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Facile synthesis of tungsten carbide nanorods and its application as counter electrode in dye sensitized solar cells

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ABSTRACT

Tungsten carbide nanorods (WC-NRs) are synthesized by pseudomorphic transformation of chemically synthesized W_3O_8 nanorods using a high-temperature method. The WC-NRs was introduced into dye sensitized solar cell (DSSC) as counter electrode (CE) catalyst to replace the expensive platinum (Pt). The synthesized WC-NRs were characterized by field emission scanning electron microscopy (FESEM), BET surface area analysis and powder X-ray diffraction (PXRD) measurements. The electrochemical properties of WC-NRs counter electrode were studied using electrochemical impedance spectroscopy (EIS) techniques. The photovoltaic performance of the DSSC with WC-NRs counter electrode was evaluated under simulated standard global AM 1.5G sunlight (100 mW/cm^2). The solar to electrical energy conversion efficiency (η) of the WC-NRs with binder and binder free based DSSC was found to be 1.92% and 0.59% respectively. The cell performance can be attributed to the WC-NRs network, catalytic redox activity and 1-D efficient charge-transfer network. Such WC-NRs configuration as CE provides a potential feasibility for counter electrodes in DSSC applications.

1. Introduction

The dye sensitized solar cells (DSSCs) have attracted considerable attention as cost-effective photovoltaic systems from the time of their discovery. DSSCs offer advantages over bulk Si-based solar cells, which are widely used in photovoltaic systems at present. DSSCs can provide transparent and flexible solar cells and operate at high efficiencies at low light intensities, including scattered, angled or shaded light [1–3]. Consequently, it is generally accepted that DSSCs are well suited for both building integrated photovoltaic (BIPV) systems and portable flexible solar cells. Due to low fabrication cost, its permanence, environmental compatibility and simple process, interest in DSSC has grown considerably. Although the cost of DSSC fabrication is 20% compared with silicon solar cell, for practical application the improvement of efficiency is inevitable [4].

During the DSSC operation process, oxidized dyes are regenerated by the iodide in the electrolyte and finally triiodide converted to iodide at the counter electrode (CE). The function of the counter electrode is to collect electrons

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from the external circuit and catalyze the reduction of the redox couple [5]. Most commonly, the counter electrodes in DSSCs have been prepared by platinum (Pt) vacuum deposition or thermal annealing of a Pt precursor on a transparent conductive oxide (TCO) substrate to reduce the over potential for reduction of I_3^- to I^- in redox electrolytes [6]. Pt has high conductivity, catalytic activity and stability, for the counter electrode, Pt nanoparticles have generally been accepted as providing the optimal solution. However, Pt is expensive and rare and it is already in high demand as a catalyst in a variety of chemical and electrochemical fields. Pt is one of the most expensive components that will hinder the commercialization of DSSCs [7]. Alternatively, other materials including carbon materials (graphite, activated carbon, carbon black, single-wall carbon nanotubes) [8–13] are attempted to achieve the similar performance like Pt based DSSCs. Although carbon based counter electrodes show high catalytic activity, their chief weakness is the poor bonding strength between carbon material and the substrate (FTO glass) [14]. This may cause instability in those DSSCs using carbon CEs. Poly(3,4-ethylenedioxythiophene) (PEDOT) [15–19], poly(3,3-diethyl-3,4-dihydro-2H-thieno (-3,4-b) (1,4) dioxepine) ($PProDOTEt_2$) [20], polypyrrole [21] and polyaniline [22] have been introduced. For these polymer catalysts, the film thickness was important, because it affected both catalytic activity and resistance. Recently inorganic materials, such as CoS, TiN and WO_2 have been proposed as CE catalysts all of which show great potential [23].

Transition-metal carbides are considered as a potential substitute for Pt because of their low cost, high catalytic activity, selectivity and good thermal stability under rigorous conditions [24]. Tungsten carbide is a versatile material exhibiting good hardness, a high melting point, durability and conductivity. Lee et al., also prepared tungsten carbide polymer-derived WC (WC-PD) and microwave-assisted WC (WC-MW) by different synthesis methods. The reported energy conversion efficiency was 6.61% and 7.01% respectively [25]. The aim of this work is to synthesize tungsten carbide nanorods and to apply for DSSC as novel WC-NRS based CE catalysts for the regeneration of the Iodolyte redox electrolyte. The WC-NRs based counter electrodes were prepared and performance of binder free based DSSC, was compared with the performance of binder based DSSC. Binder based DSSC shows better efficiency.

2. Experimental methods

2.1. Materials

Sodium tungstate dihydrate ($(Na_2WO_4 \cdot 2H_2O)$, ACS Reagent, $\geq 99\%$), ammonium sulfate ($(NH_4)_2SO_4$, Bioxtra, $\geq 99\%$) and zirconium (IV) oxide (99%, 5 μm) powders were purchased from Sigma Aldrich. Glucose ($C_6H_{12}O_6$, 99%) was purchased from Alfa Aesar. Titanium dioxide (TiO_2) (Degussa P25) was received from Systern. N719 Ruthenizer 535-bisTBA and Iodolyte Z-100 were bought from Solaronix. Indium doped tin oxide (ITO) conducting glass slides (7 Ω/sq cm) were purchased from Xin Yan Technology Limited, China.

2.2. Synthesis of tungsten carbide nanorods

2.2.1. Synthesis of W_3O_8 nanorods

The schematic representation for the synthesis of WC-NRs is shown in Fig. 1. W_3O_8 nanorods were synthesized by hydrothermal method using $(NH_4)_2SO_4$ as a capping agent as follows. $Na_2WO_4 \cdot 2H_2O$ and $(NH_4)_2SO_4$ were taken in the 1:2 M ratio, dissolved in deionized water (15 ml) and then HCl (3 M) aqueous solution was added to adjust the pH value to 2. The obtained solution was transferred into a teflon lined stainless autoclave where the reaction was maintained at 180 °C for 8 h. Then the precipitate was isolated by filtration and then washed sequentially with water and ethanol for three times. Finally the solution was centrifuged and resultant precipitate was dried at 60 °C.

2.2.2. Synthesis of WC nanorods

In a typical synthesis procedure of WC-NRs, suitable amounts of as-prepared W_3O_8-NRs and glucose (molar ratio W/C = 1:12.8) were dissolved in deionized water (15 ml) and vigorously stirred for 20 min. The mixture was hydrothermally treated in a sealed teflon lined stainless steel autoclave at 180 °C for 8 h to form carbon coated W_3O_8 nanorods. The as-prepared precursors were calcinated at 900 °C under a flow of H_2/Ar ($V_{H_2}/V_{Ar} = 1:3$, 300 ml min^{-1}) for 3 h and finally WC-NRs were obtained.

2.3. Preparation of WC-NRs counter electrode

2.3.1. Binder free WC-NRs preparation

200 mg of WC-NRs powder was finely ground in mortar and then mixed into the 8 ml of ethanol and vigorously stirred overnight until homogeneous suspension was obtained. The resultant homogeneous WC-NRs suspension was coated onto the conducting side of ITO glass substrate by spin coating method. The WC-NRs coated films were dried at room temperature and heated at 450 °C for 1 h.

2.3.2. WC-NRs prepared with the mixture of TiO_2 and ZrO_2 binder

A mixture of 200 mg WC-NRs material and 4 g zirconium dioxide (ZrO_2) pearl was dispersed in 8 mL of isopropanol. The mixture was then milled for 4 h using mortar and pestle. Finally the prepared material was ultrasonically dispersed for 48 min (6 segments) and 50 mg of TiO_2 (P25, Degussa) was prepared by the same method. The WC-NRs with the mixture of TiO_2 and ZrO_2 binder coated films were dried at room temperature and the product was heated at 450 °C for 1 h.

2.4. Fabrication of DSSCs and evaluation of their performance

The TiO_2 modified photoanode (prepared by doctor blade technique [26]) was immersed into the ethanolic solution of 0.3 mM N719 (Ruthenizer 535-bisTBA) dye for 24 h at room temperature. The dye-adsorbed photoanode was withdrawn from the solution and immediately cleaned with ethanol. A WC-NRs (with binder and binder free) modified ITO plate was placed on dye-absorbed