

Supporting Information

Triggering photocatalytic activity of carbon dot-based nanocomposites by self-supplying peroxide

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1. Experimental Procedures

1.1 Materials and reagents

The anthracite was purchased from Yangquan Coal Industry in Shanxi province, China, and the powder used for the CDs preparation was obtained through the ball-milling. Other chemicals including copper (II) chloride dihydrate ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$), 3,3',5,5'-Tetramethylbenzidine (TMB), o-Phenylenediamine (OPD), H_2O_2 (30 wt%), cupric nitrate ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$), acetic acid (CH_3COOH), sodium acetate (CH_3COONa), ethylenediaminetetraacetic acid disodium salt (EDTA-2Na), vitamin C (VC), terephthalic acid (TA), nitro blue tetrazorium (NBT), isopropanol (IPA), sodium sulphate (Na_2SO_4), ethanol absolute, were purchased from Aladdin, and they were directly used without further purification. $1 \text{ g} \cdot \text{L}^{-1}$ standard Cu^{2+} solution was purchased from Guobiao (Beijing) Testing & Certification Co., Ltd, China. All aqueous solutions in the experiment were prepared using ultrapure water.

1.2 Preparation of CDs

The preparation strategy of CDs was as mentioned in our previous work¹. 200 mg anthracite powder was mixed with 30 mL H_2O_2 (30wt.%) in the beaker and stirred for 24 h at 80 °C. Then the precipitate was separated with the supernatant through the centrifugation of 10000 rpm, and the supernatant was filtrated with the 0.22 μm filter paper and dialysis in water for 2 days. After vacuum drying at 60 °C for 3 h, the dark brown CDs powder of was collected.

1.3 Preparation of CDs@ CuO_x and CuO_x

Just as the procedure mentioned above, the prepared CDs/ H_2O_2 solution was reserved after the microfiltration with the 0.22 μm filter paper. Then 1.2 mmol of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ was slowly added into 30mL CDs/ H_2O_2 solution and stirred for 15 h at room temperature. Since Cu^{2+} can catalyze H_2O_2 to generate O_2 with intense heat

release, so a small amount was added each time to avoid the explosive boiling. Then 2.4 mmol NaOH was dissolved in 5 mL water and dropped into the liquid and reacted for 30 min. After centrifugation, washing and drying, the dark atrovirens powder was collected and we labelled it with CDs@CuO_x. In the contrast experiment, different addition amount of CuCl₂·2H₂O(0.4 mmol, 0.8 mmol, 1.2 mmol, 1.6 mmol, 2.0 mmol) and NaOH (0.8 mmol, 1.6 mmol, 2.4 mmol, 3.2 mmol, 4.0 mmol) was added to adjust the pH of the solution to higher than 8 to facilitate the formation of the oxide of copper. It turned out that the sample with the 1.2 mmol CuCl₂ exhibited the best photocatalytic effect to TMB (Figure S11b). For comparison, with the same preparation process mentioned above, just CDs/H₂O₂ solution was changed to H₂O₂ solution alone, the dark brown powder was prepared and marked as CuO_x.

1.4 Preparation of the pure CuO

The procedure referred to the previous report², thus 20 mL 0.8 M NaOH was dropped into the 20 mL 0.2 M Cu(NO₃)₂·3H₂O, the solution with the blue precipitate was transferred into a Teflon-lined reactor and heated from room to 180 °C and kept for 2 h. After cooling to room temperature, the bottom of Teflon lining would have precipitates. The collected precipitates were centrifuged and washed three times with water, and dried in a vacuum oven at 60 °C for 4 h.

1.5 Photocatalysis process of TMB and OPD

30 mM TMB solution was prepared in the ethanol absolute while 0.1 M pH=4 buffer solution was prepared with CH₃COOH and CH₃COONa. 1 mg sample was added into the mixture of 10mL buffer solution and 200 μL 30 mM TMB. The solution was irradiated with the light intensity 200 mW/cm². The product TMB-ox shows a characteristic absorption at 652 nm, which was monitored using UV-vis spectrophotometry by taking aliquots at regular intervals.

10 mM OPD solution was prepared and 10 mL was measured to conduct the photocatalysis experiment with 1 mg samples on the irradiation of simulated sunlight (100 mW/cm²) with the Tris-HCl buffer. The characteristic absorption peak of OPD-ox was at 417 nm and the measurement was conducted with the UV-vis spectrophotometry.

The visible light irradiation was provided using a solar light simulator (CEL-HXUV300, CEAULIGHT, China) with optical cut-off filters that were utilized to remove wavelengths below 420 nm. The wavelength intensity distribution curve of the visible light spectrum is shown in Figure S4.

1.6 Recycle of CDs@CuO_x

The recycle of CDs@CuO_x in OPD system was simple, thus collecting and drying the sediment after centrifugation and washing from the OPD-ox solution that after reaction. While since the composite can partly dissolve in the TMB solution with the acid condition of pH=4.0, so the recycle process was a little complex. The pH condition should be adjusted to be >8.0 with the addition of 0.1M NaOH, 10μL of H₂O₂ were also added to facilitate the formation of CDs@CuO_x. Then the precipitate was washed for three times and dried in the vacuum oven.

1.7 Experiment of reaction dynamics

The reaction dynamics was then studied in a series of TMB solutions with a range of concentration. The absorbance displayed a linear increase in each concentration (Figure S8) and the value of the slop rised gradually. The absorbance data should be converted to TMB-ox concentration according to the Lambert beer's law (1) when calculate the velocity.

$$A = \varepsilon \times b \times C \quad (1)$$

where A is absorbance which can be measured; ε is the molar extinction coefficient of TMB-ox, ($\varepsilon=39000 \text{ M}^{-1}\text{cm}^{-1}$); b is the path length of light ($b=1 \text{ cm}$).

Then the reaction rates were fitted by Michaelis-Menten equation:

$$v=V_{\max} \times \frac{[S]}{[S] + K_m} \quad (2)$$

where V_{\max} is the maximal reaction velocity; K_m is the Michaelis constant; $[S]$ is the concentration of reaction substrate.

Therein, K_m is a key parameter that indicates the enzyme affinity for a substrate. The lower K_m value means the higher affinity of catalysts to the substrates. V_{\max} refers to the reaction rate when the substrate concentration is saturated.

1.8 Sample characterization

TEM and HRTEM were performed on a FEI Tecnai G2 F20 microscope with a field-emission gun operating at 200 kV. X-ray diffraction (XRD) patterns of different samples were obtained on a Bruker D8 ADVANCE powder diffractometer at Cu $K\alpha$ with a scanning rate of 2° min^{-1} in the 2θ range of $10\text{--}90^\circ$. Light absorption spectra were collected on a Shimadzu UV-2550 UV-vis spectrometer. Fluorescence spectra were recorded with a Hitachi F4500 fluorescence spectrophotometer. Fourier transform infrared (FT-IR) spectrum of samples were recorded as KBr pellets with a Bruker Vertex 70 spectrometer from 4000 to 500 cm^{-1} . X-ray photoelectron spectroscopy(XPS) was tested on the Thermo Scientific ESCALAB 250Xi electron spectrometer with an Al $K\alpha$ Xray source for determining the composition and chemical bonding configurations. The atomic absorption spectroscopy (AAS, analytischejena ContrAA 800D(Germany)) was used to measure the content of Cu^{2+} in the solution.

1.9 Electrochemical measurement

The electrochemical measurement was conducted in the solution system of $0.1 \text{ M Na}_2\text{SO}_4$ with the three electrodes unit. The work electrode, counter electrode, and reference electrode were the sample-coated ITO glass, the Ag/AgCl standard

electrode and the Pt plate, respectively. The electrochemical data was tested and recorded by the SP-200 Bio-logic electrochemical workstation.

Mott-Schottky (MS) curves was measured in the Na₂SO₄ solution and four frequencies was chosen simultaneously to obtain the flat band potential of CDs@CuO_x and CuO_x (Figure S12). Their plots show a negative slope, which is typical for n-type semiconductor⁴. According to the relation of conduction band potential(E_c) and the flat band potential(E_{fb})^{5, 6}:

$$E_c = E_{fb} - kT \ln \frac{N_D}{N_C} \quad (3)$$

Therein, k presents the Boltzmann constant, T stands for the temperature. N_D and N_C refer to the donor impurity concentration and the effective conduction band state density. The second term depends mainly on the doping concentration of the semiconductor, and to the heavily-doped n-type semiconductor, it approaches to 0 that can be neglected. Therefore, the equation can be written as $E_c \approx E_{fb}$, so the conduction band of CDs@CuO_x and CuO_x were respectively -0.18 and 0.38 V (vs. NHE). Meanwhile, the carrier concentration (N_d) can be calculated to be $N_{d-composite}=6.0 \times 10^{20} \text{ cm}^{-3}$ and $N_{d-CuO}=4.59 \times 10^{20} \text{ cm}^{-3}$ on the basis of the following equation⁷:

$$N_d = \frac{2}{e_0 \epsilon \epsilon_0} \left| \frac{dC^{-2}}{dV} \right|^{-1} \quad (4)$$

in which e_0 refers to the electron charge, ϵ and ϵ_0 is the dielectric constant and vacuum permittivity, respectively.

1.10 Detection of free radicals

Hydroxyl radical test. Since terephthalic acid (TA) can react with $\cdot\text{OH}$ and the production 2-hydroxy terephthalic acid (TAOH) possess unique fluorescence at around 426 nm with excitation of 312 nm,⁸ we adopted this method to detect the presence of $\cdot\text{OH}$. 0.02 g NaOH was dissolved in 50 mL DI water, and 0.024 g TA was then put into the solution to stir for about 2 hours to ensure the completely dissolution.

Then 10 mg CDs@CuO_x or CuO_x was added into the prepared solution to stir for a certain time, then a small amount of the solution was centrifuged, and supernatant fluid was taken to test the fluorescence.

Superoxide radical test. NBT can be reduced by the ·O₂⁻ radical to generate blue formazan⁹ and the characteristic absorption peak of nitro blue tetrazorium (NBT) at around 260 nm can be detected with the UV-visible spectrophotometer. 1mg NBT was dissolved in 100 mL DI water with magnetic stirring for 30 min to dissolve completely. Then 10mg of CDs@CuO_x powder was added into 30 mL of the prepared NBT solution. After 10min with irradiation under visible light, 3 mL of the solution was extracted with a syringe (without a needle) and the liquid was filter through a matched 0.22 μm filter membrane to obtain the clear liquid for the test. By contrast, the test without the light was also conducted.

1.11 Measurement of the concentration of dissolved Cu²⁺

We chose atomic absorption spectroscopy (AAS, analyticjena ContrAA 800D (Germany)) to measure the content of Cu²⁺ in the solution. The wavelength λ=324.754 nm was chosen as the characteristic wavelength.

Preparation of the AAS samples. 10mg CDs@CuO_x sample was added into the 50 mL NaAc-HAc buffer (pH =4.0), after stirring with the magnetic stirrer for 5 min, more than 5 mL solution was extracted with a syringe to filter by the 0.22 μm microfiltration membrane. Then 5 mL of the clear liquid was put into the 100 mL volumetric flask to dilute and the solution obtained was marked as Cu²⁺-5 min. Similarly, the dissolve time of 10 and 15 min were also prepared as the steps mentioned above and marked with Cu²⁺-10, Cu²⁺-15 min, respectively. The standard Cu²⁺ solution with the concentration of 1, 2, 3, 4 mg·L⁻¹ was prepared by attenuation from the 1 g·L⁻¹ standard Cu²⁺ solution.

2 Supporting Figures

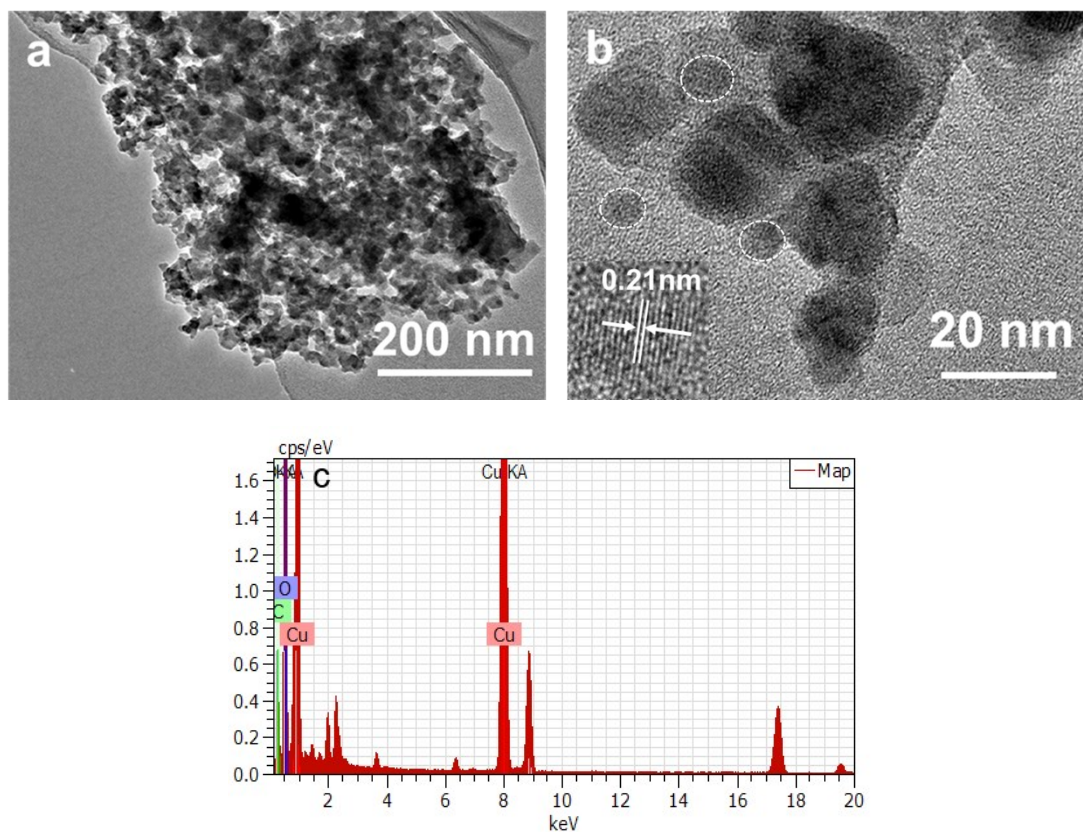


Figure S1. The TEM images of CDs@CuO_x with different scales (a) 200 nm, (b) 20 nm (CDs are marked with white circles and the inset shows the interplanar spacing of one carbon dot). (c) Elements concentration result of CDs@CuO_x in the STEM elemental mapping.

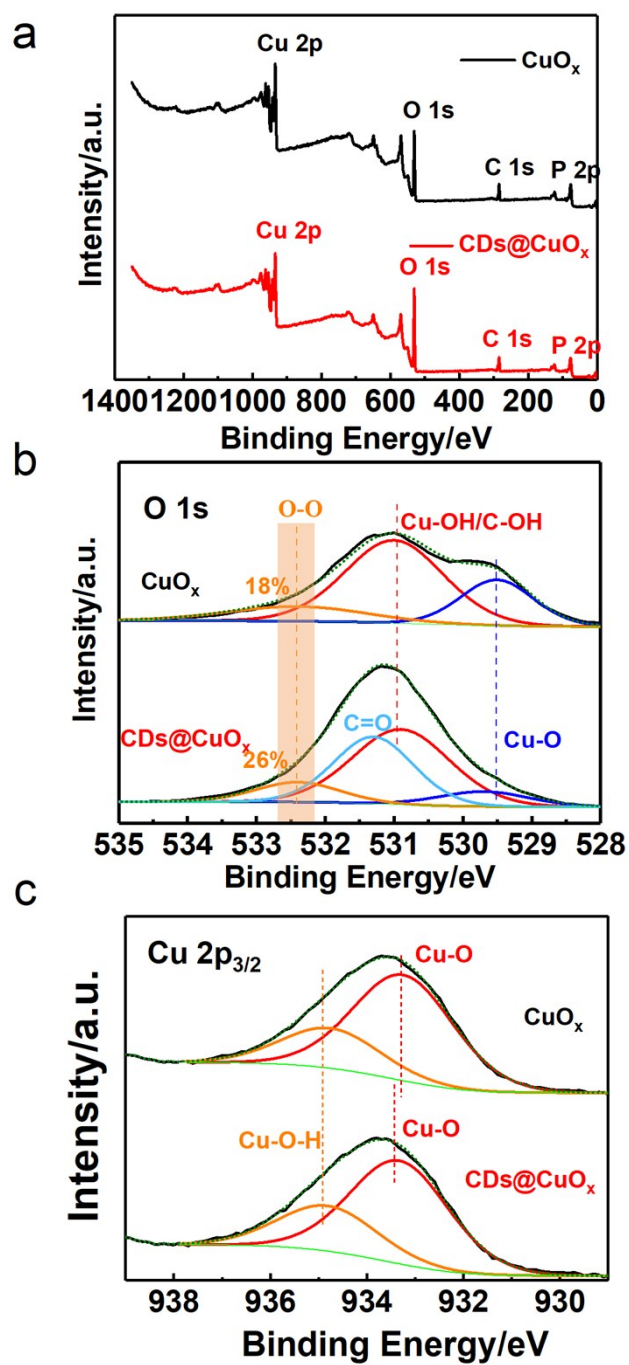


Figure S2. XPS analysis of CDs@CuO_x and CuO_x. (a) The survey patterns, (b) The high-resolution of O 1s spectra, (c) The high-resolution XPS Cu 2p_{3/2} spectra.

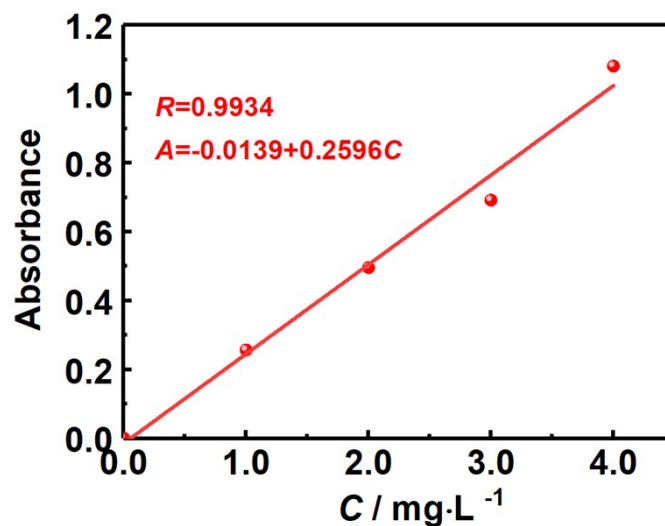


Figure S3. The standard Cu^{2+} curve obtained by the standard Cu^{2+} solution with a series of concentration.

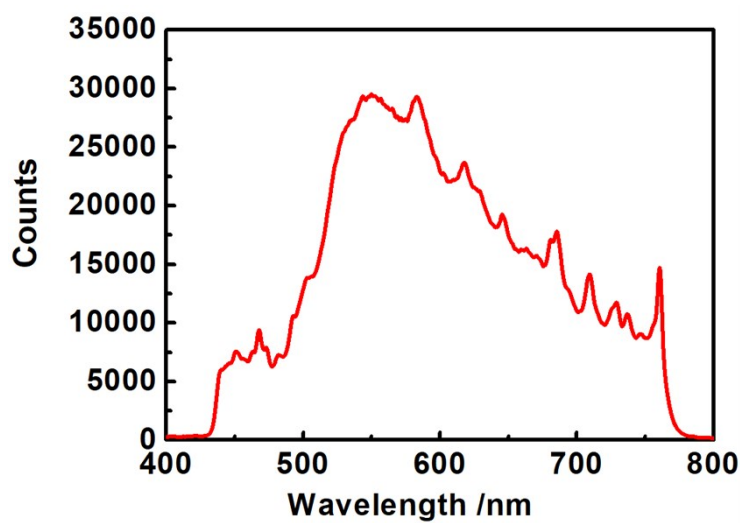


Figure S4. The spectrum of the solar light simulator with 420 nm cut-off filter.

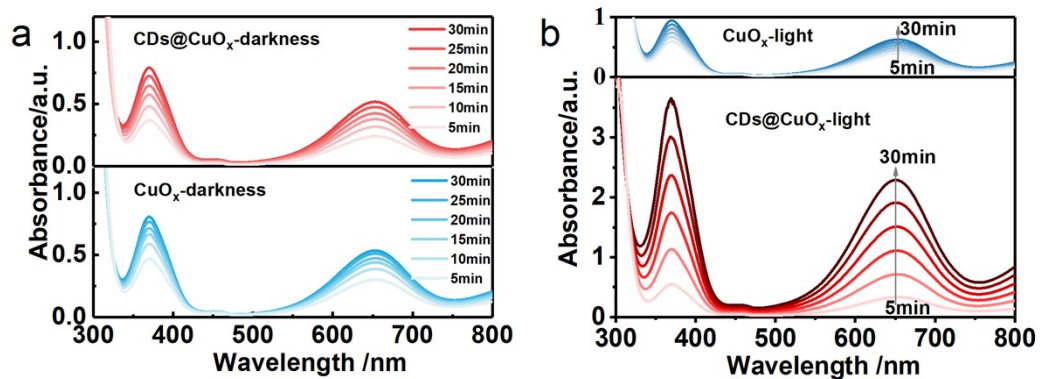


Figure S5. The catalytic effect of samples to TMB in different conditions. (a) The result of CDs@CuO_x and CuO_x in the darkness. (b) The result of CDs@CuO_x and CuO_x with light.

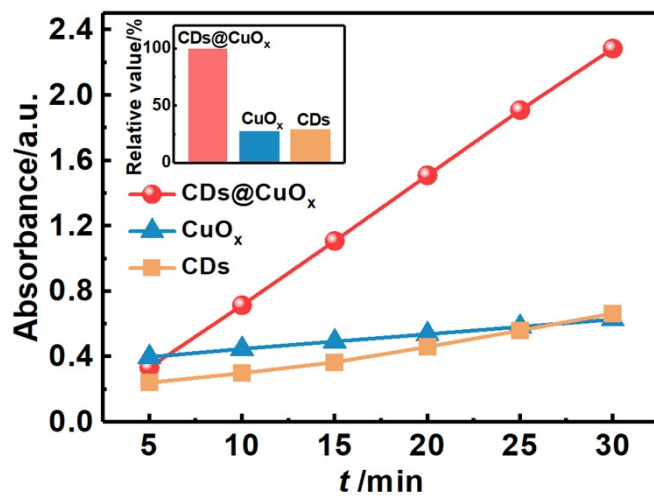


Figure S6. The photocatalysis performance comparison of CDs@CuO_x, CuO_x and CDs.

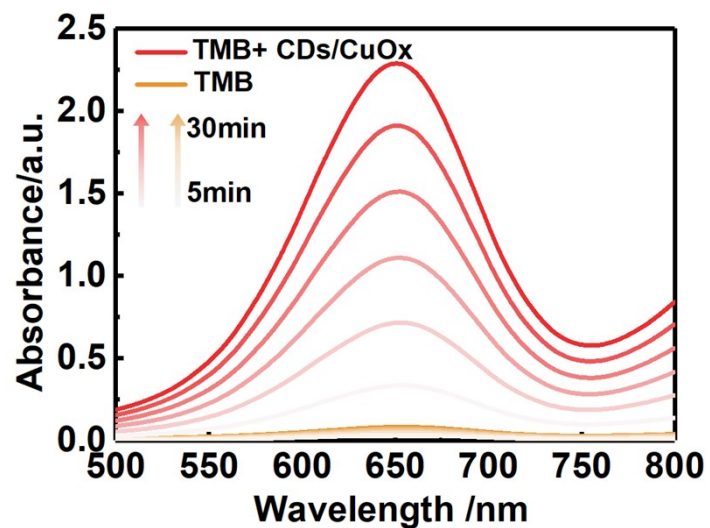


Figure S7. The comparison of the oxidation activity of TMB with and without CDs/CuO_x.

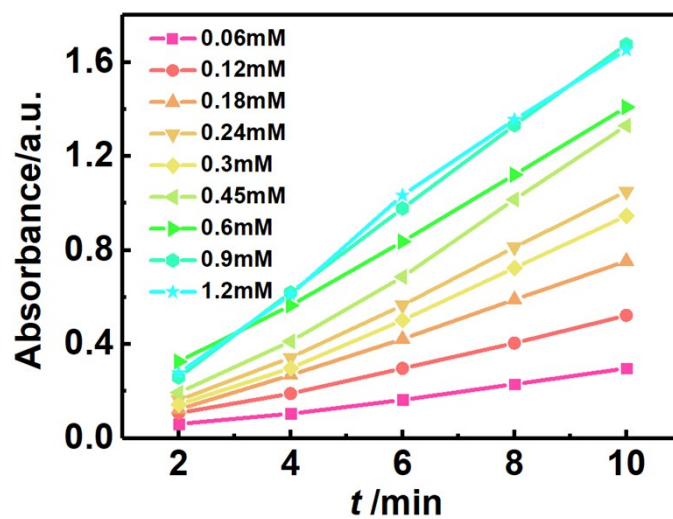


Figure S8. The absorbance of the solution with CDs@CuO_x in different TMB concentration.

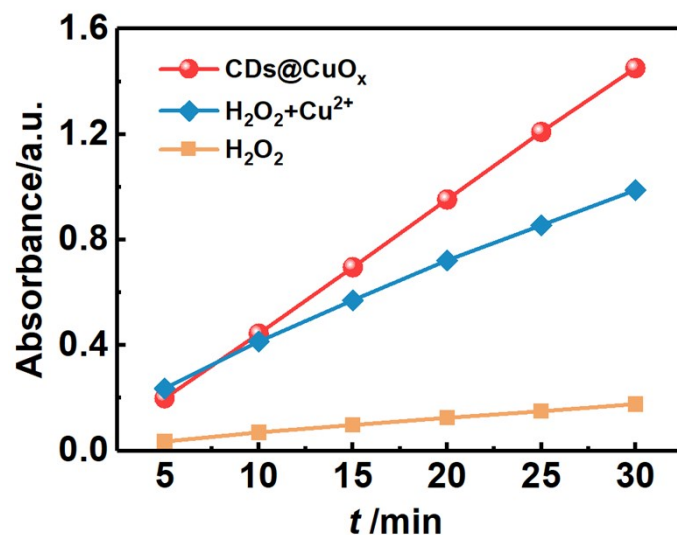


Figure S9. The comparison of the Fenton-like system Cu²⁺ (CuCl₂·2H₂O 1 mg) /H₂O₂ (10 μL) with CDs@CuO_x (1 mg), H₂O₂ (10 μL) was as the blank control group.

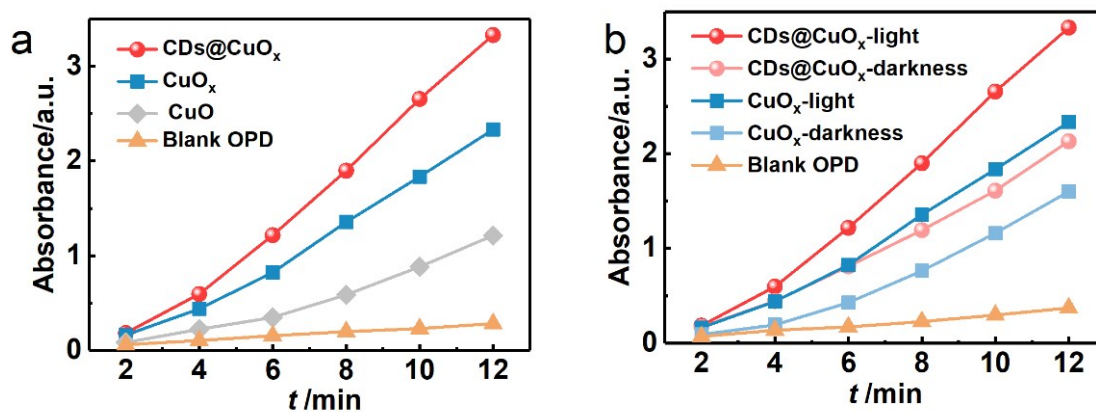


Figure S10. (a) The comparison of CDs@CuO_x, CuO_x and pure CuO on photocatalysis of OPD. (b) The photocatalytic performance of CDs@CuO_x and CuO_x with or without light.

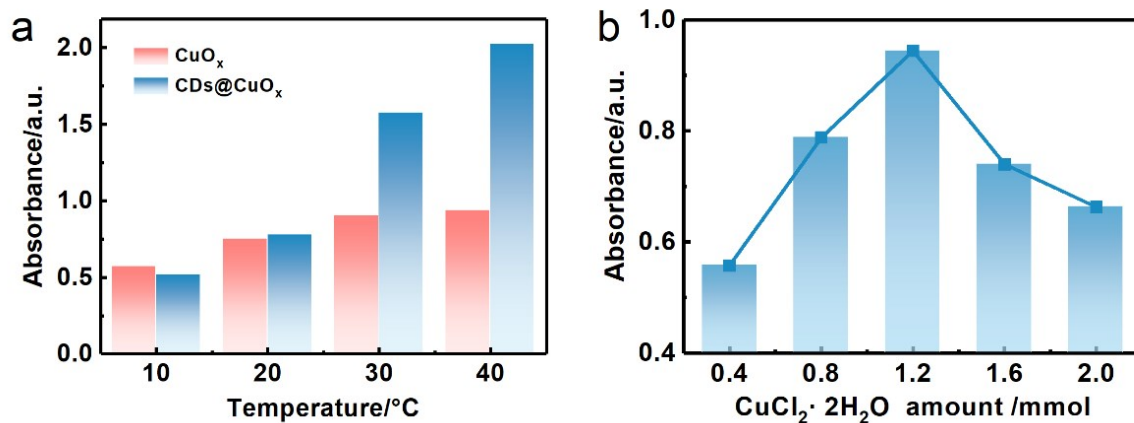


Figure S11. (a) The influence of temperature on the photocatalytic effect of CDs@CuO_x and CuO_x (b) The photocatalysis performance of the samples of CDs@CuO_x with different addition amount of CuCl₂·2H₂O (0.4 mmol, 0.8 mmol, 1.2 mmol, 1.6 mmol, 2.0 mmol)

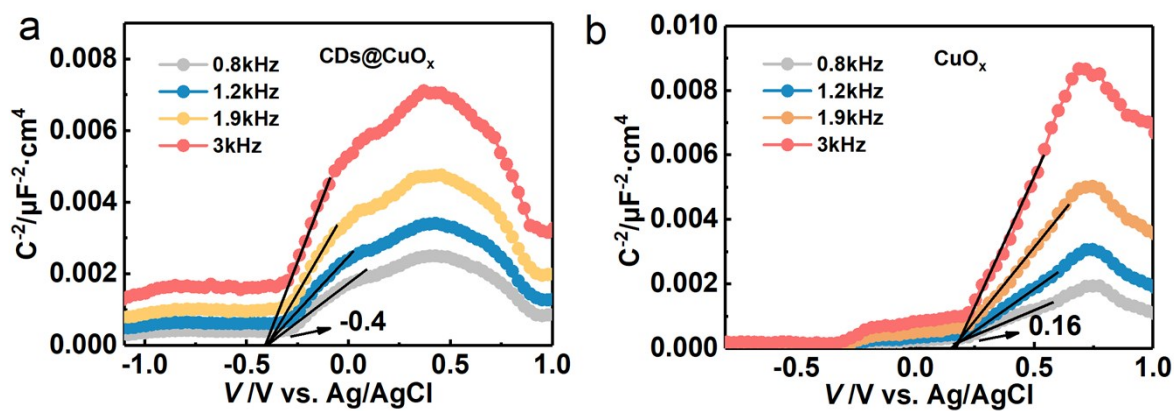


Figure S12. The MS curves of (a) CDs@CuO_x and (b) CuO_x.

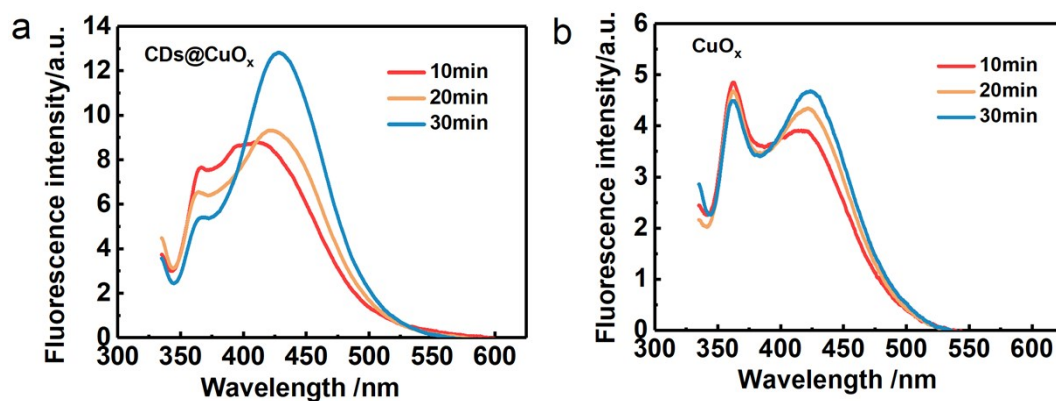


Figure S13. The fluorescence intensity of TAOH in the solution with (a) CDs@CuO_x and (b) CuO_x, respectively, which is associated with the concentration of ·OH.

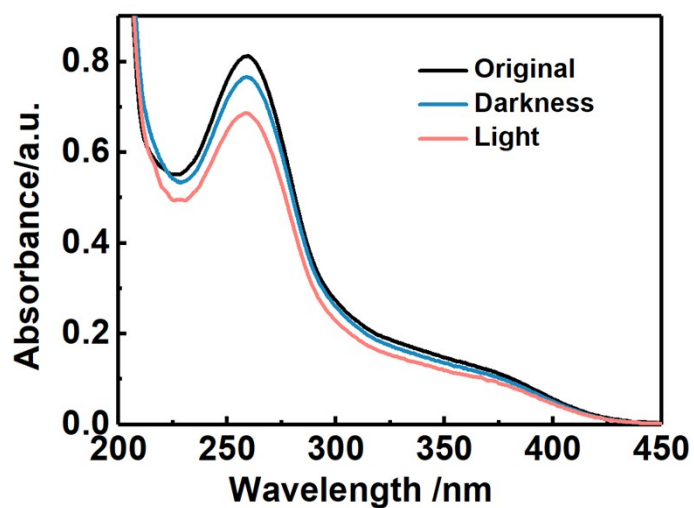


Figure S14. The UV-visible absorbance of NBT with the addition of CDs@CuO_x in darkness and light, respectively.

Table S1. The AAS result of the solution with dissolved Cu²⁺.

Samples	Concentration/mg·L ⁻¹	Absorbance
Cu ²⁺ -5min	3.951	1.0118
Cu ²⁺ -10min	3.955	1.0127
Cu ²⁺ -15min	4.106	1.0519
Reference solution	0	0.00067
Standard Cu ²⁺ solution	1.0	0.25672
	2.0	0.49616
	3.0	0.69206
	4.0	1.0810

Table S2. Comparison of the kinetic parameters of different artificial enzymes for TMB oxidation

Catalyst	K_m /mM	V_{max} /μM min ⁻¹	Additive	References
Fe ₃ O ₄ @Cu/C	1.87	81.24	H ₂ O ₂	10
Cu/Cu _x O/NC	1.61	54	H ₂ O ₂	11
Cu@Cu ₂ O	0.94	5.71	H ₂ O ₂	12
PtNPs@MnO ₂	0.015	9.36	/	13
CeO ₂ +F ⁻	0.14	3.78	/	14
CoMo hybrids	0.236	3.414	/	15
Cu-NC	0.223	1.81	/	16
CDs	0.31	1.716	/	17
Acr+-Mes	0.129	0.269	/	18
N-PCNSs-3	0.084	0.252	/	19
CDs@CuO_x	0.34	5.95	/	This work

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