

Supporting Information

Facile green synthesis of dahlia-like anatase/TiO₂(B) phase junction for boosting photocatalytic degradation of persistent tetracycline

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1. Experimental Section
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1. Experimental Section

1.1 Materials

Oxalic acid, urea, betaine, ChCl , ethanol and ethylene glycol were all purchased from Sinopharm Group Chemical Reagent Co., Ltd., Beijing, China. Tetrabutyl titanate (TBOT), Titanium(III) chloride solution, tetracycline (TC), ciprofloxacin (CPFX) and chloramphenicol (CAP) were provided by Macklin Biochemical Co., Ltd., Shanghai, China. All the reagents are utilized without any purification.

1.2 Synthesis of DES and DABTO

Mixed hydrogen bond acceptor betaine with hydrogen bond donor oxalic acid and urea in a 2:1:1 molar ratio, and stirred at 95°C for 2 h until a clear and transparent liquid appears, which is DES. Then, 1 mL of TBOT was added dropwise into a mixed solution of 15.5 mL DES and 0.5 mL distilled water with vigorous string, and the resulting mixture was transferred to a 25 mL Teflon-lined stainless steel autoclave. Subsequently, the autoclave was placed in an oven and heated at 180°C for 18 h. After being naturally cooled to room temperature, centrifuged to obtain a white precipitate, which was washed alternately with distilled water and absolute ethanol, and then placed in an oven and dried at 60°C overnight. Fig. 1a is the schematic diagram of the synthetic process of DABTO. The pure anatase phase TiO_2 and pure bronze phase TiO_2 were respectively prepared according to the preparation methods reported by references.

1.3 Characterizations of DES and DABTO

Fourier transform infrared (FT-IR) spectra were characterized with a Varian 3100 FT-IR spectrometer. The crystal structure of the sample was determined by an X-ray diffractometer (XRD, Bruker D8, Germany) using $\text{Cu K}\alpha$ radiation. The morphology and microstructure of the sample were examined by scanning electron microscopy (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 collected on a Thermo Scientific Escalab250Xi spectrometer equipped with an $\text{Al K}\alpha$ Source (1486.6eV). Diffuse reflectance spectroscopy (DRS) spectrum of samples and the absorption intensity of antibiotic were measured by an UV-Vis spectrometer

(METASH UV-8000). The hydroxyl radicals and superoxide radicals were tested by using electron spin resonance spectroscopy (ESR, Bruker EMXPLUS). Brunauer-Emmett-Teller (BET) specific surface area of the sample was measured by the Micromeritics ASAP 2020 system at the temperature of liquid nitrogen. The sample were degassed at 150 °C for 8 h before BET measurements. Photoelectrochemical performance measurements were conducted in a three-electrode system on a CHI660E electrochemical workstation.

1.4 Photocatalytic activity test

TC was selected as the main model pollutant to investigate the photocatalytic activities of the synthesized TiO₂ catalysts. Typically, 5 mg DABTO was added into a quartz tube containing 20mL antibiotic 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 276 nm with a UV-Vis spectrophotometer to calculate the TC degradation rate. The catalytic degradation conditions of CPF_X and CAP are the same with that of TC, while their absorption intensities were tested at 273 nm and 277 nm, respectively.

1.5 Photoelectrochemical performance measurements

Photoelectrochemical performance measurements were carried out in a standard three-electrode PEC cell, with TiO₂, mercury/mercuric oxide electrode, and Pt wire as the working electrode, reference electrode and counter electrode, respectively. A 0.5 M Na₂SO₄ solution was used as the electrolyte. Photocurrent responses test was carried out under 350 W Xenon lamp illumination with a bias voltage of 0.6 V. A 1 M NaOH solution was used as the electrolyte. Electrochemical impedance spectroscopy (EIS) was carried out was at open circuit voltage over a frequency range of 0.01-100000 Hz with a bias voltage of 0.5 V.

2. XRD patterns of DABTO before and after reuse four times

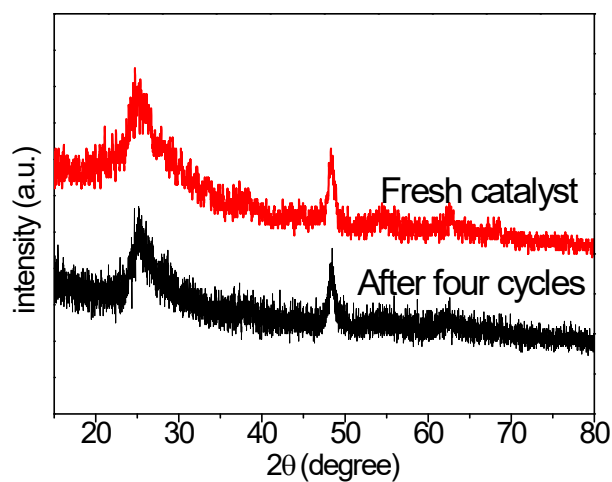


Fig. S1 XRD patterns of DABTO before and after reuse four times.

3. Catalytic degradation activity for chloramphenicol

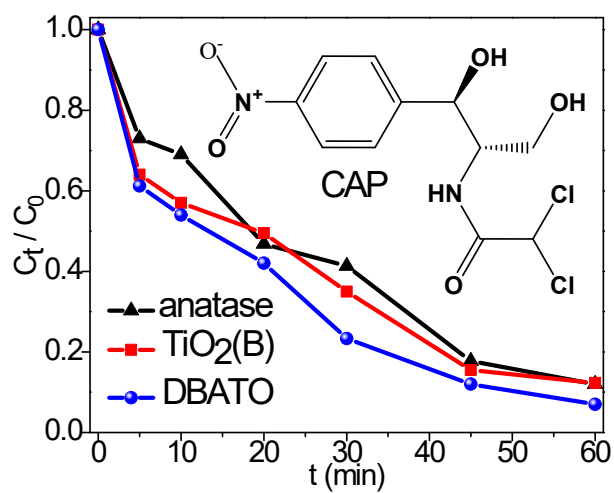


Fig. S2 CAP photodegradation efficiencies catalyzed by pure anatase, pure TiO₂(B) and DABTO (degradation conditions: 0.25 g/L catalyst, 10 mg/L antibiotic solution).