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Supplementary Information

Bifunctional Nest-Like Self-Floated Microreactor for Enhanced Photothermal Catalysis and Biocatalysis

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Materials

Tetrabutyl titanate (TBOT), absolute ethanol (EtOH), ceftazidime, ceftriaxone sodium, cefazolin sodium, hydrofluoric acid (HF, 40%), silver nitrate, concentrated nitric acid, aluminum phosphate, and glacial acetic acid (HAc, 99.5%) were purchased from Tianjin Kermel Chemical Reagent Co. Ltd, China. Sodium boron hydride ($NaBH_4$, 98%) was purchased from Aladdin Reagent Company, China. All of the chemicals used in this work were analytical grade and were employed without further purification. Deionized (DI) water was used throughout this study. The polyurethane foam (abbreviated PUF, Beijing Siqingyuan biological Technology Co, Ltd) had a three-dimensional macroporous network structure. The PUF carriers were cubic shaped with an average length of 1 cm per side and an average pore size of 2 mm. The density of the PUF was 0.8 g cm^{-3}, so the PUF could fluidize easily in the water under the normal aeration intensity.

Synthesis of Ag-doped single crystal black TiO_2 nanosheets

The Ag-doped single crystal TiO_2 nanosheets were prepared by a one-step hydrothermal method. In detail, 1.95 mL of deionized water, 0.3 mL of 40 wt% HF, and 28.6 mL of HAc were mixed together to form a clear solution in a Teflon cup. Then, 1.7 mL of TBOT was added dropwise to the solution with continuous stirring. After magnetic stirring for 30 min, the mixture was transferred into a 50 mL Teflon-lined stainless steel autoclave, which was heated at 180 °C for 24 h. After hydrothermal reaction, the white powders obtained were collected and washed with distilled water and ethanol three times and dried overnight at 60 °C. Finally, the as-prepared samples were calcinated at 450 °C in air for 2 h. The samples were denoted TiO_2 nanosheets. A total of 300 mg of the as-prepared TiO_2 nanosheets were mixed with 50 mL of DI water, and the mixed solution was ultrasonicated for 10 min. Then, 3 mL of $AgNO_3$ solution (1 g L^{-1}) was added to the above dispersion. The mixed solution was irradiated by a Xe lamp (PLXQ500W) 365 nm in wavelength for 30 min. The last product was rinsed with absolute ethanol and DI water three times (denoted Ag-TiO_2). Subsequently, 0.3 g of the sample obtained and 0.3 g $NaBH_4$ were thoroughly milled for 30 min. Then, the mixed sample was placed in a tubular furnace to anneal at 350 °C for 60 min with a heating rate of 6 °C min^{-1} under Ar atmosphere. After naturally cooling the sample in the tubular furnace under Ar atmosphere, the product obtained was rinsed with DI water and anhydrous ethanol three times. The sample was prepared and named Ag-TiO_{2-x}.

Carrier biofilm cultivation

The carrier was immersed in activated sludge for 7 days to culture the biofilm. The inoculated activated sludge came from the CASS process tank of a sewage treatment plant in Harbin (44°04′N and 125°42′E). The carrier was acclimated by adding the organic pollutant (ceftazidime, ceftriaxone sodium and cefazolin sodium) solution by a sequencing batch process. The concentration of teftazidime solution was gradually increased from 5 to 30 mg L^{-1} during the acclimation stage. The experiment was carried out in the winter, and the photocatalytic circulating-bed biofilm reactor (PCBBR) was placed in a cool room. The room temperature was kept at 12±2 °C. The photocatalytic process was carried out by the PCBBR with the uninoculated Ag-TiO_{2-}

$_x$/PUF carriers. The sole biological process was carried out by the PCBBR without vis-IR Light. The schematic diagram of the PCBBR can be seen in Fig. S1. A laboratory scale quartz glass reactor with a liquid volume of 1 L (inside diameter 8 cm × height 20 cm) was used in the study. A quartz sleeve was placed in the middle of the reactor, and a lamp was placed in the quartz sleeve. The bottom of reactor was aerated, which allowed fluidization.

Characterization

X-ray diffraction (XRD, model D/max RA, Rigaku Co. Japan with Cu Kα radiation) was conducted to analyze the crystal phase and composition of the samples. Raman measurements were performed with a Jobin Yvon HR 800 microRaman spectrometer at 457.9 nm. Diffuse reflectance spectra were recorded using a Varian Cary 5000 UV-vis spectrophotometer in the 200-2000 nm range at room temperature using $BaSO_4$ as a reference. X-ray photoelectron spectroscopy (XPS) was performed on a Kratos-ULTRA AXIS DLD system with an Al-Kα X-ray source. Scanning electron microscopy (SEM) micrographs were obtained with a Philips XL-30-ESEM-FEG instrument operating at 20 kV. Energy dispersive X-ray spectrometry (EDS) microanalysis of the samples was performed. Transmission electron microscopy (TEM) was performed using a JEM-2100 electron microscope (JEOL, Japan). The total organic carbon (TOC) removal was tested by TOC analysis using an Analytik Jena multi N/C 2100 analyzer. Thermal images were taken with a thermal imager (Testo Co., Ltd., Testo 865) to perform quantitative analyses of the photothermal effects of samples. The COD was measured using a water quality detector (5B-3C, Lianhua, China) according to the manufacturer’s instructions. A scanning Kelvin probe (SKP) test (SKP5050 system, Scotland) was conducted to evaluate the work function at ambient atmosphere. The change in the surface of the carrier is clearly shown by the scanning electron microscopy. Fig. S2a shows that the unloaded PUF surface is very smooth. Fig. S2b shows the support of the catalyst. Clearly, the catalyst is distributed well on the surface of the support. Fig. S2c shows the uniform biofilm on the carrier.

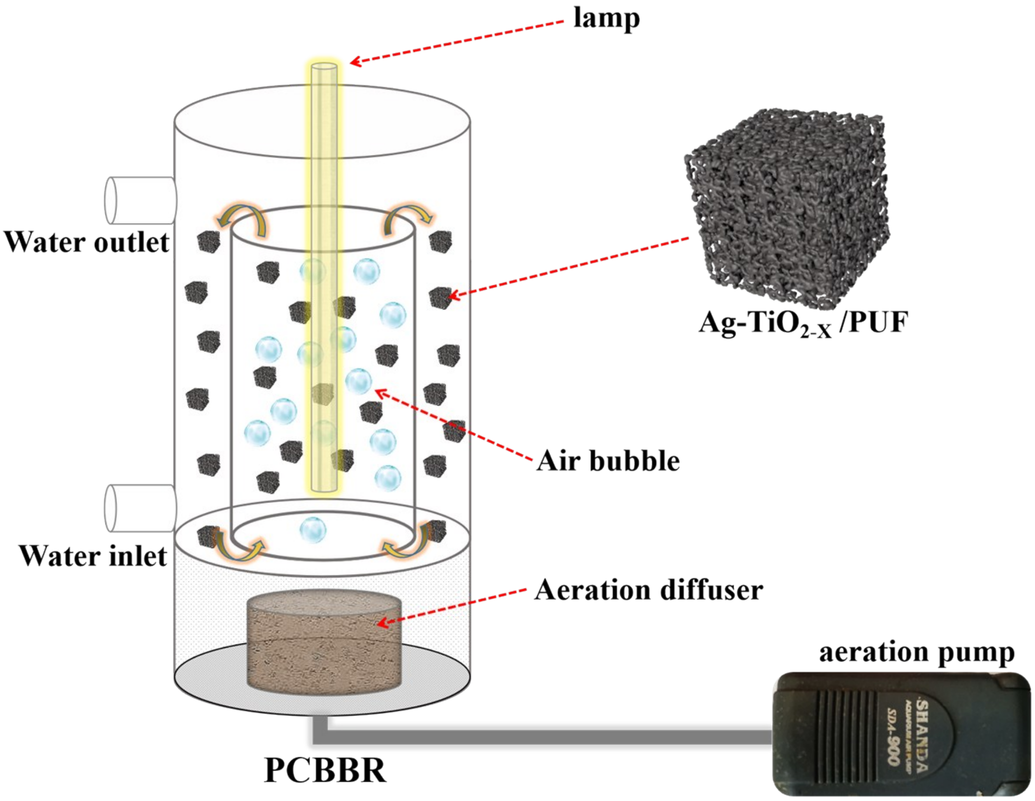

Fig. S1.The schematic diagram of PCBBR.

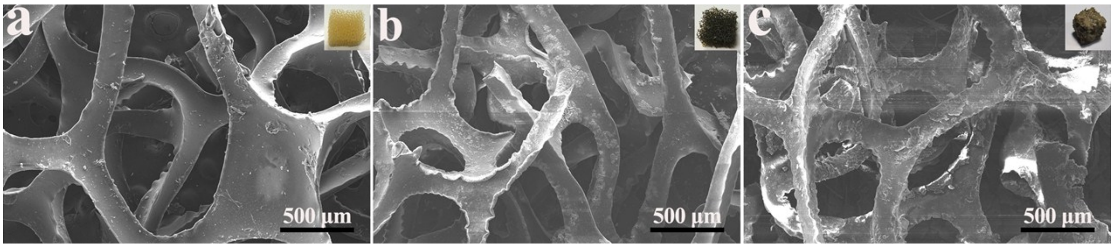

Fig.S2. SEM images of the PUF (a), Ag-TiO$_{2\text{-}X}$/PUF (b) and Ag-TiO$_{2\text{-}X}$/PUF biological membrane (c), respectively.

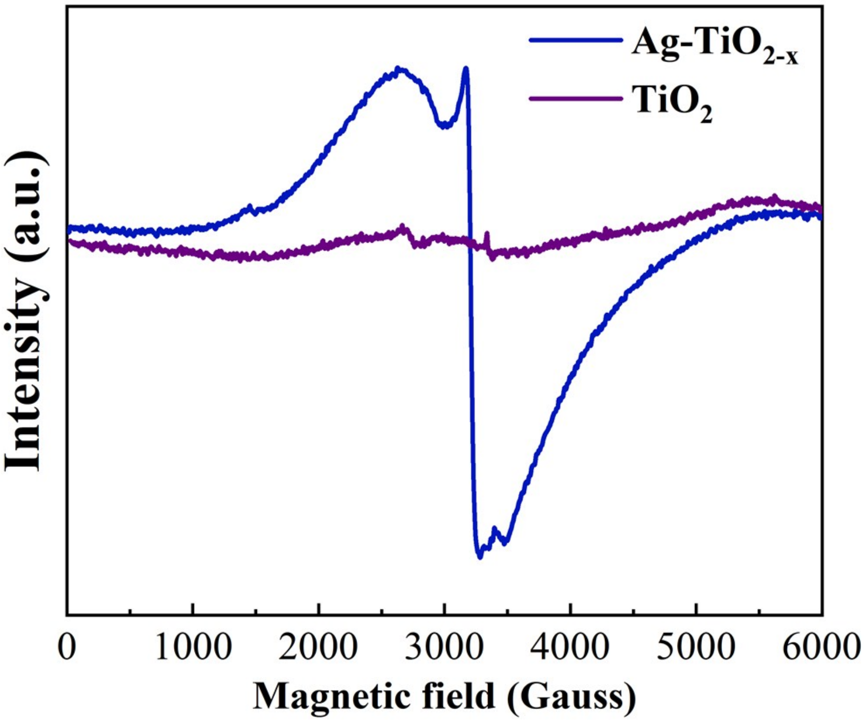

Fig. S3. The EPR spectra of Ag-TiO_{2-x} and TiO_2.

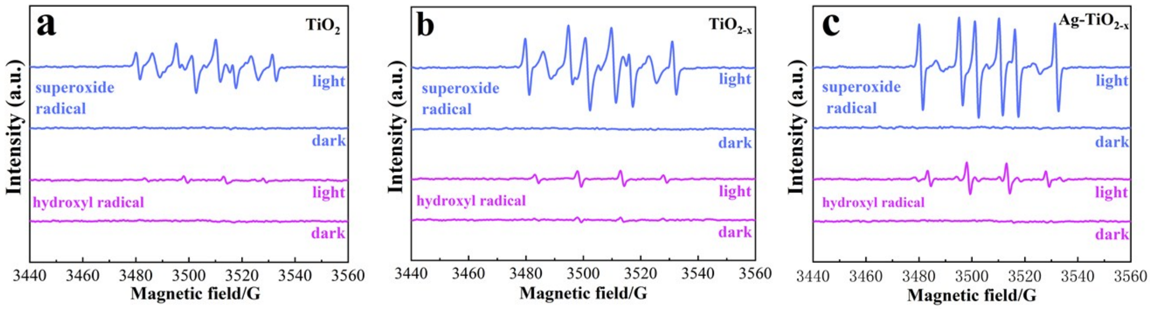

Fig. S4 The EPR radical characterizations for TiO_2 (a), TiO_{2-x} (b) and Ag-TiO_{2-x} (c).

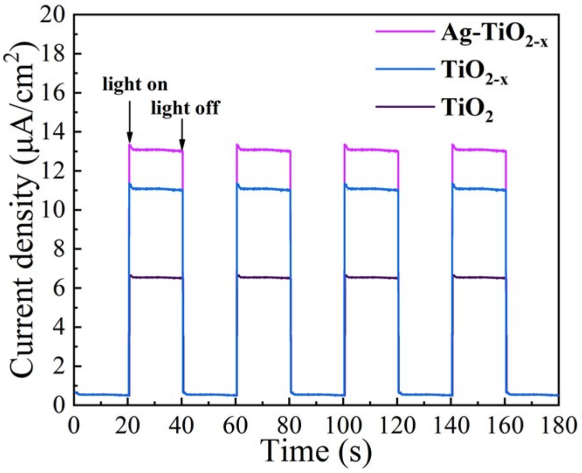

Fig. S5. The transient photocurrent responses of TiO_2, TiO_{2-x} and Ag-TiO_{2-x}