Electrochimica Acta 173 (2015) 252–259

Contents lists available at ScienceDirect

Electrochimica Acta

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

Flowerlike molybdenum sulfide/multi-walled carbon nanotube hybrid as Pt-free counter electrode used in dye-sensitized solar cells

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ARTICLE INFO

Article history:
Received 11 February 2015
Received in revised form 4 April 2015
Accepted 12 May 2015
Available online 15 May 2015

Keywords:
Dye-sensitized solar cell
counter electrode
molybdenum sulfide
multi-walled carbon nanotubes

ABSTRACT

A flowerlike molybdenum sulfide/multi-walled carbon nanotube (MoS_2/MWCNT) hybrid is prepared and used as an efficient Pt-free counter electrode (CE) for dye-sensitized solar cells (DSSCs). Field emission scanning electron microscopy observes that the flowerlike MoS_2/MWCNTs possess lamellar and large specific surface area, which benefits the enhancement of electrocatalytic activity. Cyclic voltammogram measurement indicates that MoS_2/MWCNT CE has larger current density smaller overpotential than MoS_2, MWCNT, even Pt CEs. Electrochemical impedance spectroscopy shows that the MoS_2/MWCNT with optimal MWCNT content has low charge-transfer resistance of 2.05 $\Omega \times cm^2$ and series resistance of 1.13 $\Omega \cdot cm^2$. Under simulated solar light irradiation with intensity of 100 $mW \cdot cm^{-2}$ (AM 1.5), the DSSC based on the MoS_2/MWCNT CE achieves a power conversion efficiency of 7.50 %, which is comparable with the solar cells based on the Pt CE (7.49%).

1. Introduction

Nanocrystalline dye-sensitized solar cells (DSSCs) have attracted considerable interest since it was reported by O'Regan and Gratzel in 1991 [1]. As a new kind of solar cell, DSSCs display many virtues such as low cost, easy preparation, good performance and environmental benignity compared with traditional photovoltaic devices [2,3]. Typically, a DSSC include a dye-sensitized TiO_2-nanocryatalline photoanode, electrolyte containing a redox couple, and a counter electrode (CE). The CE tasks are catalyzing the iodide/triiodide (I^-/I_3^-) redox couple and collect electrons from external circuit. Up to now, noble platinum with high conductivity and electrocatalytic activity has been widely used as CE materials. However, Pt is an expensive metal and can be decomposed to PtI_4 by I^-/I_3^- redox couple, thus resulting in the restriction for large-scale application of DSSCs [4].

Several kinds of materials, such as carbon [5–7], conducting polymers [8–10], alloy metals [11,12], metal sulfides [13–16], etc have been introduced into DSSCs as Pt-free CE. Among them, multiple-wall carbon nanotubes (MWCNTs) show a fine potential as an alternative CE due to their large specific surface area, high conductivity, and photochemical stability, as well as good mechanical strength [17]. However, pure MWCNTs do not seem to be an ideal CE material used in DSSC, in view of the limitations of electrocatalytic activity for I_3^- reduction [18].

Recently, molybdenum sulfide (MoS_2) was proposed as a potential CE material candidate, which possesses an analogous structure to graphite and graphene, is composed of three atom layers: one Mo atomic layer sandwiched between two S atomic layer in a trigonal prismatic arrangement and the layers stack through Van der Waals interactions [19,20]. MoS_2 easy synthesizes and possesses high conductivity and catalytic activity. At present, MoS_2 is extensively applied as solid lubricant and hydrodesulfurization catalysts [21], but little work has been done on MoS_2 as CE material used in DSSCs. Wu et al. [22] utilized MoS_2 as CE material in DSSC and obtained a power conversion efficiency of around 7.59 %. Further studies suggested that the electrocatalytic activity of the MoS_2 CE could be improved through adding carbon materials. Yue et al. [23] prepared a MoS_2 film with well-distributed graphene flak; the MoS_2 film possessed a high electrocatalytic activity and faster reaction for I_3^- reduction.

In this paper, a Molybdenum sulfide/multi-wall carbon nanotube (MoS_2/MWCNT) hybrid was prepared by a low-temperature hydrothermal method. Owing to the synergistic effects between MWCNTs and MoS_2, the MoS_2/MWCNT hybrid shows excellent electrochemical properties. Using the hybrid as CE material for DSSC, which exhibits a comparable photovoltaic performance to the DSSC based on Pt counter electrode, the results provide a novel promising Pt-free counter electrode materials for DSSCs.

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http://dx.doi.org/10.1016/j.electacta.2015.05.069
0013-4686/

2. Experimental

2.1. Materials

Chemical reagents including ammonium persulfate ($(NH_4)_2S_2O_8$), sodium molybdate dehydrate ($Na_2MoO_4 \cdot 2H_2O$), thiourea (H_2NCSNH_2) were purchased from Sinopharm Chemical Reagent Co. Ltd China. Sensitized dye N-719 [$RuL_2(NCS)_2$, L = 4,4′-dicarboxylate-2,20-bipyridine] and raw MWCNTs (purity: > 99.5%; average diameter: 8 nm; length: 10∼30 μm) were obtained from Deysol, Australian and Golden Innovation Business Co, respectively. All other chemical reagents were purchased from Sigma-Aldrich Co. Ltd Shanghai, China.

2.2. Preparation of CEs

The fluorine-doped tin oxide (FTO) transparent conductive glass substrate (sheet resistance, 14 $\Omega \cdot sq^{-1}$) was clean with mild detergent, aceton and deionized water in ultrasonic cleaner for 20 min, respectively, then stored in alcohol. Raw MWCNTs was pretreated using a mixed solution of H_2SO_4 (98 wt%) and HNO_3 (78 wt%) with a volume ratio of 1/3 at 120 °C for 2 h as our previous work [24,25].

Flowerlike MoS_2/MWCNT hybrid was prepared by a simple hydrothermal method: the pretreated raw MWCNTs (6 mg) were ultrasonic dispersed in 60 ml deionized water at ambient temperature. 0.187 g of $Na_2MoO_4 \cdot 2H_2O$ (0.772 mmol) and 0.177 g of H_2NCSNH_2 (2.32 mmol) were added in the above solution under vigorous stirring. After 5 min, 12 M HCl was added into the above solution drop by drop to adjust the pH value of the system less than 1. Subsequently, the mixed solution was put into a Teflon-lined stainless steel autoclave and maintained at 200 °C for 12 h. After being cooled naturally to room temperature, the black precipitates were collected by centrifugation, washed with deionized water and absolute ethanol for several times and dried at 100 °C for 12 h. The resulting black powder (40 mg) was dispersed in absolute ethanol (5 ml) by vigorous stirring for 24 h, and the suspension liquid was spin-casted on the clean FTO glass substrates at

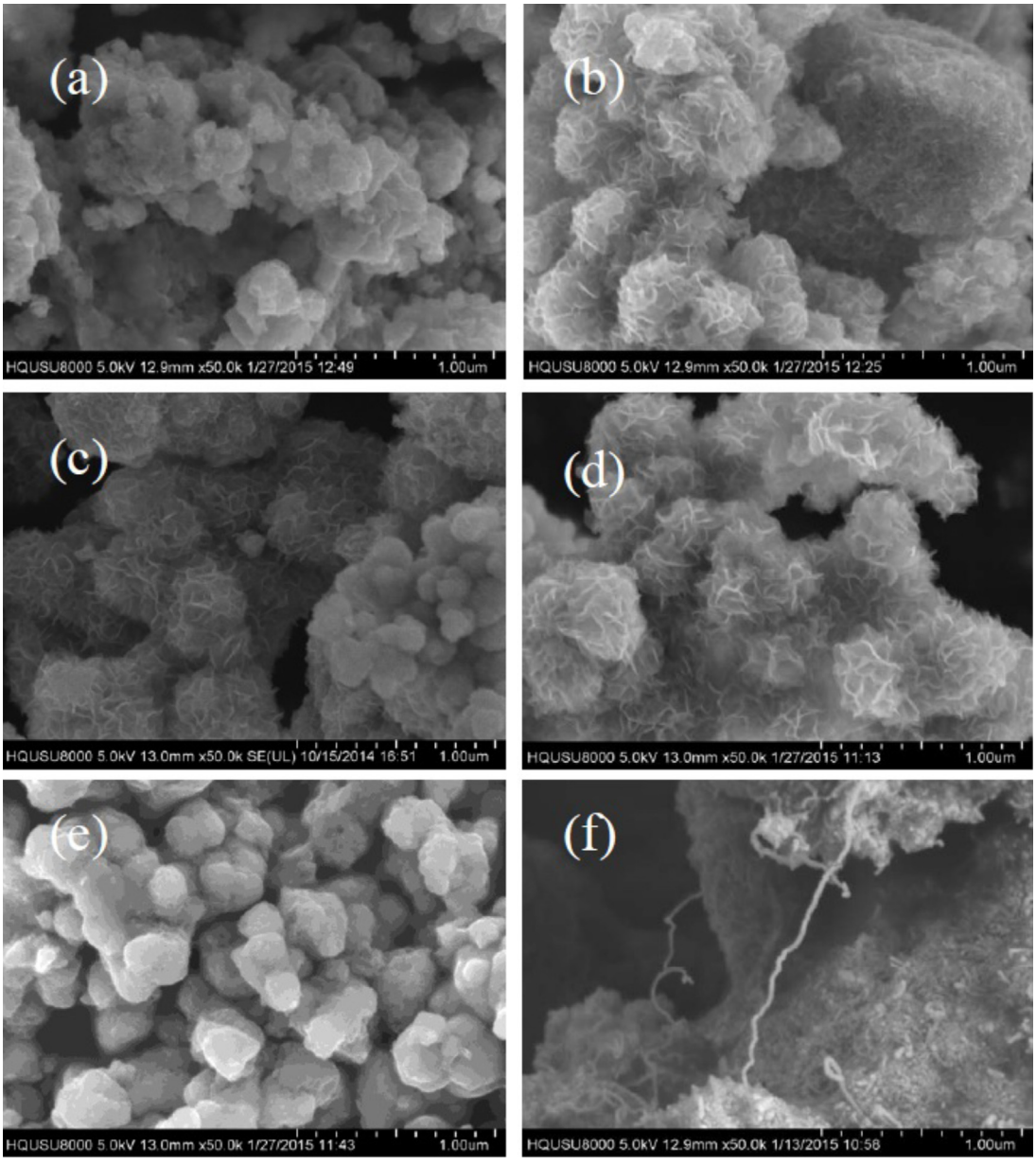

Fig. 1. SEM images of CEs: (a) CE-A, (b) CE-B, (c) CE-C, (d) CE-D, (e) CE-E, (f) MWCNTs.