Investigation on surface metal vacancy electrochemistry

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ABSTRACT

In this work, BiOCl nanosheets with and without surface bismuth vacancy (V_{Bi}-BiOCl and BiOCl) are prepared by a simple hydrothermal method. The formation of surface bismuth vacancy is confirmed mainly by XPS, EPR, PL, and UV-DRS. It is found that although BiOCl has a higher BET area ($16\,m^2g^{-1}$) and a lower electrical resistance ($2.62\,\Omega$) than V_{Bi}-BiOCl ($4\,m^2g^{-1}$, $6.33\,\Omega$), the specific capacitance (23.6 mF cm^{-2}) of V_{Bi}-BiOCl is 3.4 times higher than that (6.9 mF cm^{-2}) of BiOCl at $0.5\,mA\,cm^{-2}$. However, the improved capacitance has been mainly attributed to the formation of surface bismuth vacancies, which could provide excess electrochemically adsorption sites for Na (I) ions. This finding is obviously different from conventional viewpoint that the available electrochemically active surface and electrical conductance are usually regarded as the crucial factors for the electrochemical performance. Hence, this work provides a new idea to develop excellent electrode materials.

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1. Introduction

Today, electrochemical energy storage technology has been widely studied to meet the increased energy demands. Supercapacitors have received considerable attention, since they can store more energies than conventional capacitors and have higher power densities than batteries [1–7]. However, the performances of supercapacitors are affected by available electrochemical-active surface and electrical conductance, or irreversible Faradic reactions of electrode [1–6]. Hence, it is still a big challenge to develop high-performance electrode materials. Layer materials, such as V_2O_5 [8], graphite [9], MoS_2 [10], and BiOX (Cl, Br, I) [1,11], *etc.*, are reported as the excellent electrode materials. For example, Ye et al. have also reported BiOX (Cl, Br) as anode materials for LIBs for the first time [1]; Chen et al. have reported that BiOI can be used as a novel high-energy anode material for lithium-ion batteries [11]. In addition, BiOX (Cl, Br, I) have been widely reported as efficient photocatalysts photocatalysis field due to the open layer structure [1,12]. Thus, we could expect that such an open layer structure may favour for the charge storage. However, the supercapacitive properties of BiOX has reported scarcely. It is well known that the surface defect has been widely reported in photocatalysis field [13–16]. In the previous study [17], we have also found that BiOCl with surface bismuth vacancy has a greatly higher photocatalytic activity than BiOCl without surface bismuth vacancy. Generally, the available electrochemically active surface and electrical conductance have the crucial influences on the electrochemical properties [18–23]. The present question is whether surface defect can affect the electrochemical properties or not. Hence, it is desirable to reveal the correlation of electrochemical properties with surface defect for the development of excellent supercapacitor materials.

In this work, BiOCl nanosheets with and without surface bismuth vacancy (V_{Bi}-BiOCl and BiOCl) were prepared by a simple hydrothermal method. The correlation of electrochemical properties with surface bismuth vacancy is mainly revealed. It is found that the specific capacitance of V_{Bi}-BiOCl is 3.4 times higher than that of BiOCl at $0.5\,mA\,cm^{-2}$, although the latter has a higher BET area ($16\,m^2g^{-1}$) and a lower electrical resistance ($2.62\,\Omega$) than the former ($4\,m^2g^{-1}$, $6.33\,\Omega$). This finding is obviously distinct from the conventional viewpoint that the electrochemical properties are mainly affected by the available electrochemically active surface and electrical conductance [18–23]. This work provides a new idea to develop excellent supercapacitors materials.

2. Experiment section

2.1. Sample preparation

2.1.1. Synthesis of VBi-BiOCl

The BiOCl nanosheets with surface bismuth vacancy (V_{Bi}-BiOCl) were prepared according to our previous report [17]. Typically,

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0.5 mmol Bi_2O_3 and 8 mmol NH_4Cl were mixed together, then 20 mL of H_2O_2 was added. The resulting precursor suspension was magnetically stirred for 30 min, and then transferred into 50-mL Teflon-lined stainless steel autoclave to maintain at 180 °C for 12 h. After reaction, the autoclave was cooled to room temperature naturally. The resulting precipitate was centrifuged and washed with ethanol and distilled water three times, and then dried at 60 °C for 3 h.

2.1.2. Synthesis of BiOCl

The BiOCl nanosheets without surface bismuth vacancy (BiOCl) were prepared according to previously reported method [24]. In detail, 1.5 mmol of $Bi(NO_3)_3 \cdot 5H_2O$ was dissolved in 30 mL of ethylene glycol (EG) under stirring at room temperature. After the $Bi(NO_3)_3 \cdot 5H_2O$ was completely dissolved, 10 mmol of NaCl was added to the above solution. After stirring for 30 min, the solution was transferred into a 50-mL Teflonlined stainless steel autoclave, and then maintained at 170 °C for 6 h. After reaction, the autoclave was cooled to room temperature naturally. The sample was obtained with the same procedures as above.

2.2. Characterization

The crystal structures of the samples were determined by X-ray powder polycrystalline diffractometer (Rigaku D/max-2550VB), using graphite monochromatized Cu K_α radiation ($\lambda = 0.154$ nm), operating at 40 kV and 50 mA. The XRD patterns were obtained in the range of 20–80° (2θ) at a scanning rate of 7 ° min^{-1}. The morphologies of samples were characterized on a scanning electron microscope (SEM, Hitachi SU-1510) with an acceleration voltage of 15 keV. The samples were coated with 5-nm-thick gold layer before observations. The fine surface structures of the samples were determined by high-resolution transmission electron microscopy (HRTEM, JEOL JEM-2100F) with an acceleration voltage of 200 kV. Nitrogen sorption isotherms were performed at 77 K and $< 10^{-4}$ bar on a Micromeritics ASAP2010 gas adsorption analyzer. Each sample was degassed at 150 °C for 5 h before measurements. Surface area was calculated by the Brunauer-Emmett-Teller (BET) method. Fourier transform infrared spectra (FT-IR) were recorded on a Fourier transform infrared spectra (FT-IR, KBr disk method; Thermo Scientific Nicolet iS5) at the wavenumbers of 400–4000 cm^{-1}. X-ray photoelectron spectroscopy (XPS) measurements were done on a VG ESCALAB MKII XPS system with Mg K_α source and a charge neutralizer. All the binding energies were referenced to the C1s peak at 284.8 eV of the surface adventitious carbon. The photoluminescence (PL) spectra were detected by F-7000 FL Spectrophotometer (HITACHI) with the excitation wavelength of 325 nm at room temperature. The electron paramagnetic resonance (EPR) spectra were collected using a Bruker ESP 500 spectrometer at 90 K. UV–vis diffused reflectance spectra (UV-DRS) of the samples were obtained using a UV–vis spectrophotometer (UV-2550, Shimadzu, Japan). $BaSO_4$ was used as a reflectance standard in a UV–vis diffuse reflectance experiment.

2.3. Electrochemical measurements

All the electrochemical measurements were carried out on a CHI 660D electrochemical Working Station at room temperature. For a standard three-electrode cell, a 0.5 M Na_2SO_4 aqueous solution was used as the electrolyte. Carbon fibers was used as the current collector of working electrode (with an area of 0.25 cm^2), Pt wire (diameter: 0.1 cm, length: 4 cm) and Hg/HgO (S.C.E) electrodes were used as the counter and reference electrodes. To fabricate the working electrode, 80 wt% of active materials, 10 wt% of acetylene black (conducting agent) and 10 wt of polyvinylidene fluoride (binder) were dispersed in 1-methyl-2-pyrrolidinone to form homogeneous slurry. Then the slurry was dotted on the carbon fibers and dried for 24 h at room temperature. The mass of active material (V_{Bi}-BiOCl or BiOCl) on the carbon fibres is 2 mg. Cyclic voltammetry (CV) and chronopotentiometry (CP) were conducted in a potential range of 0-0.8 V and 0–1 V (vs. S.C.E), respectively. Electrochemical impedance spectroscopy (EIS) was performed from 1 Hz to 1000 KHz at an open circuit potential and an alternating current (AC) voltage amplitude of 5 mV. Areal and specific capacitances were calculated using the following Equations (1) and (2), respectively.

$$C_a = I \cdot t / (\Delta V \cdot S) \tag{1}$$

$$C_{sp} = I \cdot t / (\Delta V \cdot m) \tag{2}$$

where I is the constant discharge current, t is the discharging time, ΔV is the voltage drop upon discharging (excluding the IR drop), m is the mass of the active material, and S is the geometrical area of the electrode.

3. Results and discussion

3.1. Characterization of V_{Bi}-BiOCl and BiOCl

The X-ray diffraction patterns (XRD) of the samples are shown in Fig. 1a. All the diffraction peaks of both samples are well indexed to the tetragonal phase of BiOCl with the cell constants of $a = b = 3.891$ Å, $c = 7.369$ Å (JCPDS No. 06-0249). No other impurities peaks are detected, indicating the formation of phase-pure BiOCl. The Fourier transform infrared (FT-IR) spectra show the characteristic absorption peaks of these two samples (Fig. S1, seeing supporting information (SI)). The bands at 1623 cm^{-1} can be considered as bending vibration of O-H from the adsorbed water molecules [25]. The bands at 1043 cm^{-1} stem from C-O-C bonds, which originates from the ethylene glycol molecules on the sample surface [26]. The absorption bands at 1400 cm^{-1} could be assigned to the asymmetry and symmetric stretching vibrations of Bi-Cl bond, while the absorption bands at 522 cm^{-1} are assigned to the Bi-O stretching vibrations [25]. No significant change in FT-IR spectra can be found for both samples, indicating that the crystal structure does not change, which is in good agreement with the XRD results. Fig. 2 shows the scanning electron microscopy (SEM) and high-resolution transmission electron microscopy (HRTEM) images of both samples. The BiOCl sample is composed of the microspheres, which are assembled by the nanosheets (Fig. 2a).
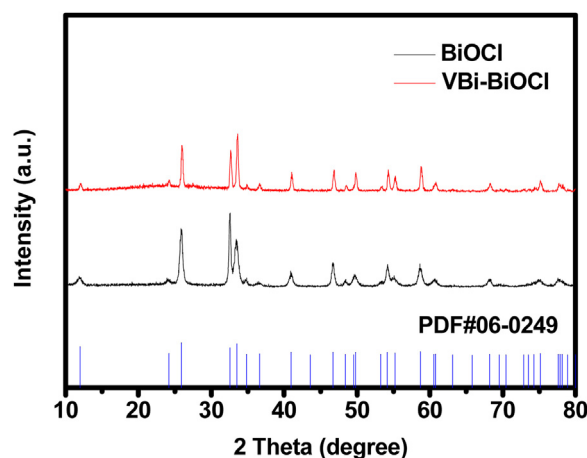

Fig. 1. X-ray diffraction (XRD) patterns.