Supporting information

Application of Long Wavelength Visible light (λ > 650 nm) in photocatalysis progress by n-In_2O_3/p-CuO Quantum Dots Heterojunction Photocatalyst

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Experimental details:

Preparation of Photocatalysts

All the chemical reagents were analytical grade and used without further purification. In a typical synthesis, $Cu(NO_3)_2\cdot 3H_2O$ (0.483 g) and $In(NO_3)_3\cdot 4.5H_2O$ (1.528 g) with a molar ratio of 1:2 were dissolved in 60 mL deionized water. The solution pH was carefully adjusted to 12 by using 1.0 M NaOH with vigorous magnetic stirring at room temperature. The obtained mixture was sealed into a 100 mL stainless autoclave and maintained at the temperature of 160 °C for 24 h, then cooled to room temperature naturally. The precipitates were washed by deionized water for several times and dried at 60 °C. The resulting products were sintered at 400 °C for 6 h to obtain the CuO/In_2O_3 heterojunction. For comparison, pure CuO and In_2O_3 were also synthesized under the same conditions.

Characterization

X-ray diffraction (XRD) patterns were recorded on a Philips X' Pert Pro MPD diffractometer with Co Kα radiation. Transmission electron microscopy (TEM) images were collected by using a JEOL JEM

2010F microscope working at 200 kV. The Brunauer–Emmett–Teller (BET) surface area of the samples was measured by N_2 adsorption at 77 K using Micromeritics ASAP2020 equipment. X-ray photoelectron spectroscopy (XPS) analysis was conducted on an ESCALAB 250 photoelectron spectroscopy (Thermo Fisher Scientific Inc.) at 3.0×10^{-10} mbar with monochromatic Al $K\alpha$ radiation. The XPS data were collected at 441 eV photon energy, while VB-XPS data were collected with a 226 eV photon energy and measured at the Fermi level (E_f) of approximately 0 eV. The UV-vis diffuse reflectance spectra (DRS) of the samples were recorded on a Varian Cary 500 UV-vis spectrophotometer equipped with an integrating sphere attachment.

Photocatalytic Activity Measurements

The photocatalytic experiment was carried out by adding an amount of 80 mg of sample into 80 mL of rhodamine B solution (1×10^{-5} mol/L). The suspension was stirred in dark for 2 h to obtain the saturated adsorption of RhB before illumination. The optical system used for the photocatalytic reaction consisted of a 500 W Xenon lamp, which focused the light onto the reaction cell, a cutoff filter (providing the visible light of different wavelength), and an IR-cutoff filter (λ < 800 nm, preventing from thermocatalytic effect). To measure RhB concentration, the suspension (3 mL) was separated by a centrifugal at given irradiation time intervals, then determined by measuring the maximun absorbance (λ = 554 nm) as a function of irradiation time with a Varian Cary 50 Scan UV-vis spectrometer. Finally, the total organic carbon (TOC) of bleaching solution was determined by a Shimadzu TOC-VCPH analyzer.

Detection of •OH Radicals and $O_2{\cdot}^-$ (ESR)

ESR spin-trapping technique appears to be one of the promising approaches for the detection of radicals' production.[1] It has been used to observe directly reactive oxygen species (ROS) generated in TiO_2 photocatalytic reactor and provides essential information for understanding of the reaction mechanism on semiconductor surfaces.[2,3] In our experiment, a Bruker model A300 spectrometer (Bruker Instruments, Inc.) was used for measurements of the electron paramagnetic resonance (EPR) spectrum. The capture agent of reactive radicals used is 5,5-Dimethyl-l-pyrroline N-oxide (DMPO), which had been dissolved in distilled water or methanol. The photocatalyst was homogeneously dispersed in DMPO solutions and analyzed in capillary quartz tube at given time intervals under visible light irradiation. The settings were as following: center field 3512.48 G, microwave frequency 9.86 GHz, and power 6.35 mW.

DPD Method for Detection of H_2O_2

The DPD (N,N–diethyl–p–phenylenediamine) method[4] employed for POD (peroxidase) measurements was used for the detection of hydrogen peroxide (H_2O_2). This method is based on the POD–catalyzed oxidation by H_2O_2 of DPD. After 2h of visible light irradiation, the CuO/In_2O_3 water (80 mg/80 mL) suspension was immediately centrifuged to remove the catalysts. After 0.05 mL DPD and POD were put into 27 mL centrifuged CuO/In_2O_3 water suspension one after another, the absorbance of suspension was measured by a Varian Cary 50 Scan UV-vis spectrometer. The sequence of reaction leads to the formation of the radical cation, $DPD^{\cdot+}$, which forms a fairly stable colour, with one absorption maxima at 510 nm and one at 551 nm.

UV-vis spectra

The UV-vis diffuse reflectance spectra of the as-prepared samples are shown in Figure S2. The CuO and the In_2O_3 show the obvious absorption in visible light region, and the CuO/In_2O_3 heterojunction presents a mixed absorption properties of both CuO and In_2O_3. For a crystalline semiconductor, the optical absorption near the band-edge follows the eq. 1[1]:

$$F(R)\cdot E=A(E-E_g)^{n/2} \qquad (1)$$

where E, E_g and A are photon energy, optical bandgap energy and characteristic constant, respectively. Moreover, n is decided by the characteristics of the transition in a semiconductor. For the CuO and the In_2O_3, the value of n is determined as 4 for the indirect transition.[2, 3]

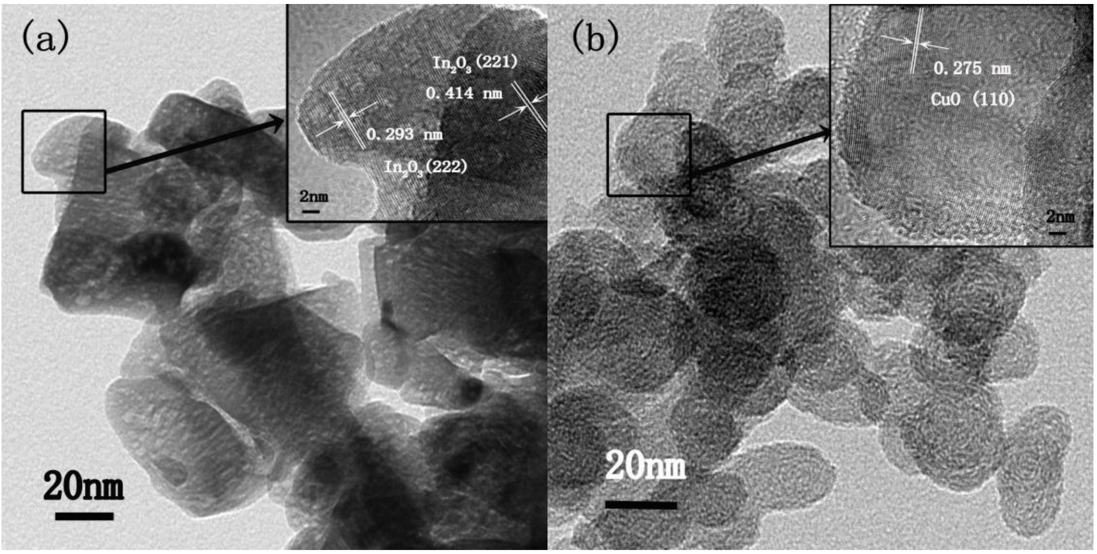

Figure S1 HRTEM images of pure In_2O_3 (a) and CuO (b).

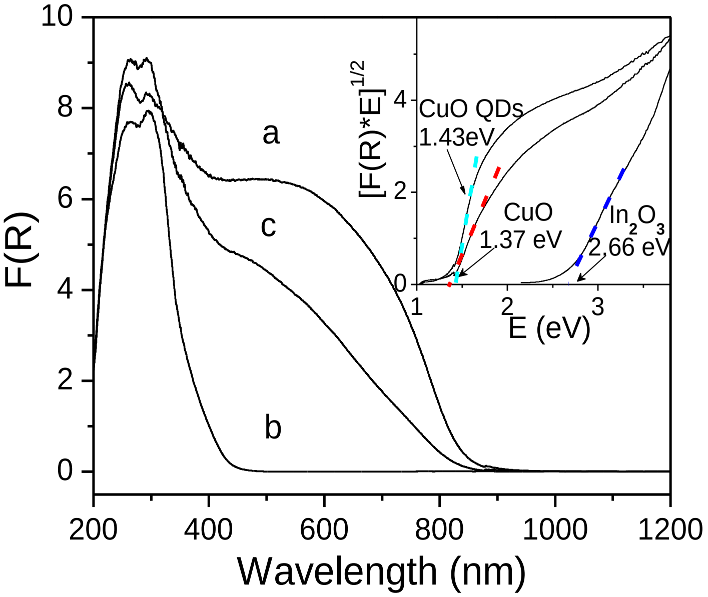

Figure S2. UV–vis diffuse reflectance spectra of pure CuO (a), pure In_2O_3 (b) and CuO/In_2O_3 heterojunction (c) with their optical band gap energy Eg (Inset)

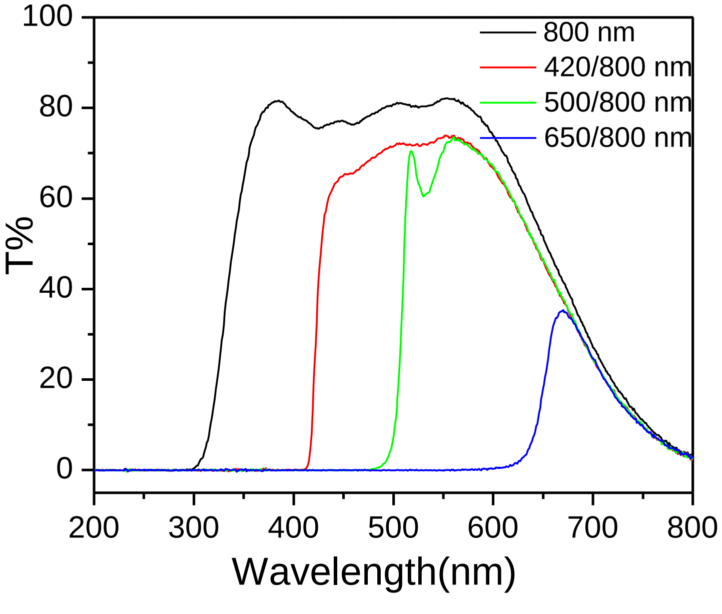

Figure S3. Optical transmission spectra of the filters used in the experiment.

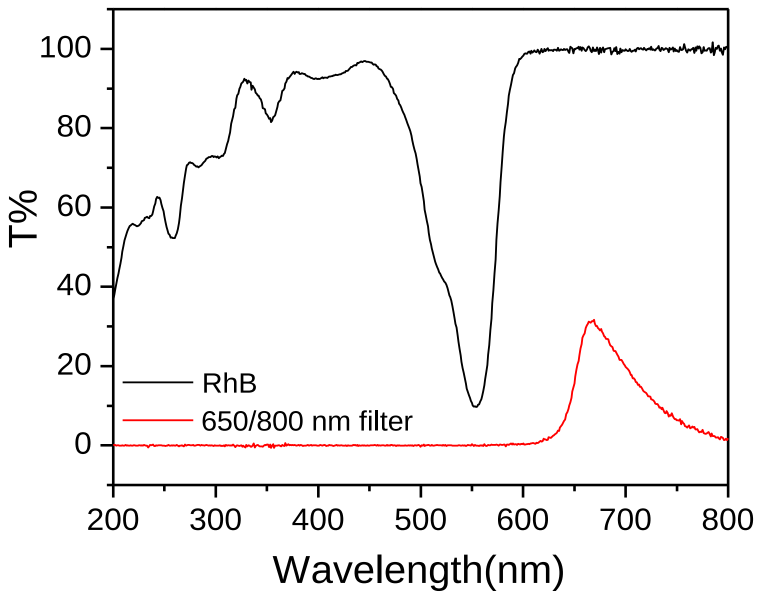

Figure S4 Optical transmission spectra of RhB solution and the 650/800 nm filter.

Notes: As seen in the figure S4, the optical transmission spectra of RhB at visible light wavelength of 600nm, 610 nm, 620nm, 630nm, 640nm, 650nm is 98.9%, 99.4%, 99.8%, 99.82%, 99.9%, 99.96%, respectively. That means that the light absorption of RhB at visible light wavelength of 600nm, 610 nm, 620nm, 630nm, 640nm, 650nm is 1.1%, 0.6%, 0.2%, 0.18%, 0.11%, 0.04%, respectively. Application of the 650/800 nm filter, the optical transmission spectra visible light wavelength of at 600nm, 610 nm, 620nm, 630nm, 640nm, 650nm is 0.35%, 0.5%, 1.5%, 2.56%, 6.24%,16.49%, respectively.

So the light absorption of RhB with the 650/800 nm filter was calculated below:

At the wavelength of 600nm:
RhB_{Abs}:=1.1 % * 0.35 % = 0.385 * 10^{-4}

At the wavelength of 610nm:
RhB_{Abs}=0.6 % * 0.5 % = 0.3 * 10^{-4}

At the wavelength of 620nm:
RhB_{Abs}=0.2 % * 1.5 % = 0.3 * 10^{-4}

At the wavelength of 630nm:
$RhB_{Abs}=0.18\ \% * 2.56\ \% = 0.46 * 10^{-4}$

At the wavelength of 640nm:
$RhB_{Abs}=0.11\ \% * 6.24\ \% = 0.68 * 10^{-4}$

At the wavelength of 650nm:
$RhB_{Abs}=0.04\ \% * 16.49\ \% = 0.66 * 10^{-4}$

Hence, we could elucidate that the light absorption of RhB under visible light irradiation with 650/800nm filter was nearly 0.

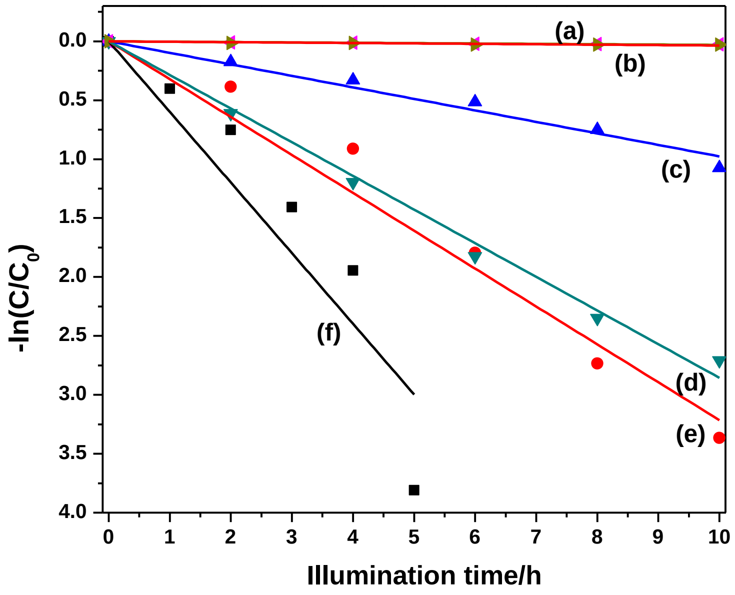

Figure S5 Photodegradation of RhB on CuO (a), In_2O_3 (b) with a 650/800 nm bandpass filter. Photodegradation of RhB on CuO-QDs/In_2O_3 with 650/800 (c), 500/800 (d), 420/800 (e) and 800 (f) nm bandpass filter, separately.

Table S1 The photodegradation rate constants of samples with different filters

Sample(filters)	k/h^{-1}
CuO(650/800nm)	0.00303
In_2O_3(650/800nm)	0.00356
CuO-QDs/In_2O_3(420/800nm)	0.321
CuO-QDs/In_2O_3(500/800nm)	0.286
CuO-QDs/In_2O_3(650/800nm)	0.0976
CuO-QDs/In_2O_3(800nm)	0.600

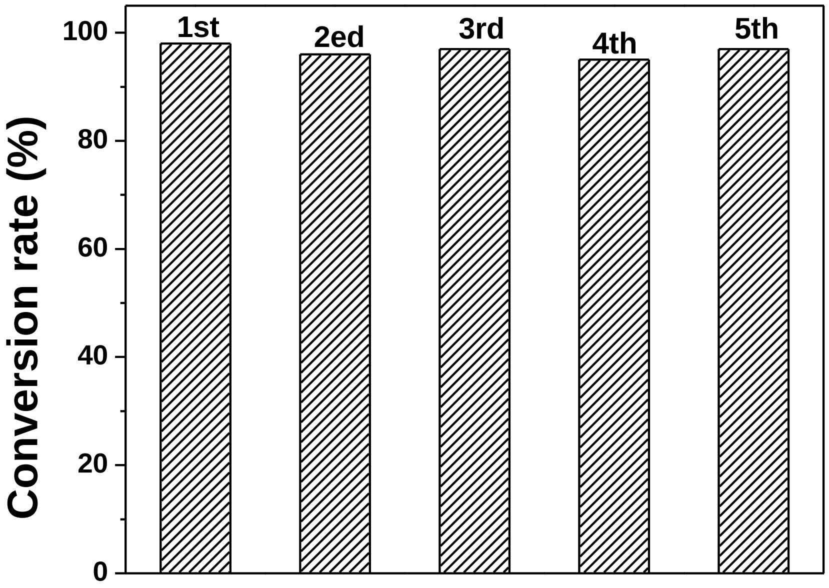

Figure S6 Degradation of RhB over CuO-QDs/In_2O_3 under visible light (650nm $<\lambda<$800nm) in five successive cycles.

Notes: In the photocatalytic stability experiments, the catalysts were recollected by centrifugation and then re-dispersed in the same RhB aqueous solution for next cycle. Other experimental parameters were same as the first testing.

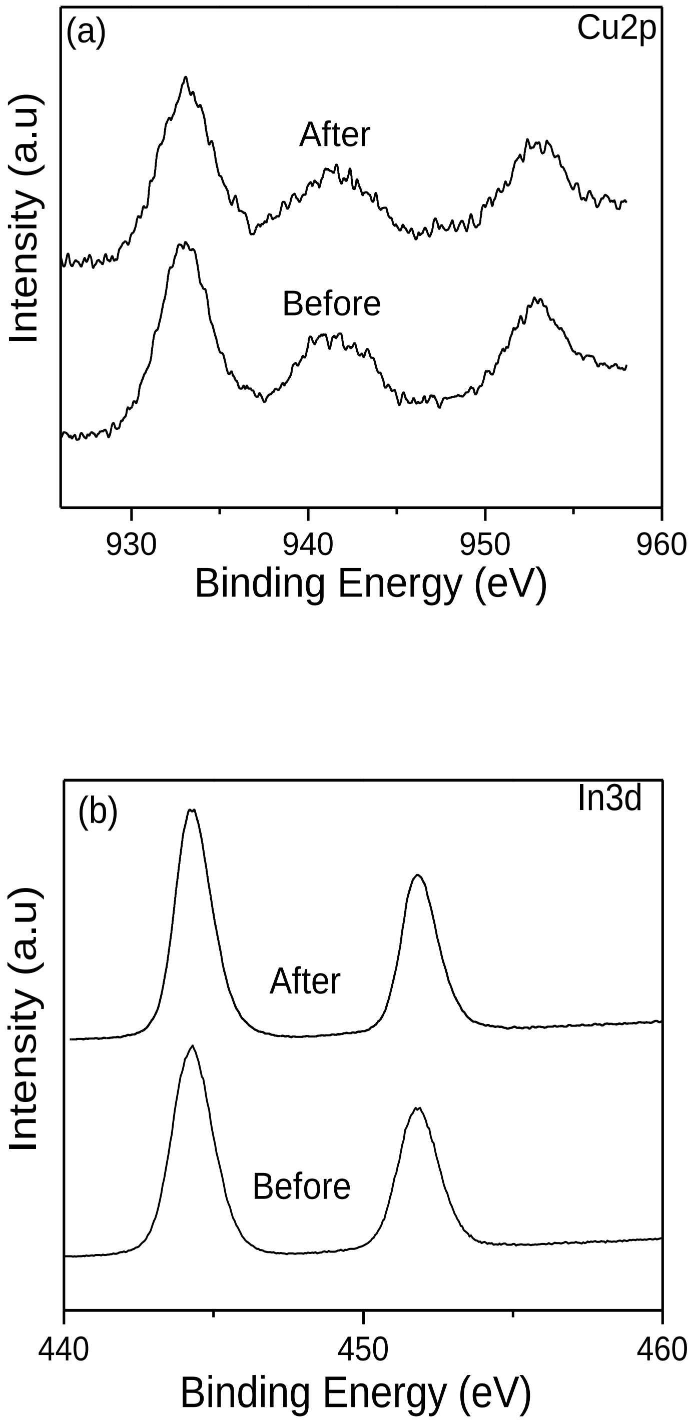

Figure S7. XPS spectra of CuO/In_2O_3 before and after 5 cycles reaction.

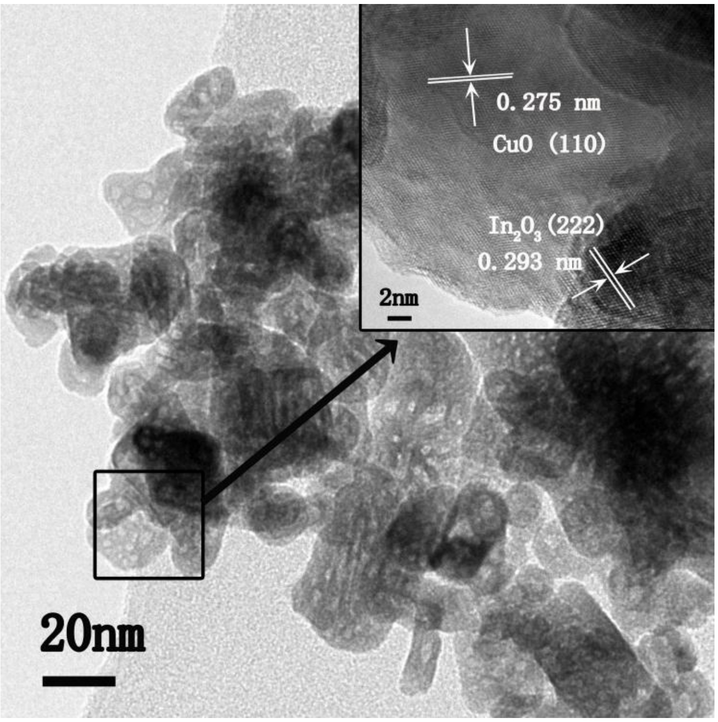

Figure S8 The HRTEM image of the as-prepared CuO/In_2O_3 with the CuO size 16nm.

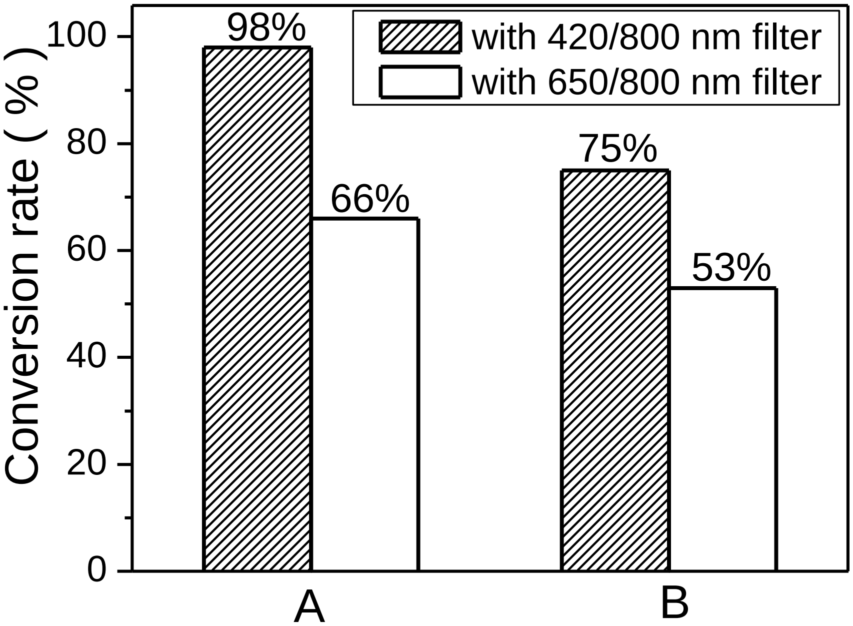

Figure S9. The conversion rate of RhB on CuO QDs/In_2O_3 (A) and CuO/In_2O_3 (B) with different cutoff filters, respectively.

Notes: The achieved high photocatalytic activity of the CuO-QDs/In_2O_3 may be attributed to two major improvements. First, the photocatalyst CuO-QDs/In_2O_3 can be excited by the much wider-ranging visible light. Second, The CuO QDs can absorb light in the visible region to generate electron–hole pairs, and the excited electrons are efficiently transferred from CuO QDs to In_2O_3. Therefore, the CuO QDs sensitized In_2O_3 photocatalyst has a beneficial role in improving charge separation and photocatalytic performance.

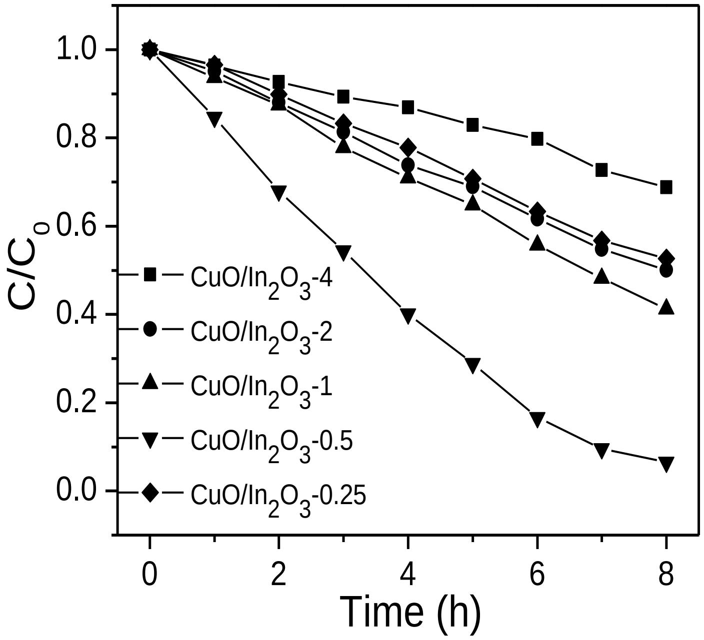

Figure S10 Photodegradation of RhB over the CuO/In_2O_3-X with different Cu/In ratios of 0.25 (-◆-), 0.5 (-▼-), 1 (-▲-), 2 (-●-) and 4 (-■-)

Notes: The samples signed as CuO/In_2O_3-X, which X represents the malar ratio of Cu/In.

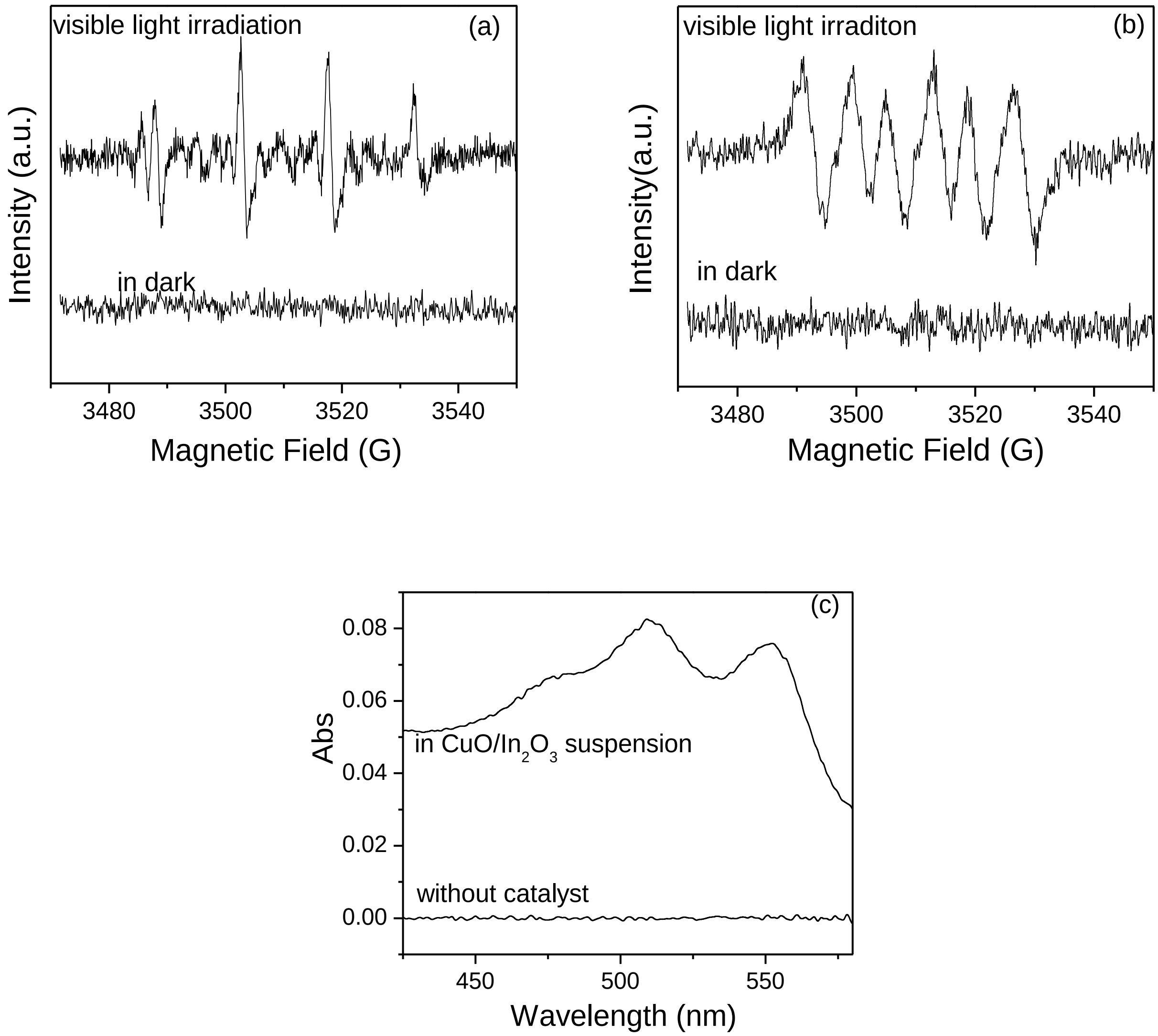

Figure S11 DMPO spin-trapping ESR spectra for CuO/In_2O_3: in methanol dispersion for DMPO-·OH (a) and in aqueous dispersion for DMPO-$O_2^{\cdot -}$(b); Detection of H_2O_2 in CuO/In_2O_3 water dispersion irradiated by visible light for 2 h (c).

Notes: ESR with DMPO spin–trapping experiments were carried out to detect the active species such as hydroxyl radicals (·OH) and superoxide radicals ($O_2\cdot^{-}$) in the CuO/In_2O_3 system under visible light irradiation. As shown in Figure S11, four characteristic peaks of the DMPO–·OH adduct were observed after 300 s visible light illumination in the water solvent, indicating small amount of ·OH was produced in the in the CuO/In_2O_3 system. On the other hand, DMPO–$O_2\cdot^-$ adducts with six obvious characteristic peaks of DMPO–$O_2\cdot^-$ species can be observed in the methanol solvent under ambient conditions. By contrast, there are no obvious signals detected in the dark. These results elucidated that $O_2\cdot^-$ and ·OH were really generated on CuO/In_2O_3 composite under visible light irradiation.

If the H_2O_2 are generated in the CuO/In_2O_3 water (80 mg/80 mL) suspension after 2h visible light irradiation, when DPD and POD were put in one after another, the radical cation $DPD^{\cdot+}$ would be formed in the system and be detected with two absorption peak, one at 510nm and the other at 551nm. The result was shown in Figure S11. For CuO/In_2O_3 water sample, there were two absorption maxima emerged at ca. 510 and ca. 551 nm, indicating H_2O_2 was actually generated in this experiment. While for the water sample, there were obvious absorbed peaks showing up. So we can indicate that the intermediate H_2O_2 species was actually generated in the CuO/In_2O_3 dispersions under visible light irradiation.

Table S2. TOC Detection Results after 10 h of irradiation.

Bandpass filters (nm)	800	420/800	500/800	650/800
TOC (mg/L)	0.36	0.83	1.32	1.62
Mineralization (%)	89.3	75.3	60.7	51.7

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