

Supplementary Information

Boosting chemoselective reduction of 4-nitrostyrene via photoinduced energetic electrons from in-situ formed Cu nanoparticles on carbon dots

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1. Experimental Section

1.1 Materials and reagents. All of chemicals including 4-nitrostyrene (4-NS), 4-aminostyrene (4-AS), 4-nitroethylbenzene (4-NE), 4-ethylbenzenamine (4-EA), 4-nitrophenol, copper (II) acetylacetonate ($\text{Cu}(\text{acac})_2$), N, N-Dimethylformamide (DMF), formic acid (88 v/v%), H_2O_2 (30 v/v%), ammonia borane (AB), and NaBH_4 were purchased from Aladdin and they were directly used without further purification in our experiments. All aqueous solutions in the experiment were prepared using ultrapure water.

1.2 Preparation of CDs. Our used CDs were prepared according to our previous method¹. Typically, coal pitch powder (200 mg) was added into the mixed solution of formic acid (30 mL) and H_2O_2 (3 mL), then the resultant solution was stirred for 20 h at room temperature. Subsequently, the supernatant liquid containing CDs was retained by centrifugation for 30 min at 10000 rpm. After removing the solvent, the powder of CDs was obtained finally.

1.3 Preparation of CDs@CuNPs. In a 50 mL beaker, 80 mg of $\text{Cu}(\text{acac})_2$, 80 mg of CDs, and 6 ml of H_2O were added into 24 mL of DMF. After stirring for 30 min, the homogeneous black solution was transferred into a Teflon-lined reactor and heated from room to 160 °C and kept for 2 h. After cooling to room temperature, the precipitates were collected by centrifugation. The collected precipitates were dried in a vacuum oven at 60 °C for 12 h after washing several times with ethanol and water, respectively. The comparison sample of Cu_2O was prepared following the same recipe and processes as for CDs@CuNPs but without adding CDs.

1.4 Sample characterization. Absorption spectra of samples were collected on a Shimadzu UV-2550 UV-Vis spectrometer. X-ray diffraction (XRD) patterns of different samples were obtained using a Bruker D8 ADVANCE powder diffractometer at Cu K α with a scanning rate of 2° min⁻¹ in the 2 θ range of 5–90°. TEM and HRTEM were performed on a FEI Tecnai G2 F20 microscope with a field-emission gun operating at 200 kV. XPS data of all samples were collected using a Kratos AXIS 165 multitechnique electron spectrometer with an Al K α X-ray source for determining the composition and chemical bonding configurations.

1.5 Electrochemical measurements. Electrochemical measurements were conducted in a three-electrode electrochemical cell system. All working electrodes were fabricated through coating ethanol suspension of the samples onto indium tin oxide (ITO) glass electrodes, then evaporating the solvent in a vacuum at 60 °C. The electrolyte solution was made using 0.5 M Na₂SO₄. A Platinum plate and Ag/AgCl reference electrode acted as the counter electrode and reference electrode. All of the data were collected on a Bio-Logic (SP 120) electrochemical workstation.

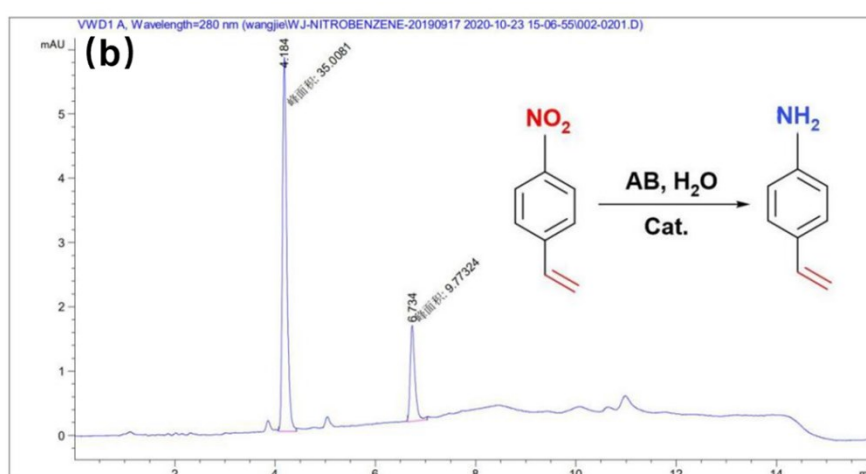
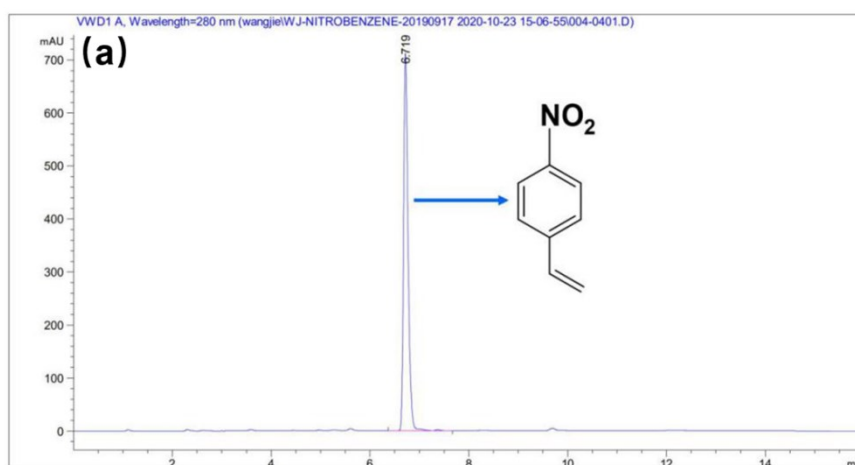
1.6 Catalytic reaction test. Typically, 3 mg of sample powder and 20 mL of aqueous solution of the reaction substrate (0.168 mM) were added into a quartz reactor placed on a magnetic stirrer and thermostatted at 25 °C. After dissolving the powder completely, 2 mg of AB and 4 mg of EDTA-2Na as a sacrificial reagent was then put into the reactor. The sealed reactor was irradiated under a Xe lamp with a cut420 filter attached ($\lambda \geq 420$ nm, 100 mW·cm⁻²). The characteristic absorption of the products was monitored using UV–Vis spectrophotometry by taking aliquots at regular intervals. The

concentrations of the products (C) were obtained using the Lambert beer's law:

$$A = \varepsilon \times b \times C$$

where A is absorbance which can be measured; ε is the molar extinction coefficient of the products; b is the path length of light ($b=1$ cm). Finally, the product contents were further confirmed by GC-MS (gas chromatography with a Thermo Finnigan chromatograph equipped with a flame ionization detector and a DB-WAX capillary column with nitrogen as the carrier gas).

2. Supporting results



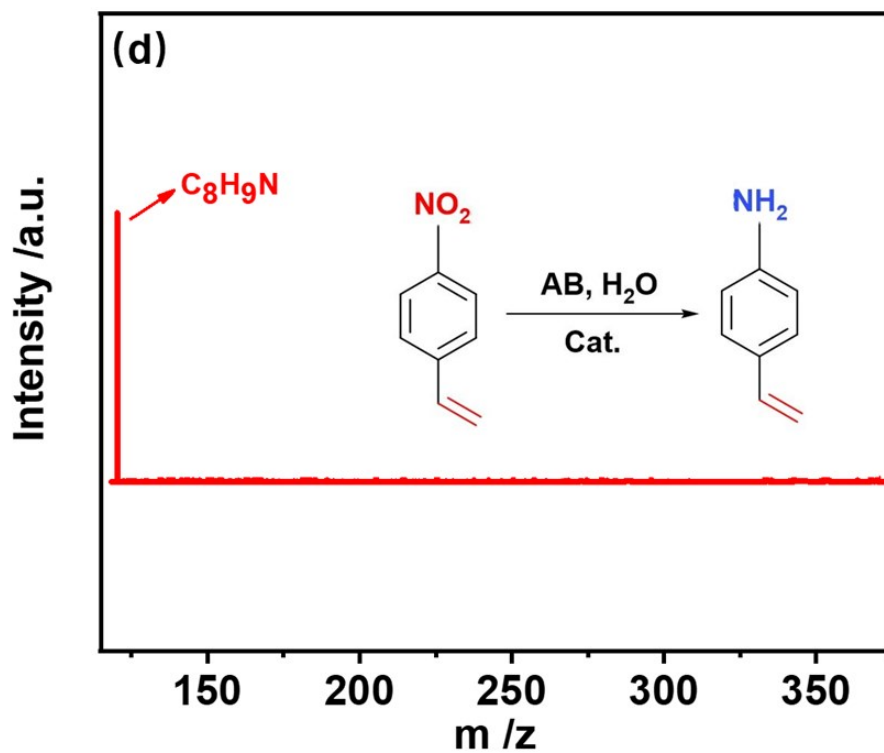
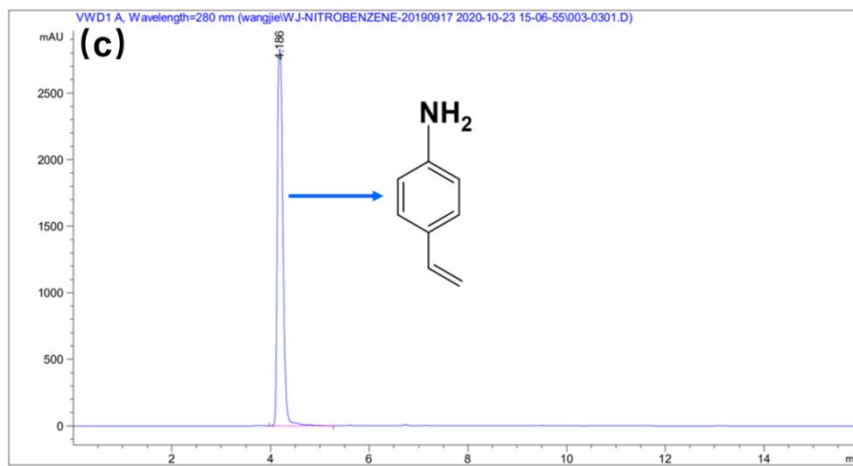


Figure S1. (a) GC spectrum of 4-NS; (b) GC spectrum of the product after catalytic reaction for 8 min; (c) GC spectrum of the product after catalytic reaction for 20 min; (d) MS spectrum of the product after catalytic reaction for 20 min.

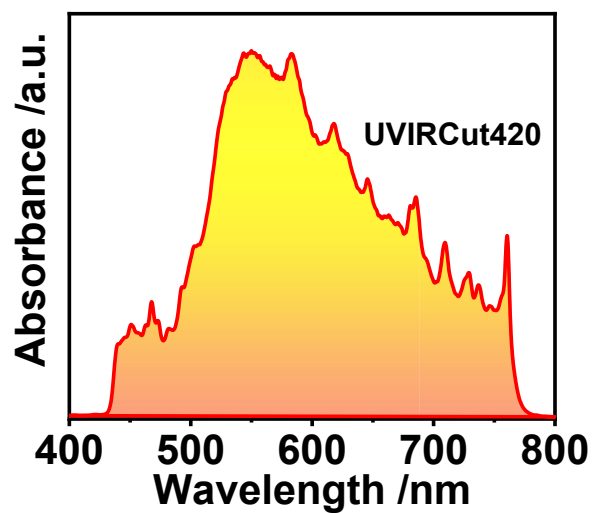


Figure S2. Visible light spectrum obtained by cut420 filter

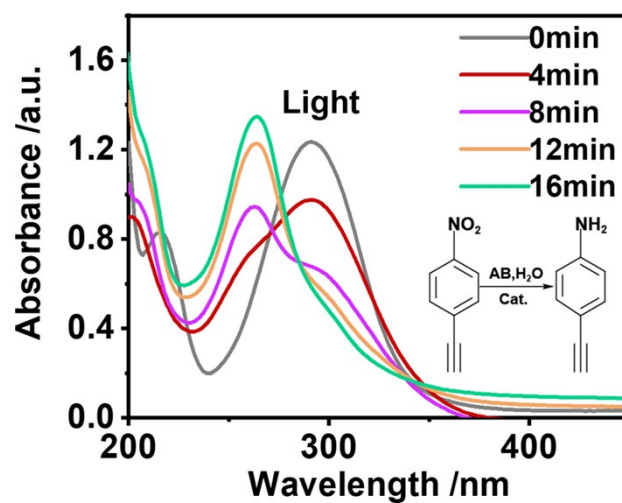


Figure S3. UV-Vis. absorption spectra of 4-nitrophenylacetylene vs. time in the presence of CDs@CuNPs (3 mg) and AB (2 mg) under visible light irradiation

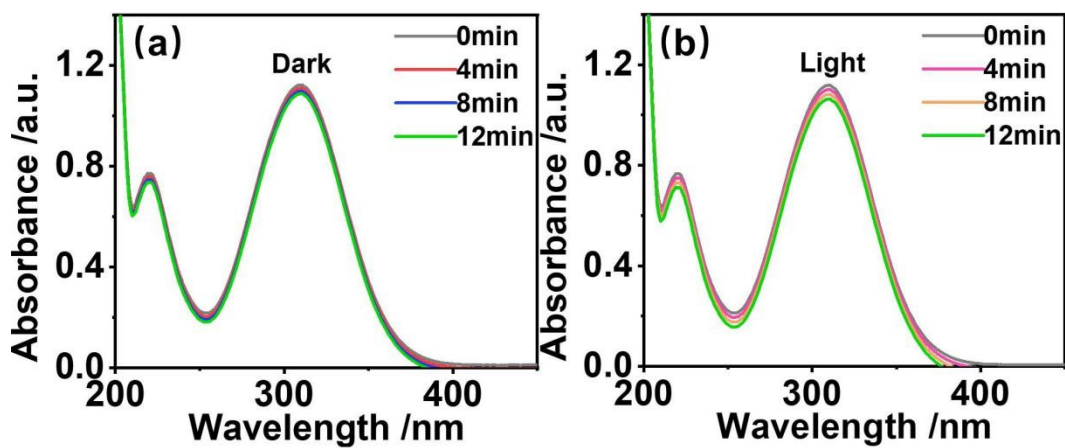


Figure S4. UV-Vis. absorption spectra of 4-NS vs. time in the presence of CDs@CuNPs but no addition of AB on dark condition (a) and on illumination (b)

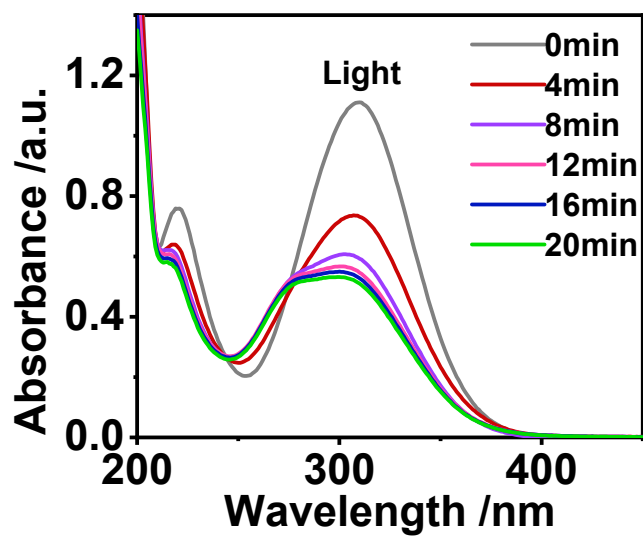


Figure S5. UV-Vis absorption spectra of 4-NS vs. time in the presence of CDs@CuNPs and AB in a mixed solution of water and ethanol

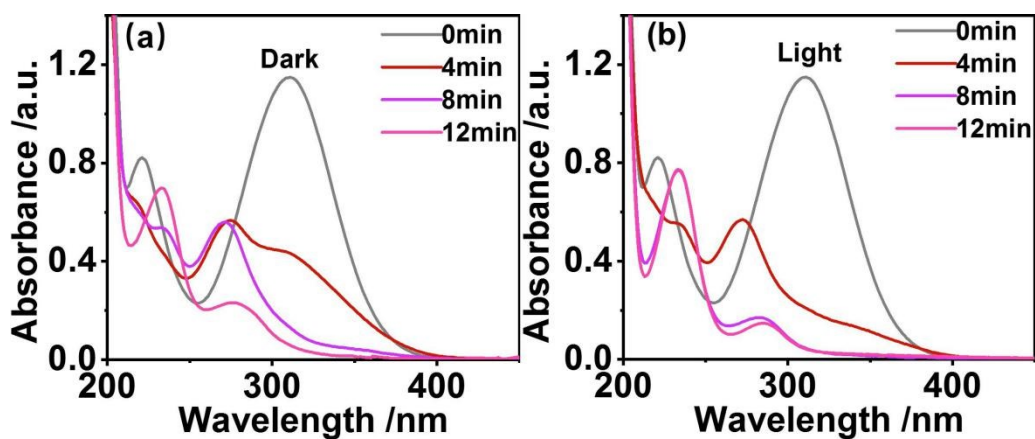


Figure S6. UV-Vis absorption spectra of 4-NS vs. time in the presence of CDs@CuNPs (3 mg) and excessive AB (10 mg) on dark condition (a) and on illumination (b).

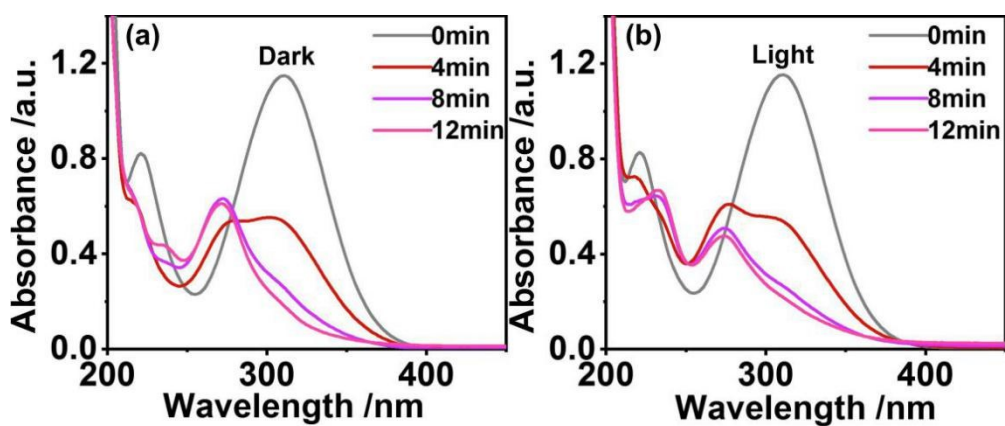


Figure S7. UV-Vis absorption spectra of 4-NS vs. time in the presence of CDs@CuNPs (3 mg) and NaBH₄ (2 mg) on dark condition (a) and on illumination (b).

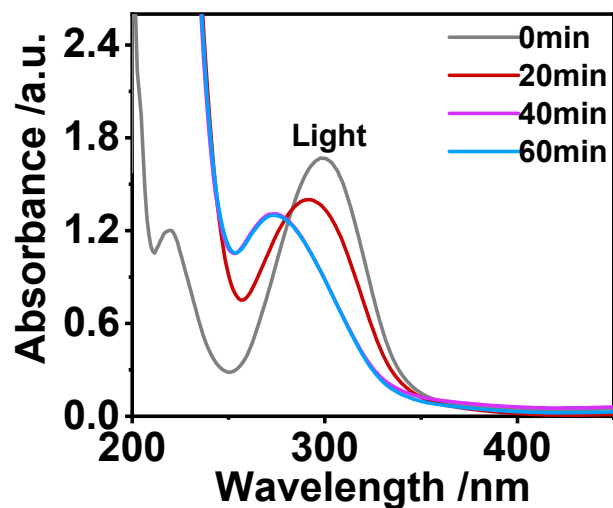


Figure S8. UV-Vis. absorption spectra of 4-NS vs. time in the presence of CDs@CuNPs (3 mg) and $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ (2 μL) under visible light irradiation

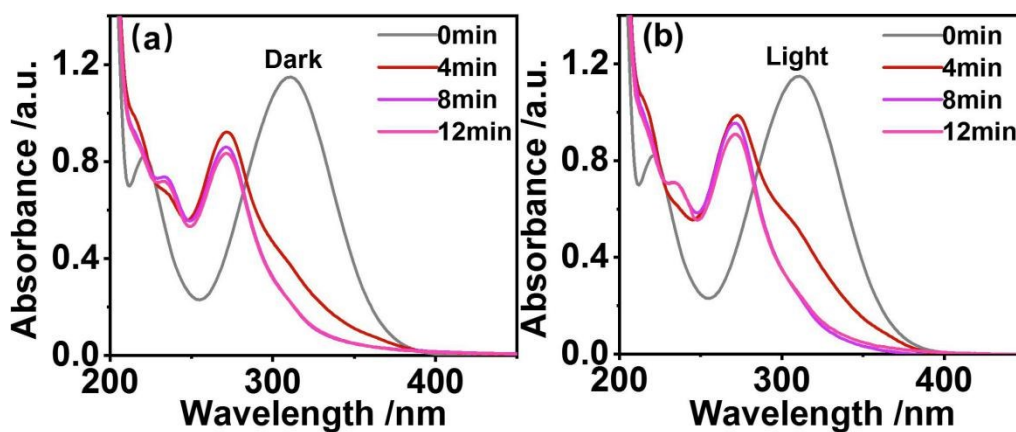


Figure S9. UV-Vis absorption spectra of 4-NS vs. time in the presence of Cu_2O (3 mg) and NaBH_4 (2 mg) on dark condition (a) and on illumination (b).

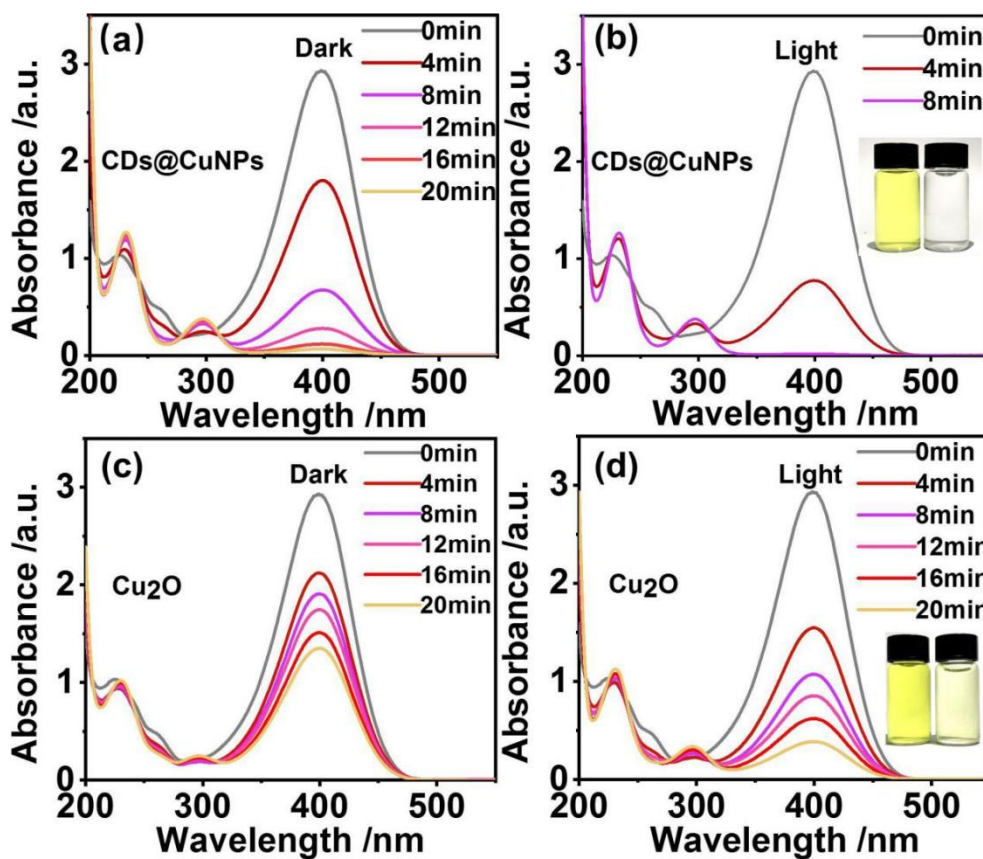


Figure S10. (a and b) The evolution of UV-Vis absorption spectra of 4-NP solution over CDs@CuNPs with time on dark condition (a) and on illumination (b); (c and d) The evolution of UV-Vis absorption spectra of 4-NP solution over Cu₂O with time on dark condition (c) and on illumination (d). The inset in (b) and (d) showing the photos of the 4-NP solution before and after catalytic reduction.

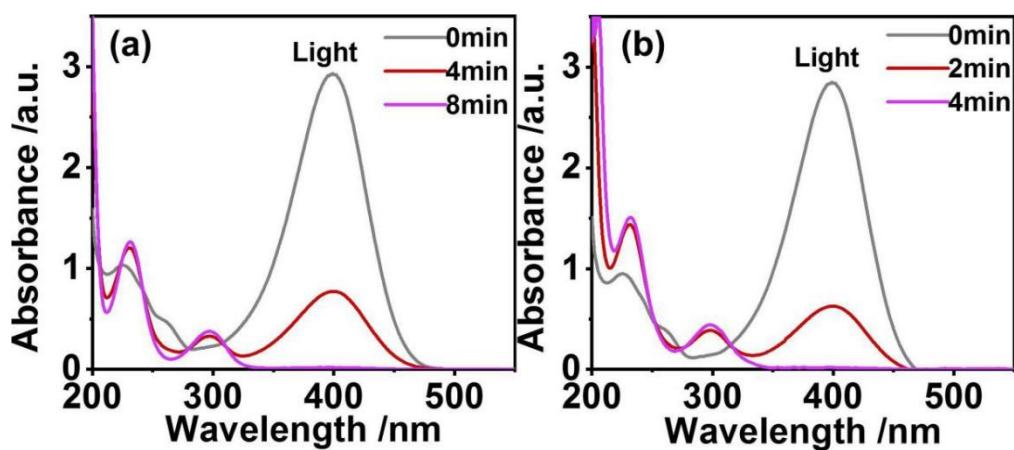


Figure S11. UV-Vis absorption spectra of 4-NP solution over CDs@CuNPs in the presence of AB (a) and NaBH₄ (b).

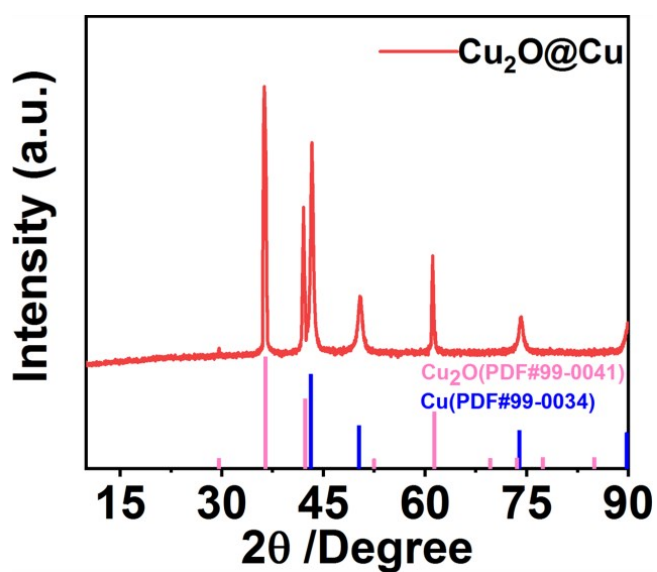


Figure S12. XRD pattern of Cu₂O@Cu.

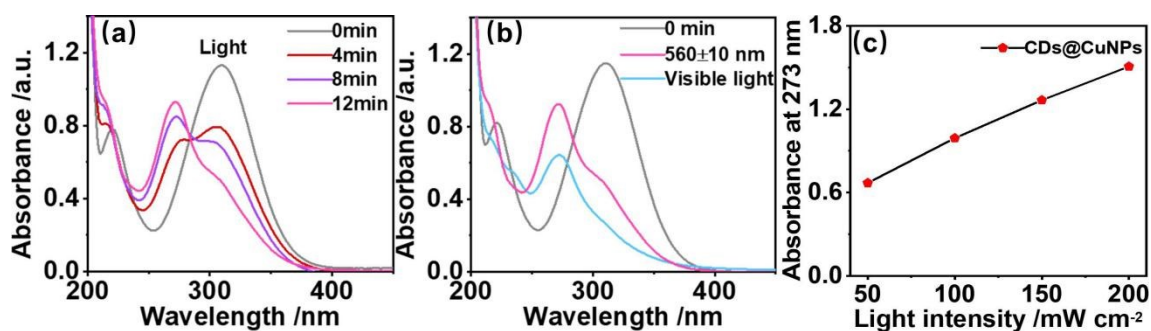


Figure S13. (a) UV-Vis absorbance spectra for the selective reduction of 4-NS irradiated with the fixed excitation wavelength at 560 ± 10 nm without adding EDTA-2Na hole scavenger. (b) The comparison of UV-Vis absorbance spectra for CDs@CuNPs irradiated with the fixed excitation wavelength at 560 ± 10 nm and visible light. (c) The dependence of conversion rate of 4-NS to 4-AS on the intensity of fixed wavelength at 560 ± 10 nm.

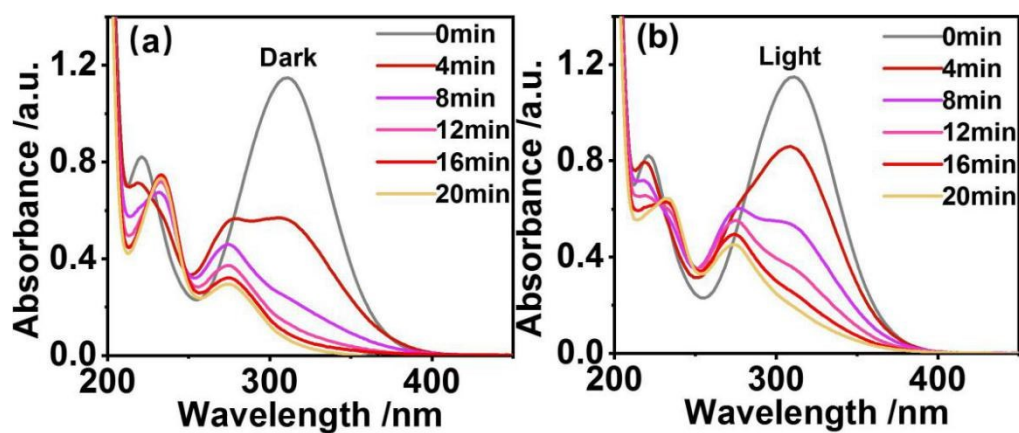


Figure S14. UV-Vis absorption spectra of 4-NS vs. time in the presence of $\text{Cu}_2\text{O}@Cu$ (3 mg) and AB (2 mg) on dark condition (a) and on illumination (b).

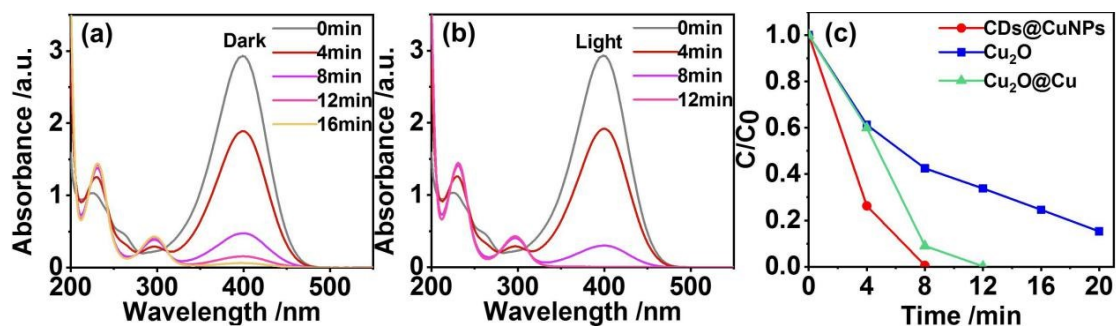


Figure S15. (a and b) The evolution of UV-Vis absorption spectra of 4-NP solution over Cu₂O@Cu with time on dark condition (a) and on illumination (b); (c) Activity comparisons of Cu₂O@CuNPs, Cu₂O and Cu₂O@Cu for 4-NP reduction under visible light irradiation.

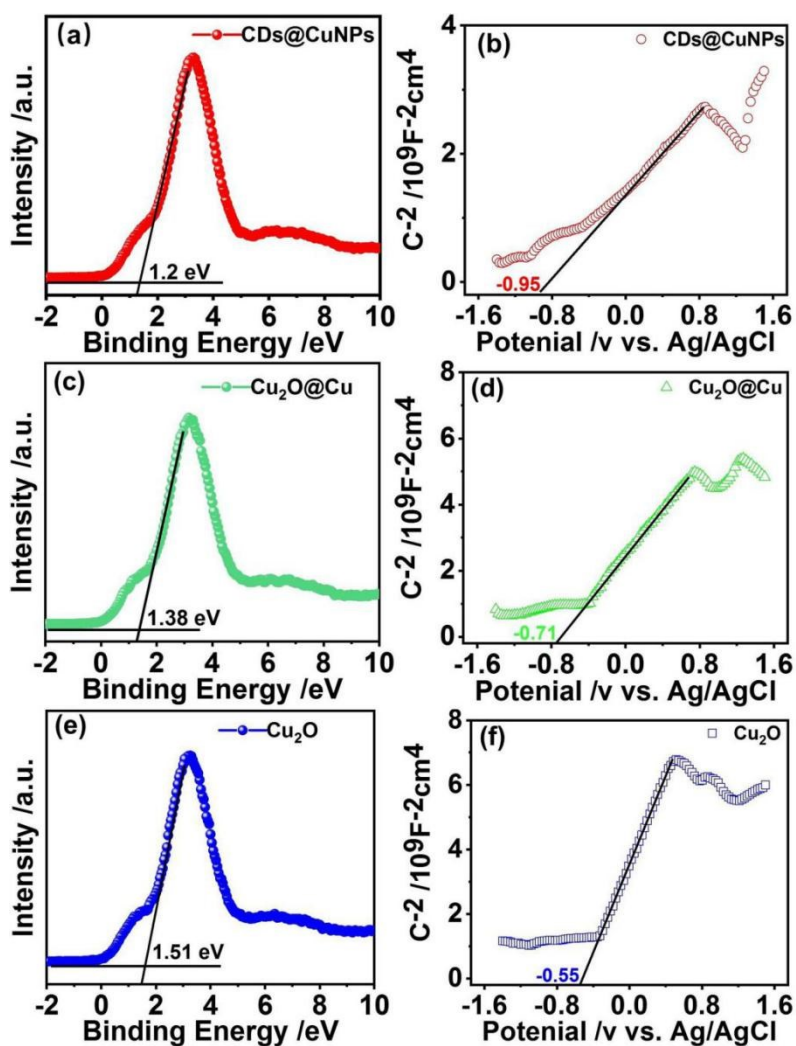


Figure S16. (a, c, and e) XPS valence spectra of CDs@CuNPs, Cu₂O@Cu and Cu₂O; (b, d, and f) MS plots of CDs@CuNPs, Cu₂O@Cu and Cu₂O.

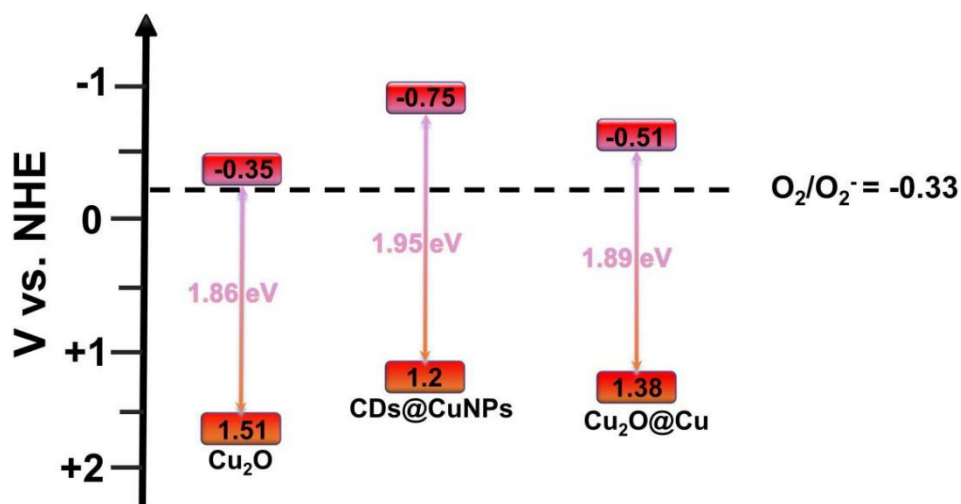


Figure S17. Diagram of the energy band positions of Cu_2O , CDs@CuNPs and $\text{Cu}_2\text{O@Cu}$.

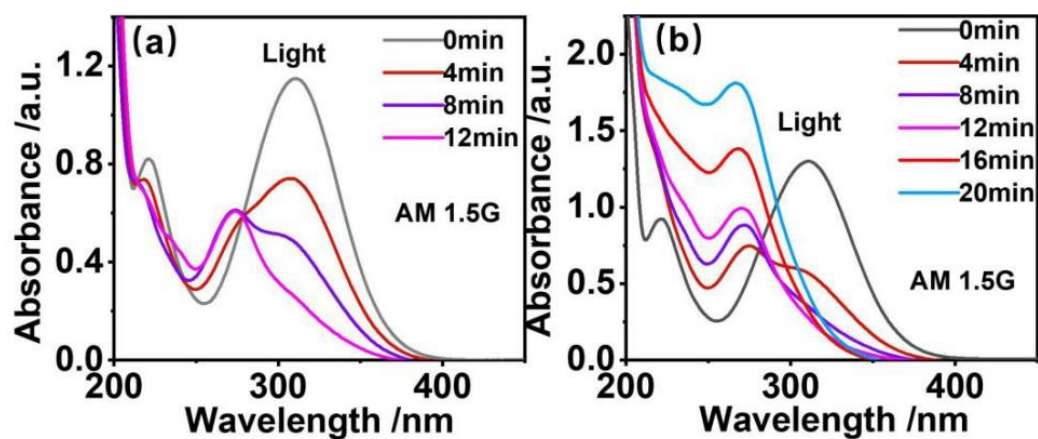


Figure S18. UV-Vis absorption spectra of 4-NS vs. time in the presence of CDs@CuNPs and AB under simulated AM 1.5G solar light (a) and adding EDTA-2Na hole scavenger (b).

Table S1. Catalytic hydrogenation of nitrostyrene with different catalysts

Catalyst	Reductant	Pressure (bar)	T (K)	Time (min)	Selectivity (%)	Conversion (%)
CDs@CuNPs	AB	/	298	20	>99	100
Cu ₂ O	AB	/	298	12	0	0
Cu ₂ O@Cu	AB	/	298	12	0	0
Au/TiO ₂ ²	H ₂	9	393	360	95.9	98.5
Au/Fe ₂ O ₃ ²	H ₂	12	403	570	95.1	95.2
Pd/C ²	H ₂	9	393	1.8	0	99
Pt/C ²	H ₂	9	393	1.8	2.9	96.7
Au-Pd/TiO ₂ ²	H ₂	9	393	1.8	0	99.5
Au-Pt/TiO ₂ ²	H ₂	9	393	1.2	1.8	93.0
Co@CN ³	N ₂ H ₄ ·H ₂ O	/	353	90	95	100
Co-NC ³	N ₂ H ₄ ·H ₂ O	/	353	90	79	97
Co@NC(al) ³	N ₂ H ₄ ·H ₂ O	/	353	90	99	74
Pd-Pd ₃ Bi/SiO ₂ ⁴	Methanol	/	343	60	10	43
Rh-RhPb/SiO ₂ ⁴	Methanol	/	343	60	94	38
Rh-RhPb ₂ /SiO ₂ ⁴	Methanol	/	343	60	93	94
Pd ₁₃ Ga ₅ -Pd/SiO ₂ ⁴	Methanol	/	343	60	0	22
0.75%Pt/FeO _x -R250 ⁵	H ₂	3	313	73	73	96.7
2.73%Pt/FeO _x -R250 ⁵	H ₂	3	313	110	92.9	97.8
4.30%Pt/FeO _x -R250 ⁵	H ₂	3	313	34	92.7	94.2
0.2%Pt/TiO ₂ -R450 ⁵	H ₂	3	313	840	94.0	96.8
0.08%Pt/SiO ₂ ⁵	H ₂	3	313	65	46.9	87.9
0.08%Pt/Al ₂ O ₃ ⁵	H ₂	3	313	158	27.8	87.3
(MeCp)0.04PtH/Zn/SiO ₂ ⁶	H ₂	3.4	313	1440	79	46
(MeCp)0.08PtH/Zn/SiO ₂ ⁶	H ₂	3.4	313	1440	75	67

References

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