

In the format provided by the authors and unedited.

Facet-dependent active sites of a single Cu₂O particle photocatalyst for CO₂ reduction to methanol

Yimin A. Wu^{1,2}, Ian McNulty¹, Cong Liu³, Kah Chun Lau^{4,5}, Qi Liu⁶, Arvydas P. Paulikas⁴, Cheng-Jun Sun⁷, Zhonghou Cai⁷, Jeffrey R. Guest¹, Yang Ren⁷, Vojislav Stamenkovic⁴, Larry A. Curtiss⁴, Yuzi Liu^{1*} and Tijana Rajh^{1*}

¹Center for Nanoscale Materials, Argonne National Laboratory, Argonne, IL, USA. ²Department of Mechanical and Mechatronics Engineering and Waterloo Institute for Nanotechnology, University of Waterloo, Waterloo, Ontario, Canada. ³Chemical Sciences and Engineering Division, Argonne National Laboratory, Argonne, IL, USA. ⁴Materials Science Division, Argonne National Laboratory, Argonne, IL, USA. ⁵Department of Physics and Astronomy, California State University, Northridge, CA, USA. ⁶Department of Physics, City University of Hong Kong, Hong Kong, China. ⁷Advanced Photon Source, Argonne National Laboratory, Argonne, IL, USA. *e-mail: yuziliu@anl.gov; rajh@anl.gov

Supplementary Information for

**Facet-Dependent Active Sites of a Single Cu₂O Particle Photocatalyst
for CO₂ Reduction to Methanol**

**Yimin A. Wu^{1,2}, Ian McNulty¹, Cong Liu³, Kah Chun Lau^{4,5}, Qi Liu⁶, Arvydas P. Paulikas⁴, Cheng-Jun Sun⁷, Zhonghou Cai⁷, Jeffrey R. Guest¹, Yang Ren⁷,
Vojislav Stamenkovic⁴, Larry A. Curtiss⁴, Yuzi Liu¹, Tijana Rajh¹**

¹ Center for Nanoscale Materials, Argonne National Laboratory, Argonne, IL 60439, USA.

² Department of Mechanical and Mechatronics Engineering and Waterloo Institute for Nanotechnology,
University of Waterloo, Waterloo, ON, N2L 3G1, Canada

³ Chemical Sciences and Engineering Division, Argonne National Laboratory, Argonne, IL, 60439, USA

⁴ Materials Science Division, Argonne National Laboratory, Argonne, IL, 60439, USA

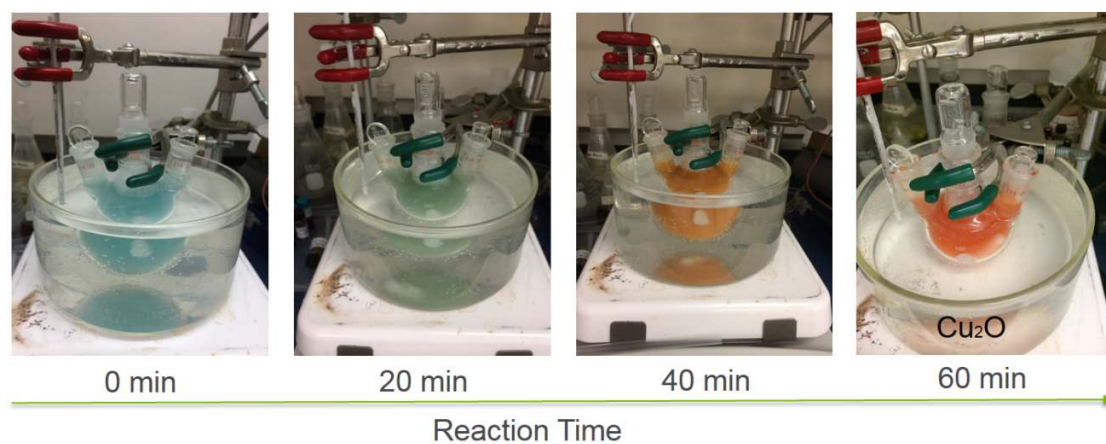
⁵ Department of Physics and Astronomy, California State University, Northridge, CA, 91330, USA

⁶ Department of Physics, City University of Hong Kong, Kowloon, Hong Kong, China

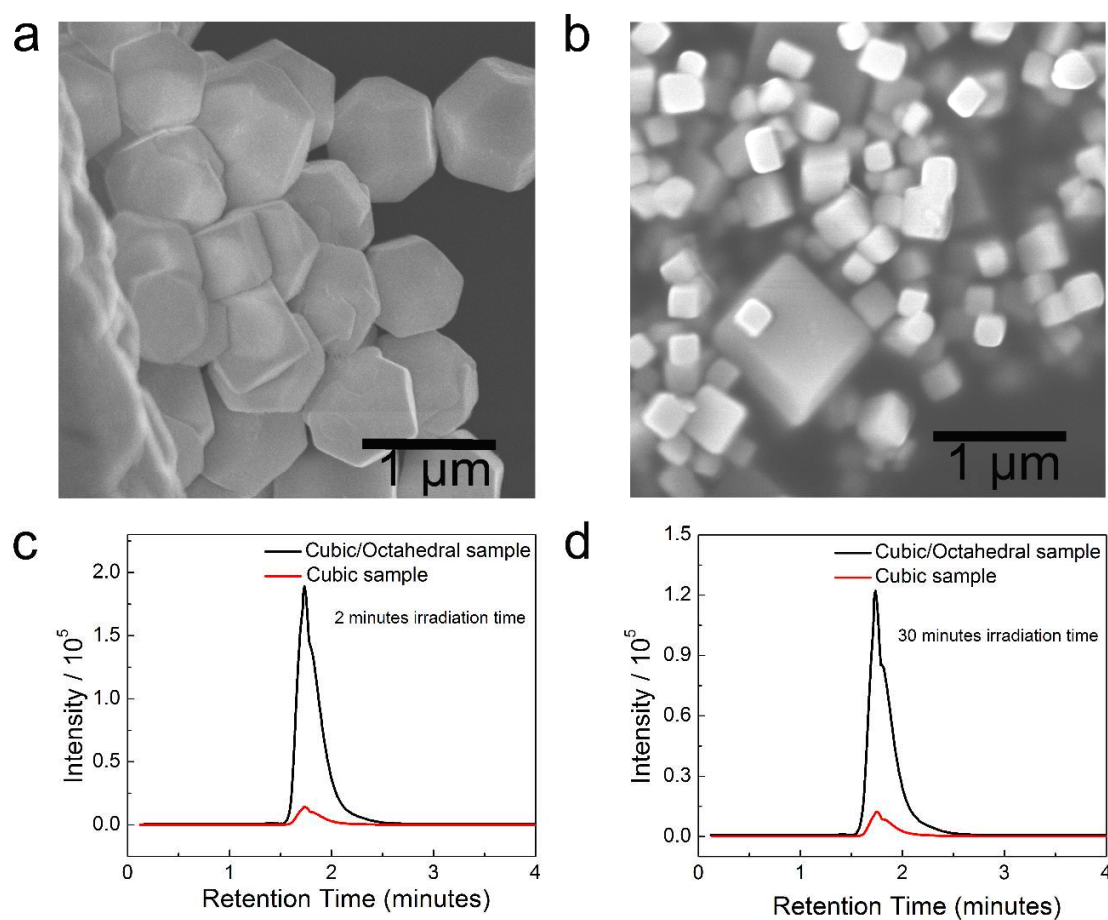
⁷ Advanced Photon Source, Argonne National Laboratory, Argonne, IL 60439, USA.

This Supplementary Information file includes:

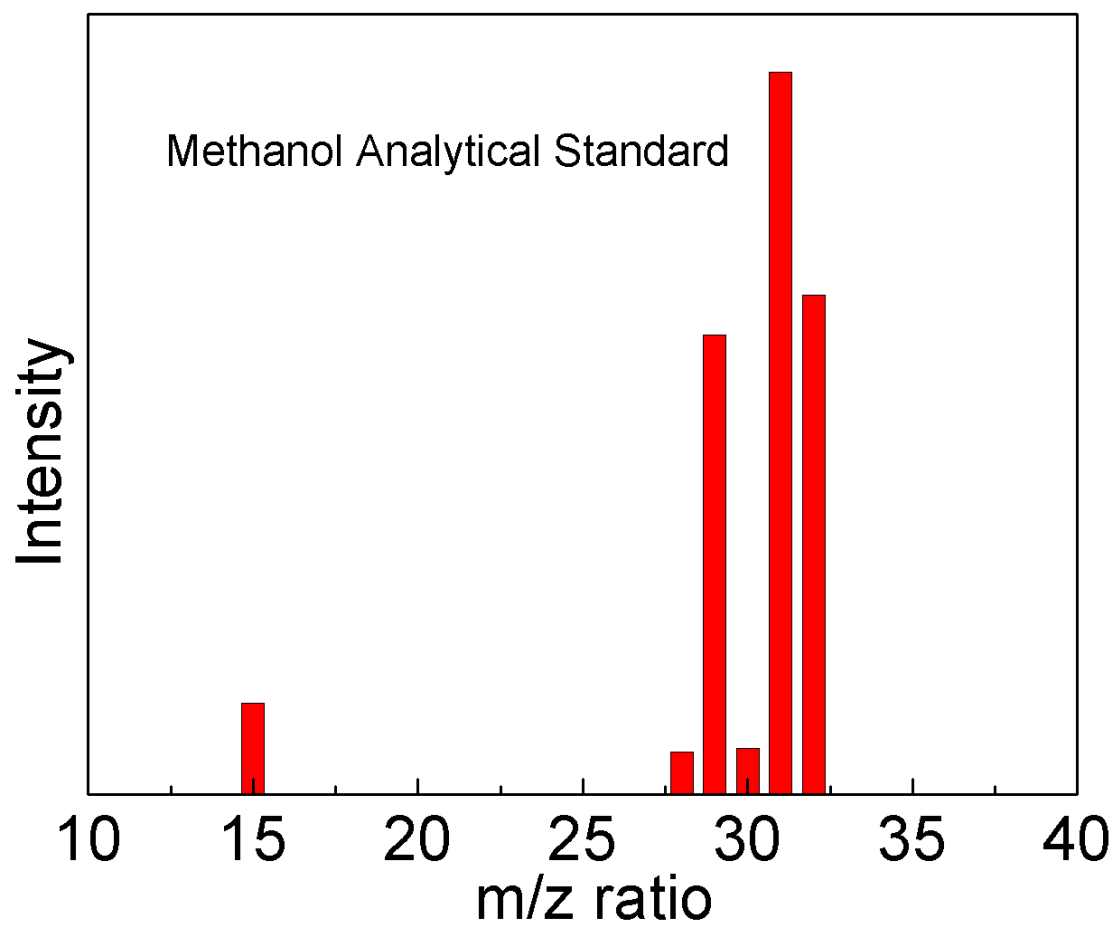
Figures S1 to S23 and Table 1:



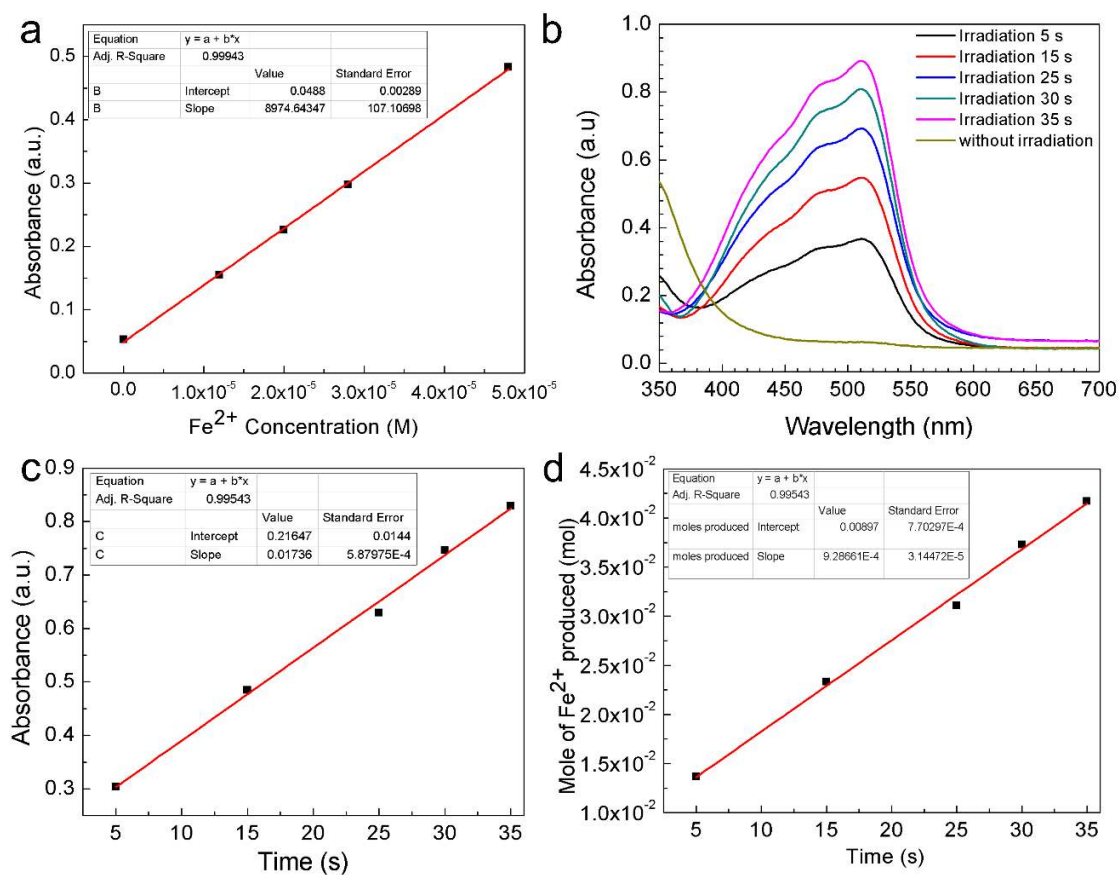
Supplementary Figure 1 | Illustration of the Cu_2O particle synthesis method. The solution color changed from blue to green, to yellow, and finally turned brick red with time.



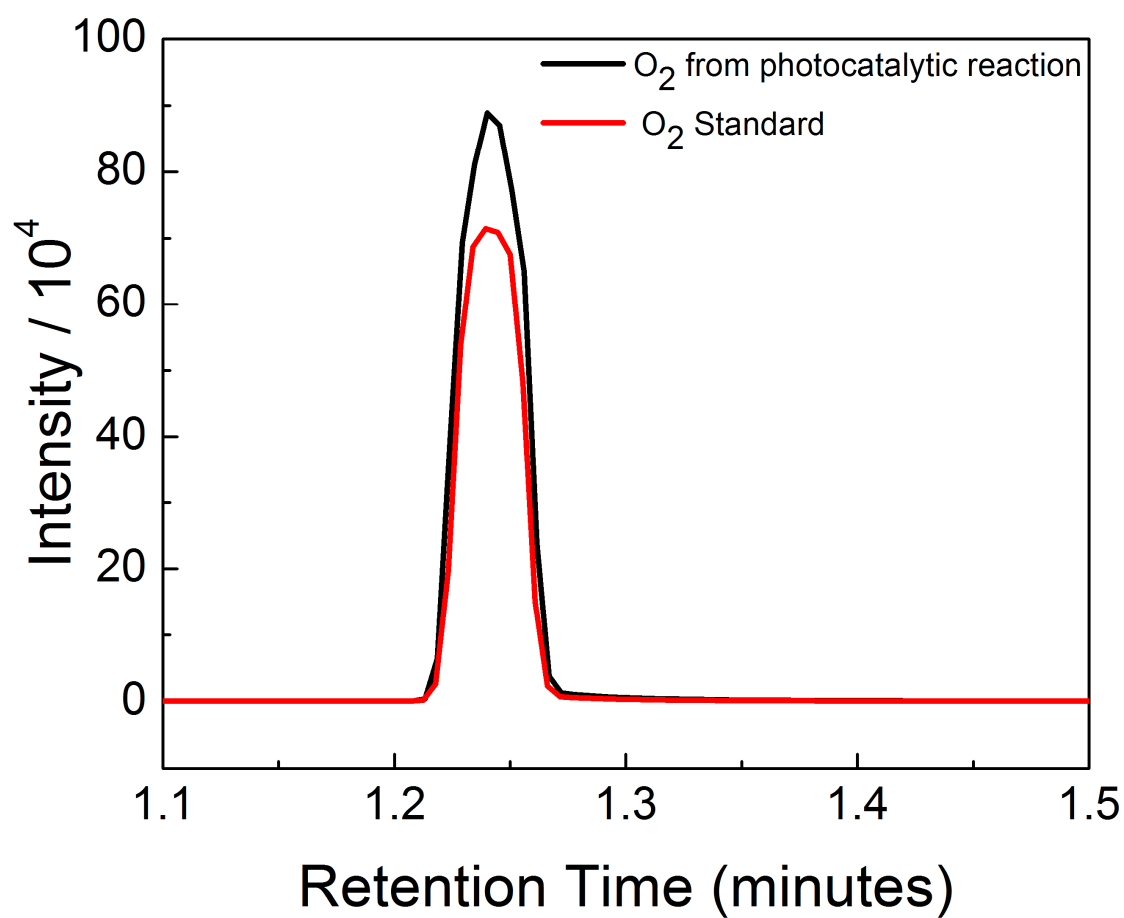
Supplementary Figure 2 | SEM images and GC results from the two Cu₂O particle samples. (a) SEM image of the cubic/octahedral sample. (b) SEM image of the cubic sample. (c) Methanol production by the cubic/octahedral sample (black curve) vs. the cubic sample (red curve), measured by GC after 2 min irradiation time. (d) Methanol production by the cubic/octahedral sample (black curve) vs. the cubic sample (red curve), measured by GC after 30 min irradiation time. The area integrated under the curve obtained with the cubic sample decreased 91% for the 2-min sample and 89% for the 30-min sample, by comparison to the cubic/octahedral sample. This indicates the cubic/octahedral sample, with its larger number of truncations and high-index facets, was more photocatalytically active than the cubic sample.



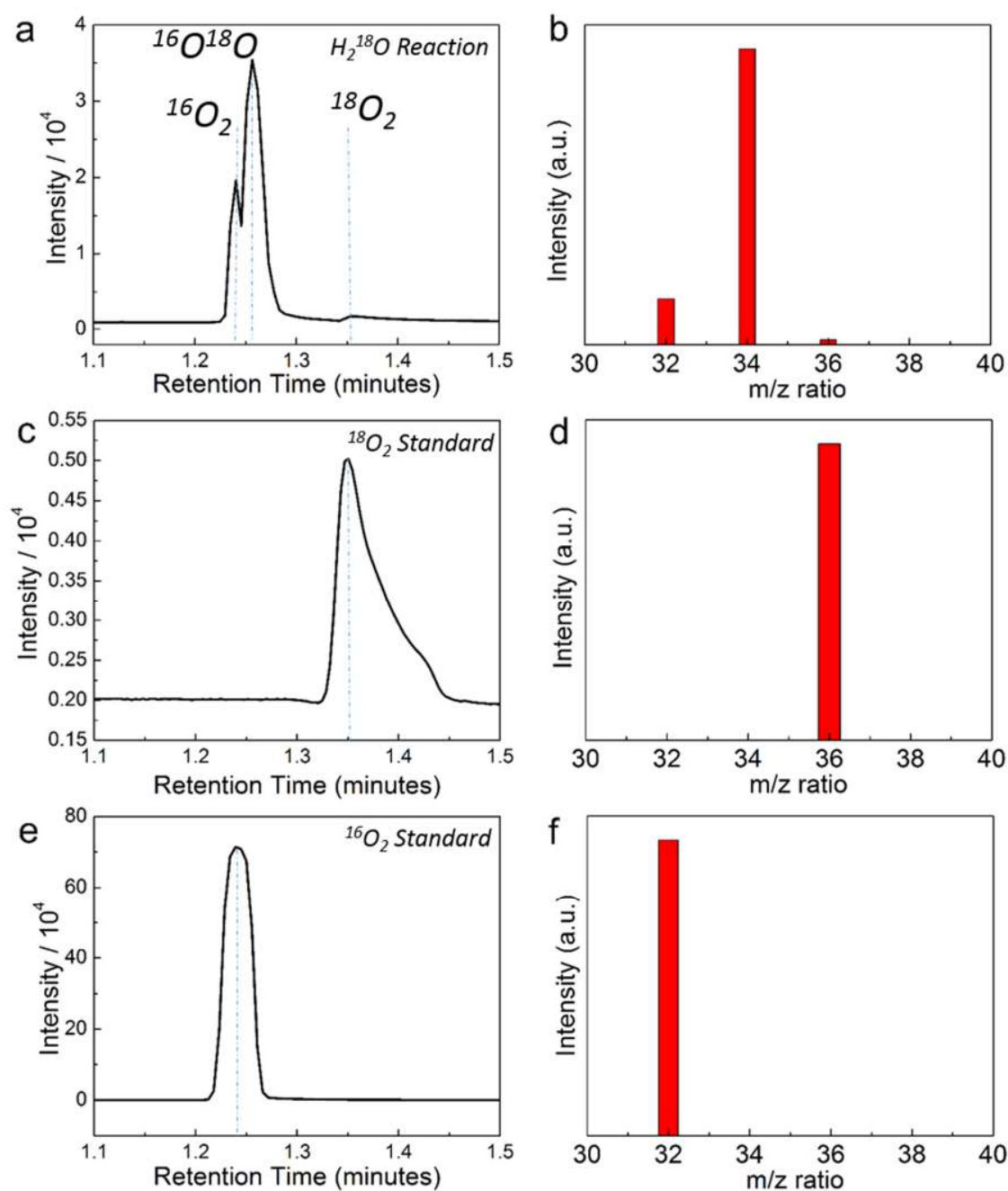
Supplementary Figure 3 | Mass spectra of a methanol analytical standard. This was measured using the same instrument and parameter for GC/MS analysis of the photocatalytic products, as in Figure 1.



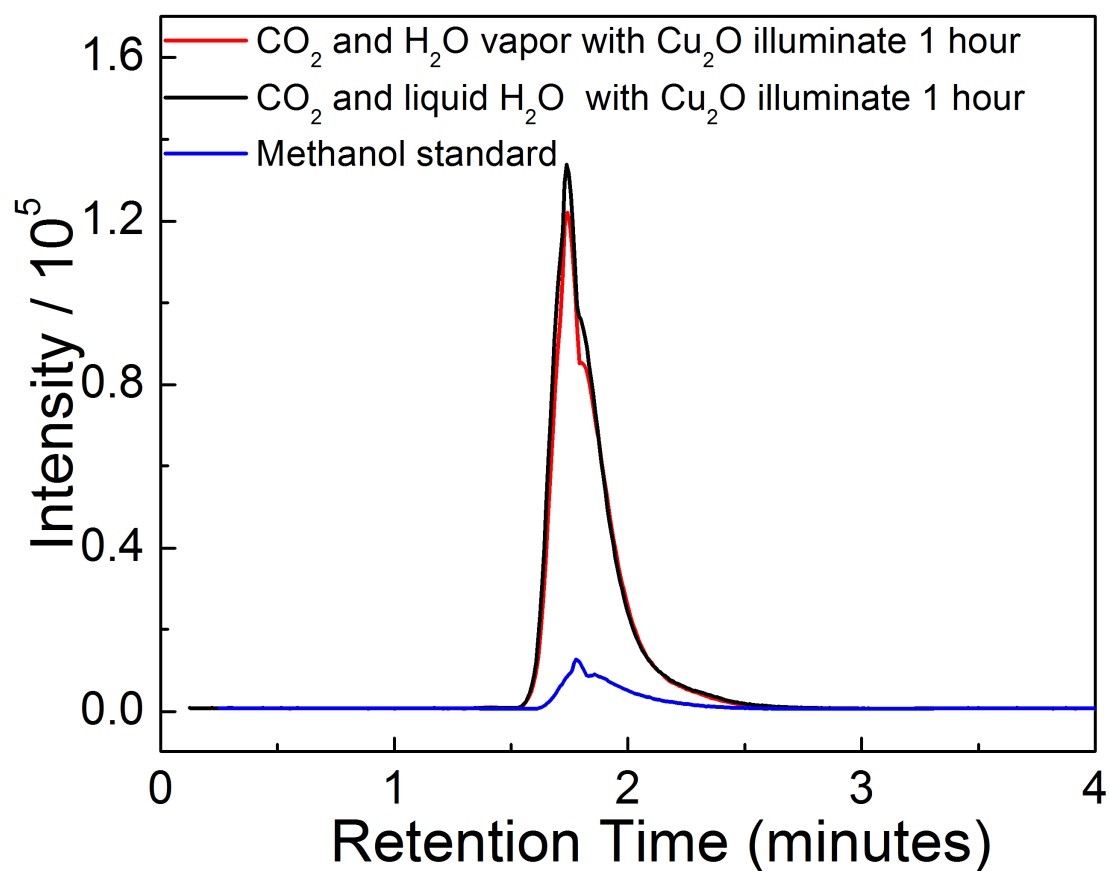
Supplementary Figure 4 | Actinometry to determine the photon flux from the white light source, which was used for photocatalytic performance measurement. (a) Molar absorptivity of $[\text{Fe}(\text{phen})_3]^{2+}$. **(b)** Irradiation time dependent UV-vis-absorption spectra of produced $[\text{Fe}(\text{Phen})_3]^{2+}$ from $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$ photochemical reaction. **(c)** The absorbance at 510 nm extracted from (b). **(d)** Mole of Fe^{2+} produced by the $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$ photochemical reaction as a function of irradiation time.



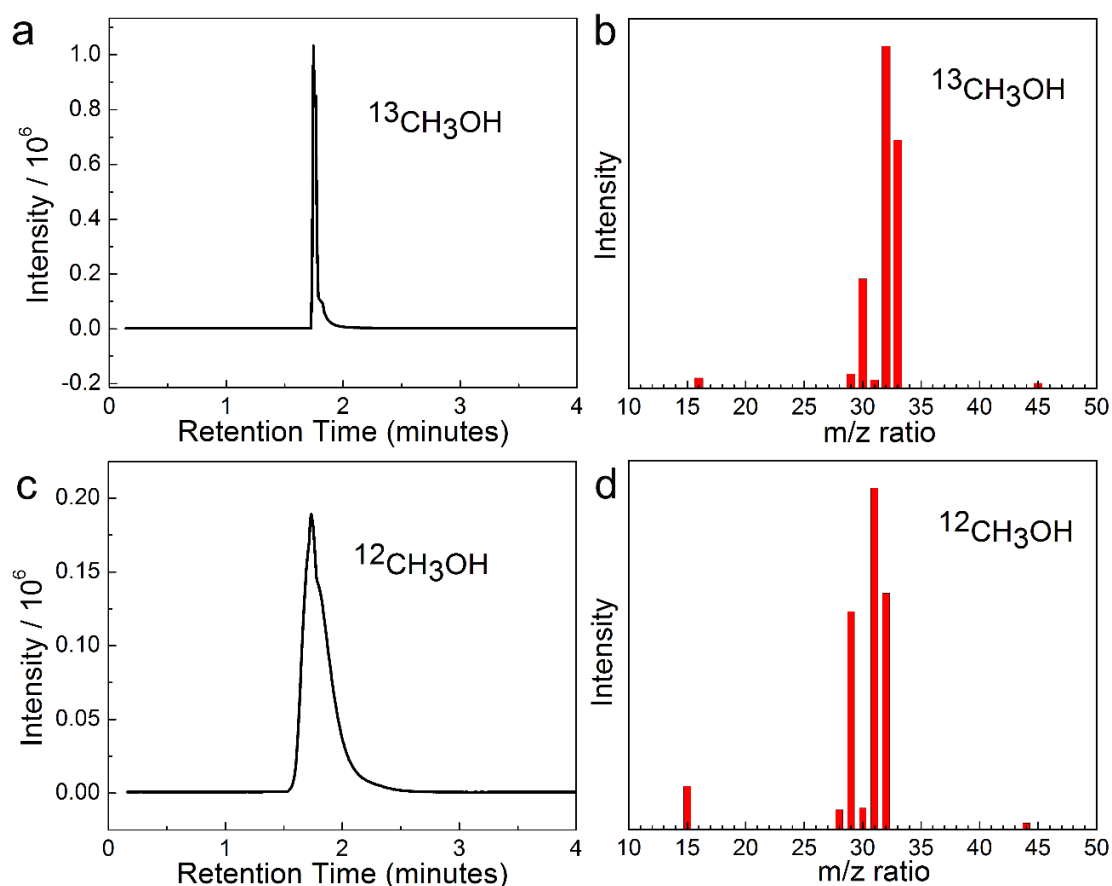
Supplementary Figure 5 | GC analysis to quantification of oxygen in the photocatalytic reaction after 2 min irradiation time.



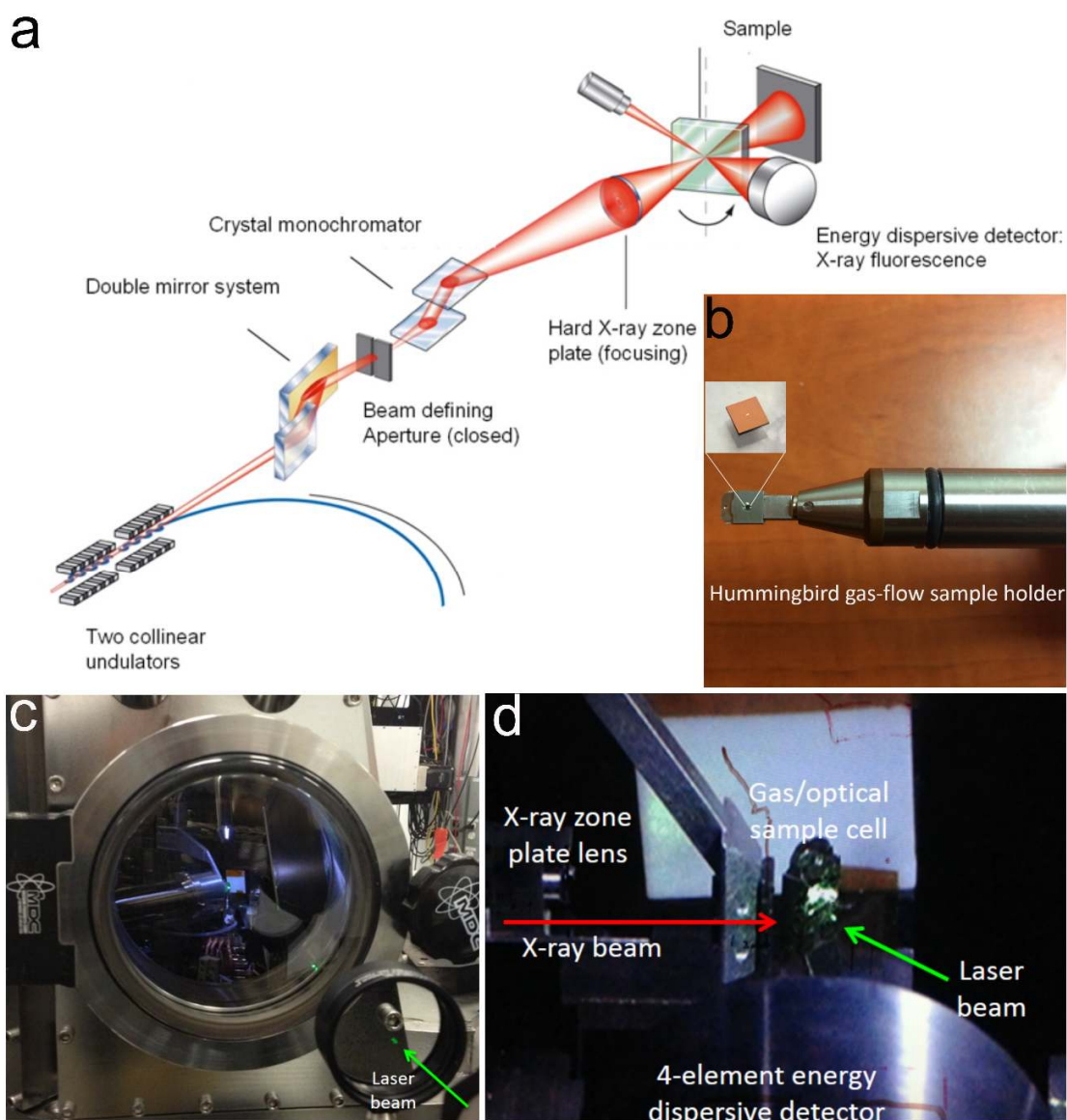
Supplementary Figure 6 | Oxygen isotope tracer measurement. (a) Oxygen production from photocatalytic reaction using H_2^{18}O and $^{13}\text{C}^{16}\text{O}_2$ with Cu_2^{16}O , measured by GC after 2 min irradiation time. (b) Mass spectra of oxygen obtained by GC/MS analysis of (a). Peaks at 32, 34, 36 correspond to $^{16}\text{O}_2$, $^{16}\text{O}^{18}\text{O}$, and $^{18}\text{O}_2$. (c) GC of $^{18}\text{O}_2$ standard. (d) Mass spectra of (c). (e) GC of $^{16}\text{O}_2$ standard. (f) Mass spectra of (e).



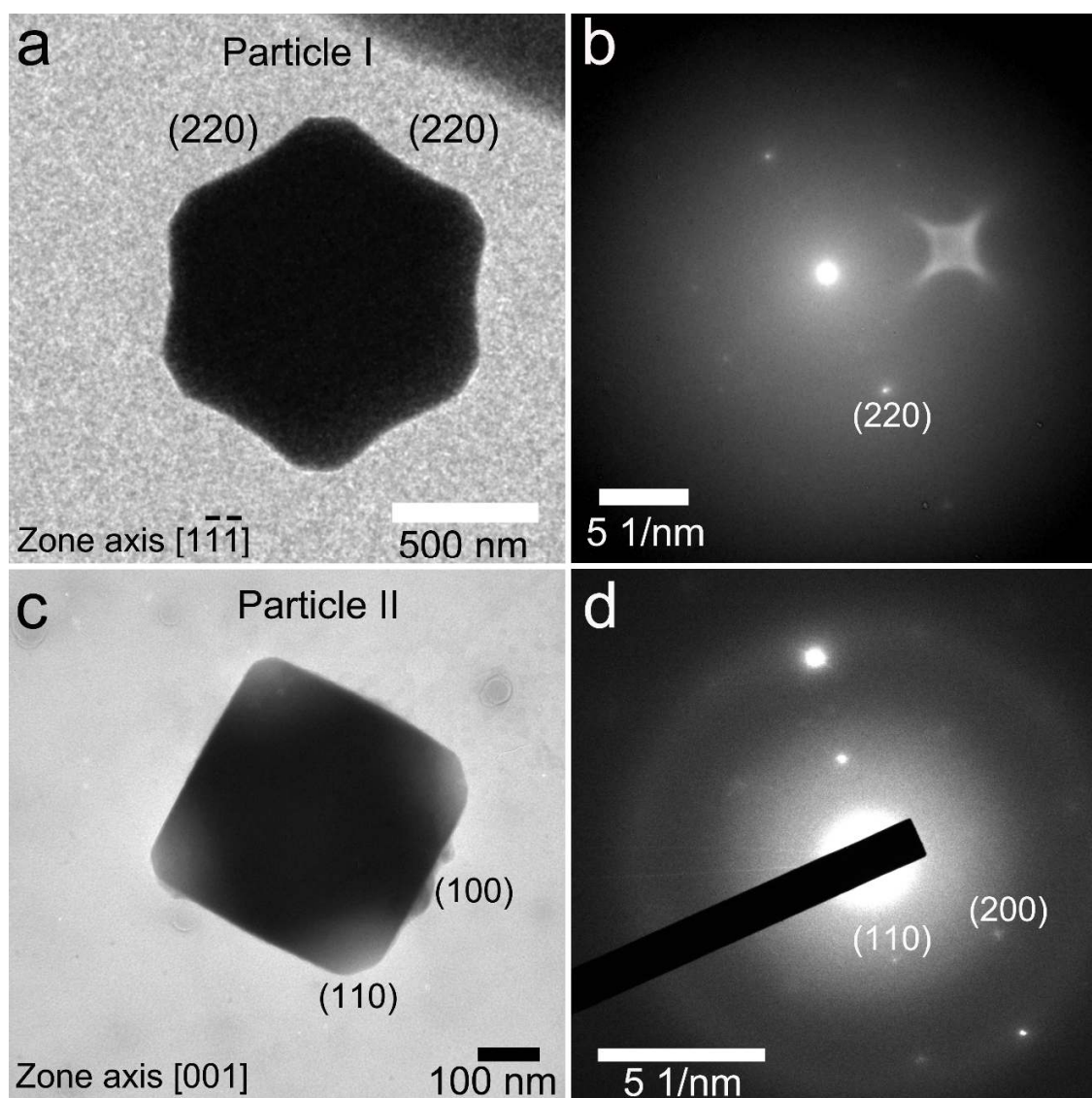
Supplementary Figure 7 | Comparison of methanol production using H₂O vapor or liquid H₂O. GC measurement using CO₂ and H₂O vapor/liquid H₂O with Cu₂O photocatalyst illuminated for 1 hour. It showed the quantity of methanol production using H₂O vapor and H₂O liquid is very similar. This indicates the same reaction mechanism using either H₂O or liquid H₂O. The liquid H₂O produces slightly more methanol than H₂O vapor. This is due to the slight difference in amount of H₂O molecules adsorbed on Cu₂O in H₂O vapor or in liquid H₂O.



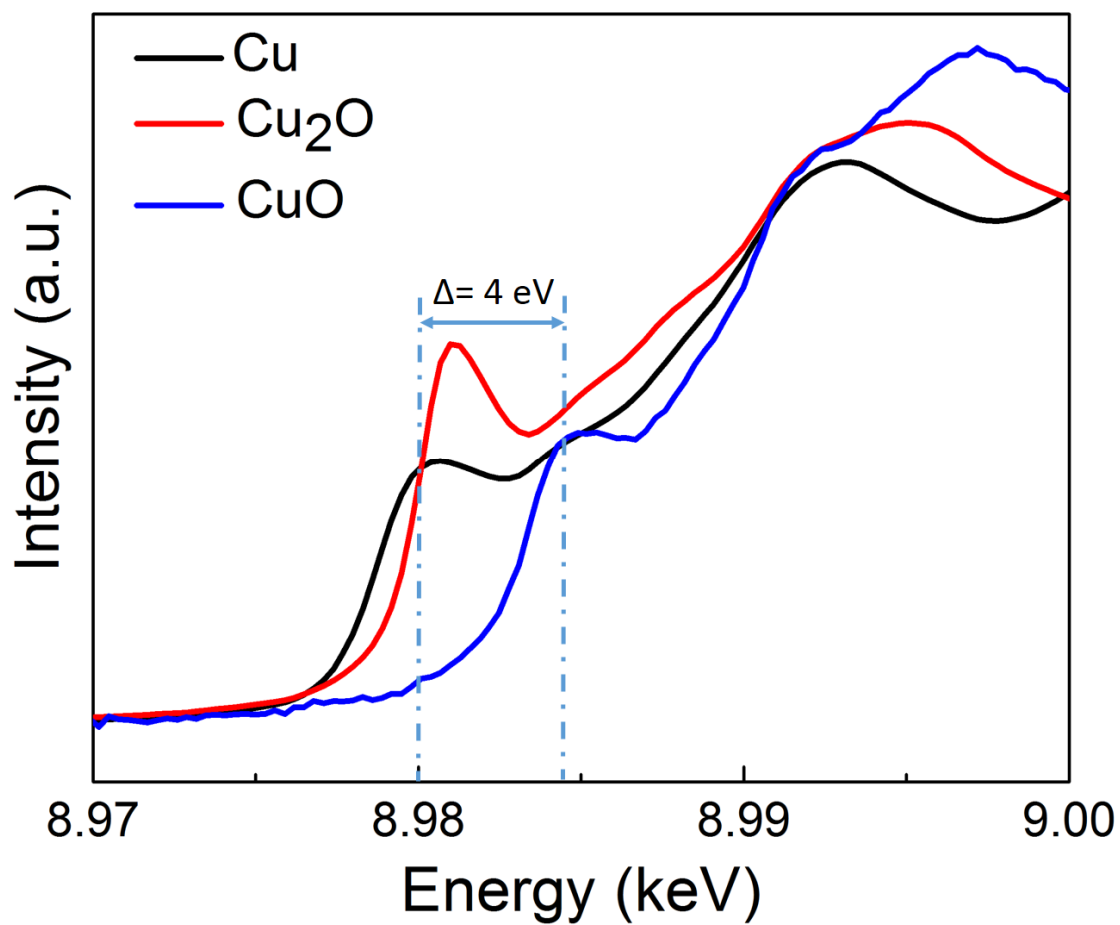
Supplementary Figure 8 | Carbon isotope tracer measurement. (a) $^{13}\text{CH}_3\text{OH}$ production by the cubic/octahedral sample measured by GC after 2 min irradiation time. The retention time was 1.74 min. (b) Mass spectra of methanol obtained by GC/MS analysis of the photocatalytic reaction products from $^{13}\text{CO}_2$. Distinct peaks at 16 and 33 were observed with no peak at mass 28. The mass-to-charge ratio of 45 corresponds to unreacted $^{13}\text{CO}_2$. (c) $^{12}\text{CH}_3\text{OH}$ production by the cubic/octahedral sample measured by GC after 2 min irradiation time. The retention time was 1.74 min. (d) Mass spectra of methanol obtained by GC/MS analysis of the photocatalytic reaction products from $^{12}\text{CO}_2$. The mass- to-charge ratio of 44 corresponds to unreacted $^{12}\text{CO}_2$.



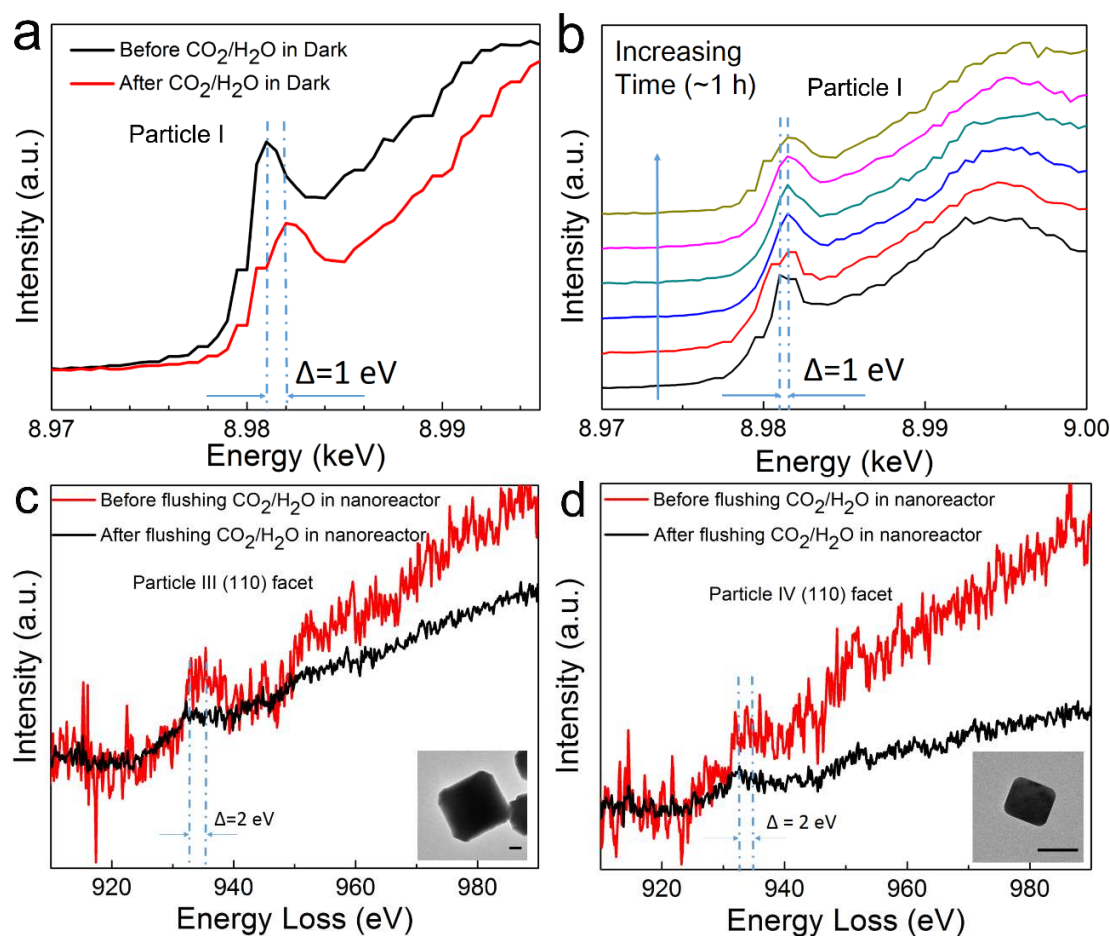
Supplementary Figure 9 | Scanning fluorescence x-ray microscopy and nanospectroscopy experiment. (a) Hard X-ray Nanoprobe at CNM/APS beamline 26-ID-C. (b) Cross-platform sample holder and nanoreactor for both TEM and SFXM. (c) Laser setup for *operando* SFXM measurements. (d) View inside the Hard X-ray Nanoprobe, showing the nanoreactor (gas/optical sample cell) x-ray beam path, x-ray zone plate lens, energy-dispersive fluorescence detector, and incident laser beam.



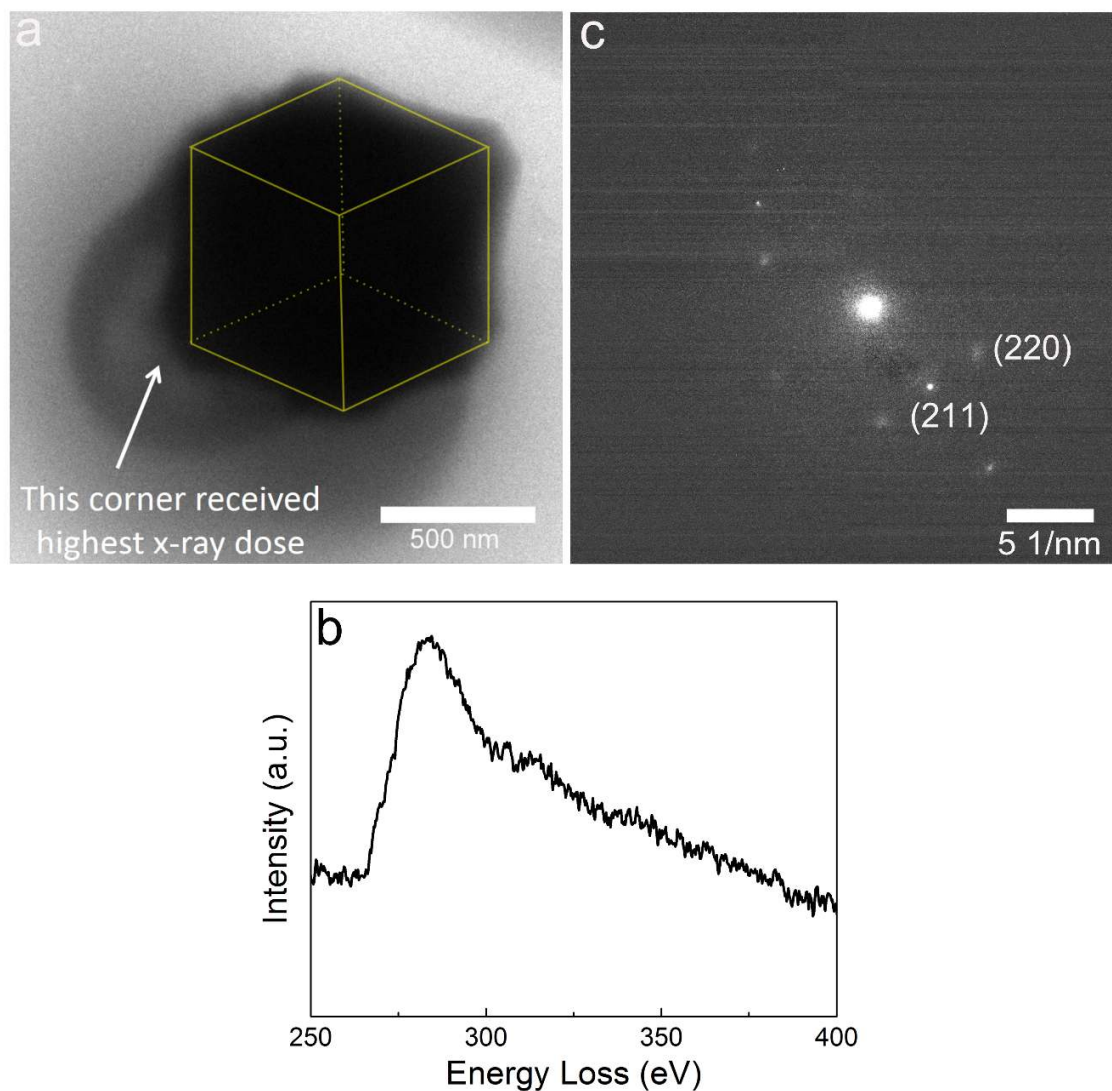
Supplementary Figure 10 | TEM and Corresponding SPED measurements. (a) TEM of particle I. (b) SPED data from particle I. (c) TEM of particle II. (d) SPED data from particle II.



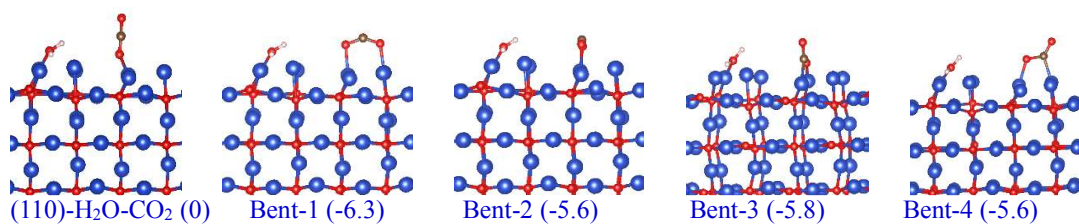
Supplementary Figure 11 | Reference XAS spectra from standard commercialized powders (Sigma Aldrich), taken at APS beamline 20-ID-B. The observed shift of the rising Cu K-edge between the metallic Cu and CuO spectra is $\sim 4 \text{ eV}$.



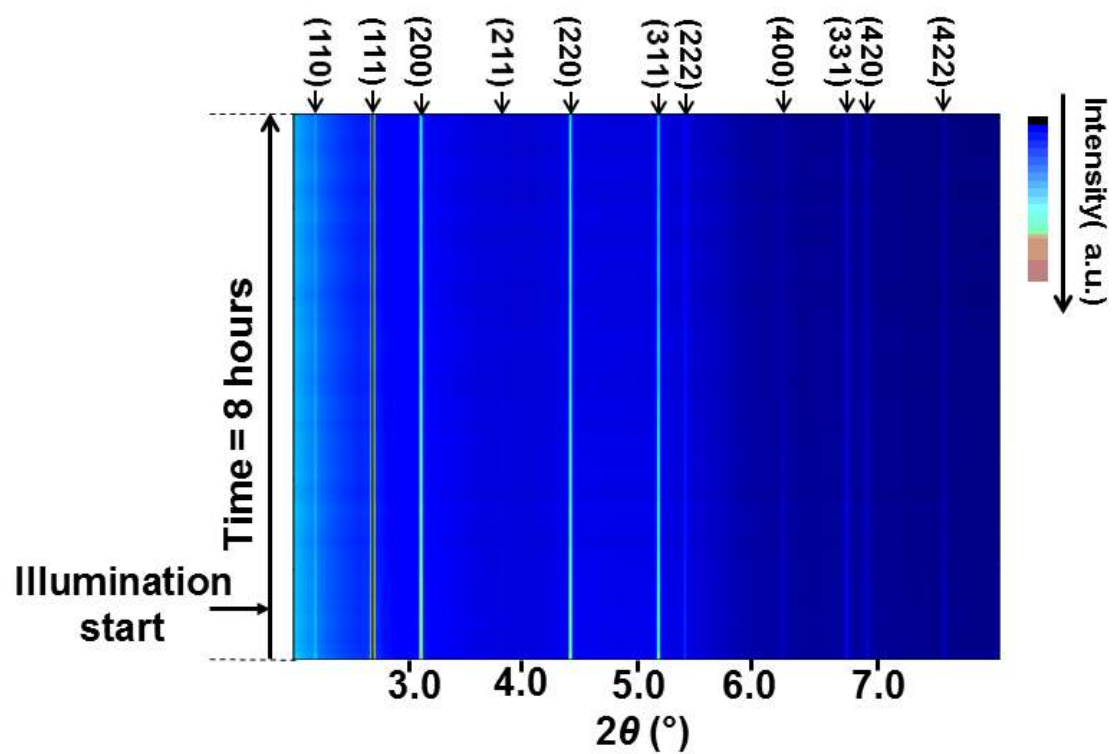
Supplementary Figure 12 | Additional x-ray nanospectroscopy spectra and EELS spectra. (a) Spectral shift due to CO₂ adsorption from the (110) facet of particle I as measured by x-ray nanospectroscopy. (b) Time-resolved x-ray point spectra from the (110) facet of particle I recorded at 10 min intervals with the induction of CO₂/H₂O gas mixture in the dark state. (c, d) Additional EELS spectra on particle III and particle IV (110) facet before and after flushing CO₂/H₂O into the nanoreactor. The lower signal-to-noise ratio with gas at atmospheric pressure is due to greater electron scattering by comparison to TEM column pressure at 10⁻⁶ Pa. Inset shows the corresponding TEM images of particle III and particle IV. The scale bar is 200 nm.



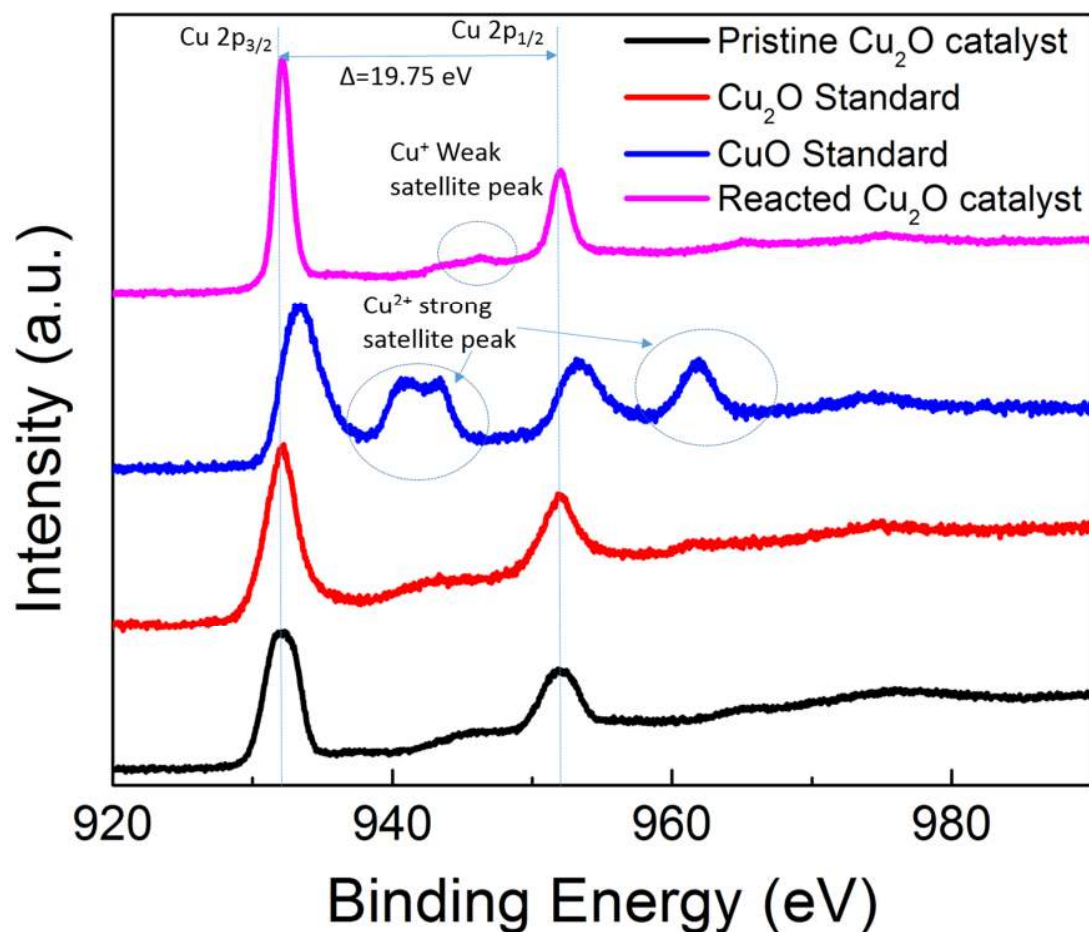
Supplementary Figure 13 | Analysis of potential x-ray beam effects. (a) TEM image of particle I as in Figure 2 after the SFXM measurements. **(b)** Some carbon deposition, determined by the presence of a carbon K-edge peak at 284 eV using EELS, was observed near the location that experienced the greatest x ray radiation dose, indicated in (a). **(c)** No obvious structural damage was observed, which was confirmed by SPED.



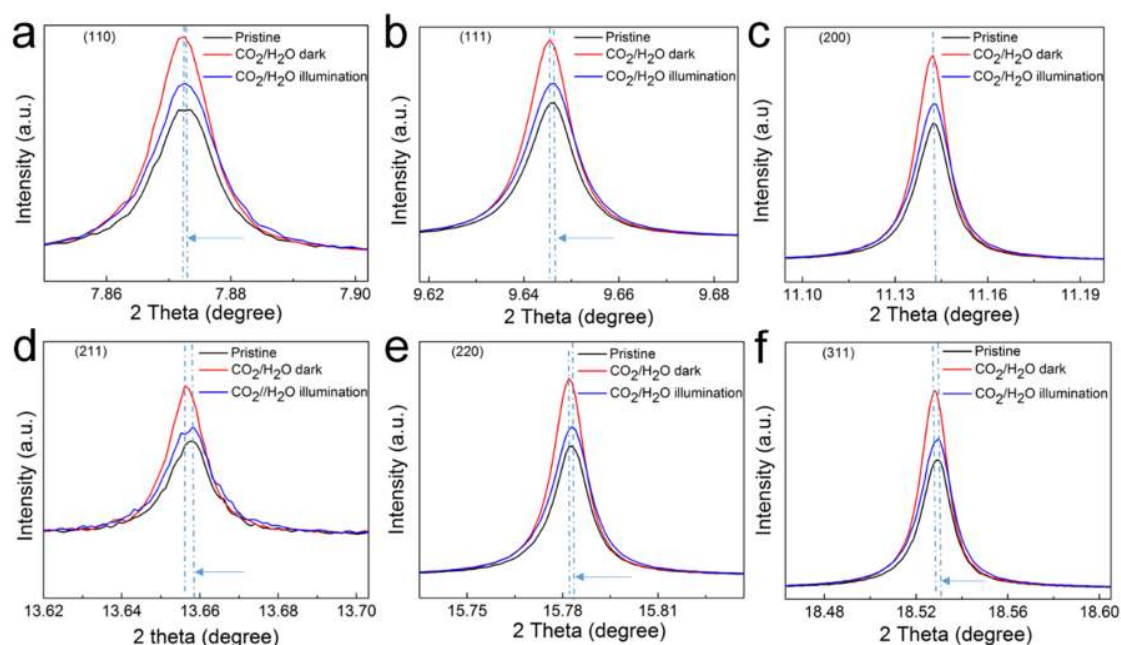
Supplementary Figure 14 | DFT figure of several "bent" CO₂ when co-adsorbed with H₂O on Cu₂O (110)-surface. Calculated conformations of linear and bent CO₂ (i.e. activated CO₂)⁷⁵ on Cu termination of Cu₂O (110) with the coadsorption of H₂O. The numbers in the parentheses are the relative total energies in eV.



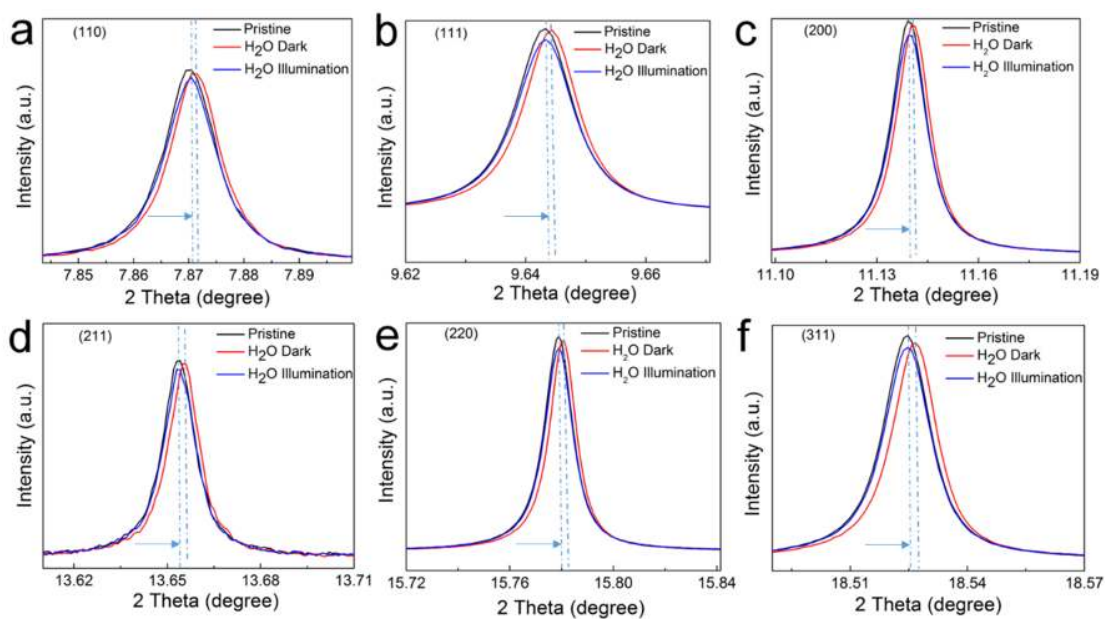
Supplementary Figure 15 | Structural stability of Cu_2O photocatalyst during the first 8 h of the photocatalytic reaction on Cu_2O as measured by *operando* HEXRD at APS beamline 11-ID-C.



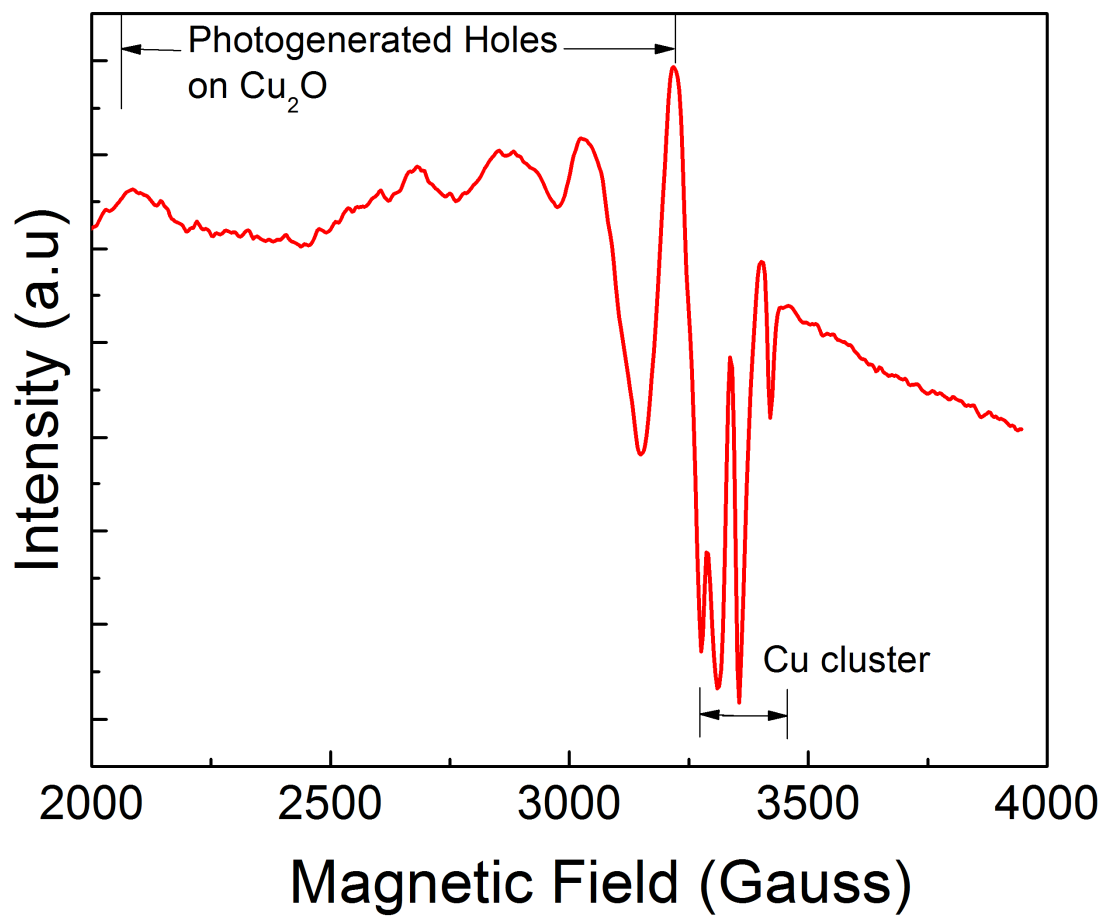
Supplementary Figure 16 | The stability of Cu₂O catalyst by *ex situ* x-ray photoemission spectroscopy measurement. Cu₂O Cu 2p peak has significant split spin-orbit components ($\Delta=19.75$ eV, intensity ratio=0.508). It is possible to distinguish Cu oxidation states using satellite features of Cu 2p. CuO has observed collection of strong satellite features around 943 eV while Cu₂O has weak satellite features around 945 eV. We do not see strong satellite peak in both pristine and reacted Cu₂O catalyst around 943 eV. This confirms the stability of Cu₂O catalyst.



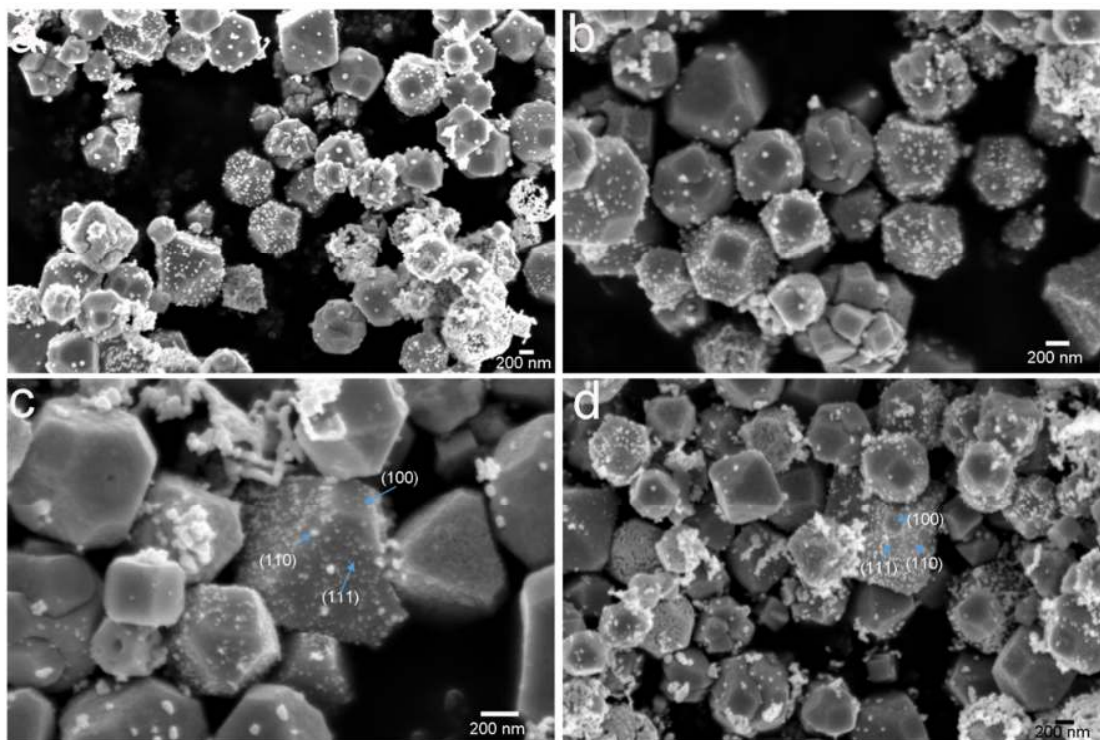
Supplementary Figure 17 | *Ex-situ* HRXRD measurements of the cubic/octahedral Cu₂O sample with a CO₂/H₂O gas mixture. All reflections showed lattice expansion (decrease of theta) upon CO₂/H₂O adsorption in the dark then and contraction upon illumination. The fraction of Cu atoms near the particle surfaces exposed to gas coadsorption, relative to the pristine Cu atoms within the particle bulk, is about 2% assuming a penetration depth of ~1 nm into a 300 nm particle with imperfect crystal surfaces. The data in figures. S10-S11 were measured at APS beamline 11-BM-B.



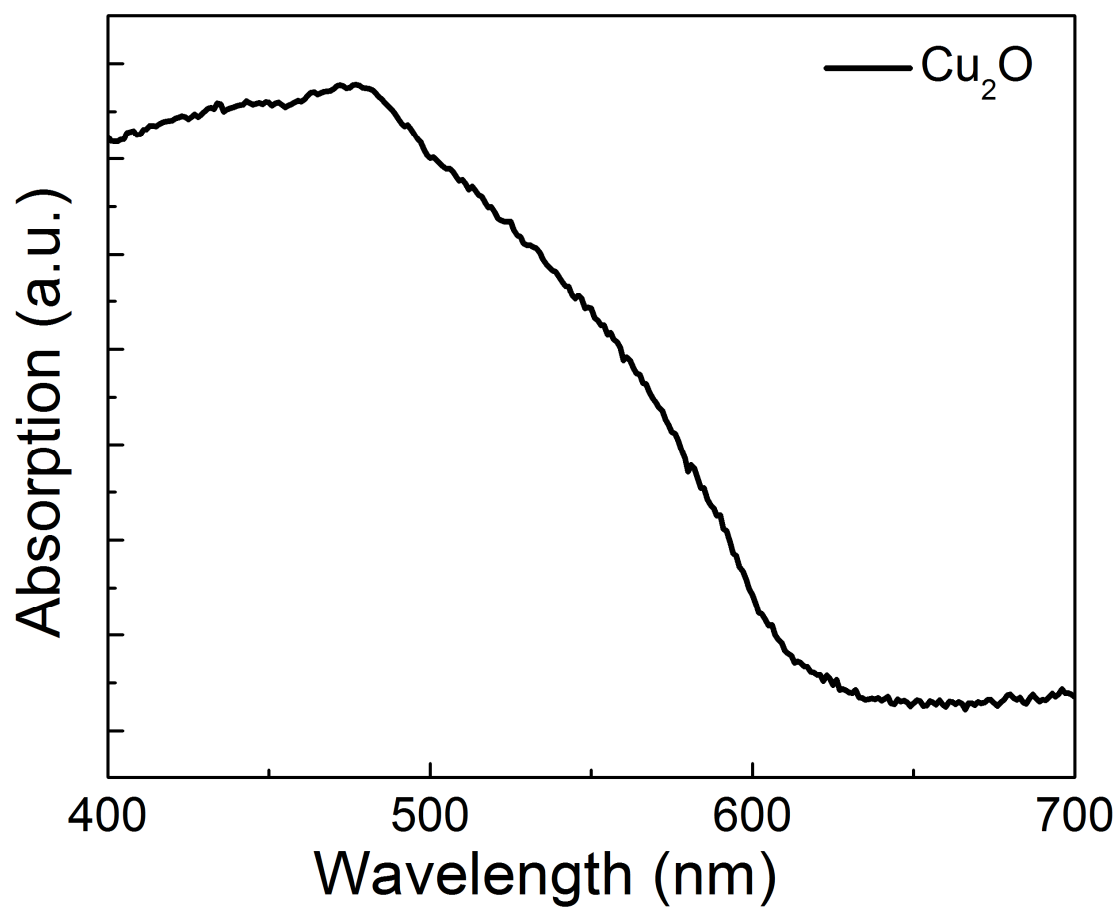
Supplementary Figure 18 | *Ex-situ* HRXRD measurements of the cubic/octahedral Cu_2O sample with H_2O gas alone. Unlike that with $\text{CO}_2/\text{H}_2\text{O}$ gas mixture, adsorption of H_2O alone by the Cu_2O crystals led to a decrease in the crystal lattice constant corresponding to lattice contraction (increase of θ).



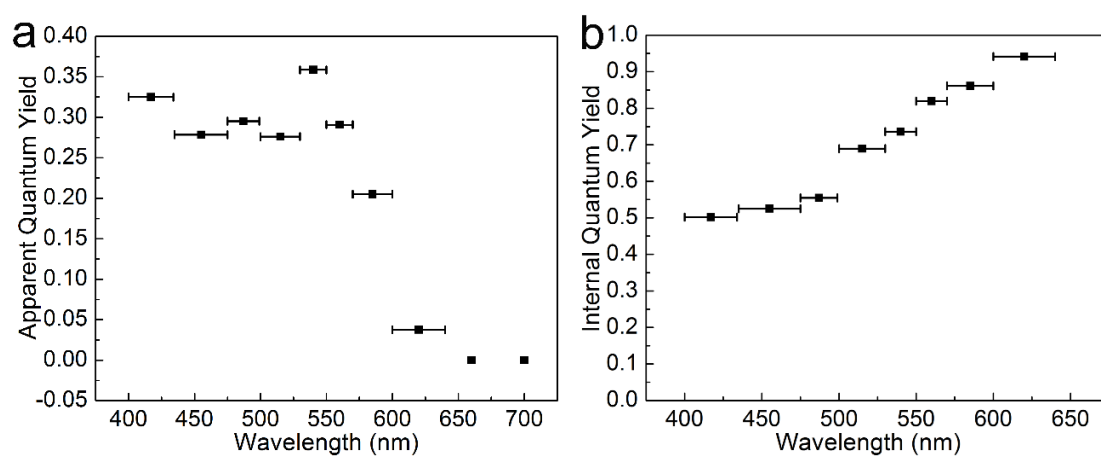
Supplementary Figure 19 | Additional EPR spectrum. Illumination of a pristine Cu₂O crystal produced photogenerated holes and Cu clusters, indicating the synthesized Cu₂O crystal is a p-type semiconductor, as measured by EPR spectroscopy.



Supplementary Figure 20 | Photoreduction of H_{Au}Cl₄ salt to form Au nanoparticles on Cu₂O particles. This shows no preferable facets for Au nanoparticles formation from photoreduction. This indicates no charge separation efficiency difference between facets of Cu₂O.

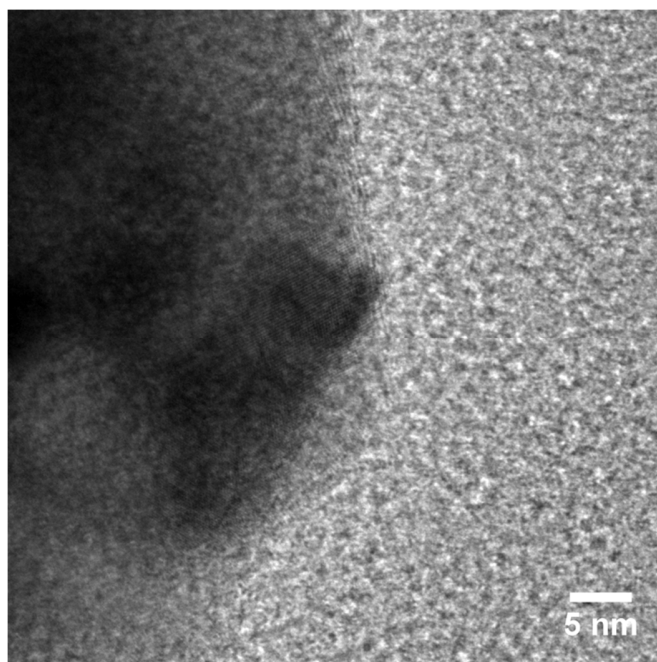


Supplementary Figure 21 | UV-vis-absorption spectrum of cubic/octahedral Cu_2O .



Supplementary Figure 22 | Wavelength dependence of apparent quantum yield (a) and internal quantum yield (b) during photocatalytic reduction of CO₂ using Cu₂O particles. The horizontal bar indicates the wavelength ranges as shown in Supplementary Table 1.

Table 1, Solar to fuel efficiency calculation					
i	Range (nm)	λ_i (nm)	$AQY(\lambda_i)$ (%)	P_i (%)	STF_i (%)
1	400-435	417	32.4	12	1.5
2	435-475	455	27.8	17	1.9
3	475-500	487	29.5	12	1.5
4	500-530	515	27.6	14	1.8
5	530-550	540	35.8	7	1.2
6	550-570	560	29.0	7	1.0
7	570-600	585	20.4	9	1.0
8	600-640	620	3.7	10	0.2
9	640-680	660	0	8	0
10	680-700	690	0	4	0
Total STF (%)					10.1



Supplementary Figure 23 | HRTEM image. A typical HRTEM image of pristine cleaned corners of a Cu₂O particle.