Electronic Supplementary Information

4-Nitrophenylacetylene-modified Cu_2O cubes and rhombic dodecahedra showing superior photocatalytic activity through surface band structure modulation

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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 (NaOH, 98%, SHOWA), sodium dodecyl sulfate ($C_{12}H_{25}NaSO_4$, ≥99.0%, J. T. Baker), potassium carbonate (K_2CO_3, 99%, Alfa Aesar), absolute ethanol (C_2H_5OH, ≥99.5%, Honeywell), acetonitrile (CH_3CN, 99.5%, Acros Organics), methyl orange ($C_{14}H_{14}N_3NaO_3S$, Alfa Aesar), 1-ethynyl-4-nitrobenzene ($C_8H_5NO_2$, 98%, Combi-Blocks), chromic(VI) acid (CrO_3, 99.5%, Acros Organics), and sodium oxalate ($Na_2C_2O_4$, ≥99.0%, Sigma–Aldrich) were used as received. A spin-trapping reagent DMPO (5,5-dimethyl-1-pyrroline-N-oxide, 98%, Matrix Scientific) needs to be treated with activated charcoal for further purification. Milli-Q water (18.2 MΩ) was used to prepare all the solutions in the experiments.

Synthesis of Cu_2O polyhedra

For the synthesis of Cu_2O nanocubes and octahedra, 9.50 mL and 9.00 mL of deionized water were respectively added in the sample vials containing 0.087 g of SDS surfactant. Next, 0.1 mL of 0.1 M $CuCl_2$ solution was added into the vials that were kept in a 30–32 ºC water bath with vigorous stirring, and 0.2 mL of 1.0 M NaOH solution was introduced. The color of solution would immediately change from colorless to light blue due to the formation of $Cu(OH)_2$. After stirring for 5 and 3 sec, 0.15 and 0.65 mL of 0.2 M $NH_2OH{\cdot}HCl$ reductant respectively were quickly injected and stirred for 10 sec. After stop stirring, and solutions were aged respectively for 50 and 25 min. The reason for shortening the aging time in making Cu_2O octahedra is because large particles and hexapods can form with a longer reaction time.

To make Cu_2O rhombic dodecahedra, 6.90 mL of deionized water was added to a vial containing 0.087 g of SDS, followed by the addition of 0.5 mL of 0.1 M $CuCl_2$ solution. The vial was kept in a 30–32 ºC water bath with vigorous stirring. Next, 0.18 mL of 1.0 M NaOH solution was added. The solution color would immediately change from colorless to light blue due to the formation of $Cu(OH)_2$. After stirring for 5 sec, 2.40 mL of 0.1 M $NH_2OH{\cdot}HCl$ solution was quickly injected and stirred for 10 sec. Finally, the solution was aged for 50 min without stirring.

All products were centrifuged at 7000 rpm for 3 min (Hermle Z323 centrifuge) and washed with 1:1 volume ratio of water and ethanol to remove unreacted chemicals, and finally washed with absolute ethanol. After washing, the particles were dried and stored in a vacuum oven.

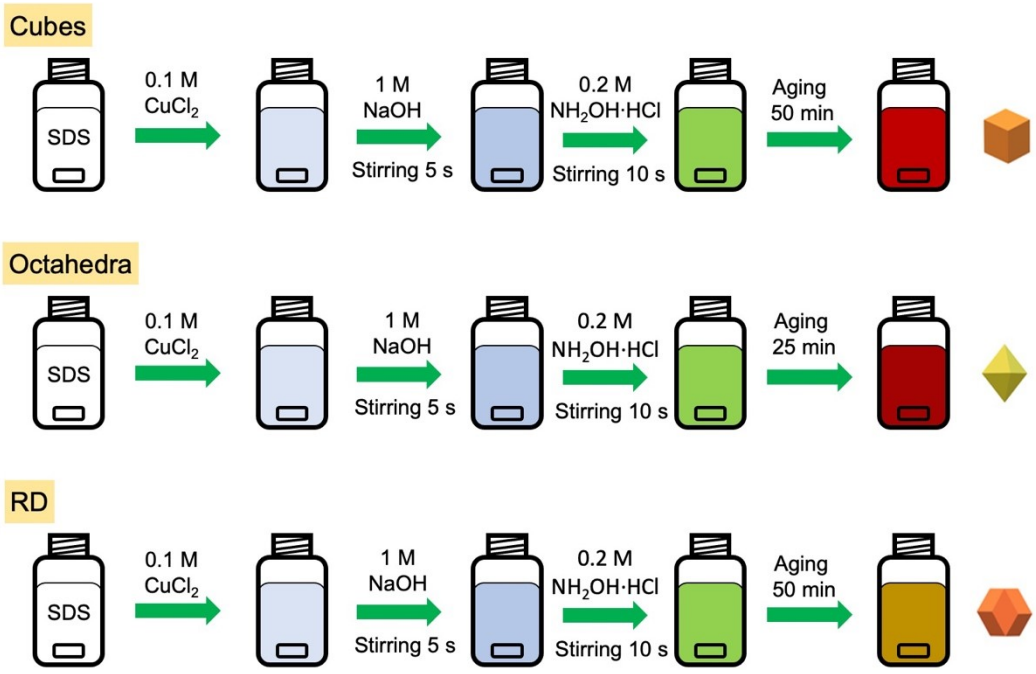

Fig. S1 Reaction conditions used to synthesize different Cu_2O crystals. The solution colors reflect the experimental observations.

Table S1 Reagent amounts used for the synthesis of different Cu_2O crystals.

	SDS (g)	0.1 M $CuCl_2$ (mL)	1 M NaOH (mL)	$NH_2OH{\cdot}HCl$ (M/mL)	H_2O (mL)
Cubes	0.087	0.1	0.20	0.2 / 0.15	9.50
Octahedra	0.087	0.1	0.20	0.2 / 0.65	9.00
RD	0.087	0.5	0.18	0.1 / 2.40	6.90

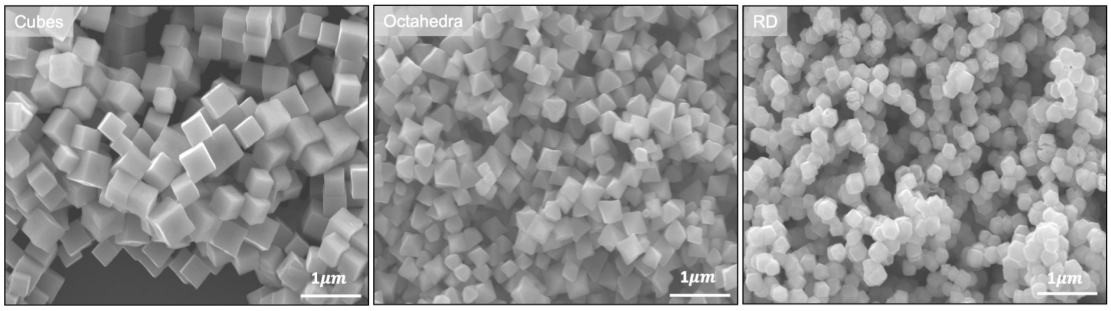

Fig. S2 SEM images of the prepared Cu_2O cubes, octahedra, and rhombic dodecahedra. The cubes can show slight depression at their face centers.

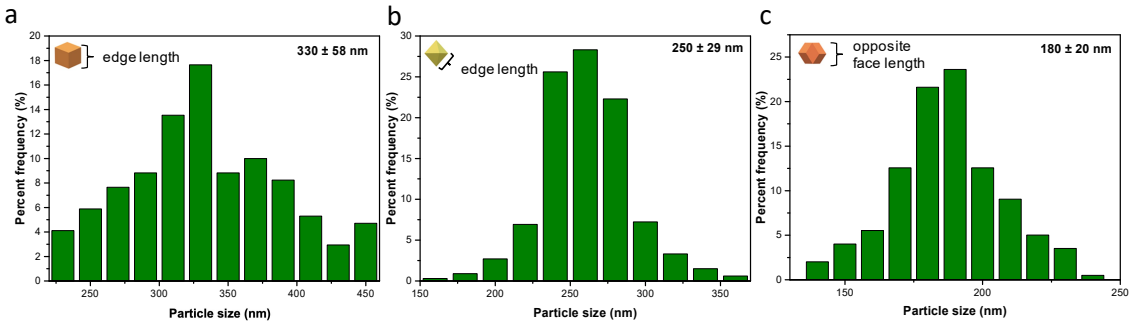

Fig. S3 Size distribution histograms of the prepared Cu_2O (a) cubes, (b) octahedra, and (c) rhombic dodecahedra. Over 250 counts were made for each sample.

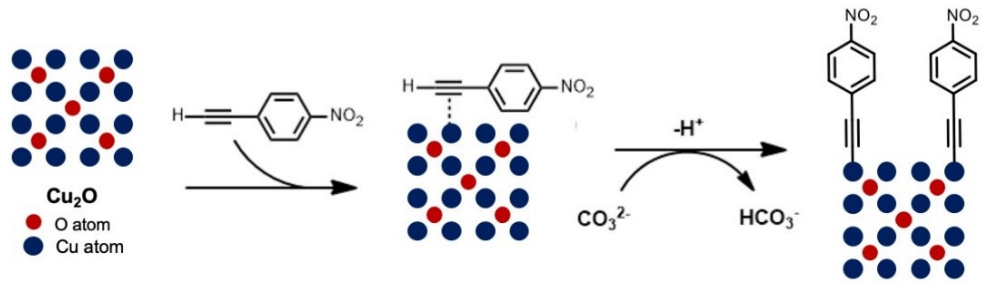

Fig. S4 Reaction mechanism of 4-NA molecules on Cu_2O surface.

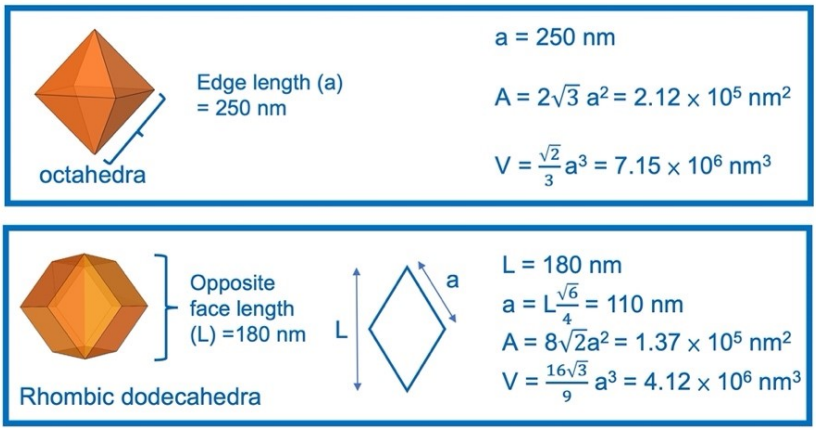

Fig. S5 Calculations of surface area and volume of a single Cu_2O cube, octahedron, and rhombic dodecahedron.

Table S2 Calculations of the amounts of Cu_2O crystals needed for photocatalysis experiments with a total particle surface area of 0.03 m^2.

	Cubes	Octahedra	RD
size (nm)	330	350	180
surface area for one particle (nm^2)	6.53×10^5	2.12×10^5	1.37×10^5
volume for one particle (nm^3)	3.59×10^7	7.15×10^6	4.12×10^6
fixed total surface area (m^2)	0.03	0.03	0.03
number of particles	4.59×10^{10}	1.42×10^{11}	2.18×10^{11}
total volume (nm^3)	1.65×10^{18}	1.01×10^{18}	8.98×10^{17}
density of Cu_2O (g/nm^3)	6.03×10^{-21}		
weight (mg)	9.9	6.1	5.4

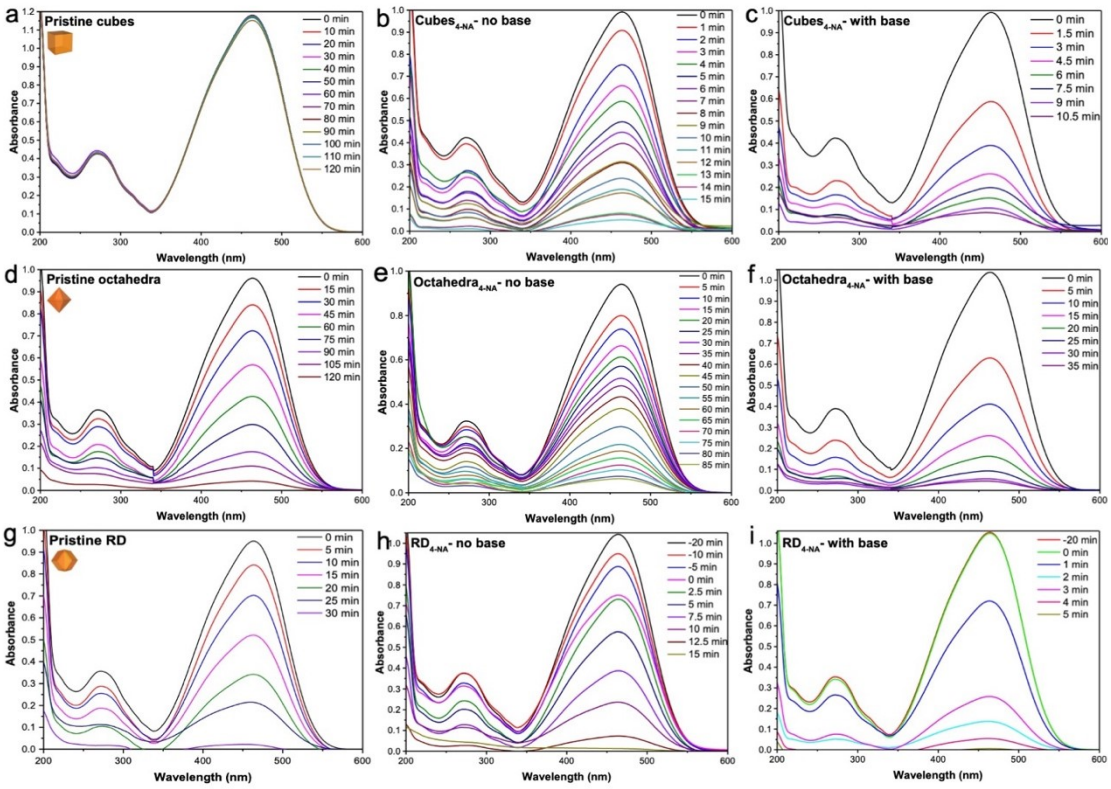

Fig. S6 UV–vis absorption spectra of methyl orange as a function of irradiation time using (a–c) pristine Cu_2O cubes and 4-NA-modified cubes with and without adding K_2CO_3, (d–f) pristine Cu_2O octahedra and 4-NA-modified octahedra with and without adding K_2CO_3, and (g–i) pristine Cu_2O rhombic dodecahedra and 4-NA-modified rhombic dodecahedra with and without adding K_2CO_3.

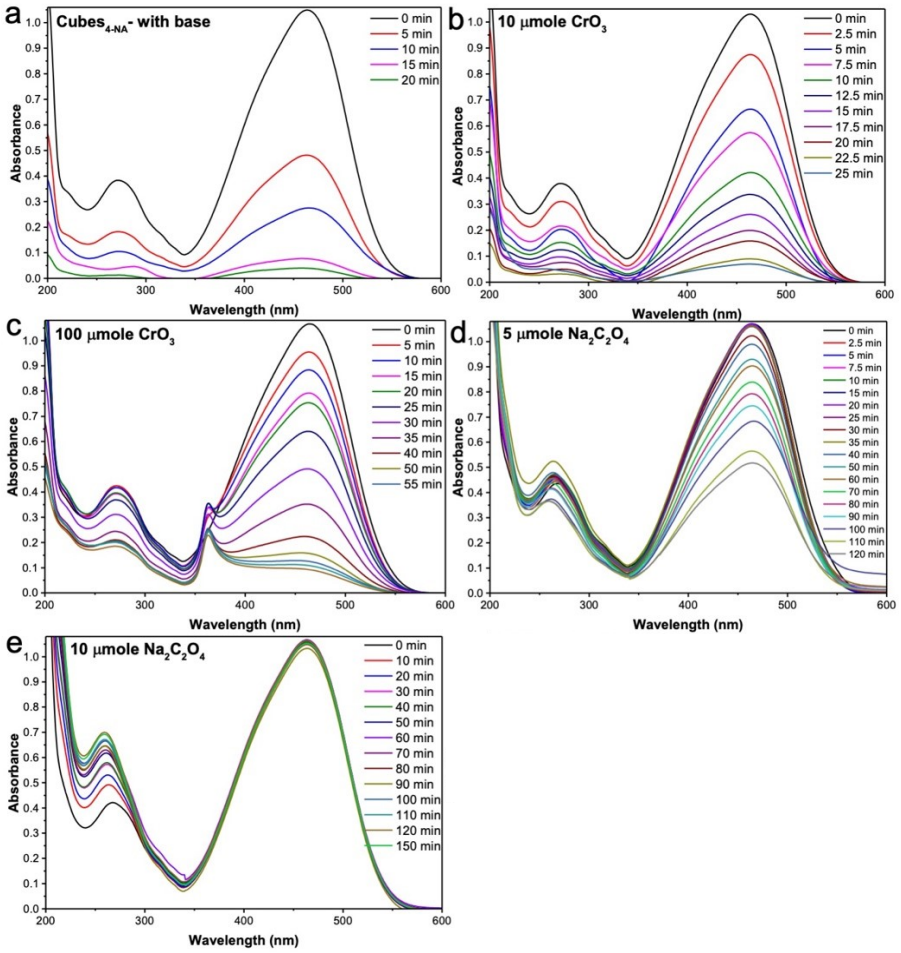

Fig. S7 Electron (CrO_3) and hole ($Na_2C_2O_4$) scavenger experiments. UV–vis absorption spectra of (a) 4-NA-modified Cu_2O cubes without adding scavengers, (b) adding 10 μmole CrO_3, (c) 100 μmole CrO_3 (d) 5 μmole $Na_2C_2O_4$, and (e) 10 μmole $Na_2C_2O_4$.

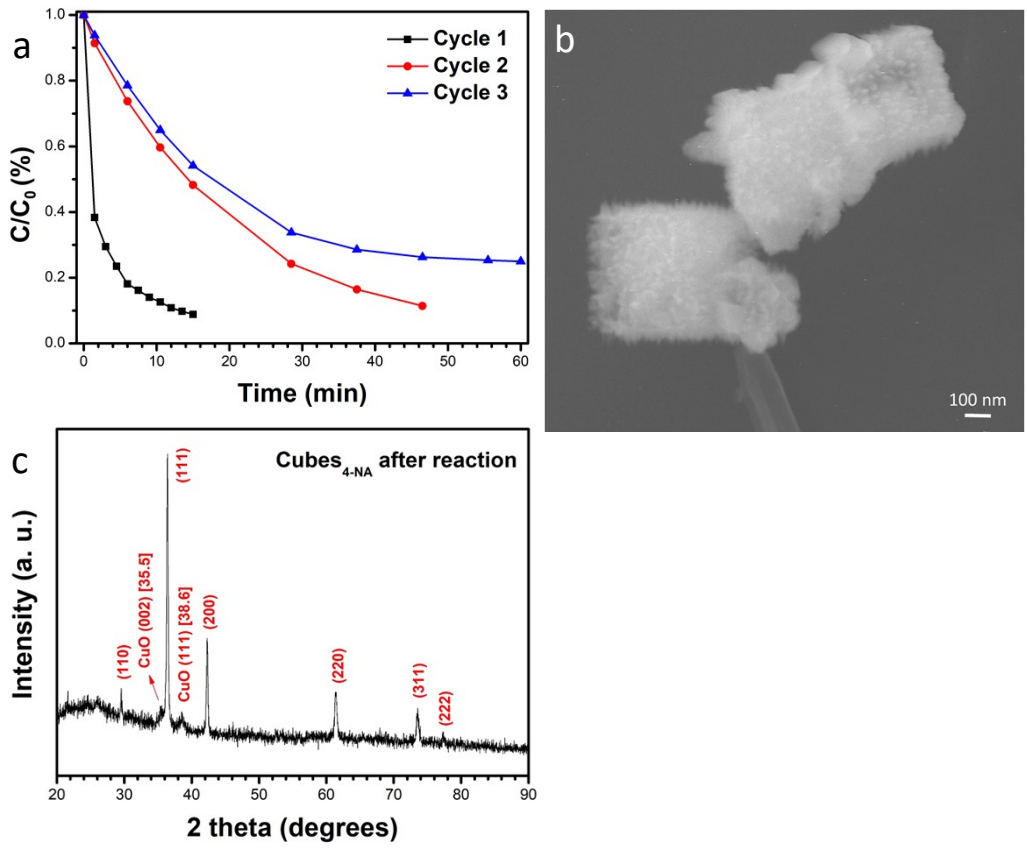

Fig. S8 (a) Plot of three cycles of MO photodegradation experiment using 4-NA-functionalized Cu_2O cubes as the photocatalyst. K_2CO_3 was added. (b) SEM image of Cu_2O cubes after three cycles of photodegradation experiment. (c) XRD patterns of the particles after three cycles of photodegradation experiment.

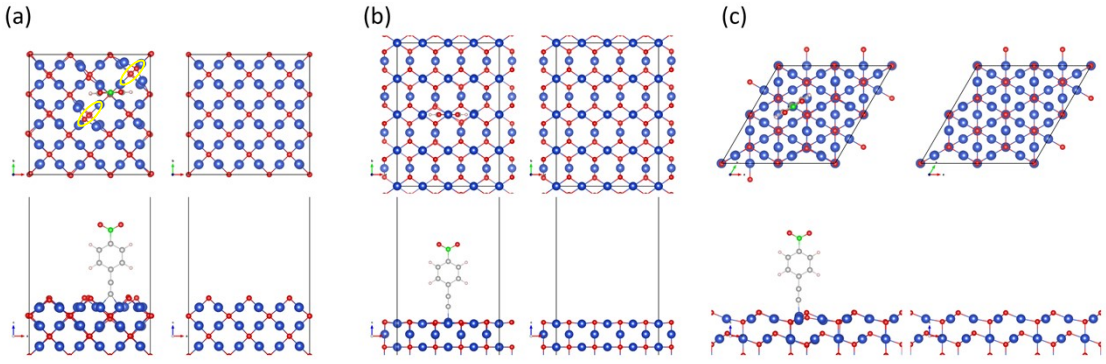

Fig. S9 Geometric structures of 4-NA before (right panel) and after (left panel) adsorption on Cu_2O (a) {100}, (b) {110}, and (c) {111} surfaces. Top and side views are shown. 4-NA adsorption does not involve significant changes to the Cu_2O surface structure, except for the {100} case with neighboring oxygen atoms moving by ~1 Å due to molecular repulsion (see circled regions).

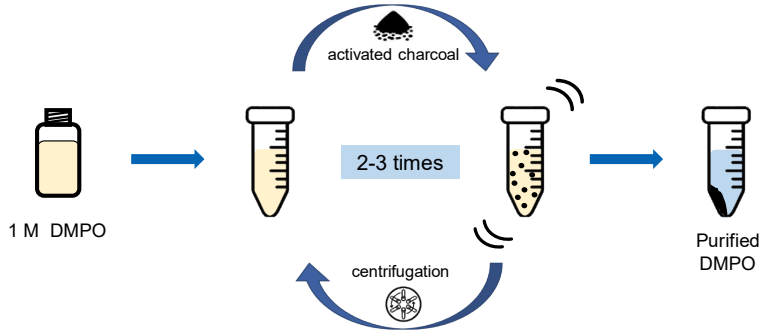

Fig. S10 Procedure used to purify DMPO.

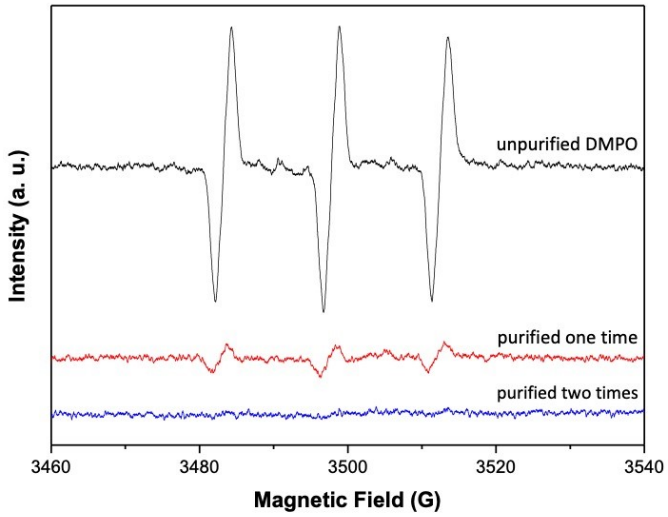

Fig. S11 EPR spectra before and after DMPO purification.