Hydrothermal growth of MoS₂/Co₃S₄ composites as efficient Pt-free counter electrodes for dye-sensitized solar cells

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ABSTRACT MoS₂/Co₃S₄ composite films were prepared via a facile one-step hydrothermal method, and used as efficient and low-cost Pt-free counter electrodes (CEs) for dye-sensitized solar cells (DSSCs). Characterizations revealed that Co₃S₄ and MoS₂ were obtained simultaneously during the facile hydrothermal process. The composites afforded a promising synergistic effect on the catalyzing of triiodide reduction. Enhanced electrocatalytic performance of the resultant composite films was confirmed through cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) analyses. DSSCs using MoS₂/Co₃S₄ composite CEs outperform the devices with pristine MoS₂ or Co₃S₄ CEs in power conversion efficiency (PCE). Furthermore, a PCE of 6.77% is obtained for the optimized devices using MoS₂/Co₃S₄ composite CEs measured under standard 1 sun illumination (100 mW cm⁻², AM 1.5G), which is comparable to that of the devices fabricated under the same conditions with conventional thermally deposited Pt CEs (7.14%). The results demonstrate that MoS₂/Co₃S₄ composites are promising alternatives to Pt to be applied as CEs for DSSCs.

Keywords: dye-sensitized solar cells, counter electrodes, composites, transition metal sulfide, hydrothermal growth, electrochemical impedance spectroscopy

INTRODUCTION

As one of the most abundant and yet least collected sources of renewable energy, solar energy has stimulated intense effort in both scientific and industrial research [1–5]. Dye-sensitized solar cells (DSSCs), which are anticipated to be a

potential alternative to silicon-based solar cells, have stood out among various photovoltaic devices as a promising renewable energy source owing to their ease of fabrication, environmental friendliness, cost-effectiveness and high efficiency [1–5]. After having been investigated for more than 20 years, liquid-state type DSSCs with power conversion efficiency (PCE) as high as 14.5% have been demonstrated [6]. Typically, the conventional liquid-state type DSSCs have a sandwich-type structure, consisting of a platinumized fluorine-doped tin oxide (FTO) glass as the counter electrode (CE), a liquid electrolyte that traditionally contains I⁻/I₃⁻ redox couples as a conductor to electrically connect the two electrodes, and a porous-structured oxide film with adsorbed dye molecules as the photosensitized anode. The triiodide/iodide redox species are commonly utilized as the redox couple in liquid-state DSSCs mainly owing to its unique performance on regeneration of various sensitizers including Ru-based dyes [7] and organic dyes [8,9]. Being as an essential and crucial component in DSSCs, the CE performs two critical functions, transferring electrons arriving from the external circuit back into the redox system and catalyzing the reduction of I₃⁻ to I⁻ so as to realize the regeneration of the sensitizer [10–12]. Thus an efficient catalytic CE should have good catalytic activity and high electrical conductivity to decrease the overvoltage for minimizing the energy losses and offer high photovoltaic efficiency [10–12]. Metal Pt thermally deposited on FTO glass has been commonly employed as CEs for DSSCs, present-

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ing the superior electrocatalytic activity and high conductivity. Unfortunately, the disadvantages such as high cost, and low abundance greatly limit the large-scale application of Pt in DSSCs [12]. In addition, Pt can be decomposed to PtI_4 in traditional I^-/I_3^- redox couple electrolyte system, which will decrease the long-term stability of the DSSCs [13]. Thus, the exploration of cheap but efficient CE material to replace Pt is a practical way to reduce the cost and realize the commercialization of DSSC application.

To date, various materials including carbon-based materials [14], conducting polymers [15], transition metal carbide [11,16], nitride [17], and sulfide [18] have been explored as catalytic materials in DSSCs to substitute platinum. Recently, molybdenum disulfide (MoS_2), one of the inorganic graphene analogues, has attracted much attention and been proposed as a promising potential CE candidate. As a typical layered transition metal sulfide, MoS_2 possesses a hexagonal structure, in which a sheet of Mo atoms is sandwiched between two hexagonally packed sulfur layers. The bonding within the three stacked atom layers (S–Mo–S) is covalent, whereas the interaction between the sandwiches is weak van der Waals force [19], which indicates that MoS_2 can be exfoliated into thin pieces. In view of these features, MoS_2 exhibits versatile applications including as a lubricant, as the catalyst for hydrogen evolution reaction as well as CE material used in DSSCs [20]. However, one of the weaknesses of MoS_2 is the intrinsic low conductivity due to its nature of semiconductor. Additionally, MoS_2 nanomaterials are prone to stacking together because of its layered nature and the high surface energy of the two dimensional structure, which will drastically reduce surface area, and thus the catalytic activity. Therefore, coupling of MoS_2 with other conductors to form composites is an efficient approach to expand the usage of MoS_2 as catalyst in the field of electrochemistry. In previous reports, MoS_2 -based composites, such as, MoS_2 /graphene [21], MoS_2 /multi-walled carbon nanotube [22], and MoS_2 /carbon [23], led to significantly improved DSSCs performance, compared to pure MoS_2 catalyst.

As well-known, cobalt chalcogenides (Co_9S_8 , CoS , Co_3S_4 and CoS_2), have been extensively applied in lithium ion batteries [24], electrochemical capacitors [25] and as catalysts in oxygen reduction reaction [26], due to their prominent characteristic of simple fabrication, abundant feedstock, high chemical stability, low electrical resistivity and superior catalytic performance [27]. Based on the slab band quantum computational principle, the calculated catalytic activity of Co_xS_y is analogous to platinum due to the corresponding surface structure which creates electron

transfer pathways for reduction kinetics [28]. Therefore, cobalt sulfides could act as the catalyst for triiodide reduction in DSSCs. In 2009, Grätzel *et al.* [18] proposed for the first time that CoS nanoparticles, fabricated by electrochemical deposition method, matched the performance of Pt as triiodide reduction catalyst in DSSCs. Besides, Co_9S_8 nanocrystal inks were employed as cathode materials to fabricate large-area DSSCs combined with spraying techniques, presenting an excellent photovoltaic performance [29]. Carbon-supported Co_3S_4 nanoparticles, hollow Co_3S_4 nanoparticles and nanotubes were successfully prepared and the as-obtained materials had an excellent catalytic ability for the oxygen reduction reaction [26]. However, only very few studies have been performed to investigate the application of Co_3S_4 as the CE for DSSCs [30–31]. Moreover, theoretical simulations and experimental evidence confirm that Co_3S_4 is of metallic behavior, which is remarkably different from CoS and Co_9S_8 [32]. Consequently, Co_3S_4 could be an ideal conductor to couple with MoS_2 to form composite as high-performance CE material for DSSCs. Taking all these factors into account, it is envisaged that the $\text{MoS}_2/\text{Co}_3\text{S}_4$ composites can possibly possess improved conductivity as well as reasonable electrocatalytic activity for I_3^- reduction due to the synergistic effect of composites.

To the best of our knowledge, the composites of MoS_2 and Co_3S_4 applied as CEs for DSSCs have not yet been reported. In the present study, we show that novel flower-like $\text{MoS}_2/\text{Co}_3\text{S}_4$ composite thin films were directly grown on FTO glass substrate as Pt-free CEs for DSSCs, via a one step *in-situ* hydrothermal method. The DSSCs assembled with the $\text{MoS}_2/\text{Co}_3\text{S}_4$ composite CEs exhibited an impressive photovoltaic performance of 6.77%, measured under one sunlight illumination ($\text{AM } 1.5\text{G}$, 100 mW cm^{-2}), which is superior to those of devices based on the pristine MoS_2 or Co_3S_4 CEs, and comparable to that of a DSSC containing a conventional thermally deposited Pt CE. Our results suggest that the $\text{MoS}_2/\text{Co}_3\text{S}_4$ composites are promising alternatives to Pt as CEs for DSSCs.

EXPERIMENTAL SECTION

Materials

The sodium molybdate ($\text{NaMoO}_4 \cdot 2\text{H}_2\text{O}$), thiourea, cobalt chloride ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$), polyethylene glycol with average molecular weight of 2000 (PEG 2000), acetonitrile, 4-*tert*-butyl-pyridine (TBP), lithium iodide (LiI) and iodine (I_2) were purchased from Sigma Aldrich. Lithium perchlorate (LiClO_4) and titanium (IV) tetrachloride were

obtained from Sinopharm Chemical Reagent Co., Ltd. TiO_2 paste (18NR-T) was purchased from Dyesol Industries Pty Ltd. All reagents are of analytical reagent grade and used without further purification. Conducting FTO glasses (20 ohm sq^{-1} , Nippon Sheet Glass Co., Japan) were used as the electrode substrates.

Fabrication of CEs

$\text{MoS}_2/\text{Co}_3\text{S}_4$ composite CEs were prepared by an *in-situ* hydrothermal growth of $\text{MoS}_2/\text{Co}_3\text{S}_4$ composite films directly on FTO substrates. The precursor solutions which were used to grow $\text{MoS}_2/\text{Co}_3\text{S}_4$ composites were prepared by dissolving appropriate amounts of $\text{NaMoO}_4 \cdot 2\text{H}_2\text{O}$, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, thiourea and PEG 2000 in deionized water. The precursor solutions with $\text{Mo/Co} = 1:1, 1:2, 1:4, 1:6$ were prepared to obtain the optimized ratio of $\text{MoS}_2/\text{Co}_3\text{S}_4$ in the CEs. The sulfur content of the precursor solution was always kept 10% higher than the value required by the stoichiometry. The cleaned FTO glass substrates were first immersed in 0.04 mol L^{-1} TiCl_4 solution and heated at 70°C for 30 min, then rinsed with water and ethanol successively, and subsequently dried under a high-purity nitrogen stream. Then, the pre-treated FTO substrates were placed at an angle against the wall of the teflon-lined stainless autoclave (50 mL) with the conductive sides facing down. Afterwards, the precursor solution was added to the autoclave up to 60% of the total volume (50 mL). Subsequently, the autoclave was sealed and maintained at 200°C for 24 h, and then allowed to cool to room temperature naturally. After the growth process, the as-prepared films were washed successively with deionized water and ethanol, and then dried at 50°C . The samples were denoted as Mo/Co-11, Mo/Co-12, Mo/Co-14 and Mo/Co-16, respectively, in terms of the Mo/Co ratios in the precursor solutions. The pristine MoS_2 and Co_3S_4 films were also prepared on FTO substrates with similar process using $\text{NaMoO}_4 \cdot 2\text{H}_2\text{O}$ or $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ together with appropriate amounts of thiourea and PEG 2000 as starting materials. Traditional Pt CEs were also prepared as reference by spin-coating of chloroplatinic acid solution (60 mmol L^{-1} in isopropanol) on FTO substrate followed by sintering at 385°C for 30 min.

Fabrication of DSSCs

All the TiO_2 photoanodes were fabricated by a standardized process as described as follows. FTO substrates were first washed sequentially with a detergent, distilled water, acetone, ethanol and isopropyl alcohol in an ultrasonic bath for 20 min. The dry clean substrates were then subjected

to TiCl_4 aqueous solution (40 mmol L^{-1}) treatment for the duration of 30 min at 70°C . Commercial TiO_2 paste was coated on the above treated FTO substrates by doctor-blading method. A portion of 0.25 cm^2 was selected as the active photoanode area. The TiO_2 -coated FTO substrates were heated on a hot plate (Fischer) in the air atmosphere at 450°C for 30 min. The thickness of TiO_2 film was $\sim 12 \mu\text{m}$. Subsequently, the TiO_2 electrodes were treated in 40 mmol L^{-1} TiCl_4 at 70°C for 30 min again, and then, washed with water and ethanol, respectively. Finally, the electrode was sintered at 500°C for 30 min and allowed naturally cool to 85°C before immersion in 0.5 mmol L^{-1} N719 dye solution (mixture of acetonitrile and tertiary butanol with volume ratio 1:1) for 18 h at room temperature under dark condition. The dye-sensitized TiO_2 photoanodes and the CEs were separated by a hot-melt Surlyn film (thickness of $25 \mu\text{m}$) and liquid electrolyte. The liquid electrolyte was composed of 0.03 mol L^{-1} iodine, 0.5 mol L^{-1} 4-*tert*-butylpyridine, 0.1 mol L^{-1} guanidine thiocyanate, and 0.6 mol L^{-1} 1-butyl-3-methylimidazolium iodide (BMII) in 3-methoxypropionitrile.

Characterization and measurements

The microstructure of the as-prepared samples was characterized by a field emission scanning electron microscope (FESEM, Hitachi S-4800) equipped with an energy dispersive X-ray spectrometer (EDS) annex. Composite films *in situ* grown on FTO substrates were scraped with a scalpel, and then ultrasonically dispersed in ethanol. Subsequently, the supernatant was dropped on holey carbon coated transmission electron microscopy (TEM) grid and dried naturally in air to prepare a sample for TEM characterization. TEM and high-resolution TEM (HRTEM) images were recorded using a Tacnai G2 F20 U-TWIN TEM (FEI, American). The X-ray diffraction (XRD) patterns were collected by a diffractometer with $\text{Co K}\alpha$ radiation ($\lambda = 1.7902 \text{ \AA}$). The photocurrent density-voltage (J - V) characteristic of the DSSCs were measured under AM 1.5G illumination (100 mW cm^{-2}) using an Oriel Newport solar simulator equipped with a 300 W xenon lamp and a digital source meter (Keithley 2420). The effective irradiated area was 0.125 cm^2 defined by a metal mask. The light intensity was calibrated using a standard Si reference solar cell (Oriel PN 91150 V). The performance of Pt, MoS_2 , Co_3S_4 , and composite CEs on catalyzing triiodide reduction was characterized by cycle voltammetry (CV) measurements. The CV measurements were implemented using a potentioinstat (CHI660E, CHI instruments) with a three-electrode system in an acetonitrile solution containing I_2 (1 mmol L^{-1}), Li-

ClO_4^- (0.1 mol L^{-1}), and LiI (10 mmol L^{-1}) at a scanning rate of 50 mV s^{-1} , in which the as-made CEs were taken as the work electrodes with working area of 1 cm^2 , a Pt wire as CE, a Ag/AgCl electrode as reference electrode. Electrochemical impedance spectra (EIS) of the CEs were measured on dummy cells consisting of two identical electrodes using an electrochemical workstation (Autolab PGSTAT302N) at the bias of 0 V with amplitude of 20 mV in the frequency range from 0.05 Hz to 100 kHz . The electrolyte used for EIS measurements is the same as that used for the DSSC fabrication. The EIS data were fitted using Zview software.

RESULTS AND DISCUSSION

After the facile hydrothermal procedure, the films were directly deposited on FTO substrates. Typical SEM images of the pristine MoS_2 , Co_3S_4 and composite samples are presented in Fig. 1. For the pristine MoS_2 sample, interlaced nanosheets which are approximately vertically grown on the substrate are observed (Fig. 1a and b), while for the pristine Co_3S_4 sample, blocky crystallites are observed on the FTO substrate (Fig. 1c and d). Shown in Fig. 1e and f are top view images taken from a representative composite sample Mo/Co-14 with the cross sectional image of this

sample given in Fig. 1g and h. The composite film consists of aggregated spheres with diameters up to several micrometers (Fig. 1e), and the image of higher magnification (Fig. 1f) reveals that the surface of the microspheres is composed of interlaced nanosheets. The thickness of the composite film is about $10 \mu\text{m}$ (Fig. 1g) and a layer of vertically grown nanosheets is observed at the bottom of the composite film (Fig. 1h). An EDS was collected on a microsphere of the sample Mo/Co-14, as shown in Fig. 2. The presence of Co in this sample is clearly identified, but the severe overlap between Mo and S peaks hinders the reliable determination of Mo/Co ratio. The weak peaks of O and Si may result from the glass substrate.

The XRD patterns of the pristine MoS_2 , Co_3S_4 and the composite samples are shown in Fig. 3. Due to the presence of FTO substrates, peaks of FTO are observed in all XRD patterns, as shown in Fig. 3. For the pristine Co_3S_4 sample, two reflections at 36.77° and 65.10° in 2θ are observed, which are (311) and (440) reflections of spinel-type Co_3S_4 , respectively. For the pristine MoS_2 sample, three very broad peaks attributed to (100), (102) and (110) reflections of MoS_2 are observed in the patterns besides the reflections resulting from FTO. It is particularly worth noting that the reflection (002) of MoS_2 , which should appear at about 16.7° , is not observed for the pristine MoS_2 sample, which could be well explained by the fact observed in SEM that the nanosheets in the pristine MoS_2 sample are approximately vertically grown on the FTO substrate, so the (001) planes have little chance to diffract X-ray in a Bragg-Brentano geometry. In the XRD pattern of the composite sample Mo/Co-14, reflections of both MoS_2 and Co_3S_4 can be identified together with peaks from the FTO substrate. Interestingly, the reflection (002) of MoS_2 appears in this case.

Figure 1 Top view SEM images of the pristine MoS_2 (a, b), Co_3S_4 (c, d) and composite sample Mo/Co-14 (e, f) as well as the cross sectional SEM images of the composite sample Mo/Co-14 (g, h).

Figure 2 EDS collected on a microsphere of the sample Mo/Co-14.

Figure 3 (a) XRD patterns of the pristine MoS₂, Co₃S₄ and the composite Mo/Co-14; (b) XRD patterns of the composite films prepared with precursor solutions of different Mo/Co ratios.

The presence of reflection (002) agrees with the SEM observation that nanosheets in the composite film are randomly oriented. XRD patterns of the composite films prepared with precursor solutions of different Mo/Co ratios are presented in Fig. 3b. As expected, intensity of reflections of Co₃S₄ increases with the Co content in the precursor. In the sample Mo/Co-16, the reflection (002) of MoS₂ disappears, as observed for the pristine MoS₂ sample. Nevertheless, other reflections of MoS₂ can still be identified, indicating the presence of MoS₂ in this composite sample.

The composite sample Mo/Co-14 was further characterized with TEM. The microspheres are too thick to be penetrated by electron beam, and only the nanosheets at the surface of microspheres can be investigated with TEM. A typical TEM image of these nanosheets is shown in Fig. 4a, and HRTEM image is given in Fig. 4b. According to the interspacing between lattice fringes in the HRTEM image, the nanosheets are few-layer MoS₂ flakes. Although Co₃S₄ has not been observed directly by TEM characterization, XRD patterns shown in Fig. 3a give solid evidence for its

Figure 4 TEM (a) and HRTEM (b) images of the composite sample Mo/Co-14.

presence in this composite film. Possibly, Co₃S₄ exists in the internal region of the microspheres. This speculation is supported by EDS shown in Fig. 2.

The composite films consisting of both few-layer MoS₂ nanosheets and Co₃S₄ are expected to be efficient CEs for DSSCs. Therefore, the as-prepared MoS₂/Co₃S₄ composite films were assembled with N719-sensitized TiO₂ photoanodes to fabricate DSSCs. The corresponding *J-V* curves of these DSSCs are shown in Fig. 5a and the detailed photovoltaic parameters are summarized in Table 1. As shown in Fig. 5a and Table 1, DSSCs based on composite CEs exhibit similar open-circuit voltage (*V*_{OC}) and short-circuit current density (*J*_{SC}) but the device using the composite film Mo/Co-14 as CE has a significantly better fill factors (FF). DSSCs based on the pristine Co₃S₄, MoS₂ and conventional Pt CEs were also prepared to be compared with devices containing composite CEs. *J-V* curves of these devices are presented in Fig. 5b and the corresponding photovoltaic performance parameters are listed in Table 1. As revealed by Fig. 5, the device based on the pristine MoS₂ or Co₃S₄ CE is much inferior in photovoltaic performance to its counterparts using the composite CEs. In comparison with the DSSC with the conventional Pt CE, the device based on the composite Mo/Co-14 CE exhibits a similar *V*_{OC}, a lower *J*_{SC} and an improved FF. The PCE of the DSSC based on Mo/Co-14 composite film is 6.77%, about 95% of that of a Pt-containing device.

The catalytic activity of MoS₂, Co₃S₄, Pt and composite Mo/Co-14 CEs on triiodide reduction was characterized with CV analysis, and the CV curves are presented in Fig. 6. Two pairs of redox peaks are observed in the CV curves for Pt and composite Mo/Co-14 electrodes. According to previous reports, [14,15,33,34] the two pairs of peaks can be assigned to the following two reactions respectively:

Figure 5 Characteristic J - V curves of the DSSCs with (a) different composite $\text{MoS}_2/\text{Co}_3\text{S}_4$ CEs, (b) pristine MoS_2 , pristine Co_3S_4 , Pt and Mo/Co-14 CEs, measured under light illumination with intensity of 100 mW cm^{-2} , AM 1.5 G.

Table 1 Photovoltaic parameters of the DSSCs with different CEs measured under 1 sun illumination (AM 1.5G 100 mW cm^{-2})

Counter electrode	V_{OC} (V)	J_{SC} (mA cm^{-2})	FF (%)	PCE (%)
Pt	0.711	16.38	0.613	7.14
MoS_2	0.661	11.55	0.608	4.64
Co_3S_4	0.705	13.16	0.550	5.11
Mo/Co-11	0.690	14.22	0.608	5.97
Mo/Co-12	0.697	14.27	0.627	6.24
Mo/Co-14	0.710	14.18	0.672	6.77
Mo/Co-16	0.683	14.17	0.634	6.14

$$3\text{I}_2 + 2e = 2\text{I}_3^- \quad (2)$$

The redox pair at relatively negative potential (Pair A) is attributed to redox reaction 1, whereas the redox pair at the much more positive potentials (Pair B) is assigned to the redox reaction 2 [14,15,33,34]. The electrochemical rate constant of the triiodide reduction is supposed to negatively correlated with the separation between the cathodic and anodic peak potential (ΔE_{pp}) [14,15,33,34]. Mo/Co-14 CE has a ΔE_{pp} of 0.50 V, slightly larger than that of Pt electrode, 0.35 V. This agrees well with the photovoltaic performance exhibited by the DSSCs based on Pt and composite CEs. No peaks can be observed on the CV curve for the pristine MoS_2 electrode, indicating its poor catalytic activity on triiodide reduction. Accordingly, the DSSC based on the pristine MoS_2 CE indeed exhibits the worst photovoltaic performance. Only one pair of peaks is observed in the CV curve of Co_3S_4 electrode. These two peaks should be attributed to reaction (1), and the corresponding value of ΔE_{pp} is 0.53 V. The results of CV measurements clearly show that the composite of MoS_2 and Co_3S_4 is comparable

Figure 6 CVs of Co_3S_4 , MoS_2 , Mo/Co-14 and Pt electrodes at a scan rate of 50 mV s^{-1} in $10 \text{ mmol L}^{-1} \text{ LiI}$, $1 \text{ mmol L}^{-1} \text{ I}_2$ solution containing $0.1 \text{ mol L}^{-1} \text{ LiClO}_4$ as the supporting electrolyte.

with Pt in catalyzing the triiodide reduction, and more active than the pristine MoS₂ or Co₃S₄.

EIS measurements were conducted to further investigate the electrochemical characteristics of different electrodes [10]. The EIS measurements were carried out with a symmetrical sandwich cell assembled with two identical electrodes, including MoS₂, Co₃S₄, Mo/Co-14 and Pt, respectively. The Nyquist plots of different electrodes are present in Fig. 7a. Two semicircles are observed for all electrodes. According to previous reports [7,10,15,35–37], the left semicircle (high frequency arc) is attributed to the charge transfer resistance (R_{CT}) at the interface of electrode/electrolyte interface, which reflects the catalytic activity of electrodes on triiodide reduction; the right semicircle (low frequency arc) is ascribed to the Nernst diffusion impedance (Z_N) of redox couple within the electrolyte. Additionally, the intercept on the real axis in the high-frequency region is attributed to the series resistance of the device, R_s . The Nyquist plots were fitted using the equivalent circuit shown in Fig. 7b. The corresponding fitted parameters including R_s and R_{CT} are summarized in Table 2. The four electrodes show similar values of R_s , whereas, R_{CT} varies with materials deposited on the sub-

Table 2 Fitted EIS parameters of the symmetric cells based on different CEs

Counter electrode	R_s (Ω cm ²)	R_{CT} (Ω cm ²)
MoS ₂	23.90	18.60
Co ₃ S ₄	21.36	3.69
Mo/Co-14	21.48	1.98
Pt	20.17	1.75

strate. The pristine MoS₂ electrode has the largest R_{CT} (18.6 Ω cm²) among the four electrodes. The pristine Co₃S₄ electrode exhibits a much smaller R_{CT} value of 3.69 Ω cm². The R_{CT} of the composite electrode Mo/Co-14 is 1.98 Ω cm², which is comparable with that of Pt electrode (1.75 Ω cm²), but significantly lower than those of the pristine MoS₂ and Co₃S₄ electrodes. The smaller R_{CT} of the composite electrode implies that electrons can be more readily transferred to I₃[−] in the electrolyte from composite electrode than from pristine MoS₂ or Co₃S₄ electrodes. The results of EIS measurements are in a good agreement with the CV characterization and photovoltaic performance exhibited by the DSSCs using different CEs.

CONCLUSIONS

The MoS₂/Co₃S₄ composite films were prepared on FTO substrates by hydrothermal growth, and applied as CEs for DSSCs for the first time. Under optimal conditions, the DSSC fabricated with the MoS₂/Co₃S₄ composite CE exhibits a PCE up to 6.77% under light irradiation of 100 mW cm^{−2}, which is about 95% of the PCE of the DDSC based on the thermally deposited Pt CE (7.14%). These results demonstrate the feasibility of using MoS₂/Co₃S₄ composite as Pt-free CE for DSSCs. In addition, the composite is more efficient than the pristine MoS₂ or Co₃S₄ as CEs for DSSCs.

Received 12 January 2017; accepted 6 February 2017;
published online 21 February 2017

Figure 7 (a) Nyquist plots for electrochemical impedance spectra of the symmetrical cells with two identical counter electrodes, including Co₃S₄, MoS₂, Mo/Co-14 and Pt; (b) the equivalent circuit used to fit the EIS data.

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Acknowledgments This work was supported by the National Natural Science Foundation of China (11574060, 51272049 and 21103032). Li Y would like to acknowledge the support from Shaanxi Provincial Natural Science Foundation (2016JM2008) and the Key Laboratory of Applied Surface and Colloid Chemistry, MOE (Shaanxi Normal University).

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Conflict of interest The authors declare that they have no conflict of interest.

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水热法制备二硫化钼/四硫化三钴复合材料作为高效染料敏化太阳能电池对电极

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摘要 染料敏化太阳能电池因其成本低、稳定性好、工艺简便而备受关注。发展高性能、廉价的材料代替传统的贵金属铂对电极是当前染料敏化太阳能电池领域的研究热点之一。二硫化钼纳米材料具有高比表面积和大量的催化位点,是较为理想的铂对电极替代材料之一,但较低的电导率限制了二硫化钼对电极性能的进一步提高。本文首次报道了由二硫化钼纳米材料与金属性的四硫化三钴复合制备染料敏化太阳能电池对电极,该复合对电极可以利用水热方法一步合成。研究结果表明,使用该复合对电极的染料敏化太阳能电池光电转换效率可达6.77%,接近于使用铂对电极的器件(7.14%),优于使用单一二硫化钼(4.64%)或四硫化三钴(5.11%)作为对电极的器件。