



Carbon-coated three-dimensional WS₂ film consisting of WO₃@WS₂ core-shell blocks and layered WS₂ nanostructures as counter electrodes for efficient dye-sensitized solar cells



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ARTICLE INFO

Article history:

Received 24 November 2017

Received in revised form

15 January 2018

Accepted 2 February 2018

Available online 3 February 2018

Keywords:

Tungsten sulphide

Sulfurization

Three-dimensional

Carbon-coated

Counter electrode

Dye-sensitized solar cells

ABSTRACT

The possibility of using solar energy for electricity generation has inspired intensive enthusiasm on the development of solar cell devices. This work reports the synthesis of a novel counter electrode (CE) composed of WO_x@WS₂@carbon core-shell film and compares its electrical and electrocatalytic performances with other two CEs of WO_x/carbon film and conventional Pt in the dye-sensitized solar cells (DSSCs). The WO_x@WS₂@carbon CE was prepared by a sulfurization treatment of a mesoporous WO_x/carbon film coated on fluorine-doped tin oxide (FTO) glass. The well-interconnected three-dimensional (3D) WS₂ structure with coated carbon film provides high electrocatalytic activity and fast reaction kinetics for the reduction of triiodide to iodide due to its sufficient active sites on 3D WS₂ framework containing surface edge-oriented nanosheets and the facile electron transfer and electrolyte diffusion via the continuously carbon layer. Photovoltaic performance tests indicate the DSSC device with the counter electrode of WO_x@WS₂@carbon core-shell achieved the power conversion efficiency (PCE) of 7.71% compared favourably with the values of 6.00% from WO_x/carbon CE and 7.34% from conventional Pt CE. Such results vividly mirror that the developed WO_x@WS₂@carbon core-shell can replace the conventional Pt film, realizing Pt-free counter electrodes for DSSCs.

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1. Introduction

The solar energy conversion research has attracted wide attention due to the energy crisis and environmental pollution arising from the heavy consumption of non-renewable fossil fuels. The dye-sensitized solar cell (DSSC) is one promising candidate of various photovoltaic conversion devices owing to its low cost, environmental benignity, facile fabrication process, and large design flexibilities [1–3]. Platinum (Pt) is the most common counter electrode (CE) material for DSSCs because of its excellent catalytic activity and high electrical conductivity. The DSSCs based on Pt CE have achieved high power conversion efficiency (PCE)

exceeding 12% [4,5]. However, Pt is an expensive noble metal and has weak chemical stability as it can be decomposed to PtI₄ or H₂PtI₆ in the triiodide/iodide (I₃⁻/I⁻) electrolyte [6,7]. Thus, it is necessary to develop new Pt-free CE materials to reduce the production cost and increase the stability of DSSC performance.

The ideal CE materials for DSSCs should have superior properties to collect electrons, catalyze I₃⁻ reduction, and long-term stability as well as being earth-abundant. For instance, graphene [8], carbon nanotubes [9], conducting polymers [10] and transition metal dichalcogenides [11] have been attempted as alternative functional materials to replace Pt as CE for DSSCs. Tungsten (W)-based compounds, including their oxides, nitrides, carbides and hybrids, also have been widely studied as CEs for the DSSC application due to their excellent properties, such as low cost, good stability and notable electrocatalytic activity [12–20]. For W-based oxides, non-stoichiometric tungsten trioxides (WO_{3-x}, where 0 < x ≤ 1), have better conductivity than tungsten trioxide (WO₃), because the carrier concentration in the system of WO₃-WO₂ increases with the

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decreasing anion coordination numbers [21]. Wu et al. reported a PCE of 7.25% achieved on the DSSC with WO_2 as CE, which is much higher than that of 4.67% based on WO_3 CE [22]. It was also found CE based on WO_3 /carbon composite showed higher PCE compared with pure WO_3 CE [23].

Similarly, tungsten sulfide (WS_2) with an analogous structure of graphite and graphene [24], is expected to exhibit a good performance in DSSCs due to its high catalytic activity, thermal and chemical stability. Wu et al. have used the pure WS_2 as CE for DSSCs [25], but the hydrothermal preparation of WS_2 is time-consuming (one week) and not eco-friendly. To compensate for the conductivity of WS_2 film, carbon materials are usually added to fabricate the CE. For instance, carbon-coated WS_2 [26] or the WS_2 composite with TiO_2 (P25) and carbon nanoparticles (WS_2 /P25/C) [27] was investigated, delivering a PCE of 5.50% or 4.56%, respectively. The discontinuous boundaries or weak interaction between carbon and WS_2 make these CEs still inferior to Pt. Moreover, the incorporation of multi-wall carbon nanotubes (MWCNTs) into the WS_2 CE system has also been attempted [28,29]. An efficiency up to 7.36% was achieved by the DSSC based on WS_2 /MWCNTs CE [29]. Nevertheless, it becomes intractable to control the carbon content in the composite, as too less carbon materials cannot improve the conductivity while too much addition would cover the active sites of WS_2 and reduce their bonding strength. On the other hand, WS_2 can also be easily obtained through a high temperature sulfurization process from W-based oxides, which can be used to prepare continuous WS_2 film in large area [30,31]. Hussain et al. fabricated the WS_2 CEs from WO_3 films deposited on fluorine-doped tin oxide (FTO) glass substrate by a sputtering and sulfurization process to be functioned as CE for DSSCs, achieving a PCE around 6.3% [30]. The relatively low efficiency compared with Pt CE (6.64%) can be ascribed to the insufficient active sites for triiodide reduction in the dense film obtained from sputtering. It was found edge-oriented WS_2 nanosheets could maximize the number of active edge sites leading to drastically enhanced catalytic activity toward triiodide reduction [31].

Here, we present a novel WS_2 electrode prepared by a simple sulfurization of a mesoporous WO_x /carbon film with rough surfaces coated on FTO Glass substrate, where WO_x not only provides the tungsten source but also acts as building blocks to scaffold continuous WS_2 layers. In the resultant film electrode, a carbon-coated well-interconnected three-dimensional (3D) WS_2 catalytic network was built up by the interconnected tetragonal WO_3 @ WS_2 core-shell blocks with surrounding irregular WS_2 layers, a small amount of WS_2 nanorods and the edge-oriented WS_2 nanosheets on the surface. The synergistic effects of the maximized active edge sites on 3D WS_2 framework's surface, and facile electron transfer and electrolyte diffusion via the continuous carbon matrix lead to drastically enhanced catalytic activity toward I_3^- reduction in the CE of DSSCs. The DSSC based on this WS_2 CE achieved a PCE of 7.71%, which is superior to the performances of the cells with Pt-based CE (7.34%) and WO_x /carbon CE (6.00%).

2. Experimental section

2.1. Materials

Sodium tungstate ($\text{Na}_2\text{WO}_4 \cdot \text{H}_2\text{O}$), hydroxylamine hydrochloride ($\text{NH}_2\text{OH} \cdot \text{HCl}$), sulfourea ($\text{CH}_4\text{N}_2\text{S}$), sulfur (S), poly (vinyl alcohol) (PVA, #341584), ethyl cellulose (EC, #46070 and #46080), titanium (IV) bis (ammonium lactato) dihydroxide solution (TALH, 50 wt% in water), titanium tetrachloride (TiCl_4), terpineol, acetonitrile, tert-butanol, lithium iodide (LiI), lithium perchlorate (LiClO_4), iodine (I_2) and fluorine-doped tin oxide (FTO) glass substrates (TEC7, 2 mm, resistance $\sim 7 \Omega/\text{sq}$) were purchased from

Sigma-Aldrich. Polyethylene glycol (PEG, 2000) was supplied by Merck while triiodide/iodide (I_3/I) electrolyte (MS005615) was purchased from Dyesol.

2.2. Synthesis of WO_x green powder

First, $\text{Na}_2\text{WO}_4 \cdot \text{H}_2\text{O}$ (0.006 mol), $\text{NH}_2\text{OH} \cdot \text{HCl}$ (0.012 mol), $\text{CH}_4\text{N}_2\text{S}$ (0.024 mol) were dissolved in 36 ml deionized water. Then, 0.216 g PEG was added into the solution under constant stirring. After complete dissolution, the solution was transferred into a 60 ml Teflon-lined stainless steel autoclave, which was sealed and heated at 180°C for 24 h in the oven. The obtained precipitates were washed three times with DI water and absolute ethanol, respectively and dried in air at 60°C for 10 h. The as-prepared powder was then calcined at 800°C for 1 h with a heating rate of $5^\circ\text{C}/\text{min}$ in a tube furnace under nitrogen (N_2) protection and the green product obtained is denoted as WO_x .

2.3. Preparation of counter electrodes

A mixture of WO_x , terpineol, and EC in the weight ratios of 1:4:0.5 was ball milled with ethanol for 2 h and then subjected to rotary evaporation process at 40°C to form a viscous paste by removing ethanol. The WO_x paste was then applied on FTO glass by using the doctor blade method. After drying at 125°C for 6 min, the coated FTO glass was sintered in a tube furnace in N_2 atmosphere at 500°C for 1 h. The obtained counter electrodes are denoted as WO_x /carbon, which were subjected to the sulfurization process at 500°C for 1 h in a tube furnace to form new counter electrodes denoted as WO_x @ WS_2 @carbon. The schematic diagram of the thermal vapor sulfurization process is illustrated in Fig. S1a, where 1 g sulfur powder and the WO_x /carbon electrodes were placed at the upwind low temperature zone and the center of the quartz tube, respectively. The quartz tube was kept in a flowing protective atmosphere of N_2 , with a flow rate of 100 sccm and the heating rate was $5^\circ\text{C}/\text{min}$. The Pt counter electrodes were prepared as described previously [32].

2.4. Fabrication of dye-sensitized solar cell

The ultrasonically cleaned FTO glass plates were immersed in a 40 mM aqueous TiCl_4 solution at 70°C for 30 min and were thoroughly rinsed with water and ethanol. A TALH-PVA aqueous solution ($V_{\text{TALH } 50 \text{ wt\%}}:V_{\text{PVA } 0.75 \text{ wt\%}} = 1:13.29$) was then spin-coated on to these FTO glasses at 3000 rpm for 30 s, followed by sintering at 500°C for 30 min to form a TiO_2 block layer (Fig. S1b). A TiO_2 bead paste, where TiO_2 beads, terpineol, and EC in the weight ratios of 1:4:0.5 respectively, was then coated on the FTO glass using the doctor blade method. The TiO_2 beads were synthesized according to our previous report (Fig. S1c) [32]. The resultant film was then sintered at 325°C for 5 min, 375°C for 5 min, 450°C for 15 min and finally at 500°C for 15 min. After being re-treated with TiCl_4 solution and re-sintering at 500°C for 30 min, the TiO_2 films were immersed into 0.5 mM N719 dye solution in acetonitrile/tert-butanol ($V_{\text{acetonitrile}}:V_{\text{tert-butanol}} = 1:1$) solution at room temperature for 24 h. The dye sensitized TiO_2 films were washed with acetonitrile to the loosely physisorbed dye molecules and dried at nitrogen steam. The solar cells were fabricated by injecting I_3/I electrolyte into the void space between the photoanode and the counter electrode.

2.5. Characterization

The crystal composition and morphology of the samples were characterized by powder X-ray diffractometer (XRD, BrukerD8

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