nanocrystals [23,24]. Among the above methods, the self-assembled monolayer technique is common and convenient method to deposit CZTS on TiO_2 films. With this method, the deposition ratio of CZTS on the surface of TiO_2 is limited, leading to a huge recombination of electron. To absorb more CZTS and generate more electrons, our group has synthesized the TrGO to construct the hierarchical structure then assembled the composite into solar cell [25]. The TrGO could create more electrons and reduce charge recombination in TiO_2-TrGO-CZTS photoanode. However the agglomerations of CZTS nanoparticles have limited the charge transferring into the pores of TiO_2 film which cause the unsatisfied performance.

In this study, the CZTS was synthesized on the surface of TiO_2-TrGO through an effective in-situ solvothermal method for solving the agglomeration of CZTS appeared in the self-assembled technique. The combination behavior and formation mechanism of TrGO and CZTS were proposed. The size and deposition amount of pure CZTS, which have great influence for the properties, can be adjusted by varying the reactant solvent and sulfur sources. The high amount of generated electrons and poor recombination rate

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give the reason for the improvement of photoelectric chemical performance and photovoltaic performance.

2. Experimental sections

All chemicals were acquired from Sinopharm Chemical Reagent Co., Ltd (China) and were used directly without further purification. The TrGO and the TiO_2-TrGO coated on the FTO substrate were prepared by following previous works [25].

2.1. In-situ synthesis of TiO_2-TrGO-CZTS composite electrodes

Firstly, the precursor solution was prepared by dissolving and stirring 0.28 mmol $Cu(CH_3COO)_2\cdot H_2O$, 0.14 mmol $Zn(CH_3COO)_2\cdot 2H_2O$, 0.14 mmol $SnCl_4\cdot 5H_2O$ and 1.12 mmol thiourea in 35 mL solvent (water, DMF or ethanol) until clarification. Secondly, the TiO_2-TrGO coated on the FTO substrate was placed at the bottom of autoclave with an angle. Then, the precursor solution was added into the stainless autoclave (50 ml) and kept at 200 °C for 24 h under autogenously pressure. After cooling down to room temperature in the air, the sample was rinsed with ethanol and distilled water successively. As a consequence, the in-situ CZTS (IS-C) composite electrodes were constructed.

2.2. Self-assembled synthesis of TiO_2-TrGO-CZTS composite electrodes and preparation of solar cells

To be sensitized with CZTS, the TiO_2-TrGO coated on the FTO substrate was immersed in the methylbenzene suspension of CZTS powders (0.3 mmol/L) overnight. After clean and dry, the self-assembled CZTS (SA-C) electrodes were obtained. The details of the preparation of SA-C were illustrated in our group's recent work [25]. The preparation of CZTS powder is the same to recent work [26].

The sandwich-like CZTS sensitized solar devices with the I^-/I_3^- redox electrolyte inside were fabricated and platinum was used as counter electrode. The active area of solar cell was 0.5*0.5 cm^2.

2.3. Characterizations and measurements

The field-emission-scanning electron microscopy (FE-SEM, SU8010, HITACHI) was used to investigate the surface morphologies of different composite films. X-ray diffraction (XRD, Ultima IV, Rigaku) and Raman spectroscopy (Horiba Jobin Yvon HR800) were served to confirm the crystal structure of TiO_2-TrGO-CZTS samples. The chemical bond among the TiO_2, TrGO and CZTS were inspected by the FTIR spectrometer (670, Nicolet). The photoelectrochemistry measurement was conducted with a three-electrode experiment system while a platinum foil serving as the counter electrode and a saturated calomel electrode (SCE) acting as reference electrode (CHI660E electrochemical workstation, Chenhua, Shanghai). The photocurrent response was measured under intermittent and regular light irradiation at an electrode potential of 0 V vs. SCE. Electrochemical impedance spectroscopy (EIS) curves were recorded at the frequency range of 10^5–10^{-2} Hz with amplitude of 10 mV in the dark. Photovoltaic properties were evaluated by employing Keithley 2400 and the light source was offered by the Newport Oriel solar light simulator (Model: 91192).

3. Result and discussion

Some impurity phases, having great influence for the photoelectric property, will be generated easily in the process of synthesize CZTS. Therefore, the glancing angle X-ray diffraction (XRD) and Raman spectroscopy are served to analyze the phase composition of CZTS. It shows in Fig. 1(a) that the diffraction peaks at $2\theta = 28.5°$, 47.3° and 56.1° in pattern corresponded to the (112), (220), and (312) planes of kesterite CZTS (JCPDS, card no.26-0575). Furthermore, some secondary sulfide phases have the same diffraction peaks with those of the kesterite CZTS. Therefore, Raman spectroscopy is served to analyze the further structural information of the sample, as shown in Fig. 1(b). The Raman scattering peaks at 287 cm^{-1}, 338 cm^{-1} are in accordance with CZTS and no other peaks demonstrate the exist of other secondary sulfide phases in the samples.

To demonstrate the functional group and the existential state of CZTS in TiO_2-TrGO, the FTIR spectra are taken in addition and shown in Fig. 2. The spectrum of TiO_2-TrGO (red line) shows three peak signals at 884 cm^{-1}, 1095 cm^{-1} and 2576 cm^{-1} assigned to C—SH, C=S and S—H bond stretching vibration [27,28]. After combine with CZTS, the absorption bands exhibit apparently change (blue and purple line). Obviously, the signals representative of C—SH and S—H bond stretching vibration apparent reduce, indicating the change of functional group in TrGO. Notably, the new peak signals at 671 cm^{-1}, 932 cm^{-1}, 962 cm^{-1} and 981 cm^{-1} which indicates the C—S, S—C=S,S=C—O, and O—H bond stretching vibration are observed and in agreement with report [29,30]. It can be speculated that the appearance of C-S bond and the disappearance of S-H are formed by losing the Hydrogen element (H) in C—SH and S—H. Therefore, this result is caused by the addition of CZTS nanoparticles. The IS-C electrode shows the weaker peak signal of C—SH at 884 cm^{-1} and a stronger peak signal of C-S at 671 cm^{-1} than the sample which prepared through self-assemble technology. It can be considered that the solvothermal synthesis CZTS nanoparticles can replace the Hydrogen element in C—SH more easily.

In order to contrast with the morphology of CZTS nanostructure synthesizing through different methods, the FE-SEM images of the IS-C and SA-C electrodes are depicted in Fig. 3. As shown in Fig. 3(c) and (d), the agglomerate CZTS particles are easy to be observed on the surface of the SA-C electrode. It means that the self-assemble technique will lead to the agglomeration of CZTS particles. For the IS-C electrode just shown in Fig. 3(a) and (b), the distribution of CZTS particles is uniform and dispersive. This is the reason why the IS-C electrode exhibits the better photoelectric property (Figs. 5 and 6). Besides, it can be seen that the TrGO deposited on the TiO_2 surface presents plicate shapes both in the IS-C (Fig. 3(b)) and SA-C (Fig. 3(d)) electrodes.

The mechanism of in-situ reaction synthesis CZTS is proposed as follows and shown schematically in Fig. 4 ripening process. During the solvothermal process, the hydrogen sulfide (H_2S), which is produced through the reaction between the thiourea and the solvent, can reduced the Cu^{2+} ions into Cu^+ [31–33]. Then, the crystal nucleus of CZTS will be composed of Cu^+ and other ions in the solution. The in-situ crystal nucleus CZTS cover on the TrGO to form CZTS nano layer and the thiol groups on the TrGO as a bridge can link the TrGO and CZTS. The thiol groups have the priority for the CZTS to growth and crystallization comparing with other groups on the TrGO. Hence the homogeneous CZTS nanoparticles on the surface of TrGO were obtained through the in-situ solvothermal method.

The photoelectrochemical properties of different electrodes are tested via the transient photocurrent response measurement. The test was performed in 0.5 mol/L Na_2SO_4 aqueous solution with the irradiated intensity of 70 mW/cm^2. As exhibited in Fig. 5, for the IS-C electrode, 130 $\mu A/cm^2$ of current density is obtained during light on and it shows higher current density and stability than the SA-C electrode. For the SA-C electrode, the current density has the obvious decline at the beginning of light on. It is caused by agglomeration, leading to the recombination of charge. The little loading of CZTS on the surface of TrGO gives rise to the low current density.