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Cost-effective, transparent iron selenide nanoporous alloy counter electrode for bifacial dye-sensitized solar cell

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HIGHLIGHTS

GRAPHICAL ABSTRACT highlights grap hical abstract

- Nanoporous FeSe alloy counter electrodes are synthesized by a mild solution method.
- Surfactant DBSA is utilized as a template for preparing nanopores.
- The resultant FeSe alloy electrode has high optical transparency.
- The transparent FeSe alloy CEs are used for bifacial DSSC applications.
- The DSSC with FeSe CE yields front and rear efficiencies of 9.16% and 5.38%, respectively.

article info

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1. Introduction

Nowadays, utilization of solar energy has been one of the promising solutions to realize low-carbon society $[1,2]$. Photovoltaic conversion [\[3\],](#page--1-0) directly converting solar energy into electricity, is considered as a cost-effective electricity-generation technique. In comparison with commercial silicon solar cells, dye-sensitized solar cells (DSSCs) display attractive merits on easy fabrication, zero emission, and scalable components $[4,5]$. Since the first prototype from Grätzel in 1991 $[6]$, a maximum efficiency of 13% has been measured under air mass 1.5 global (AM1.5G) solar light $[7]$. A typical DSSC comprises a TiO₂ anode with percolating channels for electron migration, a Pt counter electrode (CE) for

abstract

Pursuit of cost-effective and efficient counter electrodes (CEs) is a persistent objective for dye-sensitized solar cells (DSSCs). We present here the design of transparent Fe-Se nanoporous alloy CEs for bifacial DSSC applications. Due to the superior charge-transfer ability for I^{-}/I_{3} redox couples, electrocatalytic reduction toward I_3 species, and optical transparency in visible-light region, the bifacial DSSC with FeSe alloy electrode yields maximum front and rear efficiencies of 9.16% and 5.38%, respectively. A fast startup, high multiple start capability, and good stability of the FeSe alloy CE demonstrate the potential applications in driving solar panels. The impressive efficiency along with simple preparation of the costeffective Fe-Se nanoporous alloy CEs highlights their potential application in robust bifacial DSSCs.

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triiodide reduction, and electrolyte containing iodide/triiodide (I^{-}) I $_{\overline{3}}$) redox couples. However, the high expense of Pt CE is still one of the restrictions for commercial application $[8]$. One solution to this impasse is to develop cost-effective CE candidates and to utilize bifacial technique [\[9,10\]](#page--1-0). The concept of either front or rear irradiation created by Grätzel is considered as an efficient avenue of helping bring down the cost of solar energy conversion [\[11\]](#page--1-0). Such bifacial DSSC can absorb photons from either side of device, accelerating its practical application. To realize this technique of collecting sunlight from either side of a solar cell, transparent CEs are crucial in designing such bifacial DSSCs. Graphene and PANi, colored and semitransparent electrocatalyst, have been deposited on a conductive substrate for CE applications by Zhao et al. in bifacial DSSC assembly [\[12\],](#page--1-0) yielding front and rear efficiencies of 6.54% and 4.26% , respectively. However, the modest long-term stabilities and catalytic activities of carbonaceous materials and conductive polymers are limits for their commercial applications in DSSCs [\[13\]](#page--1-0). Although traditional Pt and its composites exhibit satisfactory stabilities and catalytic activities, the strong reflection to light from their metallic luster leads to a gigantic optical loss. In this fashion, it is a prerequisite to explore transparent but cost effective CE materials with excellent electrocatalysis and stability for robust bifacial DSSCs [\[14,15\].](#page--1-0)

Alloy materials have established themselves as robust electrocatalysts for energy nanodevices $[16-18]$ $[16-18]$. Aiming to reduce cost for electricity generation without sacrificing power conversion efficiency of bifacial DSSCs, here we report the synthesis of binary Fe-Se nanoporous alloy CEs by a mild solution method in the presence of surfactant. The resultant Fe-Se nanoporous CEs show superior electrocatalytic activity toward $\mathbb{I}^{-}/\mathbb{I}_{3}^{-}$ redox couples, nanoporous structure for electrolyte diffusion, and optical transparency for penetrating incident light from rear side. The utilization of surfactant is to create nanoporous structure for rapid $\rm I^-/I_3^$ diffusion within alloy electrodes. The system of interest is the utilization of transparent Fe-Se nanoporous alloy CEs, yielding maximum front and rear efficiencies of 9.16% and 5.38%, respectively.

2. Experimental

2.1. Preparation of binary Fe-Se nanoporous alloy CEs

The feasibility of this strategy was confirmed by following experimental procedures: A mixing aqueous solution consisting of 0.01 g of Se powders, 0.1 M FeCl₃ (0.71 ml for Fe_{0.6}Se, 0.94 ml for Fe_{0.8}Se, 1.18 ml for FeSe, and 1.41 ml for Fe_{1.2}Se), 1 ml of 10 mM dodecylbenzene sulfonic acid (DBSA), and 1 mL of 10 mM NaOH was made at 60 $^{\circ}$ C. The total volume of the solution was adjusted to 27.5 ml by deionized water. 2 ml of hydrazine hydrate (85 wt%) was dropped into the above solution, after vigorous agitating for 10 min, the reactant was transferred into a Teflon-lined autoclave and cleaned FTO glass substrate (sheet resistance 12 Ω sq $^{-1}$, purchased from Hartford Glass Co., USA) with FTO layer downward was immersed in. After the reaction at 120 $\,^{\circ}$ C for 12 h, the FTO substrate was rinsed by deionized water and vacuumly dried at 50 \degree C. As references, the pristine Fe and Se CEs were also prepared by the similar processes using FTO glass substrates.

2.2. DSSC assembly

The TiO₂ anodes were fabricated by coating TiO₂ colloid synthesized by a sol-hydrothermal method onto cleaned FTO glass substrates [\[19,20\].](#page--1-0) The size of the resultant anodes was controlled at 0.5×0.5 cm² with an average thickness of 10 µm. The air-dried colloids were calcined in a muffle furnace at 450 \degree C for 30 min.

The resultant $TiO₂$ film was sensitized by immersing into a 0.50 mM ethanol solution of N719 dye (purchased from DYESOL LTD) for 24 h. A DSSC device was fabricated by sandwiching redox electrolyte between a dye-sensitized $TiO₂$ anode and a CE. A redox electrolyte consisted of 100 mM of tetraethylammonium iodide, 100 mM of tetramethylammonium iodide, 100 mM of tetrabutylammonium iodide, 100 mM of NaI, 100 mM of KI, 100 mM of LiI, 50 mM of I_2 , and 500 mM of 4-tert-butyl-pyridine in 50 ml acetonitrile.

2.3. Photovoltaic measurements

The photocurrent-voltage $(J-V)$ curves of the assembled DSSCs with an active area of 0.25 cm^2 were recorded on an Electrochemical Workstation (CHI600E) under irradiation of a simulated solar light (Xe Lamp Oriel Sol³A™ Class AAA Solar Simulators 94023A, USA) at a light intensity of 100 mW cm^{-2} (calibrated by a standard silicon solar cell) in ambient atmosphere. Each DSSC device was measured at least five times to eliminate experimental error and a compromise $J-V$ curve was employed. A black mask with an aperture area of around 0.25 cm^2 was applied on the surface of DSSCs to avoid stray light completely.

2.4. Electrochemical characterizations

The electrochemical performances were recorded on a conventional CHI660E setup comprising an Ag/AgCl reference electrode, a CE of platinum sheet, and a working electrode of FTO glass supported binary Fe-Se nanoporous alloy. The cyclic voltammetry (CV) curves were recorded in a supporting electrolyte consisting of 50 mM LiI, 10 mM I_2 , and 500 mM LiClO₄ in acetonitrile. Electrochemical impedance spectroscopy (EIS) measurements were carried out in a frequency range of 0.01 Hz $\sim 10^6$ kHz and at an ac amplitude of 10 mV. Tafel polarization curves were recorded by assembling symmetric cell consisting of Fe-Se alloy CE redox electrolyte|Fe-Se alloy CE.

2.5. Other characterizations

The compositions of the binary Fe-Se nanoporous alloy CEs were detected by inductively coupled plasma-atomic emission spectra (ICP-AES). The morphologies of the FeSe alloy CE was observed with a scanning electron microscope (SEM, S4800) and on a transmission electron microscopy (TEM, JEM2010, JEOL). X-ray diffraction (XRD) profiles of the resultant alloys were recorded on an X-ray powder diffractometer (X'pert MPD Pro, Philips, Netherlands) with Cu K α radiation ($\lambda = 1.5418$ Å) in the 2 θ range from 20 to 80° operating at 40 kV accelerating voltage and 40 mA $current$). The optical transmission spectra of binary Fe-Se alloy CEs were recorded on a UV-vis spectrophotometer at room temperature. XPS experiment was carried out on a RBD upgraded PHI-5000C ESCA system (Perkin Elmer) with Mg Ka radiation $(hv = 1253.6 \text{ eV}).$

3. Results and discussion

The resultant Fe-Se nanoporous alloys synthesized by a mild solution approach are determined by ICP-AES equipment, indicating atomic rations of 0.614: 1.000, 0.608: 1.000, 1.116: 1.000, and 1.187: 1.000 for $Fe_{0.6}Se, Fe_{0.8}Se, FeSe, and Fe_{1.2}Se, respectively. There$ is a fact that the measured atomic ratios are close to the stoichiometries of Fe-Se nanoporous alloys, therefore, the chemical formulas of the binary alloy CEs can be expressed according to their stoichiometric ratios. The FeSe nanoporous alloy CE is subjected to XRD characterization, as shown in [Fig. 1](#page--1-0)a, the diffraction peaks Download English Version:

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