



Nanocomposites of nickel selenide supported on cube-shaped lidless graphitic boxes as efficient counter electrodes for quasi-solid-state dye-sensitized solar cells

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ABSTRACT

To obtain an efficient electrocatalyst with high conductivity and hence excellent electrocatalytic performance, nanocomposites of nickel selenide supported on cube-shaped lidless graphitic boxes (Graphitic-boxes/NiSe) are prepared as the counter electrode (CE) of quasi-solid-state dye-sensitized solar cells (QSDSSCs). In view of the extraordinary three-dimensional electron transportation pathway and high specific surface area for the cube-shaped graphitic boxes, good catalytic ability of NiSe, and their synergetic effect, the Graphitic-boxes/NiSe nanocomposite exhibits excellent electrocatalytic activity towards the reduction of I_3^- . Furthermore, the Graphitic-boxes/NiSe nanocomposite shows impressive electrochemical stability against the iodine-based electrolyte compared with NiSe and Pt. The QSDSSC with the Graphitic-boxes/NiSe CE yields power conversion efficiency of 8.26%, which is superior to the graphitic boxes CE (2.01%) and the NiSe CE (7.45%) as well, and exhibits good long-term stability.

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1. Introduction

In the past few decades, there has been considerable interest in scientific research and industrial applications of dye-sensitized solar cells (DSSCs) because of dye availability, ease of fabrication and cost-effectiveness compared with silicon solar cells [1–5]. A DSSC device usually consists of three major parts: a dye-adsorbed TiO_2 film, a counter electrode (CE), and a redox-couple-based electrolyte (e.g. I^-/I_3^-). The CE serves as an electrocatalyst for the reduction of I_3^- . Platinum (Pt) has so far been recognized to be an outstanding CE material [6–9], but, as a low abundance ratio metal, Pt is not only expensive for mass production but also can be easily corroded to PtI_4 and H_2PtI_6 , worsening the catalytic performance [10–13]. Considering the above restrictions, developing alternative CE materials to Pt with low manufacturing cost, high electrocatalytic activity, good stability and excellent corrosion resistance to iodine are of vital significance for practical applications of DSSCs. A lot of low-cost and efficient materials have been proposed to replace Pt, for instance, carbonaceous materials [14–16], graphene materials [17–20], metal oxides [21,22], sulfides [23,24], nitrides

[25,26], chalcogenides [27–29], and polymers [30,31].

As compared to the two-dimensional (2D) graphene nanosheets [32–38], the chemical preparation of graphitic boxes starting from recyclable CO_2 without the use of strong oxidants is environmentally friendly. Moreover, the 3D structure of graphitic boxes can provide larger effective specific surface area than the 2D structure for electrocatalysis. Finally, the porous 3D structure is favorable for electrolyte diffusion within the film, which is essential for electrocatalytic effect. However, poor film formation of graphitic boxes on the fluorine-doped tin oxide (FTO) due to its weak adhesion to the FTO surface restricts its application in DSSCs. To improve the film quality of graphitic boxes, we tried to prepare nanocomposites of graphitic boxes with other electrocatalysts that have strong adhesion to the FTO. Nickel selenide (NiSe), as one of the most functional materials among transition metal chalcogenides, has been verified to be a promising CE material for DSSCs [39,40]. The combination of graphitic boxes with NiSe may solve the film formation problem of graphite boxes on FTO, and meanwhile the nanocomposite may bring about improved electrocatalytic performance expected from the large specific surface area and the possible synergetic effect between NiSe and graphitic boxes.

In previous reports, the catalytic performance of carbon materials has been explored mostly on liquid electrolyte systems but

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rarely on quasi-solid-state electrolytes (Table S1). In this work, we demonstrate a facile hydrothermal synthesis of nanocomposites containing cube-shaped lidless graphitic boxes and NiSe (Graphitic-boxes/NiSe), and apply this nanocomposite as the CE of quasi-solid-state DSSCs (QSDSSCs). To the best of our knowledge, it is the first time that nanocomposites of cube-shaped lidless graphitic boxes and NiSe microspheres are applied as the CEs of QSDSSCs.

2. Experimental section

2.1. Synthesis of cube-shaped graphitic boxes

The uncrowded cube-shaped graphitic boxes were prepared by burning the magnesium metal in CO₂ [41]. In a detailed experiment, Mg ribbon was ignited inside a dry ice atmosphere. After the reaction of combustion was completed, the black sample was collected and stirred in HCl solution (1 M) to remove the formed MgO and unreacted Mg metal, which was then filtered and washed with deionized water for several times to obtain the pure product. Finally, the black solid product was dried at 70 °C in an oven overnight to obtain a black powder.

2.2. Preparation of graphitic-boxes/NiSe nanocomposites

A typical synthesis of Graphitic-boxes/NiSe nanocomposites involves the following processes. First, 0.111 g SeO₂ (1.0 mmol, 99.9%, Alading) and 0.238 g NiCl₂·6H₂O (1.0 mmol, 99.9%, Alading) were dissolved in 36 mL of deionized water at room temperature (RT) to get a clear solution under vigorous magnetic stirring for 20 min. Concomitantly, NH₃·H₂O (25–28%, 20 mL) and N₂H₄·H₂O (85%, 24 mL) were added into the above solution, and a dark-blue solution emerged immediately, which was stirred for 20 min. Then, 1.7, 3.4, 10.2, and 17.0 mg of graphitic boxes powders were respectively added to the above solutions in different beakers under ultrasonication for 1 h. The volume of the solution in the different breakers remained same (10 mL). Different samples of Graphitic-boxes/NiSe nanocomposites with mass ratios of 1:10, 1:5, 3:5, 1:1 were obtained. Finally, the mixture solution was sealed in a Teflon-lined stainless steel autoclave (20 mL) and heated at 180 °C for 2.5 h followed by natural cooling to RT. The resulting black precipitate was collected and washed with absolute ethanol and deionized water, respectively, for several cycles. The obtained samples were dried at 60 °C overnight.

2.3. Fabrication of electrodes and QSDSSCs

The CEs with various electrocatalytic materials, viz. graphitic boxes, NiSe, Graphitic-boxes/NiSe, were prepared through a drop-casting method. Electrocatalyst inks were prepared by dispersing 1.8 mg of the sample in 10 mL of distilled water and ethanol (volume ratio, 1:1) under ultrasonication for 15 min. The suspensions were drop casted on the conductive glass (fluorine-doped SnO₂, 14 Ω square⁻¹, transmittance 85%, Nippon Sheet Glass Co., Ltd., Japan), which was masked by a 3 M Scotch tape with an exposed area of 0.6 × 0.6 cm². Then the films were dried in an oven at 120 °C. For comparison, pyrolytic Pt CE was prepared by drop-casting 50 μL of H₂PtCl₆ in isopropanol (5 mM) on a 1.5 × 1.5 cm² FTO glass followed by sintering at 400 °C for 30 min. The loading amount of Pt on the FTO substrate was 23 μg cm⁻². The loading amount of the Graphitic-boxes/NiSe nanocomposites, NiSe, and graphitic boxes on the FTO substrate was 20 μg cm⁻².

TiO₂ films (21 μm thick) were coated on the FTO conductive glass substrates through a screen-printing method. The TiO₂ films are composed of a 14-μm-thick transparent layer consisting of

25 nm TiO₂ nanoparticles and a 7-μm-thick scattering layer consisting of 200 nm TiO₂ nanoparticles. The TiO₂ films were soaked overnight in the N719 solution (0.3 mM in a mixed solvent of acetonitrile and tert-butanol in a volume ratio of 1:1). The dye-sensitized TiO₂ film (photoanode) and the CE were separated by a 30 μm thick Surlyn film and sealed by hot pressing. The gel electrolyte composed of 0.1 M LiI, 0.05 M I₂, 0.6 M 1,2-dimethyl-3-n-propylimidazoliumiodide, 0.5 M 4-*tert*-butylpyridine, and 5 wt% poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) with 3-methoxypropionitrile as a solvent was first melted under heat and then injected into the interspace between the photoanode and the CE. Finally, the back holes of the CE were sealed up with the Surlyn films covered with a glass slide under heat.

2.4. Characterizations

The X-ray diffraction (XRD) patterns were carried out on the powder X-ray diffraction (XRD, D8 Advance, Bruker) with Cu Kα radiation (λ = 0.154 nm). The morphology of the samples was examined by field emission scanning electron microscopy (FESEM, S-4800, Hitachi). The microstructures of the samples were revealed by transmission electron microscopy (TEM, JEM-2100 F, JEOL). The Raman spectroscopy measurements were carried out on XploRA spectrometer at 532 nm with a 100× objective for the Graphitic-boxes/NiSe nanocomposite sample and on a Renishaw spectrometer at 633 nm with a 100× objective for the graphitic boxes and NiSe samples. The valence states of elements in the samples were determined by the X-ray photoelectron spectroscopy (XPS) analysis (PHI5000VersaProbe). FT-IR spectra of dried samples were recorded with a Bio-Rad FTIR spectrometer FTS165. The specific surface area was measured on a Micromeritics ASAP2020 nitrogen adsorption-desorption apparatus. Diffused reflectance spectra were obtained on a UV-vis spectrophotometer (Shimadzu UV-2550) in reflectance mode. Cyclic voltammetry (CV) was executed on an electrochemical workstation (CHI660E Instruments, Shanghai Chenhua Instrument Corp., Shanghai, China). CV was carried out in a three-electrode system with different as-prepared CEs as the working electrode, a Pt wire as the counter electrode, an Ag/Ag⁺ electrode (an Ag wire immersed in an anhydrous acetonitrile solution of 1 M AgNO₃) as the reference electrode, which was calibrated with a ferrocene solution after the CV measurements, at a scan rate of 50 mV s⁻¹. The electrodes were dipped in an anhydrous acetonitrile solution containing 0.1 M LiClO₄, 10 mM LiI, and 1 mM I₂. Electrochemical impedance spectroscopy (EIS) and Tafel polarization measurements were executed on the symmetrical dummy cells assembled with two identical electrodes filled with the same gel electrolyte as used in the QSDSSCs. The EIS and Tafel polarization measurements were performed on an electrochemical workstation (ZAHNER ZENNIUM CIMPS-1, Germany). Action spectra of the incident monochromatic photon-to-electron conversion efficiency (IPCE) for the solar cells were obtained using an SM-250 system (Bunkoh-Keiki, Japan). The current-voltage (*J*-*V*) curves of QSDSSCs were measured on a Keithley 2420 source meter under the illumination of AM1.5G simulated solar light coming from an AAA solar simulator (Newport-94943 A) equipped with a Xe lamp (450 W) and an AM1.5G filter. A black mask with an aperture area of 0.2304 cm² was put on the surface of QSDSSCs to avoid stray light completely. A reference Si solar cell (Oriel-91150) was used to calibrate the light intensity.

3. Results and discussion

The synthesis flowchart of cube-shaped graphitic boxes is schematically outlined in Fig. 1. Burning magnesium metal in a carbon dioxide environment yields graphitic boxes following eq (1).

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