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Cotton shells -like floriform molybdenum disulfide@carbon electrocatalyst for high performance dye-sensitized solar cells

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ABSTRACT

A novel cotton shells-like composite of uniform MoS_2 with the carbon coated is prepared by a simple and efficient route. This particular MoS_2@C hybrid is beneficial for a dye-sensitized solar cell (DSSC) as an inexpensive but high efficient platinum-free counter electrode. Meanwhile, the synergistic effects of catalytically active MoS_2 flower-morphology and conductive carbon supports are conducive to improve charge transfer resistance, electrocatalytic activity and fast reaction kinetics of the reduction of triiodide. The DSSC assembled with this original MoS_2@C counter electrode (CE) indicates superior photoelectric conversion efficiency (6.93%), which exceeds that of the DSSC with a Pt counter electrode (6.68%).

1. Introduction

Dye-sensitized solar cells (DSSCs) have attracted enormous attention as a promising renewable energy source due to their effortless fabrication process, low cost, environmental friendliness, and anticipant high efficiency in the past decades (Yue et al., 2013; Yum et al., 2011; Zhang et al., 2011; Du et al., 2016). Generally, a normal DSSC based on three major parts: an electrolyte containing I_3^-/I^- redox couple, a TiO_2 photoanode attached with dye sensitizer and a counter electrode loading electrocatalysts (Plummer, 2016; Lin et al., 2017; Cheng et al., 2016). Specifically, the counter electrode usually plays an essential role in the field of conductivity and catalyzer. For example, it can not only collect the electron from the external circle but also catalyze the reduction of I_3^- diffused from the TiO_2 photoanode at the interface of electrolyte and counter electrode (Plummer, 2016; Kumar et al., 2013; Li et al., 2008; McKeown, 2016). As been known, the platinum always plays a unique role in the DSSC for the I_3^- reduction due to its reported outstanding electrocatalytic performance, chemical stability and splendid conductivity (Kim et al., 2014; Cui et al., 2016; Calogero et al., 2011; Lin et al., 2017; Cheng et al., 2016). On the other hand, it is contradictory that between its costly price, infrequent inventory and the possibility of large-scale manufacture. What is worse is that the Pt is easy to be decomposed to PtI_4 in iodine electrolyte (Jeon et al., 2015; Wang et al., 2011). Hence, the study of Pt-free electrocatalytic materials arises at the historic moment, which will be not only economic but also stable and effective. Fortunately, many abundant but optional materials, such as carbon materials, conducting polymers, and inorganic materials including transition metal sulfides (Yue et al., 2013), nitrides and carbides (Cheng et al., 2016), has been exploited and attempted to replace the Pt as CE in DSSCs (Wu et al., 2015; Kavan et al., 2011; Batmunkh et al., 2015). For example, Lin, C. H et al. reported the 3D vertically aligned MoS_2/CNT hybrid nanoarchitecture CE and achieved the higher efficiency (7.83%) than a Pt film CE in DSSCs. Also, Cheng, C. K et al. assembled the DSSC with MoS_2/nGO nanocomposite CE showed the efficiency of 5.95% under an illumination of AM 1.5 (100 mW/cm^2), which was up to 92.2 % of the DSSC with the conventional platinum CE (*PCE* = 6.43%).

The molybdenum disulfide (MoS_2) is a member of typical layered transition metal sulfide with three atom layers: a Mo layer sandwiched between two S layers. And these layers are arranged and held together by weak van der Waals interactions (Tenne et al., 1992; Pecoraro et al., 1981; Miremadi and Morrison, 1987). Because of the preferable electrical conductivity and the graphene-like structure, MoS_2 has been widely used in many electrochemistry relevant areas. For example, Wu et al. employed MoS_2 and tungsten sulfide (WS_2) as CE materials for DSSCs and showed high photovoltaic efficiencies of 7.59% and 7.73%, respectively (Wu et al., 2011a, 2011b). Wang used the MoS_2 as electrode materials for high-performance electrochemical capacitors and showed it had a specific capacitance of 168 F g^{-1} at a current density of 1 A g^{-1} and it retained 92.6% of capacitance even after 3000 cycles

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(Wang et al., 2011). Wang et a1. used the MoS_2 as the anode for lithium ion battery and showed high reversible discharge capacity up to 994.6 mA h g 611 and excellent cycling performances (Wang et al., 2010).

On the other hand, the way of carbon-coated maybe can also improve the electrocatalytic property especially the transition metal sulfide (Kim et al., 2009; Park et al., 2011). Wang et al. employed tungsten sulfide (WS_2) as CE materials for DSSCs and showed decent photovoltaic efficiency of 4.39%. When it coated carbon (Zhu et al., 2013), the efficiency gets better at 5.50%, which is equal to the efficiency of 5.56% with a Pt CE. In addition, Hyun Sik Kim et al. reported that carbon-coated SnS_2 had an enhanced performance as the anode in lithium-ion batteries (Kim et al., 2009).

It is easy to find that the carbon-based materials play pivotal role in the improvement of the battery especially for a DSSC. As a member of metal sulfide, the MoS_2 has the biggish specific surface area. However, only a few articles focused on the application of carbon-coated MoS_2 as the CE in DSSCs. So, we want to introduce carbon-coated to remedy its other insufficient to improve the performance based on this advantageous specific surface area.

In present work, the MoS_2 was synthesized by a simple hydrothermal route, then it was soaked in the glucose solution (Liu et al., 2009), and the mixture was annealed in nitrogen gas after washing, centrifugation and drying. Electrochemical performance measurements such as cyclic voltammetry, electrochemical impedance spectroscopy, and Tafel measurements show that the cotton shells-like structure MoS_2@C composite has excellent electrocatalytic activity for the reduction of triiodide. Furthermore, the preeminent electrochemical stability and feasibility for volume-produce manifesting the possibility that cotton shells-like MoS_2@C composite could replace noble metal Pt to serve DSSCs as the counter electrode.

2. Experimental

2.1. Materials and reagents

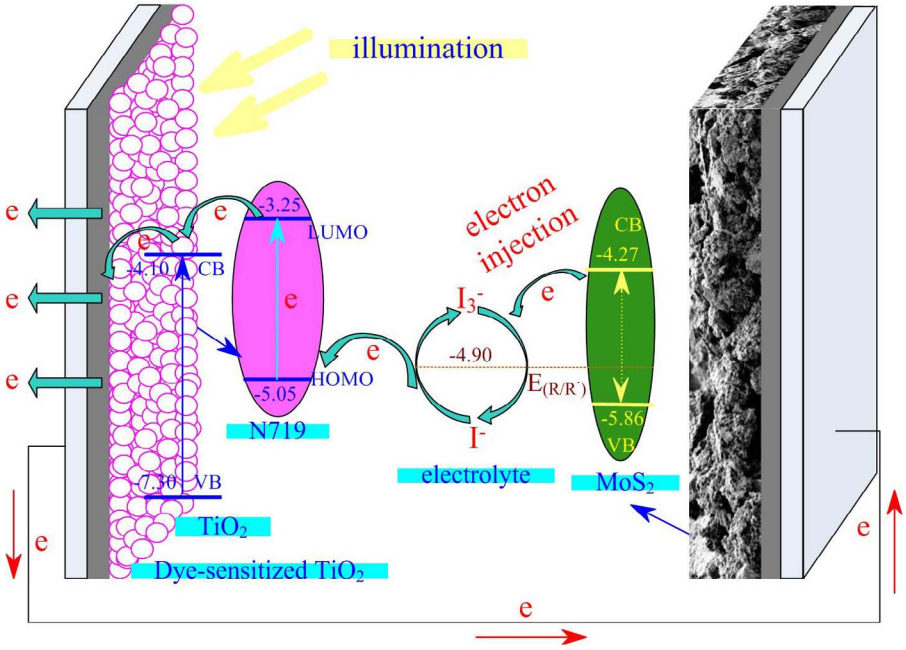
The thiourea, molybdenum trioxide, deionized water, absolute ethanol, glucose powder, polyethylene glycol with average molecular weight of 20000 (PEG 20000) purchased from the Tianjin Guangfu Fine Chemical Industry Research Institute. The sensitized dye N719 [$RuL_2(NCS)_2$·2TBA, L = 2,2-bipyridyl-4,4-dicarboxylic acid, TBA = tetrabutylammonium] was obtained from Dalian HeptaChroma Solar Tech Co., Ltd. Lithium iodide (LiI), lithium perchlorate ($LiClO_4$) and iodine (I_2) were purchased from Aladdin Reagent Co. Ltd (Shanghai, China). All reagents are of analytical reagent grade and used without further purification. FTO glass substrates were cut into 2.0 × 1.0 cm^2 carefully and ultrasonically cleaned sequentially in detergent, acetone and distilled water for 10 min each and then stored in alcohol.

2.2. Preparation of molybdenum disulfide (MoS_2)

Simply, 0.16 g thiourea was dissolved in 60 ml distilled water and stirred at less than 5 °C for 10 min. 0.16 g molybdenum trioxide was added into this solution and followed by ultrasonication and stirred for 20 min by magnetic stirrers until a clear and homogeneous solution was achieved (Wang et al., 2014). After that, the mixed solution was transferred to a 100 ml Teflon-lined autoclave and then heated in an oven at 180 °C for 24 h in an electricity heat drum wind drying oven. When the drying oven was cooled to indoor temperature, the final black products were collected by high speed centrifugation at 7000 r, then washed with distilled water and absolutely ethanol for several times until the supernatant was clear. At last, the obtained black samples were dried in a vacuum oven at 60 °C for 12 h.

2.3. Synthesis of the hybrid of MoS_2@C

Step 1: using the glucose powder and deionized water to confect a serious of glucose solution with different concentration of 0.1 mol/L, 0.3 mol/L, 0.5 mol/L, 0.7 mol/L, 0.9 mol/L. Step 2: 0.05 g pure MoS_2 was added into aforementioned solution, respectively, followed by magnetic stirrers for another 10 h (Liu et al., 2009). Step 3: Separated the final black product from slurry by high speed centrifugation at 6000 r about 6 min. Then the achieved product was dried in a vacuum oven at 60 °C for 8 h. Step 4: After the final product was dry totally, followed by annealling in a tube furnace at 500 °C for 5 h under the protection of argon. In this way, five black samples would be synthesized, which were denoted as 0.1 M, 0.3 M, 0.5 M, 0.7 M, and 0.9 M.



Scheme 1. Energy level diagram of the as-prepared MoS_2 CE and the possible mechanism diagram for the operation mechanism of the DSSCs.