

Supplementary material

Solar-accelerated chemoselective hydrogenation of 4-nitrostyrene to 4-vinylaniline with carbon dots-induced Cu over Cu₃P in the absence of any sacrificial agents

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1. Experimental Details

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), cupric nitrate ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$), Sodium hypophosphite (NaH_2PO_2), sodium hydroxide (NaOH), ammonia ($\text{NH}_3 \cdot \text{H}_2\text{O}$, 25 w%), formic acid (88 v/v%), H_2O_2 (30 v/v%), ammonia borane (AB), NaBH_4 , ethylenediaminetetraacetic acid disodium salt (EDTA-2Na) 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 method (Meng et al. *Chem. Commun.* 2017, 53, 3074). Typically, 200 mg coal pitch powder was mixed with 3 mL H_2O_2 (30 wt.%) and formic acid (30 mL) in the beaker and 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, vacuum drying at 60 °C for 5 h, the dark brown CDs powder of was collected.

1.3 Preparation of Cu_3P -CDs-Cu, Cu_3P -Cu and Cu_3P . In a 200 mL beaker, 200 mg of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ was added into 100 mL of ultrapure water and stirred for 10 min at room temperature. Subsequently, 2 mL $\text{NH}_3 \cdot \text{H}_2\text{O}$ (25 v/v%) solution was slowly added into $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ solution and reacted for 10 min. An excess amount of NaOH aqueous solution (0.5 M) was then added to the above mixture solution until sediments were formed. After centrifugation, washing and vacuum drying at 60 °C for

10 h, the blue powder was collected finally. Afterwards 50 mg of the obtained blue powder, 250 mg of NaH_2PO_2 and 100 mg CDs powder were mixed together and ground in a mortar to form a fine powder. Then, the mixture was treated at 300 °C for 2 h in N_2 atmosphere. After cooled down at room temperature under N_2 flow, dark grey-black powder was collected and subsequently washed with deionized water for several times and vacuum dried at 60 °C for 10 h, obtaining $\text{Cu}_3\text{P-CDs-Cu}$ finally. For comparison, the different contents of CDs in reaction precursors were tuned by adding different masses of CDs (50, 80, 150 mg, respectively) without changing masses of other precursors and reaction conditions. The obtaining samples were labeled as $\text{Cu}_3\text{P-CDs0.5-Cu}$, $\text{Cu}_3\text{P-CDs0.8-Cu}$ and $\text{Cu}_3\text{P-CDs1.5-Cu}$, respectively. The Cu_3P sample was prepared following the same recipe and processes as for $\text{Cu}_3\text{P-CDs-Cu}$ but without adding CDs. $\text{Cu}_3\text{P-Cu}$ was prepared using the same recipe and process as those for Cu_3P except for increasing the amount of NaH_2PO_2 to 700 mg.

1.4 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 using a Bruker D8 ADVANCE powder diffractometer at $\text{Cu K}\alpha$ with a scanning rate of 2° min^{-1} in the 2θ range of 5–90°. Absorption spectra of samples were collected on a Shimadzu UV-2550 UV-Vis spectrometer. X-ray photoelectron spectroscopy (XPS) data of all samples were obtained using a Kratos AXIS 165 mutitechnique electron spectrometer with an Al $\text{K}\alpha$ X-ray source for determining the composition and chemical bonding configurations. The compositions of the reaction mixtures were determined using a

Trace GC Ultra Gas Chromatograph system equipped with a Tri Plus RSH autosampler and an ISQ MS detector of an Agilent J&W DB-5 column (GC-MS).

1.5 Electrochemical measurements. The electrochemical measurement was conducted in the solution system of 0.5 M Na₂SO₄ with the three electrodes unit. 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. A platinum plate and Ag/AgCl reference electrode acted as the counter electrode and reference electrode, respectively. All of the data were collected on a Bio-Logic (SP 120) electrochemical workstation.

1.6 Catalytic reaction test. Typically, 12 mg of sample powder and 20 mL of aqueous solution of the 4-NS (0.146 mM) were added into a quartz reactor placed on a magnetic stirrer and thermostatted at 25 °C. After the powder was dispersed completely, 3 mg of AB was then put into the reactor. Light irradiation was provided using a solar light simulator (CEL-HXUV300, CEAULIGHT, China) with an AM1.5 filter (100 mW·cm⁻²). The light intensity can be adjusted through regulating operating current and was measured by an optical power meter (CEL-NP2000-2, CEAULIGHT, China). 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).

Besides, the yields of the product were further confirmed by GC-MS with dodecane as the internal standard. The sample solution removing catalyst by centrifugation (0.2 μL) was directly injected into the GC-MS for quantitative analysis.

1.7 Hole capturing experiment. 12 mg of sample powder and 20 mL of aqueous solution of the reaction substrate (0.146 mM) were added into a quartz reactor placed on a magnetic stirrer and thermostatted at 25 $^{\circ}\text{C}$. After the powder was dispersed completely, 3 mg of AB and 4 mg of EDTA-2Na as a sacrificial reagent was then put into the reactor. Light irradiation was provided using a solar light simulator (CEL-HXUV300, CEAULIGHT, China) with an AM1.5 filter (100 $\text{mW}\cdot\text{cm}^{-2}$). By contrast, the test without illumination was also conducted.

2. Supporting results

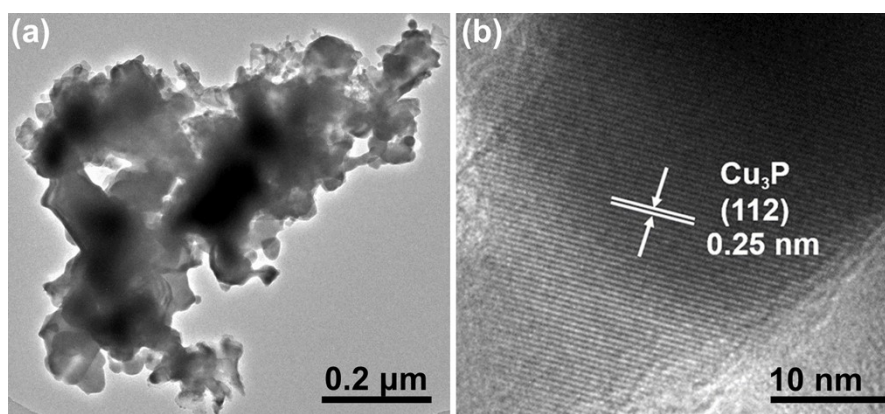


Figure S1. TEM (a) and HRTEM (b) images of Cu_3P .

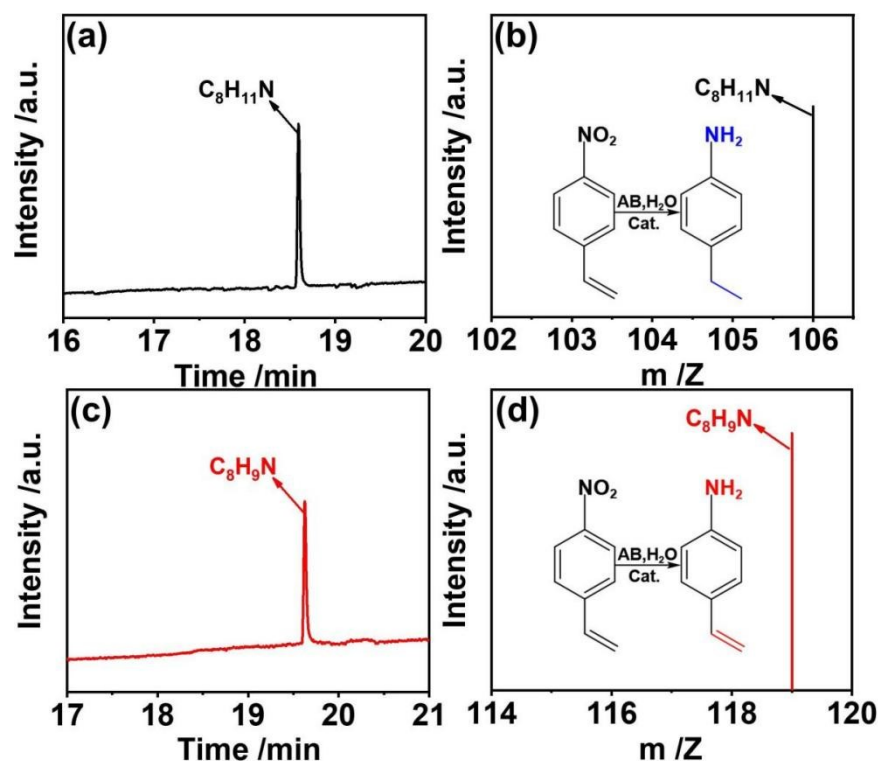


Figure S2. (a, b) GC and MS spectra of the product after catalytic reaction for 8 min over Cu_3P ; (c, d) GC and MS spectra of the product after catalytic reaction for 4 min over $\text{Cu}_3\text{P-CDs-Cu}$

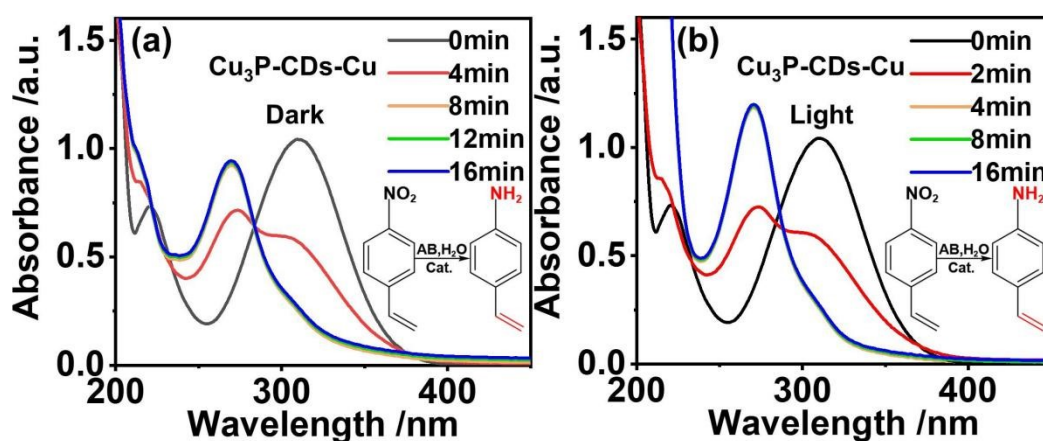


Figure S3. The evolution of 4-NS reduction over $\text{Cu}_3\text{P-CDs-Cu}$ with time on dark condition (a) and on illumination (b)

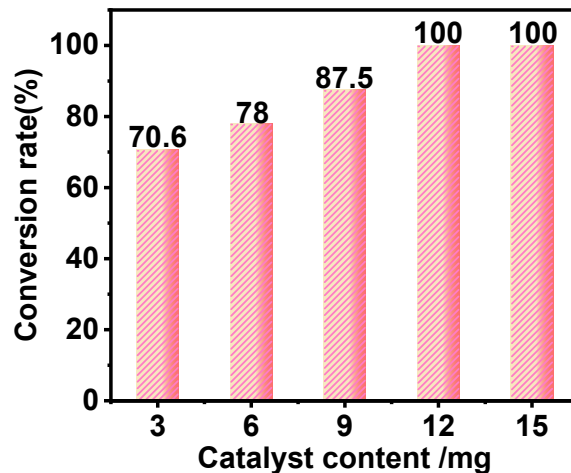


Figure S4. The relationship between the catalyst amount and the conversion rate

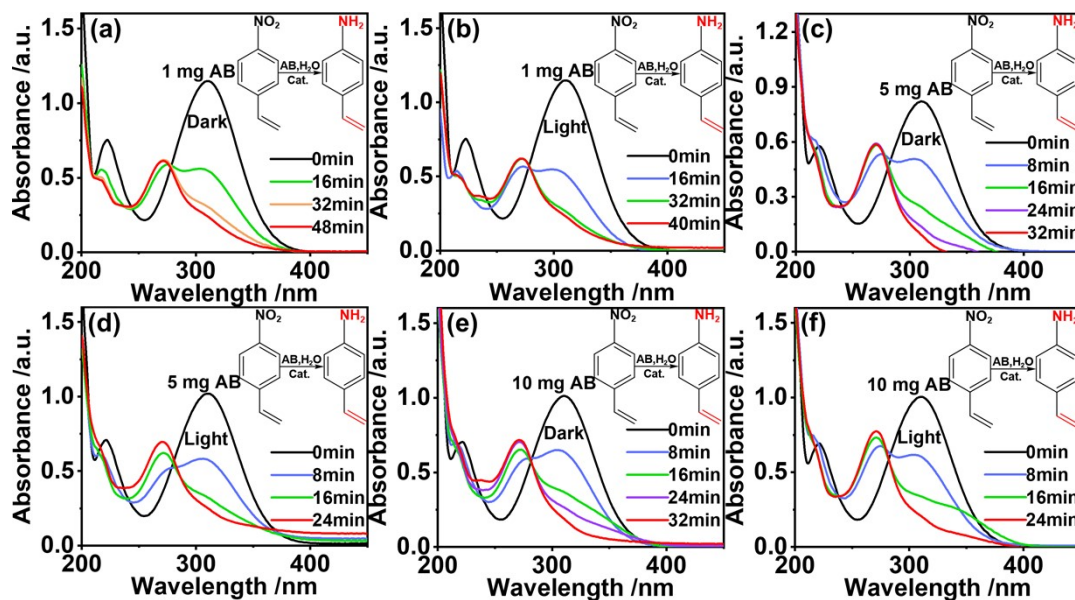


Figure S5. (a, b) UV-Vis absorption spectra of 4-NS vs. time in the presence of Cu₃P-CDs-Cu (3 mg) and AB (1 mg) on dark condition and on illumination; (c, d) UV-Vis absorption spectra of 4-NS vs. time in the presence of Cu₃P-CDs-Cu (3 mg) and AB (5 mg) on dark condition and on illumination; (e, f) UV-Vis absorption spectra of 4-NS vs. time in the presence of Cu₃P-CDs-Cu (3 mg) and excessive AB (10 mg) on dark condition and on illumination.

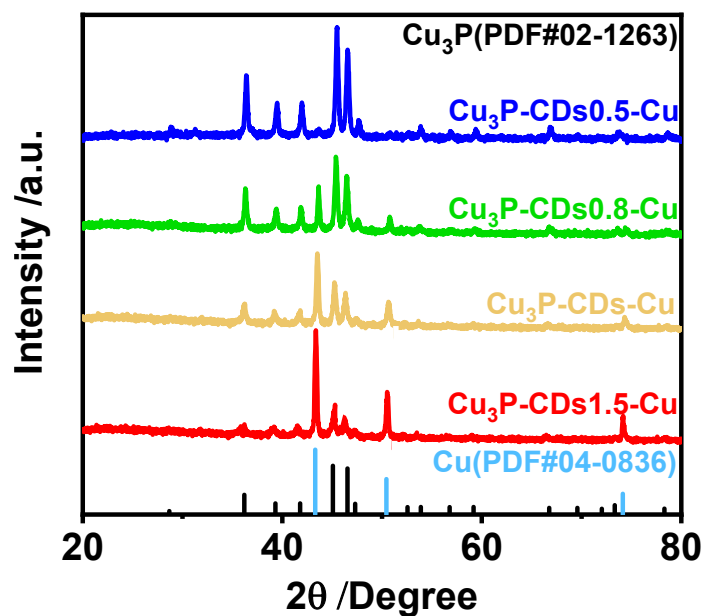


Figure S6. XRD patterns of $\text{Cu}_3\text{P-CDs-Cu}$ samples prepared by changing the contents of CDs in reaction precursors

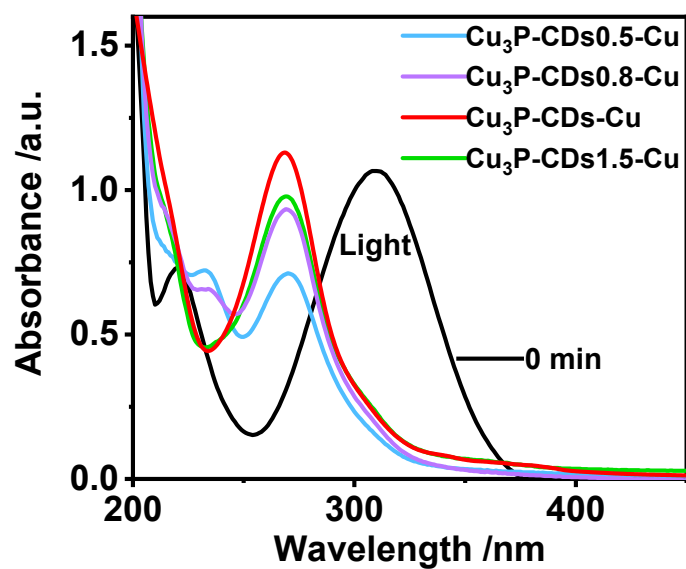


Figure S7. UV-Vis. absorption spectra of 4-NS over different $\text{Cu}_3\text{P-CDs-Cu}$ samples from different contents of CDs in reaction precursors before and after irradiating for 8 min

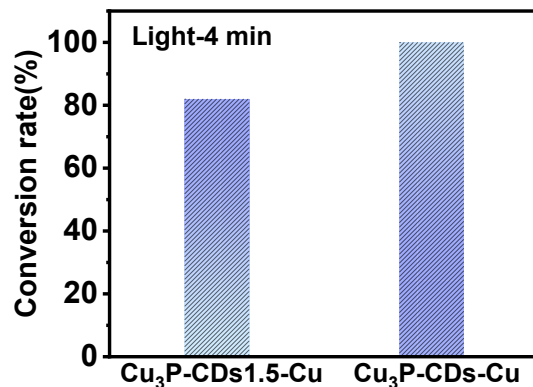


Figure S8. Comparison of reaction activity of Cu₃P-CDs-Cu samples prepared by changing the proportions of CDs in precursors after irradiating for 4 min

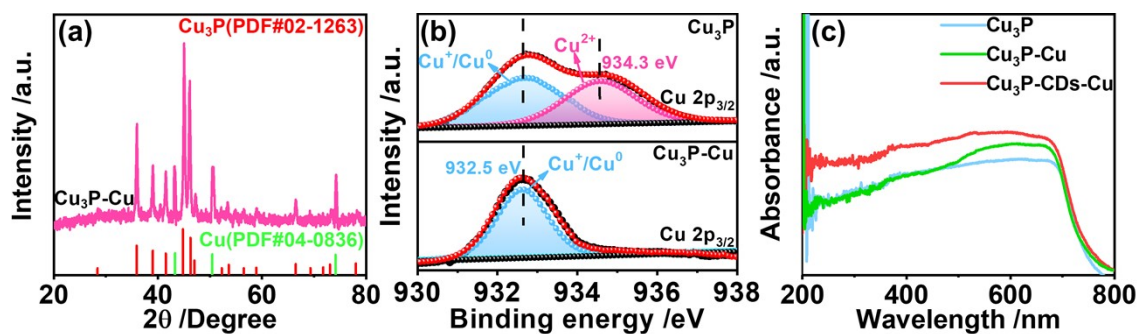


Figure S9. (a) XRD pattern of Cu₃P-Cu ; (c) XPS Cu 2p_{3/2} spectra of Cu₃P and Cu₃P-Cu; (c) UV-Vis absorption spectra of Cu₃P, Cu₃P-Cu and Cu₃P-CDs-Cu.

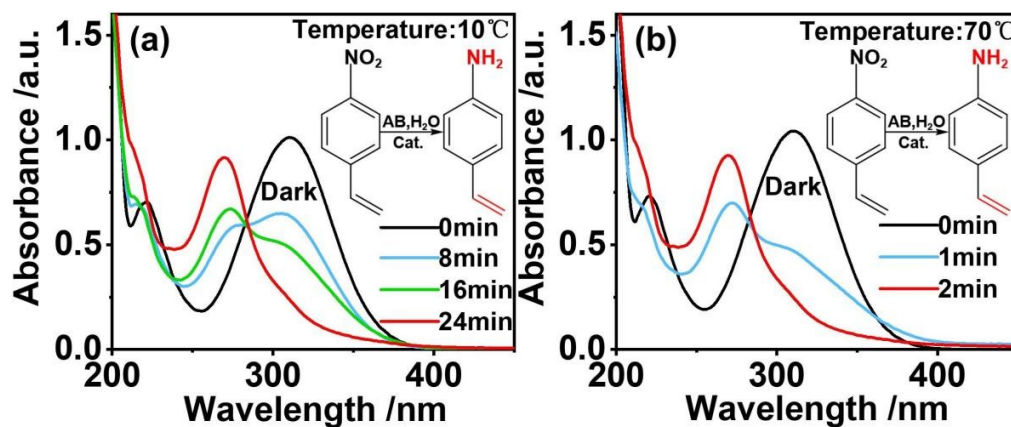


Figure S10. The evolution of 4-NS reduction over Cu₃P-CDs-Cu with time at low temperature (a) and high temperature (b) on dark condition

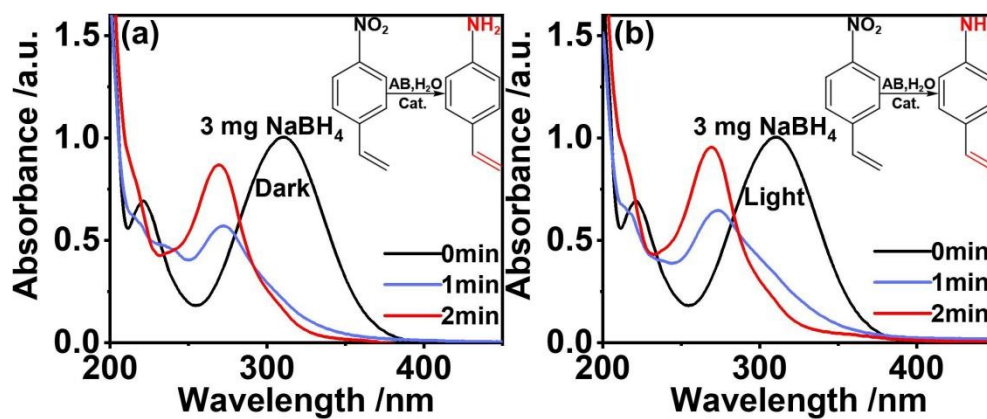


Figure S11. UV-Vis absorption spectra of 4-NS vs. time in the presence of Cu₃P-CDs-Cu (12 mg) and NaBH₄ (3 mg) on dark condition (a) and on illumination (b).

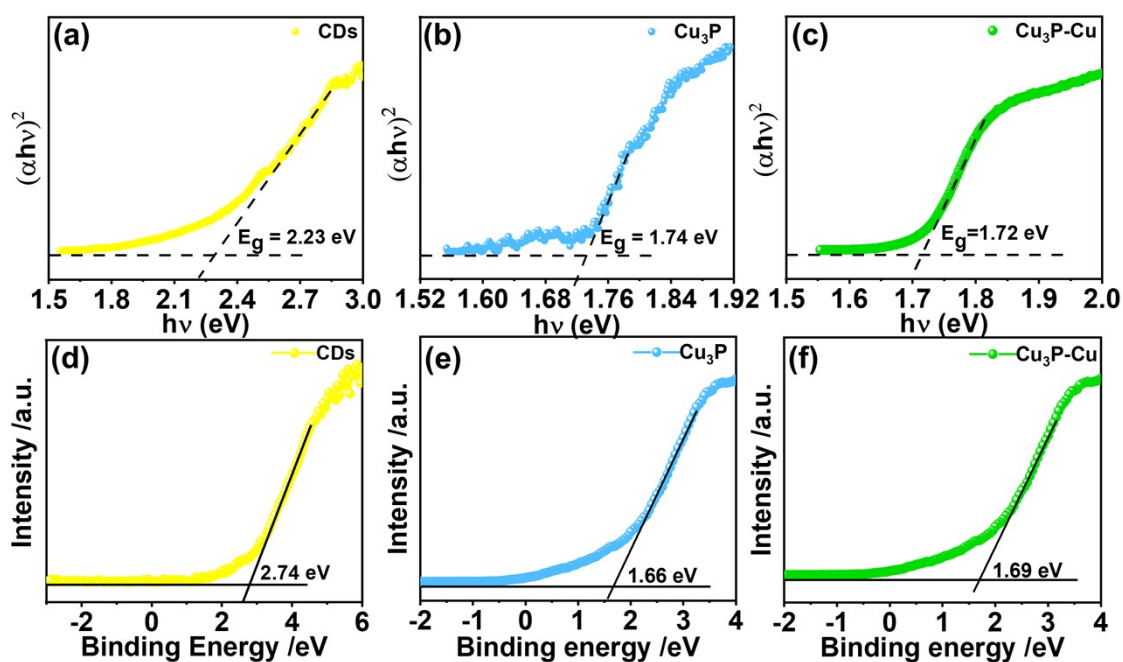


Figure S12. (a, b and c) The Tauc plots of CDs, Cu₃P and Cu₃P-Cu; (d, e, and f) XPS valence spectra of CDs, Cu₃P and Cu₃P-Cu.

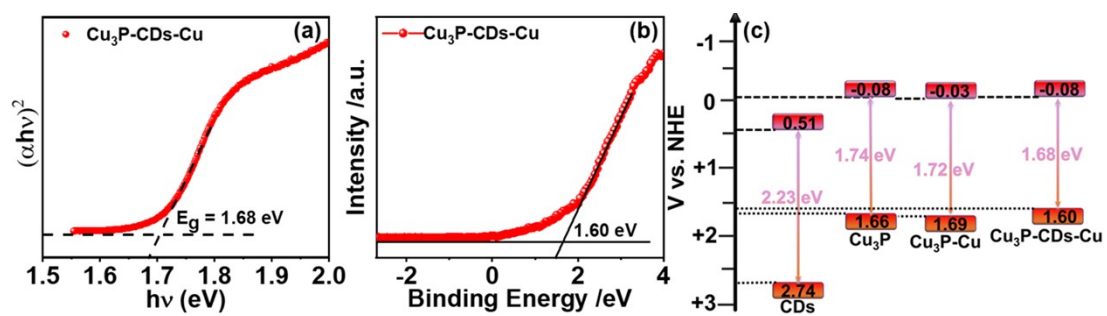


Figure S13. (a) The Tauc plots of $\text{Cu}_3\text{P-CDs-Cu}$; (b) XPS valence spectra of $\text{Cu}_3\text{P-CDs-Cu}$; (c) Energy level structure of $\text{Cu}_3\text{P-CDs-Cu}$