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DOI: 10.1557/adv.2019.91

Size-controlled Preparation of Alkylamine-stabilized Copper Fine Particles from Cupric Oxide (CuO) Micro-particles

Tetsu Yonezawa,* Jiajia Shi, Hiroki Tsukamoto, and Mai Thanh Nguyen

Division of Materials Science and Engineering, Faculty of Engineering, Hokkaido University, Kita 13 Nishi 8, Kita-ku, Sapporo, Hokkaido 060-8628

ABSTRACT

Size control of copper fine particles is highly important for their application for conductive materials. In this study, easy size tuning of the copper fine particles coated by n-hexylamine was achieved via controlling the ratio of n-hexylamine and the precursor CuO. The obtained particles were stable and had a hydrophobic surface. TG-DTA measurement revealed the formation of thin layer of n-hexylamine on the particles.

INTRODUCTION

Particle technology is rapidly developing and its products are extremely useful in various fields [1-5]. Powders, micron particles, fine particles, and nanoparticles are classified by their sizes, and all kinds of particles have a high potential for electronic, magnetic, as well as optical applications. Among these particle materials, much work on copper and silver fine particles and nanoparticles has been done in order to develop well-dispersed uniform and size controlled ones for the applications for materials for electronics [6-8]. According to the high electro and thermal conductivity of these two elements, their fine particles and nanoparticles are highly demanded for printed electronics [9,10]. Printed electronics is suitable for modern industry which requires small-volume production with large varieties and rapid remodeling. Copper can be the more promising candidate as a wiring and bonding material for printed electronics because of their lower price, lower possibility of ion migration than silver and of the similar conductivity as silver. However, comparing to silver particles, production of copper fine particles and nanoparticles are rather complicated because the obtained particles are ready to be oxidized. Recently, our group reported anti-oxidative copper

fine particles and nanoparticles using polymers as the anti-oxidative coating on the surface [6,7].

In order to apply copper fine particles as materials for printed electronics, it is highly demanded that the uniform copper fine particles can be obtained by an easy preparation process [6,7,11]. Moreover, precise tuning of the particle sizes is also required. Various preparation parameters should be controlled for this purpose. Reducing reagent, temperature, precursors, and stabilizing reagents, are important factors for tuning the particle size. In our previous study, the molecular weight of gelatin is effective to tune the sizes of the copper fine particles [7]. The quantity of the stabilizing molecules is another parameter to control the particle size. Changing the ratio of stabilizing molecules / metal atoms strongly affect the particle sizes, especially when metal coordinative ligand molecules are used as stabilizing molecules. For example, thiol/gold ratio strongly affected the size of gold nanoparticles [12,13].

In this study, we have tried to control the particle sizes of alkylamine-stabilized copper fine particles with the amine concentration. The higher concentration of *n*-hexylamine gave the smaller particle size.

EXPERIMENTAL

Materials and Preparation of Copper Fine Particles

The experiments were carried out in a fume hood. First, 16 g of CuO (particle size:1 - 2 μm) micro particles were introduced to a four-neck round bottom flask (1 dm^3). Into this flask, a designed amount of *n*-hexylamine (TCI, Japan) was introduced. After that, ethanol was added to keep the total volume of the dispersions constant as 200 cm^3. This black dispersion was stirred with a PTFE impeller under a rotation speed of 250 rpm and was heated up to 70 °C using a water bath. At 70 °C, 20 cm^3 of hydrazine monohydrate (Junsei, Japan) was quickly added to the dispersions. A violent reduction took place with instant increase of the dispersion temperature. After few minutes, the temperature went down again to 70 °C. For the complete reduction of CuO, the dispersion was kept at 70 °C for 1 h. After the reduction, the dispersion was cooled using tap water and nitrogen gas was purged to the flask. The copper dispersion was poured into centrifuge tube under nitrogen and the particles were collected by centrifuge (× 400 G, for *ca*. 10 s) and then the obtained particles were washed with 50 cm^3 of acetone twice and 50 cm^3 of methanol twice by using centrifugation of 1,000 G for 1 min. Then, the particles were dried under nitrogen atmosphere at room temperature overnight.

Characterization

Characterization of the obtained copper fine particles was carried out with FE-SEM, XRD, and TG-DTA. FE-SEM images were taken with a JEOL JEM-6701F (15 kV). X-ray diffraction patterns (XRD) were obtained using Rigaku Miniflex II (Cu-Kα, 0.1542 nm). Samples were mounted on an XRD glass sample plate. Their TG-DTA measurement was conducted using a Shimadzu DTA-60H under air. Samples were heated from 20 °C to 540 °C by 5 °C min^{-1}.

RESULTS AND DISCUSSIONS

In order to avoid oxidation of the obtained particles, the collection of the particles were carried out under nitrogen atmosphere. Stable copper fine particles were successfully and reproducibly prepared by chemical reduction of CuO micro-particles using hydrazine monohydrate in the presence of *n*-hexylamine (HA). The solvent used here was ethanol and no alkaline was added. Upon addition of hydrazine monohydrate, the color of the dispersion changed from black to brown which indicated the formation of metallic copper fine particles. After collection of the particles by centrifuge, they were dried under nitrogen and became stable. Our separation procedure was based on weak aggregation formation with a very short centrifugation time. A short time centrifuge and timesaving simple decantation were applied to collect copper fine particles. As discussed below, the obtained copper fine particle surface was hydrophobic. Therefore, in polar solvents, such as acetone and ethanol, they form weak inter-particle aggregated structures. Then, we can make the centrifugation gravity and time much smaller. These weakly aggregated particles can be re-dispersed readily, but the particles collected by long-time centrifuge with a high gravity can form very hard aggregated structures, which cannot be re-dispersed. Afterward, the particles were dried at room temperature under nitrogen flow. **Figure 1** shows FE-SEM images and the particle diameter distributions measured from the enlarged SEM images of the obtained copper fine particles prepared by hydrazine reduction of CuO. The median diameters (the midpoint of the particle size distribution, d_{50}) are 241 nm and 80 nm, when the HA/CuO molar ratio is 0.5 and 7.5, respectively. The size distributions are almost normal in some cases (Figures 1c and 1e). Contribution of smaller sized particles are slightly larger in other cases. The different agglomeration degree was observed in FE-SEM images of the obtained copper fine particles stabilized by HA. Smaller copper fine particles coated with HA tend to agglomerate and precipitate in the hydrophilic solvent used, *i.e.*, ethanol. Therefore, a higher concentration of HA has greater effect on the agglomeration.

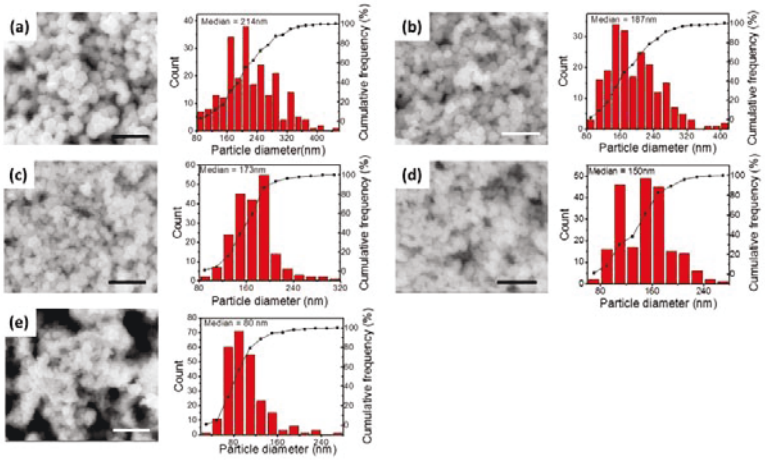

Figure 1. FE-SEM images and size distributions of *n*-hexyalamine (HA)-coated Cu fine particles prepared by hydrazine reduction of CuO micro-particles. Molar ratios of HA/CuO = (a) 0.5, (b) 2.0, (c) 5.0, (d) 5.64 and (e) 7.5. Inset gauge length = 1 μm.

The relationship between HA/CuO molar ratios and the average median particle diameters of the obtained HA-coated copper fine particles are shown in **Figure 2**. The average median sizes vary in a wide range between 80 nm to 214 nm. The median size decreases with the HA/CuO ratio increases. Smaller particles show more agglomerated structures in FE-SEM images. In many cases, the ratio of the stabilizing regent/metal is one of the key factors to control the obtained particle sizes. Leff *et al.* and our group reported that the mercaptan/gold ratio employed in the preparation step strongly affects the size of the obtained Au nanoparticles [12,13]. During the reduction reaction, particle growth and surface stabilization (termination) by organic molecules can be considered as a competitive reaction. The concentration of stabilizing reagent becomes larger, the possibility of the growth termination by capping agents becomes higher. Therefore, the particle size of the obtained fine particles becomes smaller. In this case, moreover, when the capping reagent HA binds to the particle surface, the particle surface changes to hydrophobic. The particles then formed insoluble precipitates.

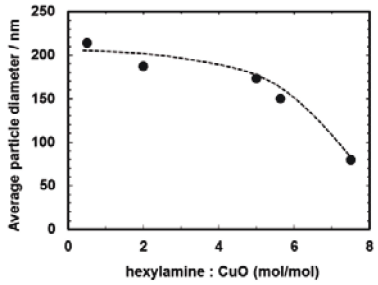

Figure 2. The relationship between the molar ratio of *n*-hexylamine/CuO and the median median particle diameters of the obtained *n*-hexylamine-coated copper fine particles prepared with various *n*-hexylamine/CuO molar ratios.

After washing, all obtained samples were dried under nitrogen flow in a centrifuge tube and then collected as a powder form. Thermogravimetric analysis (TGA) curves of the prepared copper fine particles are collected in **Figure 3**. All data was obtained under air. All the obtained TGA curves are very similar. Copper is oxidized first to Cu_2O then CuO under air and the amount of organic layer on the particle surface can be obtained by TGA curve [7]. The particles began to be oxidized at *ca.* ~120 °C, which is slightly lower than gelatin stabilized ones (~ 130 °C) [7]. The curves show a shoulder at *ca.* 220 °C, because above 220 °C, Cu_2O is oxidized to CuO. Oxidation is completed at around 320 °C. The organic component ratios of the copper fine particles prepared at HA/CuO ratios of 0.5, 2, 5, 5.64, and 8, can be estimated as 0.5, 0.5, 0.3, 0.9, and 0.6 wt%, respectively. by calculation. TGA curves measured under air provide more accurate organic component ratios than those measured under inert atmosphere. The ratios can be calculated with the clear estimation of all metallic Cu is oxidized to CuO (mass increase 25 %). It is smaller than those of gelatin or other polymer stabilized copper fine particles with similar sizes (~ 2 wt%) [7]. This small value is a very important feature of these copper fine particles for electro-conductive materials. It can be attributed to the formation of a very thin layer of HA according to the coordination between Cu and amine group. We have calculated the number of HA layers on the copper surface using topological polar surface area of HA, 0.26 nm^2 [14], the particle sizes and the density of copper. The obtained numbers of layers are in the range of 1.1 – 3.3. From these values, we can conclude that the particles are covered by HA monolayer or a very thin layer.

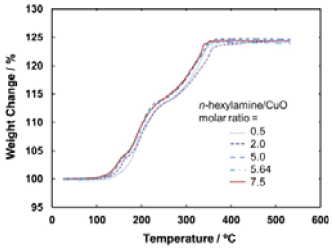

Figure 3. Thermogravimetric curves of *n*-hexylamine-coated copper fine particles prepared with various n-hexylamine/CuO molar ratios.

The samples were kept in air to check their anti-oxidation property. XRD patterns of the copper fine particles prepared with various HA/CuO molar ratios are collected in **Figure 4**. No clear oxidation peak was found in the XRD patterns of all the as-prepared dry particle samples and the samples after 1 day of the preparation (**Figures 4a** and **4b**). However, unfortunately, in the case of HA/CuO = 0.5, a small and broad hill can be observed in the pattern which can be indexed to Cu_2O after keeping under ambient conditions for 1 day (**Figure 4c**). On the other hand, the particles prepared with HA/CuO ratio of 7.5, no peak which can be indexed to Cu_2O can be found even after 1 day. Compared to polymer-stabilized copper fine particles, the stability of HA-coated copper fine particles is slightly lower probably due to the shorter molecular lengths of HA compared to polymers.

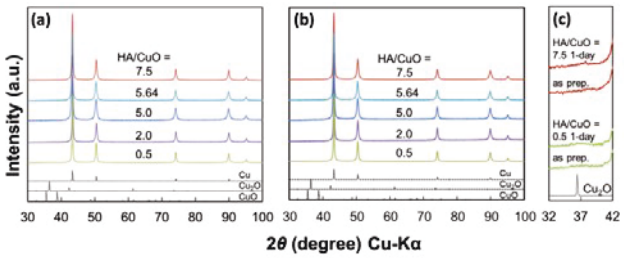

Figure 4. X-ray diffraction (XRD) patterns of (a,b) *n*-hexylamine (HA)-coated copper fine particles prepared with various HA/CuO ratios (7.5, 5.64, 5.0, 2.0, and 0.5). Measurements were carried out (a) just after the preparation and (b) after 1 day of the preparation. (c) Enlarged XRD patterns as prepared and after 1 day of the preparation of HA-coated copper fine particles prepared with HA/CuO ratios of 7.5 and 0.5 in the 2θ range of 32° – 42°.

The obtained copper fine particles were deposited on a glass plate and dried under nitrogen flow. On the particle layer, a water droplet (1 mm^3) was added. The images of the droplets are collected in **Figure 5**. The droplet shape changes with the molar ratios of HA/CuO. When the ratio is 0.5, water droplet spread on the particle layer which suggests the particle surface is relatively hydrophilic. With increasing the ratio of HA/CuO, contact angle of water droplet on the copper particle layer became much larger than 90°, which suggests that the surface of the copper fine particles were hydrophobic. This indicates that the particles were completely covered by a HA layer when the HA/CuO ratio is > 2.0. This phenomenon also is consistent of the XRD results shown in **Figure 4c**. The particles prepared with the HA/CuO molar ratio of 0.5 shows the broad peak corresponding to Cu_2O after 1 day of the preparation. It is probably due to the

imperfect coating of copper fine particle surface by HA. These particles could be re-dispersed into less polar solvents, such as ethylene glycol by using a mechanical dispersing method for production of inks or pastes.

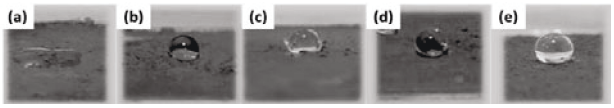

Figure 5. Digital images of a water droplet on a *n*-hexylamine (HA)-coated copper fine particle powders with various HA/CuO molar ratios. (a) HA/CuO = (a) 0.5, (b) 2.0, (c) 5.0, (d) 5.64 and (e) 7.5. (a) shows that the particles have hydrophilic surface but other images indicates that the particles have hydrophobic surfaces.

CONCLUSIONS

n-Hexyalamine (HA)-coated copper fine particles were successfully synthesized via chemical reduction of CuO micro-particles by using hydrazine as the reducing agent. The obtained particles are relatively uniform and the distribution is almost normal. The median diameters of the obtained particles change with the molar ratio of HA/CuO, especially higher than 4.0. The obtained copper fine particles are metallic but they can be slightly oxidized under ambient conditions. The particles are hydrophobic which strongly indicate that the surface was fully covered by HA when the HA/CuO molar ratio is higher than 2.0.

ACKNOWLEDGEMENTS

This work is partially supported by Canon Foundation, Hokkaido University, the Cooperative Research Program of the "Network Joint Research Center for Materials and Devices" (20181111), and the JSPS A3 Foresight Program "Organic/Inorganic Nanohybrid Platforms for Precision Tumor Imaging and Therapy". Authors thank Drs. Y. Ishida and Y. Yong (Hokkaido University), and Dr. T. Tokunaga (Nagoya University) for their fruitful discussions.

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