Supporting Information

The role of surface oxides and stabilising carboxylic acids of copper nanoparticles during low-temperature sintering

Rintaro Tokura,¹ Hiroki Tsukamoto,¹ Tomoharu Tokunaga,² Mai Thanh Nguyen,¹ and Tetsu Yonezawa^{1,*}

¹Division of Materials Science and Engineering, Faculty of Engineering, Hokkaido University, Kita 13 Nishi 8, Kita-ku, Sapporo, 060-8628, Japan ²Department of Materials Science and Engineering, Faculty of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya, Aichi 464-8603, Japan.



Figure S1. Digital images of a water droplet on 1-hexanoic acid-stabilised copper nanoparticles in a powder form. The glass substrate size is 35 mm × 50 mm.



Figure S2. X-ray diffraction patterns of (1) Cu nanoparticles after preparation and (2) CuO powders as the precursor of Cu nanoparticles before preparation.



Figure S3. RGB values of the digital images of the copper layers sintered at various temperatures. Open circle: sintered under 3%H₂-N₂ gas flow. Closed circle: sintered under nitrogen gas flow. Red, green and blue correspond to the each colour.



Figure S4. X-ray diffraction patterns of the copper layers sintered at various temperatures under 3%H₂-N₂ mixed gas flow. No peak corresponding to copper oxides can be observed. The peak height is normalised to the height of the Cu (111) peak ($2\theta = 43.3^{\circ}$).



Figure S5. X-ray diffraction patterns of the copper layers sintered at various temperatures under nitrogen gas flow. The peaks corresponding to Cu₂O can be observed in the copper layers sintered at temperatures higher than 150 °C. The peak height is normalised to the height of the Cu (111) peak ($2\theta = 43.3^{\circ}$).



Figure S6. Cross-sectional SEM images of the sintered copper nanoparticle layers after sintering at various temperatures. (a,c,e,g) Sintered under 3%H₂-N₂ mixed gas flow, (b,d,f,h) sintered under nitrogen gas flow. Sintering for 1 h at (a,b) 150 °C, (c,d) 180 °C, (e,f) 200 °C, and (g,h) 250 °C.



the structure model of $Cu_{64}O$ in [001]. The unit cell of $Cu_{64}O$ is outlined by thick lines and that of Cu by thin lines. (Reproduced with permission from Reference 33. Copyright 1985 International Union of Crystallography)



een the unit cells of Cu₆₄O (thick lines) and Cu (thin lines). \bigcirc : Oxygen atom. **a** = 9.75 Å, **b** = 10.58 Å, **c** = 16.2 Å. (Reproduced with permission from Reference 33. Copyright 1985 International Union of Crystallography)



Figure S9. (a) Projection of Cu (orange) and O (red and light red) atoms of the structure model of $Cu_{64}O$ in [001]. Copper atoms located at the corner of a rhomb with the length of 3.597 Å and the corner angles of 94.67° and 85.32°. (b) Cell structure of Cu" contains 4 Cu atoms, which can be separated from the $Cu_{64}O$ unit cell. This Cu" cell is illustrated in Figure 13 in the main text.