



Investigation of carbon nanotubes decorated with cobalt sulfides of different phases as nanocomposite catalysts in dye-sensitized solar cells



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ABSTRACT

In this study, nanocomposites of cobalt sulfide and carbon nanotube (CNT) in the forms of CNT@CoS_{1.097} and CNT@Co₉S₈ were deposited on fluorine-doped SnO₂ (FTO)-coated glasses by using a facile spray-coating approach, followed by annealing under N₂ atmosphere at 400 and 600 °C, respectively; and employed as counter electrodes (CEs) for dye-sensitized solar cells (DSCs). According to the electrochemical properties of CEs quantified by cyclic voltammetry, electrochemical impedance spectroscopy, and Tafel polarization measurements, the CNT@Co₉S₈ CE showed a superior electrocatalytic activity towards triiodide (I₃⁻) reduction to that of the CNT@CoS_{1.097} CE. As a result, the DSC based on the CNT@Co₉S₈ CE achieved an impressive photovoltaic conversion efficiency of 7.78%, which was even higher than those of the DSCs assembled with the CNT@CoS_{1.097} CE (7.29%) and Pt CE (7.46%). This signifies that the CNT@Co₉S₈ was indeed an efficient and cost-effective Pt-like alternative CE for I₃⁻ reduction reaction in DSCs.

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1. Introduction

During the last decade, dye-sensitized solar cells (DSCs) have been considered as the promising next-generation photovoltaic devices due to their acceptable efficiencies, low-cost, simple fabrication procedures and so on [1]. Typically, a DSC is composed of a semiconductor photoanode adsorbed with dye molecules, a redox electrolyte, and a counter electrode (CE). As one of the most crucial components in a DSC, the CE generally functionalizes to collect electron from external circuit and catalyze the reduction of triiodine (I₃⁻) to iodine (I⁻) species [2]. A noble metal, Pt, has been proven to be an efficient CE because of its excellent electrocatalytic activity and good electrical conductivity. Nevertheless, Pt is an expensive and rare metal, and therefore may restrict large-scale manufacturing of low-cost DSCs [3].

To address this issue, in addition to conventional Pt-free alternative CEs such as carbon materials [4–6] and conducting polymers

[7–9], transition metal sulfides including cobalt sulfides [10–19], nickel sulfides [20,21], molybdenum disulfides [22–24], and tungsten disulfides [25,26] have been proposed as the promising CE materials in DSCs due to their excellent electrocatalytic activities toward I₃⁻ reduction. Among these metal sulfides, cobalt sulfides in the forms of CoS [10–12], Co₉S₈ [13–15], CoS_{1.097} [16], Co₃S₄ [17], Co_{8.4}S₈ [18], and CoS₂ [19] have demonstrated impressive electrocatalytic activities for the redox couples of I₃⁻/I⁻ in DSCs. However, the low charge transport in cobalt sulfide nanoparticles derived from random boundaries between particles generally limits the electrocatalytic activity for I₃⁻ reduction. To further solve this problem, a useful method is the decoration of cobalt sulfide nanoparticles on highly conductive carbon materials such as carbon nanotubes (CNT) [16,27,28] and graphene [19,29]. We successfully decorated CoS_{1.097} nanoclusters on CNTs surface by means of a facile hydrothermal method and employed the nanocomposite as a CE for DSCs [16]. The CNT@CoS_{1.097} CE delivered an enhanced electrocatalytic activity for I₃⁻ reduction, which can be ascribed to the increased active sites from CoS_{1.097} nanoclusters and the incorporation of fast electron-transfer framework from the conductive CNTs. The photovoltaic performance of the device based on the CNT@CoS_{1.097} CE is comparable to that of the cell with Pt CE, indicating the high potential of CNT@CoS_{1.097} nanocomposite as a Pt-free CE in low-cost DSCs.

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In this study, we deposited the aforementioned as-synthesized CNT@CoS_{1.097} nanocomposites on fluorine-doped SnO₂ (FTO)-coated glasses by using a facile spray-coating approach, followed by annealing under N₂ atmosphere at different temperature. The objective of this work is to investigate the electrocatalytic activities of the nanocomposite CEs with different cobalt sulfide phases. It is found that the chemical composition of the cobalt sulfides in the nanocomposite kept in the form of CoS_{1.097} even after annealing at 400 °C in N₂ atmosphere (still designated as CNT@CoS_{1.097}); however, its dominative composition was transformed to Co₉S₈ (designated as CNT@Co₉S₈) after annealing at 600 °C under the same atmosphere. According to extensive electrochemical characterizations, it is noteworthy that the resultant CNT@Co₉S₈ CE showed a superior electrocatalytic activity towards I₃⁻ reduction to that of the CNT@CoS_{1.097} CE. As a result, the DSC based on the CNT@Co₉S₈ CE delivered an impressive photovoltaic conversion efficiency of 7.78%, which was even higher than those of the DSCs assembled with the CNT@CoS_{1.097} CE (7.29%) and Pt CE (7.46%).

2. Experimental

2.1. Preparation of CEs

The synthesis procedure of CNT@CoS_{1.097} and CNT@Co₉S₈ nanocomposites basically referred to our previous study [16]. In brief, 30 mg of acid-treated CNTs was dispersed in a 60 mL aqueous solution containing 0.05 M glucose in a beaker under ultrasonication for 1 h. Concomitantly, 1.6 g of CoCl₂·6H₂O was added to the solution, and the mixture was stirred vigorously for 30 min, followed by adding 5 g of thiourea into the above solution. The mixture solution was stirred for another 30 min and then transferred to a 150 mL Teflon-lined stainless steel autoclave for hydrothermal reaction at 110 °C for 4 h, followed by at 240 °C for 12 h. After the hydrothermal reaction, the black precipitate was filtered, thoroughly washed with ethanol, and distilled water three times each and finally dried at 80 °C for 12 h. After being grounded for 1 h, 50 mg of the collected precipitate was dispersed in 10 mL ethanol by ultrasonication for 1 h. Subsequently, the CNT@CoS_{1.097} and CNT@Co₉S₈ nanocomposite CEs were obtained by depositing the as-prepared suspension solution onto FTO glasses through a simple spray-coating method, followed by annealed under N₂ atmosphere for 1 h at 400 °C and 600 °C, respectively. It should be noted that the film thickness of the CNT@CoS_{1.097} and CNT@Co₉S₈ nanocomposite CEs was both controlled at ca. 6 μm to investigate their electrocatalytic activities. For comparison, the standard mirror-like Pt CE was fabricated by DC sputtering on a FTO glass with a thickness of 100 nm.

2.2. Device fabrication

To prepare the TiO₂ photoanodes for DSCs, clean FTO glasses (8 Ω sq⁻¹, Nippon Sheet Glass) were immersed in an aqueous solution containing TiCl₄ (40 mmol L⁻¹) at 70 °C for 30 min and then washed with water and ethanol subsequently. Then, the nano-TiO₂ paste (ETERDSC Ti-2105A, Eternal Chemical Co.) was screen-printed on FTO glass repeatedly via a semiautomatic screen printer (ATMA, AT45PA) until the film thickness reached 12 μm. Finally, a 4 μm light scattering film (ETERDSC Ti-2325, Eternal Chemical Co.) was further screen-printed on the as-prepared nano-TiO₂ film. The bilayer TiO₂ photoanodes with an area of 0.16 cm² were gradually sintered under an air flow at 150 °C for 10 min, 325 °C for 5 min, 375 °C for 5 min, 450 °C for 15 min in furnace. After cooling down to room temperature, the bilayer TiO₂ photoanodes were treated with TiCl₄ solution at 70 °C for 30 min and sintered again. When the TiCl₄-treated TiO₂ photoanodes

were cooled down to 80 °C, dye impregnation on the TiO₂ photoanodes was made by soaking them in a 0.3 mM N719 (D719, Everlight Chemical Industrial Corp.) ethanol solution at room temperature for 12 h. The dye-sensitized TiO₂ photoanodes were then washed with ethanol, and dried under air flow. Finally, the dye-sensitized TiO₂ photoanodes and the various CEs were assembled face-to-face and sealed with a 30 μm-thick thermal-plastic Surlyn spacer (SX1170-25, Solaronix). A proper amount of liquid electrolyte composed of 1 M 1,3-dimethylimidazolium iodide (Merck), 0.5 M 4-tert-butylpyridine (Aldrich), 0.15 M iodine (J.T. Baker), and 0.1 M guanidine thiocyanate (Aldrich) in 3-methoxypropionitrile (Acros) was slowly injected into the gap between the two electrodes through the pre-drilled holes on the CEs. The holes were further sealed with hot-melt glue.

2.3. Characterizations of the CEs and DSCs

The X-ray powder diffraction (XRD) patterns of the nanocomposites were recorded via an X-ray diffractometer (XRD 6000, Shimadzu Corp.) with Cu Kα radiation from 20° to 80°. The surface morphologies of the nanocomposites were observed by a field-emission scanning electron microscopy (FE-SEM; JSM-7600F) and a high-resolution transmission electron microscopy (HRTEM; JEOL JEM-2100F). The Brunauer-Emmett-Teller (BET) specific surface areas of the nanocomposites were analyzed using a CBET-201A (Porous Materials, Inc.) analyzer by nitrogen absorption. For characterizing the electrochemical properties of the various CEs, cyclic voltammograms (CVs) and Tafel polarization curves were conducted using a computer-controlled electrochemical analyzer (CHI 6081D, CH Instrument). Electrochemical impedance spectroscopy (EIS) was executed with an electrochemical workstation (IM-6, ZAHNER). CVs were carried out in a conventional three-electrode system. One of the various CEs, a Pt sheet, and a Pt wire served as the working electrode, counter electrode, and reference electrode, respectively. CVs were recorded at a scan rate of 10 mV s⁻¹ in the electrolyte composed of 50 mM LiI, 10 mM I₂, and 50 mM LiClO₄, with 3-methoxypropionitrile as the solvent. The symmetrical dummy cells assembled with two identical CEs with exposed film area of 0.64 cm² were used for Tafel and EIS measurements. Tafel polarization curves were obtained with a scan rate of 10 mV s⁻¹ in a two-electrode system. EIS was measured by scanning the symmetric dummy cell with the ZAHNER electrochemical workstation from 100 kHz to 0.1 Hz with 5 mV amplitude at open-circuit condition. The resultant EIS spectra were fitted with the software, ZSimpWin version 3.1. The current-voltage (IV) curves of DSCs were measured with a computer-controlled digital source meter (Keithley 2400) under exposure of a Newport solar simulator, which was calibrated to one sun light density (AM 1.5G, 100 mW·cm⁻²) with a radiant power/energy meter (Oriel, 70260).

3. Results and discussion

Fig. 1 presents the XRD diffraction patterns of the as-prepared nanocomposites. As for the nanocomposite annealed at 400 °C under high-purity N₂ atmosphere, all of the diffraction peaks can be unambiguously indexed to the crystalline CoS_{1.097} with a hexagonal structure (JCPDS #19-366) except for the weak broad peak at 25.8° from the CNTs (marked as α) [16,30,31]. After annealing at 600 °C under N₂ atmosphere; however, the most of crystalline CoS_{1.097} was transformed in the form of Co₉S₈ structure (JCPDS #65-1765) on the CNTs [32,33], as shown in the diffraction peaks. This suggests that the CoS_{1.097} based nanocomposite (designated as CNT@CoS_{1.097}) was transformed in the form of Co₉S₈-dominant nanocomposite (designated as CNT@Co₉S₈) although partial CoS_{1.097} nanoclusters still retained on the CNTs for

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