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Electrocatalytically active MoSe₂ counter electrode prepared *in situ* by magnetron sputtering for a dye-sensitized solar cell

Xueqin Cao, Hanfang Li, Guoran Li *, Xueping Gao

Institute of New Energy Material Chemistry, School of Materials Science and Engineering, Nankai University, Tianjin 300350, China

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ABSTRACT

Molybdenum selenide is a potential alternative to counter electrode of a platinum-free dye-sensitized solar cell (DSSC). In this work, an *in situ* magnetron sputtering method is developed to prepare MoSe₂ electrodes. The MoSe₂ electrodes obtained at various temperatures from 300 and 550 °C are used as counter electrode for a dye-sensitized solar cell. Photovoltaic measurement results indicate that the MoSe₂ electrodes prepared at 400 °C has the optimized performance, and the corresponding DSSCs provide an energy conversion efficiency of 6.83% which is comparable than that of the reference DSSC with platinum as counter electrode (6.51%). With further increasing the preparation temperature of the MoSe₂ electrodes, the corresponding DSSCs decrease gradually to 5.96% for 550 °C. Electrochemical impedance spectra (EIS) reveal that charge transfer resistance (R_{ct}) of MoSe₂ electrodes is rising with increase of the temperature from 400 to 500 °C, suggesting a downward electrocatalytic activity. Though the MoSe₂ electrode prepared at 550 °C show a reduced R_{ct} , its series resistance (R_s) and diffusion resistance (Z_w) increase obviously. Considering that MoSe₂ phase cannot be formed at 300 °C, it can be concluded that the prepared temperature as low as possible is favored for its final electrochemical performance. The results are very significant for developing low-cost and responsible counter electrodes for dye-sensitized solar cells.

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1. Introduction

A low-cost platinum-free counter electrode is undoubtedly important for developing economic dye-sensitized solar cells (DSSCs). In recent years, many kinds of materials such as carbonaceous materials [1–5], conductive polymers [6–9], and transition metal compounds [10–18], have been investigated to use as counter electrodes for DSSCs. Among the investigated alternatives, transition metal chalcogenides show excellent intrinsic electrocatalytic ability for electrode reaction on counter electrodes of DSSCs [19,20]. Moreover, transition metal chalcogenides are able to form transparent counter electrodes

with balance between electrical conductivity and optical transparency. Especially, molybdenum dichalcogenides i.e. MoS₂ [19] and MoSe₂ [20] have graphite-like layered structure that is helpful to improve active sites for reduction of triiodine ions on the counter electrodes.

Preparation of non-platinum counter electrodes usually employ two or more steps. Active materials are firstly prepared by chemical synthesis, and then the obtained materials are filmed on conductive substrates by spin-coating or doctor-blade coating, etc. to fabricate counter electrodes [21–24]. In these routes, besides the active materials, the film process usually has directly effect on the final electrode performance.

* Corresponding author. E-mail: guoranli@nankai.edu.cn

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Some *in situ* methods such as chemical bath deposition [25–27], chemical vapor deposition [28], and electrochemical deposition [29–32] are also developed to prepare transition metal chalcogenide counter electrodes. To compare with the conventional routes, these *in situ* methods are usually able to make better interface contact between active film and conductive substrate, reducing the interface resistance and improving electrochemical performance. Lee et al. [33] prepared the MoSe₂ electrode by the surface selenization of Mo-coated soda-lime glass with lower resistance. Chen et al. [34] obtained the MoSe₂/Mo electrode via *in situ* selenization of Mo films, in which the bottom Mo layer can act as conductive collector for electron extraction. Compared with these methods, magnetron sputtering method has advantages of simple equipment, easy control, large coating area and strong adhesion [4].

In this work, an *in situ* magnetron sputtering method is developed to prepare MoSe₂ counter electrodes. In the electrodes, MoSe₂ shows nanoplate-like morphology and forms a layer of active film with an average thickness of 1.3 μm . As counter electrode for a dye-sensitized solar cell, MoSe₂ electrodes prepared at 400 $^{\circ}\text{C}$ has relatively low charge transfer resistance (R_{ct}), and the corresponding DSSCs provide an energy conversion efficiency of 6.83% which is comparable with that of the reference DSSC with platinum as counter electrode (6.51%).

2. Experimental

2.1. Preparation of MoSe₂ counter electrode

The preparation process of MoSe₂ counter electrode is shown in Fig. 1. Transparent conductive glass (fluorine-doped tin oxide, FTO, 15 Ω/square , Nippon Sheet Glass) was used as substrate. Before used, FTO glass was cleaned up with deionized water, ethanol, and deionized water in turn. 0.5 g of Se powder (99.99%, Aladdin) was mixed with 5% aqueous solution of sodium carboxymethyl cellulose (CMC; 0.05 mL) and ground to a sticky mixture. A layer of Se film was made by doctor-blade method on the cleaned FTO substrate with a thickness of 50 nm (thickness of a layer of 3M tape). The as-prepared Se film was dried in the air, metal molybdenum was radio-frequency sputtered on the Se film when it drying, forming the Se-Mo film. In the process of sputtering, High purity argon (Ar) was used as the bombardment gas, and the sputter power is 80 W, radiofrequency sputtering 30 min in the vacuum pressure is 5×10^{-3} torr. Finally, the sample was calcined in a tubular furnace for 1 h at 300, 400, 450, 500, 550 or 600 $^{\circ}\text{C}$ separately with a heating rate of 5 $^{\circ}\text{C min}^{-1}$ under flow-

ing Ar atmosphere (80 ml min⁻¹). For the sake of comparison, pure Mo electrode was prepared in the same way. The preparation process is as shown in Fig. 1, and there is no process “a” when prepared the pure Mo electrode.

As a reference sample, the sputtering Pt counter electrode was obtained by purchase from Wuhan Lattice.

2.2. Preparation of photoanode

The cleaned FTO conductive glass was immersed into 40 mmol L⁻¹ TiCl₄ aqueous solution at 70 $^{\circ}\text{C}$ for 30 min, and then washed with water and ethanol. A commercial TiO₂ sol (20 nm, Wuhan Lattice) was coated on the FTO glass to a certain thickness by doctor-blade coating. The film was then heated in a muffle furnace at 130 $^{\circ}\text{C}$ for 8 min. After cooling to room temperature, doctor-blade coating the TiO₂ sol (200 nm, Wuhan Lattice) on the first layer, heated in a muffle furnace at 500 $^{\circ}\text{C}$ for 1 h. The obtained film was treated with TiCl₄ solution again, and then calcined at 500 $^{\circ}\text{C}$ for 0.5 h. Finally, the film was soaked in 0.3 mmol L⁻¹ ethanol solution of N719 (Solaronix SA) for 24 h.

2.3. Fabrication of DSSC

The DSSCs were assembled by clipping the TiO₂ photoanode and counter electrode together, and injecting the electrolyte into the aperture between the two electrodes. Surlyn 1702 was used as the spacer between the two electrodes. The liquid electrolyte contained 0.6 mol/L 1,2-dimethyl-3-propylimidazolium iodide (DMPII), 0.5 M 4-tert-butyl pyridine (4tBP), 0.05 mol/L I₂ and 0.1 mol/L LiI, with acetonitrile as the solvent. Solid paraffin was used as a sealant to prevent the electrolyte solution from leaking. The effective cell area was 0.20 cm².

2.4. Electrochemical measurement

Photocurrent density-voltage (J-V) characteristic curves, electrochemical impedance spectra (EIS) and cyclic voltammetry (CV) measured by Zahner IM6ex electrochemical workstation. The J-V characteristic of the DSSCs was illuminated under AM1.5 solar irradiations. The EIS measurements were carried out in a frequency range of 100 KHz to 100 mHz, with an AC modulation signal of 10 mV, and a bias DC voltage is -0.6 V. CV test was finished in the three-electrode system, metal Pt used as the counter electrode, an Ag/Ag⁺ electrode as the reference electrode, and counter electrode of DSSCs as working electrode. The electrolyte was 5 mmol/L LiI, 0.5 mmol/L I₂, 0.5

Fig. 1. Scheme of preparation process and section for MoSe₂ electrode.

mmol/L LiClO_4 dissolved in acetonitrile solution. And the scan rate was 50 mV s^{-1} when tested.

2.5. Characterization

The structure and morphology of the as-prepared materials were evaluated by X-ray diffraction (XRD, Rigaku MiniFlex II), scanning electron microscopy (SEM, SUPRA 55VP), and transmission electron microscopy (TEM, JEM-2010, JEOL).

3. Results and discussion

Fig. 2 shows the XRD patterns of FTO, Se-Mo-300, Se-Mo-400, Se-Mo-450, Se-Mo-500, Se-Mo-550, and the numbers represent the heat treatment temperature of the samples. All the patterns of the prepared samples contain the peaks of fluorine and tin oxide on account of FTO conductive substrates. In the case of Se-Mo-300, the diffraction peaks can be indexed, respectively, to crystalline selenium (JCPDS No. 1-848) and metallic molybdenum (JCPDS No. 44-1120). Clearly, this means that no reactions occur between the coating selenium layer and the sputtered molybdenum layer at 300°C . With increasing calcination temperature, Se-Mo-400 shows two diffraction peaks at $2\theta = 13.5^\circ$ and 31.6° , which can be indexed to (002) and (100) lattice planes of MoSe_2 (JCPDS No. 87-2419), respectively. The results reveals that a solid-solid chemical reaction occurs between selenium and metallic molybdenum, and MoSe_2 layer is *in situ* generated on the FTO substrate. Meanwhile, the very weak diffraction peak of (101) plane of selenium at $2\theta = 29.5^\circ$ imply existence of a small amount of selenium in the Se-Mo-400. When the calcination temperature increases to 450°C , all the diffraction peaks can be indexed to MoSe_2 , and no selenium or molybdenum is observed. With the calcination temperature rises to 550°C , the diffraction peaks of MoSe_2 become gradually strong, suggesting improved crystallinity. As a layered chalcogenide like MoS_2 , MoSe_2 similarly has (002) dominated plane as basal plane, and (100) plane in the vertical direction as edge plane. In details, the peak intensity ratios of (100) plane to (002) plane are different due to the different calcination temperatures. The ratio of (100)/(002) is 0.73, 1.1, 0.54 and 0.69 at 400, 450, 500, and 550°C , respectively. Ac-

Fig. 2. The XRD patterns of FTO, Se-Mo-300, Se-Mo-400, Se-Mo-450, Se-Mo-500, Se-Mo-550. The numbers in parentheses are indices of lattice planes.

cording to the previous results, the greater ratio means more electrocatalytically active sites for reduction of triiodide ions [19].

SEM and TEM of the Se-Mo-450 as the representative sample are performed to analyze morphology and structure details on the FTO substrate. Fig. 3(a) shows that Se-Mo-450 presents irregular particles with a size of $0.5\text{--}2 \mu\text{m}$. The irregular particles are formed by aggregation of MoSe_2 nanoplates, which is a classic morphology for layered metal dichalcogenides. Thickness of the MoSe_2 nanoplates is about 20 nm , and size of the plates is around $100\text{--}200 \text{ nm}$ (Fig. 3(b)). Fig. 3(c) shows the cross section of the Se-Mo-450 electrode. It is clear that the MoSe_2 layer is around $1.3 \mu\text{m}$ of thickness, and the nanoplates present relatively incompact but interwoven. This morphology is helpful for improving electrocatalytically active surface and infiltration of electrolyte. In addition, there is good contact between the MoSe_2 layer and FTO layer, indicating a low interface resistance. The TEM image shows the edge structure of a plate of MoSe_2 from Se-Mo-450 (Fig. 3(d)). The interplanar spacing is 0.63 nm in the edge, corresponding to the (002) plane of MoSe_2 , and the other lattice fringe spacing of 0.28 nm corresponds to the (100) plane of MoSe_2 .

Photocurrent density-voltage curves of DSSCs using Pt, Se-Mo-300, Se-Mo-400, Se-Mo-450, Se-Mo-500, and Se-Mo-550 as counter electrode are shown in Fig. 4, and the detailed photovoltaic performance parameters are listed in Table 1. In the case of Se-Mo-300, though the DSSC shows a relatively high V_{oc} , 0.791 V , the photoelectric conversion efficiency (PCE) is only 2.36% due to the poor fill factor (FF), 0.29 . This means that the metallic molybdenum and selenium in Se-Mo-300, in which no MoSe_2 is generated as shown in the XRD result, have poor electrocatalytic activity for reduction of triiodide ions [21]. The low electrocatalytic activity causes low charge transfer process on the counter electrode. Therefore, the electrons from the external circuit cannot be transferred to triiodine ions promptly, and stay on the counter electrode to result in increase of potential, which causes the high open voltage. Meanwhile, the low electrocatalytic activity means large charge transfer resistance that leads to the poor fill factor. The DSSCs using the MoSe_2 counter

Fig. 3. Surface SEM images (a, b) with different magnifications and cross-section SEM image (c), and TEM image (d) of Se-Mo-450.

Fig. 4. Photocurrent-voltage characteristic curves of DSSCs with Pt, Se-Mo-300, Se-Mo-400, Se-Mo-450, Se-Mo-500, and Se-Mo-550 as counter electrode.

Table 1

The detailed photovoltaic performance parameters of the DSSCs with different counter electrodes.

Electrode	J_{sc} (mA cm ⁻²)	V_{oc} (V)	H (%)	FF
Pt	13.37	0.773	6.51	0.63
Se-Mo-300	10.36	0.791	2.36	0.29
Se-Mo-400	13.95	0.763	6.83	0.67
Se-Mo-450	13.37	0.772	6.68	0.65
Se-Mo-500	13.39	0.773	6.55	0.63
Se-Mo-550	11.78	0.799	5.96	0.67

electrodes obtained at 400, 450 and 500 °C show the photoelectric conversion efficiency (PCE) of 6.83%, 6.68% and 6.55%, respectively. The results are comparable with that of the DSSC with Pt counter electrode (6.51%). The device with Se-Mo-550 electrode yields a reduced efficiency of 5.98%, and the one using Se-Mo-300 shows only the value of 2.36%. For Se-Mo-550, the corresponding low J_{sc} (11.78 mA cm⁻¹) is the main factor for the low efficiency. As known well, FTO substrate can be partially influenced when calcined at 550 °C.

EIS of the symmetric cells with two identical counter electrodes of Pt, Se-Mo-300, Se-Mo-400, Se-Mo-450, Se-Mo-500 and Se-Mo-550, respectively, is carried out to investigate kinetics of the electrode processes. The measurement and fitting results are shown in Fig. 5, and the detailed fitting data are listed in Table 2. All the Nyquist plots of the different electrodes obtained at the various calcination temperatures are composed of two semicircles. The semicircle in high frequency region represents charge transfer impedance (R_{ct}), reflecting electrocatalytic activity of the electrodes for reduction of triiodide ions, and the other one in low frequency region represents Nernst diffusion impedance (Z_w), reflecting diffusion rate of triiodide ions on the electrode surface [35–37]. Among the measurement results, both R_{ct} and Z_w of Se-Mo-400 are the smallest values, indicating relatively high electrocatalytic activity and fast ion diffusion rate. These reveal why Se-Mo-400 has the maximum FF and the highest power conversion efficiency in the J-V curve measurement. R_{ct} of Se-Mo-450 is 2.42 Ω, lower than the value of the Pt electrode (4.06 Ω), suggesting that its electrocatalytic

Fig. 5. Nyquist plots of the symmetric cells with two identical counter electrodes of Pt, Se-Mo-300, Se-Mo-400, Se-Mo-450, Se-Mo-500 and Se-Mo-550, respectively. The frequency ranges from 100 KHZ to 100 mHZ. The scatters and lines correspond to experimental data and fitting date, respectively. The inset is the used equivalent circuit.

Table 2

The simulated data from EIS spectra.

Sample	R_s/Ω	R_{ct}/Ω	Z_w/Ω
Pt	35.9	4.09	4.25
Se-Mo-300	40.8	403	264
Se-Mo-400	34.7	0.85	2.96
Se-Mo-450	33.6	2.42	3.84
Se-Mo-500	35.2	4.73	3.45
Se-Mo-550	37.2	1.73	5.28

activity is comparable with that of Pt electrode. Meanwhile, Z_w of Se-Mo-450 is also 3.84 Ω, close to Z_w of the Pt electrode (4.25 Ω), indicating similar ion diffusion rate for the two electrodes. This leads to the very close power conversion efficiency for the DSSCs with Se-Mo-450 and the Pt counter electrodes. To compare Se-Mo-400 with Se-Mo-450, the lower R_{ct} of the former should be attributed to a higher active surface area, considering the fact that the sample is heated at the relatively low temperature in spite of existence of the small amount of Se impurity. R_{ct} of Se-Mo-500 is 4.73 Ω, slightly higher than the value of the Pt electrode, namely, the electrocatalytic activity is slightly lower than that of the Pt electrode. However, Z_w of Se-Mo-500 is lower than that of the Pt electrode, suggesting a relatively fast ion diffusion rate. As mentioned above, the incompact but interwoven structure for MoSe₂ electrodes is helpful for mass transfer process. As the combination result of the two parameters, the power conversion efficiency of the DSSCs with Se-Mo-500 and Pt counter electrodes is very close. In the case of Se-Mo-550, R_{ct} is 1.73 Ω, and Z_w is 5.28. This means that Se-Mo-550 has high electrocatalytic activity for reduction of triiodide ions, but relatively slow ion diffusion rate due to the high calcination temperature. For the Se-Mo-300 electrode with different composition, R_{ct} is 403 Ω, much higher than those of the other electrodes, suggesting that its electrocatalytic activity is very poor. And its Z_w is also very high, resulting in the low power conversion efficiency. For series resistance (R_s), the relative gap among the MoSe₂ electrodes is small, so no further discussion here.

Fig. 6. CV curves of the symmetrical cells made of Pt, Se-Mo-400, Se-Mo-450, Se-Mo-500, and Se-Mo-550.

Electrocatalytic activity of the electrodes to iodide/triiodide ions are characterized by CV measurements. As shown in Fig. 6, in the four peaks for each, the oxidation peaks (Ox-1, Ox-2) is located in the upper portion of the curve, and the reduction peaks (Red-1, Red-2) is at the bottom. The corresponding redox reactions are as follow:

In the CV curves, peak current density and peak to peak separation (between the Red-1 and Ox-1, E_{pp}) are related to electrochemical rate constant of redox reaction, namely, the larger the current density and the thinner the E_{pp} , the greater the rate constant, and the stronger the electrocatalytic activity. In Fig. 6, peak current density decreases in the order of Se-Mo-450 > Se-Mo-400 > Se-Mo-550 > Se-Mo-500 > Pt, and E_{pp} of Se-Mo-400, Se-Mo-450 and Pt are lower than those of Se-Mo-500 and Se-Mo-550. This suggests that the reaction rate constant of Se-Mo-400 and Se-Mo-450 for reduction of triiodide ions is larger than those of Se-Mo-500 and Se-Mo-550 electrodes. The results are consistent with the above analysis from the EIS measurements.

4. Conclusions

Molybdenum selenide electrodes are prepared by *in situ* magnetron sputtering method. The obtained MoSe₂ presents nanoplate-like morphology with a thickness of around 20 nm and a diameter of about 100 nm, and the nanoplates interweave into a layer of MoSe₂ film with about an average thickness of 1.3 μm. The MoSe₂ electrodes obtained at various temperatures from 300 and 550 °C are used as counter electrode for a dye-sensitized solar cell. The MoSe₂ electrodes prepared at 400 °C has the optimized performance, and the corresponding DSSCs provide an energy conversion efficiency of 6.83% which is comparable than that of the reference DSSC with Pt as counter electrode (6.51%). The electrocatalytic activity of the MoSe₂ electrodes for reduction of triiodide ions increases with rising of the calcination temperature from 400 to 500 °C. However, the MoSe₂ electrode prepared at 550 °C has obviously

reduced electrocatalytic activity. Briefly, this work provides a simple and effective method to prepare low-cost MoSe₂ counter electrodes for dye-sensitized solar cells.

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Graphical Abstract

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Electrocatalytically active MoSe₂ counter electrode prepared *in situ* by magnetron sputtering for a dye-sensitized solar cellXueqin Cao, Hanfang Li, Guoran Li*, Xueping Gao
Nankai University

The in-situ magnetic sputtering method is used to obtain the dye-sensitized solar cell counter electrode material MoSe₂ with special structure, which not only has good electron transport performance, but also has excellent electrocatalytic performance.

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磁控溅射法原位制备电催化活性的MoSe₂用于染料敏化太阳能电池对电极

曹雪芹, 李晗芳, 李国然*, 高学平

南开大学材料科学与工程学院, 新能源材料研究所, 天津300350

摘要: 采用低成本材料取代铂对电极对于染料敏化太阳能电池的发展非常重要。金属硫族化合物MoSe₂对于I₃⁻的还原反应具有电催化活性, 有望用作染料敏化太阳能电池对电极材料。而除了材料本身, 电极的制作能够直接影响其电催化活性和稳定性。本文报道一种采用磁控溅射在FTO导电玻璃基底上原位制备MoSe₂电极的方法, 并考察其作为对电极的综合性能。

制备过程中, 首先将硒刮涂在基底, 接着在上层磁控溅射金属钼, 然后于不同温度下在氩气氛中焙烧制得MoSe₂对电极。详细研究了焙烧温度对MoSe₂对电极结构、形貌, 及其对最终电池性能的影响。形貌分析结果显示, 所获得的MoSe₂呈现纳米板状形态, 厚度约为20 nm, 直径约为100 nm, 纳米板交织成一层MoSe₂膜, 平均厚度约为1.3 μm。

光伏测量结果表明, 当焙烧温度在400和450 °C时的电池效率分别是6.83%和6.68%, 与传统的Pt作对电极时的效果(6.51%)相近。随着MoSe₂电极的制备温度进一步提高, 相应的DSSC在550 °C时逐渐降低至5.96%。对于层状MoSe₂, 其对于I₃⁻的电催化还原活性位处于层状结构的边缘面(100晶面), 而非基面(002晶面), 合适的焙烧温度能够使对电极中MoSe₂暴露更多的活性位点。

电化学阻抗谱显示, MoSe₂电极的电荷转移电阻(*R*_{ct})随温度从400 °C增加到500 °C而升高, 表明电催化活性下降。虽然在550 °C下制备的MoSe₂电极显示出降低的*R*_{ct}, 但其串联电阻和扩散电阻明显增加。考虑到MoSe₂相不能在300 °C下形成, 可见, 尽可能低的制备温度有利于提高其最终的电化学性能。

关键词: MoSe₂; 对电极; 电催化; 染料敏化太阳能电池; 原位合成; 磁控溅射

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*通讯联系人. 电子信箱: guoranli@nankai.edu.cn

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