Constructing a *p-n* heterojunction between Bi_2WO_6 and Co_3O_4 for enhanced photothermocatalyic of toluene degradation

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Experimental

Materials

Cobalt Acetate ($Co(CH_3COO)_2 \cdot 4H_2O$), cetyltrimethylammonium bromide (CTAB), Sodium tungstate dihydrate ($Na_2WO_4 \cdot 2H_2O$) and Bismuth nitrate pentahydrate ($Bi(NO_3)_3 \cdot 5H_2O$) was bought from Shanghai Shanpu Chemical Co., Ltd. Urea, glycol, deionized (DI) water, Anhydrous ethanol was bought from Guangzhou Keqi Chemical Technology Co., Ltd.

Synthesis of the Catalysts

Synthesis of Co_3O_4 precursors: the Co_3O_4 precursors were synthesized through a solvothermal method. Specifically, 15 mmol of $Co(CH_3COO)_2 \cdot 4H_2O$ were dissolved in 70 mL of glycol and stirred for 30 min. Subsequently, 30 mL of urea was added to the above red mixture and stirred for 1 h. The resulting suspended solution was moved into a 100 mL reaction vessel to undergo solvothermal reaction at 180℃ for 12 h. The obtained product was centrifuged, washed alternatively washed with water and ethanol four times, and dried at 80℃ for 12 h.

Synthesis of Bi_2WO_6/Co_3O_4 FHNs: 1 mmol Co_3O_4 precursor prepared above was dissolved in 40 mL of water. Separately, dissolve 1 mmol of $Bi(NO_3)_3 \cdot 5H_2O$, 0.025 g of CTAB and 1 mmol of $Na_2WO_4 \cdot 2H_2O$ were separately in 40 mL water and stirred for 1 h. Then, the two suspensions were thoroughly mixed and moved to 100 mL reaction vessel for a hydrothermal reaction at 160℃ for 24 h. The obtained product was separated by centrifugation, washed four times using deionized water and ethanol, and dried at 80℃ for 12 h. Finally, the composites were obtained by calcining the collected precipitates at

350°C for 2 h. The synthesized composite was denoted as Bi_2WO_6/Co_3O_4 FHNs-2. Using the identical method, only changing the molar ratios of $Bi(NO_3)_3 \cdot 5H_2O/Co_3O_4$ FHNs to 2:1 and 1:2, Bi_2WO_6/Co_3O_4 FHNs-1 and Bi_2WO_6/Co_3O_4 FHNs-3 were obtained, respectively. The pure Bi_2WO_6 catalyst was obtained using the same process without Co_3O_4 precursor.

Catalysts characterization

The crystal structure of samples was recorded by powder X-ray diffraction (XRD, Bruker D8 Advance) using Cu Kα radiation and Fourier Transform Infrared spectroscopy (FT-IR-21 Shimadzu spectrometer). The morphology and structure of samples were taken with the scanning electron microscope (SEM, GeminiSEM 500) and transmission electron microscope (TEM, FEI Talos F200x), respectively. The nitrogen adsorption-desorption isotherms were obtained on a Micromeritics-ASAP 2460 Brunauer-Emmett-Teller (BET), the pore size distribution and average pore size were determined through the Barret-Joyner-Halender (BJH) method and the adsorbed nitrongen volume. The optical characteristics of samples was characterized by ultraviolet-visible spectroscopy (UV-vis DRS, Shimadzu UV-2600, Japan). Depending on the UV-vis DRS spectra, the Tauc's equation was utilized to calculate the band gaps: $(\alpha h\nu) = A\ (h\nu - E_g)^{n/2}$. Where, α, h, ν, A and E_g denote the light absorption coefficient, planck constant, light frequency, constant and band gap energy, respectively. Furthermore, the value of n is determined by the properties of transitions in semiconductors. In the case of Bi_2WO_6, it is classified as an indirect gap semiconductor with n set to 1. while Co_3O_4 is considered a direct gap semiconductor with n set to 4.

Photoelectrochemical testing

The electrochemical measurements were carried out at CHI660D electrochemical workstation. The samples coated on conductive glass (FTO, 1*1 cm) acted as working electrodes, while saturated calomel electrode (SCE) and Pt acted as reference and counter electrode, respectively. Typically, 20 mg of prepared catalysts were added to a mixed solution containing 200 μL of water, 50 μL of ethanol and 15 μL 5 wt% Nafion solution. Then, 20 μL of the above mixture was dripped on the surface of the glassy carbon electrode, and then air-dried at room temperature to obtain a working electrode. The normal hydrogen electrode (NHE) potentials are determined using the following the equation: $E_{(NHE)} = E_{(SCE)} + 0.24$. The potential interval of the Mott-Schottky test was near the open circuit potential with a frequency of 1000 Hz, and 0.1 M Na_2SO_4 solution acted as the electrolyte.

Figure

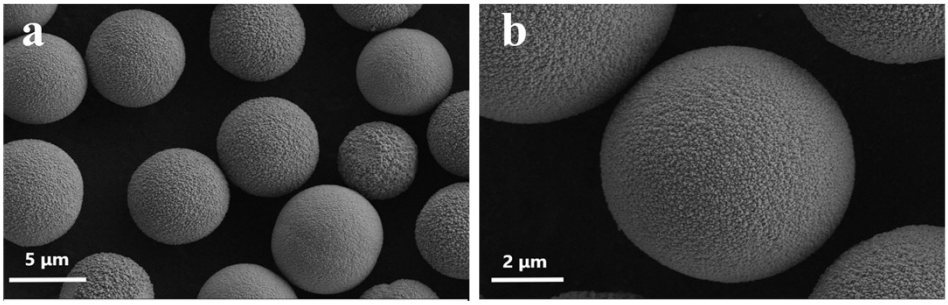

Fig. S1. SEM images of Co_3O_4.

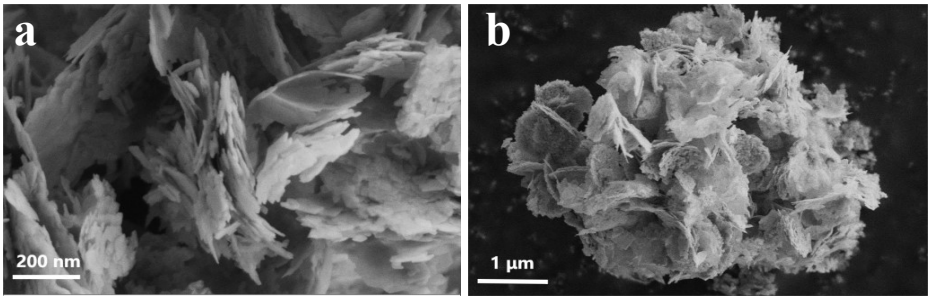

Fig. S2. SEM images of Bi_2WO_6.

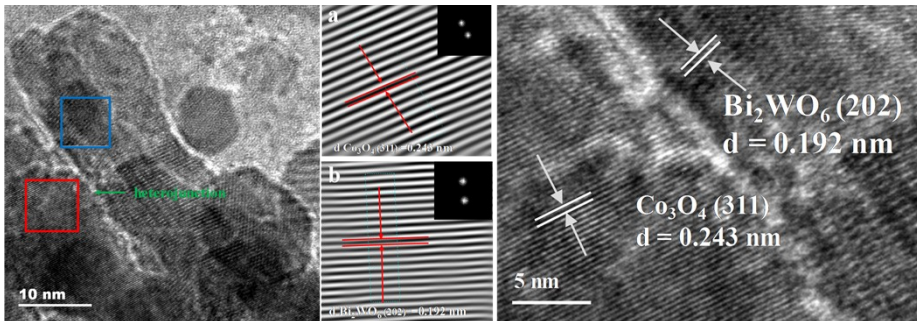

Fig. S3. HRTEM images of Bi_2WO_6/Co_3O_4 FHNs and the right images of panels a and b are the fast Fourier transform (FFT) pattern of the area tagged by the red and blue square box.

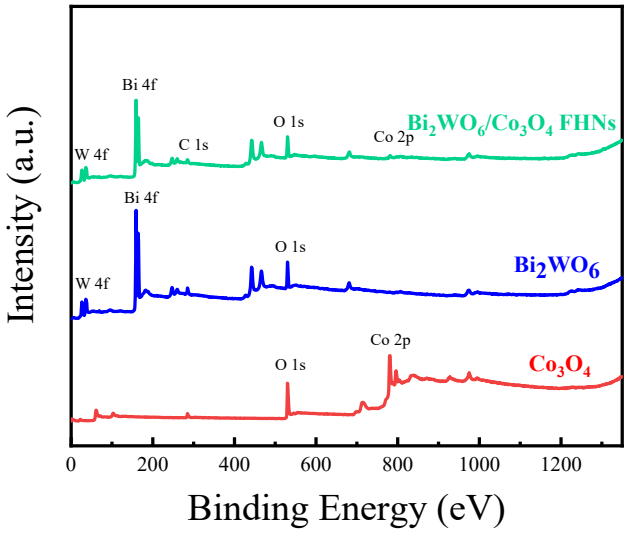

Fig. S4. XPS survey spectra of Co_3O_4, Bi_2WO_6 and Bi_2WO_6/Co_3O_4 FHNs.

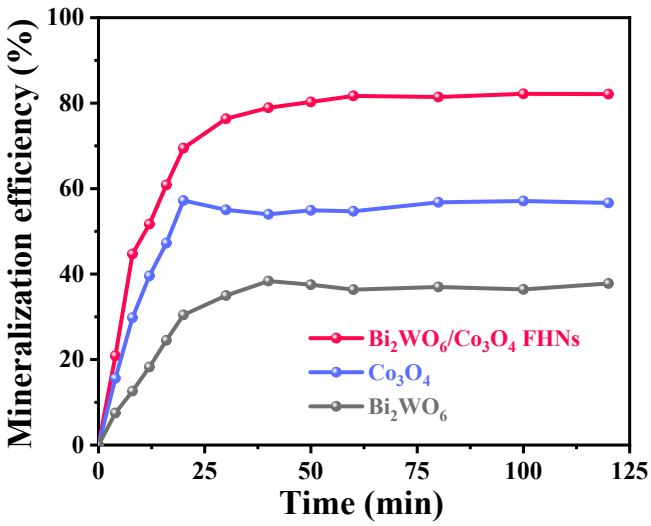

Fig. S5. CO_2 mineralization efficiency

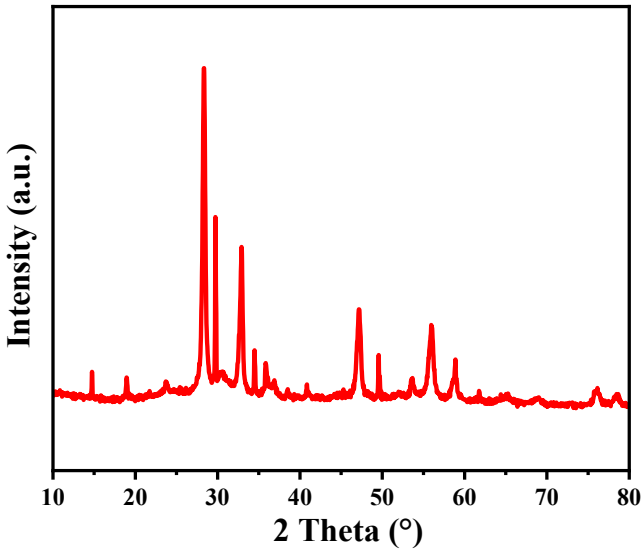

Fig. S6. XRD image of Bi_2WO_6/Co_3O_4 FHNs after cyclic tests.

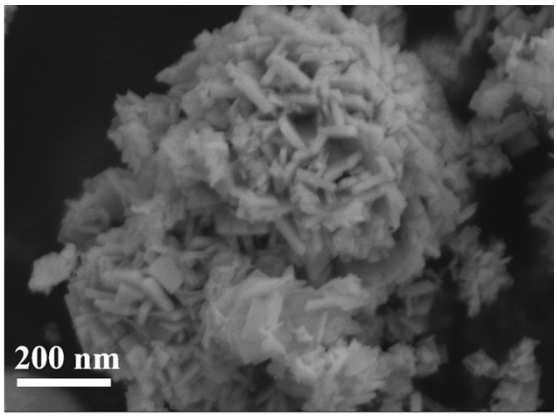

Fig. S7. SEM image of Bi_2WO_6/Co_3O_4 FHNs after cyclic tests.