Electronic Support Information for

Novel hierarchical Sn_3O_4/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 Na_2SO_4 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 cm^2. 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 (V_{fb}) was determined by equation (1):

$$\frac{1}{C^2} = \frac{2}{\varepsilon_0 \varepsilon_r e N_A}\left(V - V_{fb} - \frac{k_B T}{e}\right) \qquad (1)$$

here N_A is the carrier density, ε_0 is the permittivity in a vacuum, ε_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/Hg_2Cl_2 reference electrode were converted to the reversible hydrogen electrode (RHE) scale via the Nernst equation (2)[1]:

$$E_{\mathrm{RHE}} = E_{\mathrm{Hg/Hg_2Cl_2}} + E^0_{\mathrm{Hg/Hg_2Cl_2}} + 0.059\mathrm{pH},\ E^0_{\mathrm{Hg/Hg_2Cl_2}} = 0.2412 \text{ at } 25\ ^\circ\mathrm{C} \qquad (2)$$

where E_{RHE} is the converted potential vs. RHE, $E_{\mathrm{Hg/Hg_2Cl_2}}$ is the experimental potential measured against the Hg/Hg_2Cl_2 reference electrode, and $E^0_{\mathrm{Hg/Hg_2Cl_2}}$ is the standard potential of saturated Hg/Hg_2Cl_2 at 25 °C (0.2412 V).

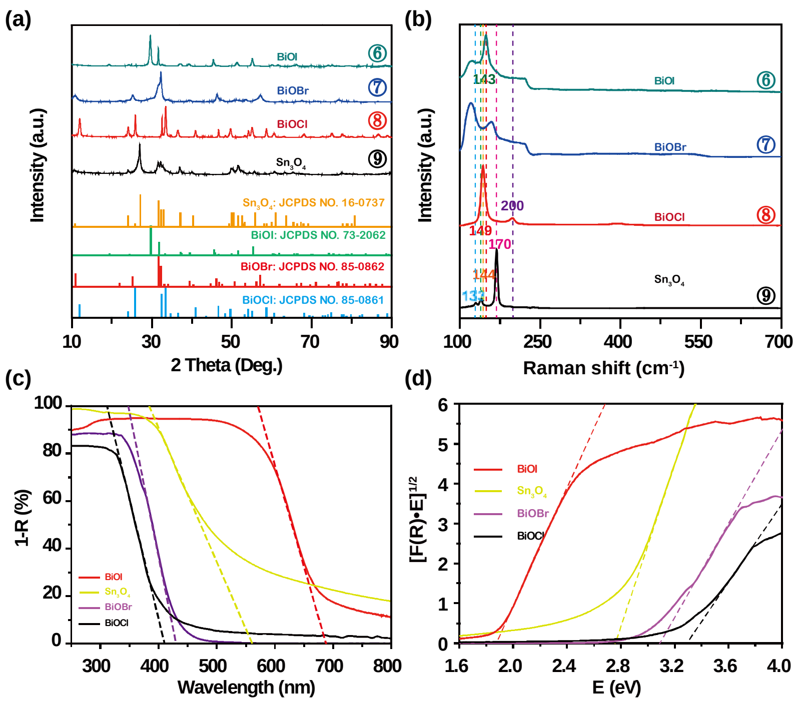

Fig. S1. (a) XRD patterns, (b) Raman spectra, (c) UV-visible diffuse reflectance spectra and (d) plots of $(F(R)hv)^{1/2}$ versus photo energy of Sn_3O_4, BiOI, BiOBr and BiOCl.

As comparison, the corresponding analyzations of each single component (Sn_3O_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_3O_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.

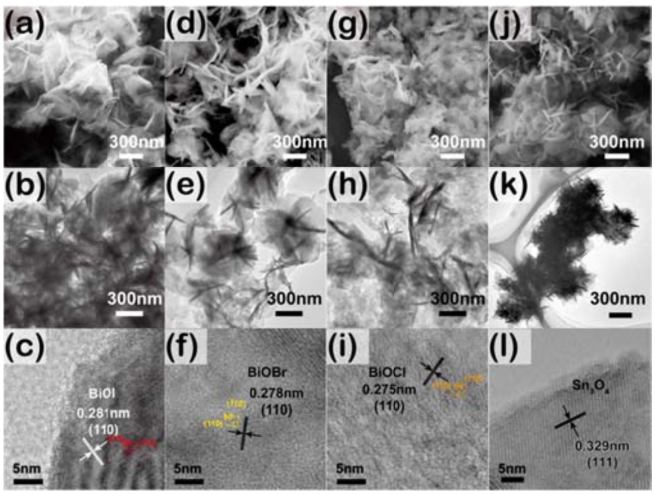

Fig. S2. SEM, TEM and HRTEM images of the pure BiOI (a-c), BiOBr (d-f), BiOCl (g-i) and Sn_3O_4.

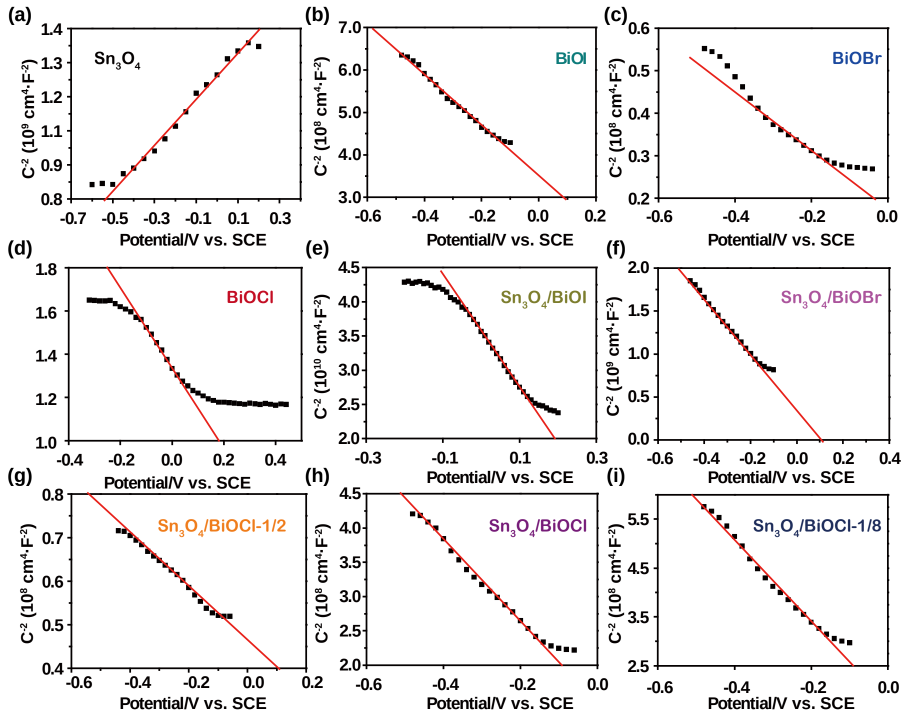

Fig. S3. Mott–Schottky (MS) plots of as-prepared Sn_3O_4 (a), BiOI (b), BiOBr (c), BiOCl (d), Sn_3O_4/BiOI (e), Sn_3O_4/BiOBr (f), Sn_3O_4/BiOCl-1/2 (g), Sn_3O_4/BiOCl (h) and Sn_3O_4/BiOCl-1/8 (i) composites

References

1. S. Hoang, S. Guo, N. T. Hahn, A. J. Bard and C. B. Mullins, *Nano Lett.*, 2011, **12**, 26-32.