



Hierarchical nickel sulfide/carbon nanotube nanocomposite as a catalytic material toward triiodine reduction in dye-sensitized solar cells



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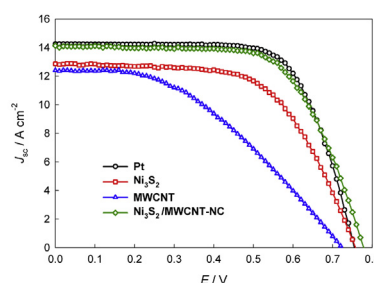
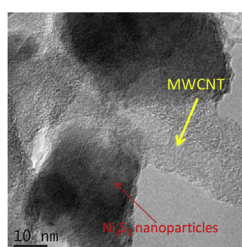
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HIGHLIGHTS

- Ni₃S₂/MWCNT-NC was synthesized via a facile glucose-assisted hydrothermal method.
- Annealed Ni₃S₂/MWCNT-NC CE showed improved catalytic activity for I₃⁻ reduction.
- Ni₃S₂ and conductive MWCNTs imparted high catalytic activity and stability to the catalyst.
- The DSC with the annealed Ni₃S₂/MWCNT-NC CE reached an efficiency of 6.87%.
- Ni₃S₂/MWCNT-NC CE served as an inexpensive and promising alternative to Pt CE for DSCs.

GRAPHICAL ABSTRACT



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ABSTRACT

In this study, Ni₃S₂ nanoparticles are successfully decorated on the backbone of conductive multi-walled carbon nanotubes (denoted as Ni₃S₂/MWCNT-NC) via a facile glucose-assisted hydrothermal method and employed as a counter electrode (CE) in dye-sensitized solar cells (DSCs). It is noteworthy that the use of glucose in the hydrothermal reaction plays a crucial role in the formation of the nanocomposite structure. Nevertheless, a thick layer of amorphous carbon derived from the hydrothermal carbonization of glucose covers Ni₃S₂ nanoparticle surface, and thus may inhibit the contact of active sites in Ni₃S₂ nanoparticles with electrolyte. It is found that the partial amorphous carbon on Ni₃S₂/MWCNT-NC can be effectively removed after annealing at 400 °C in a nitrogen atmosphere, which further increases the active sites of Ni₃S₂ nanoparticles on MWCNTs and therefore improves the electrocatalytic activity of the Ni₃S₂/MWCNT-NC CE. As a result, the DSC with the Ni₃S₂/MWCNT-NC CE yields a cell efficiency of 6.87%, which is higher than those of DSCs based on the Ni₃S₂ CE (5.77%) and MWCNT CE (3.76%). Because the Ni₃S₂/MWCNT-NC CE based DSC shows a comparable photovoltaic performance to the DSC using the Pt CE (7.24%), Ni₃S₂/MWCNT-NC CE may serve as a promising alternative to Pt CE for DSCs.

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1. Introduction

Since dye-sensitized solar cell (DSC) was reported by Grätzel and co-workers in 1991, it has become one of most promising photovoltaic devices due to its inherent virtues of simple

preparation, low cost and relatively high photovoltaic cell efficiency (PCE) [1,2]. Typically, a DSC comprises a dye-sensitized TiO₂ nanocrystalline film as a photoanode, a counter electrode (CE), and an electrolyte traditionally containing a triiodide/iodide (I₃⁻/I⁻) redox couple. As one of the crucial and indispensable component in DSCs, CEs serve to collect electrons from external circuit and accelerate the I₃⁻ reduction reaction. Therefore, a CE with the characteristics of both excellent electrocatalytic activity and high electrical conductivity is desirable [3]. Up to now, noble Pt metal with high conductivity and electrocatalytic activity has been widely used as a CE material. Nevertheless, Pt is very expensive and easily corroded by I₃⁻/I⁻ based redox electrolyte, thus possibly resulting in the restriction for large-scale production of DSCs in the future. Nowadays, a great deal of efforts have been made to explore Pt-like alternatives such as carbonaceous materials [4–12], conducting polymers, [13] transition metal oxides [14], nitrides [15], carbide [16,17], and sulfides [18–22].

Carbonaceous materials including carbon black, [4] graphite, [5] activated carbon, [6,7] carbon nanotubes (CNTs) [8–10], and graphene [11,12] have also been regarded as the potential alternatives for Pt due to their features of low cost, reasonable electron-transport ability, and high corrosion resistance. Among them, multi-walled carbon nanotubes (MWCNTs) have attracted much attention due to their exceptional specific surface area, high electrical conductivity, excellent mechanical strength and good thermal/chemical stability [23]. However, their intrinsically electrocatalytic activity for I₃⁻ reduction is not satisfactory owing to the limited number of active sites for I₃⁻ reduction on MWCNT surface. [24] To further increase the active sites for I₃⁻ reduction and improve the PCE of CNT-based DSCs, extensive studies have been recently focused on decorating the surface of CNTs with intrinsically electrocatalytic nanoparticles such as metal oxides, nitrides and sulfide [25–27]. For example, Zhang et al. [28] reported that the synthesis of the transparent conducting oxide (TCO)-free and Pt-free CE involves that the single-walled CNTs (SWCNTs) were spray-coated onto a glass substrate to form a thin film and then NiS precursor dispersed onto the resulting SWCNT film was annealed in argon to obtain the composite CE. Nevertheless, the DSC based on Ni₃S₂/SWCNT composite CE only provided a conversion efficiency of 2.76%. Very recently, Xiao et al. [29] prepared NiS/MWCNT composite CE by electrophoretic deposition of MWCNTs on Ti substrate and followed by the electrodeposition of NiS onto MWCNTs. The DSC assembled with the NiS/MWCNT/Ti CE achieved an impressive cell efficiency of 7.90%. However, the aforementioned nickel sulfide/CNT composites were prepared via two-step method which possibly results in that nickel sulfide is only deposited on the top surface of CNT layer or the inhomogeneous coating of nickel sulfides on the whole conductive CNT network.

In this study, we develop a facile one-pot hydrothermal method to directly grow the Ni₃S₂ nanoparticles on MWCNT backbones. In this hydrothermal synthesis, the addition of glucose can serve as the binder to allow the homogeneous dispersion of Ni₃S₂ nanoparticles on the MWCNT surface. We used this hierarchical Ni₃S₂/MWCNT nanocomposite (denoted as Ni₃S₂/MWCNT-NC) as the CE material in DSCs and characterized its electrocatalytic activity towards the reduction of I₃⁻ to I⁻. Due to the synergetic effect of Ni₃S₂ and MWCNTs, the DSC assembled with Ni₃S₂/MWCNT-NC CE shows the improved photovoltaic performance and excellent long-term stability.

2. Experimental section

2.1. Synthesis of Ni₃S₂/MWCNT-NC

The multi-walled CNTs were purchased from Thomas Swan & Co. Ltd. The diameters of CVD synthesized MWCNTs range from 10

to 20 nm and their wall thicknesses range from 3 to 6 nm. The purchased MWCNT product consisted of low inorganic residue (5 wt %) and 70 wt % nanotube contents. The purification of MWCNTs was achieved by refluxing MWCNTs (0.5 g) in concentrated nitric acid (100 mL) at 120 °C for 12 h. After the reaction, the MWCNT precipitate was filtered off, washed with distilled water, and dried in air. For the synthesis of Ni₃S₂/MWCNT-NC, acid-treated MWCNTs (7.5 mg) and glucose (90 mg) were added to the mixture solution of ethanol (9 mL) and distilled water (1 mL). The mixed solution was sonicated for 20 min to make a homogeneous dispersion and then nickel chloride (195 mg), thiourea (76 mg), and 1 mL of ammonia were added to the MWCNT dispersion. The mixture was then transferred to a stainless-steel autoclave (20 mL capacity). After sealing, the autoclave was heated to 180 °C for 12 h and then cooled to room temperature. Finally, the precipitate was filtered off, washed with distilled water, and dried in air. In a separate experiment, the Ni₃S₂ powder was also synthesized using the glucose-assisted hydrothermal method. Except for the addition of MWCNTs, the synthetic procedures for Ni₃S₂ powder are the same as those for Ni₃S₂/MWCNT-NC. For the synthesis of the mixture of Ni₃S₂ and MWCNTs, the synthetic procedures for Ni₃S₂/MWCNT-NC were followed except for the addition of glucose in the hydrothermal reaction. As shown in Fig. S1, Ni₃S₂ particles are separated from MWCNTs and there is no coating of amorphous carbon on the mixture when glucose is absent in the hydrothermal synthesis.

2.2. Fabrication of DSCs

The TiO₂ films (0.16 cm²) with a bilayer structure composed of a dense layer (~12 μm, ETERDSC Ti 2105, Eternal Chemical CO.) and a scattering layer (~2 μm, ETERDSC Ti 2325, Eternal Chemical CO.) were fabricated on the ultrasonically cleaned FTO glass substrates (7 Ω sq⁻¹, NSG) by using the screen-printing technique. The TiO₂ films were sintered at 450 °C for 30 min, and then subsequently cooled to 80 °C. Then, the sintered TiO₂ films were immersed in the 0.3 mM N719 dye (Everlight Chemical Industry Co.) for 12 h at a room temperature. The dye-sensitized TiO₂ photoanodes were assembled with CEs into sandwich-type configuration and sealed with hot-melt Surlyn (DuPont, 30 μm). After that, the redox electrolyte containing 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 injected into the sandwich-type cells via the predrilled holes on the CEs.

To prepare CEs, the active materials including Ni₃S₂, MWCNTs, and Ni₃S₂/MWCNT-NC, were mixed with acetylene black and polyvinylidene fluoride in a weight ratio of 8:1:1. The aforementioned mixture was added to *N*-methyl-2-pyrrolidone and the resulting slurry was grounded for 2 h. Then, the obtained slurry was coated onto the drilled FTO glass substrates by the doctor-blading technique to form the films with a thickness ca. of 4 μm. Finally, the coated FTO glass was sintered in a N₂ atmosphere at 400 °C for 1 h. For comparison, 100 nm thick Pt film was sputtered onto a FTO glass substrate as a CE by a DC sputtering instrument (ULVAC).

2.3. Material characterizations

A field-emission transmission electron microscope (TEM, JEOL JEM-2100F, operated at 200 kV with a point-to-point resolution of 0.19 nm) equipped with an energy dispersive spectrometer (EDS) was used to obtain the information on the microstructures and the chemical compositions. The X-ray powder diffraction (XRD) pattern of the composite was obtained from Philips X'Pert Pro MPD. All thermogravimetric analysis (TGA) experiments were performed

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