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Supplementary Information for

Enhanced extrinsic absorption promotes the visible light photocatalytic activity of wide band-gap $(BiO)_2CO_3$ hierarchical structure

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- Experimental Section

1.1 Synthesis of $(BiO)_2CO_3$ microspheres and $(BiO)_2CO_3$ nanoparticles

All chemicals used in this study were analytical grade (Sigma-Aldrich). Distilled water was used in all experiments. In a typical synthesis, 1.60 g of bismuth citrate and certain amount of sodium carbonate were mixed with 75 mL of water in a 100 mL autoclave Teflon vessel and stirred for 30 min. The resulting aqueous precursor suspension was then hydrothermally treated at 180 °C for 24 h. The precipitates obtained was filtered, washed with water and ethanol for three times and dried at 60 °C for 12 h to get final $(BiO)_2CO_3$ with no further treatment. Depending on the dosage of sodium carbonate (0.46 g and 0.92 g), the resultant $(BiO)_2CO_3$ materials with different structures (microspheres and nanoparticles) were labelled as BOC-R3 and BOC-R6, respectively.

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 operated at 150 W (Thermo ESCALAB 250, USA) was used to investigate the surface properties. Scanning electron microscopy (SEM; model JSM-6490, JEOL, Japan) was used to characterize the morphology of the obtained products. The morphology and structure of the samples were examined by transmission electron microscopy (TEM; JEM-2010, Japan). Fourier transform infrared (FTIR) spectra were recorded on a Nicolet Nexus spectrometer on samples embedded in KBr pellets. 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 100% $BaSO_4$ as the reflectance sample. The photoluminescence spectra (PL) for the samples were obtained using a fluorescence spectrophotometer (FS-2500, Japan) with an Xe lamp with optical filter as the excitation source. Nitrogen adsorption–desorption isotherms were obtained on a nitrogen adsorption apparatus (ASAP 2020, USA). All the samples were degassed at 150 ^{o}C prior to measurements. All photoelectrochemical measurements were conducted in a three electrode system on a CH 660D electrochemical work station, using the FTO glass with $(BiO)_2CO_3$ films as the working electrode, saturated calomel electrode as the reference electrode, and Pt wire as the counter electrode. All potentials are quoted with respect to saturated calomel electrode. For photoelectrochemical tests, the working electrode was irradiated from the $(BiO)_2CO_3$ films (250 mg of as-prepared $(BiO)_2CO_3$ samples were suspended in 0.5 mL of DMF, which was then dip coated on a 10 mm × 10 mm FTO glass electrode. The electrode was then annealed at 170°C for 2h) side under a 290W halogen lamp. Incident visible-light was obtained by utilizing a 420 nm cut-off filter. The photocurrent-time dependence of $(BiO)_2CO_3$ samples at open circuit potential was measured in 0.5 M Na_2SO_4 under chopped illumination with 60s light on/off cycles. The sample for ESR measurement was prepared by mixing $(BiO)_2CO_3$ sample in a 50 mM DMPO solution tank (aqueous dispersion for DMPO-•OH). Light of 420 nm was used to irradiate the sample.

1.3 Evaluation of photocatalytic activity

The photocatalytic activity was investigated by 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 visible light photocatalytic activity test, A 300 W commercial tungsten halogen lamp (General Electric) was vertically placed outside the reactor, and a UV cut off filter (420 nm, 450 nm and 510 nm) was adopted to remove UV light in the light beam. For photocatalytic activity testing under UV (360 nm) light, two UV lamps (6 W) were used. The photocatalyst (0.15 g) was coated on a dish with a diameter of 12.0 cm. The coated dish was then pre-treated at 70 ^{o}C to remove the water in the suspension. The NO gas was acquired from a compressed gas cylinder at a concentration of 100 ppm of NO (N_2 balance) with traceable National Institute of Standards and Technology (NIST) standard. The initial concentration of NO was diluted to about 450 ppb by the air stream supplied by a zero air generator (Thermo Environmental Inc., model 111). The desired relative humidity (RH) level of the NO flow was controlled at 50% by passing the zero air streams through a humidification chamber. The gas streams were premixed completely by a gas blender, and the flow rate was controlled at 3.3 L/min 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 (Thermo Environmental Instruments Inc., model 42c), 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 $\eta(\%) = (1-C/C_0) \times 100\%$, where C and C_0 are concentrations of NO in the outlet steam and the feeding stream, respectively.

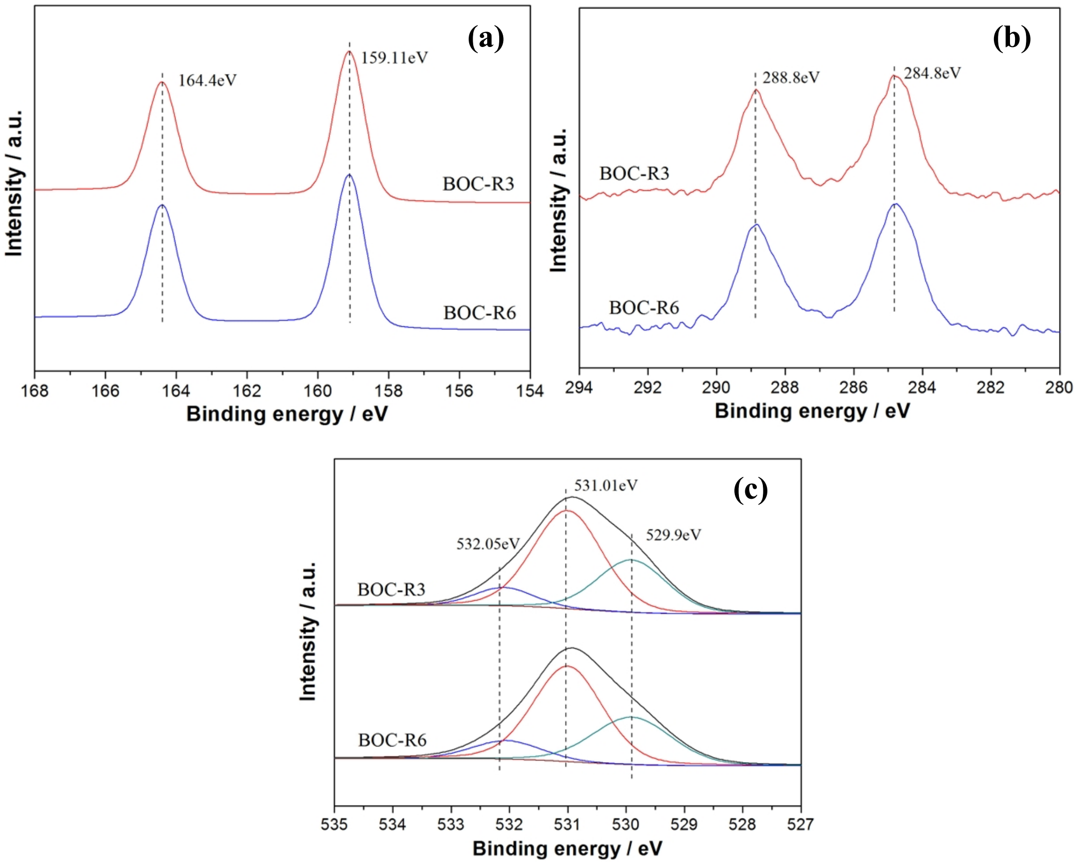

Fig. S1 XPS spectra of the BOC-R3 and BOC-R6 samples: (a) Bi4f, (b) C1s and (c) O1s.

As shown in Fig. S1a, two strong peaks at ca.159.11 eV and 164.4 eV are the Bi $4f_{7/2}$ and Bi $4f_{5/2}$ states, respectively, of the Bi^{3+} ions in $(BiO)_2CO_3$. A broad binding energy for C1s ranging from 291 to 282 eV can be observed as shown in Fig. S1b. The peaks at 284.8 eV can be attributed to adventitious carbon species from XPS measurement, while the peak at 288.8 eV can be assigned to the CO_3^{2-} ions in $(BiO)_2CO_3$. Fig. S1c presents the high-resolution O 1s peak, which can be fitted with three peaks at binding energies of 529.9, 531.01 and 532.05 eV, respectively. The peak at 529.9 eV is a characteristic binding energy of Bi–O, and the other two peaks at around 531.01 and 532.05eV can be assigned to carbonate species and surface hydroxyl groups on the sample surface. Based on this, we can conclude that the these elements in the two samples have similar chemical environment.

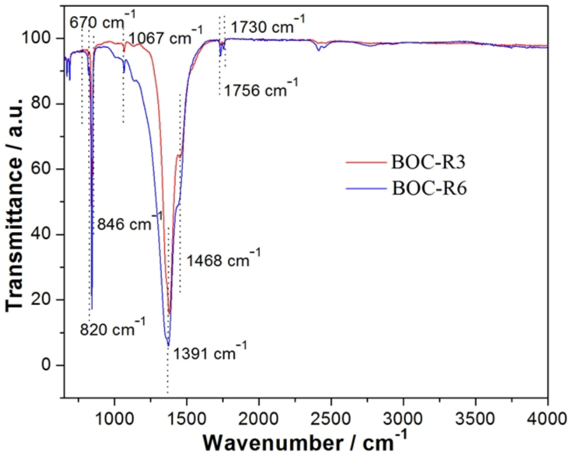

Fig. S2 FT-IR spectra of the BOC-R3 and BOC-R6 samples.

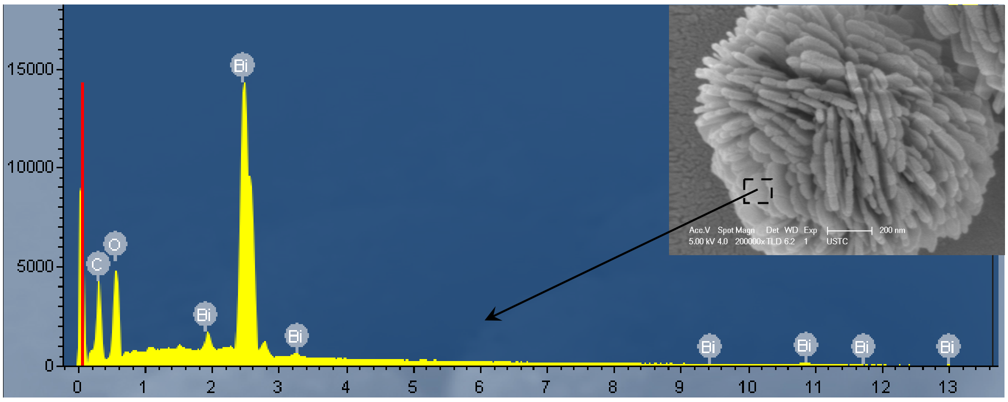

Fig. S3 EDX spectrum of the BOC-R3.

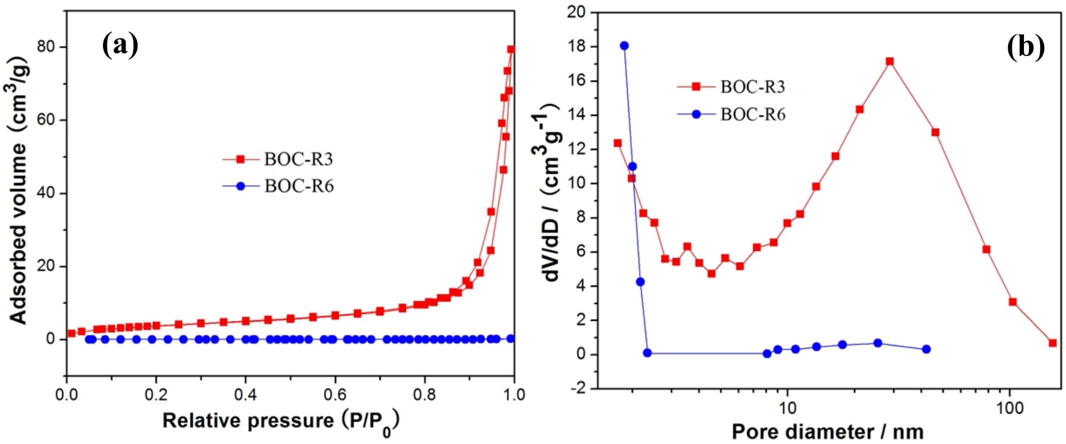

Fig. S4 N_2 adsorption-desorption isotherms (a) and the corresponding pore diameter distributions (b) of BOC-R3 and BOC-R6 samples.

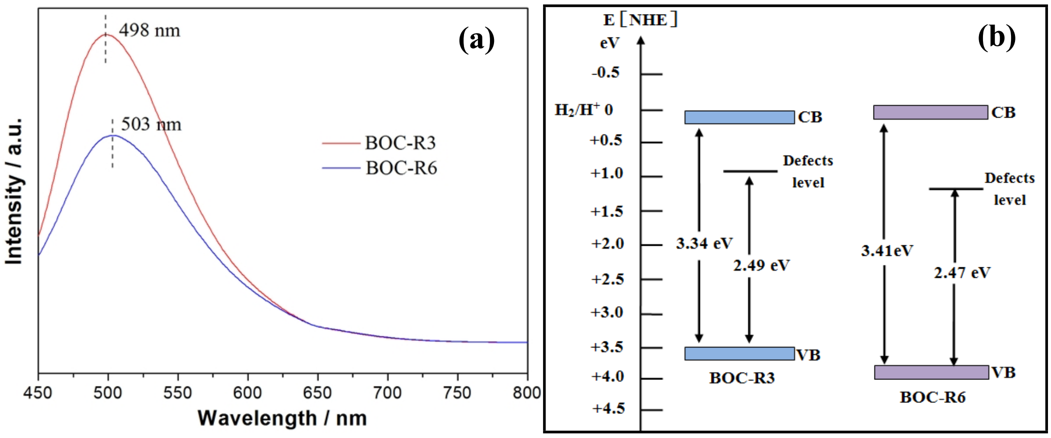

Fig. S5 PL spectra of the two samples (λ_{ex}= 430 nm) (a) and Schematic diagram of band gap and defects level for the two samples (b).

Fig. S5a shows the PL spectra of the two samples with exciting wavelengths of 430nm. It can be seen that BOC-R3 and BOC-R6 samples exhibit a strong PL signal with a obvious PL peak at about 498 and 503 nm, respectively, which is related to the defects or impurity level. Also, the defects level can be calculated by the formula: E_g=1240/λ, so we can achieve the defects level as shown in Fig. S5b.

In order to further investigate the effect of band structure on the activity of the as-prepared samples, the positions of CB edge and VB edge were calculated using a simple theoretical method. For a semiconductor, the band gap energy of a semiconductor could be calculated by the formula: $\alpha h\nu = A(h\nu - E_g)^{n/2}$,[1] where α is the absorption coefficient, hν is the photon energy, A is a constant and E_g is the band gap. For $(BiO)_2CO_3$, n = 4 for indirect transition. From the $(\alpha h\nu)^{1/2}$ versus hν plot (Fig. 4b, inset), the band gaps of the as-synthesized BOC-R3 and BOC-R6 (E_g) samples were estimated to be 3.34 and 3.41 eV, respectively. The valence band top of a semiconductor at the point of zero charge can be calculated by the empirical equation $E_{VB} = X - E_e + 0.5E_g$,[2] where E_{VB} is the valence band-edge potential, X is the absolute electronegativity of the semiconductor, taken as the weighted average of the X values of the constituents. E_e is the energy of free electrons on the hydrogen scale (about 4.5 eV), E_g is the bandgap energy of the semiconductor. Then, the conduction band bottom E_{CB} can be determined by $E_{CB}=E_{VB}-E_g$. The X value of $(BiO)_2CO_3$ is about 6.39 eV. For BOC-R3, the E_{VB} is calculated to be 3.56 eV, and then the E_{CB} is estimated to be 0.22 eV. For BOC-R6, the E_{VB} is calculated to be 3.6 eV so that the E_{CB} is estimated to be 0.19 eV. The defects level can be determined by $1240/E_g$. The corresponding schematic diagram of band structure is shown in Fig. S5b.

1 M. A. Butler, *J. Appl. Phys.*, **1977**, 48, 1914-1920.

2 Y. Xu and M. A. A. Schoonen, *Am. Mineral*. **2000**, 85, 543-556.

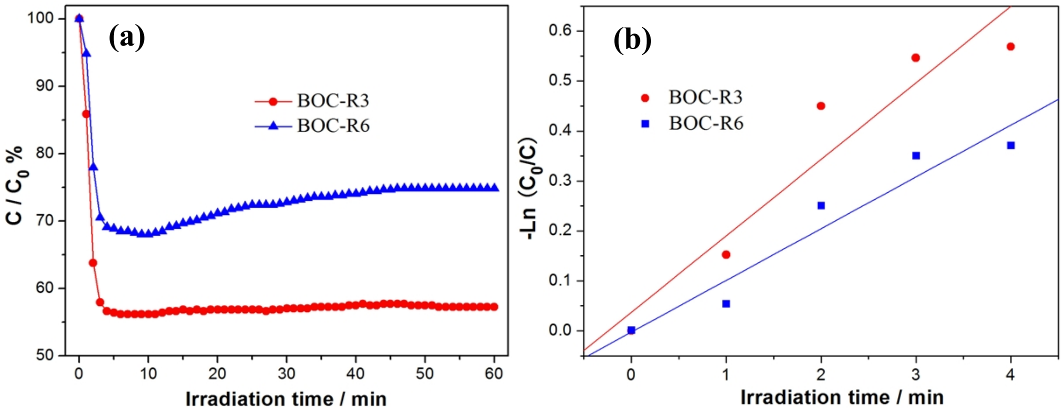

Fig. S6 Photocatalytic activity (a) and reaction rate constants k_{UV} (b) of the BOC-R3 and BOC-R6 samples under UV light irradiation.

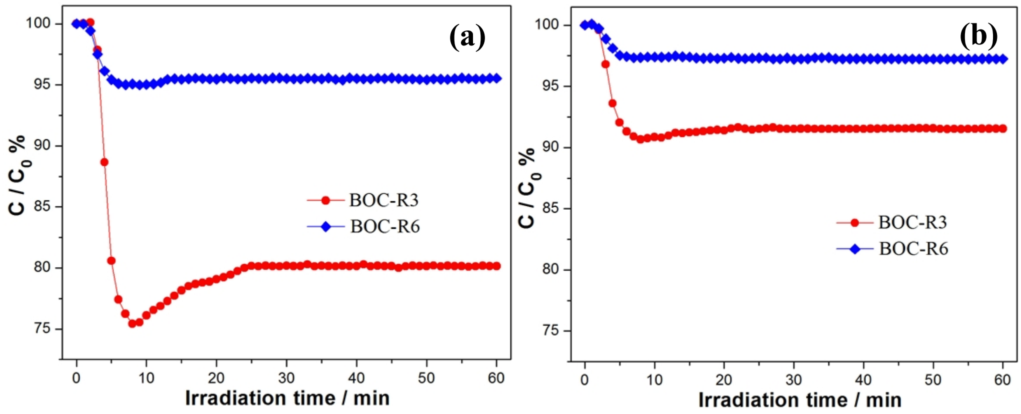

Fig. S7 Photocatalytic activity of the BOC-R3 and BOC-R6 samples under visible irradiation: (a) with a cut-filter of 450 nm and (b) with a cut-filter of 510 nm.