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Single-Crystal CoSe₂ Nanorods as Efficient Electrocatalyst for Dye-Sensitized Solar Cells

Hong Sun, Lu Zhang and Zhong-Sheng Wang

Single-crystal CoSe₂ nanorods have been prepared with a facile one-step hydrothermal method. The thin CoSe₂ films fabricated by drop-casting the CoSe₂ nanorods suspension onto conductive substrates followed by simple drying without sintering can be used as highly efficient electrocatalyst for the reduction of I₃⁻. The dye-sensitized solar cell (DSSC) with the standard N719 dye and the single-crystal CoSe₂ nanorod cathode achieves power conversion efficiency of 10.20% under AM1.5G one-sun illumination versus 8.17% for the Pt cathode. This finding implies that single-crystal CoSe₂ nanorod is a promising low-cost and high-performance cathode material for high-performance DSSCs.

Introduction

Since the seminal paper published by O'Regan and Grätzel in 1991, dye-sensitized solar cells (DSSCs) have attracted tremendous interest in scientific research and industrial applications in the past two decades. As one of the most promising photovoltaic devices, DSSCs have several advantages over silicon based solar cells such as ease of fabrication and cost-effectiveness. A typical DSSC is constructed with a working electrode (a dye-sensitized nanocrystalline TiO₂ film), a counter electrode (CE) and a redox-couple based electrolyte sandwiched between the two electrodes. The CE functions as an electrocatalyst to catalyze the reduction of I₃⁻ for effective circuit completion. Platinum (Pt) is so far the most commonly used CE for laboratory research due to its excellent electrocatalytic activity and chemical stability. Unfortunately, the high price and low abundance ratio of Pt create a big obstacle for large-scale application of DSSCs. Therefore development of cheap CE materials with high electrocatalytic activity is of significance for practical applications.

A lot of alternatives to Pt have been developed for use as CE in DSSCs. The reported CE materials include carbon, graphene, conductive polymer and metal compounds such as oxide, sulfide, nitride, carbide, and selenide. Among them, metal selenides have drawn great attention due to their distinctive electronic properties, interesting chemical behaviours, and wide variety of potential applications.

Recently, CoSe₂ has drawn much attention and several synthetic methods have been reported in the literature. We report herein single-crystal CoSe₂ nanorods for application as the CE in DSSCs. Excitingly, the single-crystal CoSe₂ nanorods exhibit excellent activity on the reduction of triiodide, and the DSSC with the single-crystal CoSe₂ nanorods CE produces a power conversion efficiency of 10.20% versus 8.17% for the Pt CE under the same conditions.

Results and discussion

Figure 1 shows the XRD pattern for the CoSe₂ powder sample. All the XRD diffraction peaks can be well indexed to orthorhombic CoSe₂ (JCPDS No. 00-053-0449). No other peaks of impurities are observed, indicating good purity of the synthesized samples. As compared to the ultrathin-layered CoSe₂ nanobelts, which exhibited Bragg peaks in the small angle region due to the lamellar structure, the CoSe₂ sample prepared in this work did not show XRD peaks below 20° of 20°. The atomic ratio of Co:Se in the sample determined by EDS is 1.0:2.1, which is close to the stoichiometric ratio of CoSe₂. The atomic ratio of Co:Se in the sample determined by ICE-AES is 1.0:2.2, which is also close to the stoichiometric ratio of CoSe₂.
Figure 1. XRD pattern of the as-prepared CoSe$_2$ sample

Figure 2 displayed the SEM image of the as-prepared sample. CoSe$_2$ nanorods were formed after the hydrothermal reaction, as seen in the SEM images. The nanorods had broad distribution in size: 50-800 nm in length and 20-150 nm in width. The nanorod morphology was further confirmed with the TEM images (Figure 3a and 3b). The HRTEM image (Figure 3c) showed that the lattice spacing was $3.71 \pm 0.01$ Å, corresponding to the (110) planes of orthorhombic CoSe$_2$ (Figure 1). The selected area electron diffraction (SAED) spots shown in Figure 3d indicated the single crystalline nature of this nanorod. The electron diffraction pattern for the orthorhombic CoSe$_2$ nanorods is different from that for the layered CoSe$_2$ nanobelt.\textsuperscript{12}
CoSe₂ thin films are fabricated by drop-casting the CoSe₂ suspension onto FTO substrates. Figure 4 shows the SEM images of the CoSe₂ film. It is evident that the nanorods are deposited on the FTO surface, but the nanorods do not cover the surface completely. For comparison, the SEM image of the Pt deposited FTO is shown in Figure S1.

Solar cell performance was optimized through varying the loading amount from 10 to 80 µg cm⁻². The efficiency increased with increasing the loading amount up to 20 µg cm⁻², and then decreased gradually with further increasing the loading amount. Therefore, the optimal loading was determined of 20 µg cm⁻², which was used for the fabrication of DSSCs and corresponding characterizations. Three parallel DSSCs with each CE were constructed and tested under AM1.5G illumination (100 mW cm⁻²) with a standard deviation error of 0.3% in absolute efficiency. Figure 5a displayed the photocurrent density-voltage (J-V) curve for the DSSC with the CoSe₂ CE and N719 dye. Impressively, the single-crystal CoSe₂ CE produced PCE of 10.20% with short-circuit photocurrent density (Jsc) = 18.55 mA cm⁻², open-circuit photovoltage (Voc) = 753 mV and fill factor (FF) = 0.73. For comparison, the DSSC with the standard Pt CE was fabricated and measured at the same conditions. According to the J-V curve shown in Figure 5a, the Pt CE generated Jsc = 15.89 mA cm⁻², Voc = 724 mV, FF = 0.71, corresponding to PCE of 8.17%. Evidently, replacement of the Pt CE with the single-crystal CoSe₂ nanorods CE causes a large increase in PCE by 25%, which is attributed to the significant improvement of Jsc and small increases in Voc and FF.

Figure 5b displays the IPCE spectra for the two DSSCs. The IPCE value for the CoSe₂ cathode is larger than that for the Pt
CE at each wavelength in the visible region. This accounts for the larger \( J_{sc} \) of the CoSe\(_2\)-based DSSC as compared to the Pt-based DSSC.

![Figure 6. EIS Bode plots for the CoSe\(_2\) and Pt DSSCs under one-sun illumination at open circuit](image)

Although the anode and electrolyte are the same, the \( V_{oc} \) is different for the two DSSCs. For the same anode and electrolyte, the different cathode likely causes the difference of \( V_{oc} \), which is determined by the photo-induced current and electron lifetime. To clarify this issue, electrochemical impedance spectroscopy (EIS) was measured. Figure 6 shows the EIS Bode plots for the two DSSCs. The left middle-frequency peak is attributed to charge recombination at the TiO\(_2\)/electrolyte interface. As compared to the Pt-based DSSC, this peak shifts to lower frequency for the CoSe\(_2\)-based DSSC, indicating a higher electron lifetime. The higher electron lifetime in combination with the higher \( J_{sc} \) for the CoSe\(_2\)-based DSSC is responsible for the higher \( V_{oc} \) as compared with the Pt-based DSSC.

The long-term stability of the DSSCs was evaluated by measuring the photovoltaic performance for eight days. The \( J_{sc} \) first decreased and then remained almost unchanged, while \( V_{oc} \) and FF first increased and then remained almost unchanged for the CoSe\(_2\)-based DSSC (Figure S2). By contrast, the \( J_{sc} \) first increased and then decreased, \( V_{oc} \) first increased followed by a plateau, FF remained stable for one day followed by a decrease, and PCE first increased followed by a slight decrease (5%) for the Pt-based DSSC. It seemed that the CoSe\(_2\)-based DSSC had better stability than the Pt-based DSSC under daylight storage.

As the DSSCs studied in this work are same in photoanode and electrolyte but different in CE, the solar cell performance should be related to the catalytic activity of the CE film. To interpret the difference of solar cell performance, electrocatalytic performances of four parallel electrodes for each sample were evaluated by measuring cyclic voltammograms (CV), electrochemical impedance spectra (EIS), and Tafel polarization. The relative standard deviation error was less than 5%. Figure 7 compares the CV curves of iodide/triiodide redox species on CoSe\(_2\) and Pt electrodes, respectively. Two typical pairs of oxidation and reduction peaks (Ox-1/Red-1, Ox-2/Red-2, as labeled in Figure 7) are well resolved in the range of -0.6 to 0.9 V (vs. Ag/Ag\(^+\)) for both materials, similar to what has been reported for the DSSC systems in the literature. According to the literature, the Red-1 peak is attributed to the reduction of I\(_3^-\) to I\(^-\) while the Ox-1 peak is attributed to the oxidation of I\(^-\) to I\(_2\). The Ox-2 peak is attributed to the oxidation of I\(_3^-\) to I\(_2\) while the Red-2 peak is attributed to the reduction of I\(_2\) to I\(^-\). The characteristics of peaks Ox-1 and Red-1 are at the focus of our analysis because the CE of a DSSC is responsible for catalyzing the reduction of I\(_3^-\) to I\(^-\). The peak-to-peak potential separation (\( E_{pp} \)) for the pair peaks is inversely correlated with the standard rate constant of a redox reaction. The \( E_{pp} \) is 0.36 and 0.44 V for CoSe\(_2\) and Pt, respectively. This indicates that the reduction rate constant of triiodide to iodide on the single-crystal CoSe\(_2\) nanorod is faster than on the Pt electrode. In addition, the CoSe\(_2\) nanorod exhibits higher peak currents than the Pt electrode. It is thus concluded that the single-crystal CoSe\(_2\) nanorod has higher electrocatalytic performance than the Pt on the reduction of triiodide due to the larger reduction rate constant and higher redox peak currents.

![Figure 7. CV curves of iodide/triiodide redox species on CoSe\(_2\) and Pt electrodes, respectively. The current is normalized to geometric area.](image)

To further elucidate the catalytic performance, electrochemical impedance spectroscopy (EIS) was recorded with a symmetric dummy cell, in which a thin layer of redox electrolyte solution was sandwiched between two identical electrodes (CE/electrolyte/CE). Figure 8a shows the EIS Nyquist plots where two semicircles were observed. As small amount of catalyst was deposited on FTO, electrolyte diffusion in catalyst pores was not observed. According to the Randles-type circuit (inset of Figure 8a), the high-frequency intercept on the real axis represents the series resistance (\( R_s \)). The left arc arises from the charge-transfer resistance (\( R_{ct} \)) at the electrode/electrolyte interface and the corresponding constant phase angle element (CPE), which describes the deviation from ideal capacitance due to the roughness of the electrode. The right semicircle reflects the Nernst diffusion impedance (\( Z_N \)) of the I\(_3^-\)/I\(^-\) redox couple in the electrolyte. \( R_{ct} \)
determined by fitting the impedance spectra using the Z-view software is 2.0 and 3.0 Ω for CoSe$_2$ and Pt, respectively. As the apparent surface area is 0.70 and 0.48 cm$^2$ for CoSe$_2$ and Pt, respectively, estimated from the product of loading amount, geometric area (0.36 cm$^2$) of the CE and BET surface area, the normalized $R_{ct}$ is 1.4 Ω cm$^2$ for both electrodes. Since $R_{ct}$ correlates inversely with the electrocatalytic performance, CoSe$_2$ and Pt CE films have comparable catalytic activity taking the apparent surface area into account, but the former exhibits higher electrocatalytic performance than the latter due to the larger apparent surface area.

Figure 8. EIS Nyquist plots for symmetric cells fabricated with CoSe$_2$ and Pt electrodes, respectively (a). The inset in (a) gives the equivalent circuit. Evolution of EIS for the dummy cells (b). The cell was first subjected to CV scanning from 0 to 1 V, then to -1 V and finally to 0 V with a scan rate of 100 mV s$^{-1}$ followed by 20 s relaxation at 0 V, and then EIS was recorded. This sequential test was repeated for ten cycles.

The $Z_N$ for the CoSe$_2$ CE (3.4 Ω or 2.4 Ω cm$^2$ normalized to the apparent area) is larger than that for the Pt CE (1.2 Ω or 0.6 Ω cm$^2$ normalized to the apparent surface area). The $Z_N$ describes the impedance of electrolyte diffusion:

$$Z_N = \frac{kT}{n^2e_0c(I_{3}^-)A_iD(I_{3}^-)i\omega} \tanh \left( \frac{i\omega A_iD(I_{3}^-)}{\delta} \right)$$  \hspace{1cm} (1)$$

where $k$ is the Boltzmann constant, $T$ is the temperature, $n$ is the number of electrons involved in the reduction of I$_3^-$ at the electrode, $e_0$ is the elementary charge, $c(I_{3}^-)$ is the concentration of I$_3^-$, $\omega$ is the angular frequency, $D(I_{3}^-)$ is the diffusion constant, $A$ is the electrode area, and $\delta$ is the diffusion layer thickness (half the distance between electrodes in the dummy cell). As $Z_N$ is inversely proportional to the concentration of I$_3^-$, the larger $Z_N$ for the CoSe$_2$ electrode indicates a lower concentration of I$_3^-$. However, the initial concentration of I$_3^-$ is same for both dummy cells. It is thus speculated that the concentration of I$_3^-$ has changed in the dummy cell, which may be influenced by the adsorption of I$_3^-$ on the electrode. To probe this possible change, we measured the adsorption of I$_3^-$ on CoSe$_2$ and Pt by means of UV-vis absorption spectra (Figure S3). It is clearly seen from Figure S1 that more than 3-fold I$_3^-$ is adsorbed on CoSe$_2$ as compared to the Pt film. Normalized to the apparent surface area, the I$_3^-$ ions adsorbed on the CoSe$_2$ CE are about 2-fold that on the Pt CE. This means that the CoSe$_2$ has higher adsorption capacity for I$_3^-$ ions than the Pt. Higher adsorption of I$_3^-$ on the CoSe$_2$ CE signifies the reduction of concentration in the bulk, which reduces the electrolyte conductivity and thus increases the $Z_N$. However, the higher adsorption of I$_3^-$ on the CoSe$_2$ CE is advantageous to fast reduction of I$_3^-$, which is at least partly responsible for its lower $R_{ct}$ as compared to the Pt CE.

Figure 8b shows the evolution of impedance spectra for the dummy cells subjected to sequential scans of CV and EIS for 10 cycles. After 10 cycles of scanning, there was almost no change of $R_e$ and $Z_N$, indicating that the potential cycling hardly influenced the series ohmic resistance and the mass transport in the redox solution. However, $R_{ct}$ increased by 0.05 Ω for CoSe$_2$ and 0.3 Ω for Pt after 10 cycles of scanning. This indicates that CoSe$_2$ had better electrochemical stability than Pt, which is responsible for the better long-term stability of the CoSe$_2$-based DSSC as compared to the Pt-based DSSC.

Figure 9. Tafel polarization curves for the dummy cells with CoSe$_2$ and Pt, respectively.

Furthermore, Tafel polarization was carried out to disclose the information of diffusion-limited current and charge exchange at the CE/electrolyte interface. Figure 9 shows the
Tafel curves of the dummy cells, in which saturation currents (i.e. the limiting current density $J_{\text{lim}}$) were observed for both CoSe$_2$ and Pt based DSSCs. Owing to the large excess of I$_3^-$ in the electrolyte, only the diffusion of I$_3^-$ limits the current.\textsuperscript{19} The $J_{\text{lim}}$ is proportional to the diffusion constant ($D(I_3^-)$) and concentration ($c(I_3^-)$) of I$_3^-$.\textsuperscript{19}

$$J_{\text{lim}} = \frac{2nFD(I_3^-)c(I_3^-)}{l}$$  \hspace{1cm} (2)

where $F$ is Faraday’s constant, $l$ is the distance between the electrodes in the dummy cell. The $J_{\text{lim}}$ for Pt is larger than that for CoSe$_2$. This indicates that the concentration of I$_3^-$ in the bulk is smaller for the CoSe$_2$ electrode, which is caused by the higher adsorption of I$_3^-$ on the CoSe$_2$ electrode (Figure S1). The result for electrolyte diffusion obtained from the Tafel curve is consistent with that from the EIS analysis.

The charge exchange current density ($J_0$) can be estimated from the slope of the anodic or cathodic branch in the Tafel curve. It is seen from Figure 9 that the CoSe$_2$ electrode gives a larger slope than the Pt electrode, indicating that the $J_0$ for the former is larger than that for the latter, which is in good agreement with the result from Tafel curves.

The above results indicate that single-crystal CoSe$_2$ nanorods supersede Pt in terms of electrocatalytic performance. The higher electrocatalytic performance is responsible for the higher FF and $J_0$ for single-crystal CoSe$_2$ nanorods, as compared to the Pt CE. To avoid current losses at the CE, the $J_0$ should be sufficiently high.\textsuperscript{20} In principle, high $J_0$ is favourable for high $J_{\text{sc}}$. The observed higher $J_{\text{sc}}$ for the CoSe$_2$ CE is likely attributed to its higher $J_0$.\textsuperscript{20}

### Experimental

**Synthesis of CoSe$_2$.** The CoSe$_2$ nanorod was synthesized via a one-step hydrothermal reaction.\textsuperscript{14} Briefly, 0.320 g Se powder (99.999%, Aladding) was dissolved in 30 mL of NaOH (4 g, Sinopharm) aqueous solution to form solution A. Solution B was prepared from 0.587 g Co(NO$_3$)$_2$·6H$_2$O (99.9%, Alfa Aesar) dissolved in 10 mL of 0.25 M EDTA-2Na (>99%, J&K). The two solutions were then added to a 100 mL Teflon-lined autoclave under stirring for several minutes. The autoclave was tightly sealed and heated at 200 °C for 6 h and then cooled down to RT naturally. A large amount of black precipitate was collected, which was washed with dilute acid and distilled water for several cycles followed by drying at 60 °C for 24 h.

**Fabrication and Evaluation of DSSCs.** 1.8 mg of CoSe$_2$ nanorods was dispersed in 10 mL of distilled water and ethanol (volume ratio, 1:1) by ultrasonication for 1 h. The CoSe$_2$ suspensions were drop-casted on conductive glass (fluorine-doped SnO$_2$, FTO, 15 Ω/square, transmittance 85%, Nippon Sheet Glass Co., Ltd., Japan), which was masked by a 3M Scotch tape with an exposed area of 0.6 × 0.6 cm$^2$. Then the films were dried in an oven at 70 °C. As a reference, pyrolytic Pt CE was prepared by drop-casting 50 µL of H$_2$PtCl$_6$ in ethanol (5 mM) on FTO glass followed by sintering at 380 °C for 30 min. TiO$_2$ films (18 µm thick) composed of transparent layer (12 µm, 25 nm TiO$_2$ nanoparticles) in contact with FTO and scattering layer (6 µm, 25 nm TiO$_2$ nanoparticles (60%) + 300 nm TiO$_2$ nanoparticles (40%)) on top of the transparent layer were prepared by a screen-printing method on FTO glass according to a previous report.\textsuperscript{21} TiO$_2$ films were soaked overnight in cis-di(isothiocyanato)-bis-(2,2-bipyridyl-4,4-dicarboxylato)ruthenium (II) bis-tetrabutyl ammonium (so-called N719, used as received from Solaronix SA) solution (0.3 mM in a mixed solvent of acetonitrile and tert-butanol in a volume ratio of 1:1). The dye-sensitized TiO$_2$ photoanode and the CE were separated by a hot-melt Surlyn film (30 µm thick) and sealed through hot pressing. The electrolyte (0.1 M LiI, 0.05 M I$_3$, 0.6 M 1,2-dimethyl-3-n-propylimidazolium iodide, and 0.5 M 4-tert-butylpyridine in absolute acetonitrile) was injected into the interspace between the photoanode and CE. Finally, the holes on the back of the CE were sealed with a Surlyn film covered with a thin glass slide under heat.

**Characterizations.** X-ray diffraction (XRD) profile was recorded on an X-ray powder diffractometer (D8 Advance, Bruker) with Cu Ka radiation ($\lambda = 0.154$ nm). The morphology and atomic ratio of the selenide sample were examined by field emission scanning electron microscopy (FESEM, S-4800, Hitachi) with energy-dispersed spectroscopy (EDS). The composition of selenide was also detected by inductively coupled plasma-atomic emission spectrum (ICP-AES, Thermo Electron Corp. Adv. ER/S). The microstructure was characterized with high-resolution transmission electron microscopy (HRTEM, JEM-2100F, JEOL). The specific surface area was measured with a Micromeritics ASAP2020 nitrogen adsorption-desorption apparatus. Cyclic voltammetry (CV) was carried out in a three-electrode system containing an anhydrous acetonitrile solution of 0.1 M LiClO$_4$, 10 mM LiI, and 1 mM I$_2$ at a scan rate of 50 mV s$^{-1}$, using a Pt wire as the CE, an Ag/Ag$^+$ electrode as the reference electrode, and the as-prepared CoSe$_2$ film as the working electrode. Electrochemical impedance spectroscopy (EIS) and Tafel polarization measurements were performed on the symmetrical dummy cells assembled with two identical electrodes filled with the same electrolyte as used in the DSSC. The active geometric area of the dummy cell was 0.36 cm$^2$ with a distance of 30 µm between the electrodes. In the EIS test, the dummy cell was scanned from 0.1 Hz to 800 kHz at 0 V bias and ac amplitude of 10 mV. The EIS of DSSCs was carried out on an electrochemical workstation at 0 V bias and ac amplitude of 10 mV, which includes a white light emitting diode and the corresponding control system. All the electrochemical characterizations were performed on an electrochemical workstation (ZAHNER...
The photocurrent density-voltage curves of DSSCs were recorded on a Keithley 2400 source meter under the illumination of AM1.5G simulated solar light coming from an AAA solar simulator (Newport-94043A) equipped with a Xe lamp (450 W) and an AM1.5G filter. The light intensity was calibrated using a reference Si solar cell (Oriel-91150). A black mask with an aperture area of 0.2304 cm$^2$ was applied on the surface of DSSCs to avoid stray light completely.

Conclusions

In summary, we have applied single-crystal CoSe$_2$ nanorods as the CE in DSSCs. CoSe$_2$ exhibits excellent electrocatalytic activity on the reduction of I$_3^-$, and the DSSC with the CoSe$_2$ CE produces higher power conversion efficiency (10.20%) than the DSSC with the Pt CE (8.17%). The results presented in this work imply that single-crystal CoSe$_2$ nanorod is a promising low-cost and high-performance cathode material for application in DSSCs.

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Notes and references