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Cobalt sulfide decorated polyaniline complex counter electrodes for efficient dye-sensitized solar cells

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ABSTRACT

The practical commercialization of dye-sensitized solar cells (DSSCs) requires persistent exploration of cost-effective counter electrodes (CEs). Aiming at increasing the active sites and accelerating charge transfer of a CE electrocatalyst, cobalt sulfide decorated aniline complexes are synthesized by a reflux technique and subsequently in-situ polymerized for Pt-free polyaniline-cobalt sulfide (PANi-CoS) electrocatalysts in liquid-junction DSSCs. The preliminary results suggest that an enhanced electrocatalytic activity for I_3^- reduction is ascribed to the fast electron-transfer ability of PANi and the high catalytic activity of CoS. The optimized DSSC device based on PANi-7 wt% CoS yields an impressive power conversion efficiency up to 8.55% under an illumination of air mass 1.5 global simulated solar light, which is much higher than 5.65% and 5.79% for the solar cells with pure PANi and pristine Pt CEs, respectively.

1. Introduction

As the third-generation solar cell, dye-sensitized solar cells (DSSCs) have emerged as one of the most promising devices to solve ever-increasing global energy consumption [1,2] due to their inherent properties such as low production cost, environmental friendliness, ease of fabrication, and relatively high power conversion efficiency [3,4]. Enhancement of reduction reaction from triiodide (I_3^-) ions to iodide (I^-) and reduction in electrode cost are two prerequisites to improve the conversion efficiency of a cost-effective DSSC [5]. Preferred Pt electrode has restricted the practical application of DSSCs owing to high expense and scarce resource in the earth [6,7], therefore cost-effective and highly electrocatalytic counter electrode (CE) electrocatalysts have been exploited to substitute for the traditional Pt-based species. Among cost-effective CE electrocatalysts, it has been found that carbonaceous materials [8,9], transition metal oxides [10], nitrides [11], sulfides [12], selenides [13], carbides [14], phosphides [15], and conducting polymers [16,17] can be proposed as candidate alternative CE materials. Polyaniline (PANi) has been of continuous interest because its widespread application in supercapacitor and electrocatalysis field owing to its low cost, easy fabrication and environmental stability as well as good conductivity [18,19]. However, its electrocatalytic activity and long-term stability of pure PANi still can't match up to Pt-based materials, resulting in the unsatisfactory power conversion efficiency when utilized in DSSC platforms.

Utilizing synergistic catalytic effect by combination of several materials provides a promising avenue to fabricate robust CE electrocatalysts [20]. Aiming at improving the electron-migration ability, the combination of carbonaceous materials with conducting polymer for complexes such as PANi-graphene and PANi-carbon nanotube has been extensively studied in our previous studies [21,22]. The electrical conduction and electrocatalysis can be elevated, arising from the easy charge-transfer between carbonaceous materials and PANi. However, one of the drawbacks of carbonaceous materials is the limited active sites for I_3^- reduction and therefore unsatisfactory redox behaviors [23]. To our best of knowledge, cobalt sulfide (CoS) is very effective in catalyzing the I_3^- reduction reaction and is comparable to that of traditional Pt material [24,25]. In order to develop other robust PANi-based composite CEs, we present here the experimental realization of aniline-CoS complexes by a reflux process and subsequent PANi-CoS complexes at F-doped SnO_2 (FTO) conductive glass after suffering an in-situ polymerization. Compared with pristine PANi, the electrocatalytic ability is dramatically enhanced by utilizing PANi-CoS complex. A potential mechanism is attributed to superior properties and the increased active sites of CoS as well as improved charge-transfer kinetics between PANi

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and CoS. The PANi can not only serve as the anchoring matrix to load and hinder agglomeration of CoS, but act as linker to improve the electrical connection between CoS nanoparticles [26]. Due to the highest electrocatalytic activity and more efficient charger migration channel, an impressive power conversion efficiency of DSSC based on PANi-7 wt% CoS complex CE is enhanced to 8.55%, which is much higher than 5.65% for PANi based solar cell and 5.79% for pristine Pt based device.

2. Experimental

2.1. Synthesis of CoS nanoparticles

In a typical synthesis of CoS nanoparticles, 1.0115 g of $CoCl_2 \cdot 6H_2O$ powders was dissolved in 30 mL of deionized water and then 0.646 g of thiourea were added into above solution under vigorous magnetic stirring. Subsequently, the reactants were transferred into a 50 mL of Teflon-lined stainless steel autoclave and heated at 160 °C for 12 h. After cooling naturally, the resultant black powders were centrifuged and rinsed repeatedly by deionized water and anhydrous ethanol, and vacuum dried at 60 °C for 24 h. The resultant CoS powders were used without post-treatment.

2.2. Reflux synthesis of aniline-CoS complexes

CoS powers at dosages of 1, 3, 5, 7, or 9 wt% were added into 10 mL of aniline and the mixtures were sonicated for 15 min. Subsequently, the mixtures were sealed in a three-neck flask and refluxed at 184 °C for 6 h in dark to prepare the aniline-CoS complexes under high-purity N_2 gas flow. When cooling down to room temperature, the complexes were stored under ambient conditions for further use.

2.3. Fabrication of PANi-CoS complex CEs

The PANi-CoS complex CEs were synthesized by an in-situ polymerization process on FTO glasses. Briefly, 1.48 mL of as-synthesized aniline-CoS complexes was dissolved in 50 mL of 1 M HCl aqueous solution and 50 mL of aqueous solution consisting of 1 M HCl and 0.125 M ammonium peroxydisulfate (APS) was dropped into above solution over a 2 h period at 0 °C under mild agitation. Prior to polymerization reaction, a freshly cleaned FTO glass substrate was placed at the bottom of vessel. Then, the polymerization reaction was continued at 4 °C for 10 h. Finally, the FTO supported PANi-CoS complex CE was rinsed thoroughly with 1 M HCl and deionized water, and stored in vacuum.

2.4. Assembly of DSSCs

A TiO_2 film with a thickness of around 10 μm was first deposited on the surface of FTO glass substrate by a traditional doctor-blade method and subsequently calcined at 450 °C for 30 min to obtain the TiO_2 film as photoanode. Afterward, the photoanode with active area of 0.25 cm^2 was sensitized by immersing into an ethanol solution containing 0.50 mM N719 dye for 24 h at room temperature. A typically sandwiched DSSC was fabricated by assembling a sensitized photoanode and a PANi-CoS complex CE with the redox electrolyte.

2.5. Electrochemical characterizations

To evaluate the electrocatalytic activity, all the electrochemical properties of CEs were recorded using a traditional Electrochemical Workstation. The cyclic voltammetry (CV) curves were recorded from −0.6 to +1.2 V and back to −0.6 V in a three electrode system comprising an Ag/AgCl reference electrode, a Pt CE, and the working electrode of PANi-CoS complex in a nitrogen-purged electrolyte solution. Tafel polarization measurements were carried out with the same equipment in a symmetric cell consisting of PANi-CoS complex CE|redox electrolyte|PANi-CoS complex CE with scanning potential window from −1 to 1 V at the scan rate of 10 mV s^{-1}. Electrochemical impedance spectroscopy (EIS) measurements were characterized with symmetric dummy cells, and the frequency range was from 10^5 kHz to 0.01 Hz with an ac modulation signal of 10 mV and zero bias potential at room temperature. The resultant impedance parameters were obtained by fitting with Z-View software.

2.6. Photovoltaic measurements

Photocurrent density-voltage (*J-V*) characteristics of DSSCs were measured under air mass 1.5 global (AM1.5G) illumination at 100 mW cm^{-2} from a 100 W Xenon arc lamp (XQ-500 W) which was calibrated by FZ-A type radiometer in the atmosphere. Each *J-V* curves were repeated measured at least ten times to control the experimental error within ±5%.

2.7. Other characterizations

The morphologies of PANi-CoS complex CEs were investigated by a field-emission scanning electron microscope (SU8020, Hitachi, Japan). The molecular structures of aniline-CoS complexes were determined on a PerkinElmer spectrum 1760 FTIR spectrometer. The optical absorption spectra were measured on a UV–vis spectrophotometer by dissolving the samples in acetone. A Fluorolog 3-P spectrophotometer was used to record the fluorescence emission spectra at room temperature with excitation wavelength of 500 nm.

3. Results and discussion

To reveal the effect of refluxing process on the interaction between CoS and aniline, the fluorescence emission spectra of CoS, pure aniline, aniline/7 wt% CoS mixture and resultant aniline-CoS complexes diluted with acetone solvent was recorded at 500 nm as shown in Fig. 1a. One can find that the maximum emissions of CoS-aniline complexes are at around 560 and 605 nm in acetone, whereas the fluorescence of pure CoS and aniline are significantly quenched. It is noteworthy to mention that the markedly distinction of the fluorescence emission spectra between CoS-aniline complexes and individual components indicates the formation of new light-absorbing species after the refluxing process. Considering the prerequisite of fabricating a robust PANi-CoS complex CEs is the rapid charger-transfer ability, in this fashion, this combination can result in enhanced electrocatalytic active. Furthermore, in order to understand more about the complexing mechanism of aniline monomers and CoS, UV–vis adsorption spectra of pure aniline, aniline/7 wt% CoS mixture and aniline-CoS complexes with various dosages of CoS in acetone are characterized. As shown in Fig. 1b, there is no obvious adsorption peak in the range from 350 to 1100 nm for pure aniline and aniline/7 wt% CoS mixture. In contrast, a new strong and broad adsorption peak between 350 and 600 nm can be observed, which may be attributed to the formation of interaction between CoS and aniline [27,28].

As indicated above, we believe that a new chemical species is produced after refluxing process at 184 °C and therefore the formation of a charge-transfer complex in its ground state because the CoS is a good electron acceptor, whereas the aniline is a common electron donor. At elevated temperature, aniline-CoS complex can be fabricated via the metal (d_π)-nitrogen (p_π)