

High Efficient Co_3S_4 Supported by Carbon Nanofibers Composite Counter Electrode Catalyst for Dye-sensitized Solar Cells

Jun-Ying XIAO^{1, a}, Jun XU^{2, b}, Mi-Dou CUI^{1, c}, Lin-Zhong ZHAN³, Liang-Xing ZHANG³, Yong-Wen PANG¹, Ling LI^{1*}, Xiao-Wei LI^{1*} and Zhi-Qiang LIU^{1*}

¹Hebei Key Lab of Optic-electronic Information and Materials, College of Physics Science and Technology, Hebei University, Baoding 071002, China

²Huizhou College of Business, Huizhou, 056025, China

³College of Chemistry and Environmental Science, Hebei University, Baoding 071002, China

^axiaojunyinghbu@163.com, ^bxujun0830@163.com, ^c15733291277@163.com

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Abstract. Cobaltosic sulfide (Co_3S_4) has been introduced into dye-sensitized solar cells (DSCs) as a counter electrode (CE) in place of Pt for the first time. The DSCs with the pure Co_3S_4 CE obtain a power conversion efficiency (PCE) of 4.2%, only reaching 79% of the comparable DSC using Pt as the CE (5.31%). To improve the catalytic activity of pure Co_3S_4 , electrospun carbon nanofibers (ECN) were fabricated by the electrospun method and the composite of ECN supported cobaltosic sulfide ($\text{Co}_3\text{S}_4/\text{ECN}$) was synthesized by hydrothermal synthesis method. And the DSCs based on $\text{Co}_3\text{S}_4/\text{ECN}$ CE achieve a high PCE of 6.44%, which increases by 21% compared to the Pt CE, indicating that the $\text{Co}_3\text{S}_4/\text{ECN}$ composites were a good choice to increase the efficiency of DSCs.

Introduction

Dye-sensitized solar cells (DSCs), as the simple fabrication procedures and low cost, attract great interest due to the special characteristics of the DSCs, such as a tunable band-gap spectrum by controlling their composition, environmental friendliness, and high extinction coefficients and power conversion efficiency (PCE)[1, 2]. A typical DSC consists of a dye-sensitized nanocrystalline semiconductor TiO_2 film using as photoanode, an electrolyte with a redox couple (triiodide/iodide), and a counter electrode (CE) [3, 4]. Among them, the conventional CE with good electrocatalytic properties for the reduction of triiodide to iodide was platinum (Pt). However, as a noble metal, Pt is scarce and expensive which restricts the long term development and practical application of DSC [5, 6]. Fortunately, develop low-cost CE catalysts is one of promising paths to reduce the production cost to replace the expensive Pt CE. A class of Pt-free catalysts has been used as CE catalysts, such as the carbonaceous materials, some transition metal, and the sulfide and oxidate of the transition metal [7, 8].

Among these materials, composite fabricated by metal and carbonaceous is tested as efficient counter electrodes recently, which show much higher performance than the single use of metal sulfides or carbon [9, 10]. Recently, cobaltosic sulfide (Co_3S_4) electrospun carbon nanofibers (ECN) were reported to be good catalysts[11, 12]. Herein, we successfully fabricated the carbon nanofibers and the composite of electrospun carbon nanofibers (ECN) supported cobaltosic sulfide ($\text{Co}_3\text{S}_4/\text{ECN}$) by the electrospun method and hydrothermal synthesis method. And the $\text{Co}_3\text{S}_4/\text{ECN}$ composites was employed as CE in DSCs for the first time. The $\text{Co}_3\text{S}_4/\text{ECN}$ based DSC obtained a PCE value of 6.44% which increased by 21% compared to the Pt CE, indicating the composite of $\text{Co}_3\text{S}_4/\text{ECN}$ was expected to be worked as effective CE to replace Pt.

Experiment

Preparation of ECN. The electrospun carbon nanofibers (ECN) were synthesized by a electrostatic spinning method as Patil reported [13]. In briefly, polyacrylonitrile (PAN, Mw = 150000) and N, N-dimethylformamide (DMF) were used as the precursor solutions. The conditions employed for

electrospun were of the order; 15 kV applied voltage and a flow rate of 1 mL h⁻¹. The electrospun nanofibers after collecting were stabilized in air at 230 °C, carbonized at 500 °C in N₂ and further heated to 1000 °C in N₂ to complete carbonization and initiate activation.

Preparation of Co₃S₄/ECN. 0.45 g Co(NO₃)₂, 3.27 g cysteine and 0.5 g ECN were added to ultrapure H₂O in a glass bottle and the final volume was 160mL. The solution was then transferred into a Teflon-lined autoclave and aged at 160 °C for 12 h. Crystalline powders after hydrothermal treatment were recovered by filtration, and washed with deionized water and alcohol, dried at 80 °C overnight. The pure Co₃S₄ was synthesized by the same procedure without addition of the ECN.

Results and Discussion

TEM and SEM analysis. The morphology of the as-obtained pure ECN and the Co₃S₄/ECN nanocomposite was characterized by TEM and SEM (shown in Fig. 1). Fig. 1a shows the SEM images of the pure ECN with connected network. The diameters of the carbon nanofibers can be estimated about 200 nm. The Co₃S₄/ECN nanostructure was investigated by the TEM (shown in Fig. 1b and 1c) which showed the Co₃S₄ nanoparticles was well-distributed on the surface of carbon nanofibers without aggregation. And the Co₃S₄ nanoparticles are polycrystalline as showed Fig. 1d.

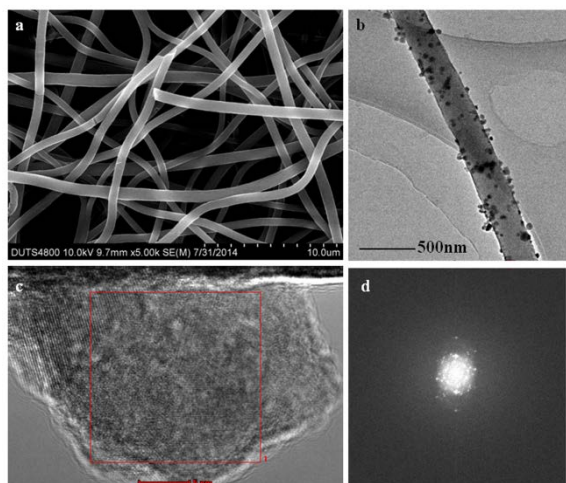


Fig. 1 TEM and SEM

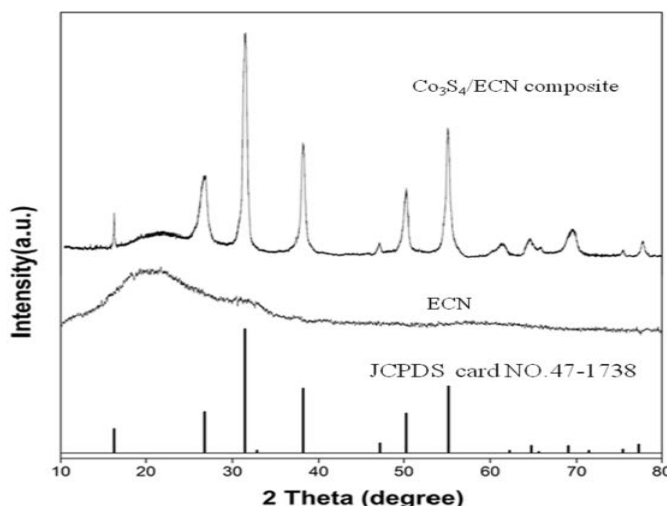


Fig. 2 XRD patterns

XRD analysis. Fig. 2 shows the XRD patterns of Co₃S₄/ECN composite and the pure carbon nanofibers. In the pattern of the carbon nanofibers, the peaks centered at the 2 θ angles of around 25 degrees were attributed to the (002) planes of the electrospun carbon nanofibers. Compared with the pattern of pure carbon nanofibers, the diffraction peaks of the Co₃S₄/ECN were perfectly indexed as pure linnaeite Co₃S₄ phase (JCPDS card NO.47-1738). Moreover, there are no obvious peaks for impurity on the patterns, which suggests that the sample was pure and no other impurities generated during the process.

Cyclic voltammetry (CV) analysis. To evaluate the catalytic activities of the different CEs for I₃⁻ reduction, cyclic voltammetry (CV) measurements were carried out using a three-electrode system, using Pt electrode as the CE and Ag/Ag⁺ as the reference electrode. Figure 3 shows the CV of the different CEs. Two pairs of reversible redox peaks were observed for all of these electrodes, which indicated high catalytic activity for I₃⁻ reduction that is favorable for the regeneration of the sensitizer. For the I₃⁻ reduction occurring at the CE surface, the cathodic peak current density of pure Co₃S₄ showed is close to Pt, while a larger cathodic peak current density was observed in Co₃S₄/ECN which implied huge surface areas, enhanced electrocatalytic activity and a higher short-circuit current would be achieved compared to Pt and pure Co₃S₄. Moreover, the cathodic peaks of the Co₃S₄/ECN exhibit a more negative potential than those of Pt and pure Co₃S₄. The outcome subsequently resulted in an enhancement of the electrochemical catalytic activity. Based

on the CV analysis, $\text{Co}_3\text{S}_4/\text{ECN}$ is expected to perform more superior catalytic activity than pure Co_3S_4 and Pt in DSCs.

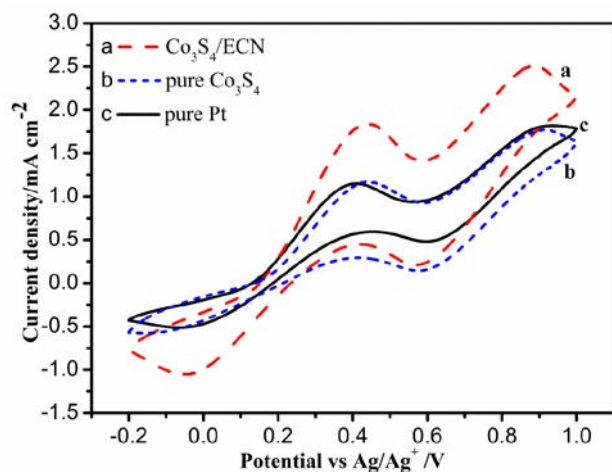


Fig. 3 Cyclic voltammograms

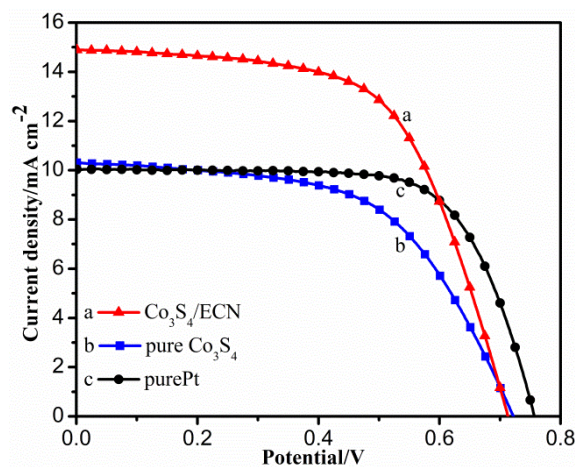


Fig. 4 J–V curves

J-V analysis. Fig. 4 shows the photocurrent density-photovoltage (J-V) curves for all of the DSCs. The DSC using $\text{Co}_3\text{S}_4/\text{ECN}$ as the CE showed an extremely high PCE of 6.44% on account of its superior catalytic behavior, which increased by 21% compared to the DSC using Pt as the CE (5.31%). The high short-circuit current density ($J_{sc}=14.89 \text{ mA cm}^{-2}$) is the main reason for the high PCE achieved in DSCs with the $\text{Co}_3\text{S}_4/\text{ECN}$ counter electrode. While the DSC using pure Co_3S_4 as the CE had a higher short-circuit current density ($J_{sc}=10.31 \text{ mA cm}^{-2}$) than Pt ($J_{sc}=10.04 \text{ mA cm}^{-2}$) and a higher open-circuit voltage ($V_{oc}=0.723 \text{ V}$) than $\text{Co}_3\text{S}_4/\text{ECN}$ ($V_{oc}=0.714 \text{ V}$), but the lowest fill factor ($\text{FF}=56.4\%$) resulted in a lower PCE (4.2%), only reaching 79% of the comparable DSC using Pt as the CE (5.31%). These values indicated that $\text{Co}_3\text{S}_4/\text{ECN}$ had the best electrocatalytic activity for I_3^- reduction compared to pure Co_3S_4 and Pt, which was in good agreement with the CV results, indicating that ECN supported Co_3S_4 to fabricate a composite electrode is feasible.

Summary

In summary, the $\text{Co}_3\text{S}_4/\text{ECN}$ composite was successfully synthesized and applied as CE catalyst in DSC for the first time. After a comprehensive analysis, it is evident that the catalytic activity can be enhanced by ECN supported Co_3S_4 to form a composite catalysis. In DSC systems, $\text{Co}_3\text{S}_4/\text{ECN}$, Co_3S_4 , and Pt acted as CE and the photocurrent density-photovoltage (J-V) curves for all of the DSCs were measured. The results showed that the DSC with the $\text{Co}_3\text{S}_4/\text{ECN}$ CE obtained a superb performance with a PCE of 6.44%, a highest J_{sc} of 14.89 mA cm^{-2} , a V_{oc} of 0.714 and a FF of 60.6%, while the PCE for Pt and pure Co_3S_4 was only 5.31% and 4.2%, respectively. Indicating that ECN supported Co_3S_4 to fabricate a composite electrode is feasible, which is a good choice to increase the efficiency of DSCs.

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