Copper Oxide Nanocrystals, Yin et al., Supporting Information.

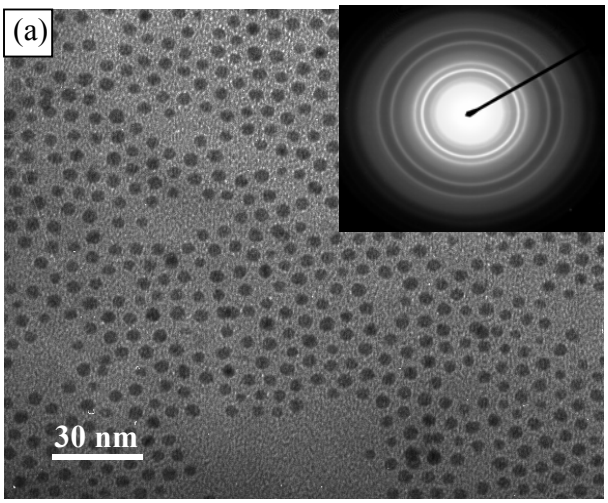

Figure S1. Transmission electron micrograph of 5.1±0.5 nm diameter Cu nanocrystal (a) and corresponding insert: Selected area electron diffraction pattern.

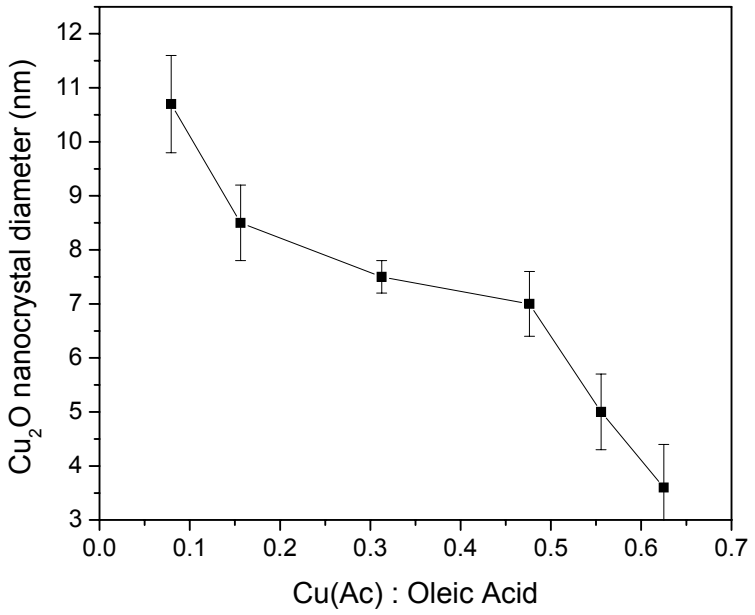

Figure S2. Plot of particle size vs the relative amount of oleic acid to copper (I) acetate, showing the diameter of the final product increases with a increased OA:$Cu(Ac)_2$ ratio.

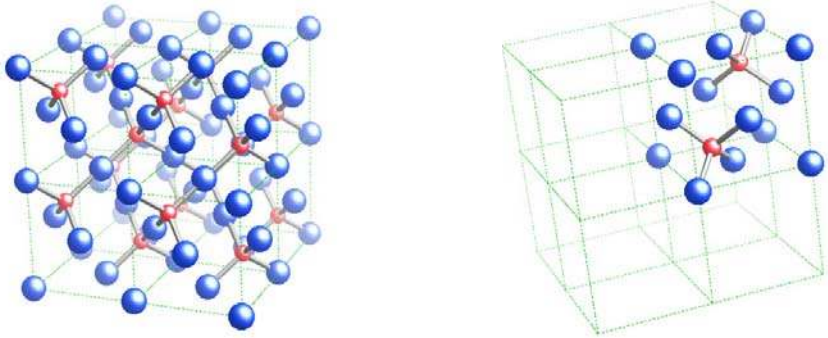

Figure S3. Crystal structure of cuprite Cu_2O.

Cu_2O/CuO Core-Shell Structure

There is always an amorphous CuO layer on the Cu_2O nanocrystal. The core (Cu_2O)-shell (CuO) structure can be characterized by XPS. J. Nanda and D. D. Sarma[1, 2] have done similar work on ZnS and CdS nanocrystallites. Here, we study not only the core-shell structure but also the reduction kinetics of the CuO layer which are induced by the X-rays.

The calculation was based on the fact that the intensity of the photoelectron from XPS decays exponentially as the sampling depth. In other words, the shell (CuO) is over counted than the core (Cu_2O). Here, we use polar coordinates other than Cartesian to characterize the photoelectron intensity.[1, 2]

$$I = I_0 \int_{R'}^{R''} \int_0^{\pi} \int_0^{2\pi} \exp\left(\frac{-f(r)}{\lambda}\right) r^2 dr \sin\theta \; d\varphi$$

$$where \quad f(r) = (R^2 - r^2 \sin^2\theta)^{1/2} - r\cos\theta$$

$$\frac{I_{Cu_2O}}{I_{CuO}} = \frac{I_{Cu_2O^o} \int_0^{R_1} \int_0^{\pi} \exp\left(\frac{r\cos\theta - \sqrt{R^2 - r^2\sin^2\theta}}{\lambda_1}\right) r^2 \sin\theta \; d\theta \; dr}{I_{CuO^o} \int_{R_1}^{R_2} \int_0^{\pi} \exp\left(\frac{r\cos\theta - \sqrt{R^2 - r^2\sin^2\theta}}{\lambda_2}\right) r^2 \sin\theta \; d\theta \; dr}$$

Assume that the nanocrystals are monodisperse with the particle size of 6 nm ($2*R_2$) (i.e. the particle size remains the same for the whole reduction process) and the capping ligands (oleic acid) are 1.2 nm thick (R= 4.2 nm). We use different values of R_1 to fit the ratio of I_{Cu2O}/I_{CuO} which we acquired from XPS. Then, the R_1 is numerically solved.

Result:

a. **The initial CuO%= 55.22%.**
b. **R_1= 2.538 nm, R_2= 3 nm.**
c. **The CuO layer is 4.62 (~ 5) Å thick.**

Reference:

1. J. Nanda and D. D. Sarma, *J. Appl. Phys.* **90**, 2504 (2001).
2. J. Nanda, B. A. Kuruvilla, and D. D. Sarma, *Phys. Rev. B* **59**, 7473 (1999).