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Preparation of carbon nanofibers supported MoO_2 composites electrode materials for application in dye-sensitized solar cells

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ABSTRACT

In this work, a counter electrode (CE) made from a composite of electrospun carbon nanofibers (CNs) and MoO_2 nanoparticles has been discussed for the first time as an efficient and low-cost Pt-free counter electrode (CE) for dye-sensitized solar cells (DSSCs). MoO_2/carbon nanofiber composites (MoO_2/CNs) were successfully prepared via a facile one-step hydrothermal method. The obtained MoO_2/carbon electrode showed good chemical stability, lower charge transfer resistance and higher electrocatalytic activity as compared to the conventional Pt electrodes. The characteristics of DSSCs based on MoO_2/CNs electrodes were analyzed using photocurrent density-voltage, cyclic voltammetry, Tafel polarization curve and electrochemical impedance spectroscopy measurements. The experimental results revealed that the MoO_2/CNs electrodes exhibited the optimal electrode characteristics. The DSSCs based on MoO_2/CNs electrodes displayed better photovoltaic conversion efficiency (7.6%) than the Pt counter electrodes (7.34%).

1. Introduction

Due to the growing demand for energy, research on dye-sensitized solar cells (DSSCs) have received extensive attention since 1991, due to the growing demand for energy, driving researchers to develop low cost, facile approaches for their fabrication [1].

A typical DSSC consists of a dye-sensitized nanocrystalline TiO_2 photoanode, an electrolyte containing I^-/I_3^- redox couple, and a noble metal (e.g. Pt) as a counter electrode [2–4]. The Pt counter electrode is used as a catalyst for the redox reaction of ions in the electrolyte and collects electrons from the external circuit. So far, the highest power conversion efficiency (PCE) has been obtained for DSSCs with Pt electrode (13%) [5]. However, Pt is expensive and scarce, which could be a limiting factor for large-scale application of DSSCs in future. Therefore, it is particularly crucial to develop alternative cost-effective counter electrode materials such as some low-Pt materials [6,7] or Pt alternative materials [8–10] to ensure the deployment of DSSCs on a commercial scale in future.

In previous studies, many researchers have attempted to obtain cost effective DSSCs with high efficiency by adjusting the synthesis method and the substrate, or by preparing a new material [11–13], such as conductive polymers [14,15], carbon materials [16–18], transition metal sulfides [19,20], oxides [21,22], carbides [23,24], and nitrides [25,26]. Among them, carbon materials have attracting more and more attention due to their low cost, high electrical conductivity, and excellent stability in corrosive electrolytes. Various allotropic forms of carbon have been widely studied as the counter electrode in DSSCs.

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Carbon materials represent an attractive alternative to platinum as counter electrodes of DSSCs to contribute to an efficient conversion of solar energy into electricity, This is possible due to their high electronic conductivity, corrosion resistance towards I_2, high reactivity for triiodide reduction and low cost [27]. Carbon nanofibers as a carrier of composite materials, is widely used in the CE, which itself has many advantages, such as the preparation of simple technology, large surface area, corrosion resistance and good conductivity [28].

The conventional synthesis strategies for CN materials, which include the substrate method and vapor growth method, are known to be complex and economically the least viable. Comparatively, electrospinning has been shown to be a simple and versatile technique for the preparation of carbon fiber materials. The continuous nature of nanofibers obtained with electrospinning offer easy handling and a high specific surface area compared to the fibers obtained from a conventional spinning method [29].

However, the electrocatalytic activity of these carbon materials is still lower than that of Pt. Li et al. synthesized Co_3S_4/electrospun-carbon-nanofibers composite was used as counter electrode for DSSCs. A combination of a new electrolyte with $Co^{3+}/^{2+}$ redox couple was employed to fabricate DSSCs. And the DSSCs based on Co_3S_4/CEs composite CE achieved a higher PCE of 9.23%, which increased by 10.1% compared to the DSSCs based on Pt CE (8.38%) [30]. Xiao et al. prepared Cr doped Pt_3Ni alloy supported on carbon nanofibers composites for application as counter electrode in DSSCs. The DSSCs based on Pt_3Ni/CNs and Cr-Pt_3Ni/CNs CEs yielded a PCE of 8.85 and 9.25% [31]. Li et al. synthesized the composite materials of Pt_3Ni and Mo-Pt_3Ni supported on carbon nanofibers, and used them as novel counter electrode catalysts in DSSCs. The surface features, morphology, and the electrochemical properties of the composite materials were studied, then they found that the fabricated Mo-Pt_3Ni/CNs composite had a much higher peak current, and significantly improved oxygen reduction reaction (ORR) activity. Moreover, it had a higher PCE than Pt_3Ni/CNs and pure Pt [32]. Huang et al. doped Mo onto the surface of octahedral Pt_3Ni/C (termed as Mo-Pt_3Ni/C), which exhibited excellent catalytic activity and stability [33].

A variety of transition metal oxide nanostructured materials (TMO) have the potential to be used as a safe and high capacity material in lithium ion batteries. Among the various TMOs, molybdenum oxides (MoO_X) are considered as an unusual and attractive anode materials owing to their rich chemistry associated with multiple valence states [34,35]. MoO_2 has high theoretical capacity, low electrical resistivity, high density, high melting point, and high chemical stability. Materials such as MoO_2/carbon-nanotube [36], MoO_2/carbon [37], and MoO_2/graphene [38] have been investigated as LIB anodes for better electrochemical performance. Liu et al. prepared three-dimensional (3D) interconnected carbon nanofibers containing monodispersed $MoO_{2+\delta}$ nanocrystals based on electrospinning and introduced them as a free-standing anode material for lithium-ion batteries. The resulting nanostructured monolithic hybrid mat made of C/$MoO_{2+\delta}$ nanofibers exhibits superior Li-storage properties. The attractive electrochemical performances of the as obtained 3D C/$MoO_{2+\delta}$ networks could be attributed to the synergistic effects of carbon nanofibers and monodispersed $MoO_{2+\delta}$ nanocrystals encapsulated in carbon nanofibers [39]. Moreover, transition metal oxide nanostructured materials (TMO) such WO_3, SnO_2 and ZnO were successfully transformed to highly active electrocatalytic material toward iodide/triiodide redox couple and have been used as efficient counter electrodes for dye sensitized solar cells. Elbohy et al. developed a novel method to convert the electro-catalytically inactive commercial n-type WO_3, SnO_{2-X}, ZnO_{1-X} SnO_2, and ZnO into highly active WO_{3-X} as counter electrodes (CEs) for DSSCs [40].

However, MoO_2/carbon-based-materials have not been well investigated as CEs of DSSCs. Therefore, we prepared MoO_2 composites on carbon nanofibers (CNs) as counter electrode in DSSCs based on the above discussed advantages. In this experiment, the composite materials of MoO_2 supported on carbon nanofibers were synthesized via a hydrothermal synthesis method and used as novel counter electrode catalysts in DSSCs for the first time, replacing the more expensive Pt CE. Ultimately, the MoO_2/CNs composite achieved a higher PCE of 7.6% compared to the DSSCs based on Pt CE (7.34%). The high catalytic performance of MoO_2/CNs was not only attributed to the synergistic effect of CNs and Mo nanoparticles, but also due to the large specific surface area of the composite materials.

2. Experiment

2.1. Preparation of CNs

Polyacrylonitrile (PAN, Mw = 150000) as the spinnable precursor of the electrospinning solution, 10% of activated carbon and PAN were dissolved in N, N-dimethyl formamide (DMF) and stirred at room temperature for 24 h, after that the mixture was dissolved sufficiently to obtain a spinning precursor solution. The solution was drawn into a 10 mL polypropylene syringe equipped with a stainless steel needle, which connected to the anode of a high voltage power supply. During the electrospunning, a voltage of 15 kV was applied over a 20 cm tip-to-collector distance while solution was pumped at a flow rate of 1 mL h^{-1}. A grounded stainless steel plate wrapped with aluminum foil was used as the collector. Electrospunning was continued until a thick sheet of CNs was obtained. This was then cut out and sandwiched between two graphite sheets. The CNs were stabilized in air at 230 °C, carbonized at 500 °C in N_2, and further heated to 1000 °C in N_2 to complete carbonization and initiate activation.

2.2. Preparation of MoO_2/CNs composite

Carbon nanofibers (CNs) supported MoO_2 composites (MoO_2/CNs) were synthesized according to previous reports [41]. Take the above CN (100 mg), ammonium molybdate ($(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ 0.625 g), deionized water (40 mL) and anhydrous ethanol (20 mL) in a beaker and sonicated for 20 min. The solution was then transferred to a Teflon-lined autoclave for reaction at 180 °C with 12 h. The mixture was obtained after the hydrothermal reaction, then washed three times with deionized water and dried at 100 °C in a blast dryer.

2.3. Preparation of CEs

The CE was prepared by a spraying process, For the preparation of MoO_2/CNs slurry, 100 mg MoO_2/CNs powder, 10 mL isopropanol and 10 g bead were placed in an agate jar and milled for 4 h using a star ball mill (QM-QX04, Nanjing Nanda Instrument Factory). The spray gun was attached to a compact compressor and the resulting MoO_2/CNs slurry was sprayed onto the FTO glass (TEC15, 15 Ω/square, Pilkington, USA), and then sintered in a tube furnace at 500 °C for 30 min in N_2 atmosphere to form MoO_2/CNs CE. Pure CNs were also prepared using the same procedure. In addition, Pt CE was prepared according to this method by Ma et al. [42–44].

2.4. Assemble DSSCs and symmetrical cells

DSSCs consists of a light anode, an electrode and an electrolyte. A semiconductor TiO_2 (Degussa, Germany) film was printed on a clean FTO glass by screen printing and used as the photocathode,