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Hierarchical Cu_7S_4 nanotubes assembled by hexagonal nanoplates with high catalytic performance for quantum dot-sensitized solar cells

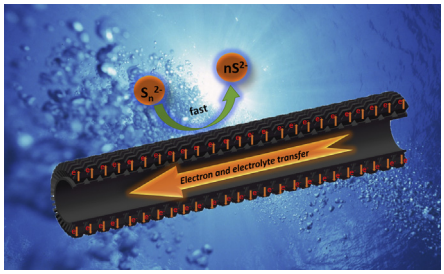
Min Wang [a], Wenlong Chen [a], Jiantao Zai [a, **], Shoushuang Huang [a], Qingquan He [a], Wei Zhang [b], Qiquan Qiao [c, ***], Xuefeng Qian [a, *]

[a] Shanghai Electrochemical Energy Devices Research Center, School of Chemistry and Chemical Engineering, State Key Laboratory of Metal Matrix Composites, Shanghai Jiao Tong University, Shanghai 200240, PR China
[b] Shanghai Key Laboratory of Catalysis of Polyolefin, Shanghai Research Institute of Chemical Industry, Shanghai 200062, PR China
[c] Center for Advanced Photovoltaics, South Dakota State University, Brookings, SD 57007, USA

HIGHLIGHTS

- Hierarchical Cu_7S_4 nanotubes (Cu_7S_4-HNT) have been synthesized at room temperature.
- Cu_7S_4-HNT combine the advantages of nanotube and hierarchical structure.
- The Cu_7S_4-HNT CE is stable in electrolyte even after 1000 CV cycles.
- The high stable CEs possess a high power conversion efficiency of 4.53%.
- The abundant active sites and fast mass/electron transfer lead to good properties.

GRAPHICAL ABSTRACT



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ABSTRACT

As a kind of promising generation solar cells, the catalytic properties of counter electrodes (CEs) play a key factor on the performance of QDSSCs (quantum dot-sensitized solar cells) at present. Here, hierarchical Cu_7S_4 nanotubes (Cu_7S_4-HNT) assembled by hexagonal nanoplates have been prepared by an *in-situ* growth route and etching process at room temperature. The formation mechanism of the unique morphology is also proposed. Because of the rapid diffusion of electrons and electrolyte, abundant catalytic sites and high stability, the as-prepared Cu_7S_4-HNT combined the characteristics of nanotube and hierarchical structure can improve the catalytic performance of CEs. QDSSCs based on the Cu_7S_4-HNT CEs possess a high power conversion efficiency of 4.53%, superior to those with the commonly used Cu_2S/brass (3.3%) or the referenced Pt (1.79%) CEs. What's more, the Cu_7S_4-HNT CE still shows excellent stability in electrolyte after 1000 CV cycles.

1. Introduction

With the continuously increasing demand for renewable and abundant energy sources in modern electronic life, solar cells have drawn tremendous attention because of the inexhaustible and easily available utilization of solar energy [1]. Among various solar

* Corresponding author.
** Corresponding author.
*** Corresponding author.
E-mail addresses: zaijiantao@sjtu.edu.cn (J. Zai), qiquan.qiao@sdstate.edu (Q. Qiao), xfqian@sjtu.edu.cn (X. Qian).

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cells, quantum dot-sensitized solar cells (QDSSCs) have become immediate areas of research focus in scientific and industrial fields [2–7]. The advantages of QDSSCs include high molar extinction coefficient, multiple exciton effect, spectral tunability of quantum effect [8] and higher theoretical energy conversion efficiency than that of dye-sensitized solar cells (DSSCs) [9–11]. However, compared with the photovoltaic performance of DSSCs, the efficiency of QDSSCs is still lower [12–17]. Extensive efforts are needed to further improve the performance of QDSSCs. As an important component in QDSSCs, counter electrode (CE) plays a crucial role in reducing polysulfide electrolytes (S^{2-}/S_n^{2-}), collecting and transporting electrons from the external circuit [8,18]. Generally, Pt is used as a standard CE because of its effective interface between the conductive transparent oxide and metal catalysts [11,19]. However, the surface activity and conductivity of Pt CEs can be suppressed because the sulfur in a polysulfide electrolyte system can cause over potential and inefficient reduction of redox polysulfide electrolyte [20,21], Therefore, it is urgent to explore alternative Pt-free CE materials for polysulfide electrolyte and further to fabricate QDSSCs with improved efficiency and stability. Since 1980 [22], metal sulfides (e.g. Co, Cu, Pb) have been proved with high electrocatalytic activity towards polysulfide redox system. Many sulfides with different composites or morphology [11], including Cu_2S or CuS [23–26], CoS [27–29], PbS [30,31], and Cu_2S/reduced graphene oxide composites [32] have been developed. Among these materials, copper sulfide based CEs displayed the highest catalytic activity toward the reduction of polysulfide in QDSSCs [33]. However, the widely used Cu_2S/brass CEs usually suffer from the continuous corrosion in the sulfide/polysulfide electrolyte [28], leading to instability as well as the poisoning of sensitized photoanode [34]. Hence, it is urgent to design more stable and rational designed efficient CEs with high performance.

Besides the intrinsic characteristics, the microstructure of CE materials also significantly affects their catalytic activity. In general, copper sulfides in 0D nanoparticles, hollow structure, 2D nanostructure or 3D architecture have been used as CE materials in QDSSCs [11,35,36]. Very recently, Wang et al. [37] synthesized $Cu_{2-X}S$ nanotubes with slightly rough surface by using Cu nanowires as self-sacrifice templates, and the QDSSCs based on the as-prepared $Cu_{2-X}S$ nanotubes showed good performance due to their high speed of electron transport. However, limited active sites can be provided by their smooth and thick wall. Hierarchical architectures constructed by nanoblocks with specific dimension can synergistically combine the advantages of nanostructures and microstructures, such as higher surface/volume ratio, porosity and accessible inner surface, which are important for the performances of CEs for the abundant active sites and quick mass diffusion characteristics. For these synergistic effects, one-dimension (1D) hierarchical architectures have gained much attention due to their high versatility and applications in catalysis, chemical sensing, energy conversion and storage devices [38–41]. Therefore, it is reasonably expected that hierarchical nanotubes may improve the performance of CEs [42,43]. However, to the best of our knowledge, few work has been reported.

Hence, hierarchical Cu_7S_4 nanotubes (Cu_7S_4-HNT) assembled by hexagonal nanoplates have been prepared by an *in-situ* growth route and etching process at room temperature. The materials combined the profitable characteristics of nanotubes and hierarchical structure. The QDSSCs with Cu_7S_4-HNT CEs yield a power conversion efficiency (PCE) of 4.53% under 1 sun illumination, superior to the PCE of Cu_2S/Brass (3.30%) and Pt CEs (1.79%), respectively. What's more, the Cu_7S_4-HNT CE still show high stability in electrolyte after 1000 CV circles.

2. Experimental

2.1. Materials

All Chemical reagents of analytic grade purity except noted additional were purchased from Shanghai Chemical Co. Ltd., and they were directly used without further purification.

2.2. Synthesis of hexagonal nanoplates based Cu_7S_4 hierarchical nanotubes (Cu_7S_4-HNT)

Copper foil (25 × 40 × 0.1 mm, 99.99%) was thoroughly precleaned by scrubbing, and then ultrasonicated in acetone, ethanol and deionized water for 20 min each, sequentially. According to the previous work [44] plus some modification, $Cu(OH)_2$ nanorod arrays were first synthesized: a mixed aqueous solution of NaOH solution (10 M, 16.0 mL), $(NH_4)_2S_2O_8$ solution (1.0 M, 8 mL), ammonia solution (25%, 8 mL) and 80.0 mL of distilled water were prepared in a beaker. Then several pieces of the pretreated copper foil were immersed in the mixed solution at room temperature and reacted for 45 min, copper foil color changed to blue. Then they were taken out of the beaker, and rinsed with deionized water and dry ethanol, respectively. $Cu(OH)_2$@Cu_7S_4 core/shell structures were fabricated by immersing the as-prepared $Cu(OH)_2$ nanorod arrays on copper foil in the mixed solution of 0.0025 M of NaOH and 0.01 M of Na_2S, and then reacted at room temperature for 1.5 h. Hexagonal nanoplates based Cu_7S_4 hierarchical nanotubes (Cu_7S_4-HNT) were prepared by introducing the obtained $Cu(OH)_2$@Cu_7S_4 core/shell arrays into an ammonia solution (14.4%) and etched for 8 h to remove the $Cu(OH)_2$ core. Then the obtained Cu_7S_4-HNT products were washed with deionized water and dry ethanol, and dried in a vacuum oven under 60 °C. For further characterization, the as-prepared Cu_7S_4-HNT were peeled off from foil substrate.

2.3. Preparation of Cu_7S_4-HNT, Cu_2S/brass and Pt counter electrodes

The obtained Cu_7S_4-HNT can be easily peeled off from copper substrate. The copper substrate is not stable in the electrolyte. Hence, Cu_7S_4-HNT were peeled off from copper substrate to prepare CEs. Cu_7S_4-HNT CEs were fabricated by a doctor-blade method. First, a paste mixture was prepared by mixing the as-prepared Cu_7S_4-HNT with acetylene black (Strem Chemicals Inc.) and poly (vinyldifluoride) (Kynar 740, ELF) (their mass ratio was 8:1:1) in N-methyl-2-pyrrolidone (ultra, ISP Technologies Inc.). Then the paste was dropped onto an edge of the drilled and thoroughly cleaned FTO conductive glass substrate to form the CE film. Furthermore, to dry and better attach the active films to FTO substrates, the as-prepared CEs were treated in a vacuum oven under 60 °C for 10 h.

Cu_2S/brass CEs were prepared according to the previous literature [24]. Pt CEs were prepared as [45]: H_2PtCl_6 (50 μL) in ethanol was drop-cast on FTO glass, and then heated at 380 °C for 30 min to form the Pt CE.

2.4. Preparation of CdS/CdSe QDs co-sensitized mesoscopic TiO_2 photoanode

Commercial FTO glass covered with 0.16 cm^{-2} mesoscopic TiO_2 (Yingkou OPV Tech New Energy Co., Ltd, the thickness was around 12 μm, including 8 μm transparent layer and 4 μm scattering layer) were used from. To fabricate CdS/CdSe QDs co-sensitized TiO_2 photoanodes, a successive ionic layer adsorption and reaction (SILAR) method was employed [46]. Firstly, TiO_2 photoanode was successively immersed into two solutions for 5 min each time to grow CdS: one is $Cd(NO_3)_2$ ethanol solution (0.5 M), another is Na_2S (0.5 M) methanol/DI water (volume ratio of 7:3) solution.