

Supporting Information for
Correlation Between Surface Redox Chemistry and the Optical Properties of Colloidal
Cu₂O Nanoparticles

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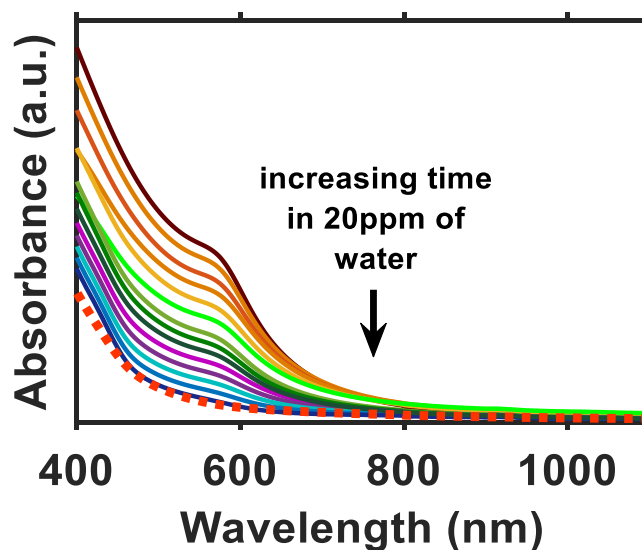


Figure S1. Cu₂O-pristine dried overnight with continuous nitrogen purging, when re-dispersed in wet hexane, containing 20 ppm of water determined by Karl Fischer titration, recovers the as-synthesized orange suspension (dotted orange line) in which the peak at 570nm has disappeared from the absorption spectrum.

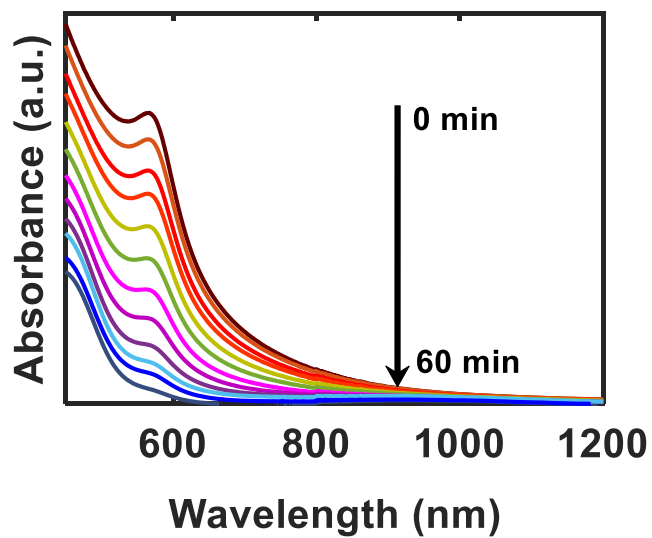


Figure S2. Addition of 5mM ferrocenium triflate to a THF suspension of **Cu₂O-pristine** causes the peak at 570nm to disappear.

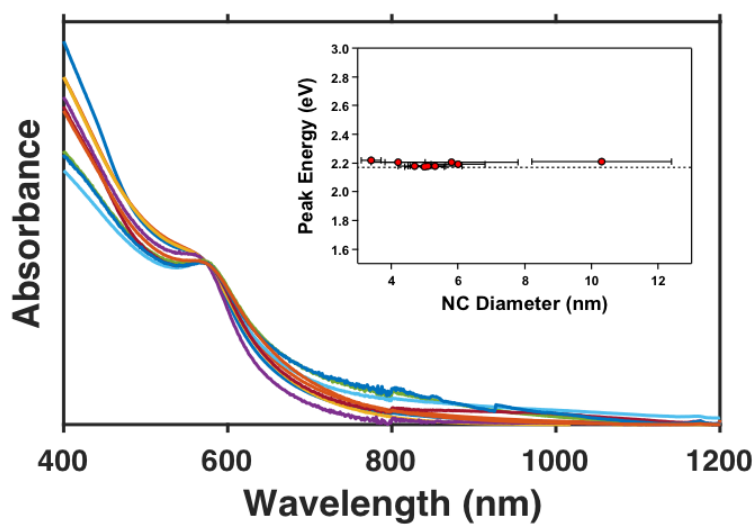


Figure S3. Normalized absorption spectra of various samples of colloidal Cu₂O nanoparticles with diameters ranging from 3.4-10.3 nm. Inset: Plot of the peak energy versus nanocrystal diameter.

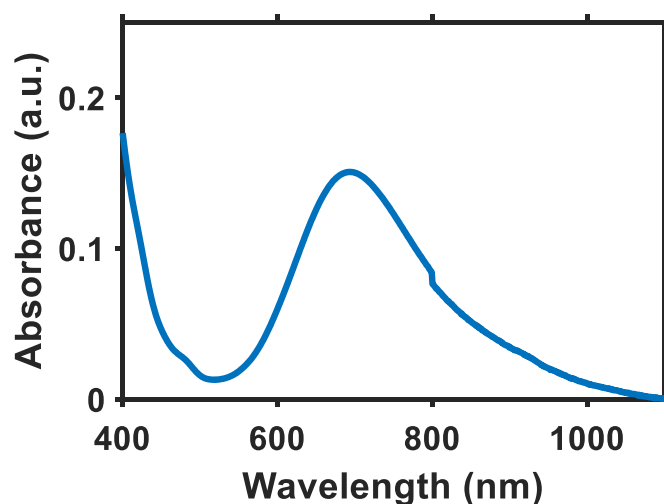


Figure S4. Absorption spectra of supernatant formed after washing **Cu-ox** nanoparticles with ethanol, showing a broad absorption peak at ~690 nm associated with the *d-d* transitions within solvated Cu^{2+} ions. We hypothesize that oxidation of **Cu-pristine** nanoparticles in air results in Cu ion leaching thereby reducing the size of the **Cu-ox** nanoparticles. Atomic absorption measurements of this supernatant revealed the presence of 0.03mM of Cu.

Atomic absorption measurements

A solution of **Cu-pristine** nanoparticles (reddish brown) was taken out of the glovebox and allowed to oxidize in air for 60 minutes to form **Cu-ox** (dark green). The **Cu-ox** solution was washed with ethanol to obtain a blue **supernatant** and green precipitate. The blue **supernatant** was dried with a flow of nitrogen to remove the ethanol and the resulting solid was digested in a 0.2% solution of nitric acid solution in Nanopure water. Known standards with copper concentrations ranging from 0 to 4 ppm were prepared by diluting a standard copper solution (100 ppm from High-Purity Standards) with a 0.2% nitric acid solution in Nanopure water. Atomic absorption (AA) measurements were done on a Shimadzu atomic absorption spectrophotometer (AA-7000 series) using a hollow cathode Cu lamp (L2433-29NB). First, the standards were used to obtain the calibration curve shown in figure S11 (red dots) and fitted to a linear curve (black line). Subsequently, the supernatant sample was measured and it showed the presence of 0.03mM of copper.

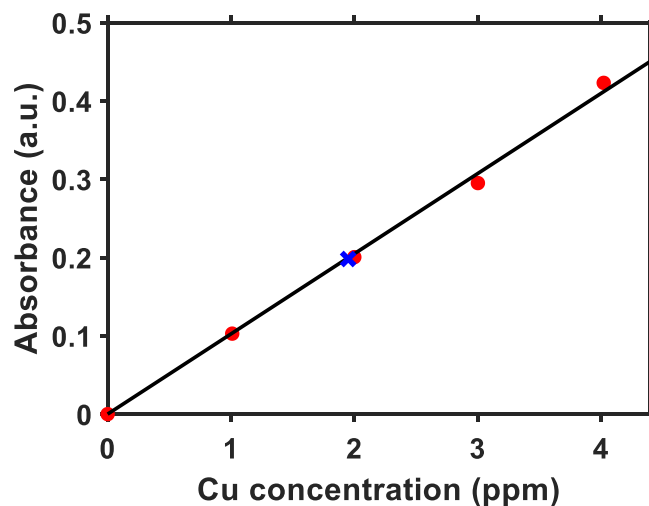


Figure S5. Calibration curve showing the absorbance dependence on the concentration of standard solutions of copper (red dots), obtained from atomic absorption spectroscopy. The blue cross shows the absorption and the concentration of Cu in the **supernatant** sample, obtained by washing **Cu-Ox** with ethanol.

Table S1. XPS peak positions for Cu₂O and Cu nanocrystals.

XPS peaks/Samples	Cu ₂ O (eV)	Cu ₂ O-oxidized (eV)	Cu (eV)	Cu-oxidized (eV)
Cu 2p _{3/2}	933.1	933.6, 936.1	932.9	933.1, 935
Cu 2p _{1/2}	952.9	953.2, 956.1	952.7	952.9, 955.4
Satellite peaks	-	944.1, 963.3	-	-
Cu LMM peaks	917.8	915.7	918.1	915.7

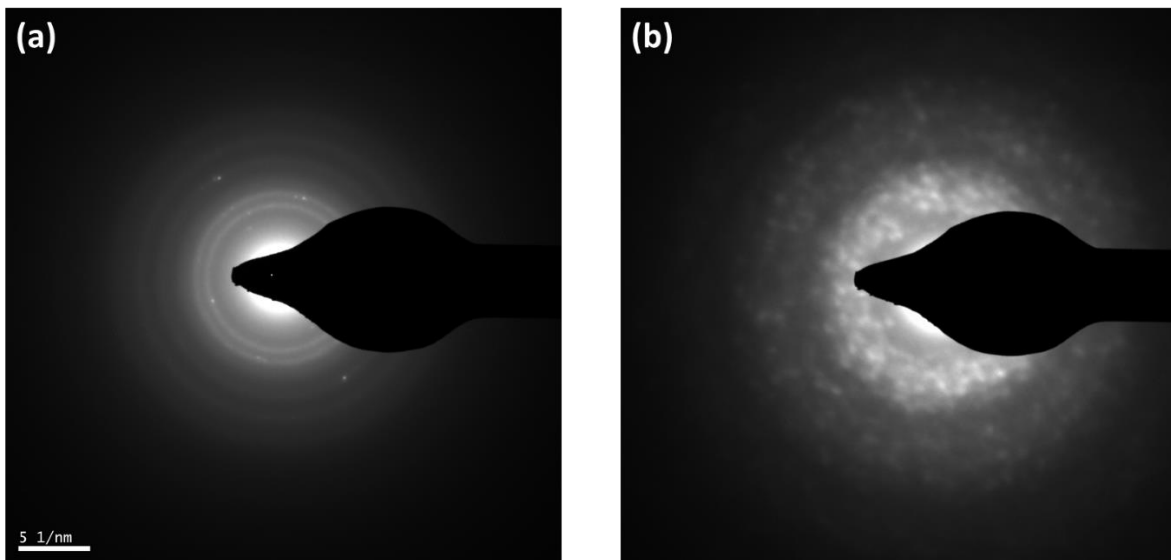


Figure S6. Selected area electron diffraction patterns of (A) **Cu₂O-pristine** nanoparticles and (B) **Cu-pristine** nanoparticles.

Table S2. *d*-spacing values corresponding to the electron diffraction pattern shown in Figure S6.

Sample	<i>d</i> spacing (Å)	2Θ	2Θ (XRD)	Crystal Structure	(h,k,l)
(A)	2.187 ± 0.01	41.24 ± 0.003	42.33	Cu ₂ O	(2,0,0)
	1.72 ± 0.07	53.21 ± 0.04	52.49	Cu ₂ O	(2,1,1)
	1.138 ± 0.1	85.19 ± 0.16	84.98	Cu ₂ O	(3,2,1)
	2.084 ± 0.08	43.38 ± 0.03	43.32	Cu	(1,1,1)
(B)	2.085 ± 0.05	43.36 ± 0.02	43.32	Cu	(1,1,1)
	1.82 ± 0.16	50.07 ± 0.08	50.45	Cu	(2,0,0)
	1.262 ± 0.08	75.23 ± 0.003	74.13	Cu	(2,2,0)
	1.084 ± 0.12	90.56 ± 0.22	89.94	Cu	(3,1,1)

Uncertainties in the *d* spacing were propagated into the 2Θ values as follows:

$$n\lambda = 2d \sin\theta$$

$$0 = 2\Delta d \sin\theta + 2d \cos\theta \Delta\theta$$

$$\Delta 2\theta = \frac{-2\Delta d \sin\theta}{d \cos\theta}$$

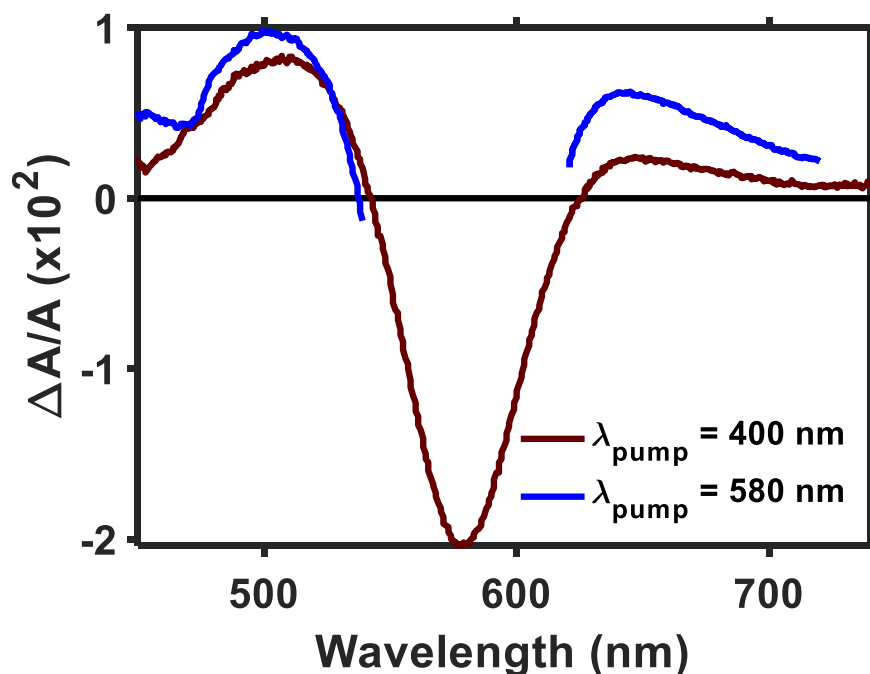


Figure S7. Transient absorption ($\Delta A/A$) spectra of **Cu₂O-pristine** nanoparticle samples at a pump-probe delay of 500 fs. The brown trace represents a sample excited with $\lambda_{\text{pump}} = 400$ nm; the blue trace a sample excited with $\lambda_{\text{pump}} = 580$ nm. Note that the region between 540 and 620 nm is removed from the blue trace due to excess of pump signal. The main features in both traces are positive signals that reach maxima at approximately 500 and 640 nm. While the full derivative shape cannot be seen in the blue trace due to noise from the pump signal, the two traces suggests the same derivative shape indicative of plasmonic behavior regardless of the initial excitation wavelength.

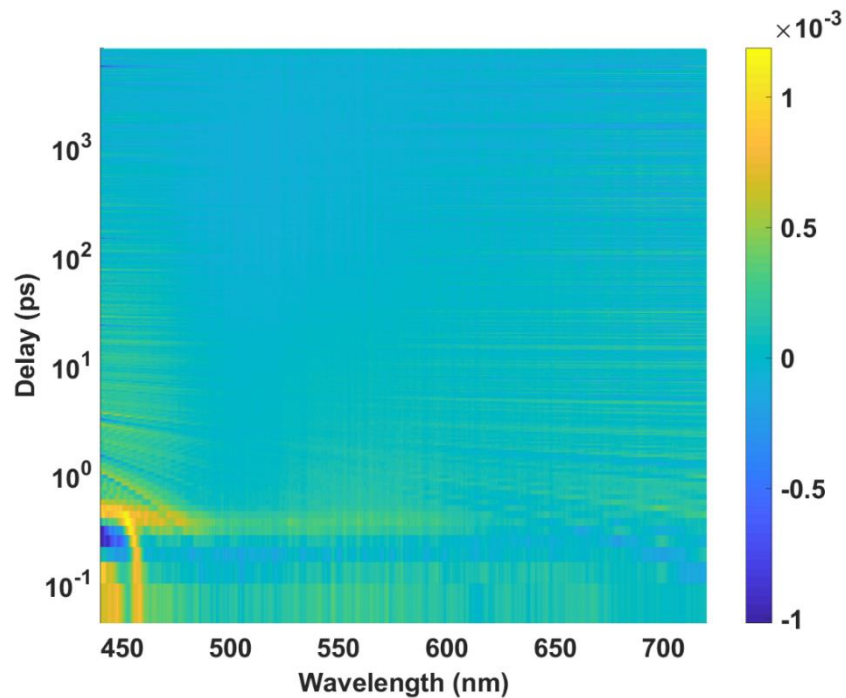


Figure S8. 3D transient absorption (ΔA) spectra of $\text{Cu}_2\text{O-Ox}$ nanoparticles with $\lambda_{\text{pump}} = 400$ nm. The only signal present, at a delay of 0 ps, is attributed to time zero oscillations within the cuvette and is also present in solvent scans. The spectrum was obtained with a gaussian beam radius of $200\mu\text{m}$ and a fluence of 0.177 mJ/cm^2 .

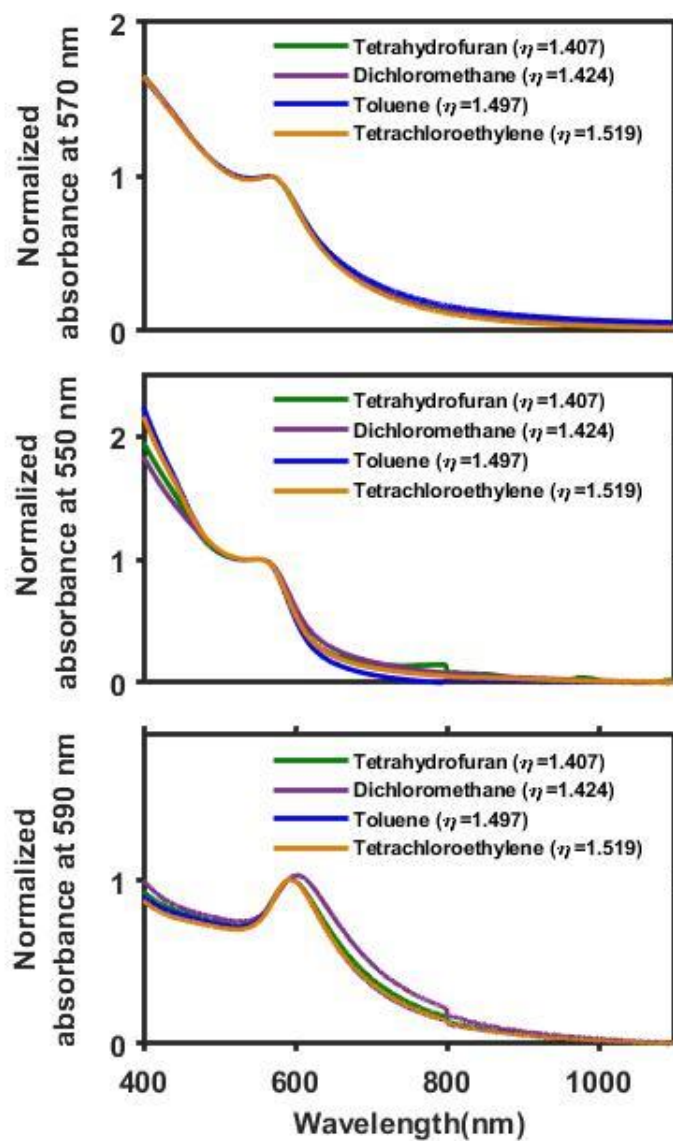


Figure S9. Normalized absorption spectra of **Cu_2O -pristine** (top), **Cu -pristine** (middle) and **Cu-ox** (bottom) in solvents with different refractive indices (η) showing no significant change in the LSPR peak position. The solvents used were tetrahydrofuran ($\eta = 1.407$), dichloromethane ($\eta = 1.424$), toluene ($\eta = 1.497$), and tetrachloroethylene ($\eta = 1.519$).

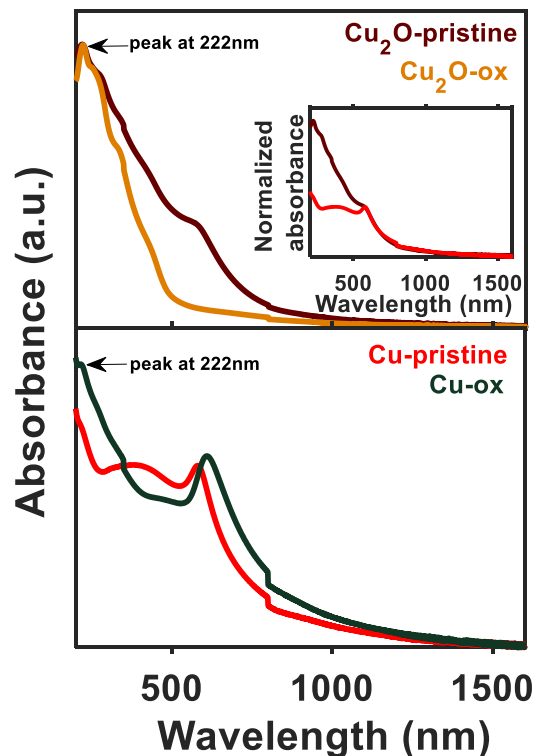


Figure S10. Absorption spectra of **Cu₂O-pristine** (brown), **Cu₂O-ox** (gold, top) and **Cu-pristine** (red) and **Cu-ox** (green, bottom) films drop cast onto thin quartz substrate. An absorption peak observed at ~222 nm in **Cu₂O-pristine** and **Cu₂O-ox** samples was also observed in **Cu-ox**, which is consistent with the presence of both Cu and Cu₂O in **Cu-ox**. Normalized absorption spectra of **Cu₂O-pristine** (brown) and **Cu-pristine** (red) demonstrate the difference in their respective absorption features (inset).

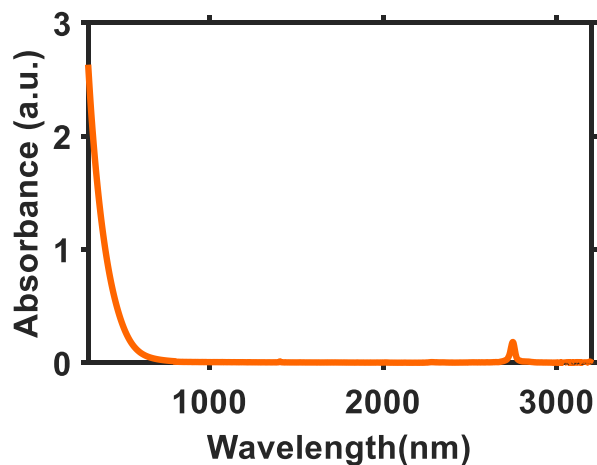


Figure S11. Absorption spectra of **Cu₂O-wet** in tetrachloroethylene showing that plasmonic features are not observed in the near-infrared region

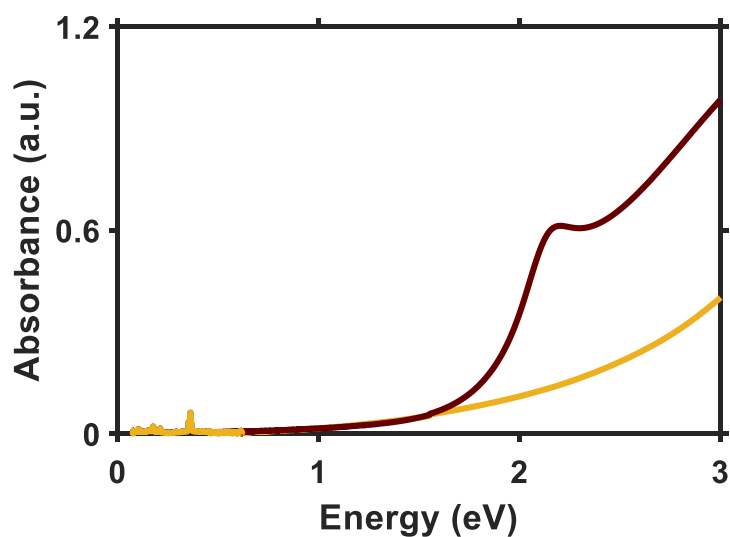


Figure S12. Air oxidation of **Cu₂O-pristine** in tetrachloroethylene showing that plasmonic features are not observed in the near-infrared or infrared absorption spectra of our oxidized Cu₂O nanocrystals.