In-situ growth of Cu₂ZnSnS₄ nanoparticles on thiol reduce graphene oxide for Cu₂ZnSnS₄-sensitized solar cells

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Abstract

Cu₂ZnSnS₄ (CZTS) as a narrow band gap semiconductor had been used to couple with TiO₂ for enhancing the utilization of solar energy. In this article, the TiO₂-thiol reduce graphene 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 TiO₂-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.

Keywords: CZTS, Thiol reduced graphene oxide, Solvothermal method, Photoelectrochemical performance.

Introduction

Titanium dioxide (TiO₂) 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 TiO₂ 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 CuInS₂ [10, 11], have been developed to couple with TiO₂. However, those toxic and rare elements limit the large

scale applications.

$\text{Cu}_2\text{ZnSnS}_4$ (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 give the reason for the improvement of photoelectric chemical performance and photovoltaic performance.

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].

In-Situ synthesis of TiO_2 -TrGO-CZTS composite electrodes

Firstly, the precursor solution was prepared by dissolving and stirring 0.28 mmol $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$, 0.14 mmol $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$, 0.14 mmol $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ 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.

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 $0.5 \times 0.5 \text{ cm}^2$.

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).

Result and discussion

Some impurity phases, having great influence for the photoelectric property, will be generated easily in the process of synthesizing 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 $2\theta = 28.5^\circ$, 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 the Fig. 3(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 Fig. 3(b), the distribution of CZTS particles is uniform and dispersive. This is the reason why the IS-C electrode exhibits the better photoelectric property (Fig. 5 and Fig. 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 $0.5\text{ mol/L Na}_2\text{SO}_4$ aqueous solution with the irradiated intensity of 70 mW/cm^2 . As exhibited in Fig .5, for the IS-C electrode, $130\text{ }\mu\text{A/cm}^2$ 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.

The current density-voltage (J-V) curves and the corresponding photovoltaic parameters of CZTS sensitized solar cell device are listed in Fig. 6(a) and Table 1. For all electrodes, the V_{oc} values show no obvious difference due to the same fermi energy of TiO_2 and electrolyte. As we know, the electron lifetime and electron transfer rate constant would influence the J_{sc} . The agglomeration of CZTS will lead to the recombination of photoelectron and generate less photoelectron. Hence the higher efficiency of 0.158% is acquired for the IS-C electrode, which increased by 18% compared with the SA-C electrode.

Electrochemical impedance spectroscopy (EIS) was implemented based on different photoanodes to analyze the dynamics of interfacial charge transfer process. Semicircles in the Nyquist plots can reflect the charge transfer procedure and the charge transfer resistance value of samples can be confirmed with diameters of the semicircles. It can be found from Fig. 6(b) that, in intermediate frequency region, the IS-C electrode has bigger radius than the SA-C one, which demonstrates a quicker charge transfer procedure at the TiO_2 -electrolyte interface. The result confirms that uniform distribution provide a smaller charge transfer resistance and higher electron mobility. The better property of photoanodes can be supported by the above FE-SEM images and the photocurrent response results.

The influence of solvothermal solvent for in-situ synthesis CZTS

Solvent plays an important role in the solvothermal reaction and has a great influence on the composition of products. In this part, the solvent-dependent detailed morphology of IS-C electrode is revealed in Fig. 7(a), 7(b), and 3(b). As shown in the picture, the particles sizes have no obvious difference and the sample with ethanol as solvent has the maximum deposition of CZTS. In general, the solvent with different surface tension have different wettability. Ethanol, possessing the lowest surface tension, has the higher wettability for TiO_2 -TrGO. It causes the benefit of nucleation

and growth for CZTS on the surface of TrGO. For the water, the lack amount of CZTS on the surface is caused by the low wettability and higher surface tension. This result shows that the solvent has the lower surface tension can promote the nucleation and growth of CZTS.

The phase structure of the IS-C electrode which is synthesized with different solvent is demonstrated in Fig. 7(c). The diffraction peaks at $2\theta=28.5^\circ$ and 47.3° are also observed in curves and the extra diffraction peaks at $2\theta=31.8^\circ$ is appeared, indicating the CuS phase is synthesized in solvothermal process. The reason why generating the CuS phase in the process of solvothermal reaction is that the weak reducibility of water cannot make reduction of Cu^{2+} into Cu^{1+} in the CZTS synthetic process. Fernandes [34] points out that the undesirable secondary phases can make great influence of the kesterite CZTS crystal growth processes. The same result was obtained from the Raman spectrum analysis as shown in Fig. 7(d). The peaks at 264 cm^{-1} demonstrate the existence of CuS phase in the sample with water as solvent. The result of XRD and Raman reflect that both ethanol and DMF can synthesis the CZTS without other metastable phases.

The electrochemical property and photoelectric property of different electrodes are obtained from the Fig. 8(a) and 8(b). The transient measurements as shown in Fig. 8(a) reveals that ethanol as the solvent has the highest current density than others. For water as the solvent, the worse photocurrent and weak stability is observed during light on, with only $50\text{ }\mu\text{A}/\text{cm}^2$ of current density. It can be deduced that the CuS phase has reduced the generation of photo electron and increased the recombination of charge. For DMF, the current density is instability and gradually reducing. The lack deposition of CZTS reduces the generation of photocurrent and results the low current density. Comparing with three samples, the amounts of CZTS particles on TrGO have great influence on the current density. The more CZTS particles loading on the TrGO, the higher current density is obtained. The J-V curves of CZTS sensitized solar cell device on account of different solvent are shown in Fig. 8(b). The detailed photovoltaic parameters are summarized in Table 2. In accordance with prediction, the solar cell which is ethanol as the solvent shows the highest efficiency and J_{sc} . The

above result shows that the purity and capacity of CZTS have the great influence for the photo-electricity of the electrodes.

The influence of sulfur source for in-situ synthesis CZTS

The sulfur-dependent detailed morphology of the IS-C electrodes is shown in Fig. 9(a) and 9(b). It shows that the morphology of CZTS is sphere-like and nanosheet and the structure size is approximately 200 nm. Comparing with Fig. 3(b), the ten times particle sizes of CZTS and serious agglomeration can be observed. This result is mainly caused by the different release rates of sulfur ions between sulfur powder and thiourea. For sulfur powder which has lower release rate of sulfur ions in the solvent, the nucleation and crystallization rates of CZTS are carried out slowly and leads to the large size of CZTS particles. The XRD pattern and Raman spectra are shown in the Fig. 9(c) and 9(d). As shown in the Fig. 9(c), the diffraction peak of FTO, TiO_2 and CZTS can be seen. According to analyze the Raman spectra in Fig. 9(d), there is no peak about the impurity phases. By analyzing the XRD pattern and Raman spectra, it is revealed that the pure kesterite CZTS nanostructure is obtained in the both sulfur source.

Fig. 10 shows the electrochemical property and photoelectric property of two electrodes. As exhibited in Fig. 10(a), with sulfur powder as source, the current density has an obvious increase process and the maximum value is approximately $110\mu\text{A}/\text{cm}^2$ during light on. The result shows that the large particles size of CZTS will reduce the electrons transport and generation rate. As the electrodes are assembled to the solar cell, the Fig. 10(b) demonstrated the J-V curves of CZTS sensitized solar cell device and the corresponding photovoltaic parameters are summarized in Table 3. In accordance with prediction, the solar cell which is the thiourea as the sulfur source shows the highest efficiency and J_{sc} . The above result shows that the particles sizes of CZTS have the great influence for the current density and then influence the photoelectric property.

Conclusion

In summary, the CZTS nanoparticles were fabricated on the surface of TiO_2 -TrGO through a feasible in-situ solvothermal method. Compared with the SA-C, the IS-C

had the uniform distributions. The IS-C electrodes exhibited better power conversion efficiency of 0.158% which was improved by 18%, compared with the SA-C electrodes. In such configuration, the thiol groups on the TrGO not only play a role in the transmission of electrons, but also acts as a site for the growth of CZTS and stabilized the connection of CZTS and TrGO. Moreover, the sulfur source and reaction solvent have influence on the size and deposition amount of CZTS nanostructure.

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Tables

electrodes	V _{oc} (V)	J _{sc} (mA/cm ²)	FF (%)	efficiency
SA-C	0.560	0.411	57.6	0.133
IS-C	0.582	0.479	56.8	0.158

Table 1 photovoltaic performance of CZTS sensitized solar devices with different electrodes

samples	V_{oc}(V)	J_{sc}(mA/cm²)	FF (%)	efficiency
Water	0.563	0.263	0.531	0.078
DMF	0.578	0.401	0.559	0.129
Ethanol	0.582	0.479	0.568	0.158

Table 2 photovoltaic performances of CZTS sensitized solar devices with different reaction solvent

samples	Voc(V)	Jsc(mA/cm²)	FF (%)	efficiency
Sulfur as source	0.579	0.432	54.9	0.137
Thiourea as source	0.582	0.479	56.8	0.158

Table 3 photovoltaic performances of CZTS sensitized solar devices with different reaction sulfur source

Figures

Fig. 1 XRD pattern (a) and Raman spectrum (b) of the TiO₂-TrGO-CZTS

Fig. 2 FTIR spectra of $\text{TiO}_2\text{-TrGO}$ (red line) and $\text{TiO}_2\text{-TrGO-CZTS}$ which are synthesized by in-situ solvothermal reaction (blue line) and self-assemble technology (purple line)

Fig. 3 FE-SEM images of the IS-C (a, b) and SA-C (c, d) electrodes

Fig. 4 Schematic illustrations for the growth of CZTS by solvothermal reaction

Fig. 5 The transient photocurrent-time measurement of different electrodes

Fig. 6 Current density-voltage (J-V) curves (a) and Nyquist plot (b) of CZTS sensitized solar cells with different electrodes

Fig. 7 FE-SEM images of the IS-C electrodes with DMF (a) and water (b) as solvent, XRD pattern (c) and Raman spectra (d) of the IS-C electrodes synthesized with different solvents

Fig. 8 The transient photocurrent-time measurement (a) of the IS-C electrodes synthesized with different solvents and the current density-voltage (J-V) curves (b) of CZTS sensitized solar cells with the different IS-C electrodes

Fig. 9 FE-SEM images of the IS-C electrodes with sulfur powder (a, b) as sulfur source, XRD pattern (c) and Raman spectra (d) of the IS-C electrodes synthesized with different sulfur sources

Fig. 10 The transient photocurrent-time measurement (a) of the IS-C electrodes synthesized with different sulfur sources and the current density-voltage (J-V) curves (b) of CZTS sensitized solar cells with the different IS-C electrodes