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MoS_2/Bi_2O_3 heterojunctions in Z-scheme for enhanced separation efficiency of charge carriers and photocatalytic degradation performance

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Experimental

1. Materials

Sodium molybdite dihydrate ($Na_2MoO_4 \cdot 2H_2O$, 99.5%) was purchased from Aladdin Reagent. Thiocarbamide ($CS(NH_2)_2$, 99.0%), sodium hydroxide (NaOH, 99.8%), bismuth nitrate pentahydrate ($Bi(NO_3)_3 \cdot 5H_2O$, 98.0%), ethanol (C_2H_5OH), isopropanol (IPA), triethanolamine (TEOA), Vitamin c (Vc) and 5,5-dimethyl-L-pyrroline N-oxide (DMPO) were all purchased from Sinopharm Chemical Reagent Co., Ltd. All materials were used as received without further purification.

2. Synthesis

First, 1.21 g $Na_2MoO_4 \cdot 2H_2O$ and 1.56 g $CS(NH_2)_2$ were dissolved in 60 mL distilled water. Then, the mixed solution was stirred for 30 min, and moved to a 100 mL Teflon-lined autoclave. Meanwhile, the mixture was put at 180 ℃ for 24 h. After that, a black precipitate was achieved by centrifuging, and it was washed using distilled water and absolute ethanol for some times. Then the black precipitate was put into the distilled water and sonicated, and with a centrifugation at 2000 rpm. Finally, the MoS_2 nanosheets were got and dried at 60 ℃ for 8 h.

Second, the Bi_2O_3 solid rods were attained by a typical synthesis. 4.8 g of $Bi(NO_3)_3 \cdot 5H_2O$ was dispersed in 100 mL distilled water stirring for 30 min. Then using NaOH (10 M) to adjust the pH of solution to 8.0 and sonicated for 60 min. The mixture was stirred overnight and then precipitated. Using distilled water and absolute ethanol to wash the precipitate for some times and dried at 60 ℃ for 12 h. Finally, the light yellow precipitate was calcined at 400 ℃ for 2 h with a heating rate of 1 °C/min in air to obtain Bi_2O_3 solid rods.

Finally, the Z-scheme MoS_2/Bi_2O_3 heterojunction was constructed a facile and practical hydrothermal method. 0.1 g Bi_2O_3 and a certain

concentration of MoS_2 were put into 40 mL absolute ethanol and stirred for 30 min. Then mixture was sonicated for 30 min and moved into a Teflon-lined autoclave heated at 140 ℃ for 6 h. In the same way, the preparation of Z-scheme MoS_2/Bi_2O_3 heterojunction with different mass ratios of MoS_2 to Bi_2O_3 (abbreviated as 5%, 10%, 15% 20% and 25% of MoS_2/Bi_2O_3) were got.

3. Characterization

In order to analyze the crystal structure and phase purity, the prepared samples are characterized by a D8ADVANCE X-ray diffractometer (Bruker AXS Co., Germany) at room temperature, and record the X-ray diffraction (XRD) patterns at 10-80º with a scanning step of 7º/min. For getting the energy dispersive x-ray spectra (EDX), an EDS Inca X-Max (Oxford, UK) is used. It uses an S-4800 field emission SEM (SEM, Hitachi, Japan) to observe the morphology and the elemental mapping of as-prepared samples with a scanning electronic microscopy (SEM). The transmission electron microscopy (TEM) of samples is investigated on JEM-2100F transmission electron microscopy (JEOL, Japan). Using Thermo ESCALAB 250X (America) to describe the X-ray photoelectron spectroscopy (XPS). The diffuse reflectance spectra (DRS) (UV-2450; Shimazu, Japan) is also performed to observe the light absorption and energy band features of photocatalysts. The surface area, pore volume and average pore size of these photocatalysts are examined by a NOVA 3020e analytical system (Quantachrome Co., U.S.A.), and it can attain the Brunauer-Emmett-Teller (BET) measure. A VersaSTAT 3 electrochemical station (Princeton Applied Research, American) is used in this part to research transient photocurrent and electrochemical impedance spectroscopy (EIS). For analyzing the intermediate degradation product, the mass spectrometry is carried out using a HPLC-MS instrument composed of Perkin-Elmer Norwalk, CT) Series 2000

HPLC with the Finnigan MAT900 mass. In the end, electron spin resonance (ESR) spectroscopy is gone on a Bruker A300 ESR spectrometer at room temperature.

4. Photocatalytic and trapping experiments

To evaluate the photocatalytic activities of as-prepared various samples, the degradation experiments of MBT, TC and RhB are carried out as bellow. A 250 W xenon lamp with a 420 nm cutoff filter is applied as a light source. The photocatalytic experiments are as following: 50 mg photocatalyst is added into 100 mL solution which contains 10 mg/mL MBT. Then the solution is stirred for 30 min to achieve the adsorption–desorption equilibrium. After that, the solution of 5 mL is sampled and centrifuged at 20 min intervals. Meanwhile, the photocatalytic degradation of TC and RhB are also processed within the same experiment conditions except for the use of 20 mg/mL TC and 10 mg/mL RhB. Furthermore, the active species trapping experiments are as same as the above photocatalytic experiments, only add 1 mL triethanolamine (TEOA, a quencher of h^+), 1 mL isopropanol (IPA, a quencher of ·OH), and 0.176 g Vitamin c (Vc, a quencher of $\cdot O_2^-$) respectively to catch various radicals during the photocatalytic reducing course. Then an UV-vis spectrophotometer is used to monitor the supernatant.

5. Photoelectrochemical measurement

In order to detect the photoelectrochemical performance, the Z-scheme MoS_2/Bi_2O_3 heterojunction is tested by the photocurrent response and electrochemical impedance spectroscopy (EIS) in a 450FRA 2A electrochemical station. Shortly, 0.05 g photocatalyst and 0.01 g polyvinyl pyrrolidone (PVP) are dissolved in 3 mL ethanol and 30 μL oleic acid. Then 0.05 ml of this mixture is dipped onto FTO substrates (1.0 cm^2) and regarded as corresponding working electrodes. And a Pt plate and a saturated Ag/AgCl electrode are as the counter electrode and

the reference electrode respectively. In addition, a 0.5 M Na_2SO_4 aqueous solution was used as the electrolyte.

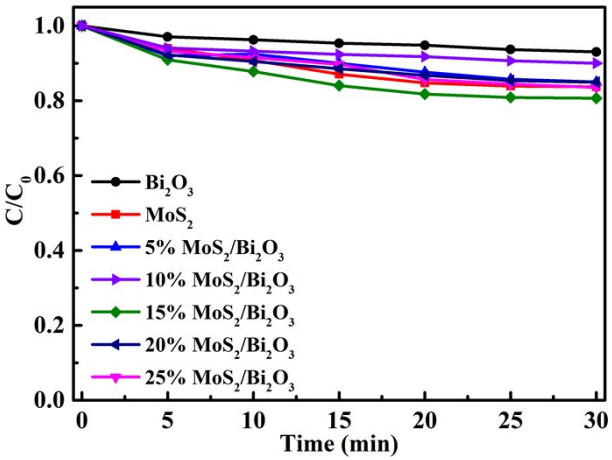

Fig. S1. The adsorption curves of MBT over different photocatalysts.

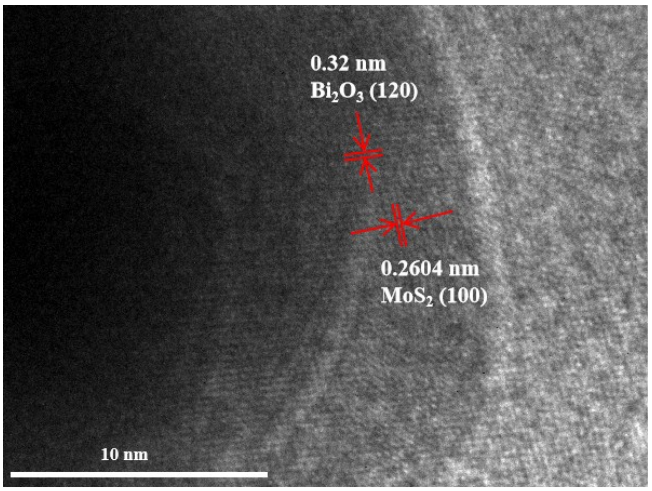

Fig. S2. HRTEM images of MoS_2/Bi_2O_3 heterojunction.

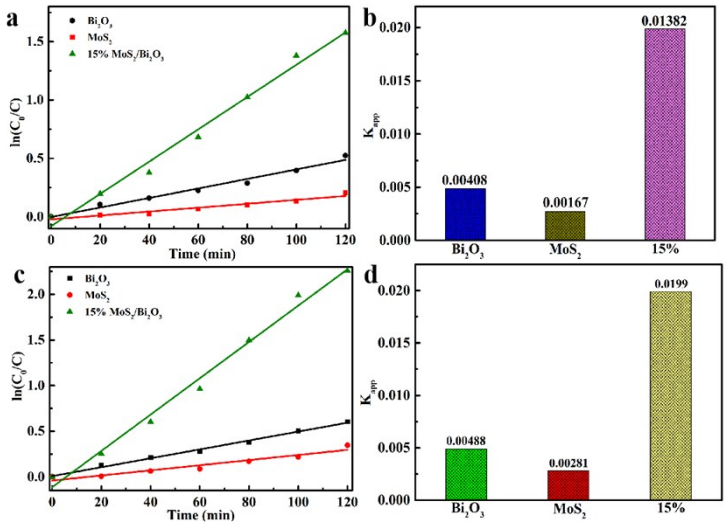

Fig. S3. (a) The pseudo-first-order reaction kinetics of TC; (b) Values of reaction rate constants of TC over the as-prepared samples; (c) The pseudo-first-order reaction kinetics of RhB; (d) Values of reaction rate constants of RhB over the as-prepared samples.