



Cobalt oxide and nitride particles supported on mesoporous carbons as composite electrocatalysts for dye-sensitized solar cells



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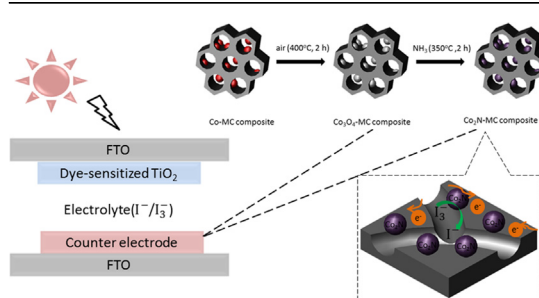
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HIGHLIGHTS

- Composites of Co₃O₄/mesoporous carbon as counter electrodes for dye-sensitized solar cells.
- Composites of Co₂N/mesoporous carbon are prepared by the nitridation of Co₃O₄/MC.
- The Co₂N/MC CEs are superior to the counterparts of Co₃O₄/MC in catalyzing I₃⁻ reduction.
- A high power conversion efficiency of 5.26% is reached, superior to that of the Pt-based one (4.88%).

GRAPHICAL ABSTRACT



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ABSTRACT

The composite electrocatalysts of cobalt oxide/mesoporous carbon and cobalt nitride/mesoporous carbon are synthesized via a convenient oxidation and subsequent ammonia nitridation of cobalt particles-incorporated mesoporous carbon, respectively. The cobalt oxide and nitride particles are uniformly imbedded in mesoporous carbon matrix, forming the unique composites with high surface area and mesopore architecture, and the resultant composites are evaluated as counter electrode materials, exhibiting good catalytic activity for the reduction of triiodide. The composites of cobalt nitride and mesoporous carbon are superior to the counterparts of cobalt oxide and mesoporous carbon in catalyzing the triiodide reduction, and the dye-sensitized solar cell with the composites achieves an optimum power conversion efficiency of 5.26%, which is comparable to the one based on the conventional Pt counter electrode (4.88%).

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1. Introduction

Dye-sensitized solar cell (DSSC) has attracted considerable attention as a potential renewable energy source compared to the

conventional silicon-based solar cell, due to its outstanding advantages, such as low cost, simple fabrication and relatively high conversion efficiency [1–3]. Within a typical DSSC, the collection of electrons from the external circuit and reduction of triiodide to iodide on the counter electrode (CE) is an extremely important process [4]. Pt is the preferred CE material with the excellent catalytic activity and good conductivity [5–7], though the high cost and limited resources severely restricts the large-scale production of DSSC. The development of abundant and cheap materials to

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replace Pt is demonstrated to be an effective strategy for reducing the cost of DSSC. To date, the carbonaceous materials [8–10], conductive polymers [11–13], transition metal nitrides [14,15], sulfides [16], carbides [17,18] and oxides [19] are regarded as promising replacements of Pt counter electrode due to their low cost and good catalytic activity in the reduction of triiodide. However, the carbon materials generally have low intrinsic electrocatalytic activity, and the transition metal compounds possess the poor electron transport efficiency between particles, which finally restricted their catalytic activity for the reduction of triiodide. Thus, rational design of the CE is a significant research area for a high-performance electrocatalyst.

Recently, the composites of transition metal compound nanoparticles and carbon material were constructed to resolve the drawbacks of individual components, such as TiN/carbon nanotubes [20], CoS/graphene [21], NiS₂/graphene [22], TaC/mesoporous carbon [23] and WO₂/mesoporous carbon [24]. Among various carbon substrates, the mesoporous carbon is a good choice due to its large surface area, well-developed mesoporous structure and good conductivity, which could provide fast electron-transport network and effective support for inorganic metal compound nanoparticles. In particular, the mesoporous carbons as the individual CE materials have exhibited good electrocatalytic activity [25,26]. Therefore, a series of inorganic metal compound, such as WO₂, MoC, TiN, and VC [24,27–29], were recently combined with the mesoporous carbon substrate and delivered the enhanced catalytic performance. Nevertheless, the composites of cobalt-based compound (such as Co₃O₄ and Co₂N) and mesoporous carbon were scarcely reported as CE materials in dye-sensitized solar cells.

In this paper, the composites of Co₃O₄ and Co₂N supported on mesoporous carbon were prepared by a facile oxidation and subsequent nitridation treatment of cobalt particles-incorporated mesoporous carbon. The catalytic activity of Co₃O₄ and Co₂N supported on mesoporous carbon for the reduction of triiodide was investigated in dye-sensitized solar cells. It is found that the electrocatalytic activity of the composites is related to the amount of Co₃O₄ or Co₂N composition, and the composite of Co₂N and mesoporous carbon exhibited better catalytic activity than the composite of Co₃O₄ and mesoporous carbon. The optimum catalytic activity of the composite of Co₂N and mesoporous carbon rendered the corresponding DSSCs a high power conversion efficiency of 5.26%, superior to that of the Pt-based one (4.88%) under the same experimental conditions.

2. Experimental section

2.1. Preparation of composite electrocatalysts

The mesoporous carbon and cobalt oxide composite catalysts were prepared as follows. In 30 ml of mixed solution of ethanol and water (volume ratio of 1:1), 1.65 g of resorcinol and 2.5 g of F127 were added and stirred for 15 min, followed by the addition of 1, 2, or 4 g of Co(NO₃)₂·6H₂O that dissolved in 10 ml of mixed solution of ethanol and water (volume ratio 1:1), as well as 0.2 g of HCl (37 wt %). After 1 h of stirring, 1.25 g of 37% formaldehyde solution was added dropwise. The reaction mixture was further vigorously stirred for another 1 h, then transferred into a Teflon-lined autoclave and heated at 80 °C for 2 days. The resulting polymer was washed with ethanol and water, dried in an oven at 60 °C for 12 h. Carbonization was carried out in a tubular furnace under an inert atmosphere (N₂ flow) with a heating rate of 1 °C/min, and then keeping the temperature at 800 °C for 3 h. The obtained solid was further calcined in a muffle furnace at 400 °C for 2 h with a heating rate of 10 °C min⁻¹, and the resultant product was denoted as

Co₃O₄-MC-*x* (*x* = 1, 2, or 4), where *x* represents the added amount of cobalt nitrate in the initial stage.

In order to produce mesoporous carbon-supported cobalt nitride catalysts, the Co₃O₄-MC-*x* was utilized as the reactant and annealed in a tubular furnace under anhydrous ammonia (99.995% purity) with a flow rate of 100 ml/min at 350 °C for 2 h, and the obtained sample was correspondingly labeled as Co₂N-MC-*x*.

2.2. Fabrication of DSSCs

The composite CEs were prepared with a simple doctor-blading method as follows: 130 mg of Co₃O₄-MC-*x* or Co₂N-MC-*x* composite sample was mixed with 15 mg of PEG-2000 in 3 ml of deionized water under ultrasonical dispersion, and the subsequent magnetic stirring for 5 h. Then the TiO₂ colloid, obtained from the dispersion of 20 mg of TiO₂ (P25, Degussa, Germany) in 3 ml of water, was added and stirred continually for 3 h to form the final paste. The paste was scraped onto an FTO (fluorine-doped tin oxide) conductive glass (sheet resistance 14 Ω/sq, Nippon Sheet Glass) by the doctor-blading method and dried at 60 °C overnight, resulting in the composite CE. For comparison, the conventional Pt CE was fabricated by thermal decomposition of 30 mM H₂PtCl₆·6H₂O solution spin-coated on the surface of FTO at 400 °C for 30 min.

The dye-sensitized TiO₂ photoanodes were fabricated by using two kinds of TiO₂ pastes. 20 nm-sized TiO₂ particles (Degussa, Germany) was firstly coated on FTO and then dried at 125 °C for 15 min to obtain a TiO₂ film of ca. 6 μm in thickness. Subsequently, the 200 nm-sized TiO₂ particles were further covered on the obtained layer, resulting in a TiO₂ light-scattering layer of ca. 3 μm in thickness. The bi-layer TiO₂ film was calcined at 450 °C for 30 min. Then the calcined electrode was treated with 40 mM TiCl₄ aqueous solution at 70 °C for 30 min, washed with distilled water and recalcined at 450 °C for 30 min. The as-made TiO₂ films were immersed in a 3 × 10⁻⁴ M N719 dye (Solaronix SA, Switzerland) ethanol solution for 24 h to obtain dye-sensitized TiO₂ films. The DSSC was assembled with a dye-sensitized TiO₂ photoanode, a counter electrode, and an acetonitrile electrolyte containing 0.05 M I₂, 0.5 M LiI, 0.3 M 1, 2-dimethyl-3-propylimidazoliumiodide (DMPII), and 0.5 M 4-tert-butyl pyridine. The apertures of the scotch tapes coated on both FTO were used as the electrolyte storage spacer. The two electrodes were clipped together and the active area was controlled to be 0.2 cm².

2.3. Characterization

X-ray diffraction (XRD) patterns were recorded on a Bruker D8 Focus diffractometer with Cu K_α radiation (λ = 1.5406 Å), operated at 40 kV and 40 mA. Transmission electron microscopy (TEM) was performed on a JEOL JEM 2010F microscope at 200 kV. All samples subjected to TEM measurements were ultrasonically dispersed in ethanol and drop-casted onto copper grids covered with carbon film. X-ray photoelectron spectroscopy (XPS) was performed on a Kratos Axis Ultra DLD (delay line detector) spectrometer equipped with a monochromatic Al K_α X-ray source (1486.6 eV). The XPS survey spectra were recorded with a pass energy of 160 eV, and high-resolution spectra with a pass energy of 40 eV. Binding energies were calibrated by using the containment carbon (C 1s 284.6 eV). Nitrogen adsorption and desorption isotherms were measured on a Quantachrome AUTOSORB-1 MP analyzer at 77 K. All samples were degassed in a vacuum at 200 °C overnight prior to the measurements. The specific surface areas (S_{BET}) were calculated by the Brunauer–Emmett–Teller (BET) method, the pore size distributions were derived from the adsorption branches of isotherms using non-local density functional theory (NLDFT) method, and the total pore volumes (V_{total}) were estimated from the adsorbed

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