Electronic Supplementary Material (ESI) for Nanoscale.
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Supporting information for

In situ Cu single atoms anchoring on MOF-derived porous TiO_2 for efficient separation of photon-generated carriers and photocatalytic H_2 evolution

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Experimental section

Characterizations. Cu and Ti species contents were measured by inductively coupled plasma optical emission spectrometry (ICP-OES) (PlasmaQuant PQ9000). The functional groups of the substances were measured by Fourier transform infrared (FTIR) spectroscopy (IR-2000, Tianjin Jingtuo Instrument Technology Co., Ltd.). The SSA was measured by specific surface and pore size analysis instrument (3H-2000PS2, Beishide Instrument Technology (Beijing) Co., Ltd.). Surface photovoltage (SPV) was measured by scanning Kelvin probe (SKP5050, Scotland KP Technology). The photoluminescence (PL) spectrum was measured by a photoluminescence spectrometer (HITACHI F-4500). Powder X-ray diffraction (XRD) was carried out on an X-ray diffractometer (RIGAKUTTRIII-18KW) with a Cu Kα source. The morphology was observed by transmission electron microscope (TEM) (JEM-2100). X-ray photoelectron spectroscopy (XPS) investigation was carried out to analyze the surface chemistry (K-Alpha+).

Photocatalytic experiments. The hydrogen production performance is tested by the high air tightness automatic online photocatalytic analysis system (Labsolar-6A, Beijing Perfectlight Technology Co., Ltd.). The catalyst (10 mg) and 90 ml of water with 20% methanol (30 mL) were mixed in a reaction cell, irradiated with a 300 W xenon arc lamp after removing the air. Meanwhile, the cooling water was used to maintain the temperature at 298.15 K. The generated H_2 was analyzed via a gas chromatograph (GC9790Ⅱ).

The determination of the apparent quantum efficiency (AQE) for photocatalytic H_2 evolution rate was performed using a Multi-channel photochemical reactor system (PCX-50C, Beijing Perfectlight Technology Co., Ltd.) under the LED light source (Wavelength: 365 nm, light intensity: 42.13 mW/cm^2). The as-prepared catalyst (20 mg) was uniformly dispersed in 30 mL methanol solution (containing H_2O/methanol, v/v=1:2) under magnetic stirring. The temperature of reaction was kept at 313.15 K by cool flowing water. The rest of the conditions were similar as stated above. The AQE is calculated by using the following equation:

$$AQE = \frac{2MN_A hc}{AIt\lambda} \times 100\%$$

where M is the amount of hydrogen molecules, N_A is the Avogadro's constant, h is the Planck constant, c is the light velocity, I is the intensity of the light, A is the irradiation area, t is the reaction time, and λ is the wavelength of light.

Electrochemical measurements. Photoelectrochemical properties are measured by photoelectrochemical test system (PEC2000, Beijing Perfectlight Technology Co., Ltd.). The working electrode was prepared by loading samples on the ITO glass (5 cm^2, 10 mg catalysis in 2800 μL ethanol and 20 μL naphthol). The reference electrode was Ag/AgCl, KCl (3 M). The Pt sheet was used as the counter electrode. EIS of Cu-TiO_2 catalysts and TiO_2 were investigated at 0.25 V in 0.5 M Na_2SO_4 electrolyte.

Supplementary Figures

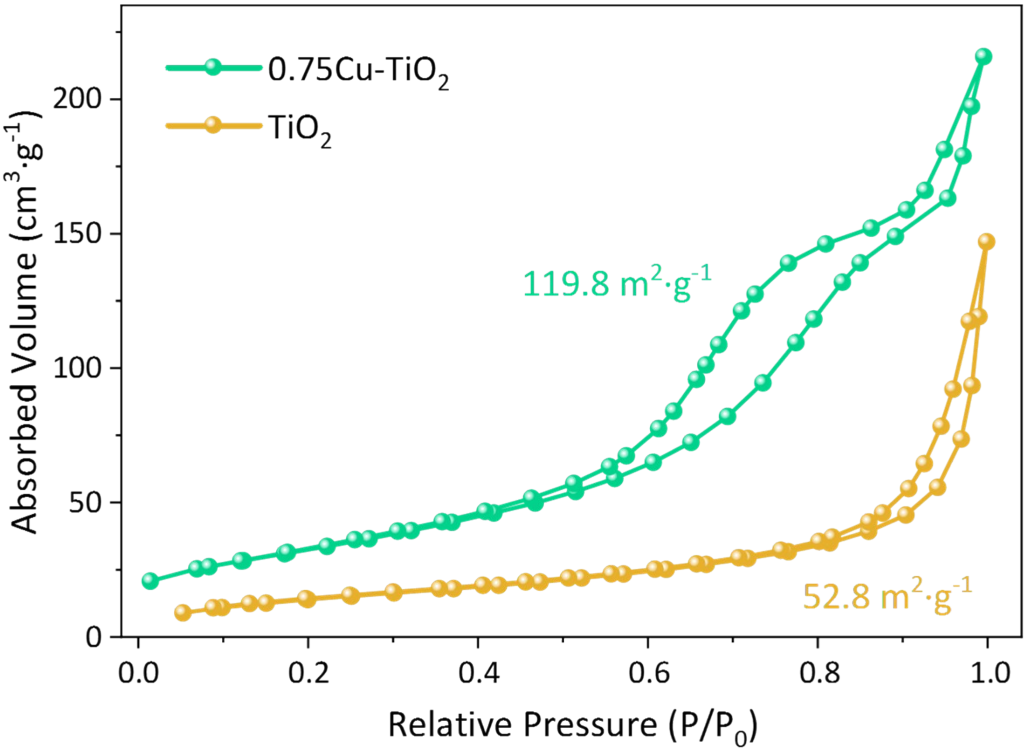

Fig. S1. The specific surface areas of 0.75Cu-TiO_2 catalyst and commercial TiO_2 (P25).

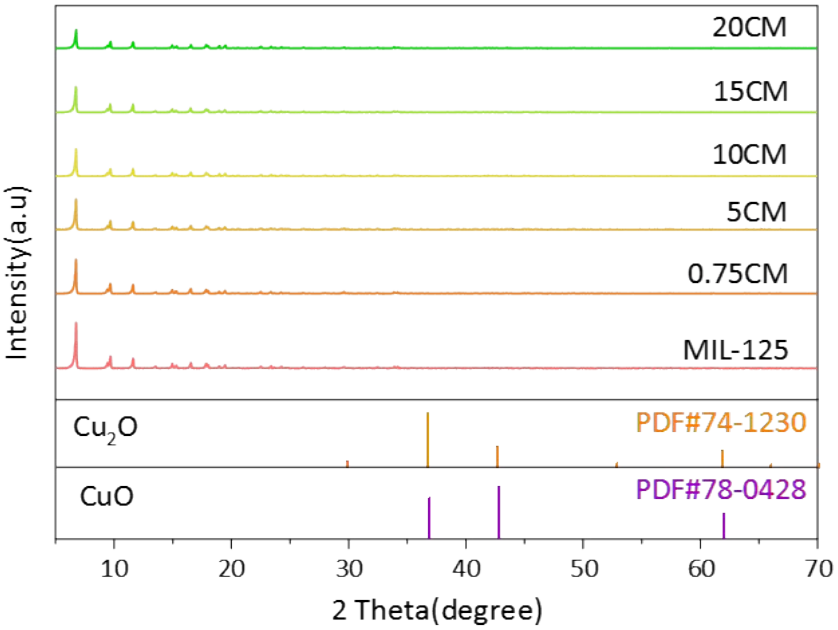

Fig. S2. XRD patterns of as-synthesized MIL-125 and Cu containing MIL-125 (CM) samples.

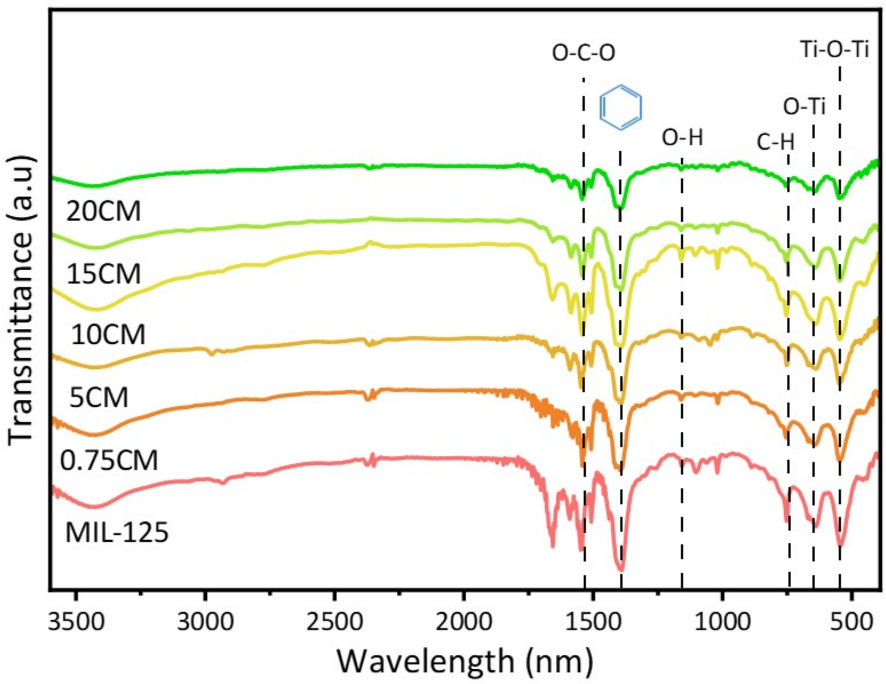

Fig. S3. FTIR spectroscopy of as-synthesized MIL-125 and CM samples.

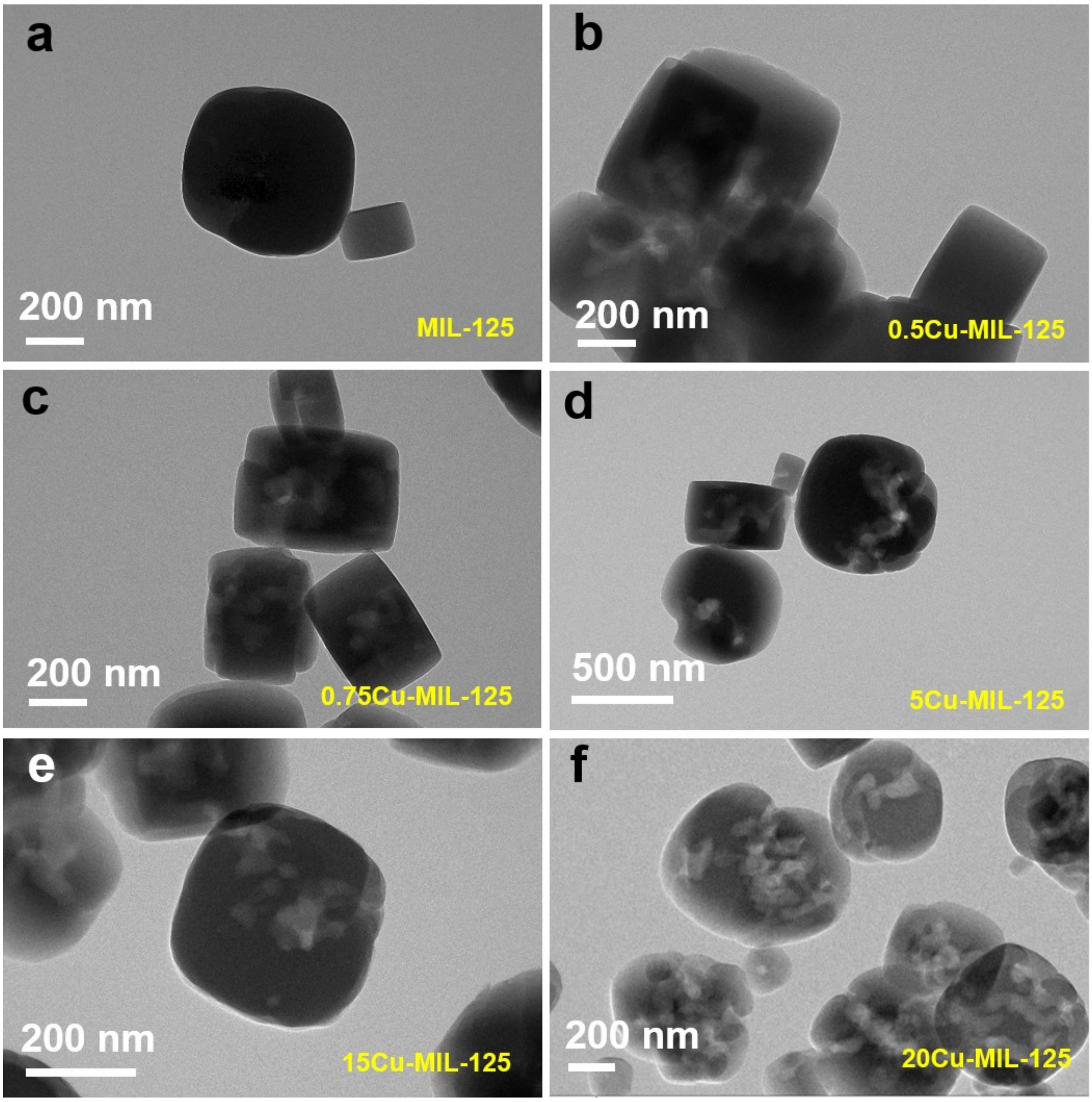

Fig. S4 TEM images of (a) MIL-125, (b) 0.5CM, (c) 0.75CM, (d) 5CM and (e) 15CM and 20CM.

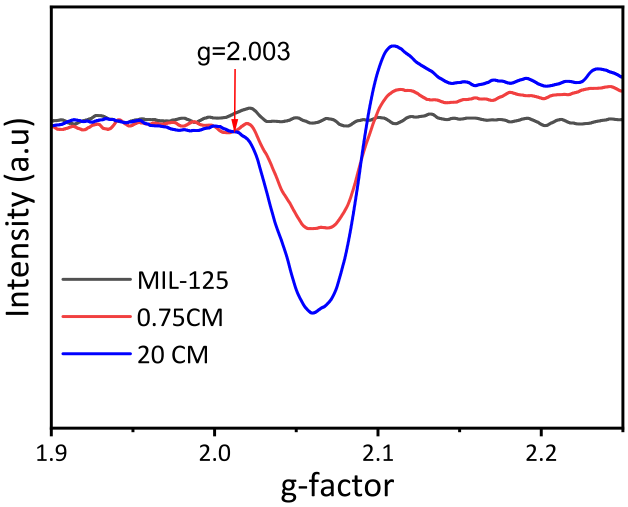

Fig. S5. EPR spectra of MIL-125, 0.75CM and 20 CM.

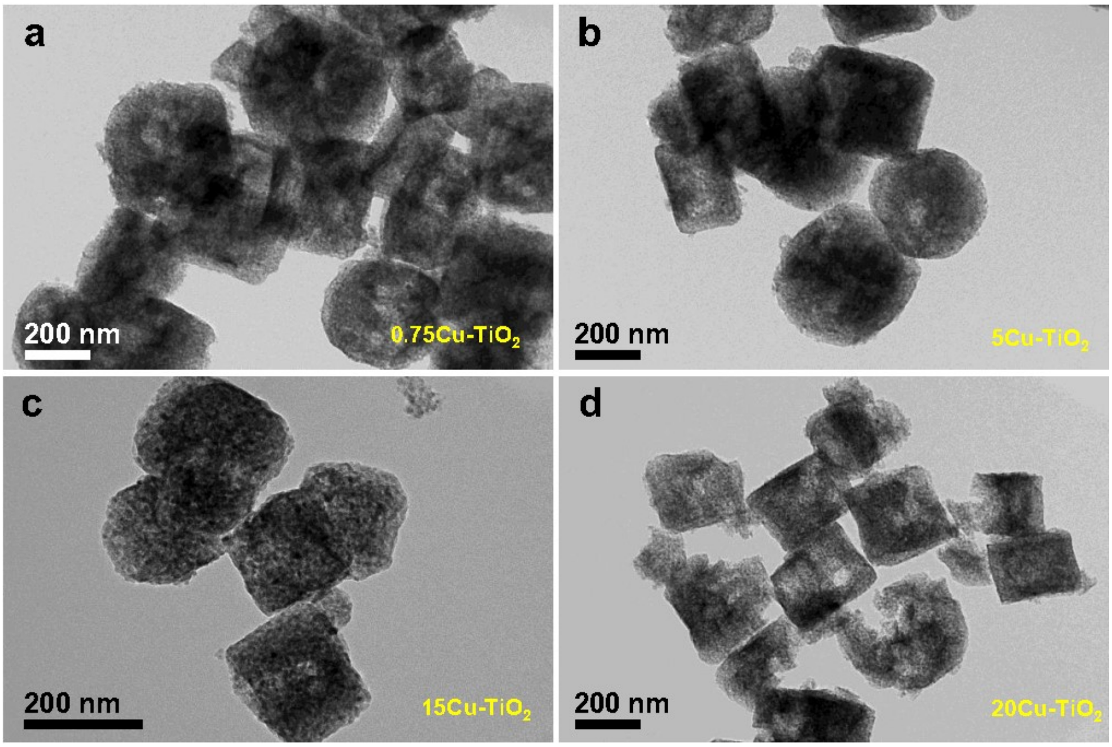

Fig. S6. TEM images of (a) 0.75Cu-TiO_2, (b) 5Cu-TiO_2, (c) 15Cu-TiO_2, and (d) 20Cu-TiO_2.

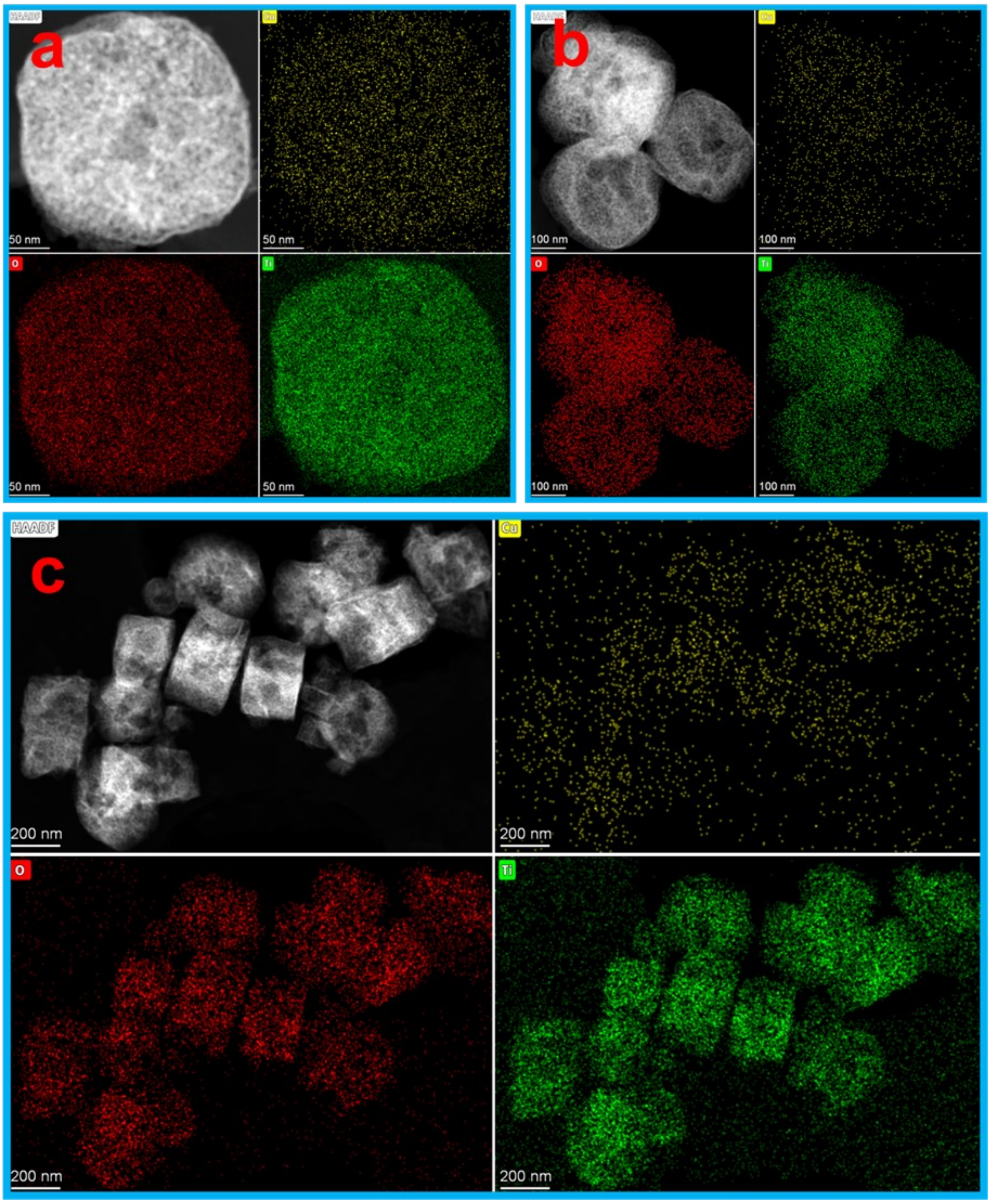

Fig. S7. (a-c) EDS mapping of 0.75Cu-TiO_2 at different magnifications.

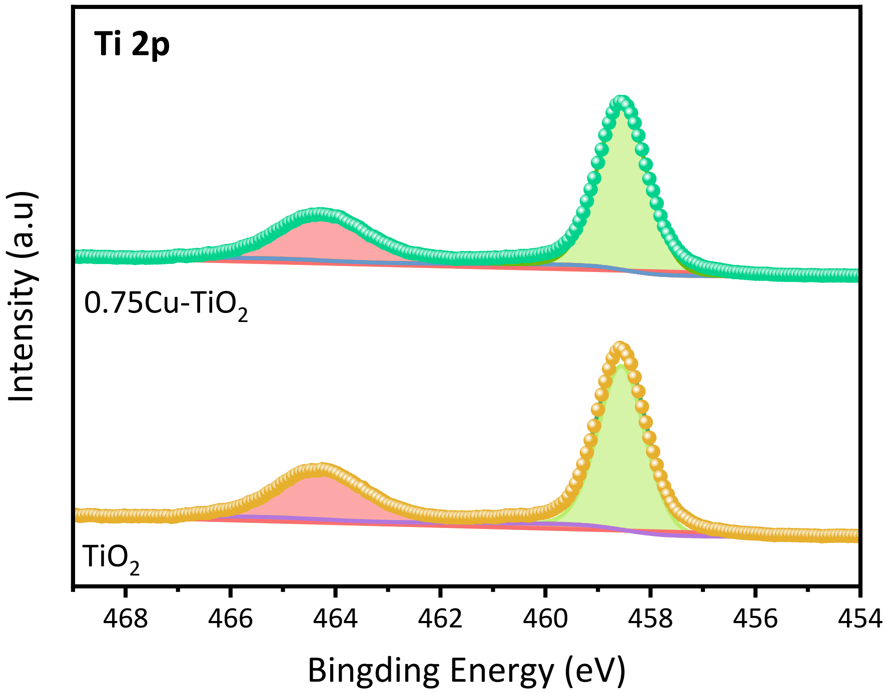

Fig. S8. Ti 2p XPS spectra of TiO$_2$ and 0.75Cu-TiO$_2$.

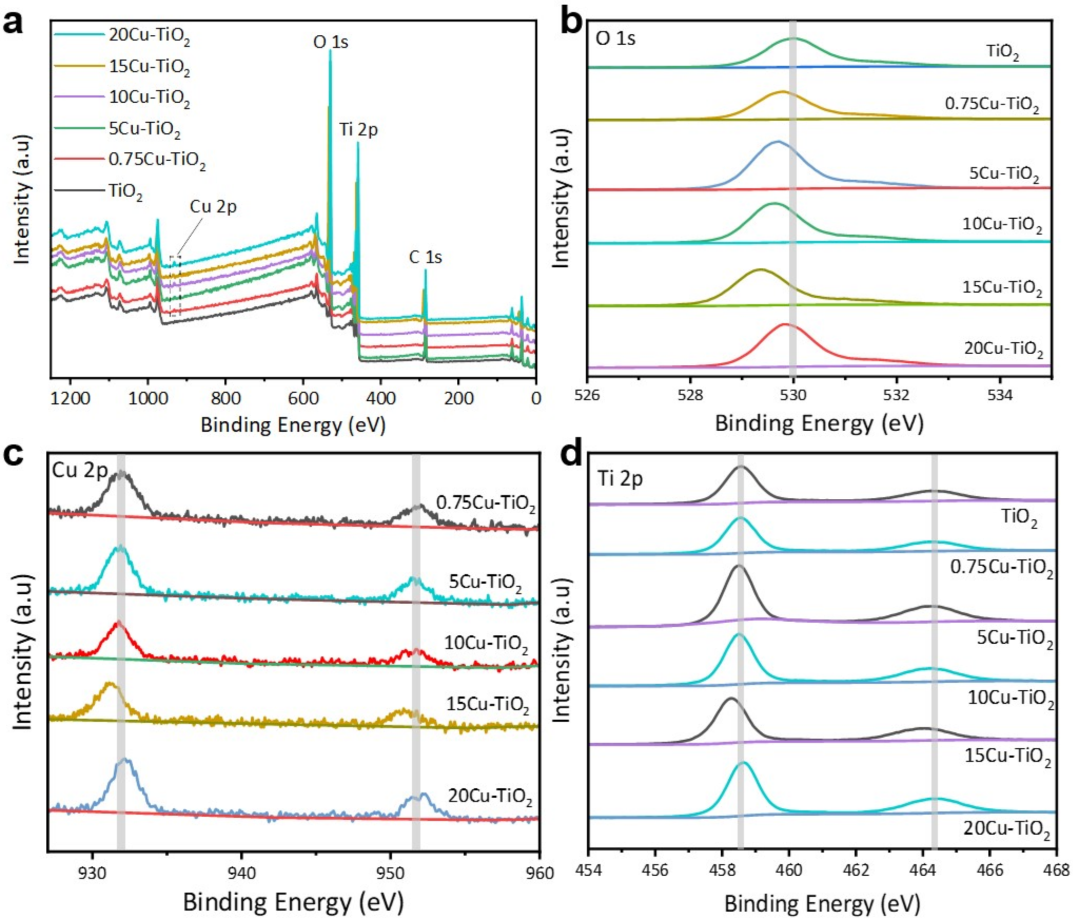

Fig. S9. (a) Full XPS spectra, (b) O 1s XPS spectra, (c) Cu 2p XPS spectra and (d) Ti 2p XPS spectra of TiO_2 with different amount of Cu loading.

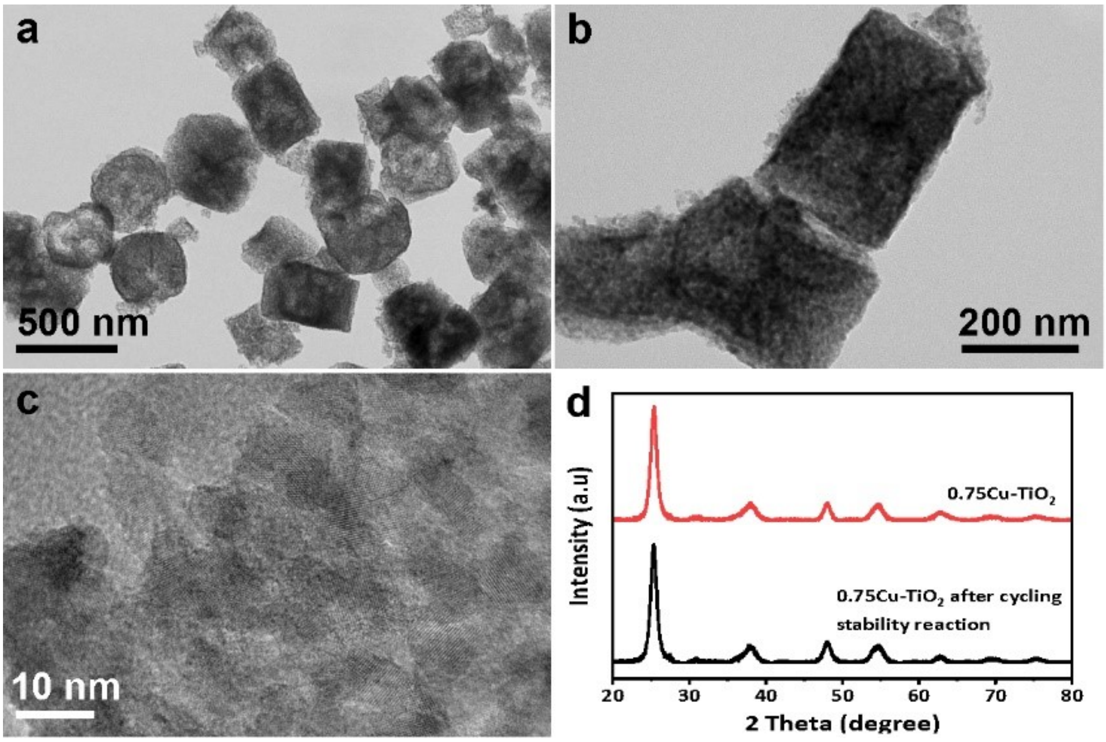

Fig. S10. (a,b) TEM images of 0.75Cu-TiO_2 after 5-cycle tests with different magnification, (c) HRTEM image and (d) XRD pattern of 0.75Cu-TiO_2 after 5-cycle tests.

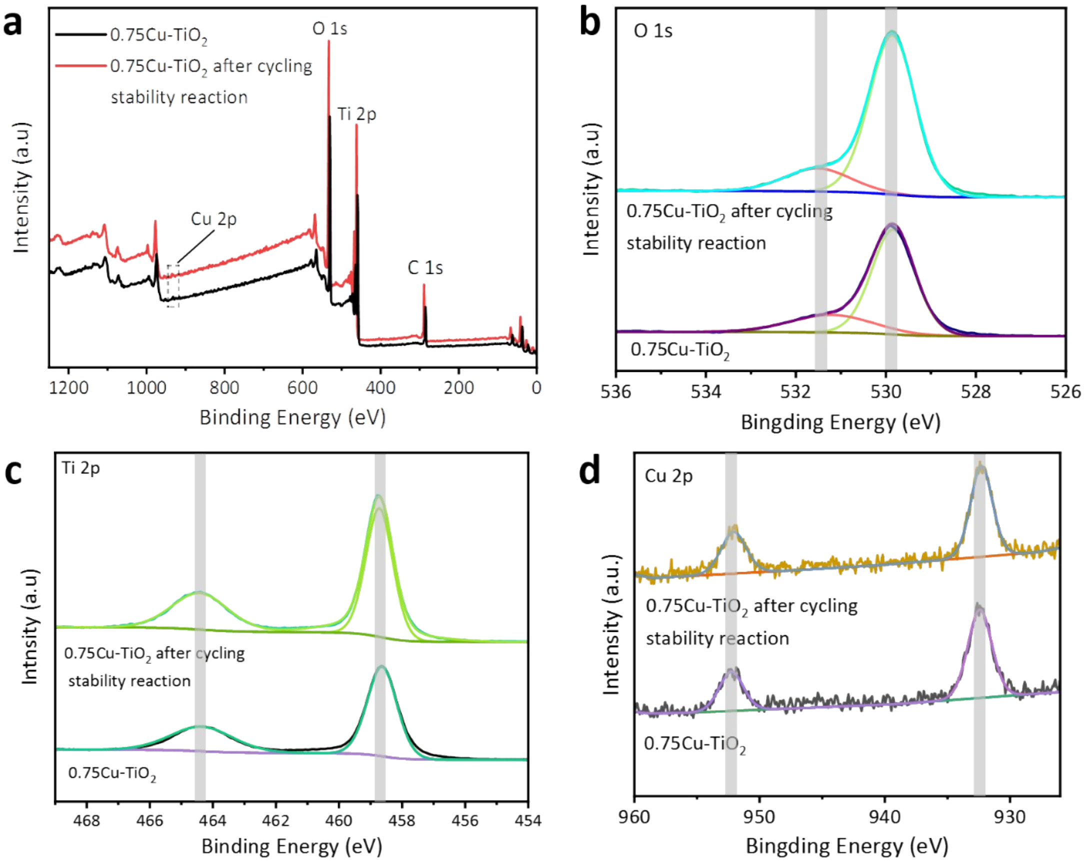

Fig. S11. (a) Survey spectrum of XPS analysis of 0.75Cu-TiO_2 and 0.75Cu-TiO_2 after cycling stability reaction. No peaks of other elements except Ti, O, Cu and C are observed. The C peak comes mainly from the atmospheric contamination for the exposure to air. (b) The XPS spectra of O 1s for 0.75Cu-TiO_2 and 0.75Cu-TiO_2 after cycling stability reaction. (c) The XPS spectra of Ti 2p for 0.75Cu-TiO_2 and 0.75Cu-TiO_2 after cycling stability reaction. (d) The XPS spectra of Cu 2p for 0.75Cu-TiO_2 and 0.75Cu-TiO_2 after cycling stability reaction.

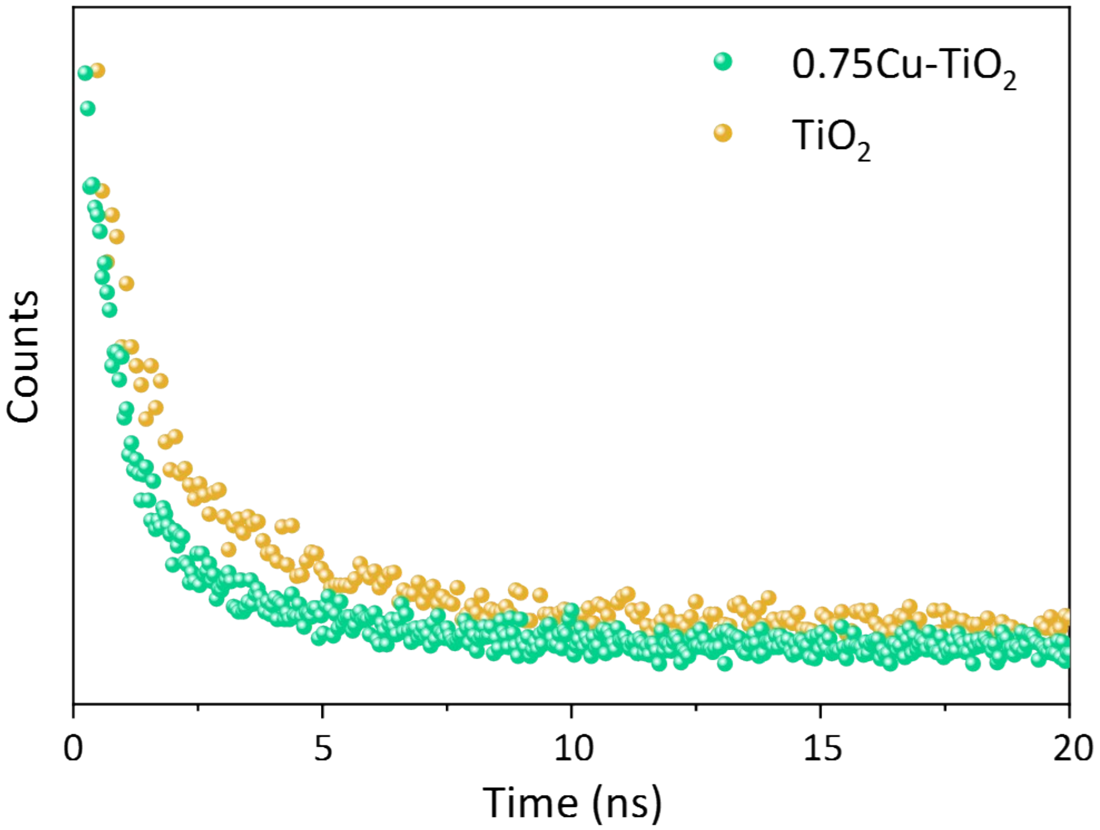

Fig. S12. The PL decay curves of $0.75Cu\text{-}TiO_2$ catalyst and TiO_2.

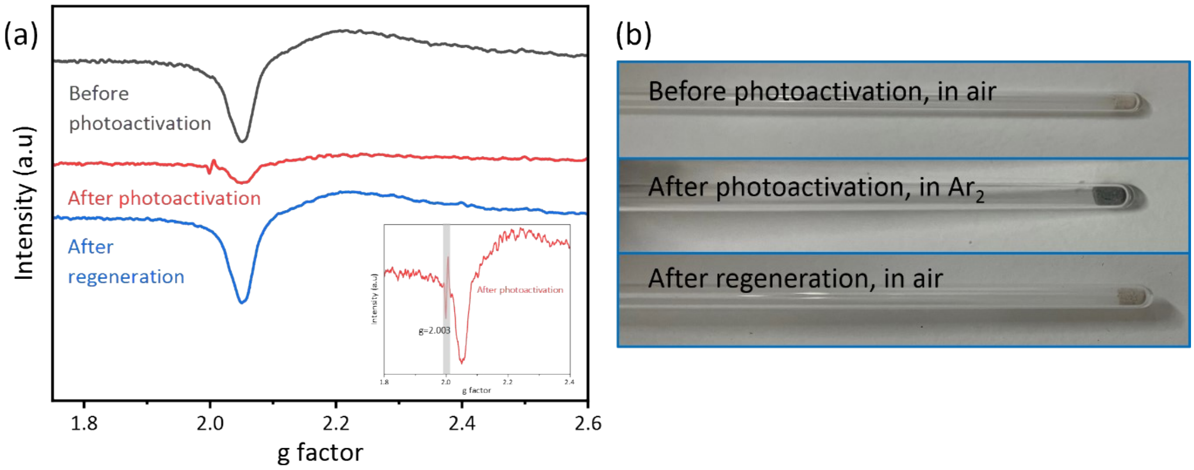

Fig. S13. (a) Color changes of Cu-TiO$_2$ before photoactivation, after photoactivation, after regeneration, respectively. (b) EPR spectra of Cu-TiO$_2$ in various states.

Supplementary Tables

Table S1. Summary of representative photocatalysts

Material	Loading amount	Reaction condition	Activity	Ref.
Cu-TiO_2	0.36 wt%	Methanol aqueous solution (30 vol%)	17.77 mmol g^{-1} h^{-1}	**This work**
Cu-TiO_2	0.75 wt%	Methanol aqueous solution (25 vol%)	16.6 mmol·g^{-1}·h^{-1}	NAT COMMUN 18 (2019) 620-626
Pt SA/Def-s-TiO_2	0.57 wt%	CH_3OH aqueous solution (20 vol%)	13.46 mmol g^{-1} h^{-1}	J ENERGY CHEM 62 (2021) 1-10
Pd/TiO_2	1.74 wt%	Methanol aqueous solution (50 vol%)	6572 μmol g^{-1} h^{-1}	ISCIENCE 24 (2021) 102938
$Pt_{0.254}$/black TiO_2	0.254 wt%	Methanol aqueous solution (10 vol%)	800.3 μmol g^{-1} h^{-1}	ENVIRON CHEM LETT 19 (2021) 1815-1821
Pt/NCD/TiO_2	0.78 wt%	0.3 M Na_2S and 0.3 M Na_2SO_3 aqueous solution	57.3 mmol·mg_{Pt}^{-1}·h^{-1}	J MATER CHEM A 8 (2020) 14690-14696
Pt-TiO_2	8.7 wt%	TEOA aqueous solution (10 vol%)	22.65 mmol·g^{-1}·h^{-1}	NANO ENERGY 69 (2020) 104409
Pd_{SA+C}/TiO_2-V_O	0.39 wt%	Methanol aqueous solution (20 vol%)	18 .2 mmol·g^{-1}·h^{-1}	SMALL 17 (2020) 2006255

Table S2. Best fitted parameters of time-resolved PL spectra.

Sample	τ1 (ns)	τ2 (ns)	A1	A2	Decay Lifetime (ns)
TiO_2	0.8744	5.197	244.6892	147.2250	2.08
Cu-TiO_2	0.5019	4.749	479.3375	35.3546	1.51

Decay lifetime is calculated by (A1τ1 + A2τ2)/(A1+A2)