Supplementary Information

Enhanced photocatalytic performance of titania nanotubes via the synergistic effect of trace copper doping and oxygen vacancies

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1. Characterization methods

The crystal structure and phase composition of the samples were obtained by powder X-ray diffraction (XRD, Smartlab, Rigaku, Japan). A field emission scanning electron microscope (FESEM, Apreo S LoVac, FEI, USA) was used to obtain the morphology of the samples, and a field emission transmission electron microscope (FETEM, JEM-2100F, JOEL, Japan) was used to further obtain the microstructure of the samples. The element distribution was obtained by transmission electron microscope (TEM, JEM-F200, JOEL, Japan) equipped with energy dispersive spectrometer (EDS). The surface electronic states of the samples were characterized by X-ray photoelectron spectroscopy (XPS, K-alpha XPS spectrometer, Thermo Fisher Scientific, USA). The specific surface area and pore size distribution of the catalyst samples were analyzed using BET (ASAP2460, Micromeritics, USA). UV-Vis spectrophotometer (UV-Vis DRS, Hitachi U4150, Japan) was used to obtain diffuse reflectance spectra of the samples. Electron paramagnetic resonance (EPR, Bruker EMX PLUS, Germany) was used to study the oxygen vacancy content of the sample and the species of free radicals generated under light, and the photoluminescence spectrum (PL) of the sample was obtained on a fluorescence spectrometer (FLS1000, Edinburgh, UK).

2. Photocatalytic experiment

Photocatalytic experiments were carried out under the illumination of a 300W Xe lamp (PLS-SXE300, Perfectlight, China) at room temperature. In a typical procedure, 50 mg of the photocatalyst was added to 200 mL of RhB aqueous solution (50 mg/L), followed by sonication for 30 min to disperse the photocatalyst evenly in the solution,

and stirred for another 30 min in the dark to ensure the establishment of an adsorption/desorption equilibrium between the catalyst and the contaminants. At regular intervals, take 5ml samples, filter them with a 0.22 um polytetrafluoroethylene filter, measure the absorbance of the filtrate with a UV-Vis spectrophotometer at the maximum absorption wavelength of 555nm, and calculate the concentration of pollutants.

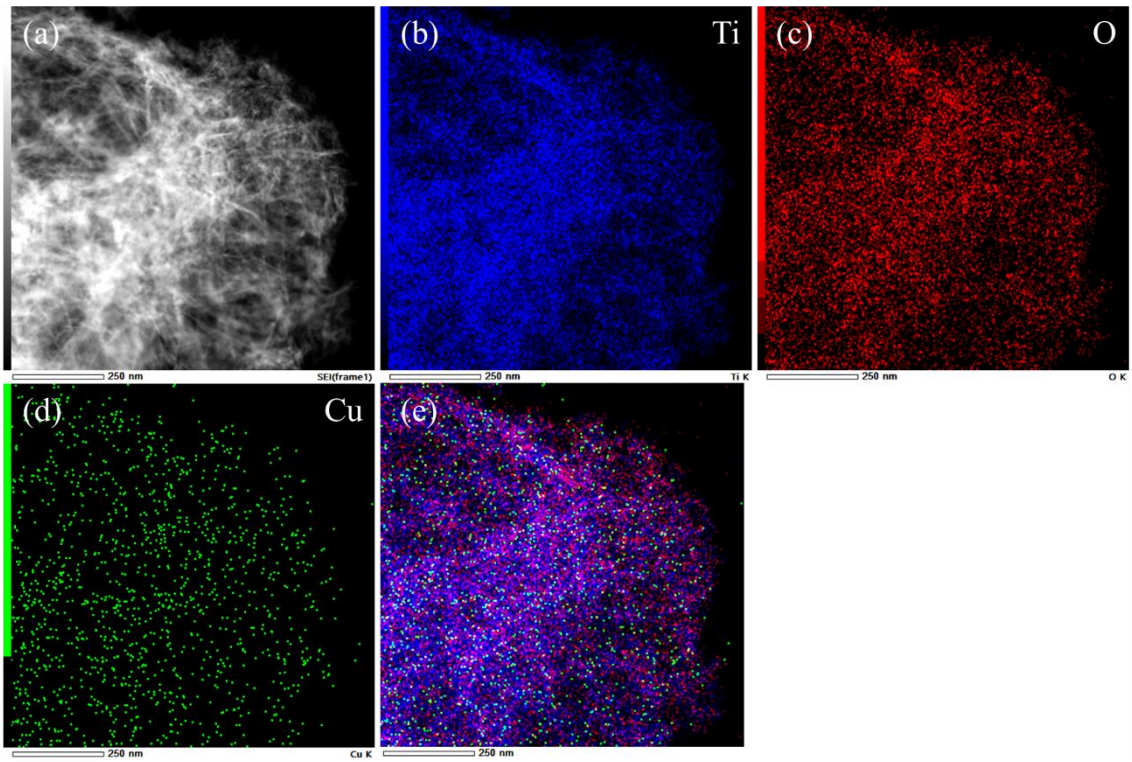

Fig. S1. EDS Mapping of Cu@ANTs.

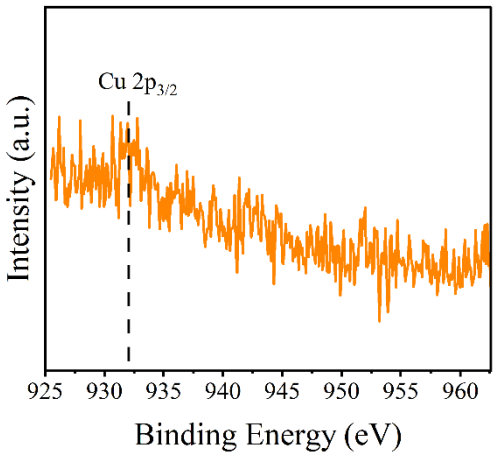

Fig. S2. The fine XPS spectra of Cu 2p.

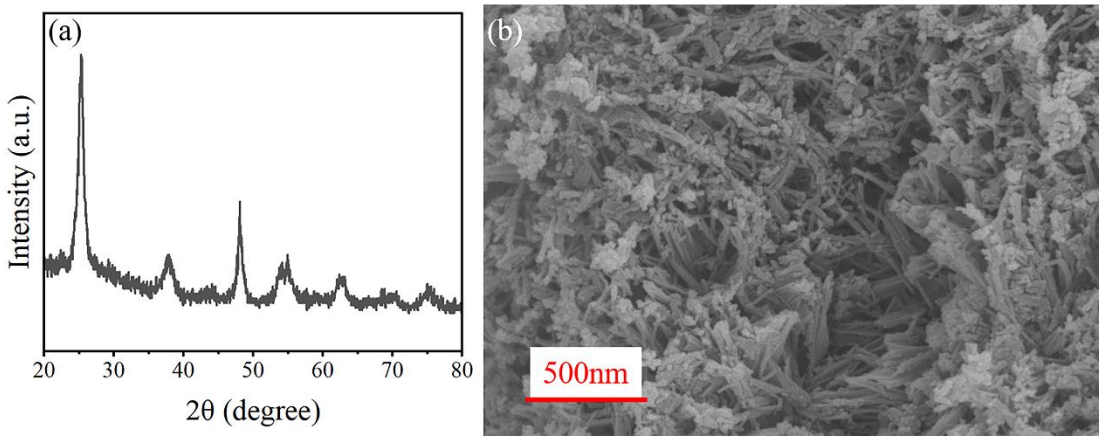

Fig. S3. (a) The XRD pattern and (b) SEM image of samples after fifth cycling.

Table S1. Performance comparison of Cu doped TiO_2 photocatalyst in present work and previous works.

Photocatalyst	Light source	Pollutant species	pollutant concentration (mg/L)	Catalyst dosage (g/L)	Degradation rate (%)	Irradiation time (min)	Rate constant (min^{-1})	Ref.
Cu-TiO_2 nanoparticles	White LED 50 kW	Rhodamine B	5	1	97.12	120	0.0147	[1]
Cu-TiO2 Hollow nanostructures	LED lamp 70W	phenol	5	0.6	99	240	0.0216	[2]
Cu-TiO_2 nanofibers	UV-A lamps 8W	methyl orange	10	0.1333	92	150	0.018	[3]
Cu- TiO2 sphere	Rayonet RPR-100 Photoreactor	paracetamol	50	4	98.8	180	0.0243	[4]
Cu-TiO2 nanoparticles	Xenon lamp 500 W	nitrobenzene	6.15	0.5	98.6	180	0.0156	[5]
Cu-TiO2 core shell nanowires	mercury lamp 50W	methyl orange	10		90	80	0.02905	[6]

Cu-TiO2 nanotube arrays	Xenon lamp 200 W	methylene blue	2		92	120	0.0206	[7]
Cu-TiO2 nanotubes	Xenon lamp 300 W	Rhodamine B	50	0.25	90	60	0.0329	This work

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