Electronic Support Information for

Novel hierarchical Sn₃O₄/BiOX (X=Cl, Br, I) p-n heterostructures with enhanced photocatalytic activity under simulated solar light irradiation

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Photoelectrochemical characterization

0.5M Na₂SO₄ aqueous solution was used as the electrolyte and indium-tin oxide (ITO) glass was chosen as the working electrode. 0.045 g photocatalyst and 0.005 g polymer binder (polyvinylidene difluoride) were dispersed in 1.0 mL of ethanol under sonication for 1 h to produce slurry. The as-prepared slurry was spread onto the conductive surface of the ITO glass to form a photocatalyst film with an area of 0.5×0.5 cm². For Mott-Schottky plots, the electrochemical impedance spectroscopy data were collected on an electrochemical workstation (CHI 760E Chenhua Instrument Company, Shanghai, China) using a conventional three-electrode cell system with Pt plate as counter electrode, saturated calomel electrode (SCE) as reference. Mott–Schottky (impedance) plots were obtained at a frequency of 1 kHz in the dark with an AC amplitude of 5 mV. The flat band potential (Vfb) was determined by equation (1):

\[
\frac{1}{C^2} = \frac{2}{\varepsilon_0 \varepsilon_r N_A} (V - V_{fb} - \frac{k_B T}{e}) \tag{1}
\]

here \(N_A\) is the carrier density, \(\varepsilon_0\) is the permittivity in a vacuum, \(\varepsilon_r\) is the relative permittivity, \(V\) is the applied potential, \(T\) is the absolute temperature, \(e\) corresponds to the electronic charge, and \(k_B\) is the Boltzmann constant. Therefore, a plot of \(1/C^2\) against \(V\) should yield a straight line from which \(V_{fb}\) can be determined from the intercept on the \(V\) axis. The measured potentials versus the Hg/Hg₂Cl₂ reference electrode were converted to the reversible hydrogen electrode (RHE) scale via the Nernst equation (2):

\[
E_{RHE} = E_{Hg/Hg_2Cl_2} + E^{0}_{Hg/Hg_2Cl_2} + 0.059pH, \quad E^{0}_{Hg/Hg_2Cl_2} = 0.2412 \text{ at } 25^\circ C \tag{2}
\]

where \(E_{RHE}\) is the converted potential vs. RHE, \(E^{0}_{Hg/Hg_2Cl_2}\) is the experimental potential measured against the Hg/Hg₂Cl₂ reference electrode, and \(E^{0}_{Hg/Hg_2Cl_2}\) is the standard potential of saturated Hg/Hg₂Cl₂ at 25 °C (0.2412 V).
Fig. S1. (a) XRD patterns, (b) Raman spectra, (c) UV-visible diffuse reflectance spectra and (d) plots of \(F(R)hv^{1/2}\) versus photo energy of Sn\(_3\)O\(_4\), BiOI, BiOBr and BiOCl.

As comparison, the corresponding analyses of each single component (Sn\(_3\)O\(_4\), BiOI, BiOBr and BiOCl) were presented in Fig. S1. Standard positions of diffraction peaks taken from the JCPDS card No. 16-0737 for Sn\(_3\)O\(_4\), JCPDS card No. 73-2062 for BiOI, JCPDS card No. 85-0862 for BiOBr and JCPDS card No.85-0861 for BiOCl were shown as denoted.

Fig. S2. SEM, TEM and HRTEM images of the pure BiOI (a-c), BiOBr (d-f), BiOCl (g-i) and Sn\(_3\)O\(_4\).
Fig. S3. Mott–Schottky (MS) plots of as-prepared Sn$_3$O$_4$ (a), BiOI (b), BiOBr (c), BiOCl (d), Sn$_3$O$_4$/BiOI (e), Sn$_3$O$_4$/BiOBr (f), Sn$_3$O$_4$/BiOCl (g), Sn$_3$O$_4$/BiOCl-$1/2$ (h), Sn$_3$O$_4$/BiOCl-$1/8$ (i) composites.

References