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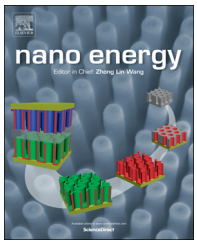

RAPID COMMUNICATION

Ni_3Se_4 hollow architectures as catalytic materials for the counter electrodes of dye-sensitized solar cells

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Abstract
Nanoparticles of nickel selenides (Ni_3Se_4) were synthesized with various hollow architectures by a simple, one-step, low temperature hydrothermal process. Using three organic solvents having different alkyl chains, precisely methanol (MeOH), ethanol (EtOH), and propan-1-ol (n-PrOH), the Ni_3Se_4 nanoparticles showed three kinds of morphologies: sea urchins-like, rice-balls-like and strawberry-fruits-like hollow nanostructures, respectively. The solvent polarity shows a trend of MeOH > EtOH > n-PrOH, and the same trend on the surface area and roughness of the corresponding Ni_3Se_4 nanoparticles can be observed. Therefore, we propose a three-step mechanism for Ni_3Se_4 growth: (1) the nucleation based on a selenium core surrounded by free selenium ions; (2) the Ni_3Se_4 formation; (3) the dissolution of selenium core to form the hollow nanoparticles. Accordingly, the first-step is the key state because the higher solvent polarity would cause the more free selenium ions and thereby the larger surface area on Ni_3Se_4 nanoparticles. For the dye-sensitized solar cells (DSSCs), the films of nickel selenide can be utilized as the electrocatalytic counter electrodes (CE) for the redox of I^-/I_3^-. The nickel selenide film obtained using methanol (hereafter urchins-like Ni_3Se_4@MeOH) shows extremely large effective surface area (5.63 times larger than traditional Pt film) and fast redox ability (1.08 times higher than traditional Pt film). The urchins-like Ni_3Se_4@MeOH CE rendered for its DSSC a power conversion efficiency (η) of 8.31%, while the expensive platinum counter

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electrode (Pt-CE) could bestow for its DSSC only an η of 8.03%. It may be said that nickel selenide is a promising catalytic material to replace the expensive platinum in a DSSC.

Introduction

In order to find sustainable and renewable power supplies, plenty of clean energy resources are developed recently; for instance, solar energy [1-2], hydrogen energy [3-5], geothermal energy [6-8] and fuel cells [9-10] have been largely researched in order to substitute for the fossil fuel. A solar-to-electricity power conversion device, a solar cell, is one of the key clean energy substitutions. Among all kinds of solar cells, dye-sensitized solar cells (DSSCs) have drawn considerable attention and have been widely investigated during the last two decades, because of their high power conversion efficiency, simple fabrication process, and low-cost production [11]. A DSSC usually consists of a dye-adsorbed TiO_2 film as the working electrode, an electrolyte with the redox couple of iodide/triiodide (I^-/I_3^-), and a platinum-coated counter electrode (Pt-CE) [12-13]. The challenging issue for DSSCs is not only to achieve high solar-to-electricity conversion efficiency, but also to manufacture them easily with least cost [14]. A conducting glass coated with a platinum (Pt) film using thermal platinization or sputtering is usually employed as the CE of a DSSC. However, Pt is very expensive and is rare on earth. Fabrication of CEs with other cheaper materials is expected to bring down the production cost of the cells, especially in large-scale production.

Many conducting polymers [15-17], carbon-based materials [18-21] and transition metal compounds [22-25] that are much cheaper than Pt, have shown great potential to replace Pt. However, some of them can hardly compete with Pt in terms of photovoltaic performance of their DSSCs; this is because of the fact that their electrocatalytic abilities are worse than that of platinum. Recently, some materials, such as sulfides [26-30], nitrides [23], carbides [31,32] and oxides [33] have rendered excellent photovoltaic performance to their DSSCs.

In this study, nickel selenides, synthesized by a hydrothermal process using three organic solvents including methanol, ethanol, and propan-1-ol, have been used as the catalytic materials for the CEs of DSSCs. Nickel selenides are very stable compounds, and can be stored in atmosphere. Among all, the DSSC with the CE of Ni_3Se_4@-MeOH showed the best efficiency of 8.31% which is higher than that of the expensive Pt-CE (8.03%). The strategy of fabricating the CE with Ni_3Se_4 is rather simple and inexpensive and is applicable to produce mass-scale DSSCs with reduced cost, compared to the case of DSSCs with Pt-CE.

Experimental section

Materials

Ethanol (EtOH, 99.5%), isopropyl alcohol (IPA, 99.5%), titanium (IV) tetraisoproproxide (TTIP, >98%), lithium perchlorate ($LiClO_4$, ≥98.0%), hydrazine (N_2H_4, >99%), 2-methoxyethanol, and tetrabutylammonium triiodide ($TBAI_3$, >97%) were obtained from Sigma Aldrich. Lithium iodide (LiI, synthetical grade), iodine (I_2, synthetical grade) and poly (ethylene glycol) (PEG, MW ~20,000) were received from Merck. Cis-diisothiocyanato bis (2,2′-bipyridyl-4,4′-dicarboxylato) ruthenium (II) bis (tetrabutylammonium) (N719 dye), TiO_2 transparent layer paste (TL paste, Ti-nanoxide HT/SP, 13 nm), and Surlyn® (SX1170-25, 25 μm) were procured from Solaronix (S.A., Aubonne, Switzerland). 1,2-dimethyl-3-propylimidazolium iodide (DMPII) was obtained from Tokyo Chemical Industry Co., Ltd. Acetonitrile (ACN, 99.99%) and nitric acid (HNO_3, *ca.* 65% solution in water) were supplied by J. T. Baker. Acetone (99%), 4-tert-butylpyridine (tBP, 96%), selenium powder (99%), and tert-butyl alcohol (tBA, 96%) were bought from Acros. 3-methoxypropionitrile (MPN, 99%), nickel (II) chloride hexahydrate ($NiCl_2 \cdot 6H_2O$, 98%) were purchased from Alfa Aesar. Commercial light scattering TiO_2 particles and ST-41 with 200 nm were acquired from Ishihara Sangyo, Ltd.

Fabrication of the various CEs, photoanodes, and DSSCs

Indium-doped tin oxide (ITO, 5 Ω sq.$^{-1}$, Uni-onward Corp., Taiwan) and fluorine-doped tin oxide (FTO, TEC-7, 7 Ω sq.$^{-1}$, NSG America, Inc., New Jersey, USA) conducting glasses were cleaned with acetone, neutral cleaner with deionized water, acetone, and isopropanol sequentially. The standard Pt-CE was prepared by sputtering a film of platinum, with a thickness of 30 nm on the ITO substrate. We synthesized three kinds of Ni_3Se_4 with different morphologies. 0.1 M solutions of NaOH were prepared using 100 ml each of three types of solvents, *i.e.*, methanol, ethanol and propan-1-ol. 11.5 ml of each of these solutions was taken in a 20 ml glass bottle. Selenium and $NiCl_2$ powders (each 0.02 mM) were added to the bottles. Finally 1.5 mL of $N_2H_4 \cdot H_2O$ was added to the bottles. The bottles were well sealed and preserved at 90 °C for 16 h. Afterwards, the supernatant liquids were removed, the Ni_3Se_4 products were washed with ethanol for four times. Five weight percent (5 wt%) of the powders was dispersed in ethanol, which acted as dispersant for the powders. The solutions were then drop-coated at 60 °C onto ITO substrates to prepare the three CEs of Ni_3Se_4. The thickness of each Ni_3Se_4 film was about 7 μm, as can be seen in the cross-sectional SEM image of the film in the "Supplementary information" (Figure S1).

A TiO_2 colloid was prepared by adding 0.5 M TTIP into 0.1 M aqueous nitric acid solution with constant stirring at 88 °C for 8 h. Afterwards, the colloid was heated at 240 °C for 12 h in an autoclave (PARR 4540, U.S.A.). Then the TiO_2 colloid was concentrated to 8 wt% of TiO_2 nanoparticles. After that, a scattering layer paste (SL paste) was prepared