

Electronic Supplementary Information

Metalloporphyrin modified defective TiO₂ porous cages with the enhanced photocatalytic activity for coupling of hydrogen generation and tetracycline removal

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Experimental Section

Materials and characterization methods

All chemical reagents were used as received. Nafion solution (5 wt% in mixture of water and 2-propanol), tetra-*n*-butylammonium hexafluorophosphate were purchased from Sigma Aldrich, and other chemicals and solvents, including copper(II) chloride ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$), 2-aminoterephthalic acid, titanium(IV) isopropoxide, L-alanine, methyl *p*-formylbenzoate, propionic acid, pyrrole, methanol, ethanol, ethyl acetate, tetrahydrofuran (THF), *N,N*-dimethylformamide (DMF), tetracycline, potassium hydroxide (KOH), ethylenediaminetetraacetic acid (EDTA) and tert-butanol (TBA) and hydrochloric acid (HCl), were purchased from Sinopharm Chemical Reagent Co., Ltd, China.

Transmission electron microscopy (TEM) and scanning electron microscopy (SEM) were used to characterize microstructures and morphologies on Tecnai F30, and HITACHI UHR FE-SEM SU8220, respectively. X-ray diffraction (XRD) was conducted in a Rigaku D/Max 2400 automatic powder X-ray diffractometer with $\text{Cu-K}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$). Cyclic voltammetry (CV), Mott Schottky (M-S) and transient photocurrent measurements were carried out by a CHI760E electrochemical workstation with a typical three-electrode cell. UV-vis absorption spectrum was collected by a HITACHI U-4100 spectrometer. N_2 sorption isotherm at 77 K were recorded by a Micromeritics 3Flex Surface Characterization Analyzer. Gas chromatography was performed on GC7900 Techcomp to analyze the gas products. X-ray photoelectron spectroscopy (XPS) was performed on Thermo ESCALAB 250Xi with $\text{Al-K}\alpha$ radiation ($h\nu = 1486.6 \text{ eV}$). Raman spectrum was collected by Jobin Yvon LabRAM HR Evolution Raman Spectrometer. Mass spectrum were collected by Agilent 6230B TOF LC/MS.

Photoelectrochemical/electrochemical measurements

Preparation of electrode: Catalysts (5 mg) were dispersed into the mixture of water and 2-propanol with volume ratio of 1:1 (0.975 mL), and then Nafion solution (0.025 mL, 5 wt%) was added. The final mixture was sonicated for 20 min to form a well-dispersed suspension. The resultant catalyst ink (5 μL) was dropped on the surface of glassy carbon (3 mm in diameter), and dried at room temperature in air. The glassy carbon loading catalyst was used as the working electrode. Ag/AgCl (3.5 M KCl) and polished Pt wire were used as the reference electrode and the counter electrode in a three-electron cell, respectively.

To assess photocurrent, photocathode was prepared by dropping of catalyst ink (20 μL) to transparent and conducting indium tin oxide (ITO) electrode ($2 \times 1 \text{ cm}$).

Electrochemical measurements: Electrochemical impedance spectroscopy (EIS) measurements were performed in 0.5 M Na_2SO_4 at 1.0 V vs. Ag/AgCl in the frequency ranging from 0.1 Hz to 100 kHz with oscillation potential amplitudes of 5 mV in the dark. The Mott-Schottky plots were obtained at different frequencies of 100, 200 and 500 Hz in the dark.

Photoelectrochemical measurements: Photocurrent measurements were performed using a three-electrode configuration in 0.5 M Na₂SO₄ at 1.0 V vs. Ag/AgCl upon simulated sunlight chopped irradiation.

Quantum yield (QY)

The photocatalytic system was irradiated by a 300 W Xe lamp with a 475-nm bandpass filter. The average intensity of incident monochromatic illumination was determined to be 100 mW cm⁻² by a handheld power meter (PL-MW2000, Beijing Perfectlight Technology Co. Ltd). The irradiation area was ~6 cm². The number of

incident photons (N) is calculated by the equation of $n_{photon} = \frac{P\lambda}{hc} \times t$, and the equation

of $QY(\%) = \frac{2n_{H_2}}{n_{photon}}$ is used to estimate QY.

$$n_{photon} = \frac{P\lambda}{hc} \times t = \frac{100 \times 10^{-3} \times 6 \times 475 \times 10^{-9}}{6.6260693 \times 10^{-34} \times 3 \times 10^8} \times 3600 = 5.15 \times 10^{21}$$

$$QY(\%) = \frac{2n_{H_2}}{n_{photon}} = \frac{2 \times 1.84 \times 10^{-3} \times 6.02 \times 10^{23}}{200 \times 5.15 \times 10^{20}} = 0.22\%$$

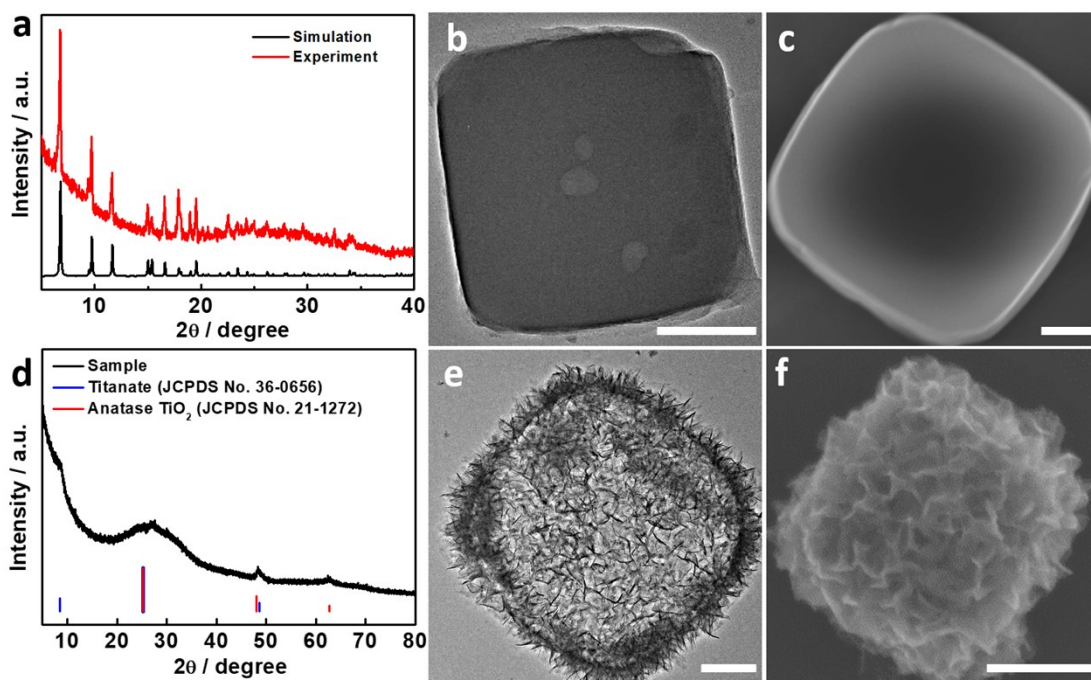


Figure S1. XRD patterns, TEM images, and SEM images of (a, b, c) NH₂-MIL-125(Ti) and (d, e, f) titanium oxide derived from NH₂-MIL-125(Ti) by an amino acid-assisted solvothermal route, respectively. All scale bars are 200 nm.

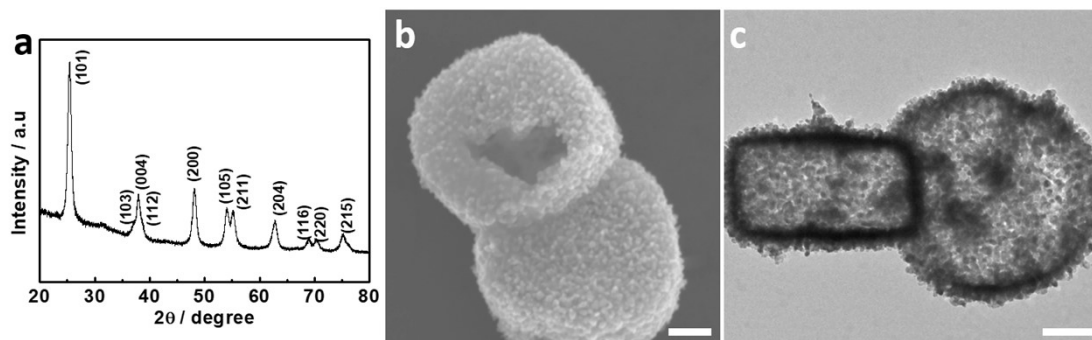


Figure S2. (a) XRD patterns, and (b) SEM and (c) SEM images of TiO₂ porous cages with oxygen vacancy defects (PC-TiO₂-*d*). All scale bars are 200 nm.

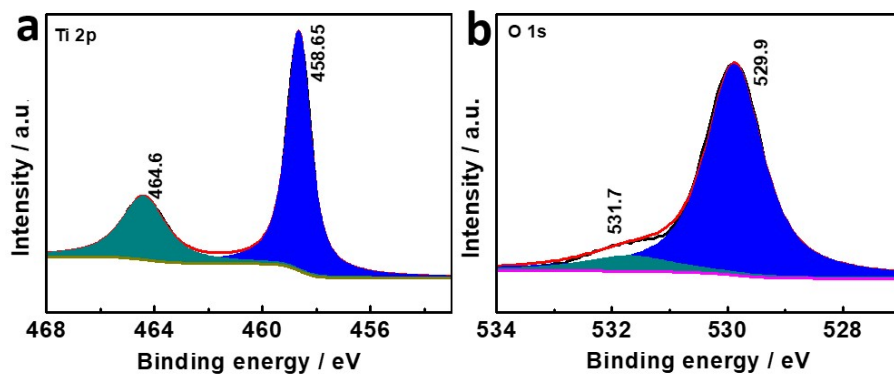


Figure S3. High-resolution XPS spectra of (a) Ti 2p and (b) O 1s of PC-TiO_{2-d}.

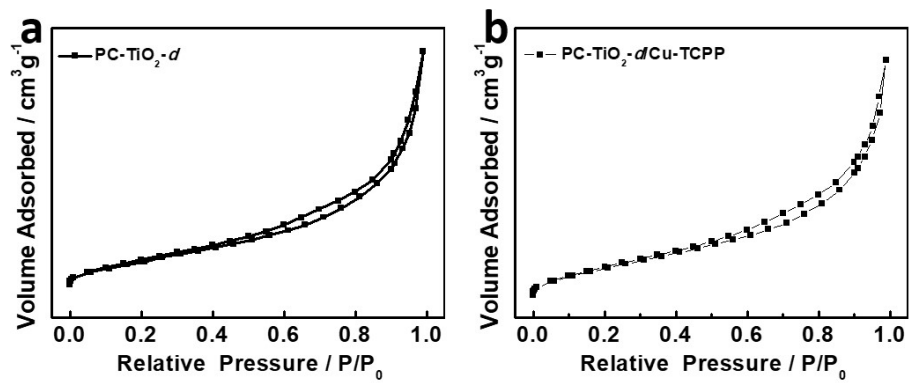


Figure S4. N₂ sorption isotherms of (a) PC-TiO₂-d and (b) PC-TiO₂-d/Cu-TCPP measured at 77 K.

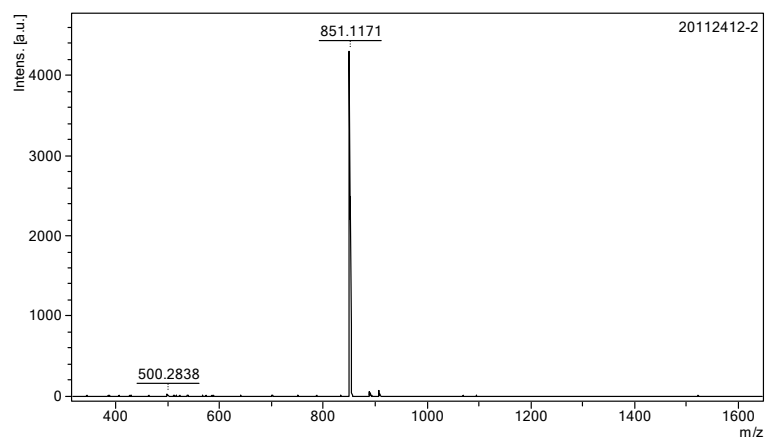


Figure S5. Mass spectrum of Cu-TCPP.

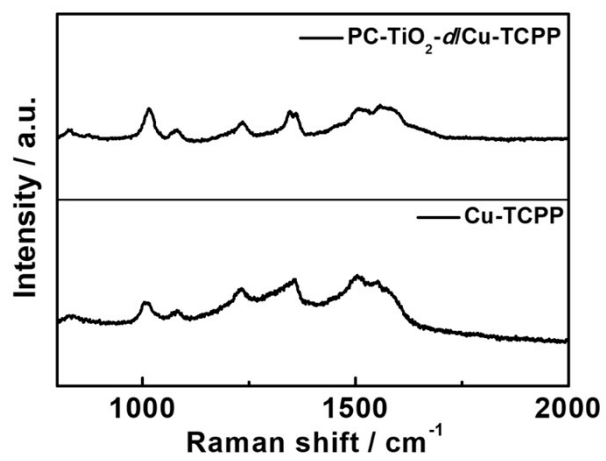


Figure S6. Raman spectra of PC-TiO₂-d/Cu-TCPP and Cu-TCPP.

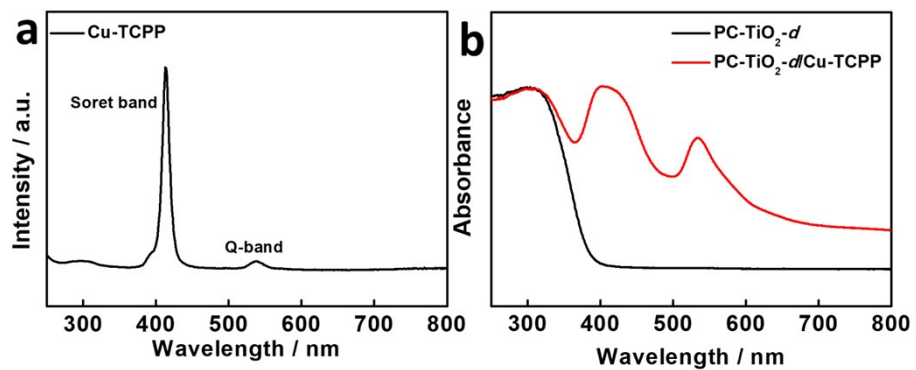


Figure S7. (a) UV-vis absorption spectrum of Cu-TCPP in ethanol solution and (b) solid diffuse reflectance UV-vis absorption spectrum of PC-TiO₂-d and PC-TiO₂-d/Cu-TCPP.

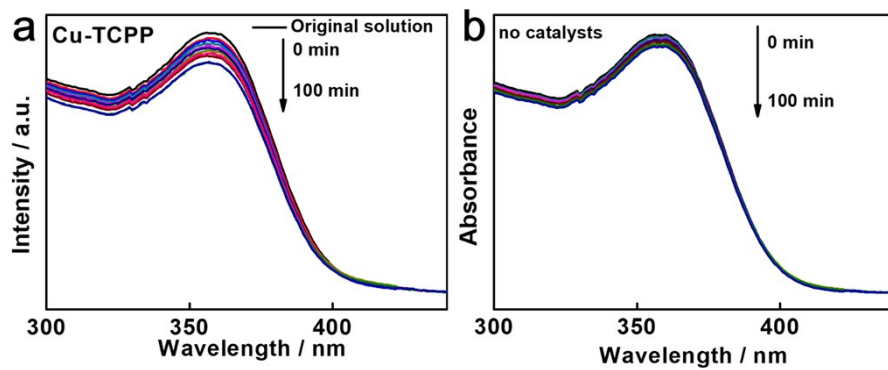


Figure S8. UV-visible absorption spectra of tetracycline aqueous solution in the presence of (a) Cu-TCPP and (b) no catalysts under irradiation of visible light.

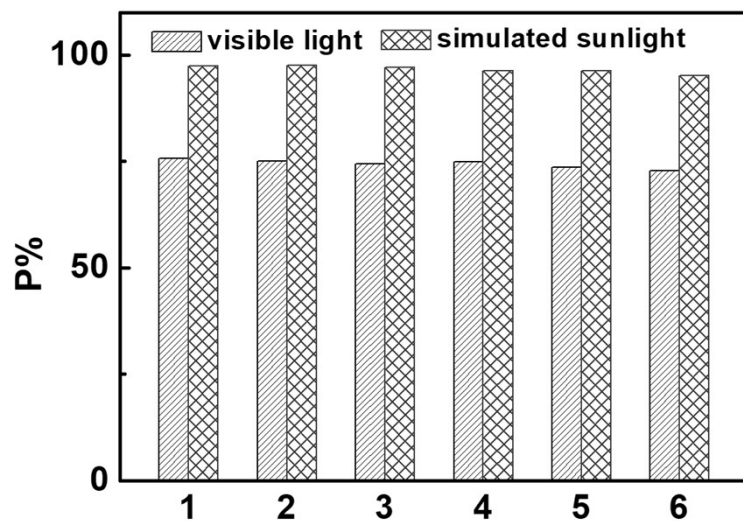


Figure S9. The recyclability of PC-TiO₂-d/Cu-TCPP towards tetracycline degradation under visible light or simulated sunlight irradiation.

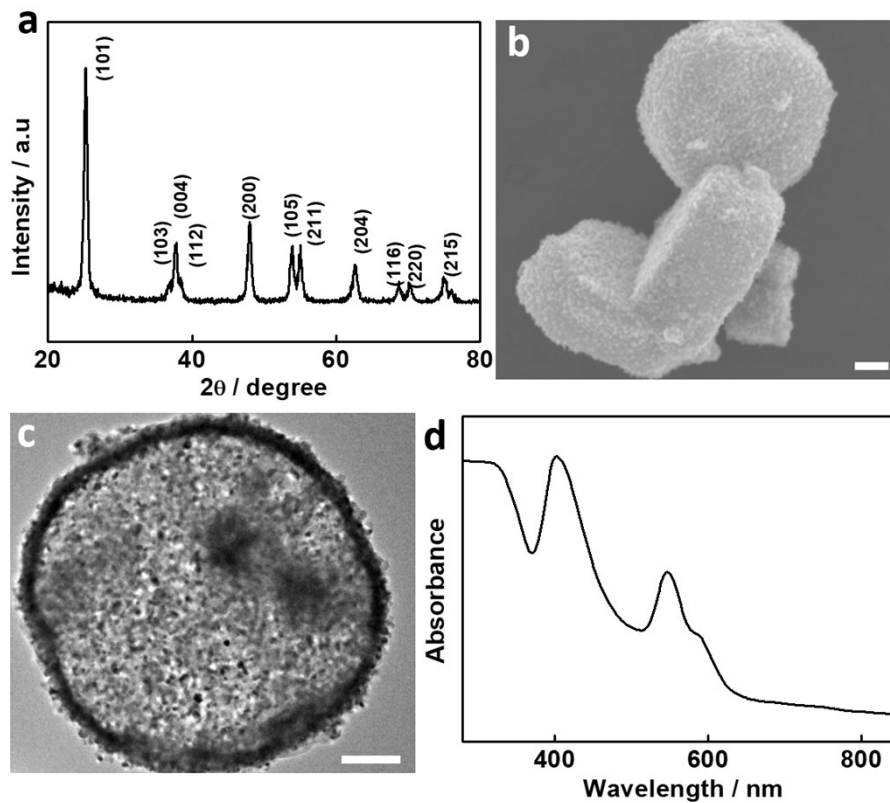


Figure S10. (a) XRD pattern, (b) SEM and (c) TEM images, and (d) UV-visible spectrum of PC-TiO₂-*d*/Cu-TCPP after being used for tetracycline degradation via six times upon visible irradiation. All scale bars are 200 nm.

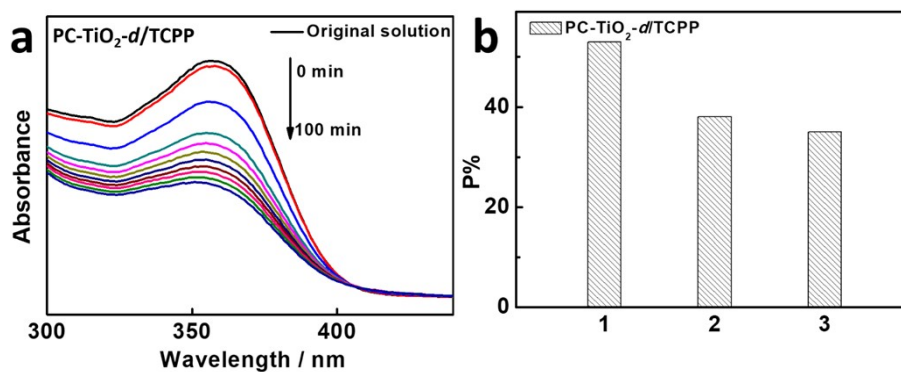


Figure S11. (a) UV-visible absorption spectra of tetracycline aqueous solution in the presence of PC-TiO₂-d/TCPP under visible light irradiation and (b) the recyclability of PC-TiO₂-d/TCPP towards tetracycline degradation.

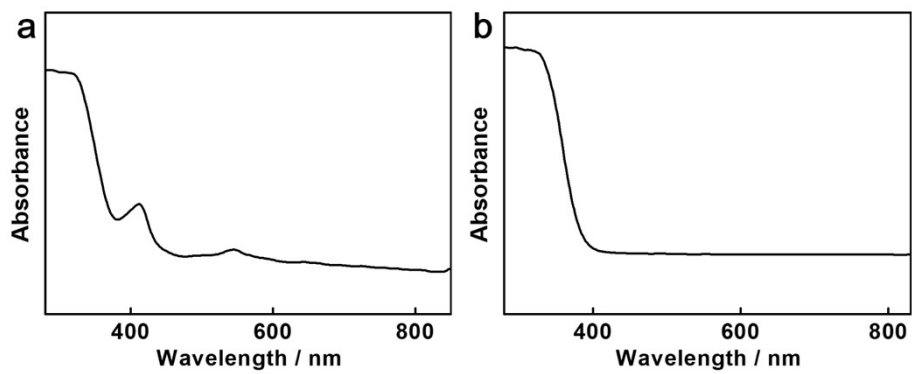


Figure S12. UV-visible absorption spectra of (a) the original PC-TiO₂-*d*/TCPP and (b) PC-TiO₂-*d*/TCPP after being used for tetracycline degradation via three times upon visible light irradiation.

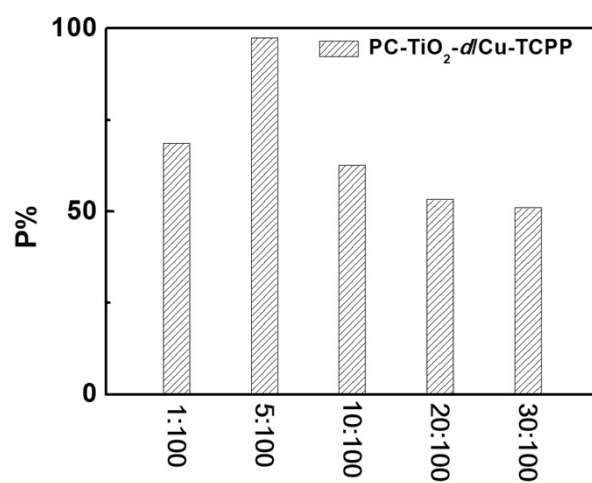


Figure S13. The photocatalytic degradation percentage of tetracycline over PC-TiO₂-d/Cu-TCPP with different amount ratio of Cu-TCPP and PC-TiO₂-d.

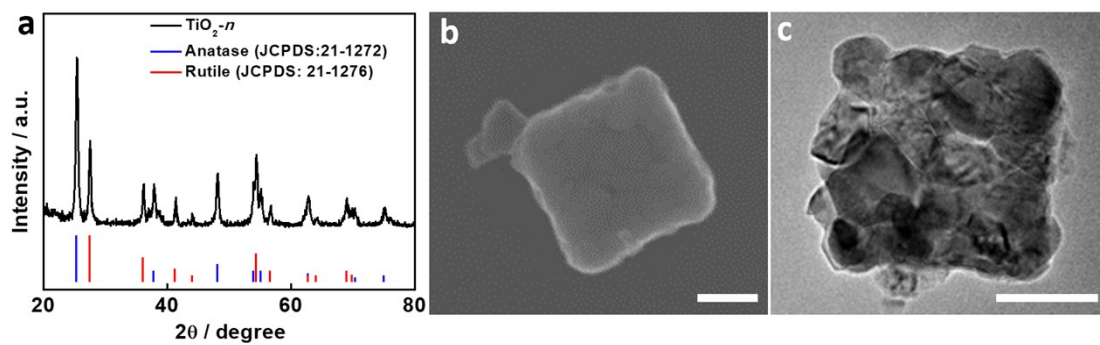


Figure S14. (a) XRD pattern and (b) SEM and (c) TEM images of $\text{TiO}_2\text{-}n$. All scale bars are 100 nm.

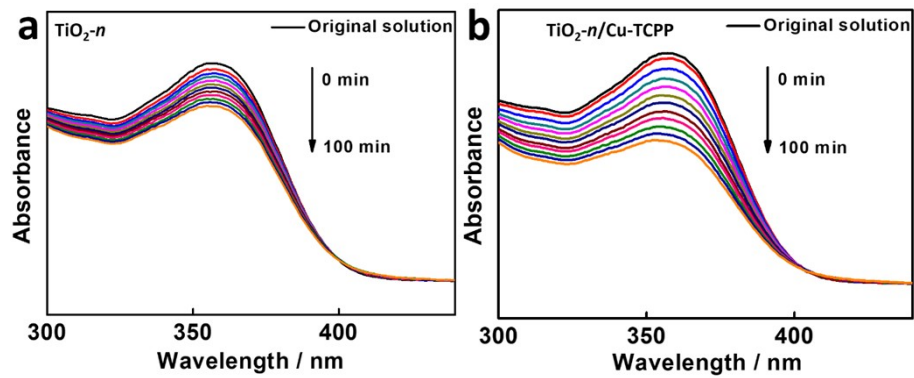


Figure S15. UV-visible absorption spectra of tetracycline aqueous solution in the presence of (a) $\text{TiO}_2\text{-}n$ and (b) $\text{TiO}_2\text{-}n/\text{TCPP}$ under visible light irradiation