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An effective general method for building advanced Z-scheme photocatalyst: case of WO_3/Bi_2WO_6

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Experimental part

1. Materials

Sodium tungstate dihydrate, nitric acid and rhodamine B were purchased from Sinopharm Chemical Reagent Co., Ltd, Lead. Bismuth nitrate pentahydrate was bought from Aladdin (China). Ethylene glycol was gotten from Tianjin Hengxing Chemical Reagent Co., Ltd. All materials are analytical reagent，using without further purification. Ultra-pure water was homemade by YL-100BD (ELION).

2. Preparation of materials

Preparation of Bi_2WO_6

Bi_2WO_6 was prepared by hydrothermal method. Firstly, 2.5 mmol of $Na_2WO_4·2H_2O$ and 1.25 mmol of $Bi(NO_3)_3·5H_2O$ were dissolved in 15 ml of deionized water and stirred for 10 min, respectively. Then, $Na_2WO_4·2H_2O$ solution was added to $Bi(NO_3)_3·5H_2O$ solution and stirred for 30 min. Finally, the mixed solution was transferred into a 50 ml Teflon-lined stainless steel autoclave, sealed and kept at 180℃ for 12 h. The obtained yellowish precipitation was washed with deionized water three times and dried at 60℃ for 12 h to obtain Bi_2WO_6.

Preparation of WO_3/Bi_2WO_6

WO_3/Bi_2WO_6 was prepared through a cation exchange method. Typically, 0.53g $Na_2WO_4·2H_2O$ was dissolved in 14 ml of ultra-pure water, 1ml ethylene glycol was added, and the mixture was stirring for 10 minutes. Then, 3 ml nitric acid was dropped into the above solution, bright yellow sediment was obtained after stirring 4 hours. Subsequently, the precipitate was washed with the ultra-pure water 6 times to ensure neutrality. The as-prepared deposit was dispersed into 20ml of ultra-pure water, adding a certain amount of $Bi(NO_3)_3·5H_2O$ with stirring for 30 minutes. Finally, the above mixture was placed into a Teflon-lined stainless steel autoclave (50 ml), sealed and maintained at 180℃ for 12 hours. The product was washed with ultra-pure water and dried at 60 ℃ for 12 hours. The prepared samples are labeled as WB-x, WO_3 were synthesized using same method without adding Bi^{3+}. The detailed information is shown in Table S1.

Preparation of $Pt/WO_3/Bi_2WO_6$

The $Pt/WO_3/Bi_2WO_6$ composites were prepared by photoreduction method. The details of the experiment are as follows: 0.2g composite WO_3/Bi2WO_6 was dissolved in a mixture of 60 ml deionized water and 20 ml methanol, and placed in an ultrasonic cleaning machine for 15 minutes. And then, the mixed solution was placed on a magnetic stirrer and stirred for 5 minutes in the dark, continuously. After the solution was evenly mixed, 4ml 50mg/100ml chloroplatinic acid solution was added, xenon lamp was turned on, and the dark gray mixed solution was obtained under the 300 W xenon lamp to irradiate for 30 min. Finally, the mixed solution was filtered, washed and dried at 60℃ for 4 h to generate $Pt/WO_3/Bi_2WO_6$.

3. Characterization

The crystallinity and purity of as-prepared samples were characterized by a powder X-ray diffractometer (XRD, RigakuD/max-2000) equipped with a Cu-Kα radiation at a scanning rate of 10° min^{-1} in the 2θ range of $10\text{-}90^{\circ}$. The morphologies and microstructures characterizations were measured on the scanning electron microscopy (SEM, TESCAN MIRA3) and transmission electron microscopy (TEM, JEOL JEM-2100F). X-ray photoelectron spectroscopy measurement (XPS) was performed on a Thermo Scientific ESCA Lab 250 spectrometer which consists of a monochromatic Al Kα as the X-ray source. All of the binding energies were calibrated by the C1 speak at 284.8 eV. UV-vis diffuse reflectance spectroscopy (UV-vis DRS) was carried out on an ultraviolet-visible spectrophotometer (UNICO 2800-A) with $BaSO_4$ was used as a reflectance standard. AUTOLAB electrochemical workstation (PGSTAT302N) with a conventional three-electrode cell was employed to measure the photoelectrochemical responses of as-prepared samples. A Pt wire and Ag/AgCl served as counter and the reference electrodes, respectively, and 0.5 M Na_2SO_4 was used as supporting electrolyte in this system. The visible light source was provided by a 300 W Xenon lamp (Perfect Light PLS-SXE300). All of the electrochemical measurements were implemented at room temperature.

4. Photocatalytic experiment

The photocatalytic activity of as-prepared photocatalysts was evaluated by degradation of RhB dye under a 300W Xenon lamp. The details were as follows: 50 mg of photocatalyst was dispersed in a 5 mg/L of RhB solution (100 mL), the suspension was ultrasonic for five minutes and stirred in the dark for 30 min to insure a complete adsorption-desorption equilibrium. When lighting commences, 2 mL of solution was withdrawn and centrifuged at fixed time intervals, the absorbance of the solution was analyzed with a UV-vis spectrophotometer.

Growth mechanism

Fig. S1 SEM images of the various samples (a, g) H_2WO_4, (b, h) WB-1, (c, i) WB-2, (d, j) WB-3, (e, k) WB-4, (f, l) Bi_2WO_6.

Homologous heterojunction WO_3/Bi_2WO_6 were synthesized by hydrothermal method using ethylene glycol as surface modifier. The specific growth mechanism of WO_3/Bi_2WO_6 samples, with different Bi^{3+} content, was revealed by the scanning electron microscope (SEM), as shown in Fig.S1. The overall morphology of as-samples shows the spherical structures (Fig.S1 (a-f)). Partial enlarged drawing of corresponding samples is shown in Fig. S1 (g-l), whose spherical structure is composed of small flower pieces with uniform size. Careful analysis shows that with the increase of Bi^{3+} content, the petals become larger and denser, and the surface clusters become more crowded and closer. This phenomenon can be explained as: when Bi^{3+} are present in H_2WO_4 system, which will insert into the $[WO_6]$ layer of H_2WO_4 to form $[Bi_2O_2]^{2+}$ layer; with the prolonging of reaction time, more $[Bi_2O_2]^{2+}$ will randomly link adjacent H_2WO_4 in the system, which displays the overlap between sheets. Under hydrothermal conditions, the $[WO_6]/[Bi_2O_2]$ structure will grow further to create Bi_2WO_6 crystal phase. At the later stage, the dehydration of H_2WO_4, due to the lower concentration of Bi^{3+}, to form WO_3. The formation mechanism of WO_3/Bi_2WO_6 is shown in Fig. S1. Thus, during the hydrothermal reaction, the [OH] are replaced by $[Bi_2O_2]$, the ion layer dissolves and recrystallizes to form the composite heterojunction with continuous transition of two-phase grain boundaries.

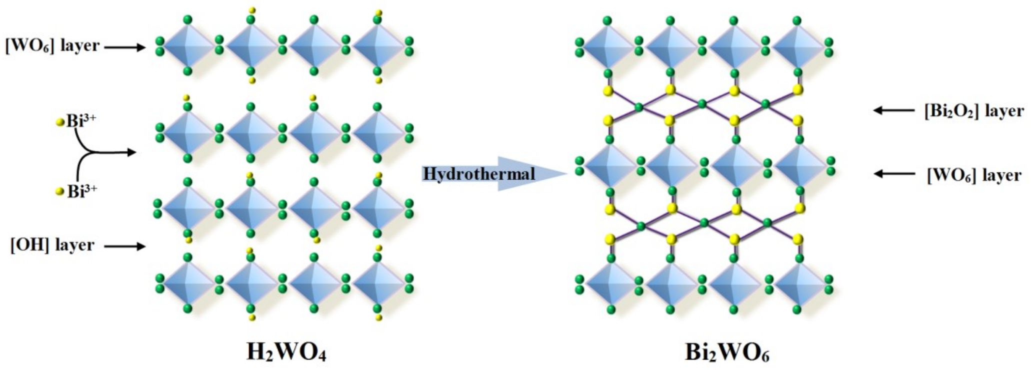

Fig. S2 The growth schematic structure of WBs.

The Bi^{3+} in the system is inserted into the $[WO_6]$ layer of H_2WO_4 to form the $[Bi_2O_2]^{2+}$ layer, and the $[Bi_2O_2]^{2+}$ is randomly connected to the adjacent H_2WO_4. Moreover, the $[WO_6]/[Bi_2O_2]$ structure grows up, to generate Bi_2WO_6 crystal phase and remaining H_2WO_4 dehydrates to form WO_3 in the system. Therefore, during the hydrothermal reaction, the [OH] are replaced by $[Bi_2O_2]$, the ion layer dissolves and recrystallizes to form the composite heterojunction with continuous transition of two-phase grain boundaries.

Fig. S3 The SEM images of (a) Bi_2WO_6 and (b) WB-3.

Fig. S3 shows that the lamellar structure of the surface of Bi_2WO_6 is much larger than that of the composite sample WB-3, and the gap between the sheets is more obvious. This may be due to the WO_3 transformed in-situ on the surface of Bi_2WO_6 and recrystallized. Under high temperature and high pressure, WO_3 and Bi_2WO_6 couple to form a three-dimensional hierarchical structure, with large specific surface area and more adsorption sites, which is helpful to improve the catalytic activity of photocatalytic materials.

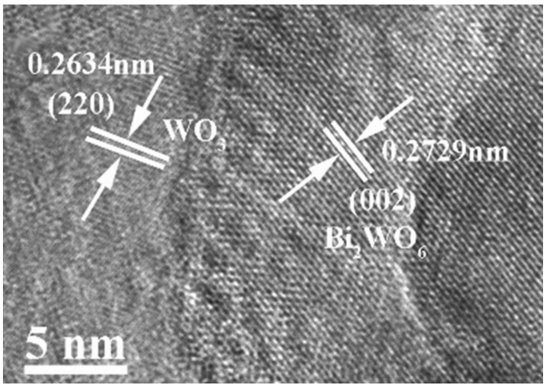

Fig. S4 The HRTEM images of WB-3 sample.

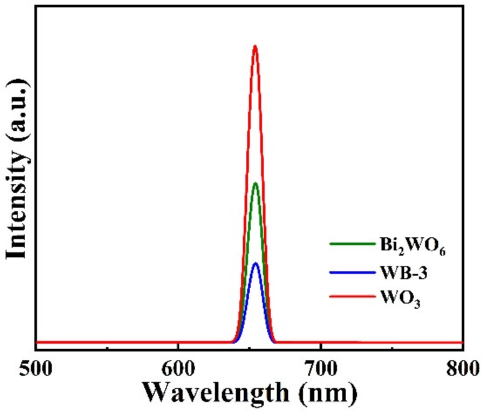

Fig. S5 (a) Steady-state PL spectra

Fig. S6 (a) Recycled photodegradation of RhB over WB-3, (b) XRD

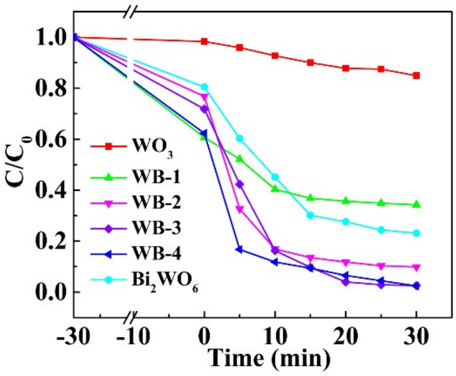

Fig. S7 Degradation TC curves of the prepared samples under visible light irradiation.

Table S1. The short name of synthesized samples with different synthesis condition

sample	Condition	lable

	$NaWO_4 \cdot H_2O$(g)	$Bi(NO_3)_3 \cdot 5H_2O$(g)	HNO_3(ml)	Ethylene glycol(ml)	
1	0.53	0	3	1	WO_3
2	0.53	0.388	3	1	WB-1
3	0.53	0.776	3	1	WB-2
4	0.53	0.97	3	1	WB-3
5	0.53	1.164	3	1	WB-4
6	0.4123	1.2127	0	0	Bi_2WO_6

Table S2. XPS data of WO_3, Bi_2WO_6, and WB-3.

	O 1s (eV)	W 4f (eV)	Bi 4f (eV)	VB (eV)	O (%)	W (%)	Bi (%)
WO_3	530.4 531.4	35.6 37.8	-	2.68	40.83	5.36	-
WB-3	529.3 531.4	35.9 38.1	159.1 164.5	-	44.17	7.78	5.43
Bi_2WO_6	529.3 530.2 531.4	35.6 37.8	159.4 164.7	1.66	30.39	8.22	16.27

Table S3. The corresponding report of Bi_2WO_6, WO_3 and composite photocatalysts for RhB degradation

Photocatalysts	RhB (mg/L)	Time (min)	Dosage (ml/mg)	Light Source	Efficiency (%)	Refs.

Bi_2S_3@Bi_2WO_6/WO_3	20	180	30/30	UV filter 400 W Xe-lamp	96 %	[1]
Bi_2WO_6@BiOI	24	300	100/100	UV filter 500 W Xe-lamp	100 %	[2]
Bi_2WO_6/BiOI	10	120	40/40	UV filter 300 W Xe-lamp	100 %	[3]
WO_3/Bi_2WO_6	24	180	100/100	UV filter 400 W metal halide lamp	100 %	[4]
BiOBr/Bi_2WO_6	24	60	150/150	Xe-lamp	97.5 %	[5]
Bi_2WO_6-Phosphate	10	60	100/50	UV filter 400 W metal halide lamp	100 %	[6]
Ag/Ag_2O/Ag_3PO_4/Bi_2WO_6	5	60	100/50	500 W Light-lamp	99.9 %	[7]
Bi_2WO_6	10	100	50/50	Xe-lamp	70 %	[8]
WB-3	5	15	100/50	300 W Xe-lamp	99.5 %	This work

Table S4. BET surface areas of the prepared samples

Samples	WO_3	WB-1	WB-2	WB-3	WB-4	Bi_2WO_6
BET Surface Area (m^2/g)	1.59	61.75	27.58	27.14	36.11	16.31

参考文献

（1） Fabrication of Bi_2S_3@Bi_2WO_6/WO_3 ternary photocatalyst with enhanced photocatalytic performance: synergistic effect of Z-scheme/traditional heterojunction and oxygen vacancy

（2）Hierarchical BiOI and hollow Bi_2WO_6 microspheres: Topochemical conversion and photocatalytic activities

（3）Insight into visible light-driven photocatalytic performance of direct Z-scheme Bi_2WO_6/BiOI composites constructed in -situ

（4）One-step hydrothermal preparation strategy for nanostructured WO_3/Bi_2WO_6 heterojunction with high visible light photocatalytic activity

（5）Microwave-hydrothermal synthesis of BiOBr/Bi_2WO_6 nanocomposites for enhanced photocatalytic performance

（6）Doping effect of phosphate in Bi_2WO_6 and universal improved photocatalytic activity for removing various pollutants in water

（7）Polyethylene glycol (PEG)-modified $Ag/Ag_2O/Ag_3PO_4/Bi_2WO_6$ photocatalyst fifilm with enhanced effificiency and stability under solar light

（8）Spiral carbon fibers modified Bi_2WO_6 with enhanced photocatalytic activity