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简易合成 Cu_2SnSe_3 作染料敏化太阳能电池对电极

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摘要: 采用简易溶剂热法合成直径为 150–250 nm 的 Cu_2SnSe_3 纳米颗粒. 以 Cu_2SnSe_3 “墨水”为前驱体采用滴落涂布法在掺氟二氧化锡基板上沉积 Cu_2SnSe_3 薄膜作为染料敏化太阳能电池(DSSC)对电极. 利用场发射扫描电镜(FESEM)、透射电镜(TEM)、X射线衍射(XRD)、拉曼光谱(Raman)、能谱仪(EDS)等对 Cu_2SnSe_3 纳米颗粒的形貌、结构和组成进行表征. 结果表明: 产物纯净无杂项且符合化学计量比. 以 Cu_2SnSe_3 为对电极的 DSSC 转化效率为 7.75%, 与铂对电极 DSSC 效率相当(7.21%). 研究表明, DSSC 的光电流密度和影响因子与 Cu_2SnSe_3 薄膜厚度密切相关, 这是由于不同厚度的 Cu_2SnSe_3 薄膜作对电极所对应的催化位置数目和电阻值不同. 电化学阻抗谱研究说明, Cu_2SnSe_3 因具有类似铂良好的电催化性能而适合作染料敏化太阳能电池对电极材料. 本文以 Cu_2SnSe_3 代替贵金属铂, 提供了一种廉价制备高效染料敏化太阳能电池对电极的新方法.

关键词: Cu_2SnSe_3 ; 纳米颗粒; 溶剂热; 对电极; 染料敏化太阳能电池

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Facile Synthesis of Cu_2SnSe_3 as Counter Electrodes for Dye-Sensitized Solar Cells

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Abstract: Cu_2SnSe_3 (CTSe) nanoparticles with diameters of 150–250 nm were synthesized by a facile solvothermal method. The nanoparticles drop-casted onto fluorine dope tin oxide (FTO) substrate were used as counter electrode in dye-sensitized solar cells (DSSCs). The morphology, structure and composition of the CTSe nanoparticles were characterized by field emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM), X-ray diffraction (XRD), Raman spectroscopy, and energy dispersive X-ray spectroscopy (EDS). The results indicated the formation of the nanoparticles with a single crystal phase and approximately stoichiometric composition. DSSCs fabricated with the CTSe-based counter electrodes exhibited a power conversion efficiency of 7.75%, which is similar to that of Pt-based devices (7.21%). The current–voltage curves of the DSSCs demonstrated that the thickness of the CTSe layer strongly influenced the photocurrent density and fill factor as a result of changes in the number of electrocatalytic sites and the resistance of the layers. Electrochemical impedance spectroscopy (EIS) measurements were performed and the results indicated that CTSe exhibited Pt-like electrocatalytic activity for the reduction of I_3^- to I^- in DSSCs. This work presents a new approach for expanding the possibilities for developing low-cost DSSCs that do not require expensive and rare Pt counter electrodes.

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Key Words: Cu_2SnSe_3 ; Nanoparticle; Solvothermal; Counter electrode; Dye-sensitized solar cell

1 Introduction

Dye-sensitized solar cells (DSSCs) have been considered as a credible alternative to the conventional silicon-related solar cells owing to their low cost and relatively high efficiency since initially reported by O'Regan and Grätzel in 1991.¹ Typically, the standard DSSC has a sandwich structure with a dye-sensitized mesoporous semiconductor photoanode, I^-/I_3^- redox electrolyte, and a catalytic counter electrode (CE).^{2,3} Among those, the CE is an important component which not only collects the electrons from external circuit but also catalyzes the reduction of I_3^- ions in electrolyte. The Pt thin layer was usually used as the CE due to its high catalytic activity and good conductivity.⁴⁻⁶ Nevertheless, both of the high cost (US \$50/gram) and low abundance ($3.7 \times 10^{-9} \text{ mg} \cdot \text{kg}^{-1}$) limit Pt as the CEs for large scale applications.⁷

Recently, a series of low cost alternatives were investigated, such as the carbon materials, conjugated polymers, inorganic materials.⁸⁻¹² Of those, inorganic compounds displayed superior plasticity and low preparation cost.¹³⁻¹⁵ Thereinto, the chalcogenides, a typical adsorbed layer of thin-film solar cells, received much attention as the CEs due to their excellent properties, such as good catalytic activity, relative good conductivity, stability in ambient conditions.^{16,17} Lin and his coworkers¹⁸ have synthesized $\text{Cu}_2\text{ZnSnS}_4$ (CZTS) nanoparticles (NPs) and fabricated CZTS-based CEs using spin-coated method for DSSCs. The resulting CZTS-based CEs exhibited an impressive electrocatalytic performance to promote the regeneration of I^- from I_3^- in electrolyte, yielding a solar energy conversion efficiency of 7.37%.¹⁸ Wu *et al.*¹⁹ demonstrated that $\text{Cu}_2\text{ZnSnSe}_4$ (CZTSe) CE had a high electrocatalytic activity, leading to a DSSC efficiency of 3.85%. Similar with CZTS or CZTSe, Cu_2SnSe_3 (CTSe) also belongs to the family of chalcogenide consisting of the three relative abundance elements, Cu ($50 \text{ mg} \cdot \text{kg}^{-1}$), Sn ($2.2 \text{ mg} \cdot \text{kg}^{-1}$), and Se ($0.9 \text{ mg} \cdot \text{kg}^{-1}$). The cost of raw material for CTSe is tens of times less than Pt.²⁰⁻²³ Moreover, the more components there are in a material system, the more difficult is the composition and phase control. Compared with CZTS or CZTSe, CTSe has simpler composition (only three elements), in favor of realizing better stoichiometricity. However, there were still few reports on the application of CTSe in DSSCs up to now.

In order to reduce the cost meanwhile maintain a high photovoltaic performance of DSSCs, it is very necessary to seek a candidate to replace expensive Pt. In this study, we synthesized CTSe NPs by a facile solvothermal method. Then, CTSe thin films were deposited on the fluorine dope tin oxide (FTO) substrates by a drop-casting method as counter electrode. We also assembled the CTSe-based DSSCs and systematically studied the effect of different thickness of the films as CEs on the solar cells.

2 Experimental

2.1 Synthesis of CTSe NPs

A solvothermal approach was employed to synthesize the Cu_2SnSe_3 NPs. Copper (II) sulfate (1 mmol, 99%, Aladdin), stannic chloride hydrated (0.5 mmol, 99%, Aladdin), and Se (1.5 mmol, 99.99%, Aladdin) were dissolved in distilled water (20 mL) under stirring, ethylenediamine monohydrate (40 mL, 98%) was added and magnetically stirred for 15 min, then the solution was transferred into a 100 mL stainless steel Teflon-lined autoclave. The autoclave was sealed and the mixture temperature was kept at 200 °C for 24 h, then autoclave was cooled to room temperature naturally. The mixture was then diluted with deionized water and precipitated with absolute ethyl-alcohol. The products were separated by centrifugation at $5000 \text{ r} \cdot \text{min}^{-1}$ for 10 min and the byproduct was decanted, then the precipitate was dispersed again in deionized water. The alternating precipitation and dispersion process was repeated for several times. The final dark product was collected after being vacuum-dried at 60 °C for 12 h. All reagents were used as received without any further purification.

2.2 Preparation of CEs and photoanodes for DSSCs

The FTO substrates (2 mm thickness, $15 \Omega \cdot \square^{-1}$) were first cut into $2 \text{ cm} \times 3 \text{ cm}$ and some of them serving as CEs were drilled two holes for injecting electrolyte. Then, all of the FTO substrates were ultrasonically cleaned for 30 min in a solution containing deionized water, acetone, and isopropanol, then rinsed with deionized water and ethanol and dried by nitrogen. The CTSe NPs were dissolved in isopropanol concentrated to $150 \text{ mg} \cdot \text{mol}^{-1}$ and ultrasonicated for 10 min to form uniform "ink". The "ink" was coated onto a thoroughgoing cleaned FTO substrate by a drop-casting method. The drop-casting area was controlled to be $1 \text{ cm} \times 1 \text{ cm}$ and the thickness of CTSe films was adjusted by the drop volume of "ink" with 0.1, 0.2, 0.3, and 0.4 mL. The films were vacuum-dried fully at room temperature for 24 h and subsequently annealed at 500 °C for 35 min in selenium vapor to obtain CTSe thin films as CEs. Pt-coated FTO glass was prepared by adopting a dipping-pulling method to coat the $5 \text{ mg} \cdot \text{mol}^{-1} \text{ H}_2\text{PtO}_6$ on the FTO glass and sintered at 390 °C for 20 min as Pt CE. TiO_2 NPs (P25, Degussa) were prepared by mixing 1 g P25, 2 mL distilled water, 0.3 g PEG 20000, and 3 drops of Triton X-100 in an agate mortar. Then, the mixture was grinded for 4 h.²⁴ TiO_2 NPs layer was spin coated on the FTO glass. After sintering at 500 °C for 3 h and cooling down to 80 °C, the TiO_2 NPs-coated FTO glass was immersed into TiCl_4 aqueous solution and kept in an oil bath at 70 °C for 1 h and sensitized in a $3 \text{ mg} \cdot \text{mol}^{-1}$ N719 ethanol solution for 24 h.²⁵

2.3 Assembly of DSSCs

The solar cell was assembled in a typical sandwich-type cell by placing an as-prepared CTSe-coated or Pt-coated FTO con-

ducting glass on the dye-sensitized photoanode. CE is separated from photoanode by applying a 60 μm thick thermal-plastic surllyn (DHS-SN1760) as the spacer then the assembled DSSC was clipped together and heated to 100 $^\circ\text{C}$ for 10 min for encapsulation. The redox electrolyte used in this study was an ionic liquid containing 0.50 $\text{g} \cdot \text{mol}^{-1}$ 4-*tert*-butylpyridine in the mixture of acetonitrile and valeronitrile (volume ratio, 85:15). A commercially available ionic electrolyte solution (Dalian Hepta Chroma) was injected between two electrodes through the holes of the CE. Finally, the holes were blocked with the melting thermal-plastic surllyn which was rewarmed by electric soldering iron and cooled down to room temperature.

2.4 Structural, morphological and photoelectrical characterization

The morphologies, crystal structure, and chemical constitution of the Cu_2SnSe_3 NPs and films were characterized by field-emission scanning electron microscope (FESEM, Hitachi S-4800, Japan), transmission electron microscopy (TEM, Jeol-2010, Japan), X-ray diffraction (XRD, Bruker D8 Advance, Germany), Raman spectrometry (Bruker Senterra, Germany), and energy dispersive spectrometer (EDS, Hitachi S-4800, Japan). The photocurrent density–voltage (J – V) measurements were carried out under illumination of 100 $\text{mW} \cdot \text{cm}^{-2}$ using a Keithley model 2420 digital source meter. A solar simulator was used to simulate sunlight by a 500 W xenon lamp light source fitted with an AM1.5G filter (Beijing Trusttech). The illumination intensity of 100 $\text{mW} \cdot \text{cm}^{-2}$ was calibrated with a standard monocrystalline silicon solar cell which passed the American Society for Testing and Materials (ASTM) calibration. Electrochemical impedance spectroscopy (EIS) analysis was conducted by using electrochemical test station (CHI660D) under an illumination intensity of 100 $\text{mW} \cdot \text{cm}^{-2}$.

3 Results and discussion

Fig.1(a, b) show the morphology of as-synthesized CTSe NPs by FESEM images with various magnifications. It could be seen that the CTSe NPs presented relatively uniform sphere shape with the diameter of 150–200 nm. Fig.1(b) shows a high-magnification FESEM image of CTSe NPs, it can be seen that the NPs are composed of many tiny nanocrystal and the surfaces are considerably rough, this can increase the specific surface

area of the NPs. Fig.1(c) displays the TEM images of CTSe NPs, the diameters of the NPs are about 150–250 nm, which are in accordance with the FESEM results. Some of the tiny nanocrystals with the size of about 20 nm can be seen from the edge of some NPs. The lattice fringe of 0.33 nm (Fig.1(d)) matches the spacing distance of (111) plane and agrees well with that determined from the diffraction peak at 27.15 $^\circ$ in XRD pattern. The NPs are well dispersed in isopropanol (inset of Fig.1(a)). This stable NP suspension remained during the whole observation period (15 days). The cross-sectional FES-EM images of the CTSe thin film after annealing are presented in Fig.2(a–d), increasing the drop volume (0.1, 0.2, 0.3, 0.4 mL) gives rise to an increase in film thickness, 2.2, 2.9, 3.4, 4.2 μm , respectively. Fig.2(e) displays the top-view FESEM image of CTSe films annealed at 500 $^\circ\text{C}$. As seen, the film is composed of many interconnected CTSe NPs. No any obvious change was observed in the morphology after annealing.

Fig.3 shows a typical XRD pattern of the annealed CTSe nanocrystals. The major XRD diffraction peaks appeared at 2θ of 27.15 $^\circ$, 45.08 $^\circ$, 53.42 $^\circ$, 65.65 $^\circ$, and 72.41 $^\circ$, which could be attributed to (111), (220), (311), (400), and (331) planes, respectively. All the diffraction peaks could be assigned to the crystal planes from standard structure of CTSe without any other peaks being observed (JCPDS No. 65-4145). Noted that all of the peaks were acute, suggesting that the films were crystallized well after annealing. On the basis of the XRD pattern, CZTSe has the following crystal structures: $\bar{I}43m$ cubic structure ($a=0.5684$ nm), which was in accordance with the data reported by the previous report.²⁶ Based on the calculation by Debye-Scherrer formula from XRD result, the nanoparticles are composed of numerous tiny nanocrystals with an average crystallite size of 21.5 nm, which are in accordance with the TEM results. Nevertheless, it was known that the SnSe had almost the same diffraction pattern with CTSe. That is to say, XRD data is insufficient to confirm the purity of the obtained products. To further confirm the phase structure, the Raman spectrum of the as-synthesized sample is shown in Fig.4. The Raman spectrum further confirmed that our CTSe has the cubic structure. As we know, the characteristic peaks of second-phase SnSe are positioned at 185.5 and 116 cm^{-1} .²⁷ Yet three main peaks appeared in Fig.4 at 278, 492.5, and 623 cm^{-1} , while no evidence of SnSe related peaks was found in the

Fig.1 FESEM images of CTSe NPs with (a) low and (b) high magnifications; (c) TEM and (d) HRTEM images of the as-obtained CTSe nanocrystals with the spacing distance of (111) plane

The NPs are well dispersed in isopropanol (inset in figure (a)).

Fig.2 Cross-sectional FESEM images of CTSe thin film with drop volumes of (a) 0.1 mL, (b) 0.2 mL, (c) 0.3 mL, and (d) 0.4 mL. Corresponding top view FESEM image of CTSe thin film after annealing as shown in (e).

Fig.3 XRD pattern of CTSe NPs after annealing

range. That suggested that the CTSe sample was of the single phase without any byproduct. Fig.5 indicates the compositional analysis of the as-synthesized CTSe after annealing. The result indicates that the atomic ratio of Cu:Sn:Se was approximately 1.97:1.06:3.00. Considering the error of the EDS detector (approximately $\pm 2\%$ (atomic ratio)), that ratio was almost stoichiometric. Thus, the obtained samples were demonstrated to be single phase and nearly stoichiometric.

Fig.6 shows the current density–voltage curves of DSSCs fabricated with different thicknesses of CTSe-based CE and Pt CE. The corresponding photovoltaic parameters were summarized in Table 1, including the short-current density (J_{sc}), the open-circuit voltage (V_{oc}), the fill factor (FF), and the power conversion efficiency (η). When the drop volume was 0.2 mL,

Fig.4 Raman scattering analysis of CTSe NPs after annealing

Fig.5 Elemental composition of Cu_2SnSe_3 NPs after annealing measured by EDS

Fig.6 Current density–voltage (J – V) characteristics of DSSCs with different thicknesses of Cu_2SnSe_3

CEs and Pt CE under AM1.5 sunlight illumination intensity of $100 \text{ mW} \cdot \text{cm}^{-2}$

a highest efficiency of $\eta=7.75\%$ was achieved with $J_{sc}=14.69 \text{ mA} \cdot \text{cm}^{-2}$, $V_{oc}=0.71 \text{ V}$, and $\text{FF}=72.95\%$. It is clear that the photocurrent density first increases from 13.39 to $14.69 \text{ mA} \cdot \text{cm}^{-2}$ with increasing the thickness of the thin film from $2.2 \mu\text{m}$ (drop volume 0.1 mL) to $2.9 \mu\text{m}$ (0.2 mL). However, while further increasing the thickness of the film to 3.4 and $4.2 \mu\text{m}$, the photocurrent density decreases significantly to 12.18 and $11.20 \text{ mA} \cdot \text{cm}^{-2}$, respectively. This may be due that the value of J_{sc} is influenced by the number of the electrocatalytic sites and different resistance in films with dissimilar thickness.²⁸ There are more electrocatalytic sites in thicker films, which would be beneficial to the electrocatalytic activity meanwhile larger re-

Table 1 Series resistance (R_s), charge transfer resistance (R_{ct}), short-current density (J_{sc}), the open-circuit voltage (V_{oc}), the fill factor (FF), and the power conversion efficiency (η) of DSSCs fabricated with different thicknesses of CTSe CEs and Pt CE under AM1.5 sunlight illumination intensity of $100 \text{ mW} \cdot \text{cm}^{-2}$

Drop volume mL	Thickness μm	R_s/Ω	R_{ct}/Ω	J_{sc} ($\text{mA} \cdot \text{cm}^{-2}$)	V_{oc}/V	FF/%	$\eta/\%$
Pt	0.5	16.45	10.05	13.10	0.77	71.48	7.21
0.1	2.2	18.85	7.50	13.39	0.72	71.99	6.94
0.2	2.9	21.11	5.34	14.69	0.71	72.95	7.75
0.3	3.4	23.38	4.21	12.18	0.71	74.12	6.41
0.4	4.2	26.19	3.59	11.20	0.70	75.26	5.90

sistance would be harmful for charge transport which is caused by more abundant grain boundaries and defects. When the thickness reached $2.9 \mu\text{m}$, we got a satisfactory result due to the synergic effects of the amount of electrocatalytic sites and the value of resistance. The FF increases from 71.99% to 75.26% with the increase of the film thickness. This is due that the CTSe film is composed of small interconnected nanocrystals and interspace (Fig.2(e)). With the increase in the film thickness, CTSe film has more contact area with electrolyte. Hence, thick CTSe-based CE can provides relatively larger amount of electrocatalytic sites which is beneficial to the electrocatalytic activity and leads to the increase of the FF.^{29,30}

In order to further clarify the photovoltaic behavior of the CE, the EIS measurement was performed. The Nyquist plots and the equivalent circuit were shown in Fig.7. The high frequency (corresponding to low Z') intercept on the real axis (Z' axis) represents the series resistance (R_s). The little semicircle in the high-frequency range results from the charge-transfer-resistance (R_{ct}) and the corresponding constant phase-angle element (CPE) at the electrolyte/CE interface.³¹ The large semicircle in the low-frequency range (corresponding to high Z') arises from the Nernst diffusion impedance of the I^-/I_3^- couple in electrolyte/dye/ TiO_2 interface. The values of R_s , R_{ct} obtained by

fitting the spectra in Fig.7 with an EIS spectrum analyzer are summarized in Table 1. The R_s of CTSe-based CEs were larger than that of the Pt-based CE, which was most likely due to the relatively large conductivity of Pt as compared to semiconductor CTSe. Furthermore, for the CTSe-based CEs, the R_s is increased with increasing the thickness. This is due to the increase of the distance of electron transport in the thicker CE. The R_{ct} of all Cu_2SnSe_3 -based CEs were less than that of Pt-based CE, indicating a superior catalytic property of Cu_2SnSe_3 . Note that as increasing the thickness of Cu_2SnSe_3 thin film, the R_{ct} is decreased. It is illustrated that thicker film has a better catalytic activity which may be due to more electrocatalytic sites provided. The EIS results agreed well with the current density–voltage curve. It suggested that the CTSe was excellent to be a candidate for replacing the conventional Pt-based CEs.

4 Conclusions

In summary, a facile solvothermal method was employed to synthesize CTSe NPs. The structure, morphology, and composition of the prepared NPs were characterized by various methods. XRD and FESEM illustrated that the CTSe NPs were cubic structure with the average size of 150–250 nm. Raman spectrometry and EDS indicated that CTSe NPs were single-phase and just about stoichiometric composition. Then a new structure CTSe film as CE was fabricated *via* a drop-casting process. The current density–voltage curves of DSSCs and the EIS measurement indicated that the obtained cells based on low-cost ternary CTSe exhibited a superior performance with the highest power conversion efficiency of 7.75%, which was similar to those conventional Pt-based ones (7.21%). Photocurrent density and fill factor were affected by the thickness of the film remarkably due to the difference of electrocatalytic sites and resistance. Considering the simple method and mild conditions, the CTSe-based film as a candidate is very promising to replace Pt-based CE by virtue of its great cost advantage.

Fig.7 Nyquist plots of the DSSCs with different thicknesses of CTSe CEs and Pt CE from EIS under AM1.5 sunlight illumination intensity of $100 \text{ mW} \cdot \text{cm}^{-2}$

The inset indicates an equivalent circuit used for fitting the EIS results, including the series resistance, charge-transfer resistance, and constant phase-angle element (CPE).

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