Preparation and Photoelectric Properties of MoS₂ Microspheres

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Abstract. MoS₂ microspheres were synthesized by a hydrothermal method using sodium molybdate as the molybdenum source and thiourea as the sulfur source, were used as the counter electrode of dye-sensitized solar cells. This paper discussed the influence of the thiourea concentration on the preparation and photoelectric properties of MoS₂ microspheres. The results show that the crystallinity, microsphere structure, photoelectric conversion efficiency and catalytic activity of MoS₂ reach the best state when the Mo/S molar ratio is 1:4. Therefore, the thiourea concentration has an important effect on the structure, morphology and photoelectric properties of MoS₂. The conclusion will provide the basis for us to improve the electrode material performance of MoS₂ to replace Pt counter electrode.

Key words: MoS₂; hydrothermal method; thiourea; dye-sensitized solar cells; counter electrode.

1. Introduction

Dye-sensitized solar cells (DSSCs) have become a hot spot in the field of new thin-film solar cells because of its advantages of low material cost, simple fabrication and high conversion efficiency. DSSC consists of photoanode, sensitizer, electrolyte and counter electrode. The counter electrode is mainly used to collect electrons from external circuits and to reduce oxidized electrolytes [1]. Pt used as DSSCs traditional electrode material is easy to be corroded by electrolyte, resulting in the deterioration of device stability. Pt as a scarce precious metal in the world is expensive, which is not conducive to the industrialization of DSSCs [2]. Therefore, the development of low-cost, high-stability non-Pt counter electrode materials is a key problem to be solved urgently in DSSCs industrialization.

MoS₂ generally has three crystal forms of 1T, 2H and 3R. 1T and 3R are metastable. 2H is stable. 2H-MoS₂ has a layered structure similar to graphite and is arranged periodically in the hexagonal system. There are a lot of unsaturated bonds at the edge of the molecular layer, and it has high energy, so its catalytic activity is high [3]. MoS₂ has semiconductor properties. Its forbidden band width can be controlled within a certain range (1.2eV-1.9eV) with the change of layered structure [4]. MoS₂ has good abilities of chemical stability, thermal stability, corrosion resistance and so on, so it has been widely used in tribology, catalysts, lithium batteries, memory devices, solar cells and other fields [4].

In this paper, MoS₂ was prepared by hydrothermal method. The effects of thiourea concentration on the morphology and structure of MoS₂ were investigated. The effects of thiourea concentration on the photoelectric properties of MoS₂ counter electrodes were also investigated. The results show that
thiourea concentration will seriously affect the preparation of MoS$_2$ and its photoelectric properties, and also indicate that MoS$_2$ has the potential to be a new counter electrode material for DSSCs applications.

2. Experimental

2.1. Preparation of MoS$_2$

MoS$_2$ was prepared by hydrothermal method. MoS$_2$ was prepared using molybdenum sources and sulfur sources at different Mo/S molar ratios (1:2, 1:3, 1:4, 1:5, 1:6). At room temperature, 20 mmol sodium molybdate (Na$_2$MoO$_4$·2H$_2$O) was dissolved in 80 ml deionized water with 40 mmol, 60 mmol, 80 mmol, 100 mmol and 120 mmol thiourea (CS (NH$_2$)$_2$), respectively. The solution was moved into the PTFE inner tank, sealed and placed in a blast drying box at 220°C for 12 hours, and then naturally cooled. The black precipitates were centrifuged for several times with deionized water and absolute ethanol. Finally, the samples were dried and labeled as A, B, C, D and E respectively.

2.2. Preparation of counter electrode

MoS$_2$ counter electrodes were prepared by knife coating process. 0.2g MoS$_2$ particles and 0.02g CMC were added to a certain amount of secondary water and anhydrous ethanol mixture. The counter electrode slurry was prepared by grinding. The slurry was scraped onto the surface of the transparent conductive glass (FTO) with a scraper. After drying at 60°C, MoS$_2$ counter electrodes were obtained by pyrolysis at 450°C in argon atmosphere tube sintering furnace for 30 minutes.

The fabrication process of Pt counter electrodes is as follows. At room temperature, 7mM chlorproplatin acid isopropanol solution was magnetically stirred 4h. The solution was dripped on FTO and automatically blooming, forming a coating after drying. Repeat dripping and drying one more time. Pt counter electrodes were obtained by pyrolysis at 400°C in air atmosphere for 15 minutes.

2.3. Configuration of device

The DSSC was assembled with a photoanode and a counter electrode, sandwiching an electrolyte. The two electrodes were separated by a 50-μm-thick spacer. The area of electrode film is 6mm×6mm. The electrolyte is 0.5M LiI, 0.05M I$_2$, 0.5M 4-tert butyl pyridine (TBP) acetonitrile solution. The photoanode was prepared by knife coating process. The TiO$_2$ absorbing layer and the TiO$_2$ scattering layer were deposited on the FTO surface in turn. After sintered at 450°C for 30min, the double-coated TiO$_2$ film was further treated with TiCl$_4$ aqueous solution followed by heat treatment at 450 °C for 30min. The photoanode was obtained by further immersing the double-coated TiO$_2$ film into 0.3 M N719 ethanol solution at room temperature for 24h.

The symmetric cell was assembled with two identical counter electrodes, sandwiching an electrolyte. The two electrodes were separated by a 100-μm-thick spacer. The area of electrode film is 6mm×6mm. The electrolyte was the same as the one used in the DSSCs. The symmetric cell was used in EIS and Tafel measurements.

2.4. Characterization and measurement

The crystal structure of samples was analyzed by X ray diffractometer (XRD, D8ADVANCE). Copper target Kα ray, the initial scanning angle was 10°, the ending scanning angle was 80°, and the step length was 0.2°. Sample morphology was analyzed by scanning electron microscopy (SEM, ZEISS EVO MA10). Photocurrent-voltage(J-V) performances of the fully functional DSSCS were measured under the illumination of a Xenon light source (CHF-XM500, Trustech, China). The light intensity was 100 mW cm$^{-2}$. Electrochemical impedance spectroscopy (EIS) measurements were conducted at 10mV of amplitude over the frequency range of 0.01Hz to 100kHz. The Tafel polarization curve (Tafel) scan rate is 10 mV/s.
3. Results and discussion

3.1. Structure and morphology analysis of MoS$_2$

A, B, C, D, and E were prepared using Mo/S molar ratios of 1:2, 1:3, 1:4, 1:5 and 1:6. The XRD of samples A, B, C, D and E is revealed in Figure 1. Compared with the standard card PDF#65-0160, the corresponding diffraction peaks of (002), (100), (102), (110) crystal planes of 2H-MoS$_2$ were observed in all samples at 14.4°, 32.7°, 35.9° and 58.3°. This indicates that 2H-MoS$_2$ was successfully synthesized at different Mo/S molar ratios. According to the reaction formula[4].

$$4\text{Na}_2\text{MoO}_4+12\text{SC(NH}_2\text{)}_2+12\text{H}_2\text{O} \rightarrow 4\text{MoS}_2+12\text{CO}_2+24\text{NH}_3+\text{Na}_2\text{SO}_4+3\text{Na}_2\text{S}$$

The reactants can react perfectly at 1:3. When the concentration of thiourea is increased, the diffraction peaks increase more obviously at 1:4. Particularly, the diffraction peaks of (002) become very sharp. It indicates that the synthesized MoS$_2$ grows preferentially along (002). When thiourea concentration continues to increase, the intensity of each diffraction peak decreases, but the characteristic diffraction peak of MoS$_2$ remains unchanged. It shows that the crystallinity of MoS$_2$ is enhanced by appropriate excessive thiourea, but a large amount of excessive thiourea will form lattice defects and weaken the crystallinity of MoS$_2$.

![Figure 1. XRD patterns of MoS$_2$ prepared at different Mo/ S ratios](image1)

![Figure 2. SEM Morphologies of MoS$_2$ prepared at different Mo/S ratios](image2)
SEM of MoS$_2$ prepared at different Mo/S molar ratio is revealed in Figure 2. When Mo/S molar ratio is 1:2 and 1:3, MoS$_2$ microspheres have been formed. The surface of the microspheres is relatively smooth, the diameter of the microspheres is larger, and the size of the microspheres is not uniform. Increasing thiourea concentration, at the Mo/S molar ratio of 1:4, 1:5 and 1:6, a large number of thin sheets appeared on the surface of microspheres, and the layered structure was very obvious, similar to petals. With the increase of thiourea concentration, the diameter of MoS$_2$ microspheres decreased, about 2 $\mu$m, and the size was relatively uniform. The microsphere flower-like structure interwoven by a large number of thin sheets has a large specific surface area. For the counter electrode material, this structure will have more catalytic active points, and then can improve the electrical properties of MoS$_2$ as a DSSCs material.

3.2. Photoelectric performance of DSSCs
The J-V curves of the DSSCs using MoS$_2$ as counter electrode and Pt as counter electrode are revealed in Figure 3, and the photoelectric performance parameters are listed in Table 1. The filling factor (FF) and conversion efficiency ($\eta$) increase with the decrease of Mo/S molar ratio. When Mo/S molar ratio is 1:4, the parameters reach the optimum state, the $\eta$ is 3.47%, which reaches 65% of Pt ($\eta$ = 5.31%). When the concentration of thiourea continues to increase, the FF and $\eta$ decrease. When Mo/S molar ratio is 1:4, the product MoS$_2$ has high purity, good crystallinity and very large specific surface area, so it has the highest photoelectric conversion efficiency as a counter electrode material.

| samples | $V_{oc}$/V | $I_{sc}$/A | $J_{sc}$/mA cm$^{-2}$ | $\eta$/% | FF        |
|---------|-----------|-----------|----------------------|--------|-----------|
| A       | 0.581     | 1.20      | 7.500                | 2.06   | 0.4726    |
| B       | 0.636     | 1.43      | 8.938                | 2.66   | 0.4681    |
| C       | 0.625     | 1.66      | 10.375               | 3.47   | 0.5347    |
| D       | 0.657     | 1.54      | 9.625                | 3.29   | 0.5203    |
| E       | 0.617     | 1.47      | 9.188                | 2.92   | 0.5145    |
| Pt      | 0.642     | 2.22      | 13.875               | 5.31   | 0.5958    |

**Table 1.** Photoelectric performance parameters of the DSSCs

Figure 3. J-V curves of the DSSCs

3.3. Catalytic properties of MoS$_2$ counter electrode
The EIS can evaluate the catalytic performance of the counter electrodes. Figure 4 shows the electrochemical impedance comparison of MoS$_2$ symmetric cells and Pt symmetric cell. The corresponding impedance parameters are fitted by Zview software, as shown in Table 2. The ohmic serial resistance ($R_s$) reflects the block resistance of the electrodes, the charge transfer resistance ($R_{ct}$)
reflects the catalytic activity of the electrodes, and the Nernst diffusion resistance ($Z_w$) reflects the diffusion ability of $I_1^+/I^-$ on the electrodes. Smaller $R_s$, $R_{ct}$, $Z_w$ means higher catalytic activity for electrode materials, which will lead to better photoelectric performance of devices [1].

![Figure 4. EIS patterns of the symmetric cells](image)

**Table 2. Impedance parameters of the symmetric cells**

| Samples | $R_s$ ($\Omega \text{ cm}^2$) | $R_{ct}$ ($\Omega \text{ cm}^2$) | $Z_w$ ($\Omega \text{ cm}^2$) |
|---------|-------------------------------|-------------------------------|------------------------------|
| A       | 42.7                          | 216.4                         | 4042                         |
| B       | 43.47                         | 148.4                         | 2492                         |
| C       | 37.5                          | 57.39                         | 28.96                        |
| D       | 48.69                         | 78.49                         | 184.6                        |
| E       | 42.42                         | 86.57                         | 639.7                        |
| Pt      | 27.25                         | 6.155                         | 3.353                        |

![Figure 5. Tafel polarization curves of the symmetric cells](image)

The experimental results show that the $R_s$, $R_{ct}$ and $Z_w$ of Pt counter electrode are the smallest. It is proved that Pt has the best catalytic performance for counter electrodes. $R_s$ of MoS$_2$ counter electrodes
prepared at different Mo/S molar ratios slightly fluctuated. \( R_{ct} \) and \( Z_w \) decreased first and then increased with the increase of thiourea concentration. Comparing all samples, the results showed that the \( R_{ct} \) and \( Z_w \) of sample C prepared with Mo/S molar ratio of 1:4 are the smallest. It indicates that the material prepared with Mo/S molar ratio of 1:4 has the best catalytic activity and the strongest \( I_3^-/I^- \) diffusion ability. MoS\(_2\) has good catalytic activity due to its microparticle structure and large specific surface area. The concentration of thiourea will directly affect the catalytic performance of MoS\(_2\). Compared with Pt, the catalytic performance of MoS\(_2\) still needs to be improved.

The Tafel polarization curves of the symmetric cells using MoS\(_2\) as electrode and Pt as electrode are revealed in Figure 5. Comparing the steepness of the curves, the steeper the curve, the higher the catalytic activity of the electrode material\(^{[1]}\). In the Figure 5, the sample C with Mo/S molar ratio of 1:4 is the closest to Pt, followed by D, E, B and A, which indicates that sample C has the best catalytic activity. This is consistent with the result of the EIS.

4. Conclusion
MoS\(_2\) microspheres were successfully synthesized by hydrothermal method using molybdenum molybdate as molybdenum source and thiourea as sulfur source. The effect of Mo/S molar ratio on the structure and morphology of MoS\(_2\) was studied. When Mo/S molar ratio is 1:4, MoS\(_2\) have good crystallinity and a large number of fine sheet structures on the surface of the microspheres. This structure makes MoS\(_2\) have a very large specific surface area, which provides more catalytic active sites for MoS\(_2\) as counter electrode materials.

The photoelectric performance parameters of MoS\(_2\) increase with the increase of thiourea concentration. When Mo/S molar ratio is 1:4, the parameters reach the optimum value. Nevertheless, the concentration of thiourea continued to increase, the parameters began to decline. When Mo/S molar ratio is 1:4, the \( \eta \) of MoS\(_2\) is 3.47%, which reaches 65% of Pt(\( \eta =5.31\% \)). MoS\(_2\) has potential as low-cost and high-efficiency non-Pt counter electrode materials.

The catalytic activity of MoS\(_2\) was evaluated by EIS and Tafel polarization curves. The results show that MoS\(_2\) has good catalytic activity for the electrode when Mo/S molar ratio is 1:4, which is closest to that of Pt.

Thiourea is not only a sulfur source providing S atom for MoS\(_2\) and a reductant reducing Mo (VI) to Mo (IV), but also acts as a surface modifier. Therefore, the concentration of thiourea will seriously affect preparation and Photoelectric Properties of MoS\(_2\). To improve the catalytic activity of MoS\(_2\) as counter electrodes and enhance the photoelectric performance of DSSCS devices, it is a potential and effective way to investigate the types of reactants, the concentration of reactants, reaction time, reaction temperature and the addition of surfactants.

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