Supplementary Materials

Facile Synthesis of Bismuth Oxide/Bismuth Vanadate Heterostructures for Efficient Photoelectrochemical Water Splitting

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Experimental

Photocatalysts preparation

The fabrication process of Bi2O3/BiVO4 heterostructures involves two processes, as shown in Figure 1. Firstly, the Bi nanobelts were grown on a FTO substrate by a template-free electrochemical deposition. In general, a piece of FTO (around 2.0 cm²) served as the working electrode, a Pt electrode as the counter electrode and an Ag/AgCl electrode as the reference electrode. Cathodic electrodeposition was performed at a constant current of 2 mA cm⁻² at 60 °C in solutions containing 0.005 mol L⁻¹ Bi(NO₃)₃, 0.05 mol L⁻¹ ethylenediamine tetraacetic acid disodium (Na₂EDTA) and 0.1 mol L⁻¹ sucrose. The second step was the conversion of Bi to Bi₂O₃/
BiVO₄ heterostructures, which was achieved by impregnating Bi electrodes in the solution of 0.1 mol L⁻¹ NH₄VO₃ for 3 h, 6 h, and 12 h, followed by annealing in air at 550 °C for 6 h to prepare Bi₂O₃/BiVO₄ heterostructures and pure BiVO₄. At last, the annealed electrodes were soaked into 1 mol L⁻¹ KOH for 1 h to remove the excess V₂O₅. On the other hand, Bi electrodes were annealed in air at 550 °C without impregnating. In comparison, pure Bi₂O₃ was also synthesis by directly calcined the as-prepared Bi nanobelts in air.

In the presence of the air, the Bi and NH₄VO₃ can reacted with the oxygen under heating conditions:

\[
2\text{Bi} + 2\text{NH}_4\text{VO}_3 + \text{O}_2 \rightarrow 2\text{BiVO}_4 + 2\text{NH}_3 + \text{H}_2\text{O}
\]

\[
2\text{Bi} + 3\text{O}_2 \rightarrow 2\text{Bi}_2\text{O}_3
\]

The product can be controlled by controlled the amount of NH₄VO₃ with different immersion times in the NH₄VO₃ solution.

**Characterizations and measurements**

The morphology, phase and composition of the as-synthesized products were characterized by field emission scanning electron microscope (FE-SEM, JSM-6330F), X-Ray Diffractometer (XRD, D8 ADVANCE), transmission electron microscopy (TEM, JEM2010-HR, FEI Tecnai G² F30), X-ray Photoelectron Spectroscopy (XPS, ESCALab250) and Raman spectroscopy (Renishaw inVia). The optical properties of the products were measured with UV-Vis-NIR Spectrophotometer (UV-Vis-NIR, Shimadzu UV-2450).

PEC measurements were carried out in a three-electrode cell with a flat quartz window to facilitate illumination of the photoelectrode surface in 0.1 mol L⁻¹ Na₂SO₄ solution. The working electrode is the as-synthesized products, while Pt electrode and Ag/AgCl electrode were used as
counter and reference electrode, respectively. The illumination source was a 300 W Xe arc lamp (PLS-SXE-300/300UV, Beijing Trusttech Co. Ltd.) directed at the quartz photoelectrochemical cell. The intensity of the light is about 100 mW/cm². The current densities were recorded with CHI 760D electrochemical workstation (CHI, Shanghai).

Incident-photon-to-current-conversion-efficiency (IPCE) measurements were conducted with a solar simulator (Newport 69911 300 W xenon lamp), coupled to an aligned monochromator (Oriel Cornerstone 260 1/4m). IPCE can be expressed as:

$$\text{IPCE} = \frac{(1240I)}{\lambda J_{\text{light}}}$$

Where $I$ is the measured photocurrent density at a specific wavelength, $\lambda$ is the wavelength of incident light, and $J_{\text{light}}$ is the measured irradiance at a specific wavelength. The carrier density was calculated by the following Mott-Schottky equation:

$$N_d = \frac{(2/e_0\varepsilon\varepsilon_0)}{d(1/C^2)/dV}^{-1}$$

where $e_0$ is the electron charge, $\varepsilon$ the dielectric constant of BiVO$_4$ ($\varepsilon =$ ~86) [20], $\varepsilon_0$ the permittivity of vacuum, $N_d$ the dopant density and $V$ the electrode applied potential.

![SEM of Bi$_2$O$_3$/BiVO$_4$ heterostructures.](image)

**Figure S1.** SEM of Bi$_2$O$_3$/BiVO$_4$ heterostructures.
Figure S2. SEM of pure BiVO$_4$.

Figure S3. SEM images of pure Bi$_2$O$_3$. 
Figure S4. XRD patterns of Bi, Bi$_2$O$_3$, BiVO$_4$ and Bi$_2$O$_3$/BiVO$_4$.

Figure S5. High-resolution Bi$_{4f}$ XPS spectra of pristine Bi. The peaks located at 157.1 and 162.5 eV are consistent with the characteristic Bi 4f/7/2 and Bi 4f/5/2 of metallic Bi peaks. The coarse of the Bi core level XPS spectrum is because the intensity of C 1s peak is too strong since the carbon is used as the reference in XPS measurements.

Figure S6. i-E curves of p-type Bi$_2$O$_3$. 

Figure S7. Absorption spectra of Bi$_2$O$_3$, Bi$_2$O$_3$/BiVO$_4$, and BiVO$_4$. 

(Abs.)$^{1/2}$/hv$^{1/2}$ (eV)$^{1/2}$ versus Photon energy (eV).
Figure S7. Plots of \((\alpha h\nu)^2\) versus the photon energy \((h\nu)\) of the Bi\(_2\)O\(_3\), Bi\(_2\)O\(_3\)/BiVO\(_4\) and BiVO\(_4\).

Figure S8. XPS valence band spectra of the Bi\(_2\)O\(_3\), Bi\(_2\)O\(_3\)/BiVO\(_4\) and BiVO\(_4\).

Figure S9. Mott-Schottky curves of p-type Bi\(_2\)O\(_3\).