Facile, room-temperature synthesis of NiSe₂ nanoparticles and its improved performance with graphene in dye-sensitized solar cells

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Abstract

Metal selenides have been proposed as counter electrodes (CEs) to substitute for Pt in dye-sensitized solar cells (DSSCs) due to their good catalytic activity for the reduction of triiodide. In this paper, NiSe₂ nanoparticles were synthesized by a facile, room-temperature process and used as the CEs. In order to further enhance the photovoltaic property, graphene was introduced by facile physical mixing. Eventually, with the assistance of graphene, NiSe₂ + 6wt% graphene CE exhibited better power conversion efficiency (*PCE*) compared with Pt CE.

Keywords: Nanoparticles; Semiconductors; Solar energy materials

1. Introduction

Dye-sensitized solar cells (DSSCs), type of low-cost and easily-fabricated cells, have attracted much attention as powerful devices for converting solar energy directly to electric power.[1-3] A typical DSSC structure is composed of TiO₂ nanocrystalline photoanode, dyes, electrolyte, and counter

electrode (CE).[4] Conventionally, depositing platinum (Pt) on the conductive glass as the CE always results in a high performance due to its superior electrocatalytic activity and high electrical conductivity.[5] Nevertheless, as an expensive and rare metal, Pt can easily corroded by the electrolyte to PtI_4 and H_2PtI_6 which would worsen the CE performance;[6] therefore, it is necessary to synthesize inexpensive and efficient materials to replace. [7] Recently, metal selenides, which with narrow band gap and metallic conductivity, own many catalytic active sites, fast electron-transfer channels, as well as their good catalytic activity for the reduction of triiodide (I_3^-), have been proposed as CEs to substitute for Pt in DSSCs.[8-10] Among them, NiSe_2 has been considered as an ideal alternative as CE of DSSCs due to high electrical conductivity, excellent catalytic activity, inexpensive and abundant.[11] Meanwhile, introducing carbon-based materials, especially the graphene, have been attempted to improve the electrocatalytic activity.[12] Graphene possesses a high surface area for the dispersion of nanostructures and good electrical conductivity for electron transfer, which are beneficial for the electrocatalytic reaction.[13]

In this report, we synthesized NiSe_2 nanoparticles by a facile, room-temperature process, and examined their feasibility as CEs for Pt-free DSSCs. Electrochemical measurements demonstrated that NiSe_2 nanoparticles showed lower power conversion efficiency (power conversion efficiency, $PCE = 6.49\%$) than Pt CE ($PCE = 7.28\%$). In order to further enhance the photovoltaic property of DSSCs based on NiSe_2 nanoparticles CE, different amount of graphene were introduced by facile physical mix. The resultant DSSCs based on $\text{NiSe}_2 + 3\text{wt}\%$ graphene, $\text{NiSe}_2 + 6\text{wt}\%$ graphene and $\text{NiSe}_2 + 9\text{wt}\%$ graphene showed promising $PCEs$ of 6.91% , 7.47% , and 7.14% , respectively, which are comparable even better than that of the cell using precious Pt.

2. Experimental

Nickel acetate tetrahydrate, sulfur powder, sodium borohydride, and ethanolamine were analytical grade and purchased from Shanghai Chemical Co. Ltd., China. NiSe₂ nanoparticles synthesis was adopted from the protocols which used for the synthesis of PbSe QDs in the inert gas environment.[14] Two three-neck flasks were used in the synthesis system, 0.248 g nickel acetate tetrahydrate were dissolved in 100 mL ethanolamine in a three-neck flask (flask-1). H₂Se gas generated by 0.0789 g selenium powder and 0.0378 g sodium borohydride while drop-wise with 10% v/v HCl under argon atmosphere in another three-neck flask (flask-2). Two flasks were tightly connected with Teflon tubing and purged with argon gas. After drop-wise with HCl, the H₂Se was continuously transferred to flask-1 under constant argon flow and the NiSe₂ nanoparticles formed instantaneously at room temperature. Argon was purged for an additional 20 min after reaction ensures the formation of stable nanocrystals. The products were collected and washed with distilled water and ethanol for 6 times each step and dried at room temperature for further use.

3. Results and discussion

Powder X-ray diffraction (XRD) was performed to verify the phase structures of the final products. As shown in Fig. 1, diffraction peaks of the obtained samples were unambiguously indexed and assigned to NiSe₂ (JCPDS NO. 14-1495), which revealed the successful synthesis of NiSe₂. X-ray photoelectron spectroscopy (XPS) spectra were employed to further prove the sample has high purity (Fig. S1). XRD pattern of graphene is presented in Fig. S2.

The morphology of the NiSe₂ products was examined by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). As shown in Fig.2a, the nanoparticles with very small diameter. The TEM image reveals that the nanoparticles are very small (Fig.2b), and the mean diameter of NiSe₂ nanoparticles is about 10-20 nm. HRTEM image (Fig.2c) confirms the high crystallinity of

NiSe₂ nanoparticles by a visible set of lattice fringes of 0.277 nm, which can be indexed to the characteristic of the (311) plane of NiSe₂. TEM images of graphene are presented in Fig. S3.

To elucidate the intrinsic interfacial charge-transfer and charge-transport kinetics at the electrode/electrolyte interface, electrochemical impedance spectroscopy (EIS) was carried out on dummy cells with symmetric sandwich-like structure—CE/electrolyte/CE. Fig. 3a shows the Nyquist plots of the corresponding symmetrical cells, and detailed EIS parameters calculated from the fitting results of the equivalent circuit are summarized in Table 1. High frequency (corresponding to low Z') intercept on the real axis (Z' axis) represents the series resistance (R_s), and the semicircle in the high-frequency range results from charge-transfer resistance (R_{ct}).^[15] The R_{ct} value (2.95 Ω) of the pure NiSe₂ nanoparticles is higher than that of the standard Pt CE (1.43 Ω). The R_{ct} values reduced obviously when NiSe₂ nanoparticles mixed with graphene. In detail, the R_{ct} values of NiSe₂ + 3wt% graphene (1.68 Ω) and NiSe₂ + 9wt% graphene (1.47 Ω) CEs are almost half of the NiSe₂ nanoparticles. Most obviously, NiSe₂ + 6wt% graphene CE exhibited much lower R_{ct} value (0.57 Ω) than NiSe₂ nanoparticles and Pt CE, showing its best charge transfer ability among all CEs. The EIS measurements demonstrated that the addition of graphene greatly enhanced the charge transfer ability of NiSe₂ CE, and the ideal amount is 6wt% graphene.

Tafel polarization was performed on the symmetric cells used in the EIS experiments, which can be used as a powerful method to examine catalytic activity for reducing I₃⁻ and diffusion coefficient of I₃⁻.^[16] The slope for the anodic or cathodic branches in Fig. 3b indicates the exchange current density (J_0), which indicates the catalytic activity toward triiodide reduction of CEs.^[17] The intersection of the cathodic branch with the Y-axis can be considered as the limiting diffusion current density (J_{lim}), which is determined by the diffusion properties of the redox couples and the CE materials.^[18] From the Tafel

polarization curves of different CEs, it can be apparently observed that the all mixed CEs of NiSe₂ and graphene exhibited both higher J_{lim} and J_0 than the pure NiSe₂ nanoparticles. This condition is due to that graphene could improve the charge transfer ability and electrolyte diffusion rates, and then reduced the electrochemical polarization and concentration polarization. Furthermore, NiSe₂ + 6wt% graphene CE owned the best J_{lim} and J_0 values among all CEs, which revealed its high catalytic activity for reducing I₃⁻ and diffusion coefficient of I₃⁻.

Photoelectric conversion efficiencies of different CEs were measured to evaluate the overall electrocatalytic effect between NiSe₂ nanoparticles and graphene (Fig. 3c and Table 1). Due to the same photoanode and the electrolyte, all DSSCs assembled from different CEs owned similar open circuit voltage (V_{OC} , 0.75 ~ 0.76 V). As similar with EIS and Tafel polarization results, NiSe₂ nanoparticles exhibited lower short-circuit photocurrent density ($J_{SC} = 13.96 \text{ mA cm}^{-2}$) than that of Pt CE ($J_{SC} = 15.25 \text{ mA cm}^{-2}$). With the enhancement effect of graphene, NiSe₂ + 3wt% graphene (14.86 mA cm⁻²) and NiSe₂ + 9wt% graphene (14.67 mA cm⁻²) CEs exhibited higher J_{SC} values than the NiSe₂ nanoparticles alone, but still lower than the Pt CE. Furthermore, the ideal proportion is NiSe₂ + 6wt% graphene CE (16.32 mA cm⁻²) showed the highest J_{SC} value. The enhanced J_{SC} values, resulting from the addition of graphene, originated from high catalytic activity for I₃⁻ reduction.[19, 20] NiSe₂ nanoparticles yielded total *PCE* of 6.49 %, which is lower than that of Pt CE (7.28 %), while *PCEs* of 6.91 %, 7.47 %, and 7.14 % are obtained when the different amounts of graphene in the composites CEs is 3wt%, 6wt%, and 9wt%.

4. Conclusion

In conclusion, NiSe₂ nanoparticles were successfully synthesized by a facile, room-temperature

process. With the simple physical mix of graphene, NiSe₂ + graphene CEs exhibited excellent electrocatalytic activity for reducing I₃⁻ and comparable even better *PCE* performance than that of the DSSCs using precious Pt. These NiSe₂ products have great potential applications as the CE of DSSCs and can be an efficient method to substitute for Pt in DSSCs.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online.

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Table. 1

Photovoltaic and EIS parameters of the DSSC with different CEs.

CEs	V_{oc} (V)	J_{sc} (mA cm ⁻²)	FF (%)	PCE (%)	R_s (Ω)	R_{ct} (Ω)
NiSe ₂ nanoparticles	0.75	13.96	0.62	6.49	16.81	2.95
NiSe ₂ + 3wt% graphene	0.75	14.86	0.62	6.91	16.80	1.68
NiSe ₂ + 6wt% graphene	0.75	16.32	0.61	7.47	16.51	0.57
NiSe ₂ + 9wt% graphene	0.76	14.67	0.64	7.14	16.60	1.47
Pt	0.76	15.25	0.63	7.28	16.69	1.43

Figure Captions

Fig. 1. XRD pattern of as- prepared NiSe₂ nanoparticles samples.

Fig. 2. Typical (a) SEM, (b) TEM, and (c) HRTEM images of NiSe₂ nanoparticles.

Fig. 3. (a) Electrochemical impedance spectroscopy (EIS), (b) Tafel polarization curves, (c)

Photocurrent density-voltage (J - V) characteristics, and schematic diagram (d) of DSSCs with different
CEs.

Figure 1