

Supporting Information

Green preparation of porous hierarchical TiO₂(B)/anatase phase junction for effective photocatalytic degradation of antibiotics

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1. Experimental Section
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3. Photodegradation efficiency of two other typical antibiotics

1. Experimental Section

Materials

Lactic acid, urea, ChCl and ethanol were purchased from Sinopharm Group Chemical Reagent Co., Ltd., Beijing, China. Tetrabutyl titanate (TBOT), OFX, CPFx and CAP were obtained by Macklin Biochemical Co., Ltd., Shanghai, China. All the reagents are directly utilized without further purification.

Synthesis of DES and PHPATO

DES was synthesized by mixing three components ChCl, urea and lactic acid with 2:1:1 molar ratio to form a clear and transparent liquid at 80 °C under continuous stirring for 2 h. TiO₂ sample was prepared by dropwise adding 1 mL TBOT into the mixed solution including 15.5 mL DES and 0.5 mL distilled water under vigorous stirring, transferring the got resulting mixture into a 25 ml Teflon-lined stainless steel autoclave, and then placing the autoclave in an oven at 180°C for 18 h. After natural cooling to room temperature, a white precipitate can be collected by centrifugation, washing alternately with distilled water and absolute ethanol, and drying at 60°C for 4h. Scheme 1 is the graphical synthetic illustration. The synthesis process of pure anatase phase TiO₂ are the same as that of PHBATO, except that the used DES is ChCl/urea prepared by mixing ChCl and urea in a ratio of 1:1.

Characterizations of DES, PHBATO and OFX degradation intermediates

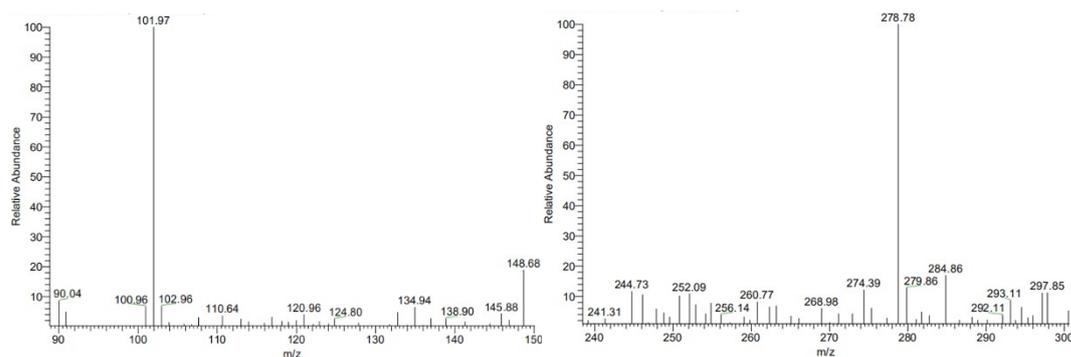
Fourier transform infrared (FT-IR) spectra were characterized by a Varian 3100 FT-IR spectrometer. The crystal structure and crystal phase of the sample were determined by an X-ray diffractometer (XRD, Bruker D8, Germany) with Cu K α radiation. The morphology and microstructure of the sample was tested by scanning electron microscope (SEM, Hitachi S4800), transmission electron microscopy (TEM) and High-Resolution TEM (HRTEM, JEM 2010 EX). Nitrogen adsorption/desorption curves were collected by a Micromeritics ASAP2020. X-ray photoelectron spectroscopy (XPS) spectra were obtained via a Thermo Scientific Escalab250Xi spectrometer equipped with an Al K α Source (1486.6eV). Diffuse reflectance spectroscopy (DRS)

spectrum of the samples and the absorption intensity of antibiotic were measured by an UV-Vis spectrometer (METASH UV-8000). Brunauer-Emmett-Teller (BET) specific surface area of the sample was measured by the Micromeritics ASAP 2020 system at the temperature of liquid nitrogen. Before the BET measurement, the sample was degassed at 150°C for 8 hours. The pore diameter distribution was estimated by the Barrett-Joyner-Halenda (BJH) model. HPLC-MS was utilized to determine the intermediates of OFX degradation process. HPLC system equipped with a C18 column (2.1 mm × 150 mm × 3.0 μm, thermo fisher) was operated at a flow rate of 0.3 mL/min. The mobile phase consists of water (mobile phase A) and methanol (mobile phase B). The gradient elution was programmed as follows: 0-2.0 min, 5 % B; 2.0-10 min, 5 %-95 % B; 10-12 min, 95% B; 12-14 min, 95 %-5 % B; 14-15 min, 5 % B. The sample injection volume was 20 μL.

Photocatalytic activity test

OFX were selected as the main model pollutant to evaluate the catalytic performance of the synthesized TiO₂ catalyst. In general, 5mg PHBATO was added into a quartz tube containing 20mL OFX solution (C₀=10 mg/L) at room temperature, and then the mixture was placed under a 500W mercury lamp for photocatalytic reaction. After the reaction, the supernatant was obtained by centrifugation, and its absorption intensity was measured at 293 nm by an UV-Vis spectrophotometer to calculate OFX degradation rate. The catalytic degradation conditions of CPFX and CAP are the same with that of OFX, while their absorption intensities were tested at 277 nm and 278 nm, respectively.

2. Mass spectra of main intermediates and possible OFX photodegradation pathways



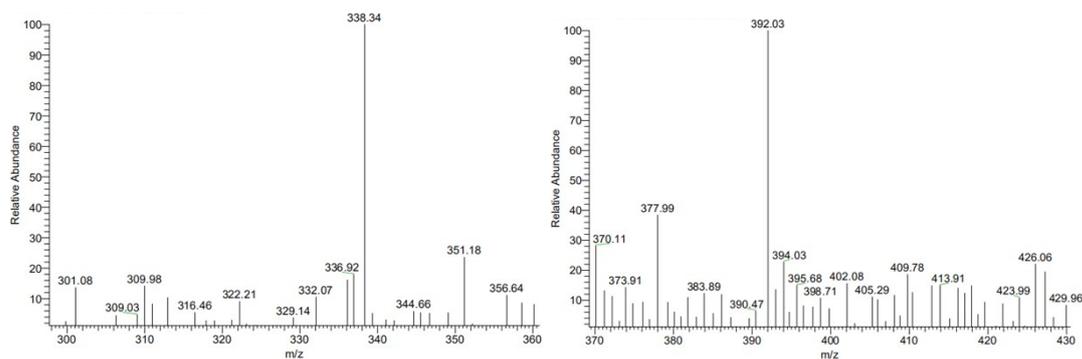


Fig. S1 Mass spectra of main intermediates during OFX degradation process catalyzed by porous hierarchical bronze/anatase phase junction TiO_2 .

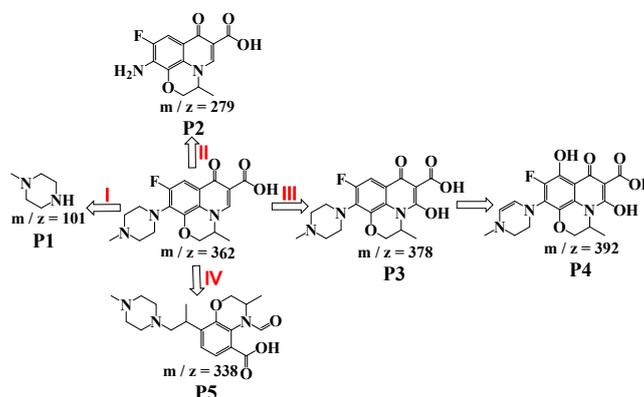


Fig. S2 Possible OFX photodegradation pathways catalyzed by PHBATO.

3. Photodegradation efficiency of two other typical organic pollutants

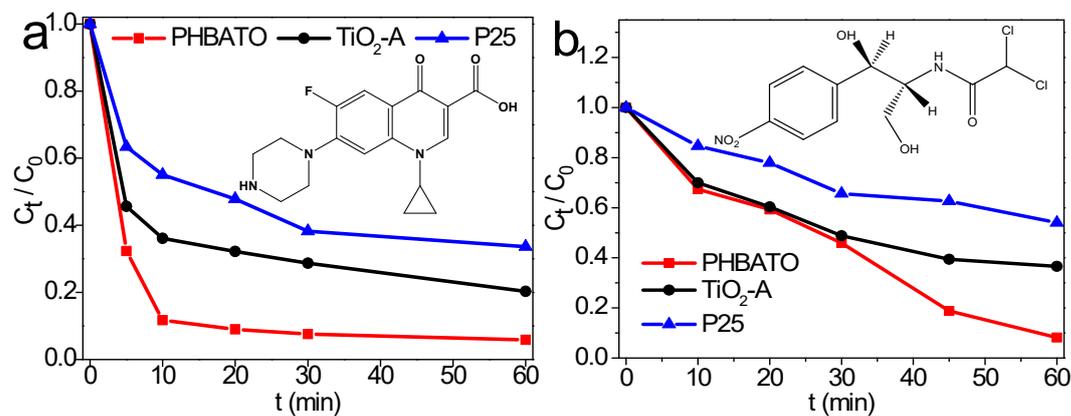


Fig. S3 Effect of catalyst type on photodegradation efficiency of two other typical antibiotics: (a) CPFX and (b) CAP under 0.25 g/L catalyst and 10 mg/L antibiotic.