Supplementary Information

Facile fabrication of faceted copper nanocrystals with high catalytic activity for \( p \)-nitrophenol reduction

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Calculation of turnover frequency (TOF) for each of the catalysts:

TOF was defined as the number of molecules reacted at each available catalytic site per time.\(^1\) Although only a small portion of surface Cu atoms can actually serve as catalytic active sites—many will be bonded to capping ligands and unavailable for catalysis, in practice, it is common to take the total number of surface atoms as the number of active catalytic sites when the value is not known. Hence, the surface-specific
activities (TOF) were calculated using the atomic rate and the dispersion.²

\[
\text{TOF} = \frac{\text{Atomic rate}}{\text{Dispersion}} \quad (1)
\]

Dispersion (D) is defined as the fraction of total atoms or molecules of the active phase available at the surface for catalysis. When the nanoparticles are spheres or cubes, dispersion can be calculated using the following formula¹

\[
\text{Dispersion} = \frac{6\rho_s}{d \rho_d} \quad (2)
\]

where \(\rho_s\) is the surface concentration of metal atoms, \(\rho_d\) is the bulk atomic density, \(d\) is the diameter of spheres or side-length of cubes. For face-centered cubic metals, \(\rho_d = 4/a_0^3\) (\(a_0\) is the lattice constant of copper), the \(\rho_s\) of low-index planes (111), (100) and (110) are equal to \(2.3a_0^{-2}\), \(2.0a_0^{-2}\), \(1.4a_0^{-2}\), respectively. Herein, the polyhedrons approximately regarded as spheres to facilitate the calculation. TOF was calculated for each of the catalysts carried out at 20 °C. Using eq1, 2 and the average nanocrystal diameter measured using TEM, TOF=0.0368 \(s^{-1}\) for ~9.5 nm Cu cubes, while 0.0057 \(s^{-1}\) and 0.0053 \(s^{-1}\) for ~18 nm and ~21.5 nm Cu polyhedrons, respectively. The increase in TOF of the Cu cubes indicates that the cubes surfaces are more catalytically active with catalytic reaction than that of polyhedrons. Therefore, the enhancement of catalytic activities of Cu cubes are most likely as a result of exposed \{100\} facets.

