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Supplementary Information

Crystal-to-Crystal Conversion of Cu_2O Nanoparticles to Cu Crystals and the Applications on Printed Electronics

Woo-ram Lee,[a] Young S. Lim,[b] Sowon Kim,[a] Jaehoon Jung,[a]† Young-Kyu Han,[c] Sungho Yoon,[d] Longhai Piao[e] and Sang-Ho Kim[e]*

[a] Corporate R&D, LG Chem., Ltd. Research Park, 104-1 Moonji-dong, Yuseong-gu, Daejeon 305-380 Republic of Korea, [b] Green Ceramics Division, KICET, 233-5 Gasan-dong, Geumcheon-gu, Seoul 153-801 Korea, [c] Division of Materials Science, Korea Basic Science Institute, Daejeon 305-333, Republic of Korea, [d] Department of Bio & Nano Chemistry, Kookmin University, 861-1, Jeongneung-dong, Seongbuk-gu, Seoul 136-702 Republic of Korea, [e] Department of Chemistry, Kongju National University, 182 Shinkwan-dong, Kongju-Si 314-701 Republic of Korea

†Present address: Department of Advanced Materials Science, The University of Tokyo, Chiba 277-8561, Japan and RIKEN Advanced Science Institute, Wako, Saitama 351-0198, Japan

* Corresponding authors. E-mail: sangho1130@kongju.ac.kr

1. XPS analysis of heat-treated Cu patterns

The heat-treated Cu patterns were etched from the surface with etching rate ~1Å /sec and the atomic concentration was measured by XPS. The zero atomic concentration of oxygen after 2000 sec. indicates that no oxidation occurred in the core of Cu patterns. The carbon is suspected to be from the imperfect removal of surfactant molecules.

2. Computational details, calculated results and discussion

Kohn–Sham density-functional theory (DFT) calculations were performed to examine the hydrogen transfer mechanism during the crystal-to-crystal conversion process from Cu_2O nanoparticle to Cu crystal. The Perdew–Burke–Ernzerhof (PBE) functional[1] and the double numerical plus polarization (DNP) basis sets were employed. The energy-consistent relativistic effective core potential was used for Cu atoms.[2] The structures of two model clusters, $Cu_{16}O_{11}H_6$ (**M1**) and $Cu_{22}O_{11}$ (**M2**), were constructed from the non-polar $Cu_2O(111)$ surface (see Figure S1).[3] To keep the neutral charge of the model cluster, the six oxygen atoms at bottom of **M1** cluster were terminated by hydrogen atoms. The Cu and O atoms at the surface layer (and the H atoms in **M1**) were relaxed during the geometric optimization, whereas other atomic positions were fixed at their experimental bulk values.[4] Polyacrylamide (PAM) was modeled by isobutyramide ($(CH_3)_2CHCONH_2$). Figure S2 clearly shows that the hydrogen transfer reaction from PAM to Cu_2O nanoparticle is thermodynamically favourable for both the two model clusters, **M1** and **M2**. The adsorption energies (ΔE) are defined as E(isobutyramide–**M*n***) – E(**M*n***) – E(isobutyramide) (***n*** = 1 and 2). All the calculations were carried out by using the DMol3 software package implemented in Materials Studio from Accelrys Inc.[5,6]

3. Control experiment with other surfactants.

To characterize the function of PAM, we have done some control experiment with some other surfactants including PVP, PVP, PEG, CTAB, acryl amide, acetamide, N,N-dimethyl acetamide and anthranilamide. First, Cu_2O NPAs were synthesized according to the method described in experimental section, with the exception of the kind of surfactant used. Then the reduction of the Cu_2O NPAs was conducted similar to the samples with PAM. It is shown from Figure S3 that the conversion behaviours

of Cu oxide to Cu metal were much different from that of PAM. Figure S3 (a) and (c) show that the reduction reaction was very slow without additional surfactant and the complete conversion of Cu_2O to Cu was difficult. In the case of PVP, the conversion reaction seems to conduct inside the Cu_2O NPAs and no extraction of Cu^+ ions form the aggregates is observed. (Figure S3 (b))

1. J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1996, **77**, 3865.
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3. T. Bredow and G. Pacchioni, *Surf. Sci.*, 1997, **373**, 21.
4. A. Werner and H. D. Hochheimer, *Phys. Rev. B*, 1982, **25**, 5929.
5. B. Delley, *J. Chem. Phys.*, 1990, **92**, 508.
6. B. Delley, *J. Chem. Phys.*, 2000, **113**, 7756.

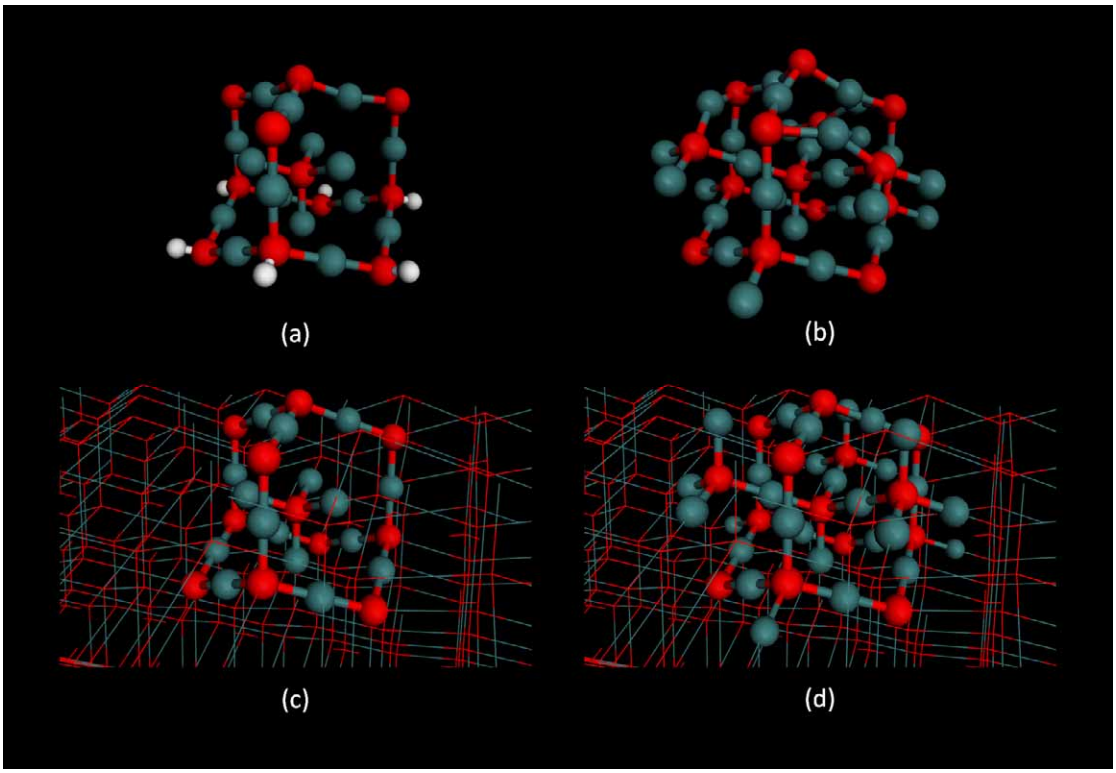

Figure S1. Optimized structures of model clusters (a) **M1** ($Cu_{16}O_{11}H_6$) and (b) **M2** ($Cu_{22}O_{11}$). The initial structure of (c) **M1** and (d) **M2** model clusters are constructed from the non-polar $Cu_2O(111)$ surface.

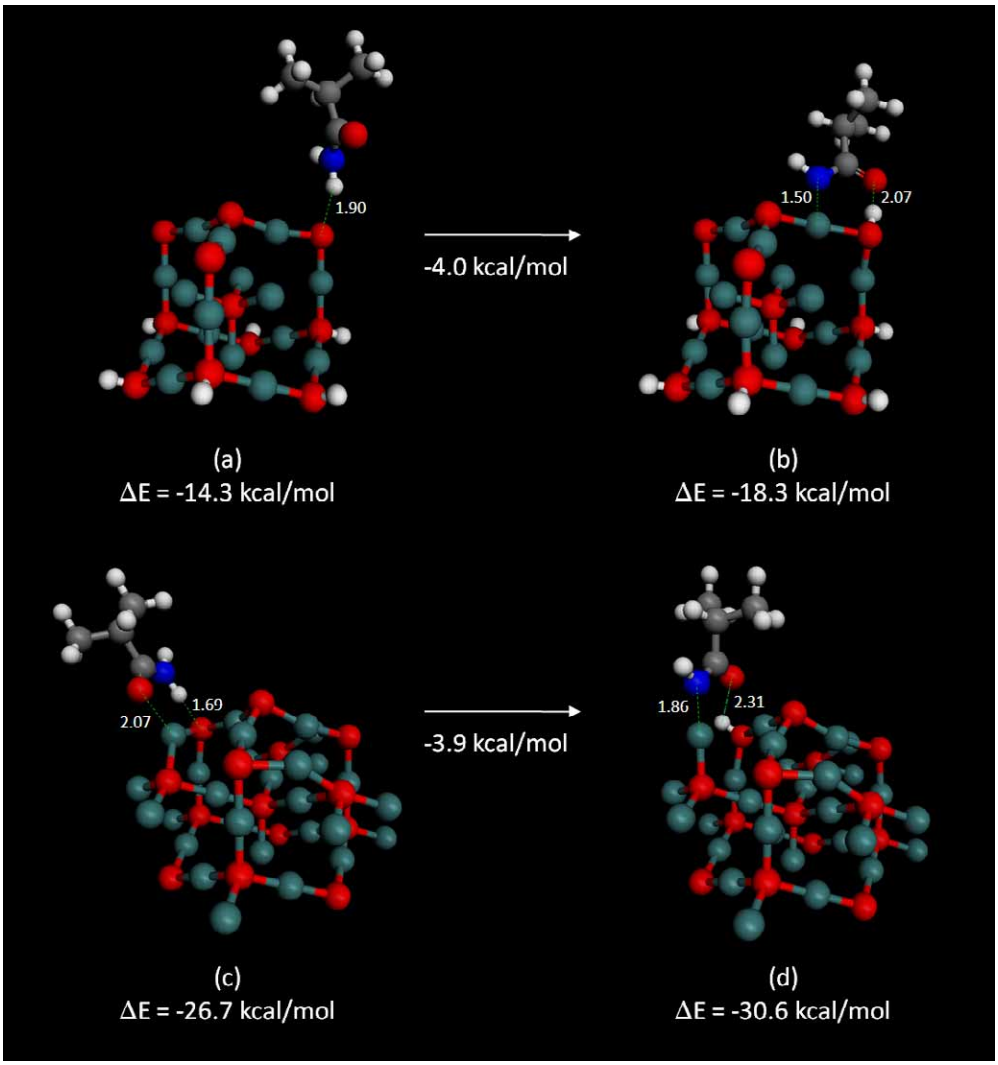

Figure S2. Optimized structures, adsorption energies (ΔE), and hydrogen transfer reaction energies of isobutyramide–Cu_2O model cluster systems: (a-b) **M1** and (c-d) **M2**. Bond lengths are given in Å.

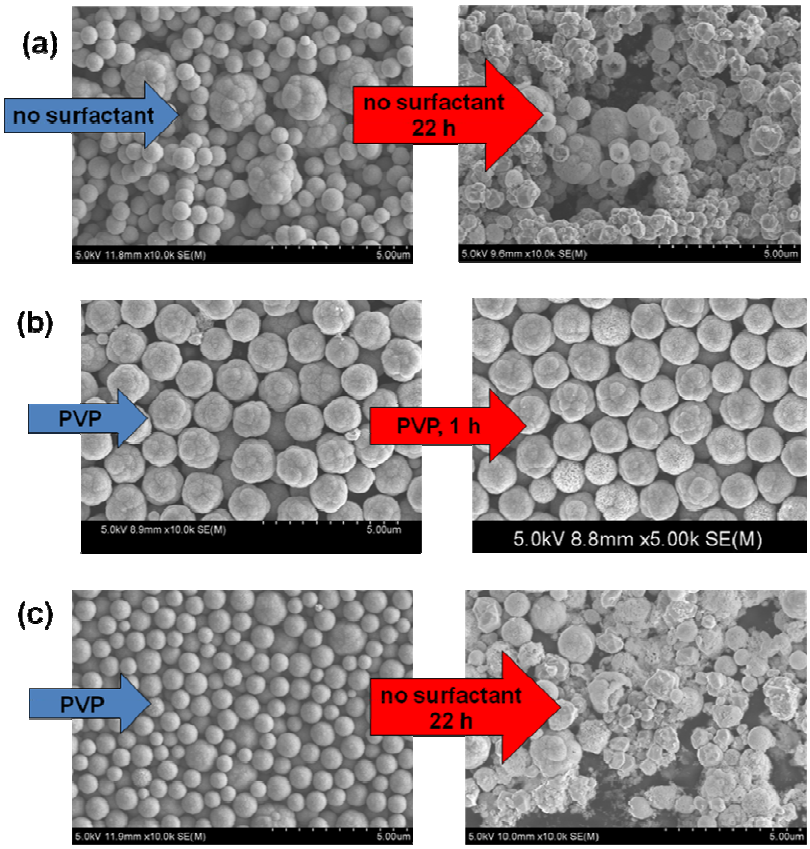

Figure S3. The conversion process of Cu2O nanoparticle aggregates to Cu crystals. The Cu_2O nanoparticle aggregates were prepared without surfactant (a) or using PVP as surfactant (b, c). The reduction reaction was conducted without additional surfactant (a, c) or with PVP as surfactant.