Metallic Copper Nanostructures Synthesized by a Facile Hydrothermal Method

Huiyu Chen¹, Jong-Hak Lee², Yu-Hee Kim¹, Dong-Wook Shin², Sang-Cheol Park², Xianhui Meng¹, and Ji-Beom Yoo¹,∗

¹School of Advanced Materials Science and Engineering (BK21), Sungkyunkwan University, Suwon 440-746, Republic of Korea
²SKKU Advanced Institute of Nanotechnology (SAINT), Sungkyunkwan University, Suwon 440-746, Republic of Korea
³Display Lab, Samsung Advanced Institute of Technology (SAIT), Yongin 446-712, Republic of Korea

A facile hydrothermal route has been developed for the synthesis of nearly spherical copper nanoparticles, copper nanocubes and ribbon-like network nanostructures. The as-prepared copper nanostructures were characterized by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), transmission electron microscopy (TEM), high-resolution TEM (HRTEM), and UV-vis spectrum analysis. These copper products were fabricated in the presence of surfactant sodium dodecyl benzene sulfonate (SDBS) acting not only as stabilizer but also as size and shape controller via hydrothermal reduction process. HRTEM revealed that the surface of the copper nanostructures was packed with a thin layer of impurities such as oxide combined surfactant or amorphous surfactant. The influence of surfactant concentration and temperature on the resultant copper nanostructures was investigated in details. UV-vis spectra indicated that strong red shift existed for the copper ribbon-like network nanostructures due to the novel morphology as well as the presence of impurities on the surface.

Keywords: Copper, Nanostructures, Hydrothermal Synthesis.

1. INTRODUCTION

During the past decade, nanomaterials have received increasing attention due to their excellent physical and chemical properties different from their corresponding bulk counterparts.¹,² It is widely accepted that these properties are often determined by their size, shape, composition, crystallinity, and structure.³,⁴ Therefore, controlling the synthesis of nanomaterials with definite morphology and uniform size is one of the most effective ways to achieve desirable properties. Considerable attention has been paid to fabricate metal nanostructures because of their great potential applications in microelectronics, nanodevices, catalysts and biology.⁵–⁸ A variety of wet chemical methodologies have been employed to synthesize metal nanomaterials with regular geometric morphologies, such as wires,⁹–¹¹ rods,¹²–¹⁴ belts,¹⁵–¹⁶ polyhedra¹⁷ and so on.¹⁸–²⁰ Among these approaches, the hydrothermal method has been considered as one of the most promising routes because it is simple and inexpensive for large-scale production. However, as the reaction mechanism is usually unpredictable, it still remains a challenge for this approach to synthesize metal nanostructures with well-defined shapes.

Elemental copper having a superior electrical conductivity and excellent catalytic property is of great importance and has been used in a wide variety of commercial applications such as electronics, sensors, nanofluids, and catalysts.²¹–²³ Its properties could be greatly enhanced by processing it into various nanostructures with well-controlled dimensions and shapes. Up to now, one-dimensional (1D) copper nanostructures have been produced by a number of synthetic routes, including soft and hard template processes,²²,²⁴–²⁷ electrochemical depositions,²⁷ reverse micelle systems,²⁸ vacuum vapor deposition (VVD),²⁹ hydrothermal method,³⁰–³² and so on.³³,³⁴ Wang and co-workers reported that cubic copper nanocages were synthesized in the aqueous phase with sodium oleate (SOA) as a stabilizer.³⁵ Copper nanocubes have also been obtained using ethylene glycol (EG) as solvent and poly(vinylpyrrolidone) (PVP) as a capping agent,³⁶ or by using special instruments.³⁷

Herein, we report a facile hydrothermal reduction process for the synthesis of nearly spherical copper nanoparticles, copper nanocubes and ribbon-like network...
Nanostructures using sodium dodecyl benzene sulphonate (SDBS) as stabilizer as well as shape and size controller. Hydrazine acts as reducing agent, which has strong reducing ability and is often employed for the preparation of some metal nanostructures. In this study, copper nanoparticles with different mean diameters were synthesized at 100 °C. Both temperature and surfactant SDBS played important roles on the morphology of the resultant product. Copper nanocubes and ribbon-like network nanostructures were obtained at 75 °C and 150 °C, respectively. The formation of metallic copper nanostructures in this work can be described on the basis of the following reactions:

\[
Cu^{2+} + 2DBS^- \rightarrow Cu(DBS)_2
\]

\[
2Cu(DBS)_2 + N_2H_4 + 4OH^- \rightarrow 2Cu + N_2 + 4DBS^- + 2H_2O
\]

2. EXPERIMENTAL DETAILS

In a typical procedure for the synthesis of copper nanoparticles, 7.04 mmol CuCl_2·2H_2O (99% purity, Sigma-Aldrich) and 5.74 mmol dodecyl benzene sulphonate (SDBS, Sigma-Aldrich) were dissolved in 270 mL water with vigorous stirring for 15 min. Then 5 mL N_2H_4·H_2O (98%, Sigma-Aldrich) was added dropwise to the above solution. Finally, the mixture was transferred into a Teflon-lined stainless steel autoclave of 375 mL capacity and maintained at 100 °C for 10 h in an electric oven. After the reaction, autoclave was then cooled naturally to room temperature, and the precipitate was rinsed several times with distilled water and absolute ethanol by centrifugation. The final products were collected and stored in absolute ethanol at room temperature. Other controlled experiments were carried out by changing SDBS concentration and temperature, respectively, while kept other synthetic conditions constant.

The X-ray diffraction (XRD) pattern of the as-prepared Cu products was examined using X-ray powder diffractometry with Cu Kα radiation (λ = 0.15406 nm) in the 2θ range from 30° to 100°. Several drops of the copper dispersed in ethanol solution were deposited onto glass substrate and the samples could be investigated by XRD measurement after evaporation of the solvent. The X-ray photoelectron spectroscopy (XPS) measurements were carried out on an ESCA 2000 spectrometer using an Al Kα X-ray as the excitation source. Scanning electron microscopy (SEM) images and energy-dispersive X-ray spectroscopy (EDX) were taken with a JEOL JSM7000F field emission scanning electron microscope. The samples for SEM measurements were deposited on Si(100) wafer. Transmission electron microscopy (TEM) images, high-resolution TEM (HRTEM) images, and the selected area electron diffraction (SAED) patterns were performed on a JOEL JEM2100F transmission electron microscope with an accelerating voltage of 200 kV. The ethanol solution with dispersed Cu nanoparticles was under ultrasonic vibration for 20 min and evaporated one drop of the suspension onto a carbon-coated copper grid for TEM measurement. UV-vis absorption spectra were obtained using a Shimadzu UV-3600 UV-vis-NIR spectrophotometer.

3. RESULTS AND DISCUSSION

The phase and purity of the as-synthesized copper product was examined using X-ray diffraction (XRD). Figure 1(a) is a typical XRD pattern of the sample. All the reflection peaks at 2θ = 43.3, 50.5, 74.2, 90.0 and 95.1° can be indexed as (111), (200), (220), (311) and (222) planes of face-centered cubic (fcc) copper, respectively, in good agreement with the reported data (JCPDS No. 4-836, a = 0.3615 nm). At the same time no characteristic peaks of any other phases or impurities are detected, which indicates that metal copper products obtained under current synthetic conditions are pure. The surface information of the freshly obtained copper product was analyzed by XPS as shown in Figures 1(b–c). The binding energies obtained in XPS analysis were corrected with the reference to C 1s (284.6 eV). Two strong peaks are observed at 952.3 eV and 932.5 eV, corresponding to Cu 2p_1/2 and Cu 2p_3/2, respectively. The Cu 2p_1/2 satellite peak characterizing Cu^{2+}, which is usually centered at about 942 eV, does not appear in the spectrum. The peak position/binding energy, line-shape and peak-to-peak separation (19.8 eV) of the XPS spectrum are consistent with the reported data for elementary Cu. However, the main O 1s peak is located at 530.6 eV as shown in the Figure 1(c). This peak can be assigned to Cu_2O in that the binding energies of O 1s for Cu_2O and CuO are 530.4 eV and 529.6 eV, respectively. The composition of the outer surfaces thus can be determined to contain a very small fraction of Cu_2O phase that can not be detected in XRD spectrum. The introduced O came from the very thin film of oxides packed on the Cu nanoparticles and the redox reaction probably occurred during the characterization process.

The morphology of the as-prepared Cu products was examined by FESEM. The typical SEM image in Figure 2(a) shows that the product mainly consists of particle-like Cu nanoclusters with panoramic view and the size ranges from 150 to 200 nm. However, further observation with high magnification (Fig. 2(b)) reveals that these Cu nanoclusters are assembled by smaller nanoparticles, which exhibit good uniformity and the average diameter is about 40 nm. The smaller Cu nanoparticles have a strong tendency to aggregate to form larger nanoclusters. As a matter of fact, the dark red absolute ethanol solution with dispersed Cu nanoparticles could be preserved for only two days. After that, all the nanoparticles fell on the bottom due to the presence of larger aggregated Cu nanoclusters.

References


Acknowledgments

This work was supported by the National Research Foundation of Korea (NRF) grant funded by the Korea government (MSIP) (2014R1A1A2058695).
Fig. 1. (a) XRD pattern of the as-obtained Cu product and X-ray photoelectron spectra of Cu 2p (b) and O 1s (c).

and then the color of the solution changed to transparent gradually. Energy-dispersive X-ray spectroscopy (EDX) analysis shows the Cu sample contains oxygen element with minute quantity (Fig. 2(c)), in good agreement with XPS analysis. Figure 2(d) displays a representative TEM image. The copper nanoparticles exhibit nearly spherical shape and most of them aggregate together even under ultrasonic vibration for a long time. The average size of these nanoparticles is about 40–45 nm, almost in accordance with that from SEM observations.

Surfactant is often used as stabilizer and size controller for the fabrication of materials within micro- or nanoscale, especially in the field of soft chemistry synthesis. In this study, it was found that the concentration of surfactant SDBS played an important role in controlling the size of Cu nanoparticles. When the hydrothermal reaction was performed in the absence of SDBS, copper nanoparticles with irregular shapes and even some nanopatches were observed, as is clearly shown in the SEM image (Fig. 3(a)). These particles have size of 100–300 nm and exhibit a broad size distribution. Once the surfactant with 1.44 and 2.87 mmol were employed in the system, the mean size of Cu nanoparticles reduced to 80–200 nm and 40–60 nm, respectively (Figs. 3(b–c)). This indicates that the size of copper nanoparticles and its distribution are dramatically reduced with the presence of SDBS in appropriate amounts. The initially formed copper nanoparticles are relatively small in dimension with the protective agent. However, Figure 3(d) shows the SEM image of Cu nanoparticles synthesized with 10.05 mmol surfactant, from which the diameter can be observed at about 35–50 nm, almost equivalent to those prepared in the typical procedure. It implied that the excessive SDBS could not further decrease the size of Cu nanoparticles effectively once the size reached a definite value. Therefore, the magnitude of copper nanoparticles could be tuned with the assistance of suitable amount of SDBS in a relative low concentration range. The effect of redundant surfactant for the size control was not obvious.

The role of surfactant SDBS is to act not only as protective agent and size controller, but also probably as morphology directing agent. Generally, surfactant is considered to kinetically control the growth rates of different crystallographic facets of Cu nanoparticles through preferentially adsorbing and desorbing on these facets. Therefore, the morphology can also be controlled effectively through this route. In the present work, both surfactant and temperature were found to be crucial to the formation of Cu nanostructures with various shapes.

To investigate the influence of temperature on the resultant copper nanostructures, a series of temperature-dependent experiments were carried out in details. When the experiment was performed at 60 °C while kept other synthetic parameters unchanged, the morphology of Cu nanoparticles is almost the same as those synthesized at 100 °C, but the diameter is in the range of 20–50 nm (Fig. 4(a)). The growth rate of nanoparticles is relative slow in the low temperature region, leading to the final smaller size during the given growth time. However, it is interesting that copper nanocubes can be fabricated at 75 °C on a large scale. Figure 4(b) presents the representative SEM image, from which it is clearly seen that nearly...
Metallic Copper Nanostructures Synthesized by a Facile Hydrothermal Method

**Fig. 2.** SEM images of the as-obtained Cu nanoparticles by (a) panoramic view with low magnification and (b) high magnification view; (c) EDX spectrum and (d) TEM image of the Cu nanoparticles.

**Fig. 3.** SEM images of the Cu nanoparticles obtained at 100 °C in the presence of SDBS with (a) 0 g, (b) 0.5 g, (c) 1 g and (d) 3.5 g. The size is about 100–300 nm, 80–200 nm, 40–60 nm and 35–50 nm, respectively.
all the nanocubes are isolated without aggregation as well as only a minute portion of copper polyhedra exist. In comparison with the solution containing aggregated copper nanoparticles prepared at 100 °C, the dark red ethanol solution with well dispersed nanocubes could be preserved for at least three weeks without color change, which indicated that the solution could exist stably over a long time without deposition.

The microstructures of the as-obtained copper nanocubes were further examined with TEM, high-resolution TEM (HRTEM), and selected area electron diffraction (SAED). It was found from the panoramic TEM image (Fig. 5(a)) that the Cu nanocubes are obtained with high yields. The inset in Figure 5(a) shows several typical nanocubes with a high magnification view, which illustrates the cubes have an average edge size of 40 nm and some corners with slight truncation are also observed. Further fine structure of the nanocubes was then characterized by HRTEM, as shown in Figure 5(b). The HRTEM image was observed along [001] zone axis and the fringe spacing of the HRTEM image is examined to be 0.180 nm, which is close to the (200) lattice spacing of the fcc copper crystal. A thin layer of impurities with a thickness of about 3–4 nm was also observed on the surfaces of copper nanocubes. It seemed that the impurities could be ascribed to oxide combined surfactant or amorphous surfactant because the fringe spacing of the impurities could not be clearly detected from the HRTEM image. The corresponding SAED pattern shown in the inset of Figure 5(b) was obtained by directing the incident electron beam perpendicular to one of the square facets of the cube. The exact square spot array can be indexed to [200] and [020] of the fcc copper. On the basis of HRTEM and SAED analyses, it can be concluded that each copper nanocube is a single crystal and the surface is bounded primarily by {100} facets.

Based on the controlled experiments, it was found that the optimal temperature for the synthesis of Cu nanocubes is about 75 °C. When the temperature was increased to 125 °C, the copper product included nanoparticles with the size of about 50–60 nm and a small portion of nanoribbons. The width and length of the nanoribbons reach 20–50 nm and micro-meters (Fig. 4(c)), respectively. Cu nanoribbons could be prepared with high yield in 150 °C as displayed in Figure 4(d), and only a few nanoparticles co-existed. Probably the long alkyl chain in SDBS molecule mainly acted as soft template for the formation of ribbon-like network nanostructures. Compared to the surfactant role in the system below 100 °C for the synthesis of copper nanoparticles, the template effect of SDBS was more evident in 150 °C. Here, the instantaneously produced nuclei with high surface energy
were apt to aggregate along the long chain of surfactant molecule. Then the aggregated nuclei would grow in situ, and finally connected together to develop into ribbon-like structures. Some ribbons with length of several microns twisted together and some curled up to demonstrate the typical characteristic of ribbons. However, from the TEM image in Figure 5(c), one can find that the Cu nanoribbons exhibit network structures. The width of single ribbon was not preserved uniformly along the growth axis and the thickness also seemed to be quite different. A number of ribbons split more or less even in the middle part. When the reaction temperature was high enough, the Brownian movement of surfactant SDBS became so intense that they might have destroyed the interaction of Cu crystal faces, which implied that Cu nanoribbons gradually split into smaller ones with narrower width. What should be noted is that the byproduct N₂ would also contribute to the splitting process simultaneously. Both the HRTEM image and SAED pattern (Fig. 5(d)) illustrate that these Cu nanoribbon networks are polycrystalline. It is still very unclear that the morphologies of copper nanostructures can be modified conveniently just by varying the reaction temperature. In order to investigate the influence of surfactant type, we examined some other surfactants including cetyltrimethylammonium bromide (CTAB), sodium dodecylsulfate (SDS) and PVP. No copper cubes or ribbons were produced under the present synthetic conditions, Cu nanoparticles with irregular shapes were obtained even various amounts of above mentioned surfactants were used. It is reasonable that anionic surfactant has a stronger interaction with the copper ion compared to the cationic or nonionic surfactant (e.g., CTAB and PVP, respectively). In addition, the longer carbon chain length exists in SDBS molecules than that in SDS. The results reveal that the difference in molecular structures between SDBS and other surfactants may be one of reasons leading to the different Cu nanostructures. As a matter of fact, surfactant is not the only crucial factor to determine the final morphologies. Instead, it often cooperates with temperature, solvent, concentrations of starting materials, etc., to guide the crystal growth. It was reported that well-defined copper nanocubes were synthesized in ethylene glycol (EG) solvent using PVP as a capping agent. Thus, the mechanism of controlling Cu nanostructures using SDBS as a
soft template in this work needs more investigations and the related work is currently under way. Besides, some reports revealed that anionic types of metal salts have great effect on the as-synthesized nanomaterials probably due to the differences in kinetics such as growth rates, adsorption of anions on growing crystal faces and so on.\(^ {42,43}\) We substituted Cu(NO\(_3\))\(_2\) or CuSO\(_4\) as the starting materials and other synthetic parameters were maintained the same as those in the typical synthesis, almost the same copper nanostructures with CuCl\(_2\) used were produced. It can be concluded from the present study that these anions of copper salts have no noticeably different effect on the final copper shapes and this probably because the anions act nearly the same roles in the present synthetic system.

Figure 6 shows the UV-vis absorption spectra taken from the as-obtained copper nanoparticles and nanoribbon networks dispersed in ethanol. A strong absorption peak centered at 603 nm was observed for the Cu nanoparticles prepared at 100 °C and this peak could be assigned to the absorption of Cu nanoparticles.\(^ {39}\) On the other hand, the Cu nanoribbons showed a broad absorption from 625 to 800 nm, exhibiting strong red shift compared with that of Cu nanorods or nanorod junctions.\(^ {30,40}\) We believe that two factors may be responsible for this interesting phenomenon. One is the unique ribbon-like network nanostructures. One dimensional nanostructure such as nanorods or nanowires is considered to be advantageous to the absorption of visible light along the major axis (the longitudinal plasmon band). The larger the aspect ratio, the more redshifted the longitudinal plasmon band will exhibit.\(^ {2}\) The Cu ribbon-like network nanostructures consist of a large number of nanoribbons, whose collective contributions to the red-shift are larger than that of an individual Cu nanoribbon. Another factor is probably due to a thin layer of oxide or impurities on the surface of Cu products. The broadness of the absorption peak most likely originated from the various sizes of Cu nanoribbons.

![UV-vis spectra](image)

**Fig. 6.** UV-vis spectra of (a) Cu nanoparticles synthesized at 100 °C and (b) Cu ribbon-like network nanostructures synthesized at 150 °C.

4. CONCLUSIONS

In summary, metallic copper nanoparticles with a variety of diameters, nanocubes and ribbon-like network nanostructures have been successfully prepared in high yield via a facile hydrothermal reduction process at different temperatures. The surfactant SDBS acted not only as stabilizer but also as size and shape controller. Both reaction temperatures and SDBS played important roles for the formation of resultant copper nanostructures with various shapes. These diverse copper nanostructures may have important applications in optoelectronics device and catalyst. Such soft-template hydrothermal approach is considered to be versatile for the synthesis of transition metallic nanostructures and can be generally adapted to other nanomaterials.

Acknowledgments: The authors gratefully acknowledge the financial support from the BK21 Project through School of Advanced Materials Science and Engineering and from Samsung Advanced Institute of Technology (SAIT) through SKKU Advanced Institute of Nanotechnology (SAINT).

References and Notes

Metallic Copper Nanostructures Synthesized by a Facile Hydrothermal Method

Chen et al.


Received: 13 February 2009. Accepted: 26 March 2009.