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Article

WB crystals with oxidized surface as counter electrode in dye-sensitized solar cells

Jian Pan [a,b], Chao Zhen [a], Lianzhou Wang [b,*], Gang Liu [a,*], Hui-Ming Cheng [a]

[a] Shenyang National Laboratory for Materials Science, Institute of Metal Research, Chinese Academy of Sciences, Shenyang 110016, China
[b] ARC Centre of Excellence for Functional Nanomaterials, School of Chemical Engineering and AIBN, The University of Queensland, QLD 4072, Australia

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ABSTRACT

Tungsten boride (WB) crystals, whose surface tends to be oxidized when exposed to air, were demonstrated to have a comparable activity to platinum as counter electrode material in dye-sensitized solar cells. The synergistic effect of both catalytically active surface layer WO_x and electronically conductive internal WB is considered to be responsible for the high activity of the WB crystals.

1. Introduction

Dye-sensitized solar cells (DSSCs), which are typically composed of a photoanode (dye-sensitized metal oxide films such as TiO_2 and ZnO), electrolyte and a counter electrode, are considered to be a class of competitive devices for converting solar energy to electricity, particularly in term of easy fabrication processes [1–3]. Although the new perovskite solar cell is a hot topic nowadays [4,5], it has been limited by some essential issues as toxicity, stability etc. [6,7]. Therefore, the research of DSSCs is still significant for developing low-cost solar cells. The search for highly active and affordable counter electrode materials to replace the widely used but high-cost noble metal Pt in DSSCs has been a focus in both scientific and industrial areas [8–12]. The excellent performance of Pt based counter electrode is attributed to both the high catalytic activity of Pt in inducing triiodide reduction reaction and its high electrical conductivity [8], which enable fast electron transfer from the counter electrode to electrolyte in the cell. In the past years, various earth-abundant materials including carbon [13–16], transition metal sulfides [17–19], carbides [20,21], nitrides [22,23], phosphides [24,25] and oxides [26–35] have been explored and shown a great potential as counter electrode materials. It is anticipated that the continuous extension of the database of Pt-free counter electrode materials will make it possible to develop low-cost high-efficiency DSSCs for large-scale applications.

Owing to their unique physicochemical properties, metal borides traditionally as an important class of structural ceramics have shown their additional potential in both functional applications [33] and synthesizing corresponding metal oxides or metal oxide/-boride heterostructures when used as precursors [36–39]. Despite the high chemical stability of most metal boride crystals, their surfaces are prone to be oxidized spontaneously when exposed to air even at room temperature. This feature allows us to consider that the particles of metal borides are covered by an ultrathin layer or clusters of corresponding metal oxides, as illustrated in the inset of Fig. 1. Given the versatile functionalities of metal oxide surface layer and high electronic conductivity of internal metal borides, such metal boride crystals might serve as an effective counter electrode material. Here, we used commercially available micrometer-sized tungsten boride (WB) crystals as counter electrodes. The DSSCs based on WO_x/WB counter electrodes show an energy conversion efficiency of 7.07%, which is close to that (7.75%) with Pt counter electrode.

2. Experimental

2.1. Characterization

XRD patterns of the samples were recorded on a Rigaku diffractometer using Cu kα irradiation. Their morphology was determined using scanning electron microscopy (SEM, Nova NanoSEM 430). The Brunauer–Emmett–Teller (BET) surface area was determined by nitrogen adsorption–desorption isotherm measurements at 77 K (ASAP 2010). Chemical compositions were analyzed using

* Corresponding authors.
E-mail addresses: l.wang@uq.edu.au (L. Wang), gangliu@imr.ac.cn (G. Liu).

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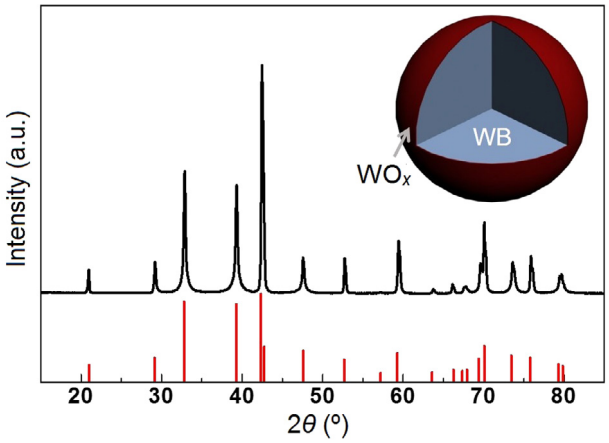

Fig. 1. (Color online) X-ray diffraction (XRD) patterns of commercial WB particles and standard diffraction patterns of WB from PDF database (JCPDS No. 35-0738). The inset is the schematic of a WB crystal particle with oxidized surface.

X-ray photoelectron spectroscopy (XPS) (Thermo Escalab 250, a monochromatic Al Kα X-ray source).

2.2. Counter electrode fabrication

Commercial WB crystals were spin-coated on a fluorine-doped tin oxide (FTO) transparent conductive glass substrate at low speed. In detail, 500 mg of WB was suspended in 5 mL of ethanol. The deposited electrode was then heated at 500 °C for 30 min in argon.

2.3. Photoanode fabrication

The three layers of TiO_2 (Dyesol) nanocrystalline film sensitized with N719 dye (Dyesol) was used as photoanode. In detail, a thin layer TiO_2 was coated on FTO conductive glass with screen printing technique. Then the TiO_2 film was sinter at 110 °C for 15 min. Repeat this process another two times and a three layers of TiO_2 film was obtained. Then, the film was calcined at 475 °C for 30 min. Then the TiO_2 film was pre-heated to 80 °C and immersed in a 0.3 mmol/L solution of N719 dye in acetonitrile/tert-butyl alcohol (1:1, v:v) for 20 h and the photoanode was obtained.

2.4. Cells fabrication

DSSCs was assembled with a photoanode and a counter electrode clipping the electrolyte and sealed by 120 μm hot-melt surlyn film. A symmetrical cell was assembled with two counter electrodes. The active area of the DSSCs is 16 mm^2. The active area of the symmetrical cells is 64 mm^2. The DSSCs were used for the photocurrent density–voltage and electrochemical impedance spectroscopy test, while the symmetrical cells were used for the Tafel-polarization measurement test.

2.5. Photovoltaic and electrochemical measurement

The photocurrent density–voltage (*J-V*) curve measurements were conducted with an AM 1.5 solar simulator (Newport 100 mW/cm^2). Cyclic voltammetry (CV) was conducted in a three-electrode system in an acetonitrile solution of 0.1 mol/L $LiClO_4$, 10 mmol/L LiI, and 1 mmol/L I_2 at a scan rate of 20 mV/s by using a PARSTAT 2273 electrochemical workstation. Pt served as a counter electrode (CE) and the Ag/Ag^+ couple was used as a reference electrode. Electrochemical impedance spectroscopy (EIS) measurements were characterized with symmetrical cells using a Parstat 2273 electrochemical workstation (Princeton Applied Research). The applied bias voltage and alternating current (AC) amplitude were set around the open-circuit 0.7 V and 10 mV, and the frequency range was from 0.1 to 10^5 Hz.

3. Results and discussion

The WB crystals used have a large particle size of several micrometers (Fig. S1a online) and thus a low surface area of 0.30 m^2/g. A WB film with around 20 μm in thickness (Fig. S1b online) was spin-coated on FTO glass and calcined at 500 °C in an argon atmosphere to increase the contact of particles. Fig. 1 gives XRD patterns of WB. All the diffraction peaks can be indexed to tetragonal WB (space group, $I4_1/amd$, JCPDS No. 35-0738). No peaks from tungsten oxides can be detected.

The composition of the WB crystals used and their chemical state were determined by XPS. Three strong characteristic peaks originated from W 4f, B 1s and O 1s were detected from the pristine surface of WB crystals, shown in Fig. 2. The atomic percentage of W, B and O is determined to be 15.8%, 21.6% and 62.6%, respectively. The high percentage of oxygen suggests that the surface of WB crystal particles was oxidized, also confirmed by studying the chemical state of W and B. Two main peaks located at 38 eV (W $4f_{5/2}$) and 35.8 eV (W $4f_{7/2}$) in the XPS spectrum are attributed to the W species in the form of W–O bonds. In contrast, only a weak peak located at 33.5 eV (W $4f_{5/2}$) is attributed to the W species of W–B bonds. This result indicates that most surfaces of WB crystals have been spontaneously oxidized, which is also confirmed by the chemical state of boron. Three oxidation states of boron with their B 1s level binding energies at 192.4, 190.2 and 188.5 eV can be identified to be B–O bonds, interstitial boron in the framework of WO_x and W–B bonds, respectively. Correspondingly, two states of oxygen with the O 1s level binding energies at 532.3 and 530.9 eV are identified to be the O–B bonds and O–W bonds, respectively. On the other hand, the absence of WO_x in the XRD pattern of WB crystals suggests that the WO_x layer formed on the surface of WB particles, revealed by XPS, has an ultrathin thickness (several atomic layers thick).

Fig. 3 shows the photocurrent–voltage (*I-V*) curves of DSSCs based on WO_x/WB and Pt counter electrodes, respectively. The detailed photovoltaic parameters are summarized in Table 1. The cell based on Pt counter electrode gives an open-circuit voltage (V_{oc}) of 715 mV, a short-circuit current density (J_{sc}) of 15.49 mA/cm^2, a fill factor (FF) of 0.70, and an energy conversion efficiency (η) of 7.75%. This efficiency is consistent with the reported value for DSSCs with Pt as counter electrode [30]. The cell based on WO_x/WB counter electrode gives a conversion efficiency of 7.07%, V_{oc} of 715 mV, J_{sc} of 15.68 mA/cm^2, and FF of 0.62. The fact of the slightly higher J_{sc} of the cell with WO_x/WB than that with Pt indicates that the WO_x/WB counter electrode material can effectively react with adsorbed I_3^- ions by reducing triiodide to I^-. On the other hand, the FF (0.62) of the cell with WO_x/WB is lower than that (0.70) of the cell with Pt largely because of the weak interface contact between the micron-sized WB particles used and thus limited electron transfer in the electrode. It is anticipated that decreasing the particle size of WB down to submicrometers or even tens of nanometers could improve both the FF and conversion efficiency of the cell with WO_x/WB as CE material.

EIS was used to investigate the electrochemical characteristics of WO_x/WB electrode in full cells. Fig. 4a shows the EIS results of WO_x/WB electrode together with Pt electrode in the form of Nyquist plots. The equivalent circuit used to fit the EIS plots is given in the inset of Fig. 4a. The series resistance (R_s) of the full cell, namely the series resistance of the device, can be determined by the high frequency intercept on the real axis. R_s is composed of