Electronic Supplementary Information

Photocatalytic activity enhancement with 4-cyanophenylacetylene-modified Cu_2O cubes and rhombic dodecahedra and use in arylboronic acid hydroxylation

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Synthesis of Cu_2O crystals

All Cu_2O crystals were synthesized in a 31 ºC water bath. For the synthesis of Cu_2O cubes, 114.6 mL of deionized water was added to a beaker containing 1.044 g of SDS. Next, 1.2 mL of 0.1 M $CuCl_2$ solution was added into the beaker and kept stirring for 25 min. After that, 2.4 mL of 1 M NaOH solution was introduced and stirred for 5 sec. Finally, 1.8 mL of 0.2 M $NH_2OH{\cdot}HCl$ solution was quickly added and stirred for 10 sec. After stop stirring, the solution was aged for 50 min.

To make Cu_2O octahedra, 26.26 mL of deionized water was added to a sample vial containing 0.348 g of SDS. 0.8 mL of 0.1 M $CuCl_2$ solution was added into the vial and kept stirring for 25 min. After that, 0.8 mL of 1 M NaOH was introduced and stirred for 3 sec. Finally, 2.6 mL of 0.2 M $NH_2OH{\cdot}HCl$ solution was quickly added and stirred for 10 sec. After stop stirring, the solution was aged for 25 min.

To form Cu_2O rhombic dodecahedra, 27.68 mL of deionized water was added to a sample vial which containing 0.348 g of SDS. Then 2 mL of 0.1 M $CuCl_2$ solution was added into the vial and kept stirring for 25 min. After that, 0.72 mL of 1M NaOH was added and stirred for 5 sec, then 9.6 mL of 0.1 M $NH_2OH{\cdot}HCl$ was quickly added and stirred for 20 sec. After stop stirring, the solution was aged for 50 min.

The solid product was centrifuged at 7500 rpm for 3 min, and washed with 1:1 volume ratio of water and ethanol for 3 times to remove residual chemicals and SDS, and then washed with 95% ethanol once. After washing, the particles were stored in absolute ethanol to avoid oxidation.

Electron paramagnetic resonance spectral measurements

Commercially available 5,5-dimethyl-1-pyrolin-N-oxide (DMPO) would cause high

EPR background from impurities. Thus, DMPO needed to be purified before EPR measurements. First, a 1.0 M DMPO solution was prepared by adding 0.2264 g of DMPO to 2 mL of 0.1 M phosphate buffer solution (PBS) to give a solution pH of 7.4 or adding methanol. Then 2 mL of 1.0 M DMPO solution was repeatedly sonicated with activated charcoal and centrifuged for 3 times, and used a syringe filter to remove residual activated charcoal.

After purification of DMPO, each shape of pristine and 4-CNA-modified Cu_2O particles were dispersed in phosphate buffer solution or methanol with a concentration of 1 mg/mL, and 0.1, 0.2 and 0.5 mL of cube, rhombic dodecahedron, and octahedron solutions were added to vials, respectively. Then 0.1 mL of 1.0 M DMPO solution was added to the vials and filled up to 1 mL with phosphate buffer solution or methanol. The reagent amounts are listed in Table S1. The solutions were placed 30 cm from xenon lamp with a long-pass Y-43 cutoff filter between the xenon lamp and vial, and irradiated with stirring for 2 min. Then sent for EPR measurements immediately. The settings of EPR instrument are: center field 3497.7 G, sweep width 100 G, sampling time 20 ms, microwave frequency 9.82 GHz, microwave power 15 mW, receiver gain 30, and receiver time constant 327.7 ms.

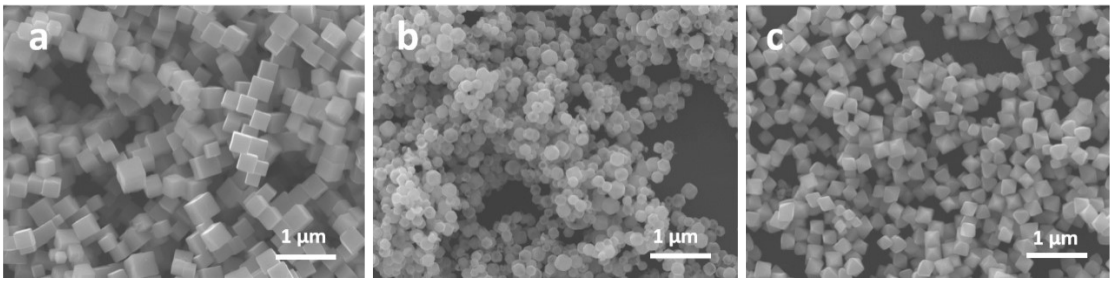

Fig. S1 SEM images of the synthesized Cu_2O (a) cubes, (b) rhombic dodecahedra, and (c) octahedra.

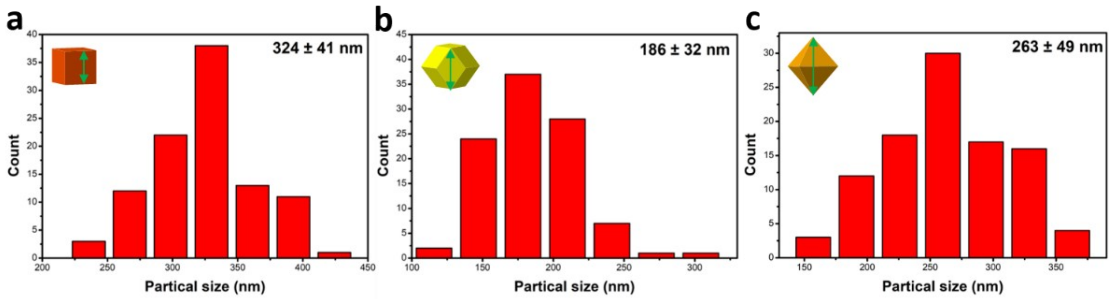

Fig. S2 Size distribution histograms of synthesized Cu_2O (a) cubes, (b) rhombic dodecahedra, and (c) octahedra.

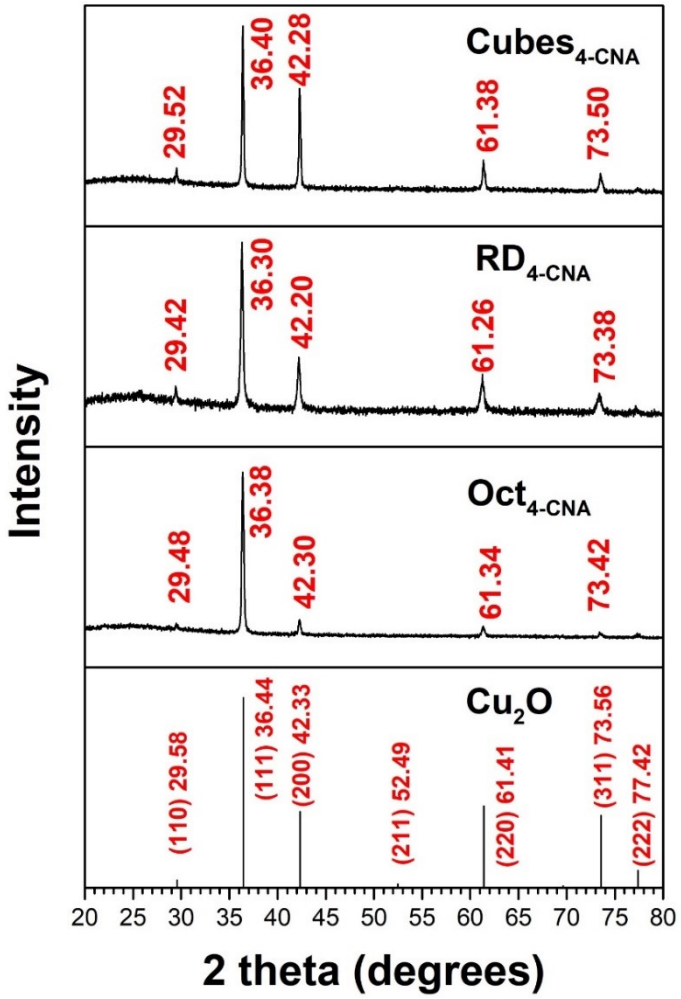

Fig. S3 XRD patterns of 4-CNA-modified Cu_2O crystals. Standard XRD pattern of Cu_2O is also shown.

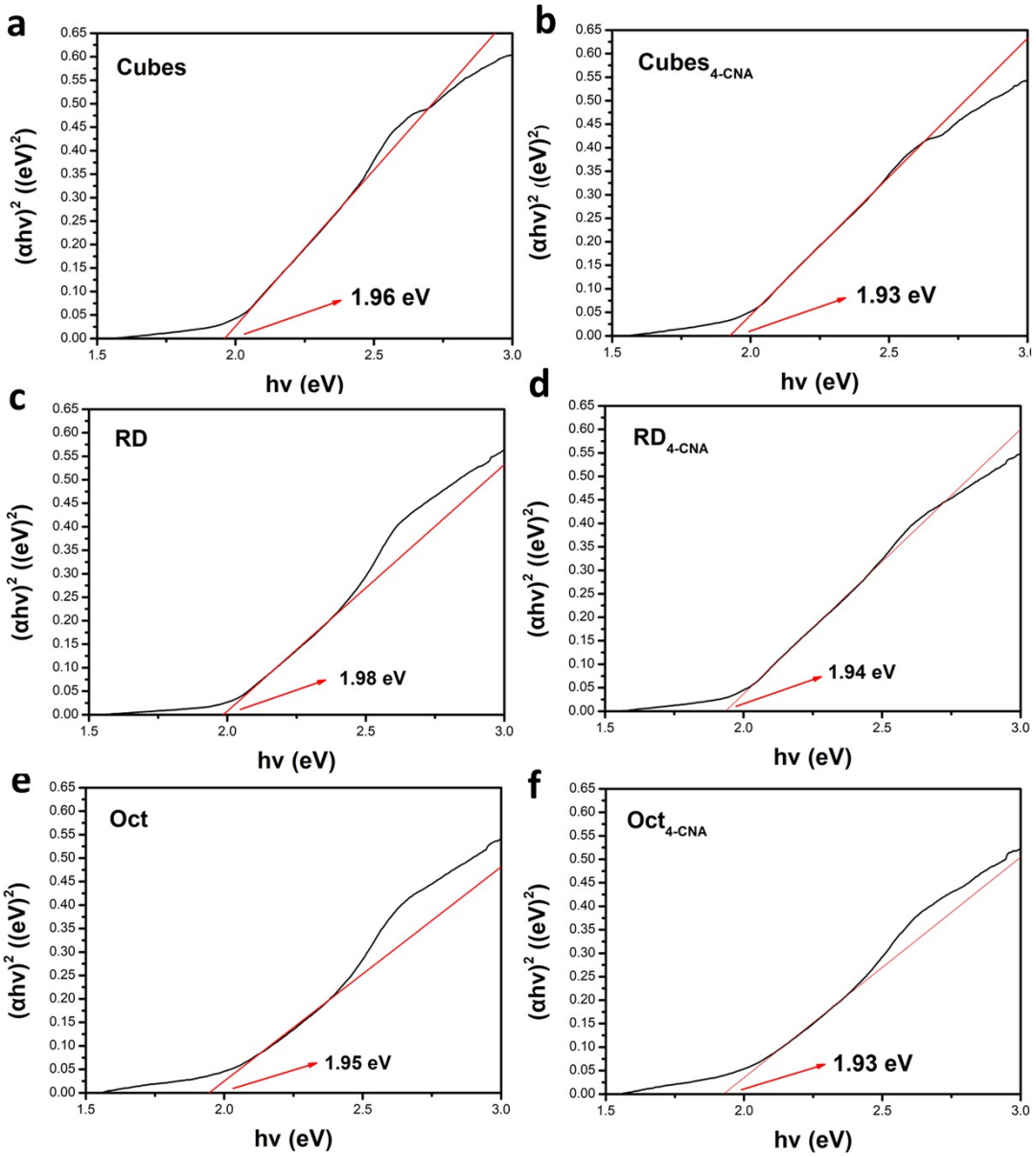

Fig. S4. (a–f) Tauc plots of pristine and 4-CNA-functionalized Cu_2O crystals for band gap energy determination.

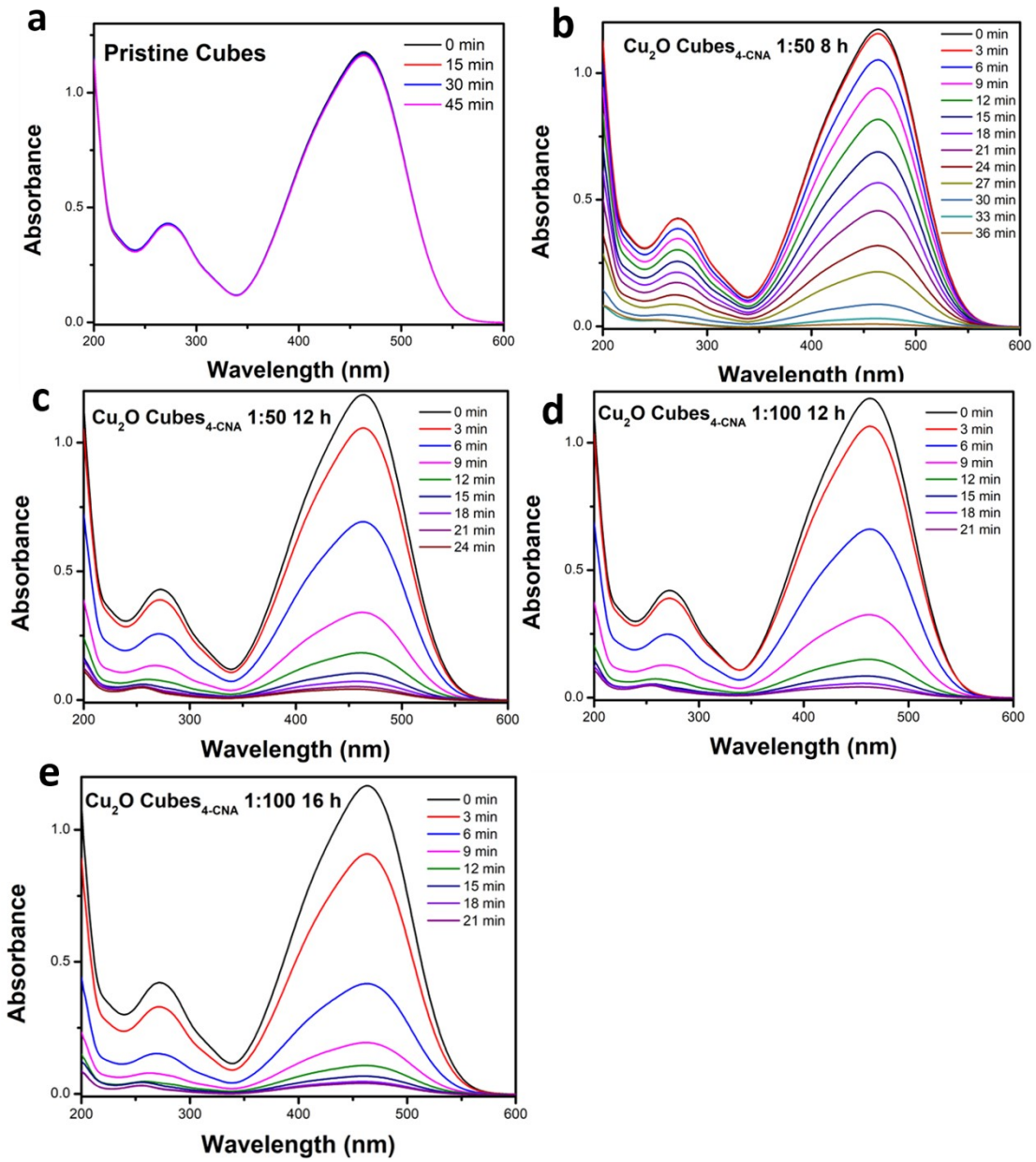

Fig. S5 Time-dependent UV–vis spectra of methyl orange photodegraded by (a) pristine Cu_2O cubes and (b–e) Cu_2O cubes modified with different 4-CNA molar ratios and functionalization times.

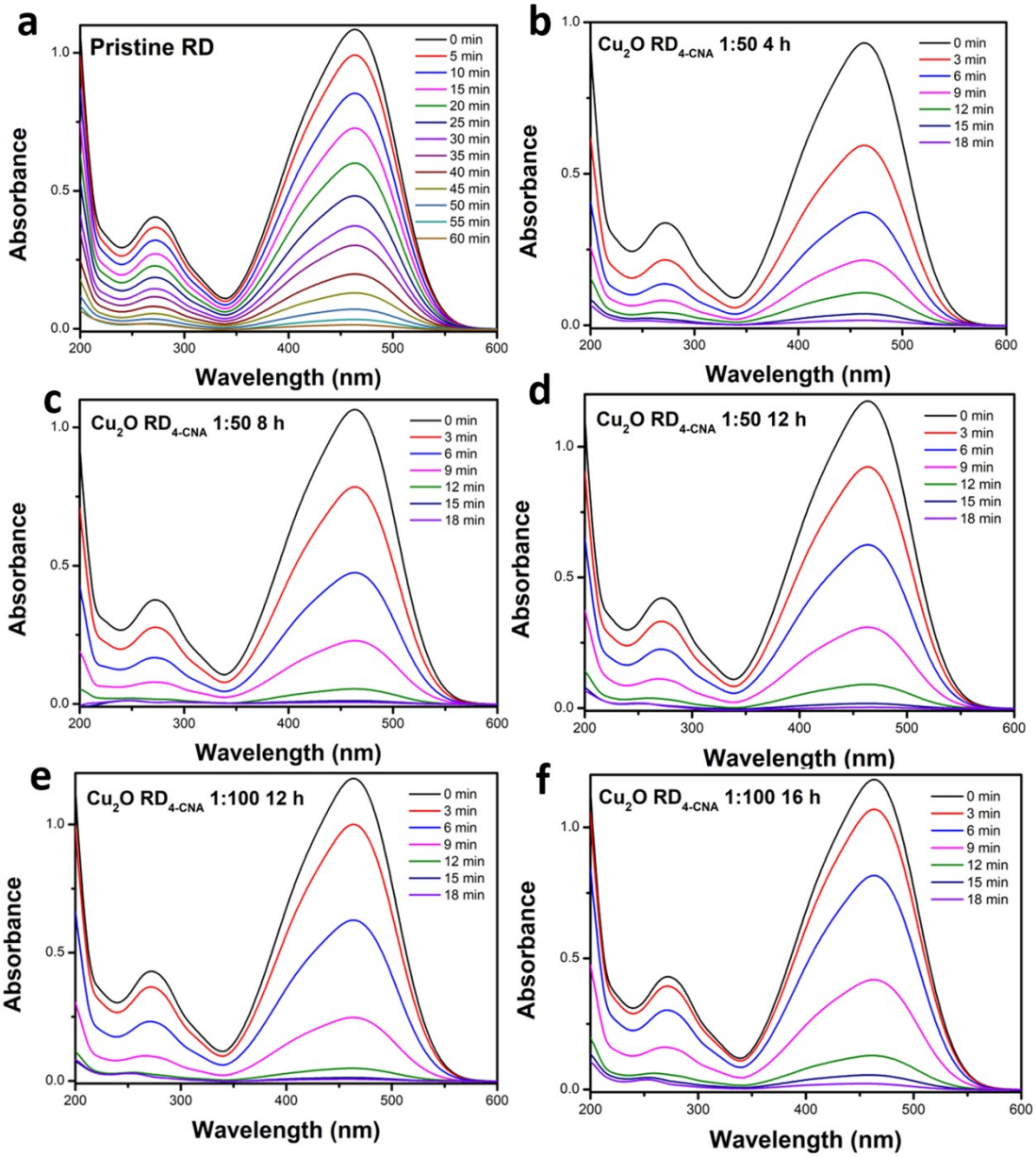

Fig. S6 Time-dependent UV–vis spectra of methyl orange photodegraded by (a) pristine Cu_2O rhombic dodecahedra and (b–f) Cu_2O rhombic dodecahedra modified with different 4-CNA molar ratios and functionalization times.

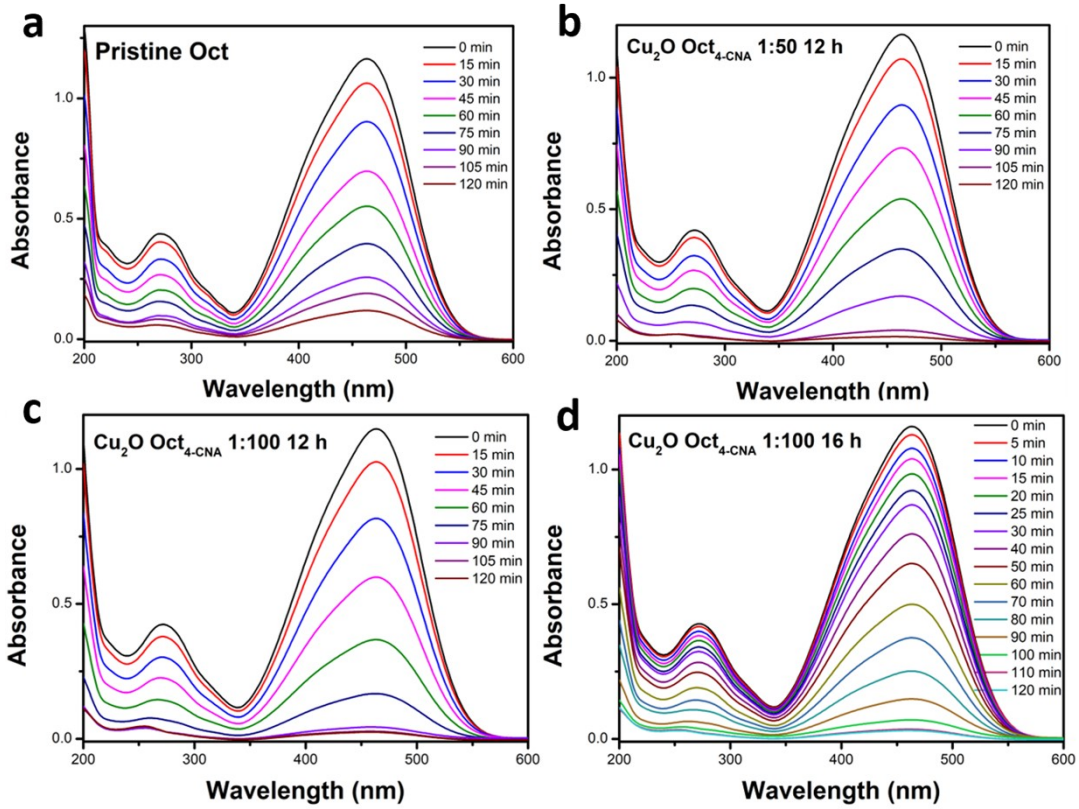

Fig. S7 Time-dependent UV–vis spectra of methyl orange photodegraded by (a) pristine Cu_2O octahedra and (b–f) Cu_2O octahedra modified with different 4-CNA molar ratios and functionalization times.

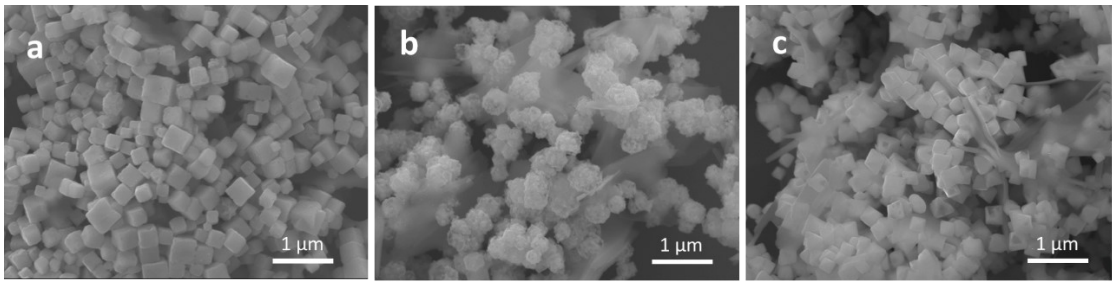

Fig. S8 SEM images of 4-CNA-modified Cu_2O (a) cubes, (b) rhombic dodecahedra, and (c) octahedra after the photodegradation experiments.

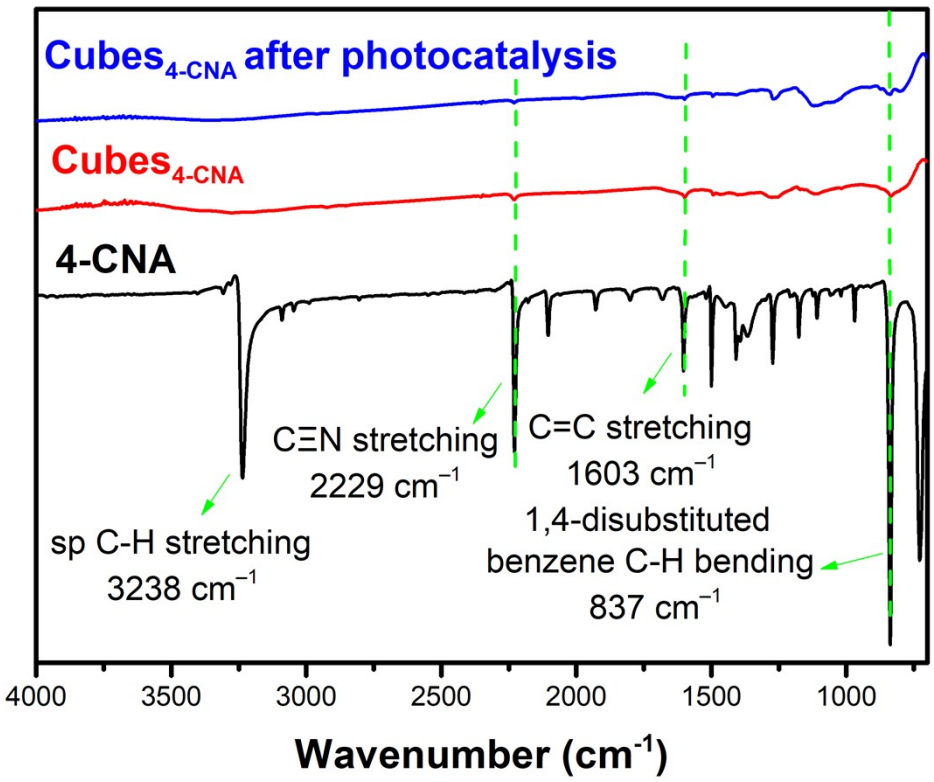

Fig. S9 FT-IR spectra of 4-CNA and 4-CNA-modified Cu_2O cubes before and after the photodegradation reaction.

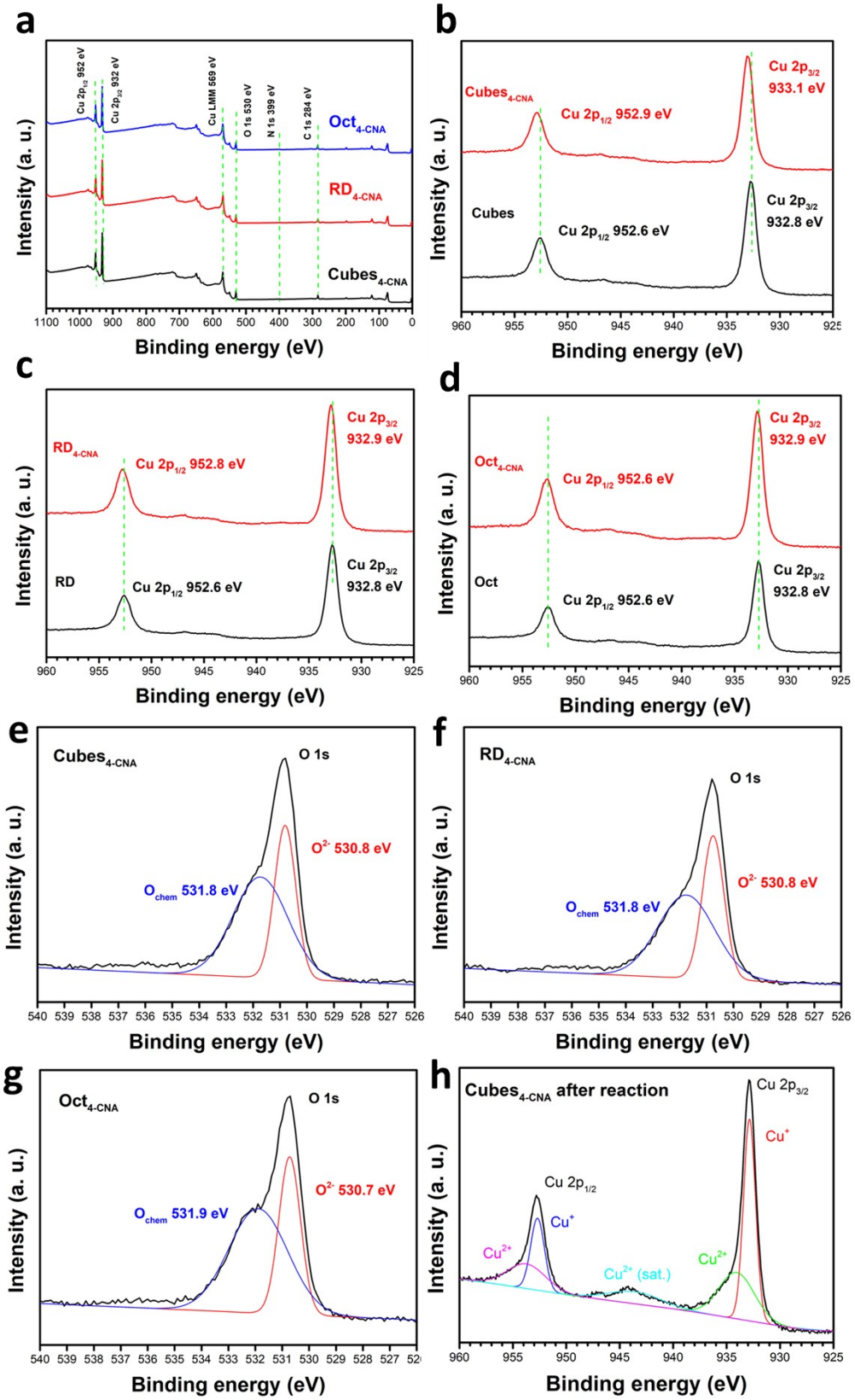

Fig. S10 (a) Full XPS data of 4-CNA-functionalized Cu_2O crystals. (b–g) XPS data of the copper and oxygen peaks before and after modification. (h) XPS data of the Cu_2O cubes after the photodegradation reaction.

Table S1 Reagent amounts used for EPR measurements.

	Cu_2O (1 mg/mL)	1 M DMPO (mL)	PBS or methanol (mL)	Total (mL)	Time (min)
Cubes	0.1	0.1	0.8	1.0	2
RD	0.2	0.1	0.7	1.0	2
Octahedra	0.5	0.1	0.4	1.0	2

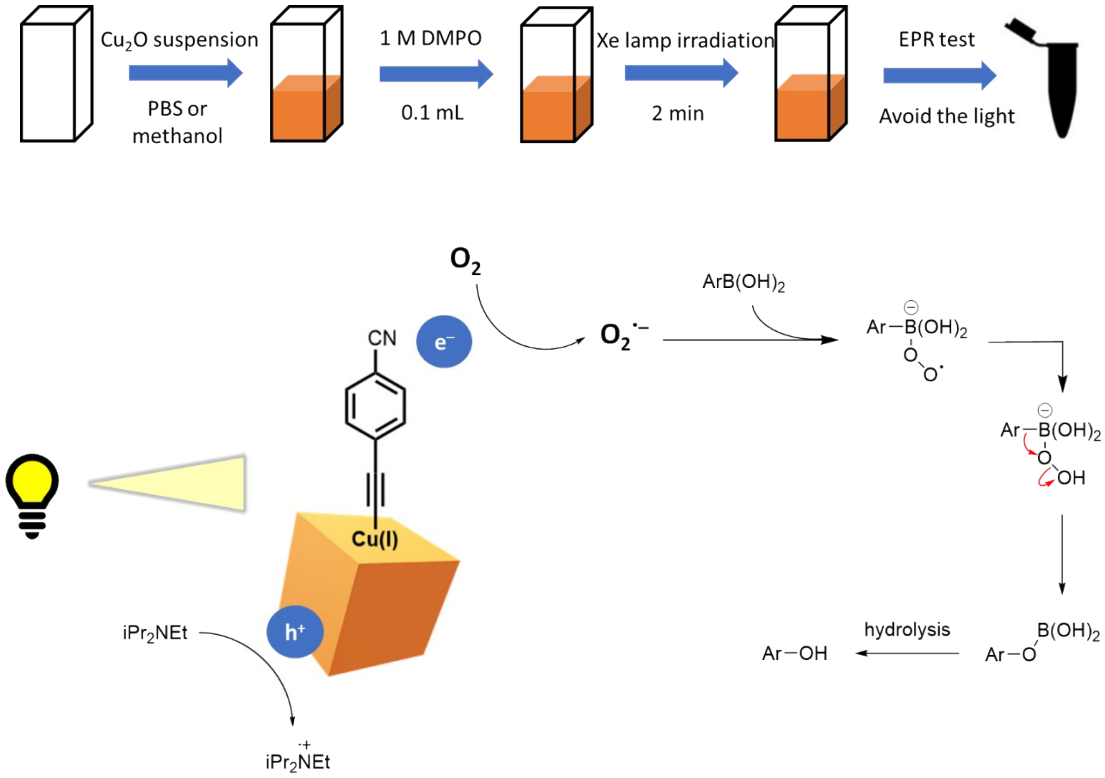

Fig. S11 Reaction mechanism for photocatalytic hydroxylation reaction catalyzed by 4-CNA-modified Cu_2O cubes.

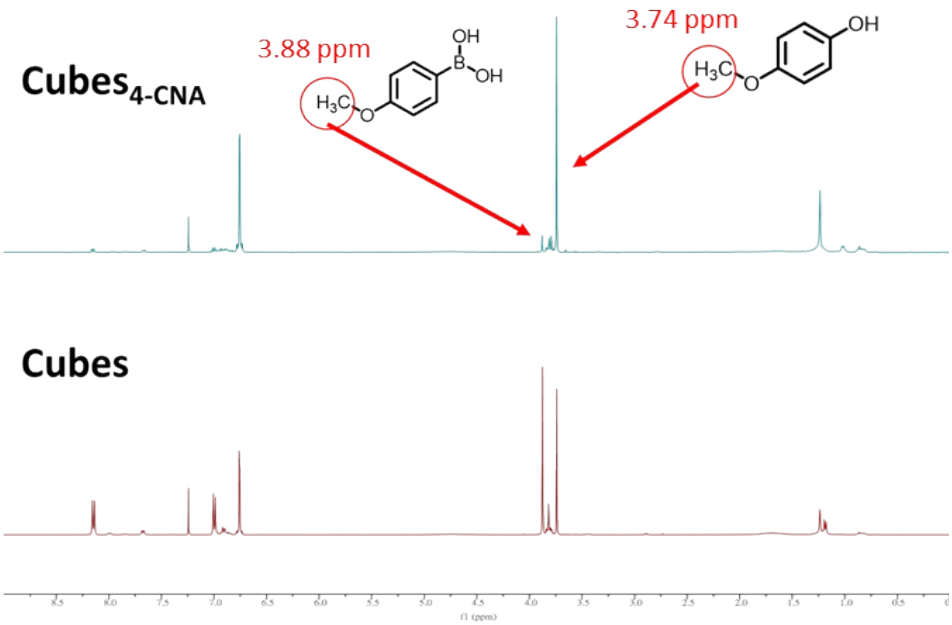

Fig. S12 Crude ^{1}H-NMR spectra collected after 4-methoxyphenylboronic acid hydroxylation catalyzed by Cu_2O cubes and 4-CNA-modified Cu_2O cubes.

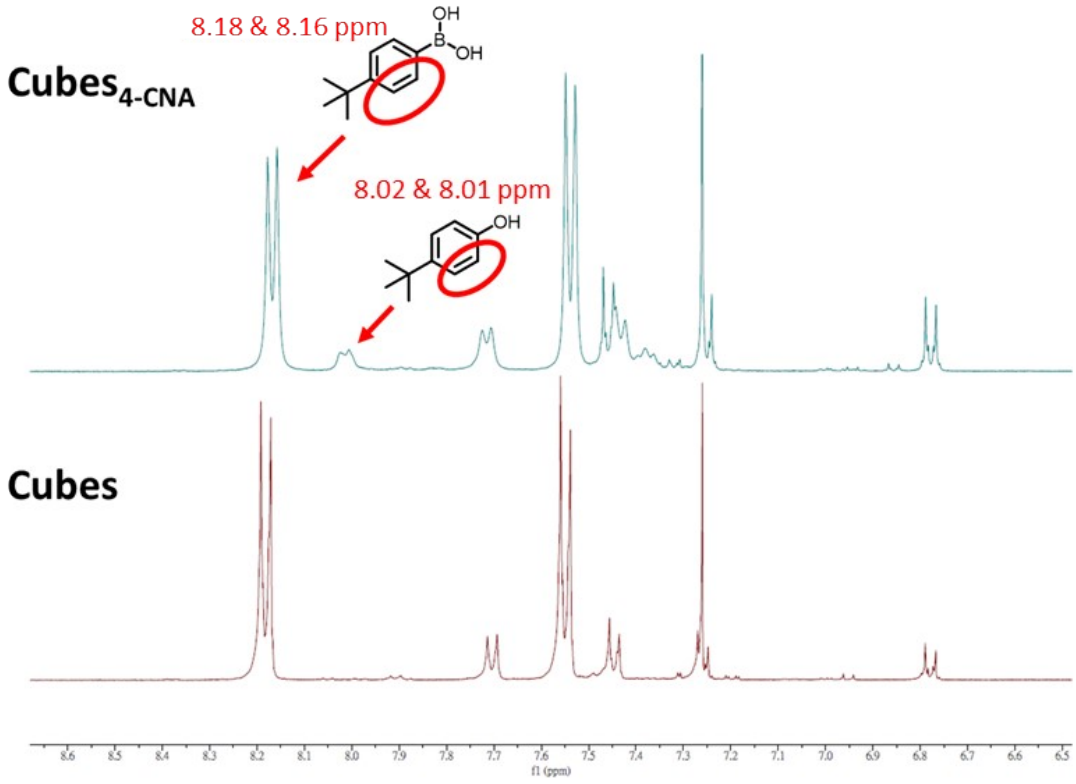

Fig. S13 Crude ^{1}H-NMR spectra collected after 4-tert-butylphenylboronic acid hydroxylation catalyzed by Cu_2O cubes and 4-CNA-modified Cu_2O cubes.

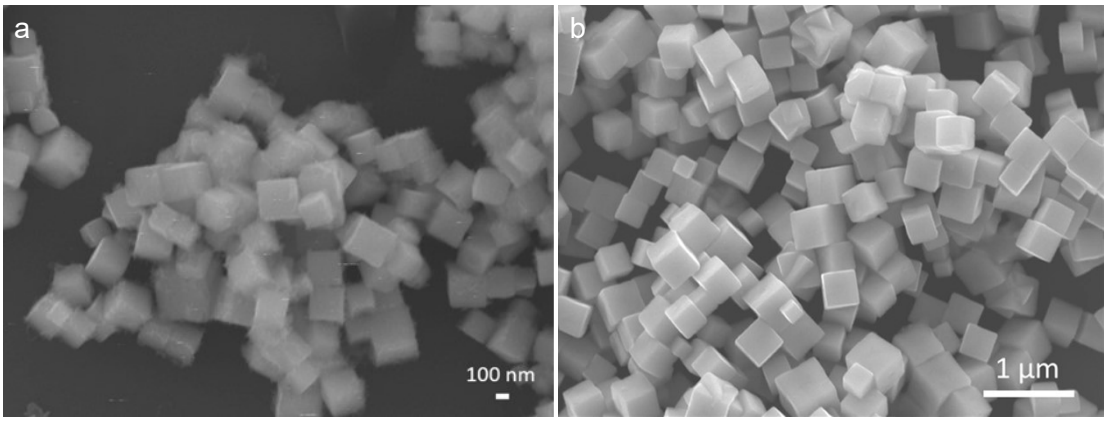

Fig. S14 SEM image of pristine Cu_2O cubes after photocatalytic hydroxylation of (a) 4-methoxyphenylboronic acid and (b) 4-tert-butylphenylboronic acid.

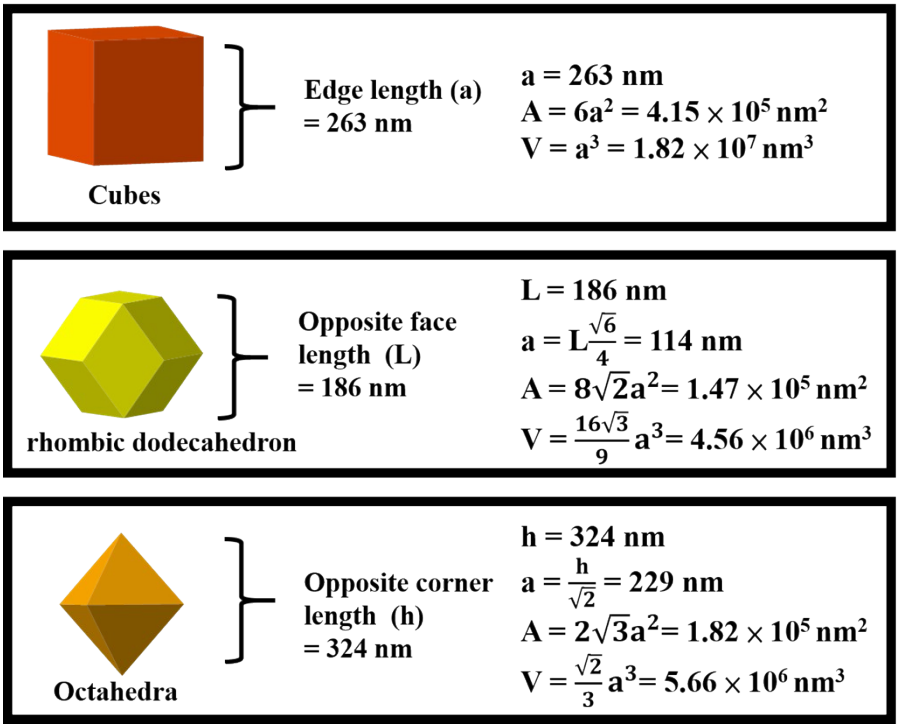

Fig. S15 Calculations of surface areas and volumes of different Cu_2O crystals.

Table S2 Calculations 4-CNA weights needed for Cu_2O surface functionalization.

	Cubes	RD	Octahedra
Size (nm)	263	186	324
Density of Cu_2O (mg/nm^3)	6.03×10^{-18}		
Weight of one particle (mg)	1.09×10^{-10}	2.74×10^{-11}	3.40×10^{-11}
Weight of Cu_2O (mg)	10		
Number of particles	9.16×10^{10}	3.65×10^{11}	2.94×10^{11}
Total surface area (m^2)	3.80×10^{16}	5.37×10^{16}	5.35×10^{16}
Surface Cu atom density (nm^{-1})	10.98	7.76	14.27
Number of surface Cu atoms	4.17×10^{17}	4.17×10^{17}	7.63×10^{17}
Weight of 4-CNA (mg) (Cu:4-CNA = 1:50)	4.4	4.4	8.1
Weight of K_2CO_3 (mg)	4.8	4.8	8.8
Weight of 4-CNA (mg) (Cu:4-CNA = 1:100)	8.8	8.8	16.1
Weight of K_2CO_3 (mg)	9.6	9.6	17.5

Table S3 Determination of particle weights for the photodegradation experiment.

	Cubes	RD	Octahedra
Size (nm)	263	186	324
Surface area for one particle (nm^2)	4.15×10^5	1.47×10^5	1.82×10^5
Volume for one particle (nm^3)	1.82×10^7	4.56×10^6	5.66×10^6
Fixed surface area (m^2)	0.03		
Number of particles	7.22×10^{10}	2.04×10^{11}	1.65×10^{11}
Density of Cu_2O (mg/nm^3)	6.03×10^{-18}		
Weight of one particle (mg)	1.09×10^{-10}	2.74×10^{-11}	3.40×10^{-11}
Weight (mg)	7.9	5.6	5.6