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# Supporting Information

## 2 Bioinspired hierarchical 3D flowers-in-ridges hybrid structure for persistent organic

## 3 pollutants photodegradation

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## 5 1. Experimental Details

## 6 1.1 Materials and Chemicals

Euploea mulciber (E. mulciber) butterfly, also known as 'striped blue crow', is commonly 7 found in Eastern Asia nations such as Malaysia, Laos, Thailand, Singapore, Vietnam and China. 8 E. mulciber belongs to subfamily Danainae of family Nymphalidae, with wingspan of 80-90 9 mm. Dorsal side of male's forewing is dark brown and distinctly adorned with iridescent blue 10 and many white spots. E. mulciber butterfly wings were acquired from Sichuan Insects 11 Education and Science Base (Sichuan, China). Bismuth nitrate pentahydrate (Bi(NO<sub>3</sub>)<sub>3</sub>.5H<sub>2</sub>O), 12 sodium tungstate dihydrate (Na<sub>2</sub>WO<sub>4</sub>·2H<sub>2</sub>O), ethylenediaminetetraacetic acid (C<sub>10</sub>H<sub>16</sub>N<sub>2</sub>O<sub>8</sub>  $\geq$ 13 99.5%), sodium tetrahydroborate (NaBH<sub>4</sub>  $\ge$  98%), gold (iii) chloride hydrate (HAuCl<sub>4</sub>·3H<sub>2</sub>O) and 14 15 absolute ethanol were purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). Sodium hydroxide (NaOH  $\geq$  96.0%) was purchased from Shanghai Ling Feng Chemical 16 17 Reagent Co. Ltd. (Shanghai, China). Isopropanol (IPA), benzoquinone (BQ), ammonium oxalate (AO) and silver nitrate (AgNO<sub>3</sub>) were purchased from J&K China Chemical Co. Ltd. 18 (Shanghai, China). Rhodamine B (RhB) and methylene blue (MB) were purchased from 19 Shanghai Aladdin Biochemical Technology Co. Ltd. (Shanghai, China). All chemicals acquired 20 21 in this experiment were used as acquired without any further refinement.

#### 22 1.2 Characterization

BW-Bi<sub>2</sub>WO<sub>6-x</sub> and P-Bi<sub>2</sub>WO<sub>6</sub> sample morphologies and energy dispersive X-ray spectroscopy 23 (EDS) were characterized by Raman image-scanning electron microscope, fitted with an EDAX 24 detector (Rise-Magna, Czech Republic), while transmission electron microscopy and high-25 resolution transmission electron microscopy (HRTEM) were performed using field emission 26 transmission electron microscope (FE-TEM; STEM F200x, U.S.A). Additionally, powder X-27 Ray diffraction (XRD) measurements were performed on a Rigaku Mini flex diffractometer 28 29 (Mini Flex 600, China) with Cu Ka radiation filtered through Ni absorber. FTIR spectra of the samples was obtained by a Nicolet 6700 Fourier transform infrared spectrometer in the range 30 of 4000-400 cm<sup>-1</sup>. Furthermore, X-ray photoelectron spectroscopy (XPS) data was recorded by 31

a Kratos Analytical Axis UltraDLD UHV spectrometer with a monochromatized Al Ka X-ray 32 33 source (1486.6 eV) scanning a spot size of 700 µm × 300 µm (Shimadzu, Japan). Raman spectra were recorded using a Renishaw inVia Qontor Raman spectrometer (Renishaw, UK) equipped 34 with an Argon ion laser (514 nm) having 1 cm<sup>-1</sup> spectral resolution, a confocal microscope with 35 different objective lenses and a CCD detector. The surface area and pore size distribution were 36 characterized through the Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) 37 methods on a Quantachrome Autosorb-IQ3 adsorption analyzer at 77 K. The UV-vis diffuse 38 reflectance spectra were obtained using a Perkin Elmer Lambda 750s UV/Vis spectrometer 39 (Waltham, MA, U.S.A) equipped with an integrating sphere assembly at a wavelength range of 40 250-800 nm and a 1.0 nm sampling interval. Rhodamine B intermediates mineralization were 41 42 analyzed through ultra-high-performance liquid chromatography-electrospray tandem mass 43 spectrometry using an Acquity UPLC System (Waters) equipped with an Acquity UPLC BEH 44 C18 column (2.1 mm x 100 mm, 1.7 µm particle size) coupled to a triple-quadrupole mass spectrometer (Xevo TQ-S MS; Waters, U.S.A) kept at 40 °C, and sample vials were kept at 20 45 46 °C. Methanol/water (95/5) containing formic acid at 0.001 % was chosen as the mobile phase. The flow rate was 0.2 mL/min, and the injection volume was 2 µL. 47

### 48 1.3 Photocatalytic Cycles Test and Reactive Species Test

49 Photocatalytic cycle tests were done by degrading rhodamine B (RhB) under the visible light using BW-Bi<sub>2</sub>WO<sub>6-x</sub> photocatalyst, as described in the photocatalytic activity procedure. After 50 51 each cycle, the photocatalyst was retrieved by centrifugation, washed with de-ionized water and dried before being suspended into fresh aqueous RhB solution. Subsequently, photocatalytic 52 53 process was repeated to obtain the individual cycles. Radical trapping experiments were performed by adding 2 mM ammonium oxalate (AO, traps h<sup>+</sup>), 2 mM Silver nitrate (AgNO<sub>3</sub>, 54 55 traps e<sup>-</sup>), 0.05 mM benzoquinone (BQ, traps ·O2<sup>-</sup>) or 2 mM isopropanol (IPA, traps ·OH) into rhodamine B (RhB) solution before the photocatalytic reaction. 56

# 57 2. Figures and Tables



- 58
- 59 Fig. S1 (a) Scanning electron micrograph illustrating low and higher magnification images
- 60 (inset) of  $P-Bi_2WO_6$  sample. (b) TEM and HR-TEM (inset) images of  $P-Bi_2WO_6$  sample. (c)
- 61 scanning electron micrograph of as-synthesized BW-Bi<sub>2</sub>WO<sub>6-x</sub> sample and (d) HR-TEM image
- 62 of BW-Bi<sub>2</sub>WO<sub>6-x</sub> sample with yellow dotted lines demarcating areas of surface distortion.



64 Fig. S2 Degradation graphs depicting use of  $BW-Bi_2WO_{6-x}$  photocatalyst in degrading (a) MB,

65 (b) RhB and (c) 4-CP. In comparison, P-Bi<sub>2</sub>WO<sub>6</sub> photocatalyst was used in the degradation of

66 (d) MB, (e) RhB and (f) 4-CP, under UV light ( $\lambda$ =365 nm) irradiation.



68 Fig. S3 Degradation graphs depicting use of BW-Bi<sub>2</sub>WO<sub>6-x</sub> photocatalyst in degrading (a) MB,

69 (b) RhB and (c) 4-CP. In comparison, P-Bi<sub>2</sub>WO<sub>6</sub> photocatalyst was used in the degradation of

70 (d) MB, (e) RhB and (f) 4-CP, under Vis light ( $\lambda$ >400 nm) irradiation.



72 Fig. S4 Degradation graphs depicting use of BW-Bi<sub>2</sub>WO<sub>6-x</sub> photocatalyst in degrading (a) MB,

73 (b) RhB and (c) 4-CP. In comparison, P-Bi<sub>2</sub>WO<sub>6</sub> photocatalyst was used in the degradation of

74 (d) MB, (e) RhB and (f) 4-CP, under NIR light ( $\lambda$ >700 nm) irradiation.

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Fig. S5 ESI mass spectra of *N*-de-ethylated intermediates from the RhB degradation using BW-Bi<sub>2</sub>WO<sub>6-x</sub> photocatalyst, detected by UPLC. (a-d) Shows ionic spectra for specific intermediates ( $t_R$ ).

HPLC	m/z	Identified Intermediates	Structural Formula
Peaks			
RhB	443.2328	Rhodamine B	(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> N (C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> N (C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> N (C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>
I	415.2016	N,N-Diethyl-N'- Ethylrhodamine	(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> N O N <sup>+</sup> HC <sub>2</sub> H <sub>5</sub> COO <sup>-</sup>
II	387.1703	N,N-diethylrhodamine	$(C_2H_5)_2N$ $O$ $N^+H_2$ $COO^-$
III	387.1703	N-ethyl-N'-ethylrhodamine	C <sub>2</sub> H <sub>5</sub> NH COO <sup>-</sup>
IV	331.1084	Rhodamine 110	

79 Table S1 Identification of RhB degradation intermediates by UPLC



