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ARTICLE TYPE

SnX (X = S, Se) thin films as cost-effective and highly efficient counter electrodes for dye-sensitized solar cells

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Solution-deposited SnSe and SnS thin films demonstrate excellent electrocatalytic activity toward the triiodide reduction in dye-sensitized solar cells (DSCs), even better than that of the conventional noble Pt electrode used in DSCs.

An enhanced photovoltaic efficiency with maximum value of 9.4% was thus achieved, higher than that with Pt (9.0%).

Dye-sensitized solar cells (DSCs) remain a promising candidate for the development of next-generation photovoltaics owing to their cost-effective, environment-benign fabrication processes, and respectable efficiency.¹⁻² A typical DSC consists of a dye-sensitized mesoporous nanocrystalline TiO₂ film interpenetrated by a liquid electrolyte containing an iodide/triiodide redox couple, and a counter electrode (CE) serves to collect electrons and meanwhile catalyze the redox couple regeneration.³⁻⁴ After several years of development, a general consensus has been reached that further enhancement of CE materials in DSCs with alternatives being less expensive and more efficient compared to the conventional noble metal Pt is warranted to boost the photovoltaic performance and to reduce the cost of the solar cells.⁵⁻⁷ A considerable number of candidate alternative CE materials with excellent catalytic activity have been proposed for DSCs in recent years.⁸⁻¹⁵ However, few of them can compete with Pt considering from the two aspects on catalytic performance and potential of large-scale production.

Metal chalcogenide semiconductors possess profound importance in areas as diverse as photovoltaics,¹⁶ batteries,¹⁷ light-emitting diodes,¹⁸ and photocatalysis,¹⁹ etc. In particular, FeSe₂,²⁰ Ni_{0.85}(Co_{0.85})Se,²¹ CoS,²² NiSe₂,²³ NiS,²⁴ and CZTS(Se),²⁵⁻²⁶ etc. have been studied as CE materials in recent years and they have shown excellent catalytic activity with I₃⁻/I⁻ electrolyte DSCs. Among them, notably, environmentally benign tin-based chalcogenide materials SnSe and SnS comprised of earth-abundant elements have received considerable attention over the past several years because of their promising applications in photo- and thermo-electric devices. Specifically, it is widely known that SnSe is a kind of excellent material for thermoelectric applications due to its ultralow thermal conductivity and also a promising anode material for ion batteries;²⁷⁻²⁹ and for SnS, it is an attractive candidate as light-absorbing semiconductor in photovoltaic devices for its favorable band gap of ~1.32 eV (bulk material) that is well matched to harvest visible photons of the solar spectrum.³⁰⁻³¹ For both SnSe and SnS thin film materials, they are electrically conductive,

making them highly attractive for both electrode and electrocatalysis applications, as the lower resistivity films could have significant benefit for larger cells where series resistance is prominent, and, moreover, the use of a conductive substrate, such as FTO/glass, may not be necessary.⁸ However, the potential use of SnSe and SnS materials as efficient catalytic electrodes in photoelectrochemical devices has otherwise remained mostly uncharted. Although similar compound SnS_x-based materials, SnS nanosheets, SnS nanowires, and SnS₂ nanosheets have been previously investigated as promising CEs for DSCs, the catalytic performance is still less satisfactory when compared with Pt.³² It is noted that the synthesis required to prepare SnS_x nanoparticles involves use of organic species as capping ligands, yet these insulating capping layers would eventually limit the conductivity of the films, which is important for CEs.³³ We consider further enhancement of catalytic performance of those SnS_x-based materials can be expected by optimizing the processing of materials, which should lead to an improved quality of the CE films and thus the electrochemical properties. In addition, it has been demonstrated that apart from the intrinsic catalytic property of the material, the difference in stoichiometry as well as electrode morphology should also be responsible for the variation in the electrocatalytic activity of a given electrode.^{5, 8, 23, 34-35} In this paper, SnS and SnSe thin films with high catalytic performance were demonstrated and their catalytic activity toward the triiodide reduction in DSC system was rigorously examined by impedance spectroscopy, cyclic voltammetry and Tafel polarization studies. It is noteworthy that these tin chalcogenide crystalline thin films were prepared via a low-temperature solution-based route employing their as-prepared semiconductor inks, paving the way for large-scale commercialization.

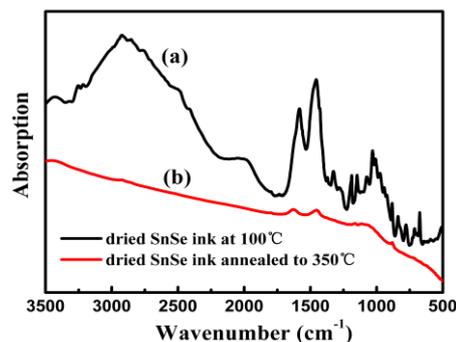


Fig. 1 FT-IR spectra of (a) the dried SnSe ink obtained by heat-treating at 100 °C and (b) dried SnSe ink after annealing to 350 °C under flowing nitrogen.

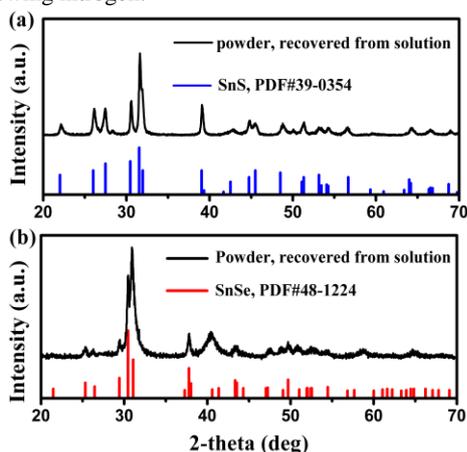


Fig. 2 XRD patterns of the powders recovered from solution by a heat treatment at 350 °C under nitrogen. (a) SnS sample and (b) SnSe sample.

An extremely facile route was employed to prepare chalcogenide semiconductor inks, i.e., the purchased SnSe and SnS solid powders were directly dissolved in a novel and relatively nonhazardous solvent mixture comprised of ethanedithiol and ethylenediamine which was first used by Brutchey's group.³⁶ SnSe and SnS thin films were then obtained by drop-casting or spin-coating the prepared inks onto a FTO glass, with a mild post-heat treatment at 350 °C under nitrogen. It is noted that the utility of this facile solution-phase deposition route to SnS thin film has been previously demonstrated by Brutchey et al.,³⁷ while the trial of the recovery for SnSe thin film from solution herein was conducted for the first time. Therefore, we mainly focus on the characterization of the SnSe films obtained from this facile and novel approach. FT-IR spectra of the SnSe sample (Fig. 1) show that the strong $\nu(\text{C-H})$ and $\nu(\text{N-H})$ stretching bands (at ca. 3300-2800 cm^{-1}) along with other bands that originate from organics in the solvent were greatly reduced after annealing the dried ink to 350 °C, suggesting the complete loss of the organic species after heating, this is also consistent with literature precedent described for the other chalcogenides.³⁶ The crystallographic phases of the obtained tin chalcogenides were investigated by XRD measurement. Fig. 2 shows the powder XRD patterns of the recovered materials after annealing the dried inks to 350 °C. The main peak positions were identical to those of the parent samples (XRD patterns of the as-bought commercial SnS and SnSe materials were shown in Figure S1, ESI), confirming that the parent chalcogenide solids were successfully recovered from solution with high crystallinity and pure phase. Additionally, EDS spectra of five randomly selected areas of the powdered samples reveal a high degree of compositional agreement between the as-bought material and those recovered from solution for both SnS (50.35% S, 49.65% Sn, which is in good agreement with the reported value³⁷) and SnSe (48.78% Se, 51.22% Sn).

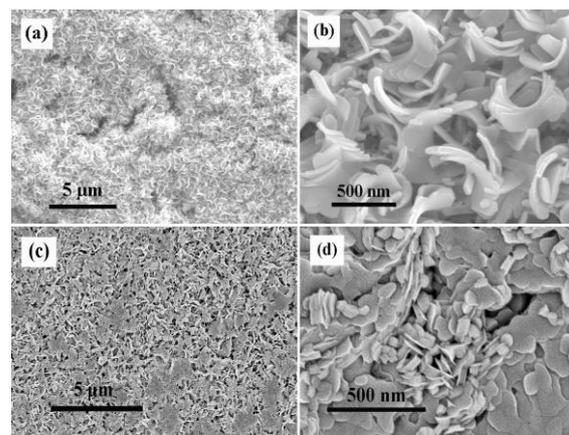


Fig. 3 SEM images of the annealed films on FTO glass. (a, b) SnS. (c, d) SnSe.

The morphology of the obtained chalcogenide films on FTO glass was investigated with SEM imaging. No major microscopic cracks or pinholes were observed for the resulting films (Figure S2, ESI). Plane SEM images demonstrate that the obtained chalcogenide films were both polycrystalline in nature and present a rough morphology formed by large laminar sheets (Fig. 3). It will be advantageous as a CE material to offer more catalytic sites and obtain improved catalytic performance.³⁸⁻³⁹ Specific surface areas of the SnSe and SnS films were measured to be 30.85 m^2g^{-1} and 28.85 m^2g^{-1} , respectively, which would undoubtedly contribute to providing an increased number of catalytic active sites for the redox process. It is interesting to note that specific surface areas of the resulting films are even more than twice the value of $\text{Co}_{0.85}\text{Se}$ thin film (11.8 m^2g^{-1}), an outstanding CE material which exhibits high electrocatalytic activity in I_3^-/I^- electrolyte.²¹

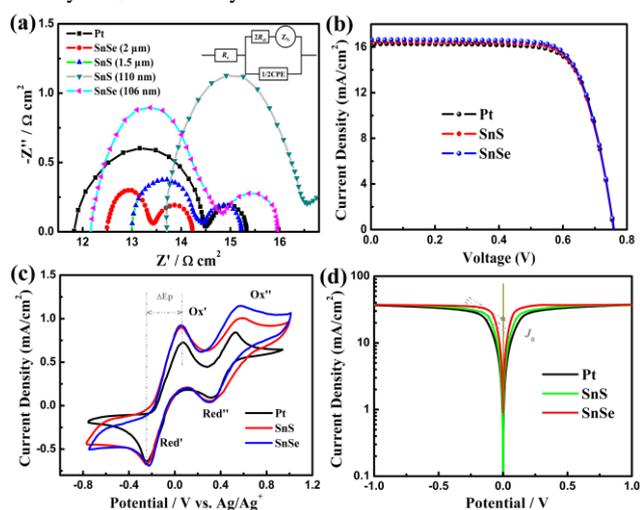


Fig. 4 (a) Nyquist plots of EIS for thin-layer symmetrical cells fabricated with SnSe and SnS (spin-coated and drop-cast) films and Pt loaded electrodes. The inset shows the equivalent circuit used to fit the EIS spectra. (b) Representative J - V characteristics of devices with Pt and drop-cast CEs under simulated AM1.5G irradiation (100 mW cm^{-2}). (c) Cyclic voltammograms of I_3^-/I^- redox couple for SnSe, SnS and Pt electrodes. (d) Tafel polarization curves of SnSe, SnS, and Pt symmetrical cells, measured at 20 °C.

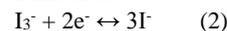
In the following, we shall investigate the electrochemical characteristics of the prepared SnSe and SnS films in iodide/triiodide redox system as a CE catalyst. We first performed studies varying the chalcogenide layer thickness. Solution processing techniques offer the distinct advantage of the direct and easy control of the thickness of the films. Herein, SnSe and SnS films of varying thicknesses were obtained by drop-casting and spin-coating the prepared inks onto a FTO glass. The thickness of the SnSe layer was about 106 nm for the spin-coated sample and 2 μm for the drop-cast one; similarly, about 110 nm for the spin-coated SnS layer and 1.5 μm for the drop-cast sample (thickness was determined by an Ambios-Step profilometer for thick films and cross-section SEM image for thin films). It is important to note that these chalcogenide films were strongly bound to the FTO substrate, and sonication in electrolyte solution for 1 h was not able to peel them off, suggesting the good mechanical stability of the prepared CEs. Electrochemical impedance spectroscopy (EIS) is a widely used technique to characterize the charge transfer between the semiconductors and electrolytes, which is a key parameter for a given CE.⁴⁰ Fig. 4a shows the Nyquist plots of EIS measurements for the thin-layer symmetrical cells fabricated with tin chalcogenide films and Pt electrode. The semicircle in the high-frequency range results from the charge transfer resistance (R_{ct}) at the electrolyte/counter electrode interface.⁴¹ The electrochemical parameters of the symmetrical cells extracted by fitting the EIS spectra are summarized in Table S1. It is found that both of the drop-cast chalcogenide films give R_{ct} values smaller than that of the spin-coated counterparts, indicating a better catalytic activity obtained by these thicker films. The explanation for this observation can be intuitively assumed to originate from the thicker films corresponding to a larger number of catalytic sites and in fact a higher catalytic activity was also observed for those thicker and more porous electrodes in previous studies.^{8, 42} It is also worth noting that both of the spin-coated and drop-cast films exhibit R_{ct} values that are well below the $10\Omega\text{cm}^2$ level needed for high-performance solar cells,⁴³⁻⁴⁴ and even the inferior thinner films give resistance values approach that of Pt, suggesting the eximious catalytic activity of these tin-based chalcogenide CEs. Fig. 4a further compares the catalytic performance of the thicker SnSe and SnS electrodes with those of Pt electrode. As expected, the R_{ct} values of those thicker SnSe and SnS electrodes were less than that of the Pt electrode, evidencing a higher catalytic activity of the prepared chalcogenide films. In addition, the Nernst diffusion-limited impedance (Z_N), which is given by eqn (1), exhibited smaller values for both SnSe and SnS, indicating a larger diffusion coefficient and, thus, a superior catalytic activity since the diffusion rate of the iodide species has a positive correlation with the reduction rate of the triiodide on the surface of catalyst.⁴³ Further improvement in photovoltaic performance of the integrated solar cells assembled with SnSe and SnS CEs is thus expected, as shown in Fig. 4b (photovoltaic parameters are summarized in Table S1, ESI), concordant with their improved electrocatalytic performance. In addition, to demonstrate the durability and reproducibility of the prepared CEs, we present the photovoltaic device performance measured for solar cells assembled with photoanodes from different batches and a reused CE in Table S2 (ESI). We found that solar cells fabricated with

reused SnSe (or SnS) CE exhibited near-identical efficiencies, indicating high reproducibility and stability of SnSe and SnS CEs in iodine-based electrolyte.

$$Z_N = \frac{kT}{n^2 e_0^2 c A \sqrt{i\omega D}} \tanh\left(\sqrt{\frac{i\omega}{D}} \delta\right) \quad (1)$$

where k is the Boltzmann constant, T the temperature, n the electron number involved in the reaction, e_0 the elementary charge, c the concentration of triiodide, A the effective electrode area, ω the angular frequency, D the diffusion coefficient of triiodide and δ is the thickness of the diffusion layer.

To support our EIS data, cyclic voltammetry (CV) measurement was carried out. Fig. 4c presents the cyclic voltammograms of iodide/triiodide redox species for these two tin chalcogenides and Pt loaded electrodes. Ten consecutive cycles at a scan rate of 20 mV s^{-1} were performed and no significant changes were observed in both curve shape and peak current density, suggesting the good electrochemical stability of the CEs during the redox process. It is seen that all of the electrodes exhibit two pairs of oxidation-reduction peaks (Ox'/Red', Ox''/Red''), as labeled in Fig. 4b). The left and right pairs are assigned to the redox reaction of I^-/I_3^- and I_2/I_3^- , which can be described by eqn (2) and (3), respectively. Since the CE is responsible for catalyzing the reduction of I_3^- to I^- , the characteristics of peaks Ox' and Red' are the focus of our analysis. The cathodic and anodic peak currents with chalcogenide electrodes were found to be higher than that of Pt, signifying the superior electrocatalytic activity of the SnSe and SnS films. In addition, the peak to peak separation value (ΔE_p), which correlates with the standard electrochemical rate constant of the redox reaction, exhibited smaller values in the case of chalcogenide CEs (270 mV, 283 mV for SnSe, SnS, respectively) than Pt (334 mV), confirming their higher catalytic activity toward the reduction of triiodide.



Tafel polarization curves on symmetrical cells were measured to further elucidate the superior activity of the chalcogenide films. As seen in Fig. 4d, the anodic and cathodic branches of the Tafel curve of the prepared electrodes show a larger slope than those of Pt electrode, implying a higher exchange current density (J_0) obtained on these chalcogenide loaded electrodes.²² J_0 can be expressed by eqn (4), which indicates J_0 varies inversely with R_{ct} , thus reconfirming the smaller charge transfer resistance on the prepared electrodes. The above observation is well consistent with the results on R_{ct} value that revealed by EIS spectra.

$$J_0 = \frac{RT}{nFR_{ct}} \quad (4)$$

where R is the gas constant, F the Faraday's constant, and R_{ct} is the charge transfer resistance, T and n retain their established meanings.

In summary, we have demonstrated two novel Pt-free CEs for DSCs based on earth-abundant tin chalcogenide materials. SnSe and SnS thin films have been deposited on FTO glass via a facile and cost-effective approach employing their as-prepared semiconductor inks, being processable in large-scale production. These solution-processed tin chalcogenide films exhibited superior catalytic activity to that of the commonly used Pt electrode. An improved photovoltaic efficiency with maximum

value of 9.4% was thus achieved, which is higher than that of the cells with Pt (9.0%). Our findings presented here expand the scope of tin chalcogenide films as competitive, low-cost, and earth-abundant catalytic materials for photoelectrochemical solar cells and meanwhile pave the way for large-scale commercialization of efficient CEs for DSCs. However, it is still noteworthy that, though relatively good short-term stability of SnX CEs in the electrolyte has been confirmed by conducting consecutive CV scans and reproducibility measurement, the long-term stability of these integrated solar cell devices is still needed to be further assessed as this should be of great importance for their practical applications, and, we will continue to work on this issue.

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Notes and references

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† Electronic Supplementary Information (ESI) available: XRD patterns of the commercial as-bought SnS and SnSe powders, top-view SEM images of SnS and SnSe thin films, photovoltaic device characteristics. See DOI: 10.1039/b000000x/

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