Electronic Supplementary Information

Experimental Section

Materials

Euploea mulciber forewings were purchased from Sichuan science and education insect company (Sichuan, China), Bismuth nitrate pentahydrate ($Bi(NO3)_3·5H_2O$), Anhydrous ethanol (C_2H_5OH) , Sodium hydroxide(NaOH), Ethylenediamine($C_2H_8N_2$), rhodamine B($C_{28}H_{31}ClN_2O_3$), Chloroauric acid($HAuCl_4$), Sodium borohydride($NaBH_4$), Tartaric acid($C_4H_6O_6$) were purchased from Sinopharm Chemical Reagent Co., Ltd(Shanghai, China). 3-chloro-1-propanol (C_3H_7ClO),6-chloro-1-hexanol ($C_6H_{13}ClO$), p-Chlorobenzyl alcohol (C_7H_7ClO), Sodium chloride (NaCl) were obtained from Aladdin Industrial Corp. (Shanghai, China). D-mannitol ($C_6H_{14}\ O_6$) were purchased from Alfa aisha (China) chemical co. LTD. All the reagents were analytical grade and used directly without further purification.

Synthesis of photocatalysts

Preparation of BiOCl microspheres

5 ml of a solution of bismuth nitrate mannitol aqueous solution, 25 ml of absolute ethanol, 30 μl of 6-chloro-1-hexanol were transferred into a 50 ml reaction vessel, reacted at 160 ° C for 3 h, then washed by centrifugation, and the products were dried at 60° C in a vacuum oven for 4 h.

Preparation of BiOCl-E Composite

We use the anti-V-shaped *Euploea mulciber* forewing as the bio-template. The specific experimental process and parameters are as follows: (1) The wings were dipped into sodium hydroxide solution at room temperature for demineralization treatment for 2 h and washed with DI water several times; (2) Dip the butterfly wing template after demineralization into ethylenediamine solution for 4 h and washed with DI water several times; (3) Immerse the aminated butterfly wing template in mannitol solution of bismuth nitrate pentahydrate for 4-5 h and washed with DI water several times; (4) Dip the

butterfly wing template into sodium chloride solution for 5-10 min and washed with DI water several times. (5) Immerse the butterfly wing template with BiOCl seeds in a reaction solution containing: 5 ml of an aqueous solution of bismuth nitrate pentahydrate mannitol, 25 ml of absolute ethanol, and 30 μl of 6-chloro-1-hexanol, and then transferred them to a 50 ml Teflon-lined stainless steel autoclave and heated at 120℃ for 3 h and allowed to cool down. Then the products were dried at 60℃ in a vacuum oven for 4 h

Preparation of BiOCl/Au-E Composite

Synthesis of Au butterfly wing[1]: The butterfly wing template is selected from the forewing of the *Euploea mulciber*. The specific experimental process and parameters are as follows: (1) Immerse the butterfly wing in aqueous sodium hydroxide solution for 2h at room temperature, and then wash it with DI water several time; (2) Immerse the butterfly wing template after demineralization in the ethylenediamine solution for 4h, and wash it repeatedly with deionized water. (3) Immerse the aminated butterfly wing template in chloroauric acid solution for 4h, and wash it repeatedly with deionized water. (4) Put it into $NaBH_4$ aqueous solution for 120s to reduce Au (III), and then wash it with DI water; (5) Put the butterfly wing on which the Au seed was deposited into a plating solution: 10 ml 2 wt% aqueous solution of chloroauric acid, 10 ml mixture solution consist of 0.8 wt% of tartaric acid, 1.2 wt% of sodium chloride, and 10.2 wt% of sodium hydroxide, 100 μl of anhydrous Ethanol. The reaction was carried out at 20 ° C for 30 min, then washed with DI water and dried at 45 ° C.

Synthesis of BiOCl/Au -P Composite: We use the Au butterfly wing mentioned above as the bio template. The next process is the same as the preparation of BiOCl-E composite.

Characterization

The composition of the material was analyzed by X-ray diffraction (XRD) with monochromatic Cu-Kα radiation (λ=1.5406 Å). X-ray photoelectron

spectra (XPS) were used to analyze the constituent elements and corresponding valence states of the materials. The instrument model is: PHI5400, which uses Mg target Kα radiation.

The microstructure and morphology of the butterfly wing and functional materials were observed by Field Emission Scanning Electron Microscopy (FESEM). The instrument model was FEI Quanta 250, the working voltage was 20kV, and the gold was sprayed for 60s before observation. Transmission electron microscopy (TEM) was used to analyze the microstructure, crystal type and interplanar spacing of the material. The instrument model was FEI Tecnai 20 and the accelerating voltage was 200 kV. The UV-visible absorption spectrum of the material was analyzed using a UV-Vis-NIR spectrophotometer. The instrument model is: Spectrum 750S, Perkin Elmer, Inc. USA, measurement range selection: 200-800 nm. The photoluminescence (PL) spectra was obtained using an Perkin Elmer Analytical Instrument LS 55 spectrophotometer and the excitation wavelength was 270 nm.

Photoelectrochemical Measurements

Cathode preparation:

BiOCl with carbon cloth: 5 mg BiOCl was added into 500 ul ethanol and 20 µl Nafion solution followed by sonication for 30 min to form a homogenous ink. Then the ink was loaded onto a carbon cloth with area of 1 x 1 cm^2 and dried under ambient condition.

BiOCl/Au-E with carbon cloth: The BiOCl/Au-E was attached to carbon cloth with electrically conductive adhesive and cut to an area of 1 x 1 cm^2 to serve as a working electrode.

All electrochemical measurements were performed using a traditional three electrode system with a 1 M Na_2SO_4 solution as electrolyte. BiOCl with carbon cloth or BiOCl/Au-E with carbon cloth, platinum foil, and Ag/AgCl in a saturated KCl aqueous solution were used as the working electrode, counter electrode, and reference electrode, respectively. Electrochemical

measurements were performed on an electrochemical workstation (Biologic VMP3). A 300 W xenon lamp was used as a light source All experiments were performed at ambient conditions.

Photocatalytic activity measurement

The visible-light-driven photocatalytic performance of the materials was evaluated by measuring the ability to degrade rhodamine B (RhB) under visible conditions[2]. The concentration of rhodamine B was 10^{-5} M and the catalyst amount was 5 mg. Prior to illumination, the solution was placed in the dark environment with stirring for 2 h to reach the adsorption−desorption equilibrium. Then the suspension was illuminated under a 300W xenon lamp (PLS-SXE 300, Beijing Trusttech Co. Ltd., China) to simulate sunlight and the 420 nm filter was used to remove ultraviolet light. During the process of photodegradation,5 ml of suspension was taken every 5 minutes to measure the absorption spectrum of the solution at 554 nm by an ultraviolet-visible spectrophotometer. The normalized temporary concentration change (C/C_0) of RhB solution during photodegradation is proportional to the normalized maximum absorbance (A/A_0), which is determined by the absorption peak of the dye in a certain time interval (RhB is 554 nm). Then, we achieve the dye degradation rate with different degradation time. The degradation rates (DR) was calculated according to following equation:

$$C/C_0 = A/A_0;$$

$$DR = (1-C_x/C_0) \times 100\% = (1- A_x/A_0) \times 100\%.$$

where A_x is the absorption peak of dye solution at 554 nm after a certain time, A_0 is the initial absorption peak of the dye solution at 554 nm.

Mechanism of BiOCl-E composites synthesized by seed-guided method

(1) Amination

The composition of the original butterfly wing is mainly chitin, and its

molecule is rich in active groups such as amino groups, hydroxyl groups, etc. These groups have the function of absorbing and sequestering metals, so in order to deposit BiOCl seeds on the surface of chitin, it is important to make full use of the reactive groups. In the case of untreated, the original butterfly wing has relatively few exposed groups on the surface, so it is necessary to pretreat the butterfly wing to expose the amino group and the hydroxyl group, generally soaking in the strong alkali or strong acid. After exposure, the active group on the surface of the butterfly wing can be further enriched by the method of “grafting”. For example, in this study, by treating in the ethylenediamine solution, the hydroxyl groups on the surface of the butterfly wing are "grafted" with large amounts of amino groups, which effectively improves the ability of the butterfly wing to adsorb and complex Bi^{3+}.

(2) Seed deposition

Depositing BiOCl seeds on the surface of chitin as the center of catalytic nucleation is beneficial to the growth of BiOCl nanosheets on the butterfly wings, which make it possible to replicate the nano-scale fine structure of the butterfly wings. This step is critical for the subsequent electroless plating process. First, the butterfly wing scales exposed a large amount of amino acid in the surface fully absorbed and chelated Bi^{3+} when immersed in mannitol solution of bismuth nitrate pentahydrate; Next, when washing the surface of the butterfly wing with water, Bi^{3+} is hydrolyzed into $BiONO_3$; Then it reacted with Cl^- to form BiOCl seeds when soaking in sodium chloride solution.

(3) Electroless plating of BiOCl nanosheets

6-Chloro-1-hexanol can release Cl^- slowly by hydrolysis, and control the nucleation rate of BiOCl. Adding ethanol to the solvent can inhibit the growth of BiOCl nanosheets, and achieve effective replication of the fine structure of butterfly wing micron, the effect was best when the ratio of water to ethanol was 1:5 (Fig. S3e, f). However, bismuth nitrate is insoluble in water and ethanol. After ultrasonication, a non-uniform suspension is formed, which is difficult to penetrate into the complex structure of the butterfly wing scales,

that is not conducive to the growth of BiOCl nanosheets. Barium nitrate can be dissolved in dilute nitric acid and some organic solvents, such as ethylene glycol, glycerin and acetone, but the three-dimensional structure of the butterfly wing is difficult to maintain and collapses due to corrosion as the reaction temperature rises when immersing in the above solution. Therefore, the plating solution needs to meet the following conditions: 1. suitable water to release Cl^- by hydrolysis of 6-chloro-1-hexanol; 2. The ratio of water to ethanol is 1:5, which promotes the replication of BiOCl nano-sheet to the nanostructure of butterfly wing. 3. Chemical plating solution that clarifies and does not destroy the scale structure of the wing. After a series of experiments, the optimum ratio of the reaction solution was: 5 ml mannitol solution of bismuth nitrate pentahydrate, 25 ml absolute ethanol, and 30 μl of 6-chloro-1-hexanol.

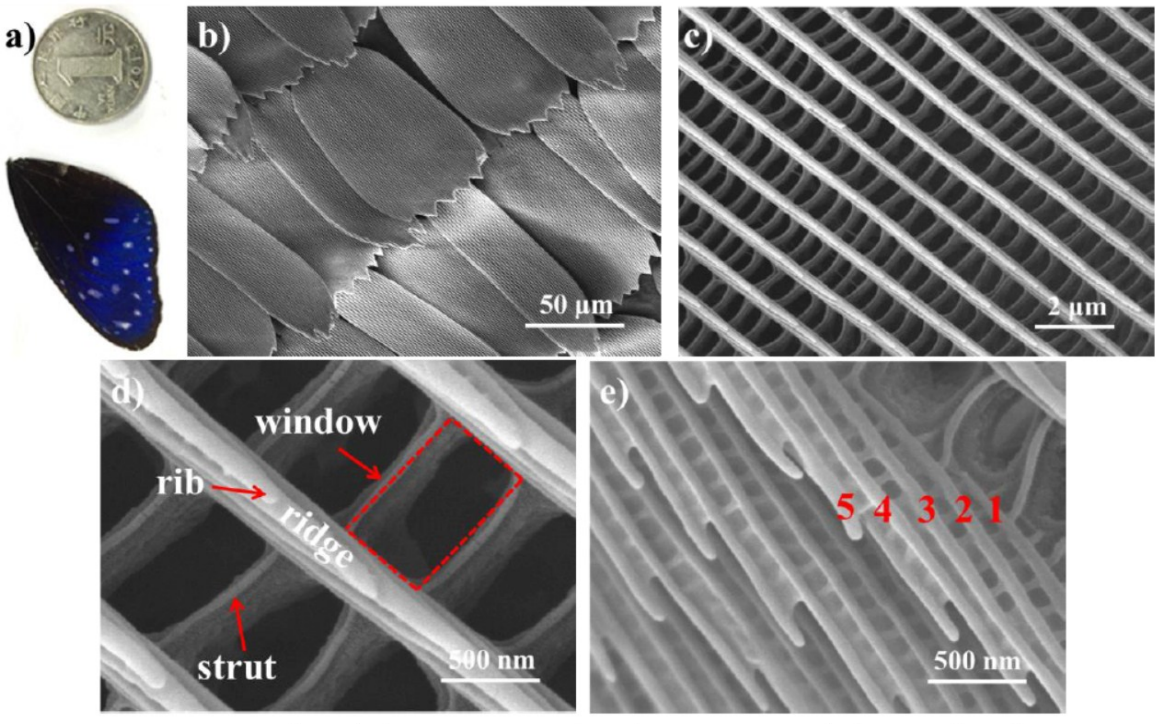

Fig. S1 (a) Optical photo of *Euploea mulciber* butterfly forewing; (b-e) SEM images of the scales of in the blue area

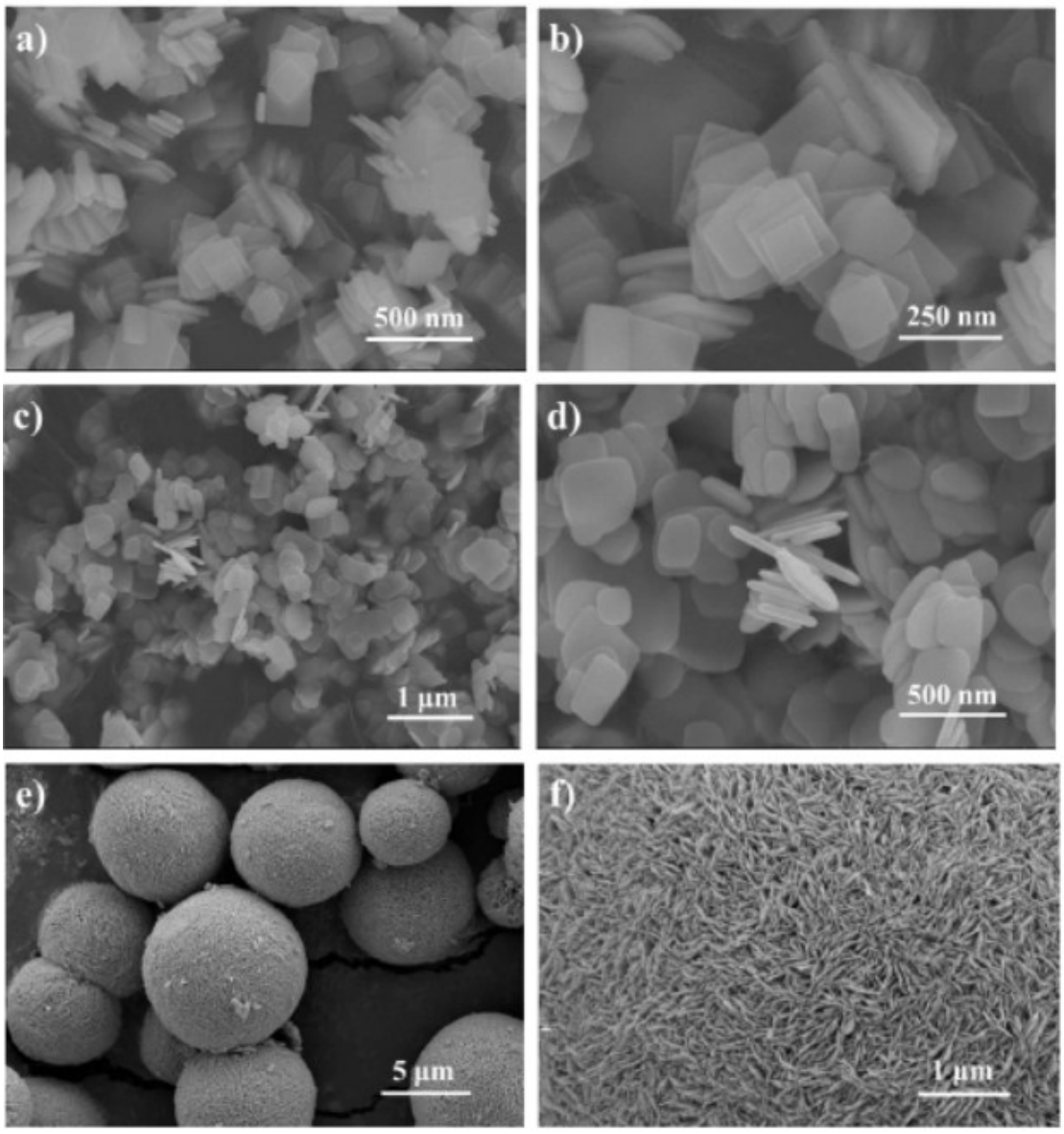

Fig. S2 SEM images of BiOCl with different halides as Cl^-sources. (a, b) sodium chloride; (c, d) 3-chloro-1-propanol; (e, f) 6-chloro-1-hexanol

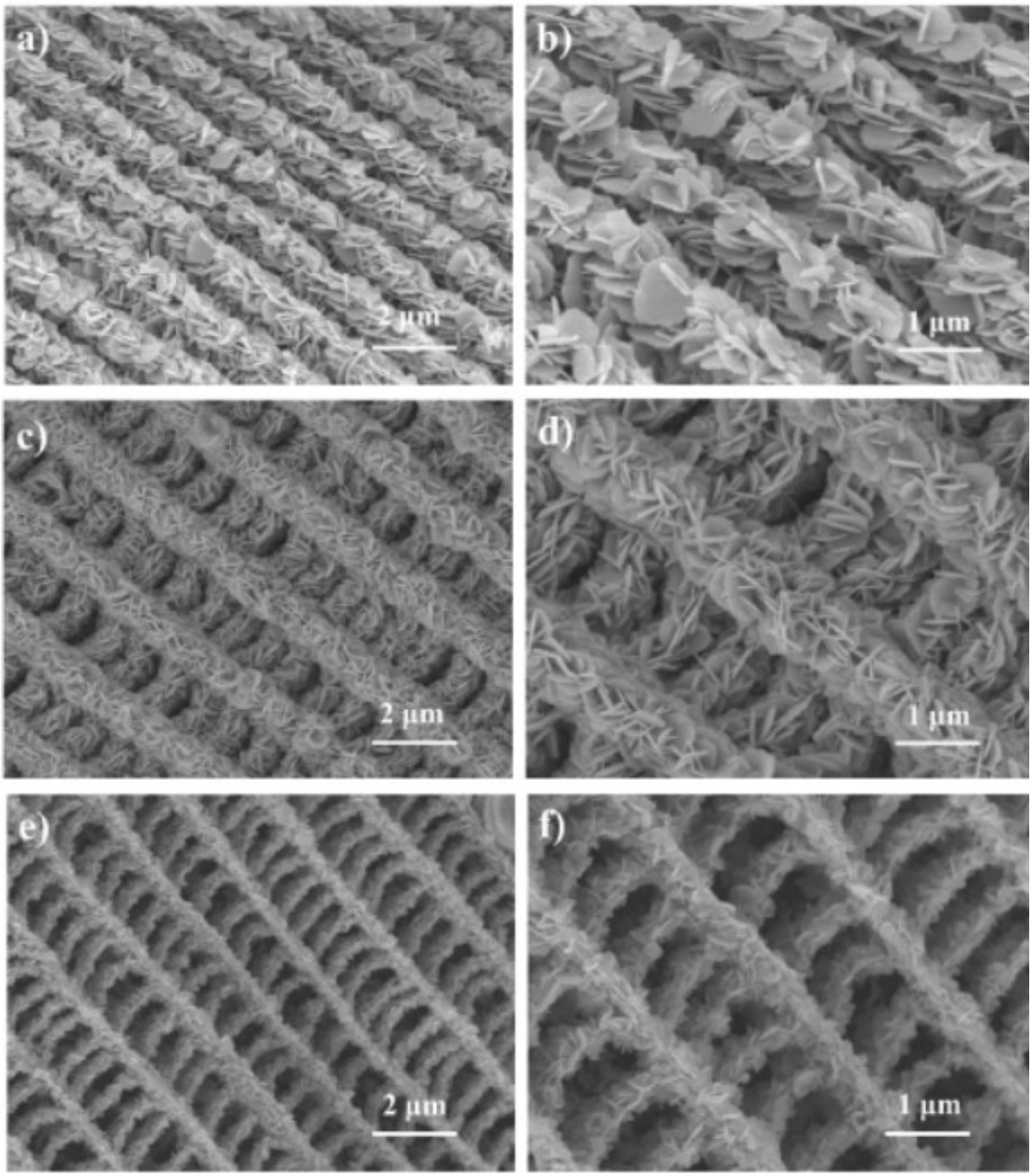

Fig. S3 SEM images of BiOCl composite with different volume ratios of water and ethanol. (a, b) 1:1; (c, d) 1:3; (e, f) 1:5

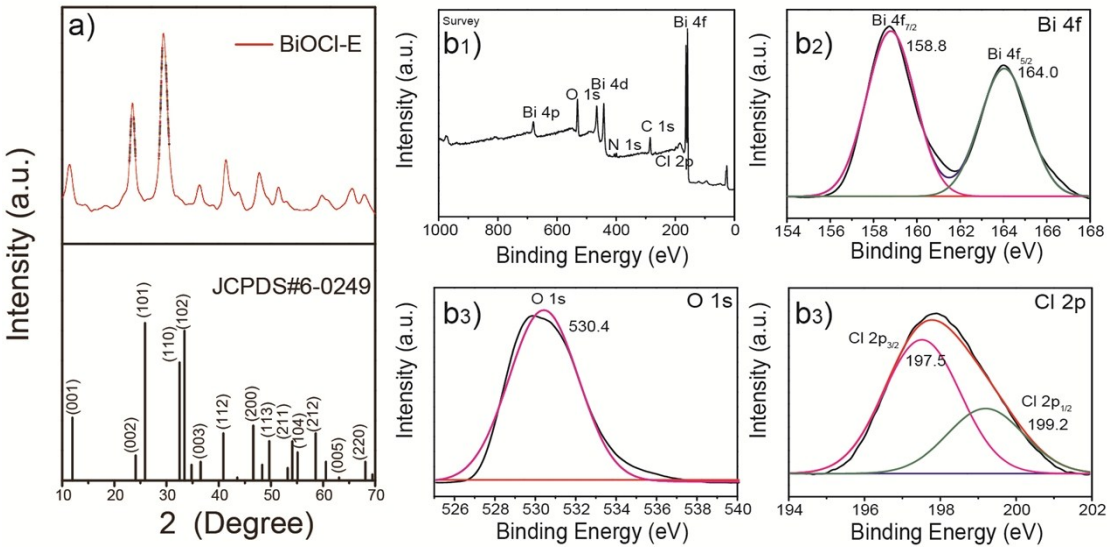

Fig. S4 Characterization of BiOCl-E sample synthesized with *Euploea mulciber* butterfly forewing as bio template. (a) XRD result. JCPDS#6-0249 refers to the corresponding standard pattern of BiOCl; (b) XPS spectrum of containing elements including Bi, O and Cl.

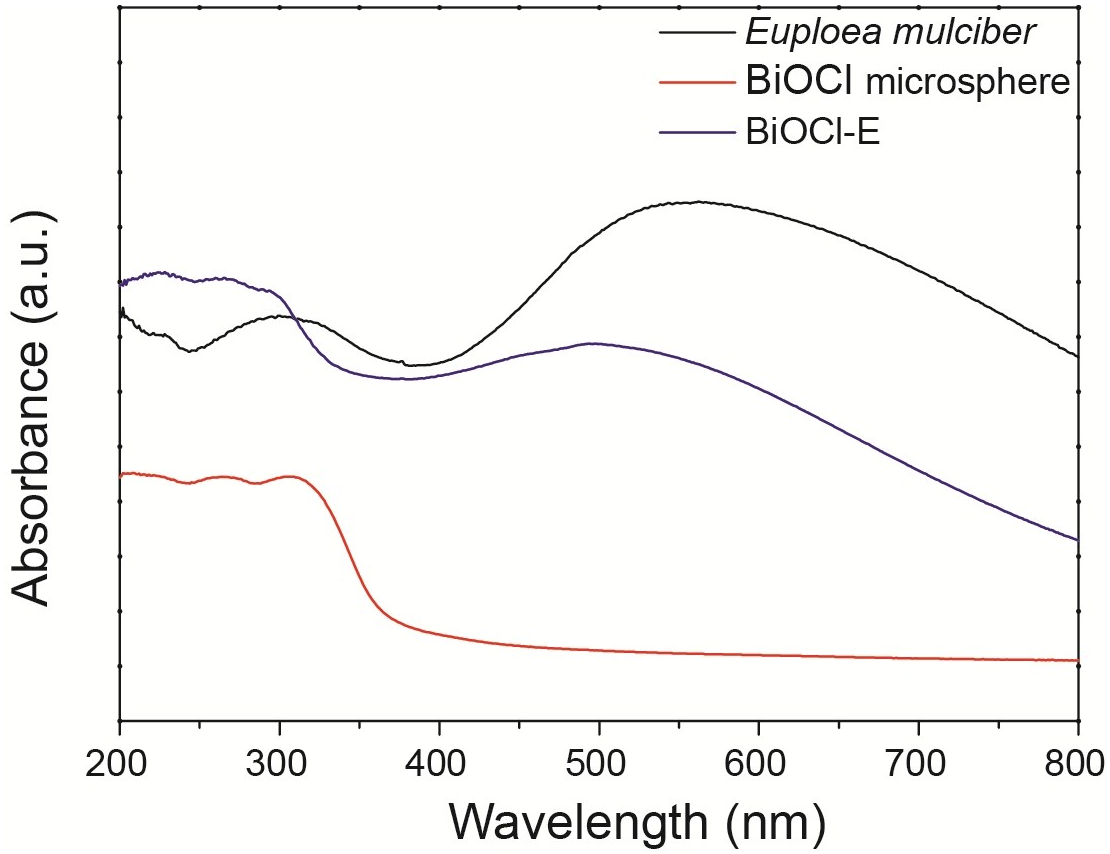

Fig. S5 UV/vis absorption spectra of *Euploea mulciber* butterfly forewing, BiOCl microspheres and BiOCl-E.

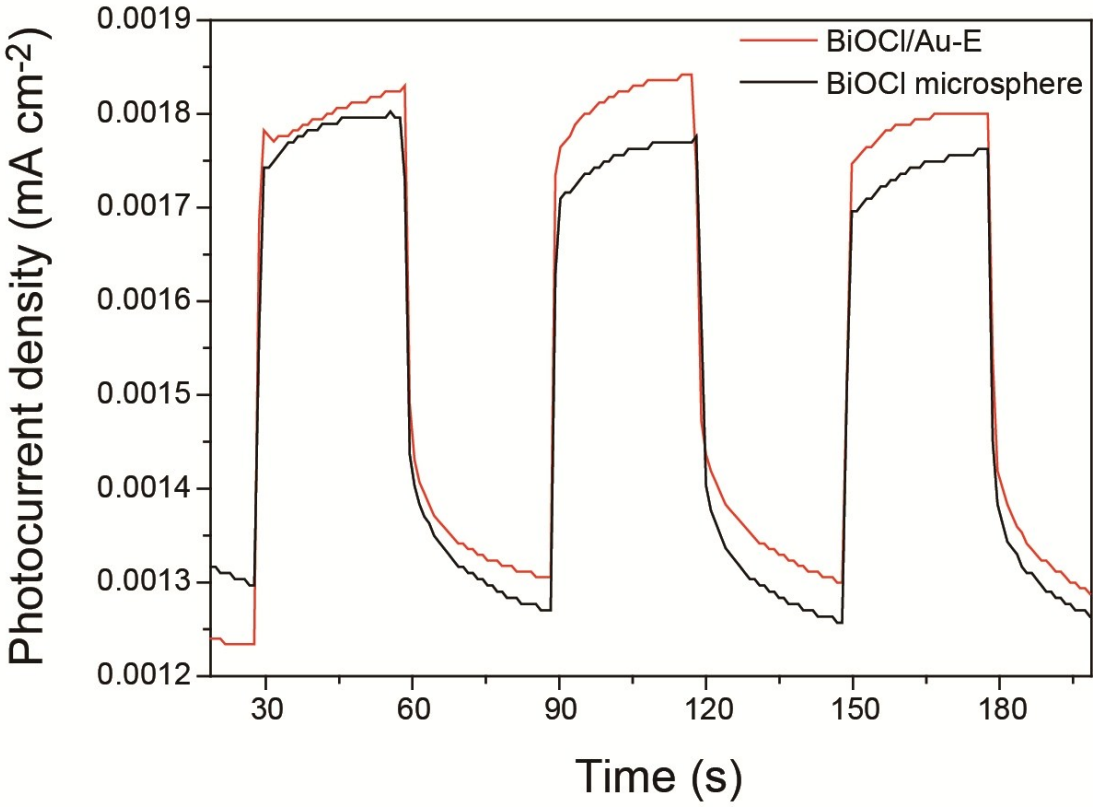

Fig. S6 Photocurrent responses of the BiOCl microspheres and BiOCl/Au-E in 1 M Na_2SO_4 aqueous solutions under UV−vis irradiation.

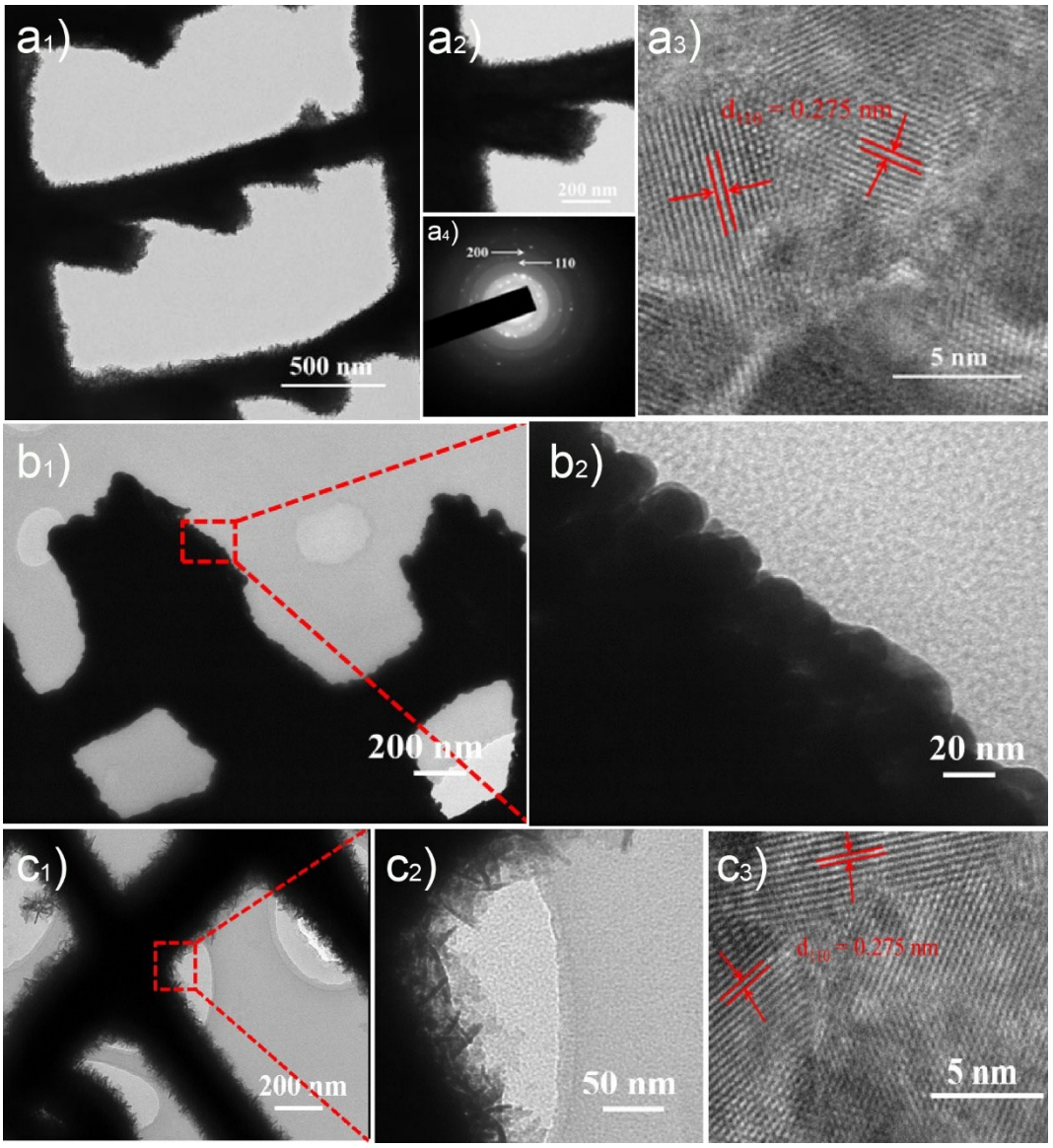

Fig. S7 TEM characterizations for slices of (a) BiOCl-E; (b) Au-E composite and (c) BiOCl/Au-E.

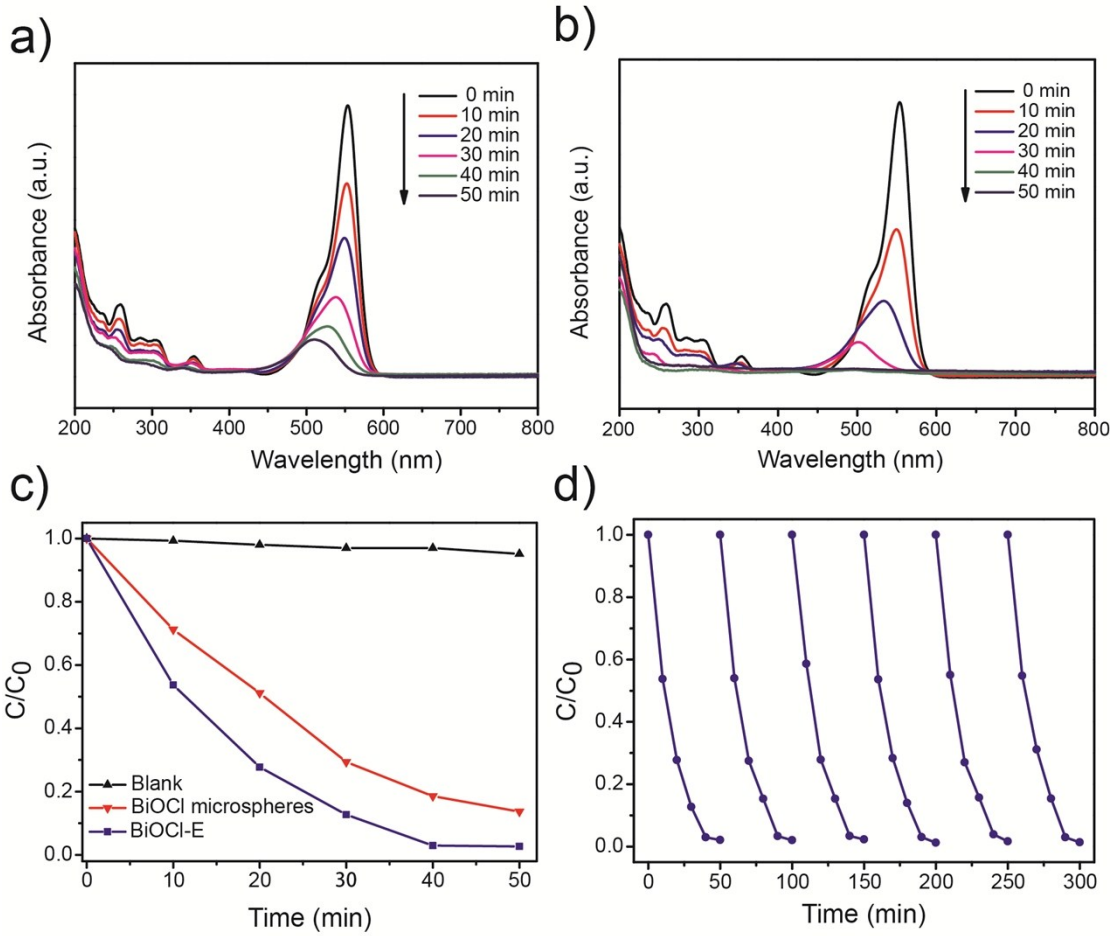

Fig. S8 Photocatalytic activity of both the BiOCl microspheres and BiOCl-E composites. (a-c) Comparison of photodecomposition of rhodamine B with BiOCl microspheres and BiOCl-E under visible light irradiation (λ>420 nm); (d) Cycling curve of photocatalytic degradation of rhodamine B for BiOCl-E.

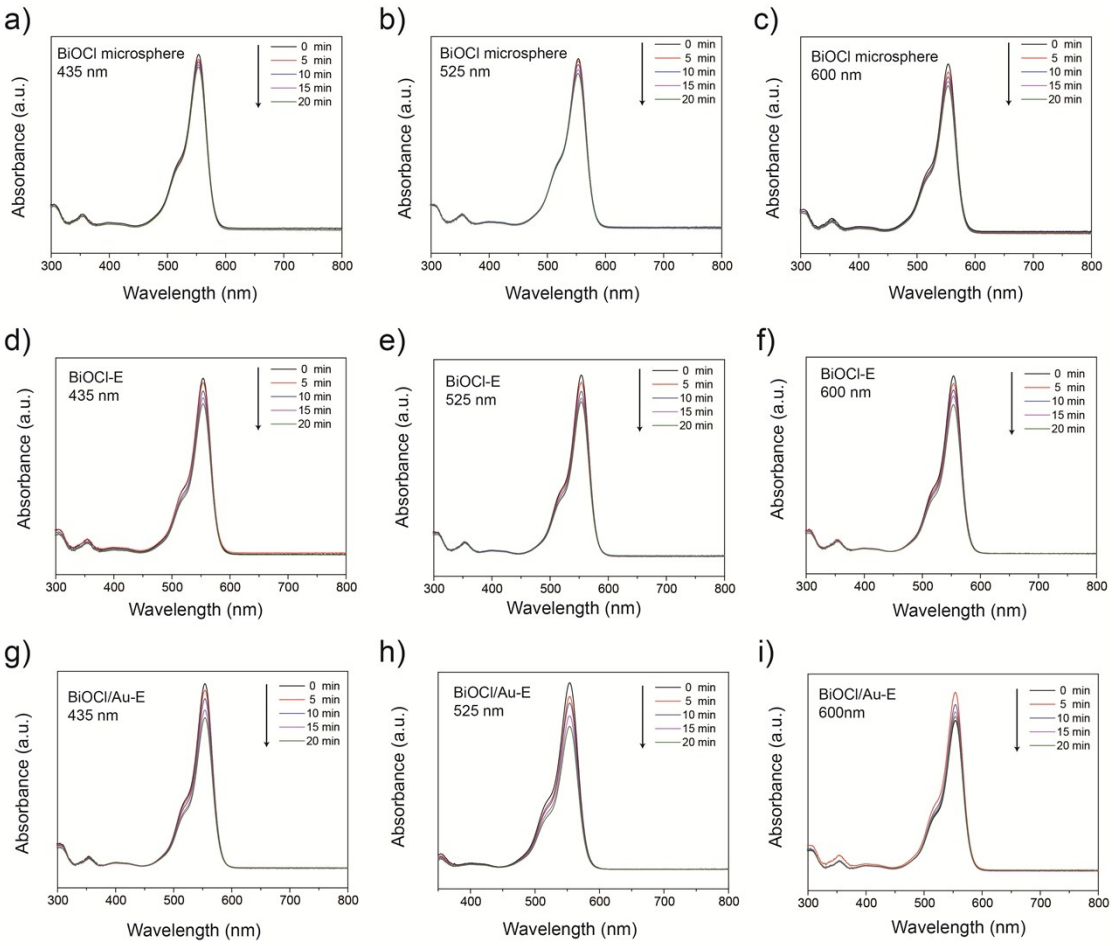

Fig. S9 UV/vis absorption spectra of rhodamine B at different photodegradation time with BiOCl microspheres (a-c); BiOCl-E (d-f); and BiOCl/Au-E (g-i) under different monochromatic light irradiation (a, d, g: 435 nm; b, e, h:525 nm; c, f, i:600 nm).

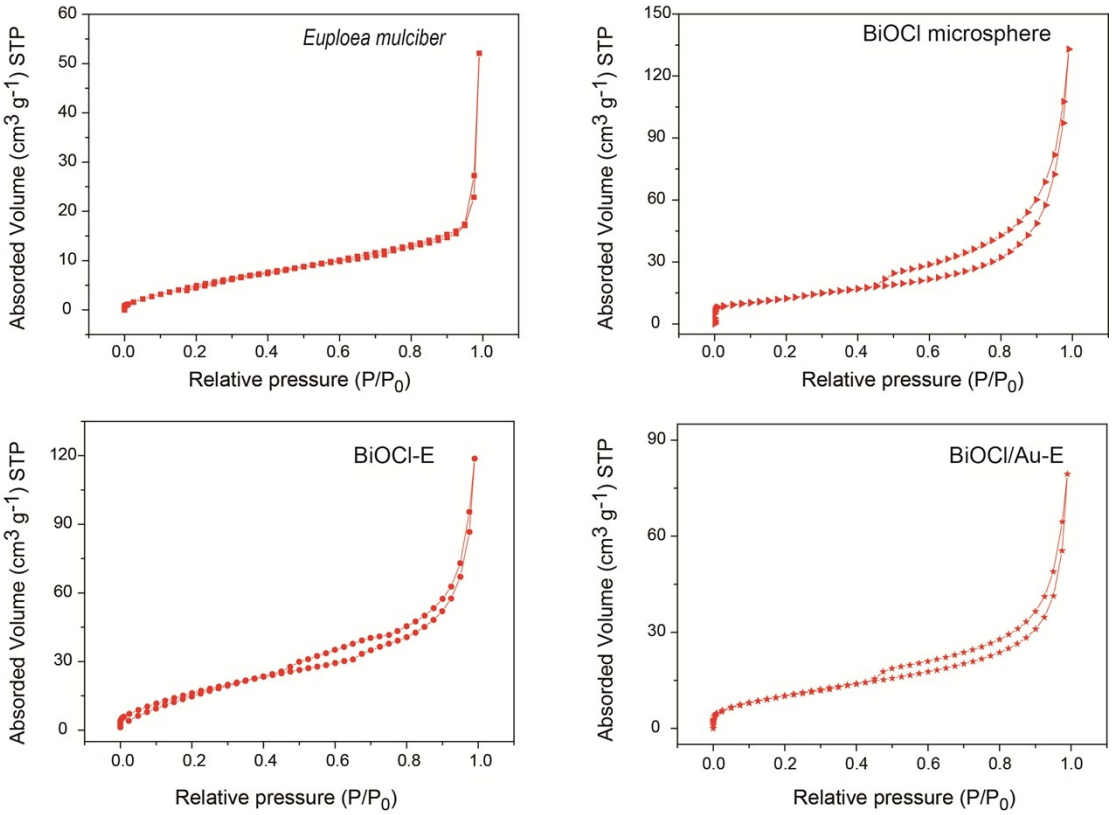

Fig. S10 N_2 adsorption-desorption on (a) *Euploea mulciber* butterfly forewing; (b) BiOCl microspheres; (c) BiOCl-E and (d) BiOCl/Au-E at 77.4 K. The surface area of *Euploea mulciber* butterfly forewing, BiOCl microspheres, BiOCl-E and BiOCl/Au-E is ~25 $m^2 g^{-1}$, ~47 $m^2 g^{-1}$, ~67 $m^2 g^{-1}$ and ~38 $m^2 g^{-1}$ respectively.

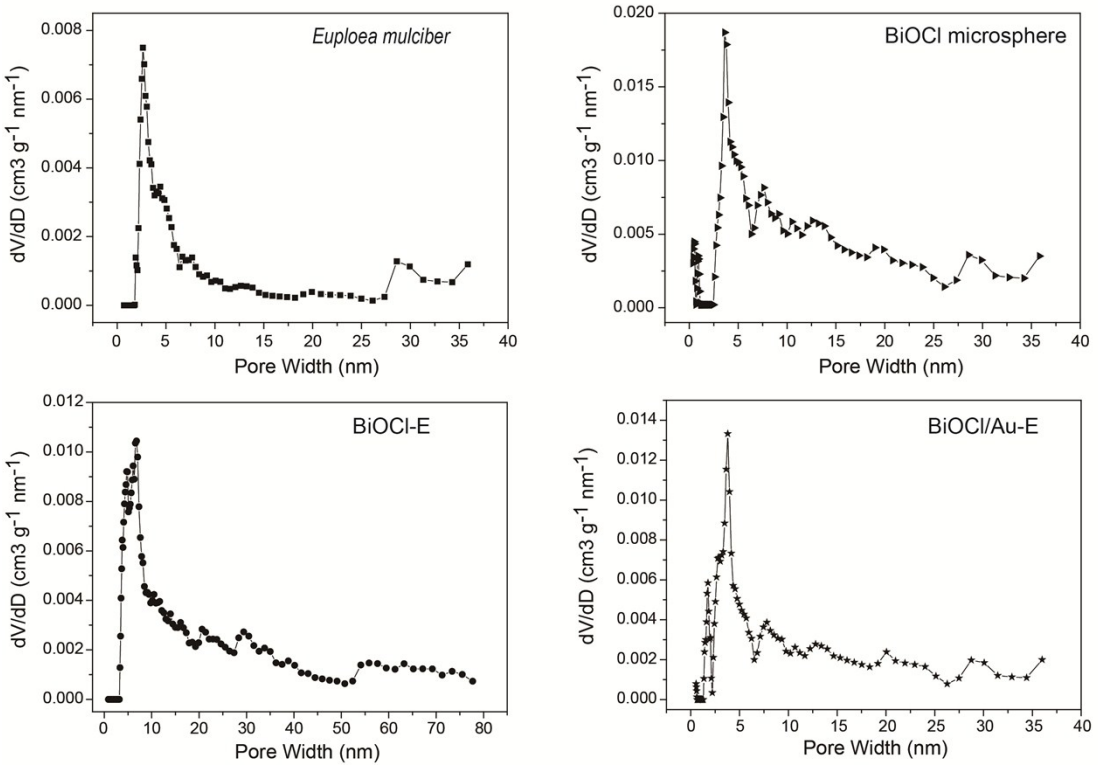

Fig. S11 Pore size distribution plots of (a) *Euploea mulciber* butterfly forewing; (b) BiOCl microspheres; (c) BiOCl-E and (d) BiOCl/Au-E.

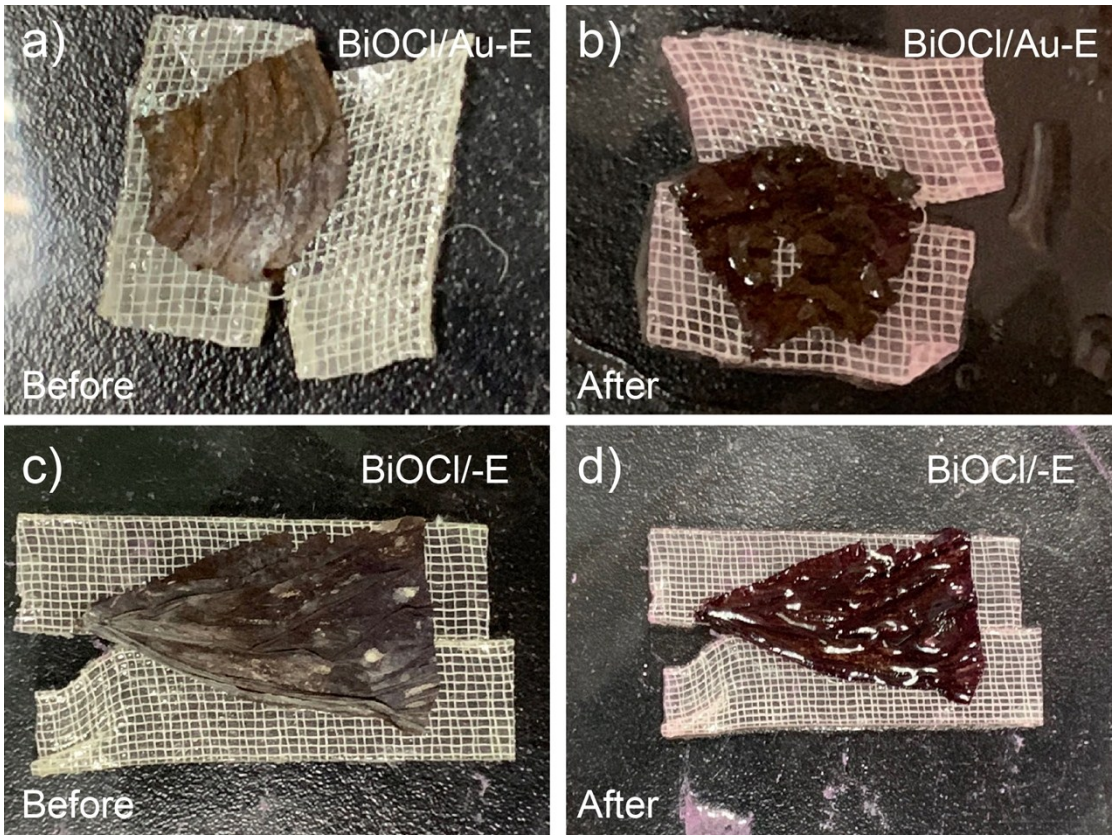

Fig. S12 Optic photos of BiOCl /Au-E and BiOCl-E before and after photocatalysis of RhB.

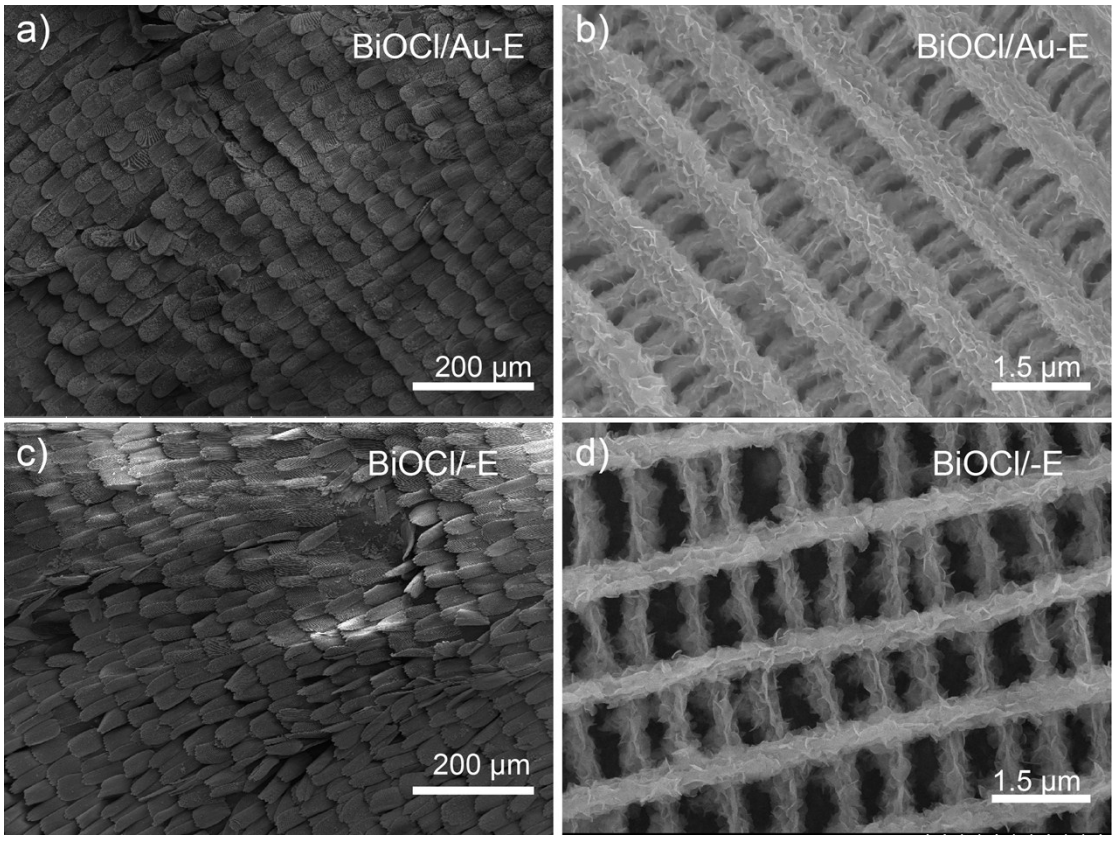

Fig. S13 SEM images of (a, b) BiOCl/Au-E and BiOCl-E (c, d) after photocatalysis of RhB.

Table S1. ICP data of BiOCl-E and BiOCl/Au-E.

Catalyst	Bismuth mass ratio (%)	BiOCl content (%)
BiOCl-E	45.86	57.23
BiOCl/Au-E	27.41	34.21

Table S2. The degradation rates (DR) of BiOCl microspheres, BiOCl-E and BiOCl/Au-E within 20-min-illumination under different monochromatic light irradiation (435 nm, 525 nm, and 600 nm respectively).

Catalyst	DR-435nm (%)	DR-525 nm (%)	DR-600 nm (%)
BiOCl microsphere	7.2	8.8	9.6
BiOCl-E	13.4	12.3	12.5
BiOCl/Au-E	16.7	23.3	17.2

References

1. Y.-C. Pu, G. Wang, K.-D. Chang, Y. Ling, Y.-K. Lin, B. C. Fitzmorris, C.-M. Liu, X. Lu, Y. Tong and J. Z. Zhang, *Nano letters*, 2013, **13**, 3817-3823.

2. M. Guan, C. Xiao, J. Zhang, S. Fan, R. An, Q. Cheng, J. Xie, M. Zhou, B. Ye and Y. Xie, *J. Am. Chem. Soc.*, 2013, **135**, 10411-10417.