



Cobalt selenide hollow nanorods array with exceptionally high electrocatalytic activity for high-efficiency quasi-solid-state dye-sensitized solar cells



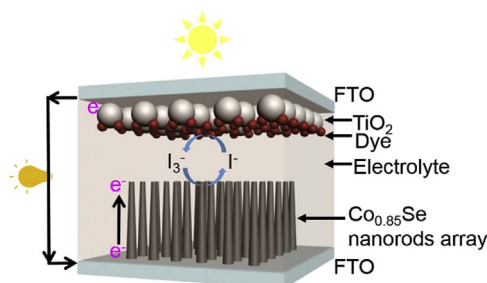
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HIGHLIGHTS

- Cobalt selenide hollow nanorods array as efficient electrocatalyst is proposed.
- The ordered cobalt selenide array exhibits excellent electrocatalytic activity.
- The ordered array structure is favorable for fast diffusion of gel electrolytes.
- Efficient and stable quasi-solid-state dye-sensitized solar cells are achieved.

GRAPHICAL ABSTRACT



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ABSTRACT

In quasi-solid-state dye-sensitized solar cells (QSDSSCs), electron transport through a random network of catalyst in the counter electrode (CE) and electrolyte diffusion therein are limited by the grain boundaries of catalyst particles, thus diminishing the electrocatalytic performance of CE and the corresponding photovoltaic performance of QSDSSCs. We demonstrate herein an ordered $\text{Co}_{0.85}\text{Se}$ hollow nanorods array film as the Pt-free CE of QSDSSCs. The $\text{Co}_{0.85}\text{Se}$ hollow nanorods array displays excellent electrocatalytic activity for the reduction of I_3^- in the quasi-solid-state electrolyte with extremely low charge transfer resistance at the CE/electrolyte interface, and the diffusion of redox species within the $\text{Co}_{0.85}\text{Se}$ hollow nanorods array CE is pretty fast. The QSDSSC device with the $\text{Co}_{0.85}\text{Se}$ hollow nanorods array CE produces much higher photovoltaic conversion efficiency (8.35%) than that (4.94%) with the $\text{Co}_{0.85}\text{Se}$ randomly packed nanorods CE, against the control device with the Pt CE (7.75%). Moreover, the QSDSSC device based on the $\text{Co}_{0.85}\text{Se}$ hollow nanorods array CE presents good long-term stability with only 4% drop of power conversion efficiency after 1086 h one-sun soaking.

1. Introduction

As one of the most promising photovoltaic technologies, dye-sensitized solar cells (DSSCs) have gained great attention from researchers and manufacturers all over the world due to their inherent low cost, environmental friendliness, easy fabrication procedure and relatively

high power conversion efficiency [1–3]. A typical DSSC is composed of a photoanode (e.g. dye-sensitized TiO_2 film), an electrolyte containing the iodide/triiodide redox couple, and a counter electrode (CE) [1]. As an indispensable component of DSSCs, the CE transfers electrons from external circuit to the electrolyte by catalyzing the reduction of triiodide ions to iodide species, and meanwhile the circuit is closed. Pt is

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commonly used as the CE material for DSSCs due to its outstanding electrocatalytic activity for the I^-/I_3^- redox reaction, but the low abundance ratio and poor long-term stability against iodine largely hinder the large-scale production of DSSCs. Therefore, developing low-cost and high-performance Pt-free electrocatalyst appears especially important [4,5].

In past years, many kinds of low-cost CE materials, such as carbon-based materials [6–8], conductive polymers [9,10], inorganic compounds [11–20] and their composites [21,22], have been studied to replace Pt. As one-dimensional (1D) materials are beneficial to electron transportation, electrocatalysts with nanorod (NR) morphology have been employed as CEs of DSSCs [13,14]. However, random packing of NRs hinders electron transfer from one NR to another NR, weakening the catalytic performance. Furthermore, the disordered nanostructure can block the electrolyte diffusion within the film, in particular for the quasi-solid-state electrolyte. By contrast, nanorod arrays (NRAs) can provide short pathway for electron transport through the NR and open channels for electrolyte diffusion. Despite these unique features, the reported NRA CEs do not show desired effect on electrocatalytic performance, and they do not show the strong points for fast electrolyte diffusion either [23,24]. Therefore, there remains a big challenge to develop highly efficient NRA based CEs, which should not only have excellent electrocatalytic activity but also be favorable for fast diffusion of redox species in quasi-solid-state DSSCs (QSDSSCs).

In this work, $Co_{0.85}Se$ NRA thin films were in situ grown on the conductive glass substrate with a two-step low temperature reaction. When the $Co_{0.85}Se$ NRA film is applied as the CE of QSDSSCs, it demonstrates exceptionally high electrocatalytic activity as judged from the extremely low charge transfer resistance. Moreover, the diffusion of the redox species in the quasi-solid-state electrolyte within the $Co_{0.85}Se$ NRA film is much faster than that within the randomly packed NRs film. As a consequence, the QSDSSC based on the $Co_{0.85}Se$ NRA CE achieves much higher power conversion efficiency than that with the $Co_{0.85}Se$ randomly packed NRs CE and the Pt CE as well. More importantly, the $Co_{0.85}Se$ NRA CE based QSDSSC exhibits good long-term stability under one sun soaking for more than 1000 h.

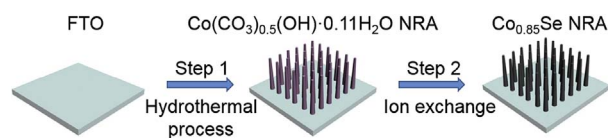
2. Experimental section

2.1. Materials and reagents

Cobalt nitrate hexahydrate ($Co(NO_3)_2 \cdot 6H_2O$, 99.9%), ethanol (99.7%), acetonitrile (99%), tert-butanol (99%) and chloroplatinic acid hexahydrate ($H_2PtCl_6 \cdot 6H_2O$, 99%) were purchased from Sinopharm. Urea (99%), sodium borohydride ($NaBH_4$, 98%), selenium (Se, 99.999%), lithium perchlorate ($LiClO_4$, 99.99%), lithium iodide (LiI, 99.9%), Iodine (I_2 , 99.99%), 1,2-dimethyl-3-n-propylimidazolium iodide (DMPII, 98%), 4-tertbutylpyridine (TBP, 96%), poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) and 3-methoxypropionitrile (99%) were obtained from Aladdin. Cis-di(isothiocyanato)-bis-(2,2'-bipyridyl-4,4'-dicarboxylato) ruthenium(II) bis-tetrabutylammonium (N719) was received from Solaronix SA. Transparent conductive glass (F-doped SnO_2 , FTO, 14Ω per square, transmittance of 90%) was purchased from Nippon Sheet Glass Co., Ltd., Japan.

2.2. Preparation of $Co_{0.85}Se$ NRA, randomly packed $Co_{0.85}Se$ NRs and Pt CEs

The $Co_{0.85}Se$ NRA was prepared via a two-step reaction, as illustrated in Scheme 1. Firstly, the cobalt carbonate hydroxide NRA, $Co(CO_3)_{0.5}(OH) \cdot 0.11H_2O$, was synthesized as the cobalt precursor for the $Co_{0.85}Se$ NRA using a hydrothermal method [25,26]. 0.4 mmol of $Co(NO_3)_2 \cdot 6H_2O$ and 2 mmol of urea were dissolved in 10 mL deionized water, and a clear pink solution was obtained after stirring for 10 min. This solution was transferred into a 15 mL Teflon-lined autoclave, and a



Scheme 1. The synthetic route of $Co_{0.85}Se$ NRA.

piece of cleaned FTO conductive substrate was immersed into the solution with the conductive side facing down. The sealed autoclave was put into an oven at $90^\circ C$ for 2 h. After cooling down to room temperature (RT), the $Co(CO_3)_{0.5}(OH) \cdot 0.11H_2O$ coated FTO as the product of step 1 was formed (Scheme 1), which was washed with ethanol for several times followed by drying at $60^\circ C$ for 6 h.

Secondly, the precursor, $Co(CO_3)_{0.5}(OH) \cdot 0.11H_2O$ NRA, was converted into $Co_{0.85}Se$ NRA via an ion exchange reaction. The NaHSe solution as the selenide source was prepared by dissolving 50 mg (1.32 mmol) $NaBH_4$ and 50 mg (0.63 mmol) Se powder in 2 mL deionized water, which was gently stirred for several minutes and diluted by adding 28 mL deionized water into the NaHSe solution. 10 mL freshly prepared NaHSe solution was loaded into a 15 mL Teflon-lined autoclave, in which one piece of as-prepared $Co(CO_3)_{0.5}(OH) \cdot 0.11H_2O$ NRA coated FTO was immersed into the NaHSe solution with the precursor film facing down. The autoclave was heated at $50^\circ C$ for 6 h, and then cooled to RT naturally. The $Co_{0.85}Se$ NRA on the FTO was obtained by ion exchange from carbonate to selenide. During the selenization process (Step 2), Se^{2-} ions react with the surface Co^{2+} on the $Co(CO_3)_{0.5}(OH) \cdot 0.11H_2O$ nanorods following a nonstoichiometric reaction. The $Co_{0.85}Se$ NRA films were washed with ethanol and acetonitrile for several times and dried at $60^\circ C$ for 3 h. The optimization of the preparation conditions for the $Co_{0.85}Se$ NRA film is detailed in the Supporting Information (Figs. S1–S4, Tables S1–S4).

$Co_{0.85}Se$ powder collected by scraping the $Co_{0.85}Se$ NRA film from the FTO was used to fabricate the randomly packed $Co_{0.85}Se$ NRs CE for comparison. 1.8 mg of the above-mentioned $Co_{0.85}Se$ NRs was dispersed in 10 mL of distilled water and ethanol (volume ratio, 1:1) under ultrasonication for 30 min. 41 μL of $Co_{0.85}Se$ suspension was drop-casted on FTO, which was masked by a 3M Scotch tape with an exposed area of $0.6 \times 0.6 \text{ cm}^2$. Then the films were dried in an oven at $70^\circ C$ and aged in a tubular furnace at $250^\circ C$ for 30 min under N_2 flow. The pyrolytic Pt CE as a control was prepared by drop-casting 50 mL of H_2PtCl_6 in ethanol (5 mM) on $1.5 \times 1.5 \text{ cm}^2$ FTO followed by sintering at $400^\circ C$ for 30 min.

2.3. Fabrication of DSSCs

TiO_2 films (17 μm thick) composed of transparent (12 μm) and scattering (5 μm) layers were prepared by a screen-printing method on FTO substrates and sintered at $500^\circ C$ for 1 h. TiO_2 films were soaked overnight in N719 (0.3 mM in a mixed solvent of acetonitrile and tert-butanol in a volume ratio of 1:1). The dye-sensitized TiO_2 photoanode and the CE were separated by a hot-melt Surlyn film (30 μm thick) and sealed through hot pressing. For quasi-solid-state DSSCs, the gel electrolyte (0.1 M LiI, 0.05 M I_2 , 0.6 M DMPII, 0.5 M TBP, and 5 wt% PVDF-HFP in 3-methoxypropionitrile) was heated at $100^\circ C$ until the gel melted. The hot gel solution was introduced into the internal space of the device, and it became motionless after cooling down to RT. Finally, the holes on the back of the CE were sealed with a Surlyn film covered with a thin glass slide under heat.

2.4. Characterizations

The crystal structure of the as-prepared samples was recorded on an X-ray powder diffractometer (XRD, D8 Advance, Bruker) using Cu K α radiation ($\lambda = 0.154 \text{ nm}$). The surface elemental component and the chemical state of the as-prepared sample were analyzed by X-ray

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