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Syntheses Cu_2O and Cu Nanoparticles by Using a Polyol Method

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Copper-containing nanoparticles were synthesized by using a polyol method. Ethylene glycol (EG), which is a typical polyol, was used as a reductant and a solvent. $Cu(OAc)_2 \cdot H_2O$ and polyvinylpyrrolidone (PVP) were employed as a reagent and a protecting agent, respectively. The product nanoparticles obtained at each reaction stage were characterized by using transmission electron microscopic (TEM), TEM-energy dispersed X-ray spectroscopic (EDS), scanning electron microscopic (SEM), X-ray diffraction (XRD), and ultraviolet (UV)-visible (Vis) extinction spectroscopic measurements. Results showed that Cu_2O particles with a mixture of various morphologies were initially formed at 175 °C. They consisted of aggregates of small nanoparticles in most cases. After further heating at 175 °C for 15 min, Cu_2O particles were reduced to Cu nanoparticles rapidly. After heating at 175 °C for 60 min, monodispersed spherical Cu nanoparticles with an average diameter of about 200 nm were finally obtained. UV-Vis extinction spectra suggested that Cu_2O particle solution was stable more than 10 days, whereas complete precipitation occurred for Cu nanoparticle solution after 3 days due to oxidation.

Key words: *Cu_2O particles, Cu nanoparticles, Polyol method, Ethylene glycol, Two-step reduction, Thermal decomposition, Stability, Oxidation, Plasmon band*

1. Introduction

Mono-metallic nanoparticles and their oxides are of great interest because they can have unique physical, chemical, and optical properties that are different from those of the atoms or of their bulk counterparts. The large surface area to volume ratio can contribute to some of the unique properties of nanoparticles.1-6) Among them, Cu and Cu_2O are industrially important materials that are widely used in fields such as magnetic storage media, solar energy transformation, electronics, sensors, catalysis, batteries, and imaging.7-13) Cu and Cu_2O have been synthesized by sonochemical methods,14) microwave irradiation,15) photochemical methods,16) hydrothermal and solvothermal methods,17,18) electrochemical methods,19-21) sol-gel methods,22,23) solid-state reactions,24) and chemical reduction and decomposition route.25-28)

Polyol method is a typical chemical reduction method for the preparation of Cu-containing nanoparticles in liquid phase. It has been used to prepare Cu and their oxides since a pioneering study of Fiévet et al. on Cu_2O.5,29-34) In the polyol process, the liquid organic compound, a polyol, including 1,2-diols and glycol ether, acts both as a reducing agent and a solvent of the precursor metallic-salt. Possible reduction processes using polyol have been reported in a review article by Rodrigues et al.4) As well as its role of reductant, the polyol medium offers several other advantages (i) their high boiling points allow syntheses at relatively high temperature, resulting in high degree of crystallinity products, (ii) the reducing medium prevents as-prepared metal particles from oxidation, (iii) its ability to

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coordinate metal precursors and particle surfaces, which minimizes aggregation and coalescence, and (iv) the high viscosity of the medium favors a diffusion-controlled growth of particles, leading to well-controlled shapes, sizes, and compositions.

We have succeeded in syntheses of such Cu-containing nanoparticles as Au@Cu, Ag@Cu, Cu@Ag, AgCu, AuAgCu, phase-separated AuAgCu/Cu, Au@Ag@Cu, and Au@Pd@Cu particles using polyol methods.[35-44] We could obtained new information on growth mechanisms of Cu-containing bi- and tri-metallic nanoparticles and effects of crystal structure and composition for antioxidative properties of Cu component in various Cu-containing nanoparticles.

In this study, we prepared Cu_2O and Cu nanoparticles using a polyol method. Crystal structures were characterized by TEM, TEM-EDS, SEM, XRD, and UV-Vis extinction spectral data. Their formation mechanisms in ethylene glycol (EG) and stability in EG solution after preparation are discussed.

2. Experiment

2.1 Materials and experimental procedures

For use in this study, $Cu(CH_3COO)_2 \cdot H_2O$ = $Cu(OAc)_2 \cdot H_2O$ (>99.0%) and EG (>99.5%) were purchased from Kishida Chemical Industry Ltd. and polyvinylpyrrolidone (PVP: Mw = 55 k) was obtained from Sigma-Aldrich Corp. A high purity Ar gas (>99.999%) was obtained from Japan Fine Products. All reagents were used without further purification.

30 mg of $Cu(OAc)_2 \cdot H_2O$ in 17 mL EG and 0.56 g of PVP in 17 mL EG (MW: 55 000 in terms of monomer units) were mixed in a 100 mL three necked flask and Ar was bubbled at room temperature for >20 min to remove oxygen dissolved in the solution. The final concentrations of $Cu(OAc)_2 \cdot H_2O$ and PVP in EG were 6 and 200 mM, respectively.

The reagent solutions were soaked in an oil bath preheated at 186 °C under bubbling Ar. The temperature profile of solution is shown in Fig. 1. The solution temperature increases rapidly from a room temperature to about 170 °C after heating for about 5 min, slowly increased from 170 to 175 °C in the 5–10 min, and it was kept at 175 °C for 60 min. The reagent solution was sampled at various reaction times to examine shape, size, composition changes of intermediate and product particles. The sample solution was rapidly cooled in a water bath after a desired reaction time finished.

2.2 Characterization of nanoparticles

Shape, size, and composition of product particles were examined by using TEM and TEM-EDS (200 kV, JEM-2100F; JEOL) and SEM (SU8000; Hitachi High-Tech Science Corp.). Samples for TEM, TEM-EDS, and SEM observations were obtained by centrifuging the colloidal solution three times at 15,000 rpm for 30 min. The XRD patterns of the samples were measured using Cu Kα radiation operating at 50 kV and 300 mA (RINT-TTR III, Rigaku Corp.). Extinction spectra of the product solutions were measured in the 300–1200 nm region using a spectrometer (UV-3600; Shimadzu Corp.).

3. Results and Discussion

3.1 Formation of Cu-containing nanoparticles from $Cu(OAc)_2 \cdot H_2O$ in EG in the presence of PVP

Figure 2 shows changes in color of reagent solution after heating. When $Cu(OAc)_2 \cdot H_2O$ was injected to the hot EG solution containing PVP, color of solution was changed from blue (125 °C) to green (160 °C), olive-green (175 °C and 175 °C 7.5 min), and red copper (175 °C 30–60 min). Figure 3 shows UV-Vis extinction spectra of products obtained from $Cu(OAc)_2 \cdot H_2O$/PVP/EG system after heating from room temperature to 175 °C and keeping at 175 °C for 7.5–60 min. Just after heating, a

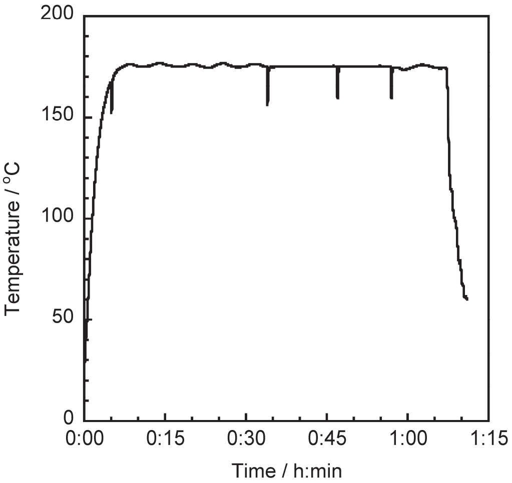

Fig. 1. Temperature profile of reagent solution after soaking reagent solution to an oil bath at 186 °C. Spikes observed in curves originate from sampling reagent solution by using a pipette.

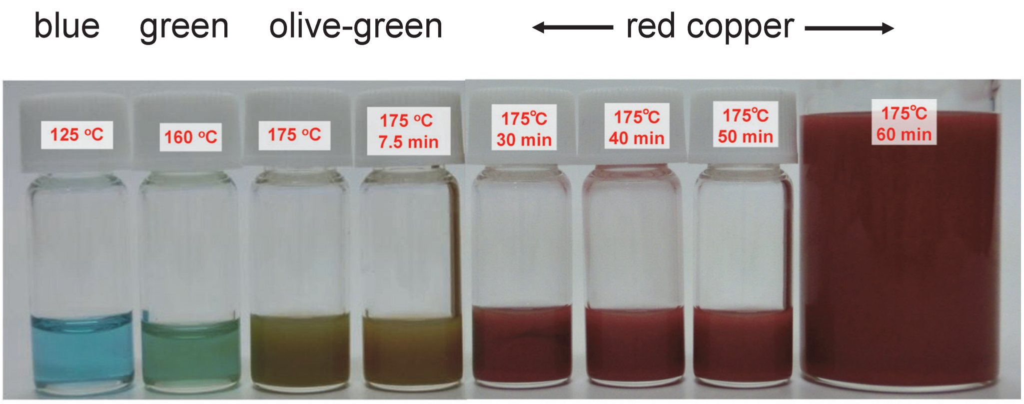

Fig. 2. Changes in color of reagent solution after heating.

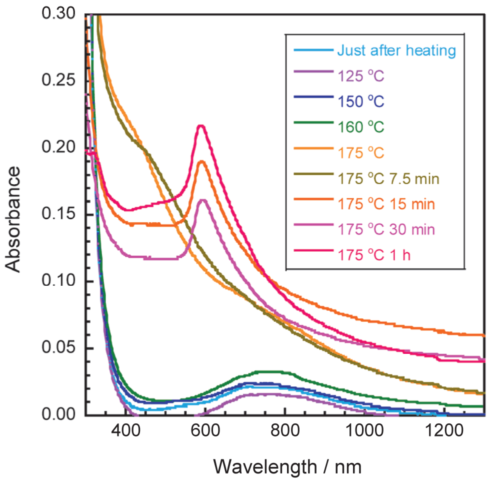

Fig. 3. UV-Vis extinction spectra of products obtained from $Cu(OAc)_2 \cdot H_2O$/PVP in EG after heating from room temperature to 175 °C and keeping at 175 °C for 7.5–60 min.

weak broad band is observed in the 450–1200 nm range with a peak at about 750 nm. At 125–160 °C, similar broad bands are observed, although peak intensity becomes slightly strong at 160 °C. After heating at 175 °C and at 175 °C 7.5 min, strong long tail bands with weak shoulder peaks at about 450 nm appear in the 350–1250 nm region. The appearance of the 450 nm peak suggests that main product is Cu_2O in this reaction time range.[32] After heating at 175 °C 15 min, 30 min, and 1 h, long tail bands change into broad bands with a peak at about 600 nm. It is known that Cu nanoparticles give a surface plasmon resonance (SPR) band with a peak at ≈600 nm.[38,44] Thus, the spectral changes indicate that major products changes from Cu_2O to Cu during heating at 175 °C for 15 min. Similar two-step formation of Cu nanoparticles via decomposition of Cu_2O in polyol solvents have

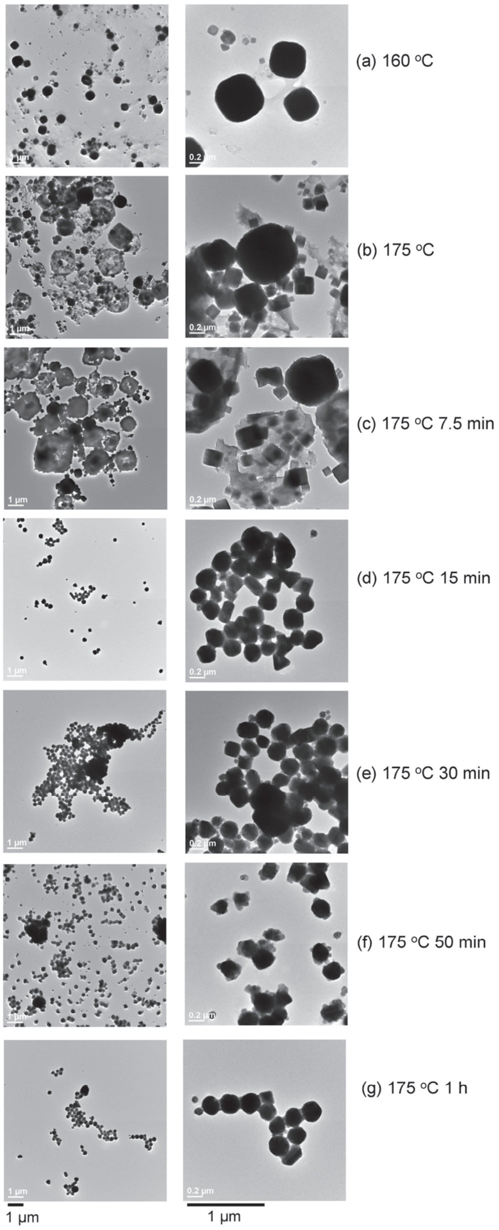

Fig. 4. TEM images of products obtained at 160 °C and 175 °C 0–60 min.

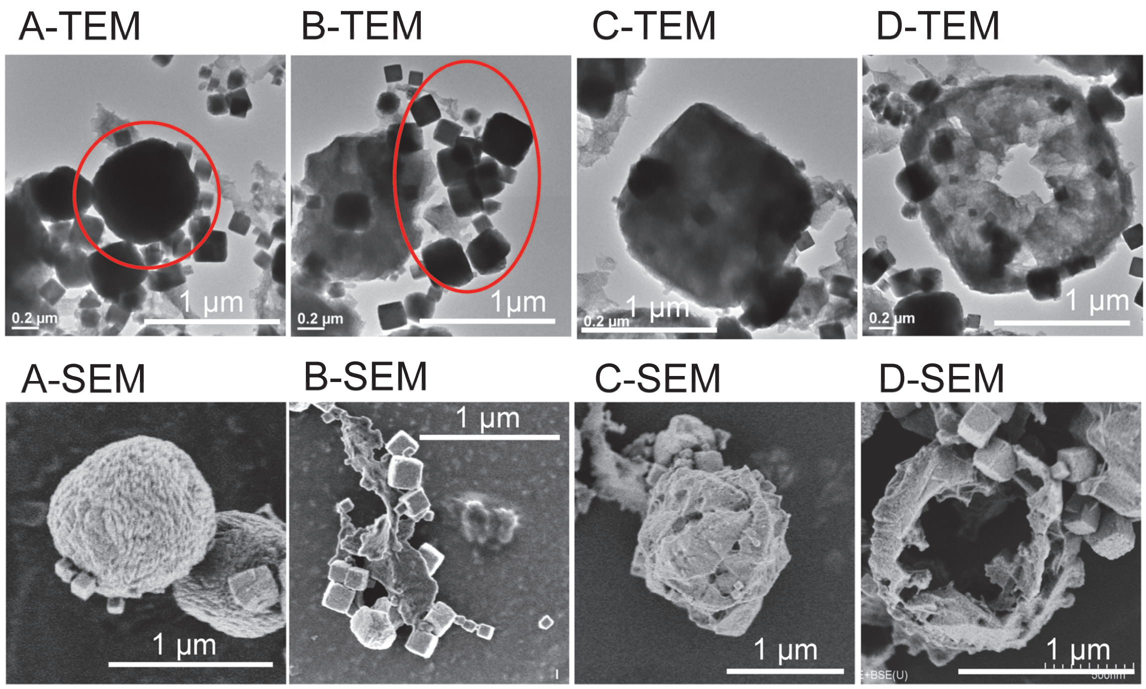

Fig. 5. TEM and SEM images of various shapes of products at 175 °C.

been reported, although the reaction temperatures, where $Cu_2O \rightarrow Cu$ reduction occurs, are higher than that observed in this work in most cases.[31,32,34] This will be discussed in more detail in Sec. 3.3.

Figures 4a-4g show TEM images of products obtained at 160 °C and 175 °C 0–60 min. At 160 °C (Fig. 4a), a mixture of small particles with an average diameter of about 100 nm and a cubic-type large particles with an average diameter of about 300 nm is obtained.

At 175 °C and 175 °C 7.5 min (Figs. 4b and 4c), mixtures of various shapes of aggregates are formed. To examine crystal structures of these aggregates in more detail, expanded TEM and SEM images at 175 °C are measured (Fig. 5A-5D). Four kinds of particles are found. They are spherical aggregates with an average diameter of about 1 µm (type A), cubic particles with an average diameter of 200 nm (type B), larger cubic-shaped aggregates with an average diameter of about 1 µm (C), and hollow spherical aggregates with an average diameter of about 1 µm (type D). All of these particles are expected to be Cu_2O on the basis of UV-Vis spectral data (Fig. 3).

To obtain information on composition of products at 175 °C, TEM-EDS measurements were carried out. Figures 6a-6f display TEM, TEM-EDS, and line analysis data, where hollow particles and cubic particles are observed. TEM-EDS and their line analysis data indicate that both particles are composed of uniformly distributed Cu and O components, and Cu : O atomic ratio was about 2 : 1. These results suggest that major products at 175 °C are Cu_2O, which is consistent with the prediction from the UV-Vis spectral data (Fig. 3).

At 175 °C 15, 30, and 50 min (Figs. 4d-4f), hollow particles disappear and mixtures of spherical and cubic-type particles with an average diameter of about 200 nm are formed. At 175 °C 1 h (Fig. 4g), spherical particles with an average diameter of about 200 nm are formed. On the basis of UV-Vis extinction spectra (Fig. 3), main component of these particles is expected to be Cu.

To obtain definite information on the crystalline structure of products, XRD patterns of products were measured. Figures 7(a) and 7(b) show XRD patterns of product powders obtained at 175 °C and 175 °C 1 h, respectively. At 175 °C, major peaks are attributed to cubic Cu_2O and weak peaks arising from cubic Cu are observed. The Cu_2O and Cu ratio was estimated to be 96 : 4. At 175 °C 1 h, only Cu peaks are found, indicating that Cu_2O is completely converted to Cu after heating Cu_2O particles in EG at 175 °C for 1 h. Results obtained from XRD analyses were consistent with drastic spectral changes from broad Cu_2O peak to more sharp Cu SPR peak observed in the UV-Vis extinction spectra (Fig. 3).

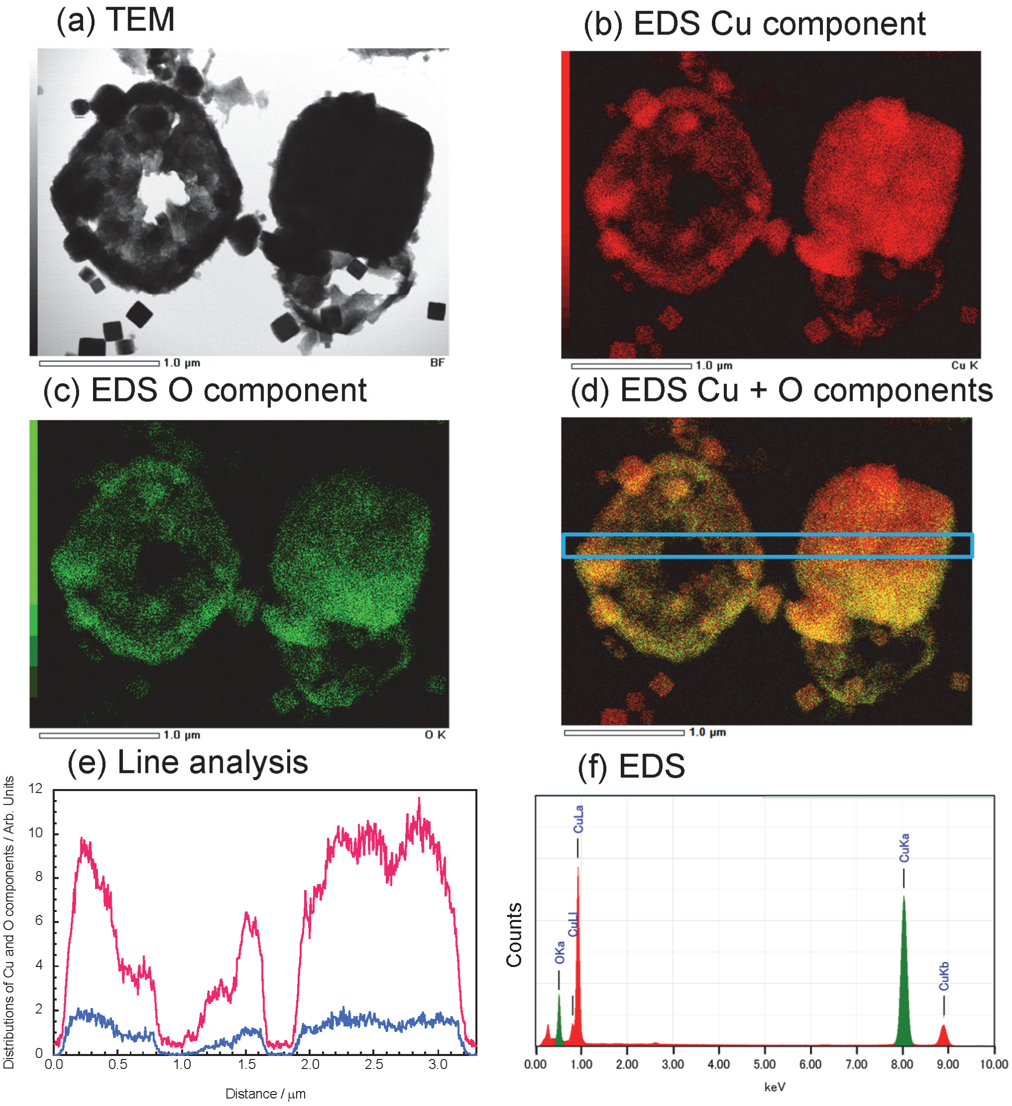

Fig. 6. TEM and TEM-EDS data of products obtained at 175 °C. Line analysis data (e) are obtained along a blue box shown in (d).

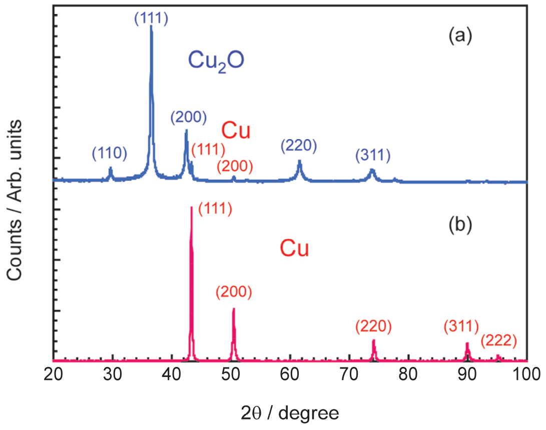

Fig. 7. XRD patterns of products obtained at (a) 175 °C and (b) 175 °C 1 h.

3.2　Stability of Cu_2O and Cu nanoparticles

Stability of Cu_2O and Cu nanoparticles after preparation was examined by monitoring time changes in UV-Vis spectra. Figure 8a shows UV-Vis spectra of Cu_2O obtained at 175 °C and 12 days after preparation. Although Cu_2O peak at 484 nm decreases by 3% after 12 days, no significant reduction of peak intensity is observed. This implies that stability of Cu_2O particles is relatively high in EG.

Oxidation of Cu nanoparticles gives rise to progressive damping of their characteristic SPR band because of the growth of the oxide outer shell.[45,46] Consequently, the extent of oxidation of Cu nanoparticles can be monitored by observing the intensity changes in the Cu band at ≈600 nm. Figure 8b shows SPR bands of Cu nanoparticles at 0–3 days after preparation. The SPR band of Cu particles at ≈600 nm decreases rapidly with increasing in the reaction time and becomes zero after 3 days because of their oxidation. These results suggest that dispersion of Cu nanoparticles is much more unstable than that of Cu_2O particles in EG, so that precipitation is formed within a few days.

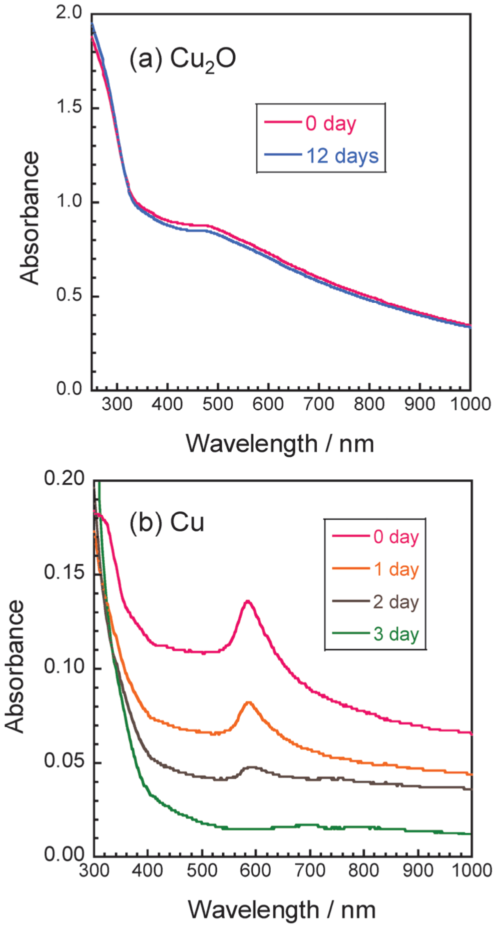

Fig. 8. Time evolution of UV-Vis extinction spectra of (a) Cu_2O and (b) Cu nanoparticles in EG/PVP solutions after preparation.

3.3 Formation mechanism of Cu nanoparticles via reduction of Cu_2O particles

Teichert et al.[34] studied the formation mechanism of Cu nanoparticles via Cu_2O in $Cu(OAc)_2$/EG system on the basis of XRD and DTA-TG analyses of intermediate and final products. They reported that $Cu(OAc)_2$ completely dissolved in EG at ca. 80 °C giving a bright turquoise solution. When the reagent solution was further heated to 120 °C, a dark green crystalline compound was precipitated. Single-crystal X-ray diffraction data suggested that the precipitation was the coordination polymer $Cu_3(OAc)_2(C_2H_4O_2)_2$. According to their analysis, this crystal belongs to the triclinic space group $P\bar{1}$ and has a 2D network structure generated by bridging bidentate acetate and deprotonated EG ligands. In their DTA-TG measurements of dry $Cu_3(OAc)_2(C_2H_4O_2)_2$ in air showed that it is stable up to 200 °C and decomposes in an exothermic reaction to Cu_2O.

In this study, we obtained a green solution at 160 °C (Fig. 2), where no precipitation was obtained. Precipitation was not found in our study, even reaction temperature increased from 160 °C to 175 °C and it was kept in this temperature for 1 h. In our work, we did not hold the temperature constant before elevating the reaction temperature from room temperature to 175 °C. Rapid increase in the reaction temperature around 120 °C in this work probably prevents the reagent solution from the precipitation. Although Teichert et al.[34] reported that $Cu_3(OAc)_2(C_2H_4O_2)_2$ is stable in air up to 200 °C, we found here the formation of Cu_2O particles from $Cu(OAc)_2 \cdot H_2O$/PVP/EG system after heating at a lower temperature of 175 °C in EG. It is therefore reasonable to assume that $Cu_3(OAc)_2(C_2H_4O_2)_2$ intermediate is not formed or rapidly decomposed into smaller soluble intermediates in our condition.

We found here that Cu_2O particles with a Cu^+ component were formed, when the reagent solution was heated to 175 °C at a relatively fast heating rate of about 30 °C/min. The following reduction potentials in aqueous solutions can be used for the reduction of Cu^{2+} to Cu^0 via Cu^+, because their relative magnitude is similar in EG and water.[47,48]

$$Cu^{2+} + 2e^- \rightarrow Cu^0 \qquad E^\circ = +0.342\ \text{V} \qquad (1)$$

$$Cu^{2+} + e^- \rightarrow Cu^+ \qquad E^\circ = +0.153\ \text{V} \qquad (2)$$

$$Cu^+ + e^- \rightarrow Cu^0 \qquad E^\circ = +0.521\ \text{V} \qquad (3)$$

It is expected that direct $Cu^{2+} \rightarrow Cu^0$ reduction (1) does not occur, but the reduction of Cu^{2+} ions into Cu^0 proceeds through two stages in EG solution:[5,31,34]

$$Cu(OAc)_2\text{-EG} \rightarrow Cu_2O \rightarrow Cu^0 \qquad (4a)$$

$$Cu^{2+} \rightarrow Cu^+ \rightarrow Cu^0 \qquad (4b)$$

At first, Cu^{2+} ions, which are stable in EG at ambient temperature, are formed from $Cu(OAc)_2 \cdot H_2O$ reagent and then they are reduced to Cu^+ through process (2). In principle, since the standard potential associated with the $Cu^+ \rightarrow Cu^0$ reduction (3) is more positive than that of the $Cu^{2+} \rightarrow Cu^+$ reduction (2), the Cu^+ species produced through reaction (2) are unstable and should be readily reduced to Cu^0. However, the Cu^+ ions immediately form sparingly soluble Cu_2O, a compound that is more difficult to reduce as predicted by the more negative redox potential associated with Eq. (5)

$$Cu_2O + H_2O + 2e^- \rightarrow 2Cu^0 + 2OH^- \quad E^\circ = -0.36\ \mathrm{V}. \qquad (5)$$

Actually, the SEM, TEM, and XRD data indicate that these Cu_2O particles are not further reduced, and therefore, they are formed by the aggregation of primary nano-sized particles at 175 °C and 175 °C 7.5 min. Similar aggregation processes have been observed in other cases.[49-51] Cu_2O particles in EG solution is stable more than 10 days.

After further heating Cu_2O/PVP/EG solution at 175 °C for more than 15 min, Cu^+ component in Cu_2O particles is rapidly reduced to Cu^0. Then, monodispersed spherical Cu nanoparticles with an average diameter of about 200 nm are finally formed. When leaving these particles in a bottle, precipitation occurs nearly completely after three days due to oxidation.

In the last section, we compared the $Cu_2O \rightarrow Cu$ conversion temperature observed in this study with those reported previously. Orel et al.[31] have first observed conversion of uniform colloidal Cu_2O spheres to copper in polyols (EG and tetraethylene glycol (TEG)) by using $Cu(OAc)_2$ as a reagent. They reported that the conversion from Cu_2O to Cu occurred at 170 °C in EG, though no detailed experimental conditions (e.g. reaction time) and XRD data were shown. They gave more detailed experimental data, when TEG was used. Pure Cu nanoparticles were prepared at 240 °C in TEG, which was much higher than 170 °C in EG. Zhao et al.[32] obtained spherical Cu particles with a similar size obtained in this study by microwave heating of $Cu(OAc)_2 \cdot H_2O$/EG solution at 197 °C. Since no protecting agent was added in their experiment, precipitate was obtained. Teichert et al.[34] prepared Cu contained products from $Cu(OAc)_2 \cdot H_2O$/EG system. After the formation of $Cu_3(OAc)_2(C_2H_4O_2)_2$ intermediate at 120 °C, solid alkoxide $Cu(C_2H_4O_2)$ was formed at 180–200 °C. Cu nanoparticles were obtained under reflux conditions of $Cu(C_2H_4O_2)$ at a higher temperature of 210 °C. As described above, there are several reports that Cu nanoparticles could be prepared through decomposition of Cu_2O in polyol solvents, our simple condition, heating at 175 °C for 15 min in EG, provides pure Cu nanoparticles at a relatively low temperature in a short heating time.

4. Summary and Conclusion

A simple polyol reduction method was applied to the syntheses of Cu_2O and Cu nanoparticles. $Cu(OAc)_2 \cdot H_2O$ was reduced in EG in the presence of PVP as a protecting agent. When the reagent solution was heating to 175 °C at a heating rate of about 30 °C/min, Cu_2O particles with a mixture of various morphologies were prepared with a yield of 96%. The remaining 4% was Cu particles. After heating at 175 °C for 15–60 min, Cu_2O particles were completely reduced to Cu nanoparticles. UV-Vis spectral changes suggested that the $Cu_2O \rightarrow Cu$ conversion occurs within a few minutes. Although the formation of Cu nanoparticles via decomposition of Cu_2O particles in polyols has been reported,[31,32,34] higher temperatures above about 200 °C were required for conversion in most cases. Thus, this work provides a new simple lower temperature synthesis method of monodispersed Cu nanoparticles in EG.

Acknowledgments

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References

1) Y. Xia, Y. Xiong, B. Lim, and S. E. Skrabalak, *Angew. Chem. Int. Ed.*, 48, 60 (2009).

2) M. B. Gawande, A. Goswami, F.-X. Felpin, T. Asefa, X. Huang, R. Silva, X. Zou, R. Zboril, and R. S Varma, *Chem. Rev.*, 116, 3722 (2016).

3) Y. Xia, K. D. Gilroy, H.-C. Peng, and X. Xia, *Angew. Chem. Int. Ed.*, 56, 60 (2017).

4) T. S. Rodrigues, M. Zhao, T.-H. Yang, K. D. Gilroy, A. G. M. da Silva, P. H. C. Camargo, and Y. Xia, *Chem. Eur. J.*, 24, 16944 (2018).

5) F. Fiévet, S. Ammar-Merah, R. Brayner, F. Chau, M. Giraud, F. Mammeri, J. Peron, J.-Y. Piquemal, L. Sicard, and G. Viau, *Chem. Soc. Rev.*, 47, 5187 (2018).

6) Y. Shi, Z. Lyu, M. Zhao, R. Chen, Q. N. Nguyen, and Y. Xia, *Chem. Rev.*, 120, Web published (2020). https://dx.doi.org/10.1021/acs.chemrev.0c00454.

7) A. Inoue and B. L. Shen, *J. Mater. Res., 18*, 2799

(2003).

8) S. Krongelb, L. T. Romankiw, and J. A. Tornello, *IBM J. Res. Dev.,* 42, 575 (1998).

9) T. Mitsuyu, O. Yamakazi, K. Ohji, and K. Wasa, *Ferroelectrics,* 42, 233 (1982).

10) M. M. Viitanen, W. P. A. Jansen, R. G. van Welzenis, H. H. Brongersma, D. S. Brands, E. K. Poels, and A. Bliek, *J. Phys. Chem. B*, 103, 6025 (1999).

11) U. Bjoerksten, J. Moser, and M. Graetze, *Chem. Mater.,* 6, 858 (1994).

12) J. Tamaki, K. Shimanoe, Y. Yamada, Y. Yamamoto, N. Miura, and N. Yamazoe, *Sens. Actuat. B,* 49, 121 (1998).

13) Y. Jiang, S. Decker, C. Mohs, and K. J. Klabunde, *J. Catal.*, 180, 24 (1998).

14) R. V. Kumar, Y. Mastai, Y. Diamant, and A. Gedanken, *J. Mater. Chem.*, 11, 1209 (2001).

15) H. Wang, J. Z. Xu, J. J. Zhu, and H. Y. Chen, *J. Cryst. Growth,* 244, 88-94 (2002).

16) G. G. Condorelli, L. L. Costanzo, I. L. Fragala, S. Giuffrida, and G. Ventimiglia, *J. Mater. Chem.*, 13, 2409 (2003).

17) Z. Liu, Y. Yang, J. Liang, Z. Hu, S. Li, S. Peng, and Y. J. Qian, *J. Phys. Chem. B*, 107, 12658 (2003).

18) S. J. Chen, X. T. Chen, Z. L. Xue, L. H. Li, and X. Z. You, *J. Cryst. Growth*, 246, 169 (2002).

19) Y. Konishi, M. Motoyama, H. Matsushima, Y. Fukunaka, R. Ishii, and Y. Ito, *J. Electroanal. Chem.*, 559, 149 (2003).

20) T. Gao, G. W. Meng, Y. W. Wang, S. H. Sun, and L. Zhang, *J. Phys.: Condens. Matter*, 14, 355 (2002).

21) D. K. Sarkar, X. J. Zhou, A. Tannous, M. Louie, and K. T. Leung, *Solid State Commun.*, 125, 365 (2003).

22) C. L. Kitchens, M. C. McLeod, and C. B. Roberts, *J. Phys. Chem. B*, 107, 11331 (2003).

23) L. Armelao, D. Barreca, M. Bertapelle, G. Bottaro, C. Sada, and E. Tondello, *Thin Solid Films*, 442, 48 (2003).

24) W. H. Wang, Y. J. Zhan, and G. H. Wang, *Chem. Commun.*, 727 (2001).

25) M. Yang and J. J. Zhu, *J. Cryst. Growth*, 256, 134 (2003).

26) W. Z. Wang, G. H. Wang, X. S. Wang, Y. J. Zhan, Y. K. Liu, and C. L. Zheng, *Adv. Mater.*, 14, 67 (2002).

27) L. F. Gou and C. J. Murphy, *Nano. Lett.*, 3, 231 (2003).

28) M. H. Cao, C. W. Hu, Y. H. Wang, Y. H. Guo, C. X. Guo, and E. B. Wang, *Chem. Commun.*, 1884 (2003).

29) F. Fiévet, J.-P. Lagier, and M. Figlarz, *MRS Bull.*, 14, 29 (1989).

30) F. Fiévet, J.-P. Lagier, B. Blin, B. Beaudoin, and M. Figlarz, *Solid State Ionics*, 32-33, 198 (1989).

31) Z. C. Orel, E. Matijević, and D. V. Goia, *J. Mater. Res.*, 18, 1017 (2003).

32) Y. Zhao, J.-J. Zhu, J.-M. Hong, N. Bian, and H.-Y. Chen, *Eur. J. Inorg. Chem.*, 2004, 4072 (2004).

33) K. J. Carroll, J. U. Reveles, M. D. Shultz, S. N. Khanna, and E. E. Carpenter, *J. Phys. Chem. C*, 115, 2656 (2011).

34) J. Teichert, T. Doert, and M. Ruck, *Dalton Tran*s., 47, 14085 (2018).

35) M. Tsuji, S. Hikino, Y. Sano, and M. Horigome, *Chem. Lett.*, 38, 518 (2009).

36) M. Tsuji, S. Hikino, R. Tanabe, and Y. Sano *Chem. Lett.*, 38, 860 (2009).

37) M. Tsuji, S. Hikino, R. Tanabe, and D. Yamaguchi *Chem. Lett.*, 39, 334 (2010).

38) M. Tsuji, S. Hikino, R. Tanabe, M. Matsunaga, and Y. Sano, *CrystEngComm*, 12, 3900 (2010).

39) M. Tsuji, D. Yamaguchi, M. Matsunaga, and Md. J. Alam, *Cryst. Growth Des.*, 10, 5129 (2010).

40) M. Tsuji, M. Matsunaga, T. Ishizaki, and T. Nonaka, *CrystEngComm*, 14, 3623 (2012).

41) M. Tsuji, M. Matsunaga, H. Kumagai, M. Ogino, S. Hikino, Y. Yoshdia, and T. Ishizaki, *CrystEngComm*, 15, 1345 (2013).

42) M. Tsuji, K. Ikedo, K. Uto, M. Matsunaga, Y. Yoshida, K. Takemura, and Y. Niidome, *CrystEngComm*, 15, 6553 (2013).

43) M. Tsuji, M. Matsunaga, Y. Yoshida, M. Hattori, and T. Ishizaki, *CrystEngComm*, 15, 7062 (2013).

44) Y. Yoshida, K. Uto, M. Hattori, and M. Tsuji, *CrystEngComm*, 16, 5672 (2014).

45) P. Kanninen, C. Johans, J. Merta, and K. Kontturi, *J. Colloid Interface Sci.*, 318, 88 (2008).

46) I. Pastoriza-Santos, A. Sánchez-Iglesias, B. Rodrıguez González, and L. M. Liz-Marzán, *Small*, 5, 440 (2009).

47) F. Bonet, C. Guéry, D. Guyomard, R. Herrera Urbina, K. Tekaia-Elhsissen, and J.-M. Tarascon, *Int. J. Inorg. Mater.*, 1, 47 (1999).

48) F. Bonet, C. Guéry, D. Guyomard, R. Herrera Urbina, K. Tekaia-Elhsissen, and J.-M. Tarascon, *Solid State Ionics*, 126, 337 (1999).

49) W. P. Hsu, L. Rönnquist, and E. Matijević, *Langmuir*, 4, 26 (1988).

50) M. Ocaña and E. Matijević, *J. Mater. Res.*, 5, 1083 (1990).

51) D. V. Goia and E. Matijević, *Colloids Surf A. Physicochem. Eng. Asp.*, 146, 139 (1999).