Electronic Supplementary Information

Photocatalytic activity enhancement with 4-trifluoromethylphenylacetylene-functionalized Cu_2O cubes and rhombic dodecahedra from band structure modulation and use in boronic acid hydroxylation

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Chemicals

Copper(II) chloride anhydrous ($CuCl_2$, 98%, Alfa Aesar), hydroxylamine hydrochloride ($NH_2OH{\cdot}HCl$, 99%, Sigma-Aldrich), sodium hydroxide (98%, Showa), sodium dodecyl sulfate (≥99%, J.T. Baker), potassium carbonate (99%, Alfa Aesar), absolute ethanol (≥99.5%, Honeywell), methyl orange ($C_{14}H_{14}N_3NaO_3S$, Alfa Aesar), 4-trifluoromethylphenylacetylene (4-TFMA, 95%, Combi-Blocks), potassium bromate ($KBrO_3$, 99%, Alfa Aesar), sodium oxalate ($Na_2C_2O_4$, ≥99.0%, Sigma–Aldrich), DMPO (5,5-dimethyl-1-pyrroline-N-oxide, 98%, Matrix Scientific), *N*,*N*-diisopropylethylamine ($C_8H_{19}N$, DIPEA, 99.5%, Acros Organics), (4-methoxyphenyl)boronic acid ($C_7H_9BO_3$, 98%, TCI), 4-fluorophenylboronic acid ($C_6H_6BFO_2$, 98%, Alfa Aesar), and 4-chlorophenylboronic acid ($C_6H_6BClO_2$, 98%, Nova-Matls) were used as received. Milli-Q water (18.2 mΩ) was used to prepare all solutions.

Synthesis of Cu_2O crystals

All Cu_2O crystals were synthesized in a 31 ºC water bath. For the growth 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 to the beaker and kept stirring for 25 min. After that, 2.4 mL of 1.0 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 synthesize 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 1.0 M NaOH solution 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. The solution was aged for 25 min.

To make Cu_2O rhombic dodecahedra, 27.68 mL of deionized water was added to a sample vial 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 1.0 M NaOH solution was added and stirred for 5 sec. Finally, 9.6 mL of 0.1 M $NH_2OH{\cdot}HCl$ solution was quickly added and stirred for 20 sec. 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 measurements

Commercially available 5,5-dimethyl-1-pyrolin-N-oxide (DMPO) would cause high EPR background from impurities. Thus, DMPO needs 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 to give a solution pH of 7.4. Then 2 mL of 1.0 M DMPO solution was repeatedly sonicated with activated charcoal and centrifuged for 3 times. A syringe filter was used to remove residual activated charcoal.

After DMPO purification, each shape of pristine and 4-TFMA-modified Cu_2O particles were dispersed in phosphate buffer solution 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. The solutions were placed 30 cm from a xenon lamp with a long-pass Y-43 cutoff filter between the xenon lamp and vial, irradiated with stirring for 2 min, and 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.

Table S1 Calculations of weights of 4-TFMA and K_2CO_3 needed for Cu_2O molecular functionalization

	RD	Octahedra	Cubes
size (nm)	**295**	**311**	**318**
density of Cu_2O (mg/nm^3)	6.03×10^{-18}		
volume of one particle (nm^3)	1.82×10^{7}	5.02×10^{6}	3.22×10^{7}
weight of one particle (mg)	1.10×10^{-10}	3.03×10^{-11}	1.94×10^{-10}
total weight of Cu_2O (mg)	**10**		
number of particles	9.09×10^{10}	3.30×10^{11}	5.15×10^{10}
total surface area (nm^2)	3.37×10^{16}	5.53×10^{16}	3.12×10^{16}
surface Cu atom density (nm^{-1})	7.76	14.27	10.98
number of surface Cu atoms	2.62×10^{17}	7.89×10^{17}	3.43×10^{17}
weight of 4-TFMA (mg) (Cu:4-TFMA = 1:100)	**7.4**	**22.3**	**9.7**
weight of K_2CO_3 (mg)	**6.0**	**18.1**	**7.9**

Table S2 Calculations of particle weights needed for photodegradation experiment with the same total particle surface area of 0.03 m^2

	RD	Octahedra	Cubes
length (nm)	**295**	**311**	**318**
surface area of one particle (nm^2)	3.70×10^{5}	1.67×10^{5}	6.06×10^{5}
fixed surface area (m^2)	0.03		
number of particles	9.10×10^{10}	3.32×10^{11}	5.18×10^{10}
weight (mg)	**8.9**	**5.4**	**9.5**

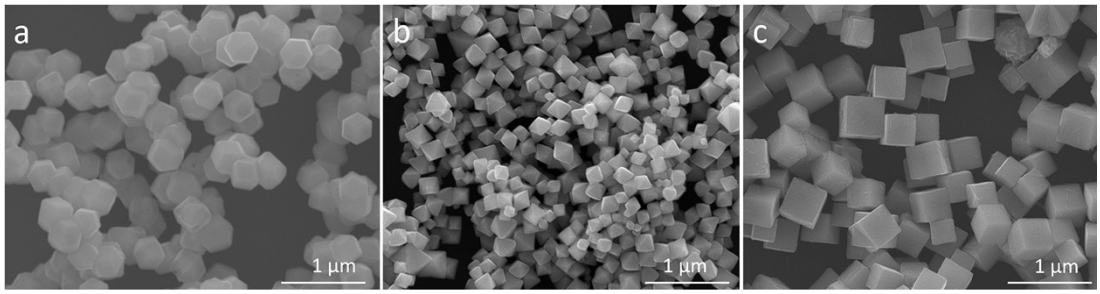


Fig. S1 SEM images of the synthesized Cu_2O (a) rhombic dodecahedra, (b) octahedra and (c) cubes.

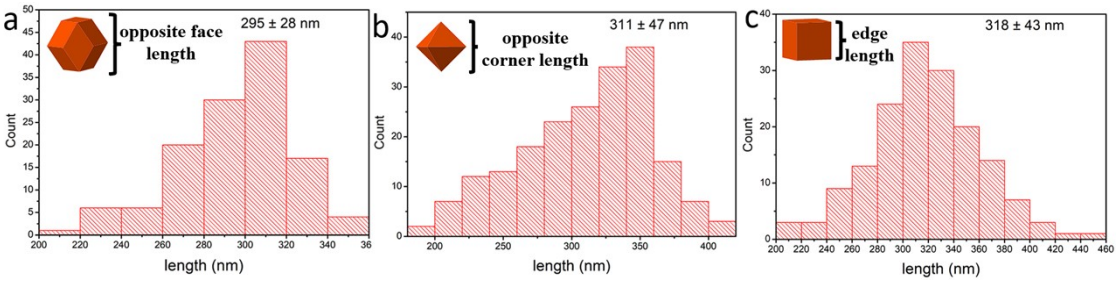


Fig. S2 Size distribution histograms of the synthesized Cu_2O (a) rhombic dodecahedra, (b) octahedra and (c) cubes.

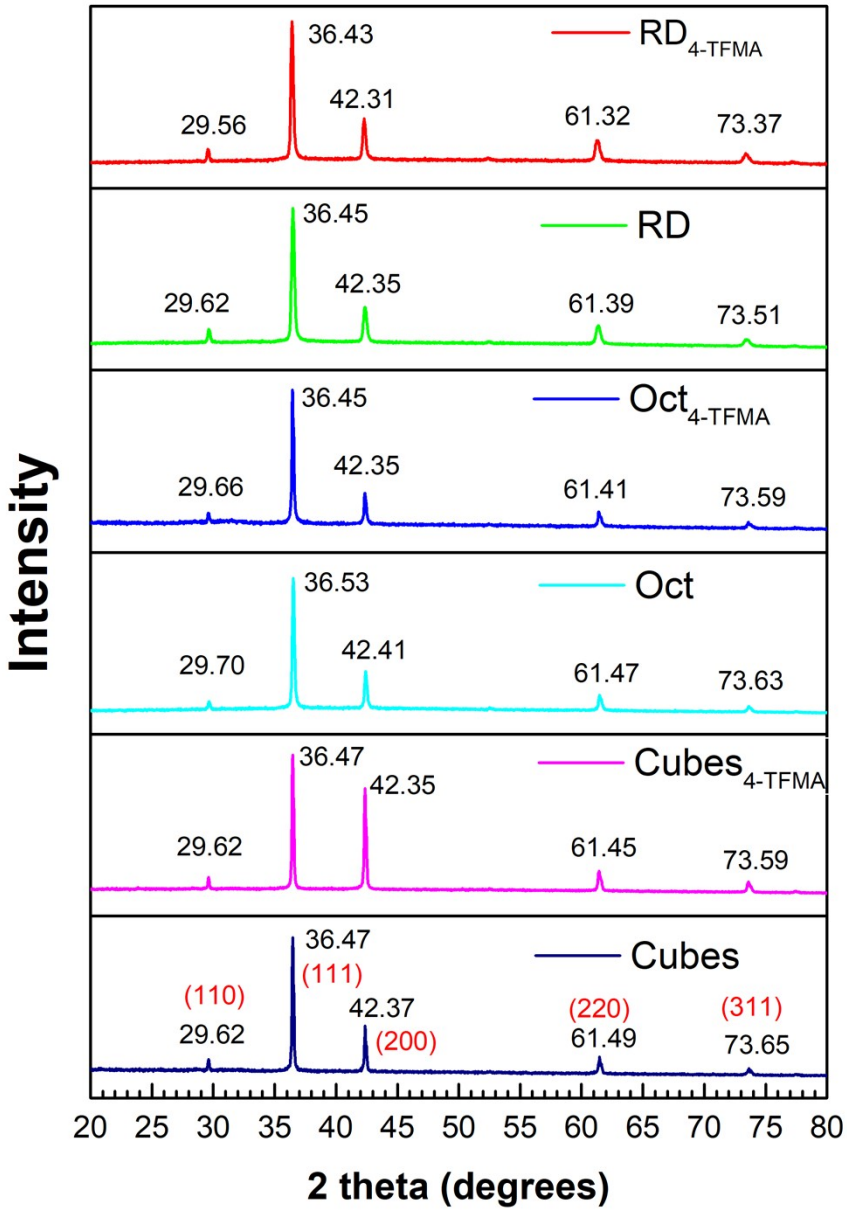


Fig. S3 XRD patterns of different pristine and 4-TFMA-modified Cu_2O crystals.

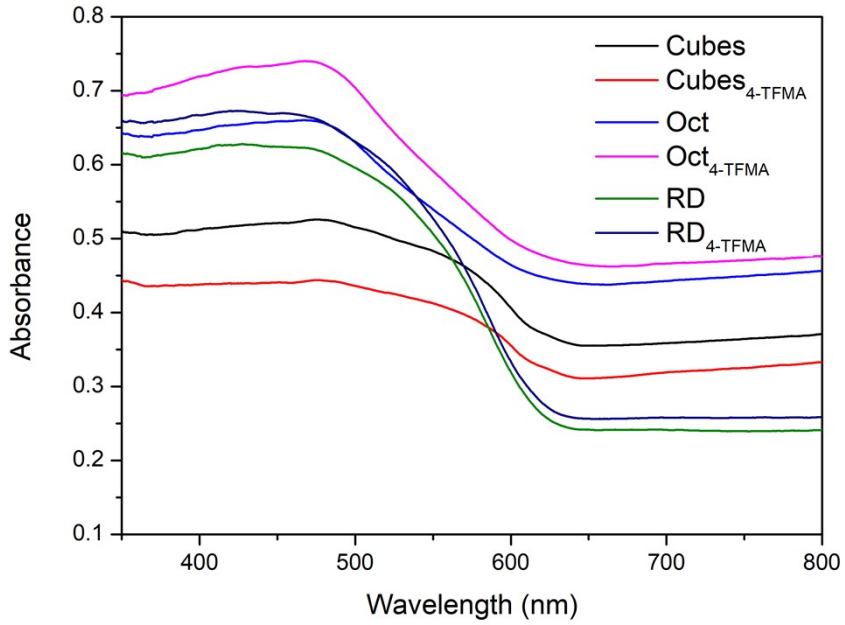


Fig. S4 Diffuse reflectance spectra of different Cu_2O crystals with and without 4-TFMA modification.

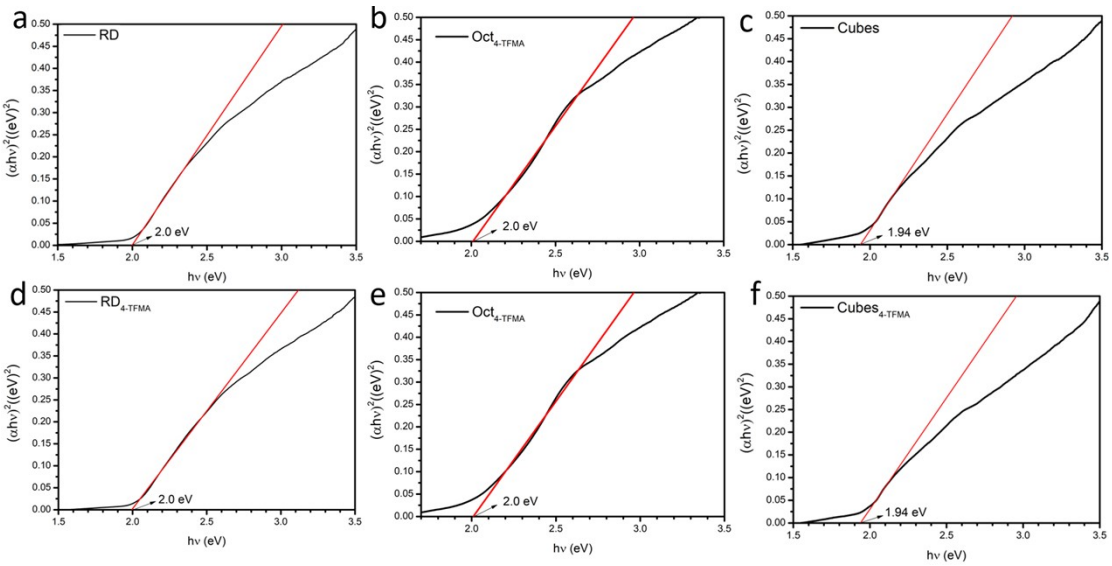


Fig. S5 (a–f) Tauc plots of pristine and 4-TFMA-functionalized Cu_2O crystals for band gap energy determination.

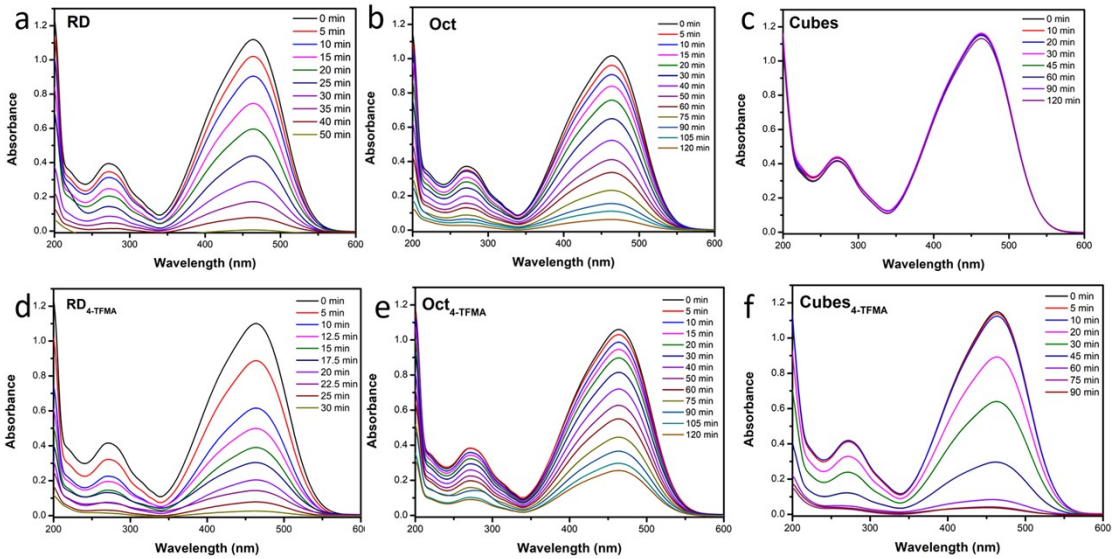


Fig. S6 (a–c) Time-dependent UV–vis absorption spectra of methyl orange photodegraded by Cu_2O rhombic dodecahedra, octahedra and cubes. (d–f) Time-dependent UV–vis absorption spectra of methyl orange photodegraded by 4-TFMA-modified Cu_2O rhombic dodecahedra, octahedra and cubes.

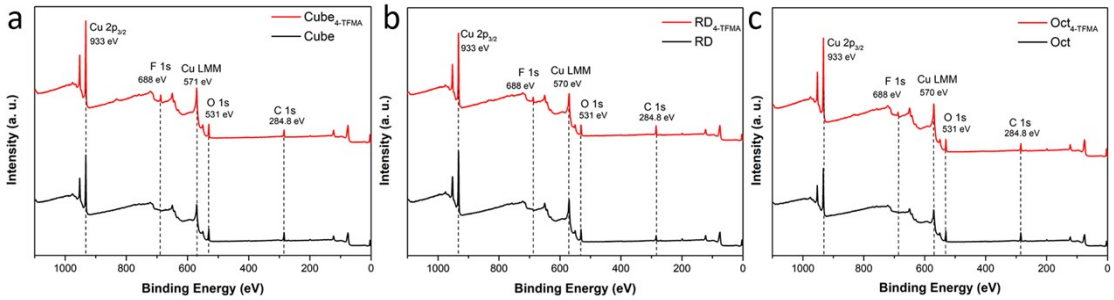


Fig. S7 XPS spectra of pristine and 4-TFMA-modifed Cu_2O (a) cubes, (b) rhombic dodecahedra and (c) octahedra.

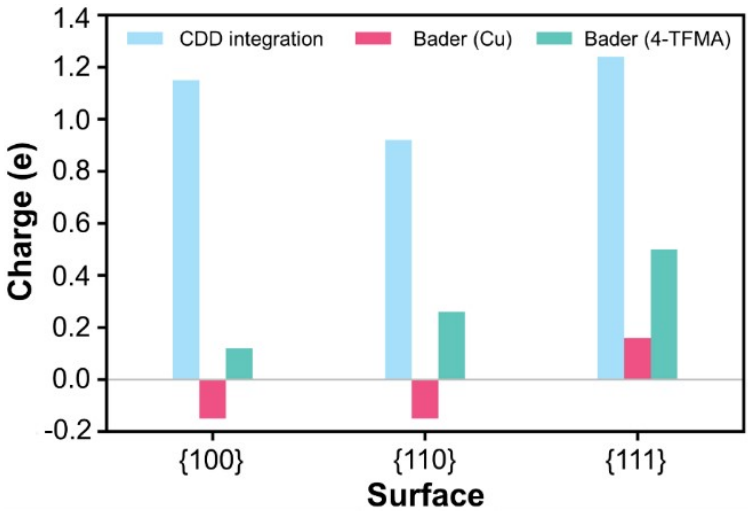


Fig. S8 The integral values of charge density difference and Bader charge difference (for surface Cu atoms and 4-TFMA molecule) of 4-TFMA-decorated Cu_2O {100}, {110} and {111} surfaces.

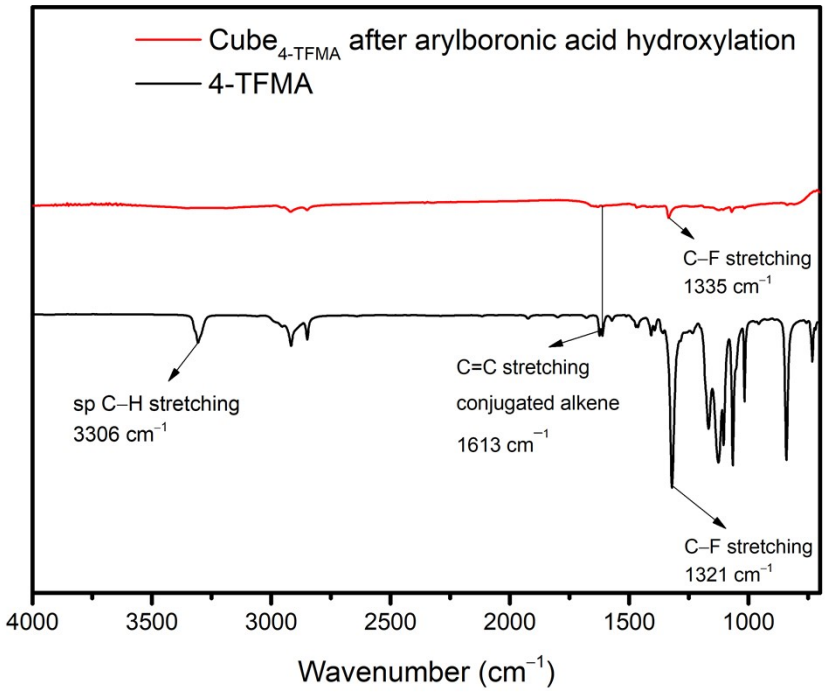
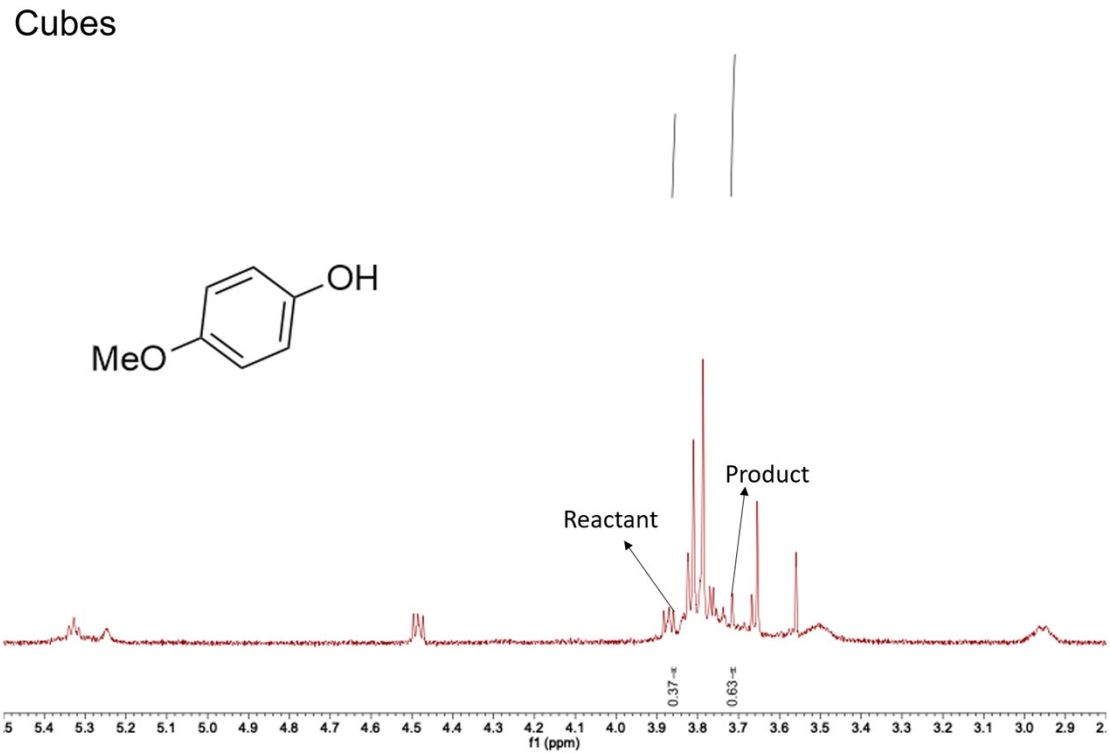
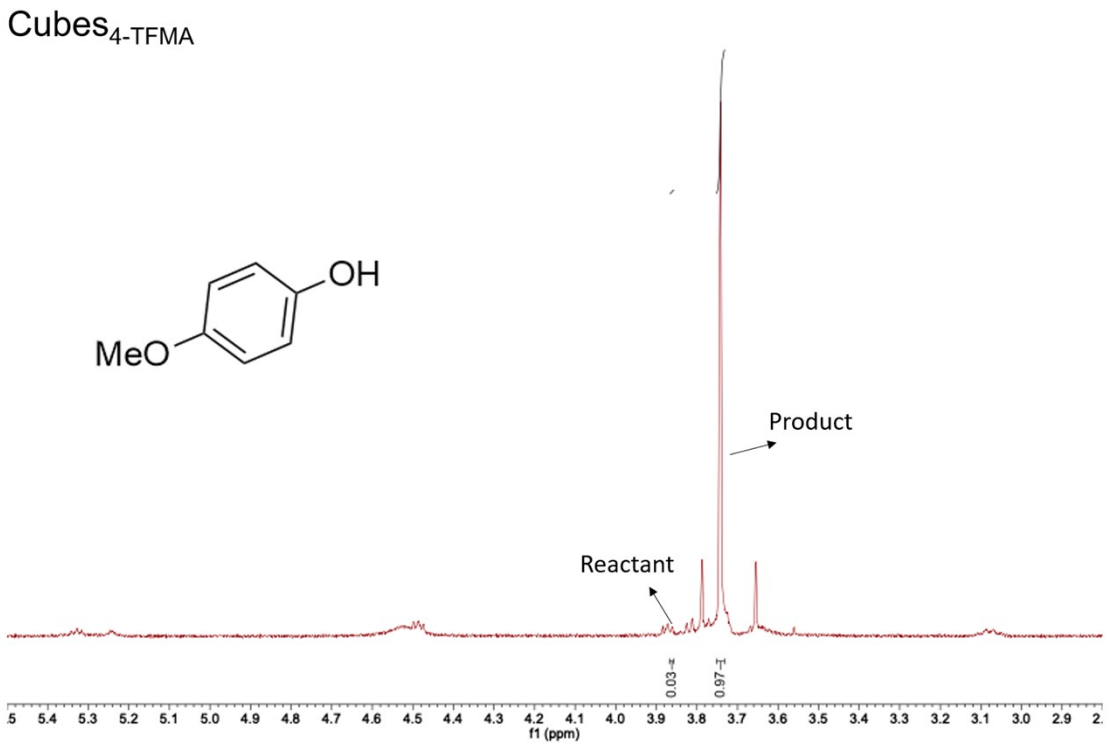


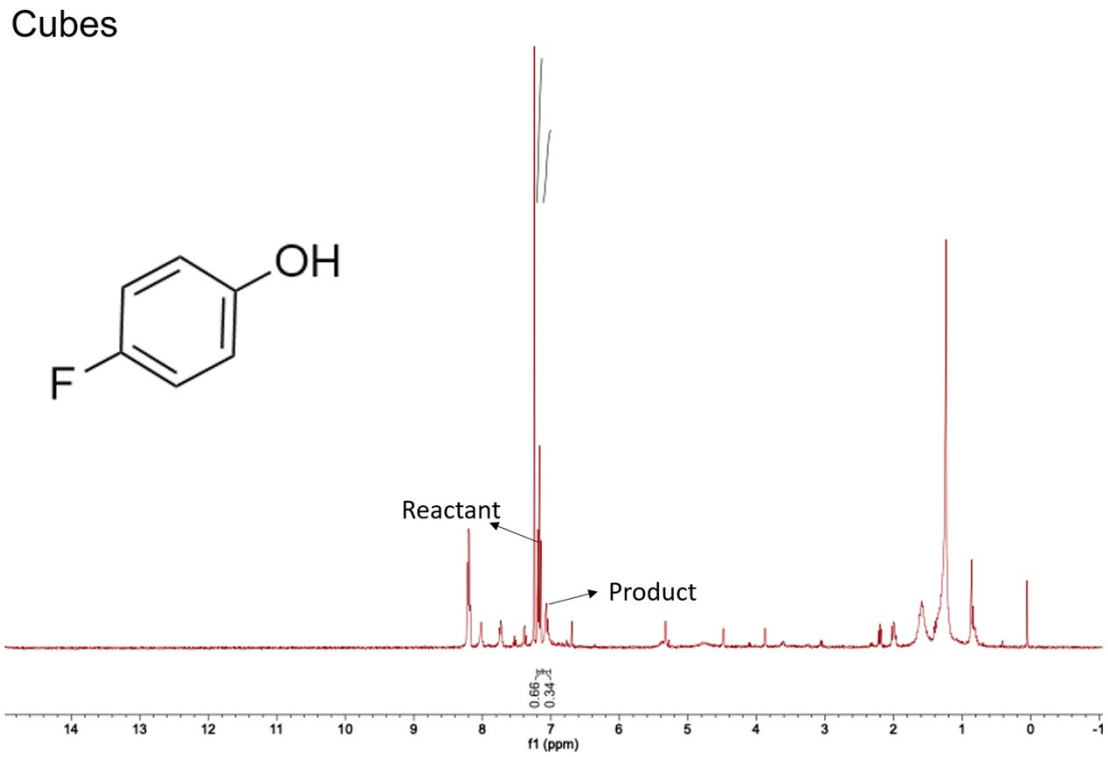
Fig. S9 FT-IR spectra of 4-TFMA and the functionalized Cu_2O cubes after the arylboronic acid hydroxylation reaction.



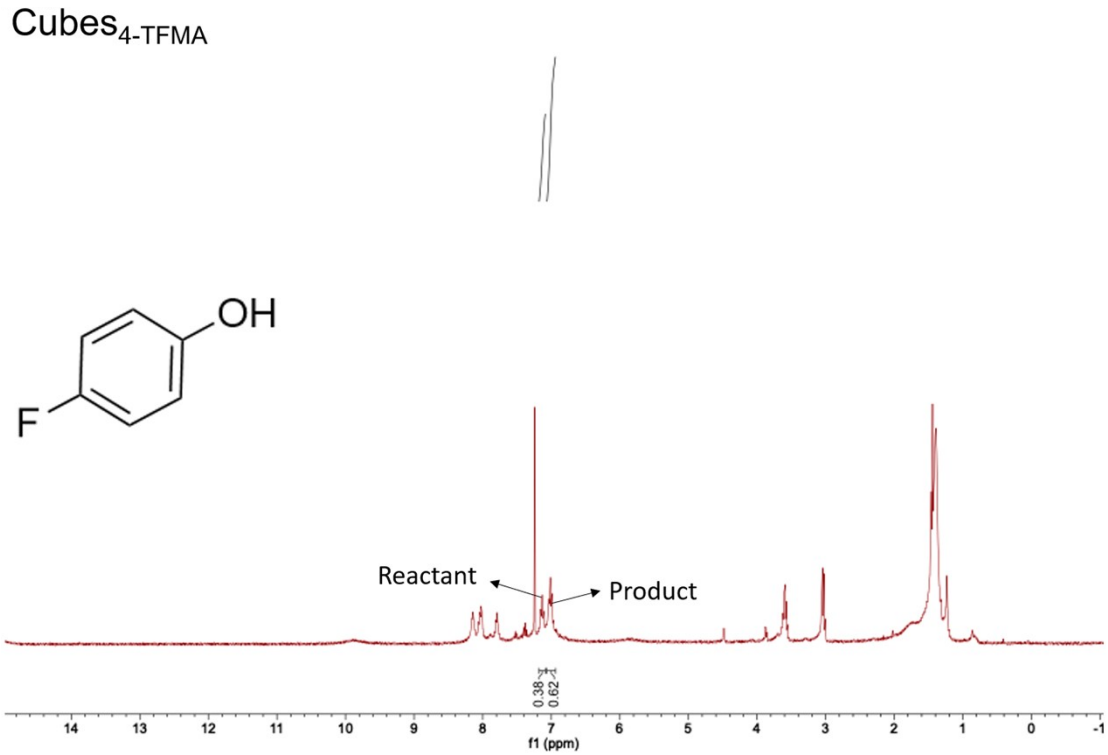
Spectrum S1 ^{1}H NMR spectrum of 4-methoxyphenylboronic acid conversion to 4-methoxyphenol using Cu_2O cubes as the photocatalyst.



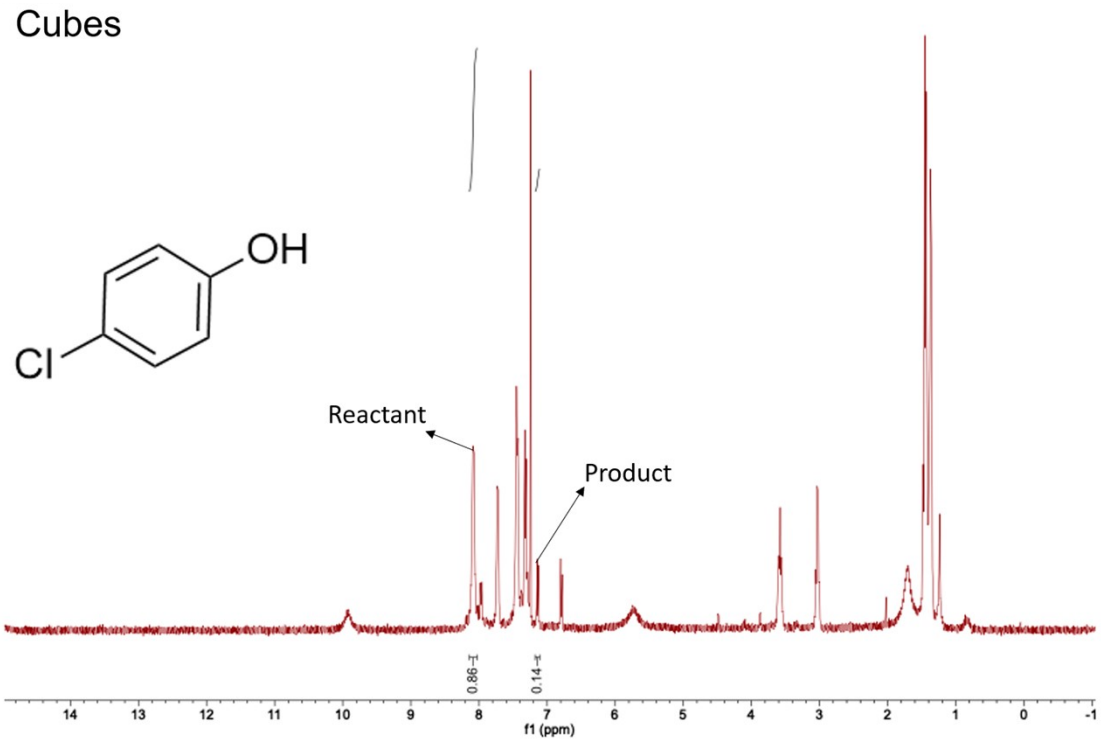
Spectrum S2 ^{1}H NMR spectrum of 4-methoxyphenylboronic acid conversion to 4-methoxyphenol using 4-TFMA-modified Cu_2O cubes as the photocatalyst.



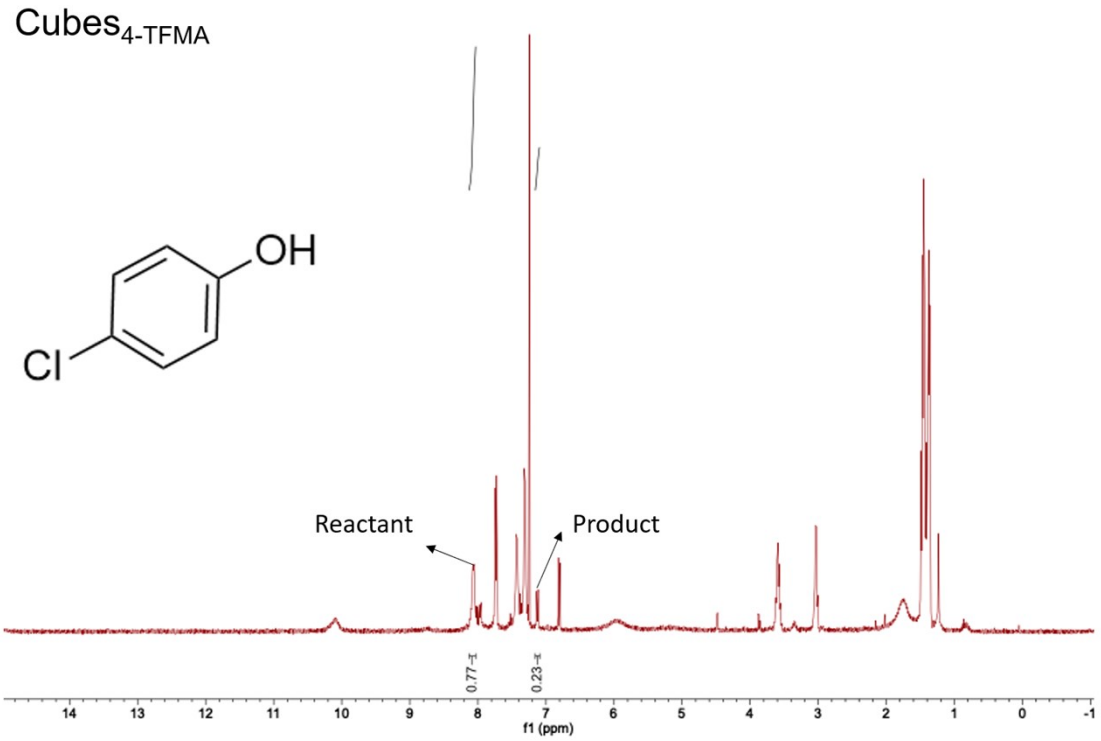
Spectrum S3 ^{1}H NMR spectrum of 4-fluorophenylboronic acid conversion to 4-methoxyphenol using Cu_2O cubes as the photocatalyst.



Spectrum S4 ^{1}H NMR spectrum of 4-fluorophenylboronic acid conversion to 4-fluorophenol using 4-TFMA-modified Cu_2O cubes as the photocatalyst.



Spectrum S5 ^{1}H NMR spectrum of 4-chlorophenylboronic acid conversion to 4-chlorophenol using Cu_2O cubes as the photocatalyst.



Spectrum S6 ^{1}H NMR spectrum of 4-chlorophenylboronic acid conversion to 4-chlorophenol using 4-TFMA-modified Cu_2O cubes as the photocatalyst.