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Economically synthesized $NiCo_2S_4$/reduced graphene oxide composite as efficient counter electrode in dye-sensitized solar cell

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ABSTRACT

Exploiting efficient Pt-free counter-electrode materials with low cost and highly catalytic property is a hot topic in the field of Dye-sensitized solar cells (DSCs). Here, $NiCo_2S_4$/reduced graphene oxide (RGO) was prepared via an economical synthesis route, and the as-prepared composite exhibited comparable electrocatalytic property with the conventional Pt electrode as the counter-electrode. Notably, the introduction of RGO into the $NiCo_2S_4$ counter-electrode induces a significantly promoted electrocatalytic rate towards the triiodide reduction than that of pristine $NiCo_2S_4$ by increasing surface area in the composite electrode, as revealed by electrochemical impedance spectroscopic measurement and Tafel polarization measurement. The easy synthesis, low cost and excellent electrochemical performance of the $NiCo_2S_4$/RGO composites enable themselves to serve as promising counter-electrode candidates for efficient DSCs.

1. Introduction

Dye-sensitized solar cells (DSCs) have been the hotspots in the photovoltaic field both scientifically and industrially in the last two decades, ascribed to their easy fabrication, impressive photovoltaic performance, low cost and wide application possibilities [1–4]. Many efforts have been devoted to improving the power conversion efficiency (PCE) of DSCs with approaches including fabricating novel photoanodes, light management by improving dye loading and tuning the energy level alignment via employing new electrolytes [5–7]. Recently, PCE up to 13% has been achieved with the cobalt trisbipyridine redox mediator coupled with a meticulous device and sensitizer engineering under standard illumination conditions (AM 1.5G, 100 mW cm^{-2}) [8]. However, platinum (Pt) has been widely used as counter electrodes due to its superior catalytic activity, which is well-known to be expensive thus potentially inhibiting the large-scale implement of such devices [9]. Therefore, to develop Pt-free electrocatalysts with both high performance and low-cost is of significant importance. Till now, candidates including carbon-based materials, conducting polymers and transition metal oxides/nitrides/sulfides have been explored and considered to be promising [10–12]. Among them, transition metal sulfides (Co_3S_4, CoS, MoS_2 and SnS[14–15]) have attracted special attention [13] due their excellent catalytic properties compared with Pt, while they can be synthesized using simple approaches. More recently, ternary metal sulfides, such as $CoMoS_4$, $NiMoS_4$ and $NiCo_2O_4$, have been attracted extensive attention as efficient counter electrode materials. Ternary transition sulfides have an enhanced catalytic property due to the existence of nickel and cobalt ions. Banerjee et al. [16] explored the performance of DSCs using $NiCo_2S_4$ as the counter electrode, who directly synthesized $NiCo_2S_4$ on tin oxide (FTO) substrates by the sulfurization of the $NiCo_2O_4$ in toxic H_2S solution. Huang et al. [17] reported an in-situ hydrothermal approach to prepare $NiCo_2S_4$ on FTO glass. However, the utilization of toxic H_2S and the high temperature treatment prohibit the development of $NiCo_2S_4$ as efficient counter electrode materials. Moreover, the relatively poor conductivity of $NiCo_2S_4$ is another issue that needs to be solved for further improvement.

In this work, we demonstrated a simple, low temperature and non-toxic method to prepare efficient $NiCo_2S_4$/reduced graphene oxide (RGO) based counter electrodes for Pt-free DSCs. The performances of the $NiCo_2S_4$ films were carefully investigated by changing the ratio of $NiCo_2S_4$ to RGO. RGO have been added to the material to improve the electrical conductivity [18] and the

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PCE of DSCs for two sakes: (i). Reduce the recombination of electrons by increasing the conductivity of sulfides. (ii).Increase the specific surface to obtain more electrocatalytic activity sites. This work provides a low cost and non-toxic synthesis procedure for the promising alternative materials serving as counter-electrodes for efficient Pt-free DSCs.

2. Experimental section

2.1. Materials

All the materials were used as received. The materials used in this work include $Ni(NO_3)_2$ (Aladdin, 99.999%), $Co(NO_3)_2$ (Aladdin, 99.99%), $Na_2S.9H_2O$ (Alfa Assar, 98%), Graphite powder (Alfa Easar, 99.99%), polyvinylidene fluoride (Alfa Assar, 44080), *N*-methylpyrrolidinone (Aladdin, 99.9%).

2.2. Preparation of RGO

Graphene oxide (GO) suspension was prepared from natural graphite though a modified Hummers and Offeman's method [19]. The GO dispersed in deionized water was reduced by using FeI_2/Ni $(NO_3)_2$ aqueous solution as reported in our previous work [20]. FeI_2 was synthesized via the direct reaction between I_2 and Fe powder in water. $Ni(NO_3)_2$ solutions was introduced to FeI_2 solution for inhibiting the hydrolysis of Lewis acids. In detail, 2 g I_2 powders were ground into powder in an agate mortar and mixed with 2 g Fe particles in a beaker, for which the reaction between I_2 and Fe started fiercely and quickly, finishing within 15 s. Then, 200 mL deionized water was added into the beaker with strong stirring until the metal iodide was completely dissolved. After this, 1.2 mM Ni $(NO_3)_2$ was added into the FeI_2 solution. By collecting the supernatant, the FeI_2/Ni $(NO_3)_2$ aqueous solution was obtained. The obtained supernatant was added to a beaker containing 100 mL 10 mg mL^{-1} GO dispersion. Finally, the GO and FeI_2/$Ni(NO_3)_2$ solutions were heated to 95 ° for 6h to obtain RGO solution followed by cooling down and being collected through centrifugation to remove the surface-absorbing residues. Finally, RGO was dried 24 h and the obtained powder was further dried at 100 ° for 48 h.

2.3. Synthesis of $NiCo_2S_4$/RGO composite

The $NiCo_2S_4$ nanoparticles were synthesized via a simple solution-based co-precipitation method with different reaction times at 180 ° without using any surfactant [21]. The counter electrodes were obtained by mixing the synthesized materials ($NiCo_2S_4$, $NiCo_2S_4$/RGO (6mg), $NiCo_2S_4$/RGO(8mg) and $NiCo_2S_4$/RGO(10mg)) in ethanol (weight ratio of 1:9). The counter electrode pastes were ultrasonically dispersed for 1h. After that, the dispersions were deposited onto FTO substrates and heated to 120° by air-brushed spraying. After the deposition of the wet composite films, the electrodes were dried at 60 ° in vacuum for 12 h.

2.4. Assembly of DSC devices

TiO_2 nanostructured films were fabricated according to our previous reports [22–23]. The TiO_2 films were then soaked in the N719 solution (0.3 mM, tert-butanol/anhydrous acetonitrile 1:1 (v/v)) for 24 h to form photoanodes. The TiO_2 photoanodes and the Pt-free counter electrodes were assembled to form DSCs devices by sandwiching I^-/I_3^- based electrolyte, which was composed of 0.3 M LiI, 0.03 M I_2, 0.5 M 4-Tert butyl pyridine in the acetonitrile solution.

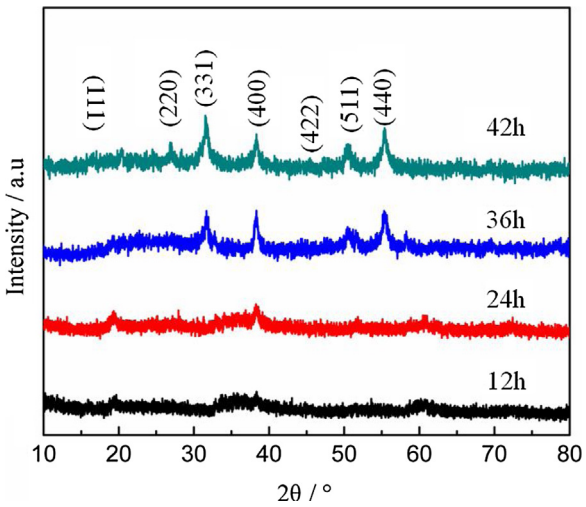

Fig. 1. XRD patterns of the as-synthesized $NiCo_2S_4$/ RGO.

2.5. Characterization

The microstructures of the samples were investigated by a scanning electron microscope (SEM, LEO 1530, Gemini, Zeiss, Germany) and TEM (Tecnai F20 TEM, FEI, USA). Composition identification of the samples were performed by the X-ray photoelectron spectroscopy (XPS) spectra (ESCALAB 250 Xi, Thermo SCIENTIFIC, USA) with Al Kα radiation (hv = 1486.6 eV) as source. The purity of the samples was analyzed by an X-ray diffractometer (XRD, D8 advance, Bruker, Germany). The surface area was investigated by low-temperature N_2 adsorption-desorption measurements using a surface area analyser (Quanta chrome, Autosorb-1, USA) and calculated using the Brunauer-Emmett-Teller (BET) method based on the absorption isotherm.

Electrochemical impedance spectra (EIS) measurements were taken at zero potential bias with the amplitude of the modulation was10 mV, and the frequency range was 0.1 Hz-100 kHz. Tafel measurements were performed with a scanning rate of 10 mV s^{-1}. Cyclic Voltammetry (CV) was carried out at a scan rate of 50 mV s^{-1} in a three electrode system with different counter electrodes as working electrodes, a Pt foil as counter electrode, and a Ag/Ag^+ electrode as reference electrode, respectively. The photocurrent-voltage (J–V) characteristic curves of the DSCs were measured with a digital source meter (2400, Keithley Instruments, USA) under AM 1.5G illumination (100 mW cm^{-2}), which was realized by a solar simulator (91192, Oriel, USA, calibrated with a standard crystalline silicon solar cell).

3. Results and discussion

$NiCo_2S_4$ were synthesized via a simple solution-based co-precipitation method with different reaction time (12 h, 24 h, 36 h, and 42 h) at 180 ° without using any surfactant. Fig. 1 shows the XRD patterns of the $NiCo_2S_4$/RGO composites with different reaction time. The sharp peaks can be assigned to the phases of $NiCo_2S_4$ (PDF 20-0782) at 42 h for 180 °. The sharp peaks at 16.3°, 26.8°, 31.6°, 38.3°, 50.5° and 55.3° are attributed to the(111), (220), (311), (400), (511) and (440) crystal planes [24,29], indicating the high purity of the as-prepared $NiCo_2S_4$. However, RGO is not detectable in XRD measurement, which is probably due to the relatively small content (<10 mg) of RGO in the $NiCo_2S_4$/ RGO composites.

The SEM images of $NiCo_2S_4$ film and $NiCo_2S_4$/RGO film are shown in Fig. 2. The $NiCo_2S_4$ film consisted of nanoparticles shows a sponge-like porous morphology with homogeneous size distribution. Concurrently, $NiCo_2S_4$/RGO film inherits the porous structure