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Investigation on Effect of Anion Layer on Photocatalytic Activity: Carbonate vs. Oxalate

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Experimental Section

Chemicals: $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, urea ($\text{CO}(\text{NH}_2)_2$) and sodium oxalate ($\text{Na}_2\text{C}_2\text{O}_4$) were of analytical grade, purchased from Beijing Chemical Reagents Industrial Company of China, and were used without further purification.

Characterizations: The crystal structures of the samples were determined by X-ray powder polycrystalline diffractometer (Rigaku D/max-2550VB), using graphite

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monochromatized Cu K α radiation ($\lambda = 0.154$ nm), operating at 40 kV and 50 mA. The XRD patterns were obtained in the range of 10-80° (2θ) at a scanning rate of 7 ° min⁻¹. The samples were characterized on a scanning electron microscope (SEM, Hitachi SU-1510) with an acceleration voltage of 15 keV. The fine surface structures of the samples were determined by high-resolution transmission electron microscopy (HRTEM, JEOL JEM-2100F), equipped an electron diffraction (ED) attachment with an acceleration voltage of 200 kV. Fourier Transform Infrared (FTIR) spectra of the ceramics were performed using a Nicolet spectrophotometer and the dielectrical measurements were performed using a HIOKI LCR meter. UV-vis diffused reflectance spectra of the samples were obtained using a UV-vis spectrophotometer (UV-2550, Shimadzu, Japan). BaSO₄ was used as a reflectance standard in a UV-diffuse reflectance experiment. Photoluminescence (PL) spectra were measured on a fluorescence spectrophotometer (Japan, Shimadzu RF-5301PC) with the 260 nm excitation line of a Xe lamp as the excitation source. Nitrogen sorption isotherms were performed at 77 K and < 10⁻⁴ bar on a Micromeritics ASAP2010 gas adsorption analyzer. Each sample was degassed at 150 °C for 5 h before measurements. Surface area was calculated by the Brunauer-Emmett-Teller (BET) method.

Electrochemistry test: The working electrodes were fabricated by mixing 80 wt% powders, 10 wt% acetylene black, 10 wt% poly(vinylidene fluoride). The mixture was dispersed in 1-Methy-2-pyrrolidinone to form homogeneous slurry under stirring. The slurry was dotted on the nickel foam and then dried for 24 h at room temperature. All the electrochemical measurements were carried out on an electrochemical working

station (CHI 660D). Electrochemical measurements were carried out in a three-electrode cell at room temperature. In the test, a platinum wire was served as a counter electrode, a saturated calomel electrode (SCE, Hg/Hg₂Cl₂) electrode was employed as a reference electrode, and 0.5 M Na₂SO₄ aqueous solution was used as the electrolyte. The surface photovoltage (SPV) measurement system is consist of a monochromatic light source, a lock-in amplifier (SR830-DSP) with a light chopper (SR540), a photovoltaic cell and a computer. The monochromatic light is provided by a 500 W xenon lamp (CHFXQ500 W, Global Xenon Lamp Power) and a double-prism monochromator (Zolix SBP500). During the SPV measurement, the samples were test without further treatment. While the measurement of surface photovoltage was performed, the contact between the samples and the indium tin oxide (ITO) electrode was not ohmic. The construction of the photovoltaic cell is a sandwich like structure, which consist of steel timber, sample and ITO. The powders were placed on the steel timber electrode and pressed to obtain a film with ITO electrode.

Photocatalytic reactions: The photocatalytic activity of the sample was evaluated by the degradation of phenol and rhodamine B (RhB) aqueous solution under UV light ($\lambda \leq 400$ nm), using a 300 W Xe arc lamp (CEL-HXF 300) as a light source. The reaction system was placed in a sealed black box with the top opened and maintained a distance of 15 cm from the light source. The samples (100 mg) were dispersed in 200 mL of 10 mg/L phenol or RhB aqueous solution in a Pyrex beaker at room temperature. Before lighting on, the suspension was continuously stirred for 30 min in the dark to ensure the establishment of an adsorption–desorption equilibrium between the catalysts and

phenol or RhB solution. During degradation, 5 mL of solution was collected by pipette at an interval of irradiation, and subsequently centrifuged to remove the catalysts. UV-vis absorption spectra were recorded on a Spectrumlab 722sp spectrophotometer to determine the concentration of phenol or RhB. The concentration of phenol was measured through 4-aminoantipyrine spectrophotometric method at the characteristic optical absorption of 510 nm. While RhB was measured at the characteristic optical absorption of 553 nm directly. The degradation reaction could be expressed by an apparent first-order rate constant (k_a), which could be calculated using the following equation:

$$\ln(C_0/C) = k_a \times t, \text{ or } C = C_0 \times \exp(-k_a \times t) \quad (1)$$

where C_0 is the initial concentration of phenol or RhB solution, and C is the concentration of phenol or RhB at t -min irradiation, respectively.

Fig. S1

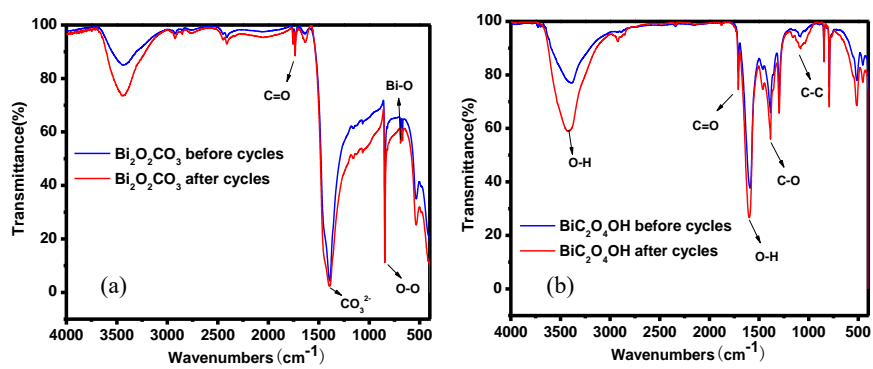


Fig. S1 FTIR spectra of the samples before and after cycle experiments: (a)

Bi₂O₂CO₃; (b) Bi(C₂O₄)OH.

Fig. S2

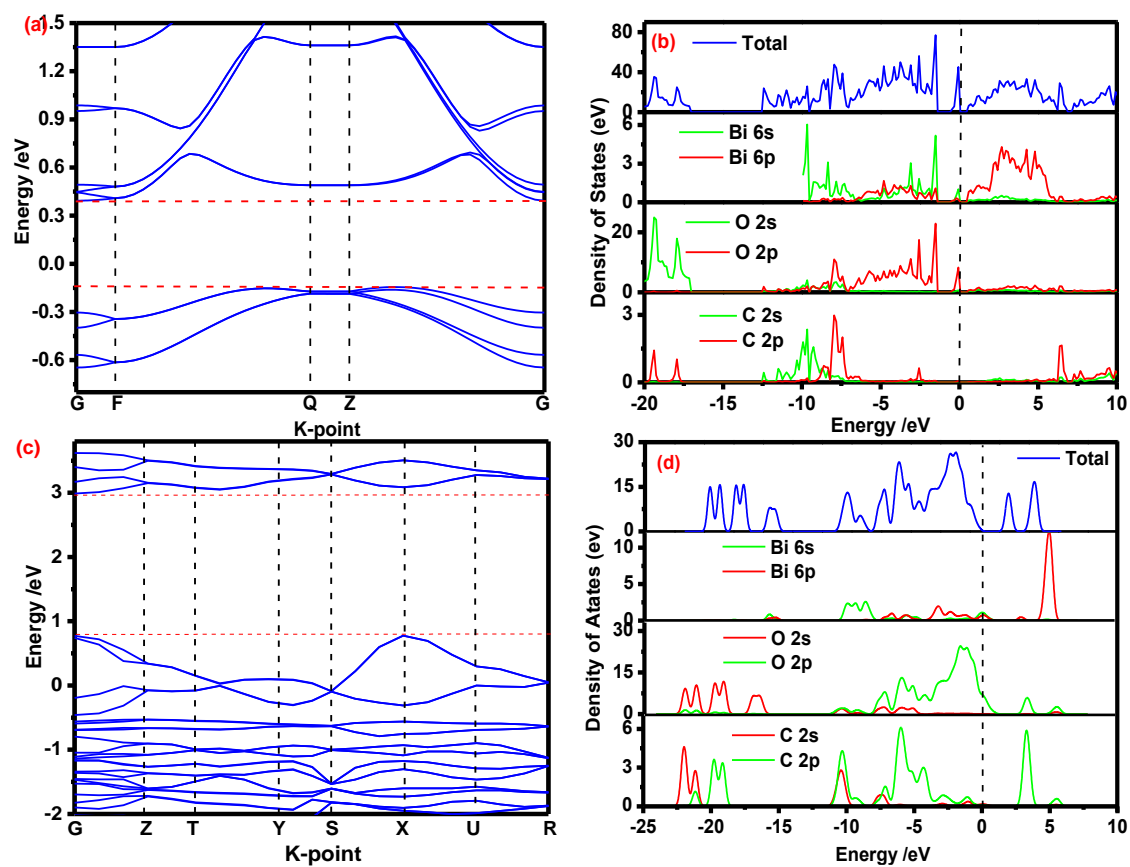


Fig. S2 Energy band structures and density of states (DOS): (a,b) $\text{Bi}_2\text{O}_2\text{CO}_3$;
(c,d) $\text{Bi}(\text{C}_2\text{O}_4)\text{OH}$.

Fig. S3

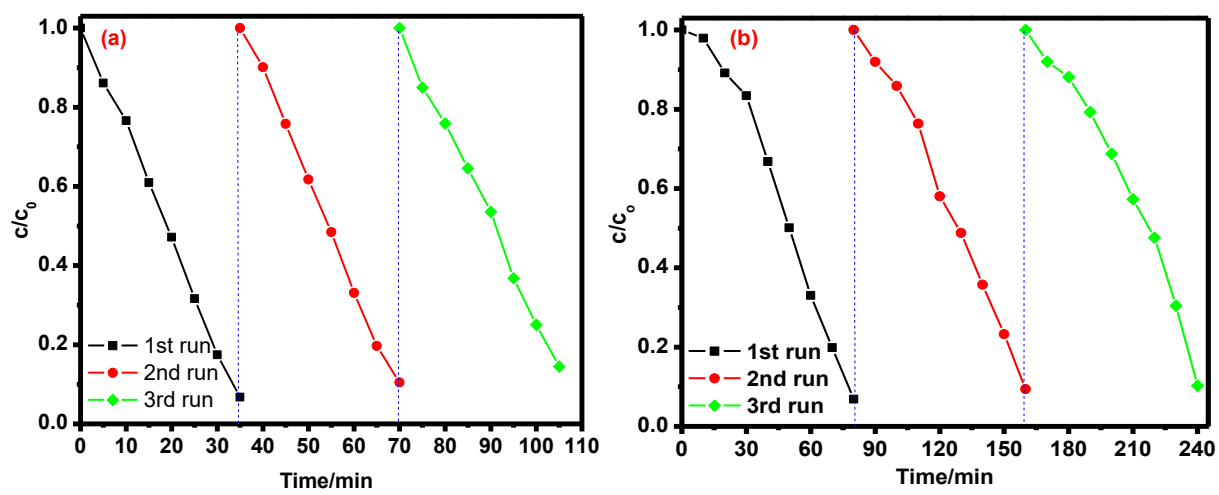


Fig. S3 Cycle degradation curves of RhB over the samples under UV light irradiation

($\lambda \leq 400$ nm): (a) $\text{Bi}_2\text{O}_2\text{CO}_3$ and (b). $\text{Bi}(\text{C}_2\text{O}_4)\text{OH}$

Fig. S4

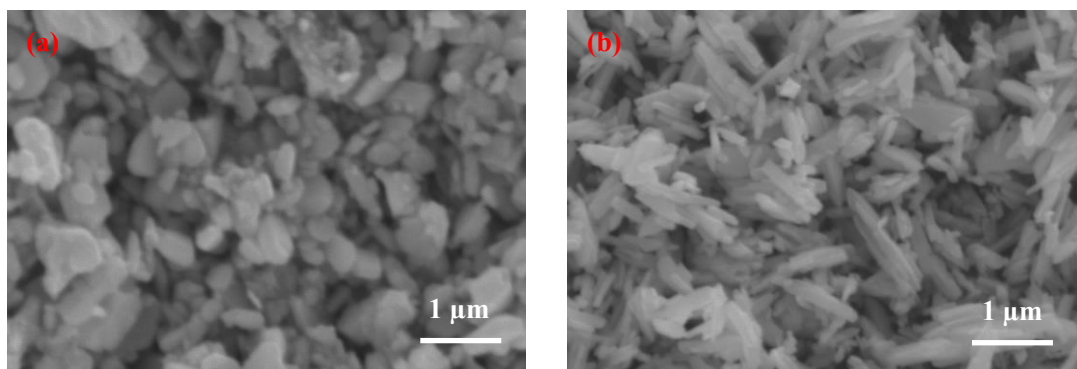


Fig. S4 SEM images of the samples after three cycles: (a) $\text{Bi}_2\text{O}_2\text{CO}_3$; (b)
 $\text{Bi}(\text{C}_2\text{O}_4)\text{OH}$.