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Highly transparent ultrathin metal sulfide films as efficient counter electrodes for bifacial dye-sensitized solar cells

Zhelu Hu [a], Kai Xia [a], Jing Zhang [a,b], Ziyang Hu [a,b], Yuejin Zhu [a,b,*]

[a] Department of Microelectronic Science and Engineering, Ningbo University, Ningbo, Zhejiang 315211, China
[b] Department of Physics and Ningbo Collabrative Innovation Center of Nonlinear Harzard System of Ocean and Atmosphere, Ningbo university, Ningbo 315211, China

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ABSTRACT

Highly transparent metal sulfides (Ni_3S_4, MoS_2) are directly deposited on fluorine doped tin oxide (FTO) substrates as effective Pt-free counter electrodes (CEs) for novel bifacial dye-sensitized solar cells (DSSCs). The blocky-like Ni_3S_4 and petal-shaped MoS_2 nanoparticles (NPs) possess large surface area, which provides amount of active site to contact with electrolyte. The films not only show high transmittance at visible wavelengths, but also exhibit prominent electrocataltytic activity and outstanding metallic conductivity in iodine/iodide based bifacial DSSCs. Under front-side irradiation (100 mW/cm^2), the bifacial DSSC based on the transparent Ni_3S_4 or MoS_2 CE presents remarkable photovoltaic conversion efficiency (E_{ff} = 6.56%, 6.11%, respectively), closing to that of conventional Pt CE (E_{ff} = 6.83%). Moreover, by appending an ordinary mirror as a photo reflector to achieve both-side illumination, the bifacial DSSC using the transparent Ni_3S_4 or MoS_2 sample as CE obtained higher short-circuit current density (J_{sc}) and more attractive power conversion efficiency (PCE) (E_{ff} = 7.06%, 6.65%, respectively). It indicates that the as-prepared transparent Ni_3S_4 and MoS_2 CEs are promising potential candidates to explore low-cost and high-efficiency bifacial DSSCs.

1. Introduction

With the growing severity of environment challenges and energy crisis, dye-sensitized solar cells have attracted significant attention since 1991, due to their low cost, simple fabrication process, good durability and relative high efficiency [1–3]. Recently, the power conversion efficiency of DSSCs has reached 13% under the illumination of 100 mW/cm^2 AM 1.5G full sunlight [4]. Generally, a standard DSSC consists of three components: a dye-sensitized nanocrystalline TiO_2 photoanode, an electrolyte containing a redox couple (I^-/I_3^-) and a counter electrode. The counter electrode, as an important part of a typical DSSC, plays a key role in rapidly collecting electrons from external circuit and catalyzing the triiodide ion reduction in the electrolyte. Commonly the preferred CE material is made of platinum, which provides excellent catalytic activity for reducing the I_3^- to I^- and high electrical conductivity [5,6]. Nevertheless, high cost and scarcity of Pt undoubtedly hinders its application to commercial production of DSSCs. It is highly necessary to develop some replaceable counter electrode materials to figure out the problems. Recently, a large amount of functional substitute materials are used to investigate, such as conducting polymers [7,8], carbonaceous materials [9,10] and inorganic compounds (metal sulfides [11], metal nitrides [12], metal carbides [13], metal phosphides [14], metal oxides [15] etc), which exhibit both high catalytic activity for reduction of triiodide ions and excellent electrical conductivity for transferring of electrons.

It is noteworthy that the abundant alternatives show opaque and thick films to achieve the optimal photovoltaic performance. By contrast, the characteristic feature of optical transparency is a substantial benefit of DSSCs for certain practical applications, such as roof panels, windows or various decorative facilities [16]. In recent years, many researchers pay closer attention to transparent CEs and more actively seek simple execution and low-cost preparation methods. The original transparent counter electrodes based on carbon materials [17], conductive organic polymers [18], metallic compounds [19,20], composite materials [21], and platinum [22], which have been widely investigated. Seo et al. developed transparent carbon nanotube as cathode material, combining with chemical assembly method [23]. Lin's group fabricated transparent honeycomb-like CoS [24] and $NiCo_2S_4$ [25] CEs through an electro-deposition process. Baroughi et al. explored

* Corresponding author. Tel.: +86 574 87600770; Fax: +86 574 87600744.
E-mail address: zhuyuejin@nbu.edu.cn (Y. Zhu).

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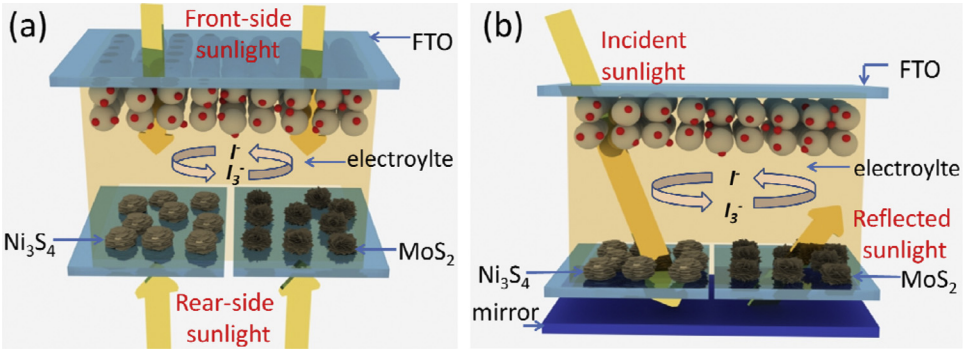

Fig. 1. (a) Schematic illustration of the conventional bifacial DSSC and Fig. 1(b) schematic diagram of the bifacial DSSC adding a mirror as an incident light reflector.

highly transparent platinum counter electrodes based on spray coating technique [26]. Though the technology of transparent electrodes has not been matured for up-scale production, it plays an important role to expedite the practicability of DSSCs.

Furthermore, it is also found that designed bifacial DSSC based on transparent CEs could enhance light harvesting efficiency of dye-sensitized solar cells, due to the incident light simultaneously from the front and the rear sides. Thus, more dye molecules are excited and more carriers are generated. The transparent polyaniline [27] and carbon [28] counters were applied in bifacial DSSC respectively, showing high PCEs and low preparation cost. Meanwhile, the PCE of bifacial DSSCs presents an apparent increase by appending an ordinary mirror or a white filter paper as a photo reflector to receive bifacial irradiation. Li et al. prepared similar bifacial DSSC based on transparent SiO_2/PEDOT:PSS electrode showing excellent photovoltaic performance [29].

Motivated by the outstanding feature of the transparent electrodes, we design the highly transparent blocky-like Ni_3S_4 and petal-shaped MoS_2 counter electrodes (shown in Fig. 1(a)) by one-step hydrothermal method, which are applied into bifacial DSSCs under front- or rear-side sunlight illumination. The blocky Ni_3S_4 and petaloid MoS_2 particles possess large surface area, generating a large amount of active site to absorb electrolyte, which benefits electrons migration and reduction for triiodide. Under the sunlight irradiation from the front-side (anode), the bifacial DSSCs based on the resultant transparent Ni_3S_4 and MoS_2 CEs achieved impressively efficiencies of 6.56% and 6.11%, which approach about 96% and 90% that of Pt CE (6.83%), respectively. It indicates that the Ni_3S_4 and MoS_2 samples present excellent catalytic activity for I_3^- reduction, comparable to that of Pt CE. When adding a mirror as a sunlight reflector to obtain bifacial illumination (shown in Fig. 1(b)), there is a significantly increased utilization rate of sun light, which achieved higher PCE of 7.06% (based on Ni_3S_4 CE) and 6.65% (based on MoS_2 CE) compared with the devices irradiated from only front- or rear-side.

2. Experimental

2.1. Preparation of counter electrodes

All chemical reagents were used as received without further purification. The prepared sulfide CEs directly were grown on FTO substrates by one-pot hydrothermal method. The typical procedure is as follows: For the nickel sulfide precursor solution, $NiCl_2{\cdot}2H_2O$ (1.5 mmol, Aladdin) and thiourea powder (15 mmol, Aladdin) dissolved in 80 mL of deionized water and stirred for 10 min until a clear and homogeneous jade-green solution was achieved. For the molybdenum sulfide precursor solution, $Na_2MoO_4{\cdot}2H_2O$ (1.5 mmol, Aladdin), thiourea powder (15 mmol, Aladdin) and 20 mg polyethylene glycol with average molecular weight of 2000 (PEG 2000) dissolved in 80 mL of deionized water and stirred for 10 min until a clear and homogeneous transparent solution was achieved. The nickel sulfide or molybdenum sulfide precursor solution was transferred into a 100 mL Teflon-lined autoclave, respectively. A piece of cleaned FTO substrate was placed at an angle against the wall of the Teflon-liner autoclave with the conductive side facing down. The nickel sulfide autoclave was sealed and heated in an oven at 160 °C for 20 h and the molybdenum sulfide autoclave was sealed and heated in an oven at 180 °C for 30 h, in that period without intentional control of ramping or cooling rate. When the process is completed and then the FTO substrate was removed from the solution, thoroughly washed several times by deionized water. After that, sulfide electrodes were dried in a vacuum oven at 60 °C for 5 h.

2.2. Fabrication of the DSSCs

The TiO_2 anode was prepared as described previously [30]. Prepared TiO_2 porous films were deposited onto FTO by doctor-blade coating. The electrode was gradually heated under an airflow at 200 °C for 5 min, at 325 °C for 5 min, at 375 °C for 5 min, and at 450 °C for 15 min, and finally, at 500 °C for 15 min. Subsequently, the electrodes were immersed in 40 mM of $TiCl_4$ aqueous solution at 70 °C for 30 min. After being sintered in airflow at 500 °C for 15 min as above process again, the prepared TiO_2 electrode was immersed into a 0.5 mM N719 dye solution (acetonitrile and tertbutyl alcohol with volume ratio of 1:1). Then the electrolyte was a solution of 0.6 M BMII, 0.03 M I_2, 0.10 M guanidinium

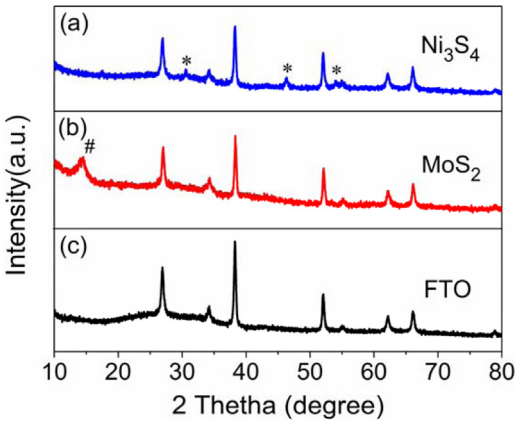

Fig. 2. XRD patterns of the obtained Ni_3S_4/FTO, MoS_2/FTO CEs and FTO substrate.