

# Synthesis of $\text{Bi}_2\text{WO}_6$ as Novel Anode Material for Lithium-Ion Battery

Wei Dang<sup>1</sup>, Shiyun Zhou<sup>2\*</sup> and Chuanqi Feng<sup>1\*</sup>

<sup>1</sup>Hubei Collaborative Innovation Center for Advanced Organic Chemical Materials & Ministry-of-Education Key Laboratory for Synthesis and Applications of Organic Functional Molecules, Hubei University, Wuhan, P. R. China

<sup>2</sup>School of Electronic and information Engineering, Anshun University, P.R China

## Research Article

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### \*For Correspondence

Chuanqi Feng, Hubei Collaborative Innovation Center for Advanced Organic Chemical Materials & Ministry-of-Education Key Laboratory for Synthesis and Applications of Organic Functional Molecules, Hubei University, Wuhan, P. R. China, Tel:+86 27 88662747; Fax:+86 27 88663043.

**Email:** cfeng@hubu.edu.cn  
asxyzsy@163.com

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### ABSTRACT

Three dimensional (3D)  $\text{Bi}_2\text{WO}_6$  microspheres are successfully synthesized by the hydrothermal method using  $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$  and  $\text{NaWO}_4 \cdot 2\text{H}_2\text{O}$  as raw materials. The structure and morphology of the samples are characterized by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM). The results show that the  $\text{Bi}_2\text{WO}_6$  takes on morphology of microspheres. As a novel anode material for lithium-ion batteries (LIBs), the as-prepared  $\text{Bi}_2\text{WO}_6$  electrode exhibits both high reversible capacity and good cycling performance at room temperature under a potential window from 3.0 to 0.01 V (vs.  $\text{Li}^+/\text{Li}$ ) at current density of  $100 \text{ mA g}^{-1}$ . The  $\text{Bi}_2\text{WO}_6$  anode has initial discharge capacity as  $1218 \text{ mAh g}^{-1}$  and retained its reversible capacity at  $922 \text{ mAh g}^{-1}$  after 129 cycles. The  $\text{Bi}_2\text{WO}_6$  with morphology of microspheres is a promising anode material for the lithium-ion battery application.

## INTRODUCTION

In recent years, lithium ion batteries (LIBs) have conquered the market of portable electronics because of their advantages of long lifetime, high energy density, etc. [1-3]. However, commercial graphite-based anodes possess a low theoretical specific capacity ( $372 \text{ mAh g}^{-1}$ ) which can't meet the increasing requirements for higher energy density [4], thus limiting its range of applications. In addition, safety problems might occur when lithium ion batteries are charged-discharged at high rates [5]. Therefore, new anode materials should be developed.

Intensive researches have been conducted to search for new electrode materials with higher capacities than that of traditional materials in recent years, for instance,  $\text{CaWO}_4$  [6],  $\text{FeWO}_4$  [7],  $\text{ZnWO}_4$  [8],  $\text{LiFe}(\text{WO}_4)_2$  [9] and  $\text{Bi}_2\text{WO}_6$  [10] have been investigated as anode materials for LIBs. In near past years, Bi-W-O systems have also attracted a lot of interests because of the high theoretical capacity ( $670 \text{ mAh g}^{-1}$ ). Zhang et al. investigated  $\text{Bi}_2\text{WO}_6$  composite as anode material for lithium-ion batteries, and its reversible capacity was maintained as  $427.8 \text{ mAh g}^{-1}$  at current density of  $50 \text{ mA g}^{-1}$  [11]. Although Wu et al. synthesized  $\text{Bi}_2\text{WO}_6$  with nanoplate-built hierarchical nest-like structure, the electrochemical properties were not satisfied [12]. In our work, 3D- $\text{Bi}_2\text{WO}_6$  microspheres were synthesized by a facile hydrothermal method. Its electrochemical performances as an anode material were studied.

## EXPERIMENTAL

### Materials

The precursor of  $\text{Bi}_2\text{WO}_6$  microspheres was synthesized by a hydrothermal method using salts ( $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ ,  $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ ) as metal source and Polyvinylpyrrolidone (PVP) as the surfactant. All the reagents were analytical grade (A.R.) reagents and used without further purification. Deionized water was used in all experiments. In a typical synthesis process,  $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$  (2.5 mmol) and PVP (0.5 g) were dissolved in 40 mL distilled water under magnetic stirring to form a mixed solution.  $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$  (1.25 mmol) was slowly added into the mixed solution. After magnetic stirring for an hour, the mixed solution was transferred into a 50 mL teflon-lined stainless steel autoclave and annealed at  $180^\circ\text{C}$  for 24 h. The precursor was washed with distilled water and ethanol for several times, and dried under vacuum at  $60^\circ\text{C}$  for 12 h. The precursor was heated at  $400^\circ\text{C}$  in air for 3 hours to obtain expected sample.

### Characterization of the Samples

The crystal structure of the  $\text{Bi}_2\text{WO}_6$  was characterized by X-ray diffraction (XRD) using  $\text{Cu K}_\alpha$  radiation source (Bruker AXS, D8 diffractometer). The particle sizes of the samples were observed by scanning electron microscopy (SEM; JEOL JSM, 6510V). Energy dispersive spectroscopy (EDS) was performed to detect the contents of metallic elements for expected compounds. The valences of elements in samples were analyzed using an X-ray photoelectron spectrometer (XPS, Escalab 250Xi) with a multi-channel detector, which can withstand high photonic energies from 0.1 to 3 keV.

### Electrochemical Measurements

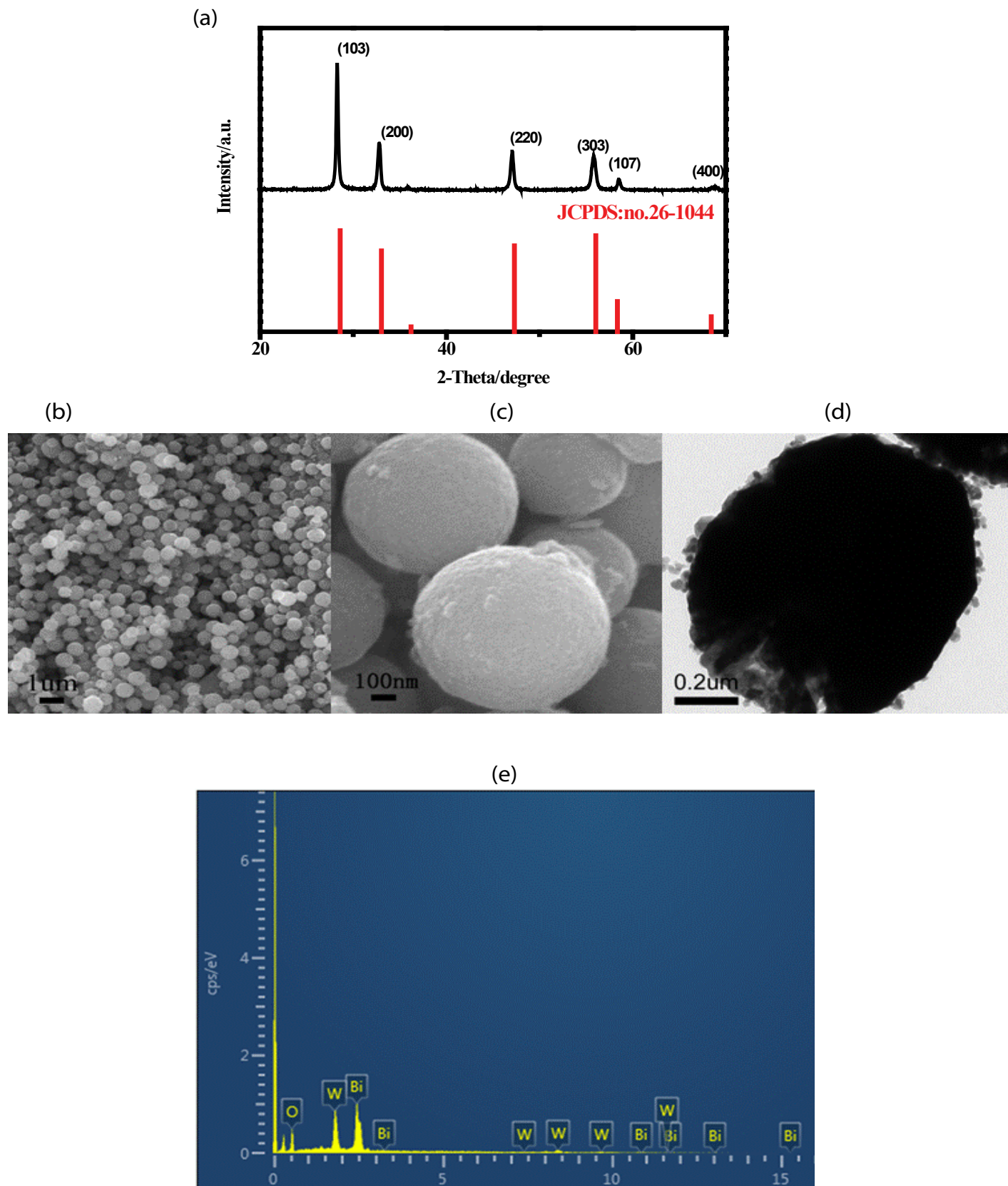
Charge/discharge tests were performed using CR2025 coin-type cells in an automatic battery tester system (Neware China). The working electrodes were made from a mixture of 60 wt.% as-prepared powders, 30 wt.% acetylene black and 10wt.% poly(vinylidene fluoride) (PVDF) binder. Prior to being used, the electrodes were dried at  $120^\circ\text{C}$  in a vacuum furnace for 24 hours. Lithium foil was used as the counter electrode, and the electrolyte was 1 M  $\text{LiPF}_6$  in a mixture of ethylene carbonate (EC) and dimethyl carbonate (DEC) (1:1, v/v). All test cells were assembled in an argon-filled glove box containing less than 1 ppm each of oxygen and moisture. The cells were discharged and charged at a constant current of  $100 \text{ mAg}^{-1}$  over a voltage range of 0.01~3.00 V (vs.  $\text{Li}^+/\text{Li}$ ) at room temperature. The typical masses of electrode materials used in the experiment were ranged from 5 to 8 mg. Electrochemical impedance spectroscopy (EIS) experiments and cyclic voltammetry (CV) experiments were conducted using a CHI 600E electrochemical workstation.

## RESULTS AND DISCUSSION

**Figure 1a** presents the XRD patterns of the  $\text{Bi}_2\text{WO}_6$  microstructures, in which the major diffraction peaks appeared at  $2\theta$  ( $28.586^\circ$ ,  $33.026^\circ$ ,  $47.305^\circ$ ,  $56.027^\circ$ ,  $58.355^\circ$  and  $68.423^\circ$ ) can be respectively correspond to the lattice planes (1 0 3), (2 0 0), (2 2 0), (3 0 3), (1 0 7) and (4 0 0) of a hexagonal  $\text{Bi}_2\text{WO}_6$  structure which belongs to a space group of  $P6/mmm$  (191) (JCPDS card No. is 26-1044,  $a = b = 5.48\text{\AA}$ ,  $c = 11.500\text{\AA}$ , and  $\alpha = \beta = 90^\circ$ ,  $\gamma = 120^\circ$ ). The  $\text{Bi}_2\text{WO}_6$  has high crystallinity. In addition, no characteristic peaks of the other impurities were observed, which indicated that pure phase of  $\text{Bi}_2\text{WO}_6$  was formed.

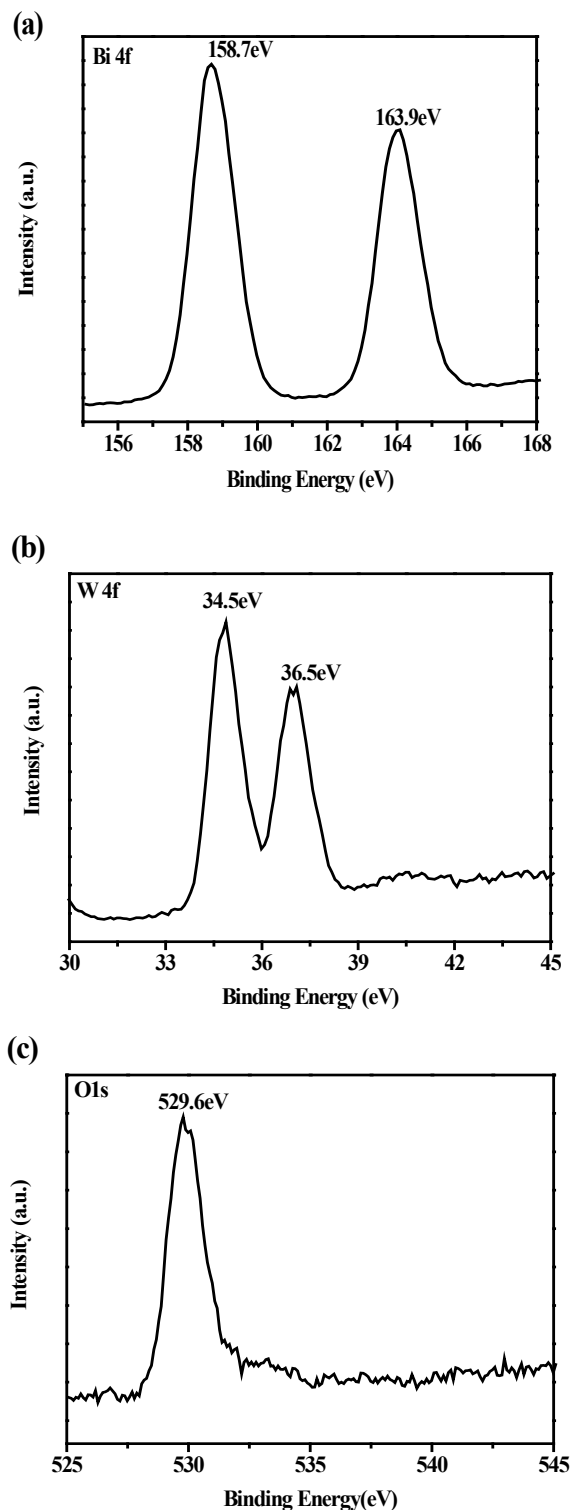
**Figure 1b and 1c** present the scanning electron microscope (SEM) images of the as-prepared  $\text{Bi}_2\text{WO}_6$  sample. **Figure 1b** is a typical low-magnification SEM image of the as-synthesized  $\text{Bi}_2\text{WO}_6$  sample, from which it can be seen that the aggregated particles have a sphere morphology with an average diameter of 700~800 nm. **Figure 1c** shows a typical surface image of the microspheres at a higher magnification, in which a smooth surface can be clearly observed.

Chemical analysis using Energy dispersive X-ray spectroscopy (EDS) indicates the presence of Bi, W, O (elements of  $\text{Bi}_2\text{WO}_6$  sample), and no other elements existed as observed in **Figure 1d**. It can be seen in **Figure 1e**, the composites contained the elements Bi, W at the molar ratio of  $\text{Bi} : \text{W} = 57.62:29.86$  (in At.%), thus, the molar ratio of Bi, W in BWO sample could be calculated to be 1.9:1, which basically agrees with the theoretical value of 2:1.



**Figure 1.** (a) XRD pattern, (b-d) SEM images and TEM images (e) EDS spectrum

The expected oxidation states of the elements in the Bi<sub>2</sub>WO<sub>6</sub> sample were further determined using X-ray photoelectron spectroscopy (XPS) spectra (**Figure 2**). The Bi 4f peaks of the sample appeared at ca. 163.5 eV and ca. 158.7 eV, which corresponded with Bi<sup>3+</sup> according to the previous results. The W 4f peaks of the sample appeared at 36.5 eV, 34.5 eV, indicating W<sup>6+</sup> in the sample, which was in agreement with the reported value in the literature [13]. The O 1s binding energy (**Figure 2c**) of 529.6 eV was in agreement with literature values of the bulk for Bi<sub>2</sub>WO<sub>6</sub>. Consequently, the as-synthesized product could be determined as pure orthorhombic Bi<sub>2</sub>WO<sub>6</sub> based on the results of XPS measurements.

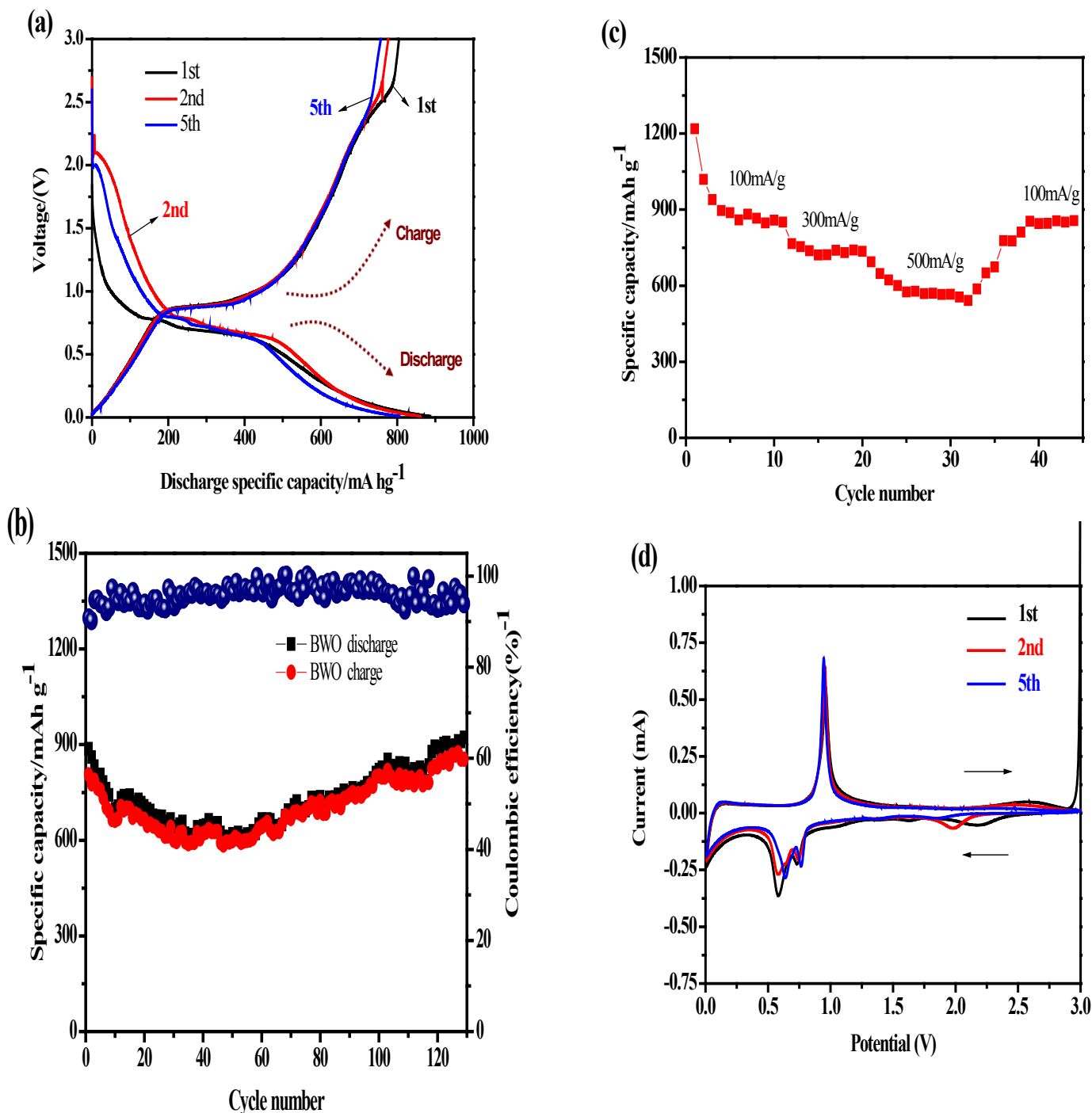


**Figure 2.** XPS high-resolution spectra of the (a) Bi 4f, (b) W 4f, and (c) O 1s regions of the as-synthesized  $\text{Bi}_2\text{WO}_6$

**Figure 3a** shows the charge/discharge profiles of  $\text{Bi}_2\text{WO}_6$  electrode at a current rate of  $100 \text{ mA g}^{-1}$  for the 1st, 2nd, and 5th cycles (0.01–3 V). The first Li-insertion and extraction capacity are as high as  $1218$  and  $805 \text{ mA g}^{-1}$ , respectively, with a coulombic efficiency of 66.1%. This can be attributed to the difficult dissolution of the SEI, as well as other factors, such as the intrinsic nature of the materials, kinetic limitations and cation deficient [14]. In addition, the discharge capacities of the  $\text{Bi}_2\text{WO}_6$  anode in the 2<sup>nd</sup>, 5<sup>th</sup> cycles are  $861$ ,  $806 \text{ mA h g}^{-1}$ , respectively; and the charge capacities of the anode in the 2<sup>nd</sup>, 5<sup>th</sup> cycles are  $805$ ,  $757 \text{ mA h g}^{-1}$ , respectively.

**Figure 3b** presents the cyclic stability and coulombic efficiency of the  $\text{Bi}_2\text{WO}_6$  electrode at a current density of  $100 \text{ mA g}^{-1}$ , and maintains a capacity as high as  $922 \text{ mA h g}^{-1}$  after 129 cycles. The capacity increasing phenomenon during cycle process has been found in many anode materials containing metal elements, while there is no accurate explanation for this phenomenon so far. Some authors ascribed this phenomenon to the reversible growth of a polymeric gel-like film resulting from kinetically

activated electrolyte degradation and the larger specific surface area obtained from fragmentation of the structure during the cycling process [15].



**Figure 3:** (a) Selected discharge and charge curves of the as-synthesized  $\text{Bi}_2\text{WO}_6$  electrode at a current density of  $100 \text{ mA g}^{-1}$ ; (b) cycling performance of the as-synthesized  $\text{Bi}_2\text{WO}_6$  electrode at a current density of  $100 \text{ mA g}^{-1}$ ; (c) rate capability of the as-synthesized  $\text{Bi}_2\text{WO}_6$  electrode at different current densities (100, 300, 500 and  $100 \text{ mA g}^{-1}$ ). The test potential window is between 0.01 and 3.0 V (vs.  $\text{Li}^+/\text{Li}$ ). (d) CV curves of  $\text{Bi}_2\text{WO}_6$  film electrodes at various scanning rates between 0.01V and 3V.

The rate capability of the  $\text{Bi}_2\text{WO}_6$  electrode at various charge-discharge rates is shown in **Figure 3c**. Typically, the discharge capacities of the  $\text{Bi}_2\text{WO}_6$  electrode at the currents densities of 100, 300 and  $500 \text{ mA g}^{-1}$  are 887, 763 and  $565 \text{ mAh g}^{-1}$ , respectively. Furthermore, it is worth to note that the capacity can also be restored to  $\sim 856 \text{ mAh g}^{-1}$  when the current density is returned to  $100 \text{ mA g}^{-1}$ .

The cyclic voltammograms of the three cycles for annealed  $\text{Bi}_2\text{WO}_6$  thin film over a potential range of 1.0–4.0 V are shown in **Figure 3d**. For the first discharge, the peak at about 2.2 V can be ascribed to the initially inserting of Li into BWO and the reduction of the Bi and W metals with the formation of  $\text{Li}_2\text{O}$ . The following two peaks between 0.5 and 1 V can be correspond to the two steps



of alloying processes between Li and Bi [16]. For the first charge process, one peak at about 0.9 V and other peak between 2 and 3 V correspond to the two steps oxidation processes of Bi and W.

During charge and discharge process, the reversible alloying processes lead  $\text{Bi}_2\text{WO}_6$  to behave excellent cycle ability, which can be seen from CV curves.

## CONCLUSION

In summary, a facile one-pot hydrothermal method combined the heat-treatment was used to synthesize the 3D- $\text{Bi}_2\text{WO}_6$  microspheres. As a novel anode material for the lithium ion battery, the as-prepared  $\text{Bi}_2\text{WO}_6$  electrode exhibits both high reversible capacity and good cycling performance at room temperature under a potential window from 3.0 to 0.01 V (vs.  $\text{Li}^+/\text{Li}$ ) at current density of  $100 \text{ mA g}^{-1}$ . The material ( $\text{Bi}_2\text{WO}_6$ ) is a promising and novel anode material for lithium ion battery applications. Besides, this work provides a new and simple approach to synthesize inorganic functional materials.

## ACKNOWLEDGMENTS

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