

Supporting Information

Construction of α -Fe₂O₃/Bi₂O₃ p-n heterojunction with exceptional visible-light photocatalytic performance for dye removal

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1 Experimental Section

1.1 Chemicals and materials

All the chemicals were analytical grade reagents and used as received. All the solutions were prepared using double distilled water (DDW). Iron foils (99.5 % purity, Goodfellow) of 1 mm in thickness were sliced into sizes of $10 \times 10 \text{ mm}^2$, sonicated in ethanol solution for a few minutes, rinsed with DDW and dried in N_2 flow.

1.2 Synthesis of $\alpha\text{-Fe}_2\text{O}_3$ NTAs

$\alpha\text{-Fe}_2\text{O}_3$ NTAs was prepared *via* the anodization-calcination method. The pure iron foil was served as the anode and graphite sheet as the counter electrode, respectively. Potentiostatic anodization reaction was carried out in a mixture of 0.35 wt% NH_4F and 3.0 vol% DDW and connected with a direct current power supply (IT6154, ITECH, Nanjing, China) at 55 V for 500 s. Then the samples were cleaned with DDW, placed in the ceramic boat and annealed in a quartz tube furnace. The temperature increased to $450 \text{ }^\circ\text{C}$ with a heat rate of $10 \text{ }^\circ\text{C}/\text{min}$ and kept for 2 h.

1.3 Preparation of $\alpha\text{-Fe}_2\text{O}_3/\text{Bi}_2\text{O}_3$ NTAs

$\alpha\text{-Fe}_2\text{O}_3/\text{Bi}_2\text{O}_3$ NTAs was synthesized through a facile hydrothermal process. 1.2 g of bismuth nitrate pentahydrate ($\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$) and 0.5 g of polyvinylpyrrolidone (PVP) were dissolved in 100 mL DDW and agitated for 60 min. The pH value of the mixture was adjusted to 8 by using NaOH solution (0.1 M). The precursor solution was transferred to a 50 mL Teflon-lined autoclave and the anodized foil was immersed in the above precursor. Then the autoclave was sealed into a stainless steel tank and maintained at $160 \text{ }^\circ\text{C}$ for 1-3 h. Afterwards, the foil was washed with DDW for three times and dried in air at $60 \text{ }^\circ\text{C}$ for 12 h. The as-synthesized $\text{Fe}_2\text{O}_3/\text{Bi}_2\text{O}_3$ composites with 1 h, 1.5 h, 2 h, 2.5 h and 3 h were named as FB-1, FB-1.5, FB-2, FB-2.5 and FB-3, respectively. Finally, the precipitate was collected by centrifugation, washed for three times with DDW and dried in air at $60 \text{ }^\circ\text{C}$ for 12 h to obtain Bi_2O_3 powder for further experiments and characterization.

1.4 Analytical characterizations

The field-emission scanning electron microscopy (FE-SEM, FEI Nova 400 Nano, Eindhoven, Netherlands) was employed to examine the morphologies of the samples. Transmission electron microscopy (TEM, JEM-2100UHR STEM/EDS, JEOL, Japan)

and high-resolution transmission electron microscopy (HRTEM) equipped with energy dispersive X-ray spectrometry (EDS) were conducted to investigate crystalline structure. The X-ray diffraction (XRD) pattern was recorded on a X-ray diffractometer with the monochromatized Cu K α radiation over the 2 θ range of 10°-90° (XRD, Philips X'Pert Pro, Eindhoven, Netherlands). The UV-Vis diffuse reflectance spectroscopy (DRS) were carried out using a double beam UV-Vis spectrophotometer (TU-1901, Purkinje General, Beijing, China) over the wavelength range between 200 and 800 nm.

1.5 Photocatalytic performance

The samples were immersed into a quartz reactor comprising 20 mL methylene blue (MB) with original concentration of 5 mg L⁻¹. The visible light source was a 500W Xe lamp equipped with an ultraviolet cut-off filter. The quartz vessel was set in a black case whose left was open. The interval between the light source and quartz vessel was 3 cm. To attain the adsorption-desorption balance on the surface of photocatalyst, the solution was agitated for 1 h without visible light irradiation. After equilibration, the concentration of MB was tested as the initial concentration (C₀). 2 mL MB was taken from the upper part of the solution at 15 min intervals. The concentration of the MB (C) was measured *via* the UV-Vis spectrophotometer at the absorbance peak of 664 nm. The adsorption capacity of the MB dye for the samples was negligible (<6%) after 12 h. The degradation efficiency (DE) of MB was determined using the formula: $DE=(C_0-C)/C_0$.

Five successive MB degradation were performed to study the stability of FB-2. After each photocatalytic run, the sample was extracted, rinsed with DDW, air-dried and reused. Then the photocatalyst was placed into the new MB solution to carry out the circular reaction.

The primary reactive species of hydroxyl radicals (\bullet OH), holes (h⁺) and superoxide radicals (\bullet O₂⁻) generated in the degradation procedure were detected through radical trapping tests. Similar experimental procedures over FB-2 were carried out except that diverse scavengers, containing 1 mM of p-benzoquinone (BQ), 1 mM of disodium ethylenediaminetetraacetate (EDTA) and 1 mM of methanol, were added into MB (25 ml, 5 mg L⁻¹). The total organic carbon (TOC) content was

determined using a Shimadzu TOC 5000A analyzer. In the TOC test, FB-2 was dispersed in MB solution (5 mg L^{-1} , 50 mL).

1.6 Photoelectrochemical measurement

Photocurrent density and electrochemical impedance spectroscopy (EIS) were measured on CHI 660E electrochemical workstation (CH Instruments, Shanghai, China). The as-prepared foil was employed as the working electrode, platinum wire as the counter electrode and Ag/AgCl (saturated with KCl) as the reference electrode, respectively. 0.1 M Na_2SO_4 aqueous solution was employed as electrolyte. The photoelectric response measurements were operated at 0.8 V bias vs Ag/AgCl with the 500 W Xenon lamp on-off switches of 20 s. EIS curves were recorded by applying an AC voltage of 5 mV.