Journal of Power Sources 315 (2016) 79–85

Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

Copper indium disulfide nanocrystals supported on carbonized chicken eggshell membranes as efficient counter electrodes for dye-sensitized solar cells

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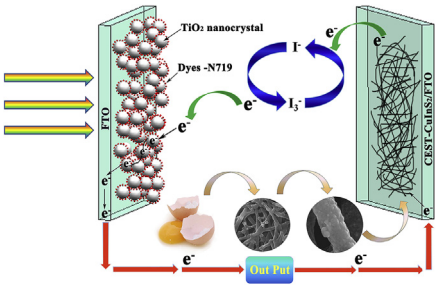
HIGHLIGHTS

- Chicken eggshell membrane is used as a skeleton to load $CuInS_2$ nanocrystals.
- CESM-$CuInS_2$ composite shows a 3D macroporous submicron fiber network structure.
- N-doped CESM loaded $CuInS_2$ nanocrystals show better electrocatalytic activity.
- DSSC fabricated using CESM-$CuInS_2$ counter electrode exhibit an efficiency of 5.8%.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 31 October 2015
Received in revised form
24 February 2016
Accepted 8 March 2016

Keywords:
Carbonized eggshell membrane
Copper indium disulfide nanocrystals
Counter electrode
Dye-sensitized solar cells
Conversion efficiency

ABSTRACT

A domestic waste, chicken eggshell membrane (ESM), is used as a raw material to fabricate carbonized ESM loaded with chalcopyrite $CuInS_2$ nanocrystals (denoted CESM-$CuInS_2$) by a simple liquid impregnation and carbonization method. The CESM-$CuInS_2$ composite possesses a natural three-dimensional macroporous network structure in which numerous $CuInS_2$ nanocrystals with a size of about 25 nm are inlaid in carbon submicron fibers that form a microporous network. The CESM-$CuInS_2$ composite is used as the counter electrode in a dye-sensitized solar cell (DSSC) and its photoelectric performance is tested. The DSSC with a CESM-$CuInS_2$ counter electrode exhibits a short-circuit current density of 12.48 mA cm^{-2}, open-circuit voltage of 0.78 V and power conversion efficiency of 5.8%; better than the corresponding values for a DSSC with a CESM counter electrode, and comparable to that of a reference DSSC with a platinum counter electrode. The favorable photoelectric performance of the CESM-$CuInS_2$ counter electrode is attributed to its hierarchical structure, which provides a large specific surface area and numerous catalytically active sites to facilitate the oxidation of the electrolyte. This new composite

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http://dx.doi.org/10.1016/j.jpowsour.2016.03.029
0378-7753/

material has many advantages, such as low cost and simple preparation, compared with Pt and pure $CuInS_2$ counter electrodes.

1. Introduction

The rising global demand for energy has promoted use of sustainable and renewable energies. Solar power is an abundant energy source and is expected to contribute substantially to world energy production in the near future [1]. During the last two decades, dye-sensitized solar cells (DSSCs) have attracted great attention for photovoltaic applications because of their low cost of fabrication and high energy conversion efficiency [2]. In general, DSSCs work by photoelectrochemistry and consist of a nanocrystalline TiO_2 film sensitized with light-harvesting absorbers that is in contact with a redox electrolyte containing the iodide (I^-)/triiodide (I_3^-) couple and a platinum (Pt) counter electrode (CE) [3]. The CE is one of the most important components in DSSCs, collecting electrons from an external circuit and catalyzing the reduction of I_3^- in the electrolyte [4,5]. The CE is usually composed of the noble metal Pt because of its high electrocatalytic activity, electrical conductivity, and stability [6]. However, the scarcity and expense of Pt limit its use in DSSCs. Therefore, it is necessary to find alternative CE materials that are inexpensive with relatively high catalytic activity to replace Pt in DSSCs.

Various materials such as graphite [7], carbon nanotubes [8], carbon nanocomposites [9], conducting polymers [10–13], inorganic semiconductors [14–16] and composite nanomaterials [17] have been investigated as alternatives to Pt in DSSCs. Among them, inorganic semiconductor materials possess the advantages of both facile preparation and diversity. Metal sulfides in particular have drawn considerable attention. Copper indium disulfide ($CuInS_2$), a ternary semiconductor (I–III–IV2) with a bulk band gap of 1.45 eV and high extinction coefficient in the visible spectral range, is well known as a promising light-absorbing material in solar cells. For example, Yu et al. [18] prepared vertically oriented $CuInS_2$ nanosheet thin films via a facile one-step solvothermal process. These films were used as the CE in DSSCs, which exhibited a power conversion efficiency (PCE, η) of 6.33%, comparable to that of a DSSC with a sputtered Pt CE (6.07%). Meanwhile, Wu and colleagues synthesized $CuInS_2$ nanocrystals by replacing organic capping ligands with inorganic S^{2-} ions [19]. When the unsintered surfactant-free $CuInS_2$ films were used as the CE in DSSCs, a η of 5.77% was achieved.

An ideal CE must possess high conductivity, catalytic activity and specific surface as well as low resistance; however, it is usually not easy for inorganic semiconductor materials to meet these requirements simultaneously [20]. For example, the electron collection efficiency and η of one-dimensional (1D) inorganic semiconductor nanomaterials are low because electrons are easily trapped at the nanoparticle–electrolyte interface due to the disorder of the nanoparticles [21]. Although DSSCs with $CuInS_2$ materials as a CE have achieved high η, their cost needs to be lowered.

In this article, we use a domestic waste product, eggshell membrane (ESM), as a skeleton to prepare carbonized fiber membranes loaded with chalcopyrite $CuInS_2$ nanocrystals. A carbonized eggshell membrane (CESM)-$CuInS_2$ composite is obtained by a simple liquid impregnation and carbonization method. The CESM-$CuInS_2$ composite has a three-dimensional (3D) porous structure and large specific surface area, which facilitate the penetration of the electrolyte and electron transmission. The hierarchical architecture of the composite provides numerous catalytically active sites for the oxidation of the electrolyte, which improves the electron collection and conversion efficiencies. Furthermore, the CESM-$CuInS_2$ electrode is cheaper than a $CuInS_2$ film CE.

2. Experimental section

2.1. Chemicals and materials

Copper sulphate ($CuSO_4$), indium(III) chloride ($InCl_3$), and thiourea were purchased from Aladdin and used without further purification. TiO_2 paste (18NR-T) and N719 dye solution were purchased from Dyesol. Hydrochloric acid (HCl) and absolute ethyl alcohol were purchased from Sinopharm. The eggs used in the experiments were bought at a local supermarket.

2.2. Preparation of the CESM-$CuInS_2$ composite

The white ESM peeled off the interior surface of fresh eggshells was immersed in hydrochloric acid (0.5 M) for 13 h. The ESM was rinsed with deionized (DI) water and dried at 60 °C for 90 min. The ESM was immersed in $CuInS_2$ precursor solution for 12 h at 25 °C. The $CuInS_2$ precursor solution consisted of 1 mol $CuSO_4$, 1 mol $InCl_3$, and 2 mol thiourea in absolute ethyl alcohol. The ESM was then annealed at 900 °C for 2 h (heating rate: 2 °C min^{-1}) under dynamic nitrogen atmosphere (gas-flow rate: 200 ml min^{-1}) to obtain the CESM-$CuInS_2$ composite.

2.3. Fabrication of CEs

First, the fluoride-doped tin oxide (FTO) substrate was cleaned with isopropyl alcohol, DI water, and acetone. All samples including the CESM-$CuInS_2$ composite and reference CESM were ground using an agate mortar for 5 h. Electrode pastes were prepared by dispersing the CESM-$CuInS_2$ or CESM powder in a mixture of 1-methyl-2-pyrrolidinone, ethyl cellulose, acetylene black and terpineol. The pastes were then ground in the agate mortar for 2 h. A layer of each paste with a thickness of 4–5 μm was coated onto a FTO-coated glass slide by the doctor printing method, and dried at 80 °C under vacuum for 2 h. For comparison, Pt-coated FTO glass slide functioned as a counter electrode.

2.4. Fabrication of photo electrodes

TiO_2 paste was doctor-bladed on FTO glass and annealed at 500 °C for 30 min. Subsequently, the TiO_2 photo electrodes were immersed in the N719 dye solution in absolute ethyl alcohol with a concentration of 0.5 mM for 12 h at room temperature then rinsed with ethanol and dried.

2.5. Fabrication of DSSCs

In the fabricated DSSCs, the dye-sensitized TiO_2 nanostructure functioned as a photoanode, and the CESM-$CuInS_2$/FTO, CESM/FTO and Pt/FTO glass slides functioned as CEs. The photoanodes and CEs were assembled together to compose a sandwich structure using a thermoplastic sealant (Surlyn 1702), and then the electrolyte (E23)