

## Supporting Information

### **Construction of three-dimensional flower-like Bi<sub>2</sub>S<sub>3</sub>/BiOCl S-scheme heterojunction and its efficient photocatalytic degradation of ciprofloxacin**

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## 2. Materials and methods

### 2.1 Materials and reagents

All the chemical reagents used in the experiment were analytically pure and used directly without further purification. Bismuth trichloride ( $\text{BiCl}_3$ ), hydrochloric acid (HCl, 36-38 %), citric acid monohydrate ( $\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$ ), polyvinyl pyrrolidone (PVP, K30), thioacetamide (TAA,  $\text{CH}_3\text{CSNH}_2$ ), cyclopropyl salicylate ( $\text{C}_2\text{H}_2\text{O}$ ) were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. The experimental water is deionized water.

### 2.2 Preparation of BiOCl

Firstly, 1.2 mmol  $\text{BiCl}_3$  was dissolved in 7 mL deionized water, then 1 mL concentrated hydrochloric acid was added and magnetically stirred until completely clarified, recorded as solution A. In addition, 1.2 mmol of citric acid monohydrate and 0.01 g of PVP were dissolved in 42 mL of deionized water and 50 mL of anhydrous ethanol, and stirred until completely dissolved, which was recorded as solution B. The solution A was slowly added to the solution B under 80 °C water bath heating and continuous stirring. After the completion of the dripping, continue to stir the reaction at 80 °C for 3 hours. After the reaction, the white precipitate was collected by centrifugation and washed several times with deionized water and absolute ethanol, respectively. Finally, the product was dried in an oven at 60 °C for 12 hours, and the pure BiOCl sample was obtained after grinding.

### 2.3 Preparation of $\text{Bi}_2\text{S}_3/\text{BiOCl}$ composites

$\text{Bi}_2\text{S}_3/\text{BiOCl}$  composites were prepared by ion exchange method. 0.1 g BiOCl powder was dispersed in 30 mL deionized water. Subsequently, TAA with different mass ratios of 0.1: 1, 0.3: 1, 0.5: 1, 1: 1 and 3: 1 to BiOCl were added to the suspension. The mixture was continuously magnetically stirred in a water bath at 80 °C for 30 minutes. After the reaction was completed, the obtained yellow precipitate was centrifuged and collected, and repeatedly washed with deionized water and ethanol to remove the residual reactants. The products were dried at 60 °C for 12 h to obtain a series of  $\text{Bi}_2\text{S}_3/\text{BiOCl}$  composites, denoted as BS-x, where x represents the mass ratio of  $\text{Bi}_2\text{S}_3$  to BiOCl ( $x = 0.1, 0.3, 0.5, 1, 3$ ).

### 2.4 Characterization method

The physicochemical properties of the catalyst were characterized by various techniques. The crystal structure of the samples was analyzed by X-ray diffractometer (XRD, Bruker D8 Advance, Cu  $K\alpha$  radiation). Scanning electron microscopy (SEM, Hitachi SU8010) and transmission electron microscopy (TEM, FEI Tecnai G2 F20,

equipped with EDS spectrometer) were used to observe the microstructure, size and element distribution of the samples. The surface elemental composition and chemical state were analyzed by X-ray photoelectron spectroscopy (XPS, Thermo Scientific K-Alpha+, Al K $\alpha$  excitation source). The optical absorption properties of the samples were studied by UV-vis diffuse reflectance spectroscopy (UV-vis DRS, Shimadzu UV-2600). The photoluminescence behavior of the samples was detected by a fluorescence spectrometer (PL, Hitachi F-7000). The electrochemical workstation (CHI 660E) was used to test in the three-electrode system. The electrolyte was 0.5 M Na<sub>2</sub>SO<sub>4</sub> solution. The working electrode was ITO conductive glass loaded with catalyst film, the counter electrode was platinum sheet, and the reference electrode was Ag/AgCl electrode.

#### **2.4 Photocatalytic performance test**

The photocatalytic activity of the samples was evaluated by degrading ciprofloxacin (CIP) solution at room temperature. A 300 W xenon lamp (Beijing Perfect Light, CEL-HXF300) is used as the light source, and a 420 nm cut-off filter is provided to provide visible light irradiation. 10 mg catalyst was dispersed in 50 mL CIP aqueous solution. First, magnetic stirring was performed for 30 minutes under dark conditions to achieve the adsorption-desorption equilibrium of CIP on the catalyst. Then, the light source was turned on for irradiation, and about 4 mL of suspension was taken out every 15 min, and the supernatant was extracted by centrifugation. Ultraviolet-visible spectrophotometer was used to determine the absorbance of the supernatant.

In order to explore the mechanism of photocatalytic reaction, the active species capture experiment was carried out. Under the same photocatalytic reaction conditions, different capture agents were added to the reaction system: tert-butanol (TBA), benzoquinone (BQ), ethylenediaminetetraacetic acid disodium (EDTA-2Na) and silver nitrate (AgNO<sub>3</sub>). By comparing the degradation efficiency of CIP before and after the addition of the capture agent, the main active species were identified.

#### **2.5 Photocatalytic cycling test**

**To evaluate the reusability of the BS-0.5 photocatalyst, four consecutive cycling experiments were performed under identical conditions. After each cycle, the catalyst was collected by centrifugation, washed thoroughly with deionized water and ethanol three times, and dried at 60 °C overnight. The recovered catalyst was then redispersed into freshly prepared CIP solution for the next run.**

**Table S1. The photocatalytic activity of BiOCl in the literature.**

<u>Photocatalyst</u>	<u>Reaction conditions</u>	<u>Pollutants</u>	<u>Photodegradation rate</u>	<u>Ref</u>
<u>Bi<sub>2</sub>S<sub>3</sub>/BiOCl S-scheme heterojunction</u>	<u>500 W xenon lamp, (<math>\lambda &gt; 400</math> nm), 10 mg catalyst</u>	<u>Ciprofloxacin (50 mL, 10 mg·L<sup>-1</sup>)</u>	<u>82.11 %, 60 min</u>	<u>this work</u>
<u>DiCoPc/BiOCl</u>	<u>400 W xenon lamp, (<math>\lambda &gt; 420</math> nm) 20mg catalyst</u>	<u>Rhodamine B (50 mL, 10 mg·L<sup>-1</sup>)</u>	<u>91.8 %, 120 min</u>	<u>1</u>
<u>Cr/Sn BiOCl nanocomposites</u>	<u>500 W xenon lamp, (<math>\lambda &gt; 400</math> nm), 20 mg catalyst</u>	<u>Ciprofloxacin (50 mL, 10 mg·L<sup>-1</sup>)</u>	<u>90.88 %, 180 min</u>	<u>2</u>
<u>Fe-doped BiOCl hierarchical microspheres</u>	<u>300 W xenon lamp, 1 g·L<sup>-1</sup> catalyst</u>	<u>Methylene blue (50 mL, 50 mg·L<sup>-1</sup>)</u>	<u>93.5 %, 60 min</u>	<u>3</u>

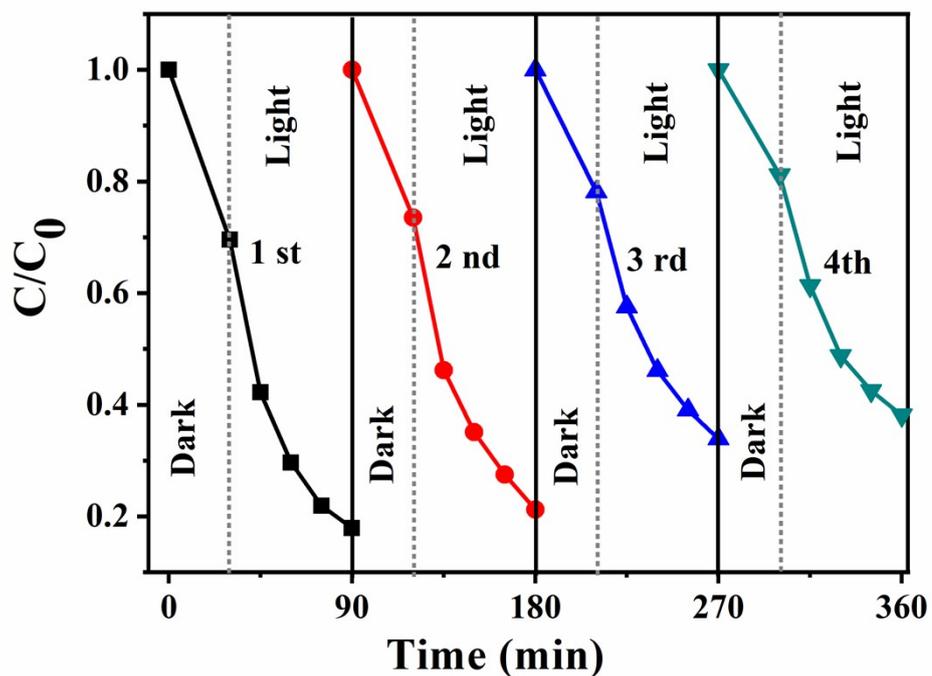


Fig. S1. The four-cycle stability test of BS-0.5.

### References

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