Supplementary Information for

Interlayer-I-doped $BiOIO_3$ nanoplates with optimized electronic structure for efficient visible light photocatalysis

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Experimental

1.1 Materials and synthesis

All chemicals used in this study were analytical grade and were used without further purification. In a typical synthesis, $BiOIO_3$ were obtained as follows. 0.485 g of $Bi(NO_3)_3·5H_2O$ was added to the 70 mL of H_2O and stirred vigorously for 30 min. Then 0.214 g of KIO_3 was added into the above mixture and continuously stirred for 10 min. The resulting aqueous suspension was then hydrothermally treated at 150 ^{o}C for 6 h. The products were recovered by filtration, rinsed by deionized water and ethanol for three times, and then dried at 60 ^{o}C for 12 h. The as-prepared sample was denoted as $BiOIO_3$.

Interlayer-I-doped $BiOIO_3$ were synthesized by a simple chemical solution method. A certain quantity of $BiOIO_3$ was added into 100 mL of H_2O, and the suspension was stirred for 30 min. Then, 30 mL aqueous solution containing KI was added into the above suspension. The obtained yellow suspension was continuously stirred for 2 h and aged for 1 h. Depending on the dosages of $BiOIO_3$ and KI, different products can be synthesized.

Table 1: Dosage of $BiOIO_3$ and KI for the preparation of Interlayer-I-doped $BiOIO_3$.

Samples	6:1	3:1	1:1	1:3	0:1
$BiOIO_3$ dosage	0.560 g	0.640 g	0.960 g	1.920 g	0.480 g
KI dosage	0.033 g	0.066 g	0.199 g	0.598 g	0.199 g

1.2 Characterization

The crystal phases of the sample were analyzed by X-ray diffraction (XRD) with Cu Kα radiation (model D/max RA, Rigaku Co., Japan). X-ray photoelectron spectroscopy (XPS) with Al Kα X-rays (hm = 1486.6 eV) radiation (Thermo ESCALAB 250, USA) was used to investigate the surface properties. Scanning electron microscopy (SEM, model JSM-6490, JEOL, Japan) and transmission electron microscopy (TEM: JEM-2010, Japan) were used to characterize the morphology of the obtained products. The UV−vis diffuse reflectance spectrometry (DRS) spectra were obtained for the dry-pressed disk samples using a Scan UV−vis spectrophotometer (TU-1901, China) equipped with an integrating sphere assembly, using $BaSO_4$ as the reflectance sample. Nitrogen adsorption−desorption isotherms were obtained on a nitrogen adsorption apparatus (ASAP 2020, USA). All of the samples were degassed at 120 °C prior to measurements. The photocurrent response and electrochemical impedance spectra measurements were performed in three-electrode quartz cells with a 0.1 M Na_2SO_4 electrolyte solution. Platinum wire was used as the counter electrode, and saturated calomel electrodes were used as the reference electrodes. The as-prepared samples film electrodes on ITO served as the working electrode. The photoelectrochemical experiment results were recorded using an electrochemical system (CHI-660B, China). All the photoelectrochemical measurements are performed under visible light of a 500 W Xe lamp coupling with 420 nm cutoff filters, and the average light power is 45 mW/cm^2.

1.3 Density Functional Theoretical (DFT) Calculations.

DFT calculations were carried out using the "Vienna *ab initio* simulation package" (VASP5.3).[1] The Perdew–Burke–Ernzerhof (PBE) exchange-correlation functional was used within the spin polarized generalized gradient approximation (GGA).[2] A plane-wave basis set was employed within the framework of the projector augmented-wave (PAW) method.[3] To get accurate results, the cut-off energy was set to 450 eV. Geometry relaxations were carried out until the residual forces on each ion converged to being smaller than 0.02 eV/Å. A 1× 1 × 2 supercell of $BiOIO_3$ was built as the simulation model. We relaxed the $BiOIO_3$ to obtain an optimal structure. Then, based on the relaxed $BiOIO_3$ structure, we constructed Interlayer-I-doped $BiOIO_3$ model by putting a I atom in the $BiOIO_3$ interlayer. The electronic structures of $BiOIO_3$ and I-intercalated $BiOIO_3$ were calculated based on the fully relaxed lattice parameters and ionic positions. For the calculation of the density of states (DOS), Monkhorst-Pack *k*-points were set to be 4×2×2.

1.4 Evaluation of photocatalytic activity

The photocatalytic activity was tested by the removal of NO at ppb levels in a continuous flow reactor at ambient temperature. The volume of the rectangular reactor, made of stainless steel and covered with Saint-Glass, was 4.5 L (30 cm × 15 cm × 10 cm). For the UV light (360 nm) activity test, a UV lamp (6 W) was vertically placed outside the reactor. For the visible light photocatalytic activity test, a 150 W commercial tungsten halogen lamp was used, and a UV cut off filter (420 nm) was adopted to remove UV light in the light beam. 0.20 g of the as-prepared sample was dispersed in distilled water (60 mL) in a beaker via ultrasonic treatment for 10 min and then coated onto two glass dishes (12.0 cm in diameter). These dishes were then pretreated at 60 ^{o}C to remove the water in the suspension and cooled to room temperature before the photocatalytic test.

The NO gas was acquired from a compressed gas cylinder at a concentration of 100 ppm of NO (N_2 balance). The initial concentration of NO was diluted to about 660 ppb by the air stream supplied by compressed standard air. The relative humidity in the present system is controlled at 50 % to simulate the indoor environmental conditions by passing the zero air streams through a humidifier in the gas flow. The gas streams were premixed completely by a gas blender, and the flow rate of the air stream and NO were controlled at 2.4 $L \cdot min^{-1}$ and 15 $mL \cdot min^{-1}$, respectively, by a mass flow controller. After the adsorption–desorption equilibrium was achieved in the dark, the lamp was turned on. The concentration of NO was continuously measured by a chemiluminescence NO analyzer (model 42i-TL, Thermo Environmental Instruments Inc), which monitors NO, NO_2, and NOx (NOx represents NO + NO_2) with a sampling rate of 0.7 L/min. The removal ratio (η) of NO was calculated as η (%) = $(1 - C/C_0) \times 100\%$, where C and C_0 are concentrations of NO in the outlet and feeding stream, respectively.

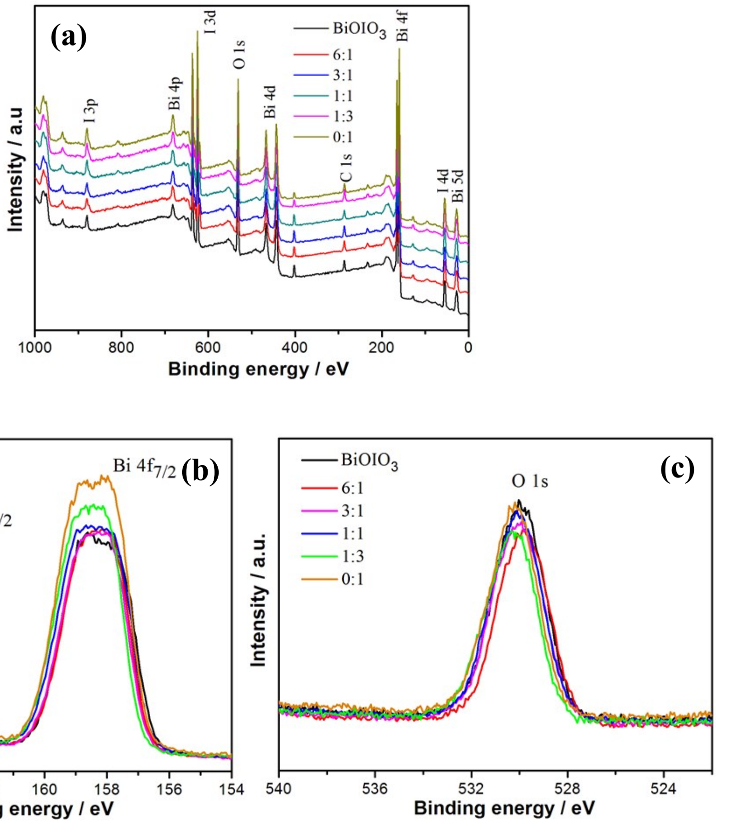

Fig. S1 Survey XPS spectra (a), Bi 4f (b) and O 1s (c) of the as-prepared samples.

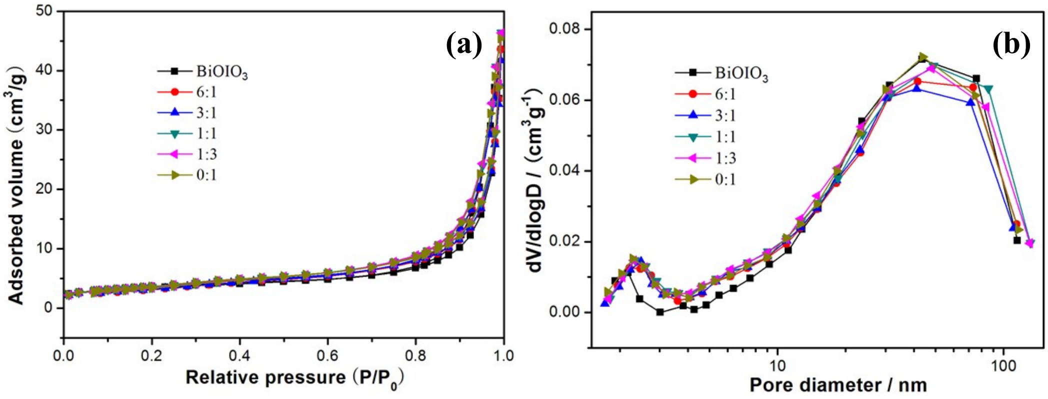

Fig. S2 Nitrogen adsorption–desorption isotherms (a) and the corresponding pore diameter distribution curves (b) of the as-prepared samples.

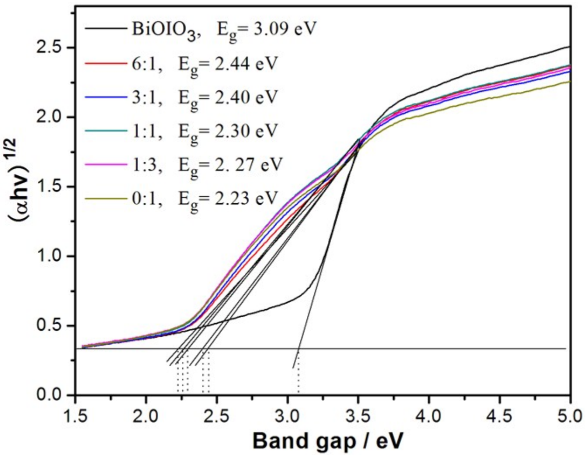

Fig. S3 The plot of $(\alpha h\nu)^{1/2}$ vs.photon energy (b) of the obtained samples.

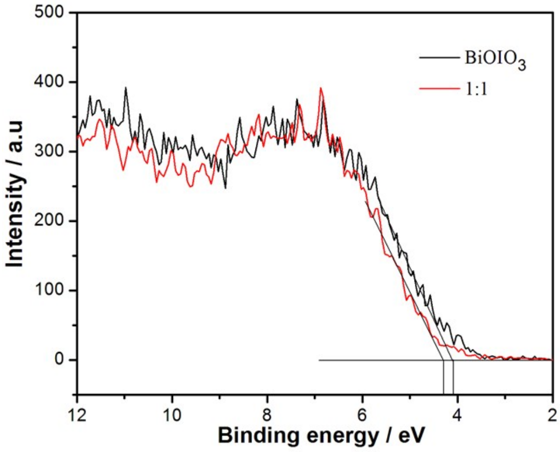

Fig. S4 VB XPS of the as-prepared $BiOIO_3$ and I-intercalated $BiOIO_3$ sample (1:1).

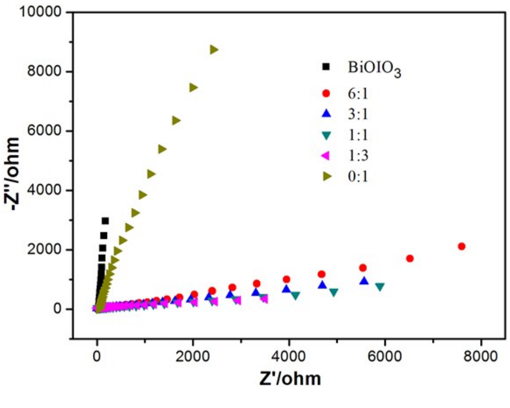

Fig. S5 Electrochemical impedance spectroscopy of the as-prepared samples in 0.1 M Na_2SO_4 aqueous solution.

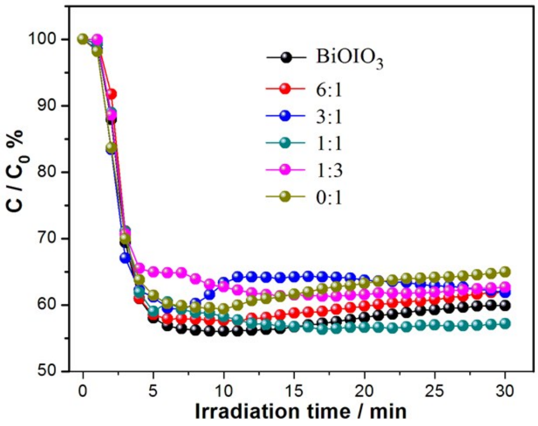

Fig. S6 UV light (360 nm) photocatalytic activities of the as-prepared products.

References

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