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Synthesis of Cu₂ZnSnS₄ thin film from mixed solution of Cu₂SnS₃ nanoparticles and Zn ions

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Abstract: The Cu₂ZnSnS₄ thin film was prepared by a facile solution method without vacuum environment and toxic substance. The formation mechanism of the film was studied by transmission electron microscopy (TEM), X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS), and Raman scattering measurements. Through cyclic voltammetry and photo-electricity tests, the electrocatalytic activity of the prepared film as the counter electrode of dye-sensitized solar cell was also studied. The results show that the mixed precursor solution mainly consists of Cu₂SnS₃ nanoparticles and Zn ions. After 550 °C annealing process on the precursor film prepared from the mixed solution, Cu₂ZnSnS₄ thin film is obtained. Besides, it is found that the prepared Cu₂ZnSnS₄ thin film has the electrocatalytic activity toward the redox reaction of I₃⁻/I⁻ and the dye-sensitized solar cell with the prepared Cu₂ZnSnS₄ thin film as the counter electrode achieves the efficiency of 1.09%. Key words: Cu₂ZnSnS₄ thin film; Cu₂SnS₃ nanoparticle; Zn ion; electrocatalytic; dye-sensitized solar cells

1 Introduction

Copper zinc tin sulfide (Cu_2ZnSnS_4) is the $I_2-II-IV-VI_4$ quaternary compound semiconductor. All constituents in Cu_2ZnSnS_4 are abundant in the crust of the earth (Cu: 50×10^{-6} , Zn: 75×10^{-6} , Sn: 2.2×10^{-6} , S: 260×10^{-6}) and are nontoxic. It not only has an appropriate energy gap (1.5 eV) and high absorption coefficient (over 1×10^4 cm⁻¹ in visible wavelength region) for solar cell application [1], but also has an excellent catalytic activity for a variety of chemical and electrochemical reactions [2,3]. So, it has attracted much attention in these years.

Many researches have reported the preparation of Cu_2ZnSnS_4 thin films via vacuum and non-vacuum methods such as evaporation [4], sputtering [5], pulsed laser deposition [6], sol-gel [7], successive ionic layer adsorption and reaction [8], electrodeposition [9], and particle-ink coating method [10–12]. Compared with vacuum methods, non-vacuum methods have the advantage of low fabrication cost. TANAKA et al [7]

first prepared Cu₂ZnSnS₄ thin films by spin-coating a sol-gel precursor solution containing Cu, Zn and Sn metal salts in 2-methoxyethanol solvent. SCRAGG et al [13] made Cu₂ZnSnS₄ thin films on Mo substrates using sequential electrodeposition of constituents metals Cu, Zn and Sn. SHINDE et al [14] reported a novel chemical successive ionic layer adsorption and reaction (SILAR) technique for Cu₂ZnSnS₄ thin films formation by sequential immersion of the substrate into the cationic precursor solutions of CuSO₄, ZnSO₄, SnSO₄ and the anionic precursor solution of thioacetamide. TODOROV et al [15] prepared Cu₂ZnSnS₄ thin films using an hybrid solution-particle approach where the slurry consists of Cu-Zn-Sn chalcogenide in hydrazine. GUO et al [10] reported the synthesis of Cu₂ZnSnS₄ nanoparticles in oleyamine. ZHOUG et al [11] synthesized high quality Cu₂ZnSn(S,Se)₄ film from the aqueous nanoink which consists of the Cu/Zn sulfide nanoparticles with $Sn_2S_6^{4-}$ and $Sn_2S_7^{6-}$ as self-component ligands.

Despite many methods have been adopted to prepare the Cu_2ZnSnS_4 film, the preparation of the Cu_2ZnSnS_4 film from mixed solution of Cu_2SnS_3

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nanoparticles and Zn ions has not been studied. As the preparation of the mixed (precursor) solution is simple and does not need vacuum environment, high temperature and any extremely toxic substance such as hydrazine and toluene, it is a low-cost and environmentally-friendly technology which is appropriate for industrial production. The formation mechanism of Cu₂ZnSnS₄ thin films from the mixed solution is studied. Moreover, the prepared Cu₂ZnSnS₄ thin film is applied as the counter electrode in dye-sensitized solar cell (DSSC).

2 Experimental

A typical synthesis process for the preparation of Cu₂ZnSnS₄ thin films from the mixed solution of Cu₂SnS₃ nanoparticles and Zn ions is as follows. First, 0.068 g CuCl₂·2H₂O, 0.048 g SnCl₂·2H₂O and 0.055 g ZnCl₂ are mixed and dissolved in 50 mL ethylene glycol at 165 °C. Then, 0.25mL mercapto-acetic acid is dropped into the solution and the color of the solution changes from green to black quickly. After stirring for 0.5 h, the precursor solution of nanoparticles and metal ions is obtained. Second, the precursor solution is drop-coated onto a Mo or glass substrate. Finally, the prepared precursor thin film is annealed in sulfur atmosphere at 550 °C to obtain the Cu₂ZnSnS₄ nanoparticals thin films. The Cu₂ZnSnS₄ thin films deposited on Mo substrates are used as counter electrodes in dye-sensitized solar cells (DSSC) which are assembled according to Refs. [16,17].

The nano-porous TiO_2 films are fabricated by pasting the colloid containing 25 nm TiO_2 nanoparticles on the fluorine-doped tin oxide (FTO) substrates, followed by sintering at 500 °C for 30 min. The sintered films are then dipped in a N719 solution for 12 h to allow the dye to adsorb on the innersurfaces of the nano-porous films. Then, the films are rinsed in ethanol and dried. Finally, iodine-based electrolyte (the electrolyte solution consists of 0.04 mol/L LiI, 0.03 mol/L I₂, 0.1 mol/L GuSCN (Guanidinium thiocyanate), 0.5 mol/L TBP(4-tert-Butylpyridine), 1 mol/L PMII (1-Methyl-3-propyl imidazolium iodide) in acetonitrile and propylene carbonate (V:V=1:1)) is dropped onto the films and these films are assembled with the Cu₂ZnSnS₄ thin film as counter electrodes to obtain DSSC samples.

The nanoparticles of the mixed precursor solution are purified by centrifugation. Then, the precipitated nanoparticles are collected and studied by transmission electron microscopy (TEM). The crystallographic properties of the prepared thin films are characterized by X-ray diffraction (XRD, Rigaku3014) and Raman spectrometer (LabRAM ARAMIS). The surface morphology and the composition of the films are analyzed by a field-emission scanning electron microscope (SEM, FEI Quanta-200) equipped with an energy dispersive X-ray spectroscopy system (EDS, EDAX-GENSIS60S). The cyclic voltammetry (CV) study is carried out in a three-electrode system on PARSTAT 4000 (AMETEK.) with a pure graphite plate as the counter electrode, a Ag/Ag^+ electrode as the reference electrode and the prepared Cu₂ZnSnS₄ film as the working electrode in an acetonitrile solution containing 10 mmol/L LiI, 1 mmol/L I2, and 0.1 mmol/L LiClO₄ at a scan rate of 50 mV/s. The current densityvoltage $(J-\varphi)$ characteristics of the DSSC with the prepared Cu₂ZnSnS₄ thin film as the counter electrode are measured using a Keithley 2400 source meter under simulated sunlight (100 mW/cm², AM 1.5).

3 Results and discussion

3.1 Characteristics of mixed precursor solution

To study the composition of the mixed precursor solution, the solution is centrifuged and the precipitate is collected and analyzed by TEM. Figure 1(a) shows the low-magnification TEM image of the nanoparticles with irregular shape. It indicates that the crystallinity of the



Fig. 1 TEM images (a, b) and SAED pattern (c) of Cu₂SnS₃ nanoparticles

nanoparticles is low which may be due to the low prepared temperature for the precursor solution. Despite of this, it would not affect the preparation of the Cu₂ZnSnS₄ thin film finally. The high-resolution TEM (HRTEM) image (Fig. 1(b)) illustrates the nanoparticles surface and lattice fringes with interplanar spacings of 3.13 and 3.34 Å that can be ascribed to the $(1\overline{3}1)$ and (131) planes of Cu₂SnS₃, respectively. The selected area electron diffraction (SAED) pattern shown in Fig. 1(c) matches with the structure of Cu_2SnS_3 (JCPDS: 35-0684), as indicated via the diffraction spots corresponding to $(1\overline{3}1)$, $(2\overline{4}3)$ and (304) planes. Figure 2 shows the XRD pattern of the film consisted of precipitated nanoparticles. The peaks at 26.89°, 28.9° and 47.79° are corresponding to (131), (131) and Cu_2SnS_3 (2010) planes of (JCPDS:35-0684), respectively. This result is in accord with the TEM results. To further confirm the composition of the mixed precursor solution, the EDS measurements are performed on the films prepared by the precursor solution and precipitated nanoparticles, respectively. The main composition of the film prepared by the precipitated nanoparticles is 34.66% Cu, 14.22% Sn and 47.64% S (mole fraction). Besides, there is a little amount of Cl (3.01%) and Zn (0.77%) which could be considered as the ion residues that are not washed off completely. The mole ratio of Cu/Sn/S is about 2:1:3 matching the composition ratio of Cu₂SnS₃. The main composition of the film prepared by the mixed precursor solution is 21.76% Cu, 10.92% Sn, 49.99% S, 6.69% Cl and 10.76% Zn. The content of Zn is the dominating difference between two films. This indicates that the precursor solution may mainly consist of two parts. One is nanoparticles Cu₂SnS₃ and the other is Zn ions in solvent.

3.2 Annealing process of prepared film

Figure 3(a) shows the XRD patterns of films prepared by the precursor solution sulfurized at 350, 450 and 550 °C. From the XRD patterns, we can observe the peaks at 28.38°, 47.45° and 55.95°. As the structures of Cu₂ZnSnS₄ and Cu₂SnS₃ are very similar, so they have the close XRD peaks at these positions and it is difficult to distinguish the origin of these peaks only by XRD measurement. Thus, the films are further examined using Raman technology. After being sulfurized at 350 °C, from the Raman spectrum of the same film (Fig. 3(b)), there are two obvious peaks at about 336 and 338 cm⁻¹ corresponding to Cu_2SnS_3 and Cu₂ZnSnS₄, respectively [18,19]. This indicates that the peaks at 28.38°, 47.45° and 55.95° of the corresponding XRD pattern belong to the planes of Cu₂SnS₃ (JCPDS: 35-0684) and Cu₂ZnSnS₄ (JCPDS: 26-0575). The



Fig. 2 XRD pattern of film prepared by precipitated nanoparticles

generation of Cu₂ZnSnS₄ is probably due to the Zn atoms diffusion into Cu₂SnS₃ lattice in the sulfur atmosphere which agrees with other reports [20]. But as the sulfurized temperature is low, Cu₂SnS₃ cannot be totally reacted and translated to Cu₂ZnSnS₄ [21]. After being sulfurized at 450 °C, the XRD peaks of the prepared film at 28.38°, 47.45° and 55.95° become intense compared with those of film sulfurized at 350 °C. This is because annealing temperature higher improves the crystallization of the film. Emerging peaks at 15.13° and 31.86° corresponding to the (001) plane of SnS₂ (JCPDS:23-0677) and the (200) plane of Cu₂S (JCPDS:30-0505), respectively, are also observed. Moreover, from the Raman spectrum of the film (Fig. 3(c)), it is observed that the peak at 338 cm^{-1} corresponding to Cu₂ZnSnS₄ appears and the peak at 336 cm⁻¹ corresponding to Cu₂SnS₃ disappears. This indicates that the XRD peaks at 28.38°, 47.45° and 55.95° are corresponding to Cu₂ZnSnS₄ only. Besides, a new peak at 313 cm^{-1} corresponding to SnS₂ is observed [22]. According to the results of XRD patterns and Raman spectra, it indicates that the decomposition of the residual Cu₂SnS₃ introduces other two second phases such as Cu₂S and SnS₂. The formation mechanism of Cu₂SnS₃ has been reported according to the reversible reaction [23,24]:

$$Cu_2S+SnS_2 = Cu_2SnS_3$$
(1)

But as SnS_2 is instable, it would easily decompose into SnS which vanishes as gas above 400 °C [25,26]. This leads the reaction above reversed towards the decomposition reaction of Cu_2SnS_3 which introduces the second phases Cu_2S and SnS_2 . Utilizing the EDS measurement, it is found that Zn/Sn mole ratio of sample sulfurized at 450 °C increases to 1.07:1 compared with 0.99:1 of the precursor film. The increase of Zn/Sn mole



Fig. 3 XRD patterns (a) and Raman spectra (b-d) of films prepared by precursor solution sulfurized at 350 °C (b), 450 °C (c) and 550 °C (d)

ratio indicates Sn loss, which verifies our speculation. After being sulfurized at 550 °C, the XRD peaks at 18.2°, 28.5°, 32.9°, 47.3°, 56.1°, 69.16° and 76.48° of the prepared film become more intense. The sharp and strong major peak is an indication of the good crystalline quality of the film. From the Raman spectrum of the same film (Fig. 3(d)), an obvious major peak at 338 cm^{-1} and a minor peak at 289 cm⁻¹ corresponding to Cu₂ZnSnS₄ can be clearly seen and no other of characteristic peaks impurity phases are observed [19,27]. So, the seven main XRD peaks mentioned above reflected the (101), (112), (200), (220), (312), (008) and (332) planes of kesterite Cu₂ZnSnS₄. The disappearance of the second phases Cu₂S and SnS₂ is likely due to the reaction of Cu₂S, SnS₂ and Zn atoms in sulfur atmosphere at relatively high temperature forming the single Cu₂ZnSnS₄ phase which is similar with the hybrid solution-particle approach for the preparation of Cu₂ZnSnS₄ using Cu-Zn-Sn chalcogenide [28]. The composition ratio of the film sulfurized at 550 °C is n(Cu)/n(Zn+Sn)=0.92:1, *n*(Zn)/*n*(Sn)=1.1:1 (25.06% Cu, 14.34% Zn, 13.01% Sn and 47.59% S) approaching the composition ratio of the high-quality Cu₂ZnSnS₄ thin film.

Figure 4 shows the SEM images of Cu₂ZnSnS₄ thin films after being sulfurized at 350, 450 and 550 °C. After being sulfurized at 350 °C, no obvious large particles can be observed because the film is poorly crystalline and there are some residual organics undecomposed on the surface of the film. After being sulfurized at 450 °C, obvious nanostructures are observed which mean the improvement of the crystalline and the decomposition of the residual organics in the film. Despite of it, the surface morphology of the film is not uniform. The particles are in different shapes like spherical and sheet, and different sizes ranging from 150 nm to 2 µm. This is because of the hybrid phases of the film with SnS₂, Cu₂S and Cu₂ZnSnS₄, which is proved by the XRD patterns and Raman spectra. After sulfurization at 550 °C, the surface morphology of the film (Fig. 4(c)) becomes uniform and the size of the particles is around 300 nm.

According to the analysis above, we can speculate the formation process of the Cu_2ZnSnS_4 thin film by the facile solution method, as shown in Fig. 5. During the solution reaction process, $CuCl_2 \cdot 2H_2O$, $SnCl_2$ and mercapto-acetic acid would react to form Cu_2SnS_3 nanoparticles. In the sulfurized process at 350 °C, Cu_2SnS_3 nanoparticles, Zn atoms and S vapor would



Fig. 4 SEM images of Cu_2ZnSnS_4 thin films after being sulfurized at 350 °C (a), 450 °C (b) and 550 °C (c)

react to form Cu_2ZnSnS_4 and partial Cu_2SnS_3 unreacted exists in the film. When the sulfurized temperature rises up to 450 °C, Cu_2SnS_3 unreacted would decompose into SnS_2 and Cu_2S . In the sulfurized process at 550 °C, SnS_2 and Cu_2S would react with Zn atoms forming Cu_2ZnSnS_4 and the film of pure Cu_2ZnSnS_4 is achieved.

3.3 Characteristics of electrocatalytic activity of prepared Cu₂ZnSnS₄ thin film

Figure 6(a) shows the cyclic voltammetry of the I_3^{-}/I^{-} system with the Cu₂ZnSnS₄ thin film working electrode. One pair of oxidation and reduction peaks (Ox/Red) is observed which could be described by [29]

$$I_3^+ 2e \longrightarrow 3I^-$$
 (2)



Fig. 5 Formation mechanism of Cu_2ZnSnS_4 film from mixed solution of Cu_2SnS_3 nanoparticles and Zn ions



Fig. 6 Cyclic voltammetry of Cu₂ZnSnS₄ thin film counter electrode in acetonitrile solution of 10 mmol/L LiI, 1 mmol/L I₂, and 0.1 mmol/L LiClO₄ at scan rate of 50 mV/s (a), and $J-\varphi$ characteristics of DSSCs using Cu₂ZnSnS₄ thin film counter electrode (b)

From Eq. (2), we can observe that the voltage separation (φ_{pp}) and currents density separation (J_{pp}) of the two peaks(Ox/Red) are 522 mV and 1.44 mA/cm², respectively, which indicate that the Cu₂ZnSnS₄ thin film has the electrocatalytic activity toward the redox reaction of I₃⁻/I⁻ [30]. It is well known that the counter electrode (CE) is an indispensable component in DSSC, which catalyzes the redox couple (I₃⁻/I⁻) regeneration after

electron injection [31-33]. Since the Cu₂ZnSnS₄ thin film has the electrocatalytic activity toward the redox reaction of I_3/I^- , it is used as the counter electrode in DSSC. Figure 6(b) illustrates the photocurrent-voltage curves of the DSSC with the Cu_2ZnSnS_4 thin film counter electrode. The open-circuit voltage (φ_{oc}), short-circuit photocurrent density (J_{sc}) , fill factor (F_f) and efficiency (E) of the cells are 628 mV, 3.43 mA/cm^2 , 0.51 and 1.09%, respectively. This indicates that the Cu₂ZnSnS₄ thin film is an alternative material for the counter electrode of DSSC. Despite that the device with Cu₂ZnSnS₄ thin film as counter electrode could operate under simulated sun light, its efficiency is low due to the weak J_{sc} . It is well know that Cu_2ZnSnS_4 is a semiconductor and the prepared film is quite thick because of the dipping coating method, so, the electron transfer at counter electrode is limited. This leads to that the performance of the corresponding device is not as good as that of DSSC devices with the traditional conductive material platinum [34]. Despite of it, because of low cost, non-toxicity and abondent constituents of the prepared Cu₂ZnSnS₄ thin film, it is still a competitive material for the counter electrode of DSSC.

4 Conclusions

1) Without any vacuum equipment and extremely toxic substance, the mixed precursor solution composed of Cu_2SnS_3 nanoparticles and Zn ions is prepared.

2) According to the analysis of the annealing process, 550 °C is an appropriate temperature to prepare pure Cu_2ZnSnS_4 film from mixed precursor solution without any second phases.

3) The prepared Cu_2ZnSnS_4 thin film has the electrocatalytic activity toward the redox reaction of I_3^-/I^- .

4) The Cu₂ZnSnS₄ thin film can be applied as counter electrode of the DSSC which shows an efficiency of 1.09% with $J_{\rm sc}$ of 3.43 mA/cm², $\varphi_{\rm oc}$ of 628 mV and $F_{\rm f}$ of 0.51.

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利用 Cu₂SnS₃ 纳米晶和 Zn 离子混合 溶液制备 Cu₂ZnSnS₄ 薄膜

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摘 要:在非真空条件下,选用无毒原材料,采用溶液法制备 Cu₂ZnSnS₄薄膜。利用透射电镜、X 射线衍射、扫描电镜、能谱以及拉曼等研究手段,对 Cu₂ZnSnS₄ 薄膜的形成机理进行分析。通过循环伏安及光电测试,探讨 Cu₂ZnSnS₄ 薄膜作为染料敏化太阳能电池对电极的催化性能。结果表明:采用溶液法制备的 Cu₂ZnSnS₄ 混合前驱 体溶液主要由 Cu₂SnS₃ 纳米晶和 Zn 离子组成,将其滴涂成膜后,经过 550 ℃ 退火,最终可以得到 Cu₂ZnSnS₄薄膜;制备的 Cu₂ZnSnS₄ 薄膜对氧化还原对 I₃⁻/□具有一定的催化作用,将其应用于染料敏化太阳能电池的对电极取得了 1.09%的光电转化效率。

关键词: Cu₂ZnSnS₄薄膜; Cu₂SnS₃纳米晶; Zn 离子; 电催化; 染料敏化太阳能电池

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2108