

Supporting Information

1. Methods and experiment section:

1.1 Preparation of nanoporous TiO₂ spheres:

All chemicals were used as received without further purification.

Tetra-n-butyl Titanate (purchased from Alfa Aesar Co. Ltd., named as TBT in this paper), placed parallel with a dosage of 4 mL, were dissolved into 100ml ultra pure ethanol (named as EtOH). After this, this mixture was transferred to a three-neck flask (capacity, 250 mL) and was heated at 393 K for 15 min in the oil bath. Stable at this temperature and with vigorous stirring, a flow of water gas (1 mL/min) was introduced into this solution to promoted hydrolysis of Tetra-n-butyl Titanate, and then a whiter suspension rapidly appeared in the reactor and water gas supply for 100 minutes. The suspension was heated to 453 K, maintained for 4 h. The whiter suspension was cooled to room temperature by removing the flask from the oil bath. The suspension was mixed with ethanol and the particles were precipitated through centrifugation at 10000 rpm for 15 min, and washed with ethanol and water several times. Finally, nanoporous TiO₂ spheres were achieved through calcinating the samples at 773 K for 5 h to promote crystallization.

1.2 Synthesis of the N-modify TiO₂ spheres:

Firstly, 1 g as-prepared nanoporous TiO₂ spheres were dispersed in 100 mL 1, 2-ethylenediamine (AR) solution. And then, treatment of the spheres suspension at 423 K in the oil bath results in the formation of a yellowish suspension. After the suspension cooled to room temperature, the precipitate was washed with ethanol and

water several times. Upon vacuum drying for 12 hours, the treated TiO₂ spheres forms deep-yellow crystallites.

1.3 Electrochemical test

Electrochemical test experiments were performed with an IM6e potentiostat (Zahner Elektrik Company, Germany) in a conventional three-electrode cell. The electrode assembly consisted of a platinum wire as the counter electrode, an Ag/AgCl/KCl (sat) electrode as the reference electrode, and a GCE as the working electrode. The measurement buffer contained 1M KCl and 5 mM [Fe (CN)₆]^{4-/3-} as redox indicator. CV was recorded in the range [-1 V to 1 V] and a scan rate of 0.1 V/s. The GC electrode was prepared as follows: prior to the surface coating, the GC electrode was polished carefully with 0.5 μm and then with 0.05 μm alumina powder, and followed by sonication in 1:1 nitric acid/water (v/v), acetone and in doubly distilled water successively. The surface of GC electrodes was allowed to dry under nitrogen atmosphere. The samples (P25, PTS, and N-PTS.) were ultrasonically dispersed in water to form a homogeneous dispersion (1mg/mL). The surface of GC electrode was coated with 5 μL of the sample and then dried in air. The surface of modified GC electrode was further coated with 5 μL of Nafion ethanol solution (0.2 wt %) and then dried in air before the electrochemical experiments.

1.4 Photocatalytic abilities test:

Photodegradation of rhodamine B (RhB):

A 100 W tungsten-halogen was positioned inside a cylindrical vessel, surrounded by a circulating water jacket for cooling. 0.1 g of photocatalyst (P 25, PTS, and N-

PTS) was suspended in 100 mL aqueous solution of 20 ppm RhB. The solution was stirred for 4 h to ensure the establishment of an adsorption–desorption equilibrium. The system was then irradiated with tungsten-halogen light and during the irradiated, 3 mL aliquots were removed at certain time intervals and analyzed on a UV-Vis spectrophotometer to record concentration.

Photodegradation of benzene:

A sealed box (64 L) was equipped with three 8 W visible light lamps on top, and the box soleplate scattered with 1 g of photocatalyst (P 25, PTS, and N-PTS), 1ml benzene was injected into this box and started the fans let the polluted gas (15.6 ppm benzene) cycled in this box for 4 h to ensure the establishment of an adsorption–desorption equilibrium. After that, the polluted gas exposure to the visible light and during the irradiated, 10 μ L aliquots were removed at certain time intervals and analyzed on a gas chromatography (Agilent 7890A), measuring the benzene concentration in the remaining gas.

Photodegradation of inorganic toxic pollution (Cr^{6+}):

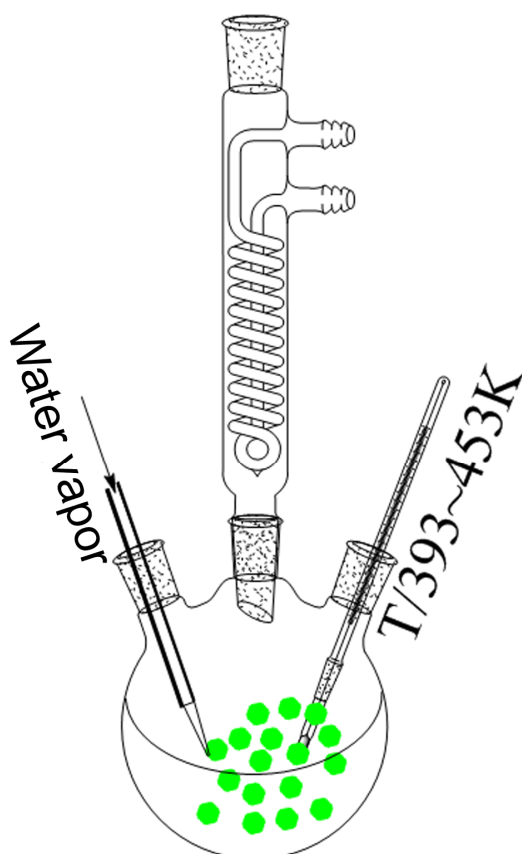
Two 50 W tungsten-halogen was positioned inside a cylindrical vessel, surrounded by a circulating water jacket for cooling. 0.1 g of photocatalyst (PTS) and 1.0404 g CHOONa were suspended in 100 mL aqueous solution of 50 ppm $\text{K}_2\text{Cr}_2\text{O}_7$. The solution was stirred for 4 h to ensure the establishment of an adsorption–desorption equilibrium. The system was then irradiated with tungsten-halogen light and during the irradiated, 3 mL aliquots were removed at certain time intervals and analyzed on a UV-Vis spectrophotometer to record concentration. There are two compare

experiments carried out. One of the experiments, the addition is CHOONa , and the other is PTS.

1.5 Measurement and Characterization.

The obtained products were characterized by X-ray powder diffraction (XRD) using a X'Pert-ProMPD (Holand) D/max- γ A X-ray diffractometer with Cu $K\alpha$ radiation ($\lambda = 0.154178\text{nm}$). XRD samples were prepared by drying a dispersion of sample on a piece of Si wafer. Scanning electron microscopy (SEM) images were taken on a FEI-quanta 200F scanning electron microscope with acceleration voltage of 20 kV. Transmission electron micrographs (TEMs) were taken on a FEI-Tecnai F20 (200 kV) transmission electron microscope (FEI). X-ray Photoelectron Spectroscopy were obtained by using a KRATOS Axis ultra-DLD X-ray photoelectron spectrometer with a monochromatised Mg $K\alpha$ X-ray ($h\nu = 1283.3\text{eV}$). XPS samples were prepared by drying a dispersion of sample on a piece of Si wafer. Room temperature UV-Vis absorption was recorded on a Lambda 750 (PerkingElmer) spectrophotometer in the wavelength range of 200-800 nm. The small-angle X-ray scattering (SAXS) was carried out on the BL16B1 beamline in the Shanghai Synchrotron Radiation Facility (SSRF), while the Scanning transmission X-ray microscopy (STXM) was carried out on the BL08U beamline in SSRF.

2. Figures



TBT-EtOH mixed solution

Figure S1. Illustration of the reaction equipment of the nanoporous TiO_2 spheres.

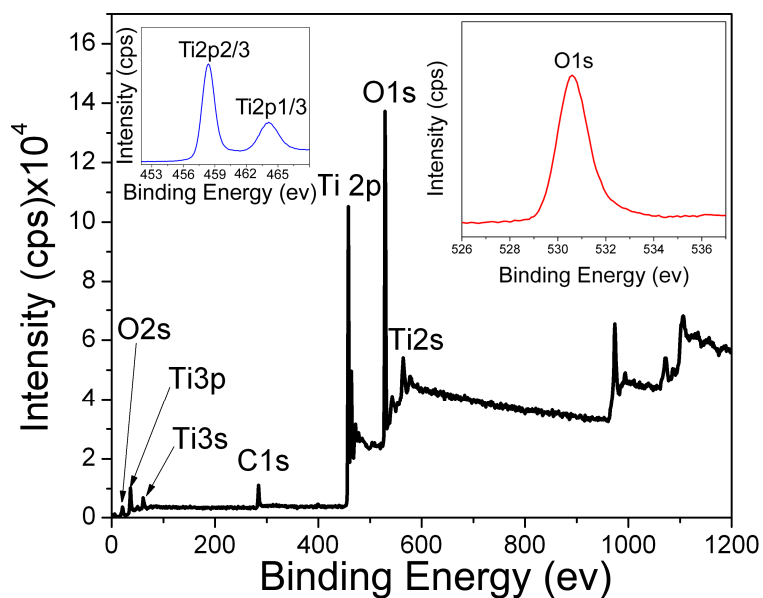


Figure S2. XPS full spectrum of the PTS. Insert picture are Ti2p (left) and O1s (right) spectrum, respectively.

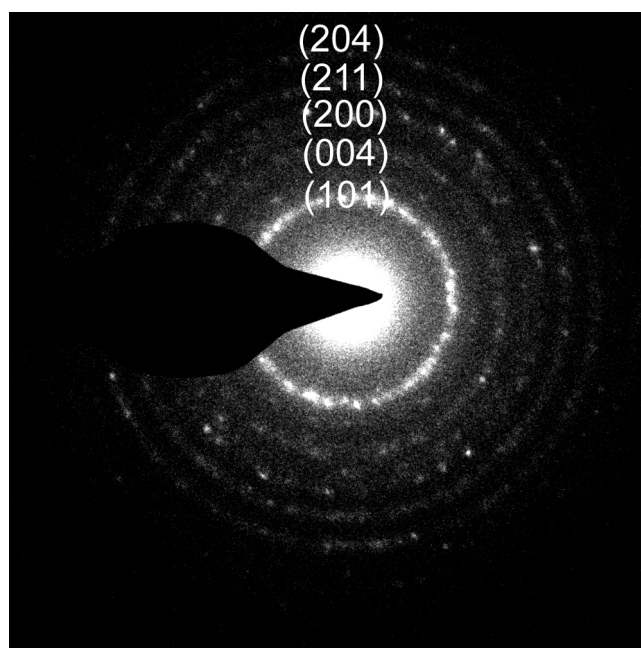


Figure S3. SAED pattern of PTS.

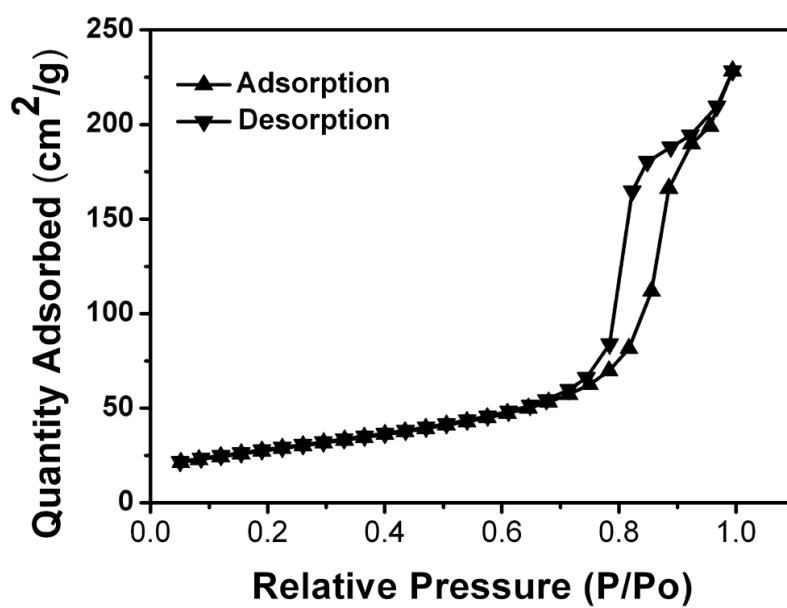


Figure S4. Nitrogen adsorption-desorption isotherm of N-PTS.

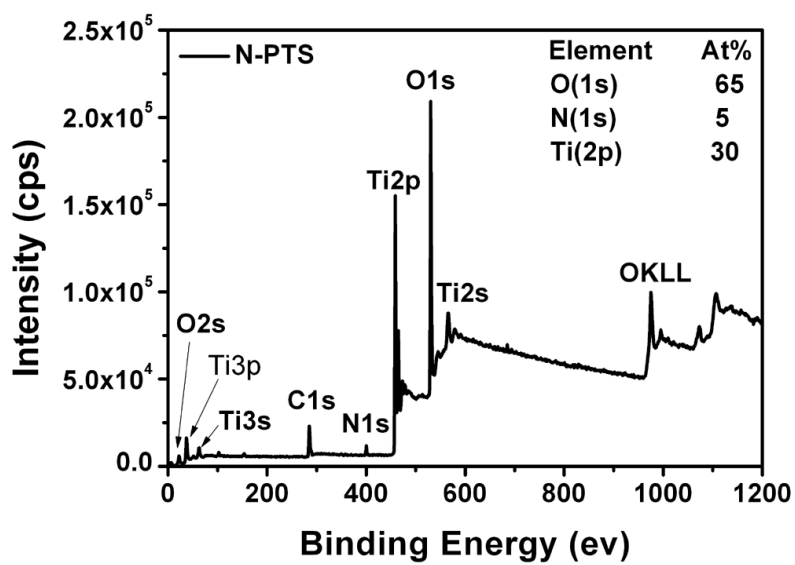


Figure S5. XPS spectrum of N-PTS.

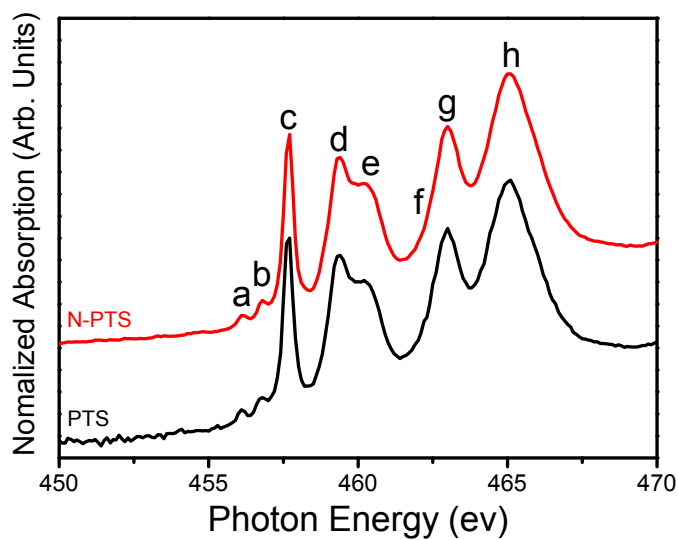


Figure S6. Ti L2, 3-edge spectra for the PTS and N-PTS.

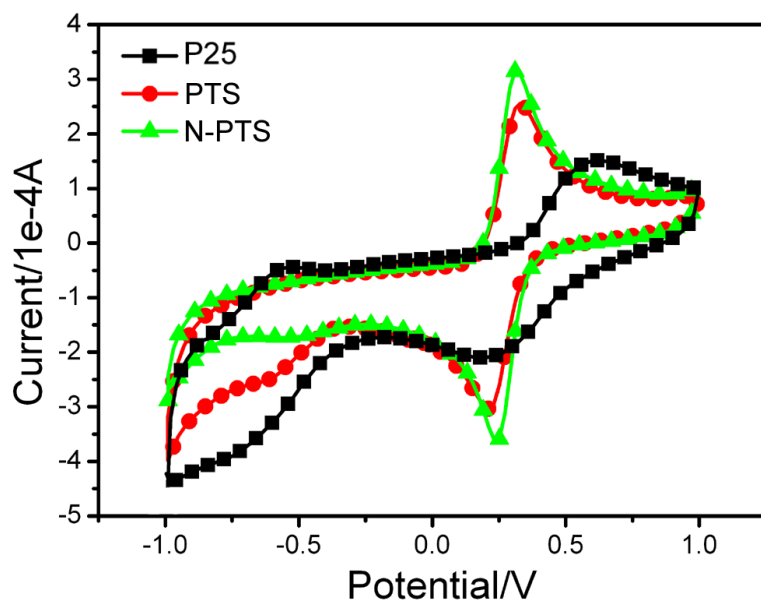


Figure S7. Cyclic voltammetry (CV) spectra of P25, PTS, and N-PTS.

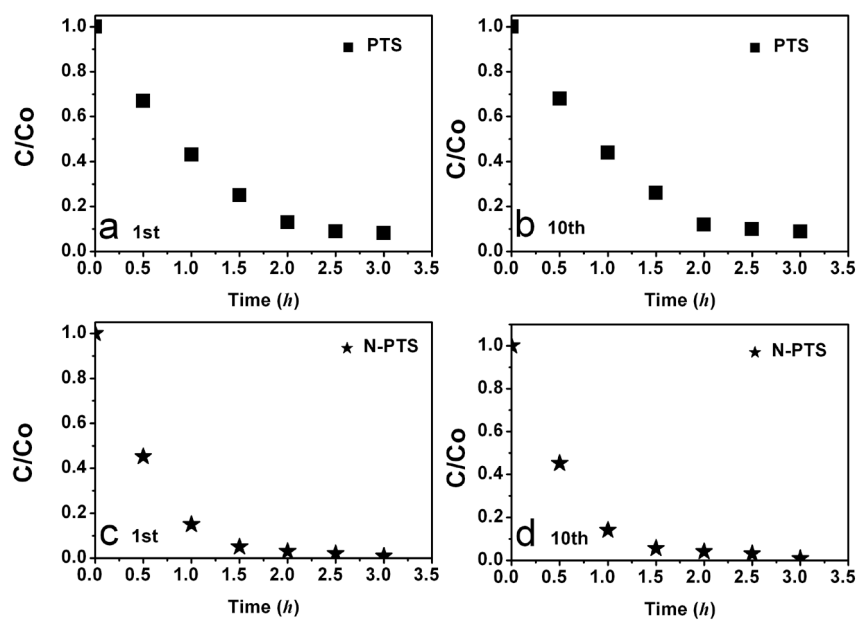


Figure S8. Reaction time dependence of the relative concentration of the RhB in solution over PTS and N-PTS during repeated photodecomposition experiments.

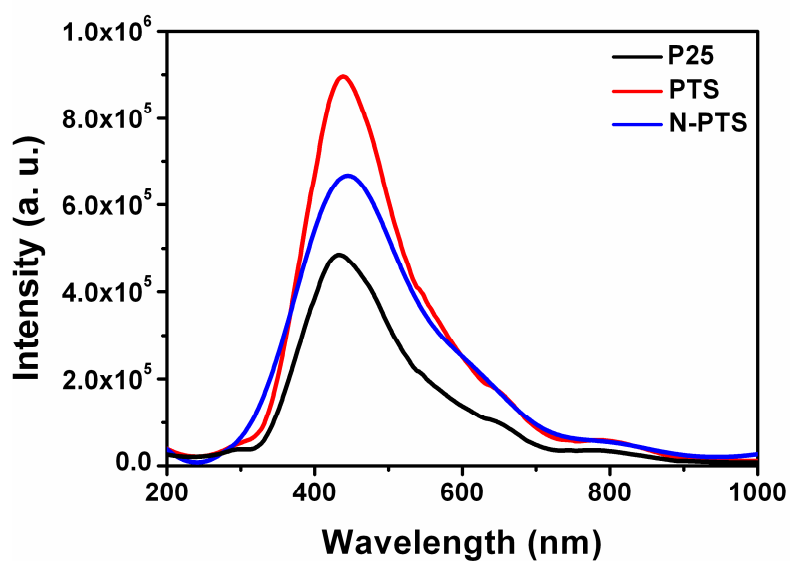


Figure S9. PL (excitation at 325 nm) spectra of P25, PTS and N-PTS.

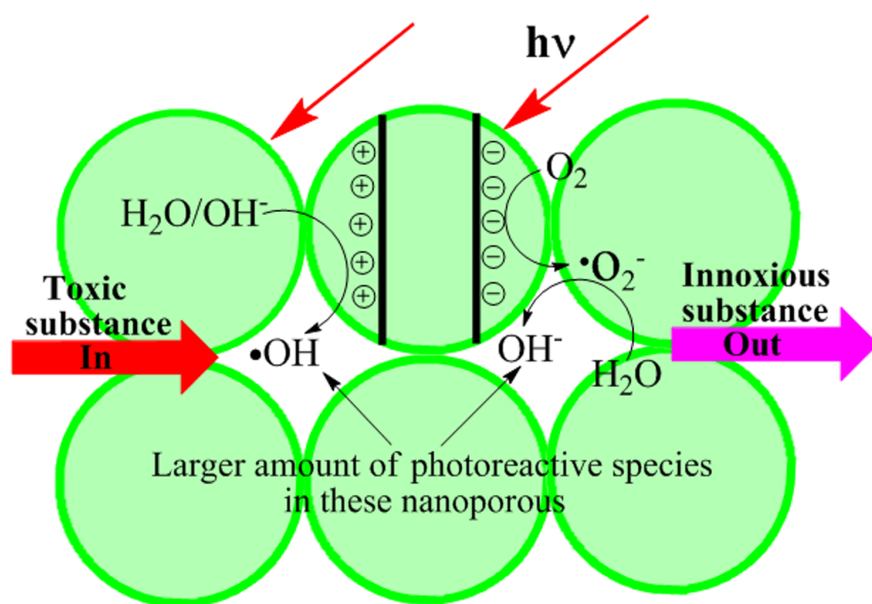


Figure S10. Scheme of the photocatalytic process of PTS and N-PTS under visible light irradiation.