Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A

Supplementary Information

Facile fabrication of faceted copper nanocrystals with high catalytic activity for *p*-nitrophenol reduction

Pinhua Zhang,[a] Yongming Sui,[a] Guanjun Xiao,[a] Yingnan Wang,[a] Chunzhong Wang,[b] Bingbing Liu,[a] Guangtian Zou[a] and Bo Zou*[a]

a State Key Laboratory of Superhard Materials, Jilin University, Changchun 130012, China

b Key Laboratory of Physics and Technology for Advanced Batteries (Ministry of Education), College of Physics, Jilin University, Changchun, 130012, China

* Corresponding authors. E-mails: zoubo@jlu.edu.cn

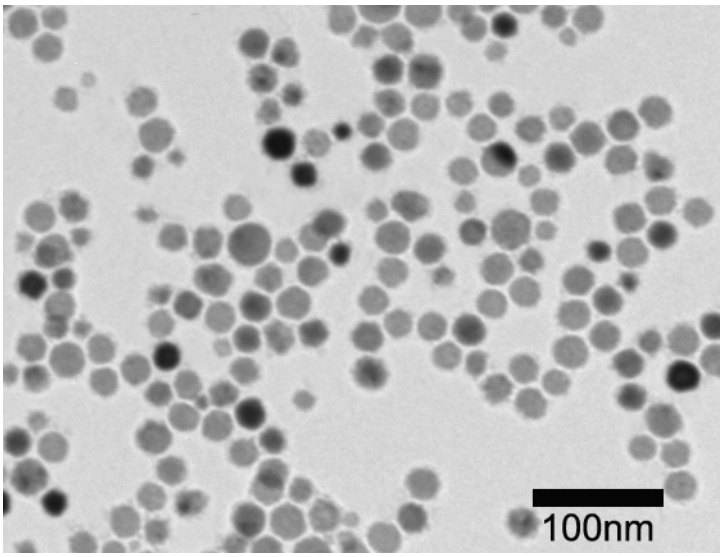

Fig. S1 TEM image of the Cu nanocrystals after washing four times.

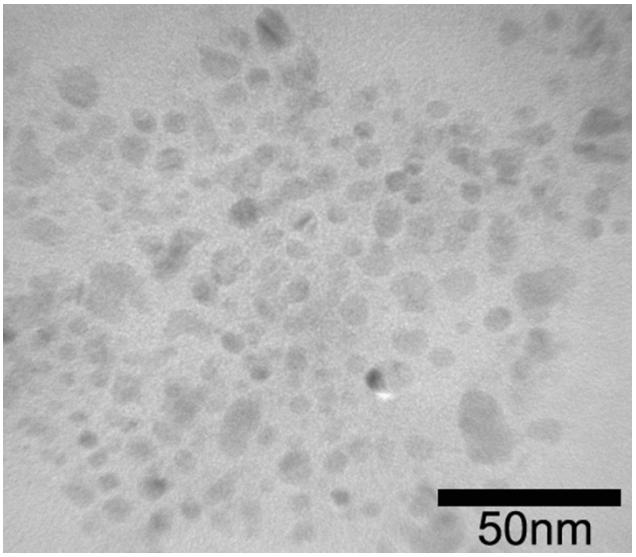

Fig. S2 TEM image of the Cu nanocrystals after re-cycling test.

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]

$$\text{TOF} = \text{Atomic rate} / \text{Dispersion} \quad (1)$$

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 formula[1]

$$\text{Dispersion} = 6\rho_s / d\rho_d \quad (2)$$

where ρ_s is the surface concentration of metal atoms, ρ_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 ρ_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 ^{o}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.

1. C. A. Stowell and B. A. Korgel, *Nano Lett.*, 2005, **5**, 1203.
2. C.H. Bartholomew and R.J. Farrauto, *Fundamentals of Industrial Catalytic Processes*, 2nd ed.; Wiley: Hoboken, NJ, 2006.
3. C. Dumonteil, M. Lacroix, C. Geantet, H. Jobic and M. Breysse, *J. Catal.*, 1999, **187**, 464.