One-Step Synthesis of Copper and Cupric Oxide Particles from the Liquid Phase by X-Ray Radiolysis Using Synchrotron Radiation

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The deposition of copper (Cu) and cupric oxide (Cu4O3, Cu2O, and CuO) particles in an aqueous copper sulfate (CuSO4) solution with additive alcohol such as methanol, ethanol, 2-propanol, and ethylene glycol has been studied by X-ray exposure from synchrotron radiation. An attenuated X-ray radiation time of 5 min allows for the synthesis of Cu, Cu4O3, Cu2O, and CuO nano/microscale particles and their aggregation into clusters. The morphology and composition of the synthesized Cu/cupric oxide particle clusters were characterized by scanning electron microscopy, scanning transmission electron microscopy, and high-resolution transmission electron microscopy with energy dispersive X-rays spectroscopy. Micro-Raman spectroscopy revealed that the clusters comprised cupric oxide core particles covered with Cu particles. Neither Cu/cupric oxide particles nor their clusters were formed without any alcohol additives. The effect of alcohol additives is attributed to the following sequential steps: photochemical reaction due to X-ray irradiation induces nucleation of the particles accompanying redox reaction and forms a cluster or aggregates by LaMer process and DLVO interactions. The procedure offers a novel route to synthesize the Cu/cupric oxide particles and aggregates. It also provides a novel additive manufacturing process or lithography of composite materials such as metal, oxide, and resin.

1. Introduction

Nanoparticles (NPs), of which sizes are in general below 100 nm, are potentially interesting for applications such as catalysis and optical devices, and the nucleation and fabrication of NPs are fundamental topics of scientific and engineering studies [1–5]. The optical properties of noble metal NPs have attracted considerable attention because these NPs exhibit extremely high absorption and scattering cross sections due to surface plasmon resonance. Metal NPs are currently synthesized by many methods such as sonochemical reaction [6–13], chemical aqueous reduction of metal ions [14–16], microwave-assisted synthesis [17], and UV-visible light or laser-induced photochemical reaction [18–23]. In these studies, the polylol reaction [24–28] plays a significant important role in NP synthesis. Recently, X-ray irradiation has also been used to generate NPs from liquid solution and tailor NP aggregation at desired locations [29–36]. To this end, noble metal NPs are typically used for surface enhanced Raman scattering spectroscopy (SERS) and plasmon-assisted photochemical reactions [1–4, 37]. Potential applications of NPs in a nanoscale material processing have been demonstrated in various fields such as catalysis, medicine, electronics, ceramics, pigments, and cosmetics [1–5].

Recently, copper (Cu) and copper oxide-nanostructured materials have attracted considerable attention due to their
fundamental importance and potential future applications [38–54]. Cupric oxide (Cu$_2$O, CuO) NPs are p-type semiconductor materials with a low band-gap energies. Recently, Poizot et al. [40] used cupric oxide NPs as anodes for lithium ion cells. Izaki et al. [47] produced solar cell plates consisting of Cu$_2$O and ZnO NPs. In addition, the cupric oxide NPs have sufficient space to absorb harmful gases. Zhang et al. demonstrated the application of copper oxide NPs as a gas sensor [51]. Thus, copper oxide NPs have additional noteworthy properties, such as nontoxicity, environmental friendliness, high stability, and recyclability. Many reports have provided methods to synthesize and characterize cupric oxide (Cu$_2$O, CuO) NPs [38–54]. For example, CuO NPs were prepared by Brookshier et al. using a spin-coating technique to control SiO$_2$ size [54] and Volanti et al. synthesized CuO flower-like nanostructures using a domestic hydrothermal microwave [38]. Clay and Cohen synthesized CuO nanoclusters within films of diblock copolymers [52], whereas Lisiecki and Pileni produced Cu and CuO NPs from inverse micelle solutions [53].

Radiolysis using synchrotron radiation (SR) has recently been investigated as a radiation-assisted method for the synthesis of NPs [29–36]. Due to the higher brilliance and controllability of X-ray from SR, the X-ray radiolysis has attracted much attention. To date, the synchrotron X-ray synthesis of Au, Fe, Ni, and AuPt alloyed NPs has been reported [29–36]. Thus, the syntheses of various metallic NPs by X-ray irradiation have been investigated. A few studies have reported the synthesis of Cu, Cu$_2$O, Cu$_4$O$_5$, and CuO materials using X-ray irradiation from SR. Recently, Oyanagi et al. [55] and Yamaguchi et al. [56] succeeded in producing Cu particles by exposing diverse copper solutions. Oyanagi et al. [55] used Cu(II) bis(1,1,1,5,5,5-hexafluoro-2,4-pentanedionato) solution with benzopinacol C$_8$H$_2$O$_3$, octylamine C$_8$H$_{17}$N and diethylene glycol diethyl ether, while Yamaguchi et al. [56] succeeded in producing Cu NPs by exposing copper sulfate (CuSO$_4$) liquid solution mixed with ethanol to X-rays. In the previous study, we simply demonstrated the synthesis of Cu NPs without any detailed analysis. Investigating the formation of Cu and cupric oxide NPs is required to understand the physical and chemical mechanisms and to develop engineering applications such as lithium ion cells [51], gas sensors [57], and solar cell plates [58].

In this paper, synchrotron X-ray radiation is used to synthesize cupric oxide and Cu particles from cupric sulfate solutions containing methanol, ethanol, 2-propanol, and ethylene glycol. Here, we investigate additive alcohol type dependence of cupric particles synthesized by X-ray irradiation. High-resolution scanning electron microscope (SEM), scanning transmission electron microscope (STEM), and high-resolution transmission electron microscope (HRTEM) image with energy dispersive X-ray spectroscopy (EDX) are used to obtain a deeper understanding of the formation mechanism. We also employ microscopic Raman spectroscopy to characterize the cupric particles obtained by X-ray irradiation.

| Table 1: Summary of solutions prepared for X-ray irradiation experiments. |
|---------------------------------------------------|------------------|------------------|
| Prepared solution                               | Base solution & amount | Additive material & amount |
| Solution #1 10% CuSO$_4$ solution 200 μL         | Methanol (CH$_3$COH) 10 μL | —                     |
| Solution #2 10% CuSO$_4$ solution 200 μL         | Ethanol (CH$_3$CH$_2$OH) 10 μL | —                     |
| Solution #3 10% CuSO$_4$ solution 200 μL         | 2-Propanol (CH$_3$CH(CH$_3$)OH) 10 μL | —                     |
| Solution #4 10% CuSO$_4$ solution 500 μL         | Ethylene glycol (HOC$_2$H$_3$OH) 0.5 μL | —                     |

2. Experimental

The stock solution was prepared by dissolving 18.6 g of CuSO$_4$·5H$_2$O (Wako Chemical, 99.99%) in 100 mL of doubly distilled water. A 100 mL aliquot of 10% CuSO$_4$ aqueous solution (solution #1) was prepared by diluting the stock solution. We siphoned off 200 μL 10% CuSO$_4$ aqueous solution into a microtube and added 10 μL ethanol to obtain the mixed solution (solution #3). In the similar way, other additives such as methanol (solution #2) and 2-propanol (solution #4) were also added into 10% CuSO$_4$ aqueous solution. In the case of X-ray irradiation experiment with ethylene glycol, the mix ratio of CuSO$_4$ solution and ethylene glycol is 500 μL to 0.5 μL (solution #5). We took off 18 μL of the mixed solution (including the CuSO$_4$ and ethanol) and added it into the X-ray irradiation system. The prepared solutions for X-ray irradiation experiments are summarized in Table 1.

The particles deposition experiments using the SR were performed on BL8S1 at the Aichi Synchrotron Radiation Center (Aichi SRC). The experimental setup is schematically shown in Figure 1 [36, 56]. The X-ray spectra evaluated by the calculation are also shown in the inset of Figure 1(a). As described in the previous work [36, 56], a silicon substrate (10 × 10 × 0.5 mm$^3$) was dipped into the solution prepared as shown in Table 1 (total amount of 18 μL). The Si substrate dipped in the solution was sealed by a 2 μm thick SiN membrane and polytetrafluoroethylene (PTFE) plates as shown in Figure 1(a). The sealed package including Si substrate dipped in the solution was fixed by the special steel used stainless (SUS) holder as schematically illustrated in Figure 1(a). In addition, a filtered patterned X-ray mask made of SUS was attached on the SUS holder to obtain the contrast by X-ray irradiation. The use of the X-ray mask allows us to easily get more, about tenfold, difference of the photon number in an area directly irradiated by X-ray with respect to the area covered with the X-ray mask, as shown in the spectra of Figure 1(a). The X-ray mask has some hole-arrays with various size through-holes. We chose the hole-array
3. Results and Discussion

When the silicon substrate with only CuSO₄ solution with no additives (solution #1) was exposed to X-rays, no particles were synthesized; particles and clusters were only generated in the presence of ethanol (solution #3). Figure 2 shows the SEM image after a 10% CuSO₄ containing ethanol (solution #3) was irradiated with X-rays for 5 min. Here, the X-ray was attenuated by 500 μm thick Al foil as shown in Figure 1 [36, 56]. As shown in Figure 2(a), a slit pattern is well defined. When magnified, the slit patterns were found to contain particles. The magnified SEM images of small particles and aggregates are represented in Figures 2(b)–2(d), showing that they are not detached from the Si substrate even after washing because of strong van der Waals interaction.

To confirm the composition of the synthesized particles, elementary analysis was carried out by EDX. The inset of the magnified SEM image in Figure 3(a) represents that the positions at which EDX are measured. The red squares correspond to the areas measured by EDX. Signals of elements C, Cu, and Si are observed in the spectra in Figures 3(a)–3(c), while an enlarged signal of O is seen in Figure 3(b). The Cu/O ratios in Figures 3(a)–3(c) are roughly estimated to be about 9/0.5, 7/2, and 9/0.5, respectively. Here, the EDX peak of Si is derived from the silicon substrate because the synthesized particles are small enough to pick up the Si elementary information as the background signal. As a result, these spectra suggest that the core particle is different from the additional particles which attach on it. Carbon (C) is in all particles, while sulfur (S) is not included in them. C is considered to be derived from contamination or the additive ethanol. C from ethanol is expected to play an important role in the nucleation process, in which the added ethanol facilitates the redox reaction and nucleates the Cu and cupric oxide particles [38].

To investigate the morphology and composition, STEM was performed and elemental maps were collected using...
Figure 2: (a) SEM image of a well-patterned CuSO$_4$ solution with ethanol (solution #3) after X-ray irradiation for 5 min. The dashed circle and arrows correspond to the slit patterned areas. (b) Magnified SEM image of Cu particles nucleated from the mixed solution under X-ray irradiation. ((c) and (d)) High-resolution SEM images of the nucleated particles. The arrow in (c) points out a cuboctahedral like particle.

Figure 3: In the inset of (a), three red squared frames (i), (ii), and (iii) on the high-resolution SEM image of the particle depict the EDX measurement positions. EDX spectra measured from the positions (i), (ii), and (iii) are shown in (a), (b), and (c), respectively. The position (ii) corresponds to the surface of the core particle, while the positions (i) and (iii) are the surfaces of attached particles.
EDX. Figure 4(a) shows the EDX spectrum of the cross-sectional area of a cluster generated by X-ray irradiation in the liquid solution shown in Figure 4(b), which is the STEM image. The spectra include necessary elemental information along with nonessential signals derived from the TEM grid mount materials (C, Al, Si, and Mo) and a Ga signal from the focused ion beam (FIB) milling process. In this manuscript, except the carbon C, elemental maps of Al, Mo, and Ga are not shown to avoid cumbersome maps of which provide nonessential phenomena. Figures 4(c)–4(f) show the elemental maps of Cu, O, Si, and C, respectively; the bright and dark contrasts correspond to high and low elemental abundance, respectively. Note that the elements Si and C remained from the polishing agent slurry and mold resin, respectively, after FIB milling. Thus, both elements reside around the particles near the TEM grid frame, as shown in Figures 4(e) and 4(f). This cross-sectional TEM elemental mapping indicates that all synthesized particles are at least including Cu as shown in Figure 4(c) and the element C does not play an important role in the ripping process of the particles. By comparison with Figures 4(c) and 4(d), the amount of oxygen (O) is higher included in the core particle, while oxygen distribution is barely visible in the small particles attached on the core particle (Figure 4(d)). One can see the single crystalline-like structure in all synthesized particles, because we recognized the several facets in morphology observation using TEM and SEM.

To understand the details of the elementary distributions in the synthesized particles, the magnified STEM images and EDX mappings are shown in Figure 5. Figure 5(a) shows the topographical STEM image of the cross section of the aggregate. Figures 5(b) and 5(c) show the EDX elementary mappings of Cu (red-colored) and O (orange-colored), respectively. The elemental mappings clearly show anisotropic distributions of Cu and O. O is almost detected in the original single crystalline core region, whereas Cu is mainly found in all particles, similarly to the results shown in Figures 4 and 5.

Furthermore, we collected the micro-Raman spectra in order to reveal crystallographic information. The photograph insets of Figure 6 show the respective aggregates consisting some particles. The labels (A), (C), and (D) correspond to the measurement positions of micro-Raman spectroscopies. The bright green positions correspond to the areas irradiated by the excitation laser. Figures 6(a)–6(d) show the micro-Raman spectra of (a) surface of metallic particle, (b) silicon substrate, (c) surface of core particle, and (d) particle on the core particle, respectively. The micro-Raman spectrometer is so sensitive that it can pick up the information at focal depth of about 500 nm. As shown in Figures 6(a) and 6(d), the broad
spectra are observed, indicating that the particles attaching on core particle are metal and are deduced that the nucleation, growth, or aggregate of Cu particles occurred.

Next, we focus on the spectrum of Figure 6(c). The peaks at 277, 324, 520, and 613 cm\(^{-1}\) appeared clearly in Figure 6(c). These peaks are possibly attributed to summation of three cupric oxides: CuO, CuO, and Cu\(_2\)O\(_3\) [38, 39]. Although a comparison of Raman spectra shown in Figures 6(a), 6(c), and 6(d) with that of the Si substrate in Figure 6(b) indicates that the peak at 520 cm\(^{-1}\) is attributed to the Si substrate, there remains the undeniable possibility that the peak at 520 cm\(^{-1}\) is derived from \(A_{lg}\) mode of Cu\(_2\)O\(_3\) because the particle volume is thick enough to shade the excitation laser reaching Si substrate. Accordingly to the previous studies of Debibichi et al. [39] and Volanti et al. [38], our observed Raman signals at 277, 324, and 613 cm\(^{-1}\) from the core particle correspond to Raman signals from Ag (283.8 cm\(^{-1}\)) and Bg (333.5 and 622.5 cm\(^{-1}\)) modes of CuO, respectively [38, 39]. In this study, the corresponding Raman shifts are a little bit lower than those reported in [40, 41]. As shown in the inset photograph of Figure 6(d) after the measurement of Raman spectra, the particles that the laser had been focused on were slightly melted. It is attributed that a red shift was induced by the heating effect from laser excitation. In addition, we understand the potential of the broad Raman peak structure ranging from 500 to 630 cm\(^{-1}\) being originated from CuO [38, 39]. The result may be explainable for CuO (at %) ratios of the aggregates by comparing with EDX measurements; however, in the present stage, it allows us to deduce that the synthesized particle is expected to be a composites cupric oxide consisting of CuO, CuO, and Cu\(_2\)O\(_3\), while some particles attached to the core particle were deduced to be Cu particles. Thus, in either case, we demonstrated one-step synthesis of Cu/cupric oxide and the aggregates induced from the liquid solution by direct X-ray irradiation.

Various investigations were performed to understand the mechanism of particle formation based on the interaction of sonochemical preparation [6–13], laser light [18–23], microwave irradiation [14–17, 38, 39, 41–51], and X-ray and γ-ray irradiation (radiolysis) [29–36, 55, 56]. For photochemical reactions, both thermal and electronic excitation effects were considered and discussed. To our knowledge, no report has discussed the particle formation mechanism from CuSO\(_4\) solution under X-ray irradiation. Therefore, we have attempted to understand the phenomenological chemical reaction process.

In our experiment, hydrated electrons, hydroxyl radicals, and hydrogen atoms were the reactive intermediates in the X-ray irradiation of the mixed aqueous solution. As described in previous studies, the X-ray irradiation from SR provides the proton radical and hydroxyl radical as the following [59–65]:

\[
\text{H}_2\text{O} \xrightarrow{\text{X-ray}} \text{e}_{aq}^\ast, \cdot\text{H}, \cdot\text{OH}, \text{H}_2\text{O}_2, \text{H}_2
\]  

As described above, in this study, the X-ray irradiation of only CuSO\(_4\) solution (without ethanol) did not result in the formation of any particles. This is because the proton and hydroxyl radicals provided by X-ray irradiation are not sufficient to form copper particles via reduction due to the hydration.

Upon the addition of an alcohol (e.g., methanol and ethanol), the \(\cdot\text{OH}\) and \(\cdot\text{H}\) radicals are scavenged to yield reducing organic radicals. In the case where ethanol is added to the solution, proton and hydroxyl radicals react as follows [59–65]:

\[
\cdot\text{OH} (\cdot\text{H}) + \text{CH}_3\text{CH}_2\text{OH} \rightarrow \text{H}_2\text{O} (\text{H}_2) + \cdot\text{CH}_2\text{OH} \quad (2a)
\]

\[
\text{CH}_3\text{CH}_2\text{OH} \xrightarrow{\text{X-ray}} \text{CH}_3\text{CHO} + 2\text{e}^\pm + 2\text{H}^+ \quad (2b)
\]

\[
(\text{CH}_3\text{CH}_2\text{OH})_n \xrightarrow{\text{X-ray}} [(\text{CH}_3\text{CH}_2\text{OH})_n]^\ast + \text{e}^\pm \quad (2c)
\]

\[
(\text{CH}_3\text{CH}_2\text{OH})_n \xrightarrow{\text{X-ray}} (\text{CH}_3\text{CH}_2\text{OH})_{n-1}^\ast \text{H}^+ + \text{CH}_3\text{CHO} + \text{e}^\pm \quad (2d)
\]
The several candidates of associated reactions are taking place in the mixed solution under the X-ray irradiation, as follows [58, 63–65]:

\[
\begin{align*}
\text{Cu}^{2+} + 2e^- & \rightarrow \text{Cu}^0 \quad (3a) \\
\text{Cu}^{2+} + 2\text{CH}_3\text{CHO} + 2(\text{OH}^-) & \rightarrow \quad (3b) \\
\text{Cu}^0 + 2\text{CH}_3\text{COOH} + \text{H}_2 & \rightarrow \quad (3c) \\
\text{Cu}^{2+} + 2(\text{OH}^-) & \rightarrow \text{Cu(OH)}_2 \quad (3d) \\
\text{Cu(OH)}_2 & \rightarrow \text{CuO} + \text{H}_2\text{O} \quad (3e) \\
\text{Cu(OH)}_2 + \text{Cu} & \rightarrow \text{Cu}_2\text{O} + \text{H}_2\text{O} \quad (3f) \\
2\text{CuO} + \text{Cu}_2\text{O} & \rightarrow \text{Cu}_4\text{O}_3
\end{align*}
\]

Here, the \(\text{CuO}, \text{Cu}_2\text{O}, \text{Cu}_4\text{O}_3\), and \(\text{Cu}\) particles are finally reduced and deposited onto the silicon substrate and SiN membrane.

Here, we can obtain cubic, cuboctahedral, and octahedral particles as shown in Figure 2. The nucleation and growth process can be basically explained by LaMer model [66] and the aggregation mechanism derived from the Derjaguin, Landau, Verwey, and Overbeek (DLVO) model [67, 68]. In addition, for the silicon substrate, the H-terminated Si substrate produced during the X-ray irradiation may play an important role in particle synthesis, as described in [46].

To investigate the functional group dependence of particle synthesis initiated by X-ray radiolysis, we added methanol, 2-propanol, or ethylene glycol to 10% \(\text{CuSO}_4\) solution. The concentration of the additives of methanol and 2-propanol was the same as the case of X-ray irradiation with ethanol. The mixture ratio of the 10% \(\text{CuSO}_4\) solution and ethylene glycol was 500 \(\mu\text{L}\) to 0.5 \(\mu\text{L}\) (solution #5), while the ratio of the others (methanol, ethanol, and 2-propanol) was 200 \(\mu\text{L}\) to 10 \(\mu\text{L}\). As a result, the synthesis of particles is confirmed. The SEM images and EDX spectra and micro-Raman spectra of morphologies of particles and surface of Si substrate after X-ray irradiation of \(\text{CuSO}_4\) solution with methanol, 2-propanol, and ethylene glycol are shown in Figures 7–9, 10–12, and 13–15, respectively. We found that the single crystalline like particles and their aggregates are also formed in the cases of additive methanol, 2-propanol, and ethylene glycol, respectively. In addition, the dappling surfaces, where the bright and dark contrasts are randomly distributed in Figures 10 and 13, on irradiated area appear in the both cases of X-ray
irradiation under the application of 2-propanol and ethylene glycol. According to the EDX analysis (not shown here), the dappled shade area is consisting of Si. This result indicates that dips are formed in the dappled shade area by etching process of Si due to X-ray radiolysis with 2-propanol and ethylene glycol.

To confirm the composition of the synthesized cupric particles with methanol and 2-propanol, we analyzed the synthesized particles or clusters by EDX spectroscopy, as shown in Figures 8 and 11, respectively. By comparison with these spectra, the EDX spectra indicate that the synthesized particles consisted mostly of Cu. Next, the micro-Raman
spectra of the aggregate of these particles are shown in Figures 9 and 12. Comparing the spectrum in Figure 9(c) with that in Figure 12, we found the two spectra are almost the same and are deduced to be derived from Cu$_4$O$_3$. The spectra shown in Figures 9(a) and 9(b) are similar with Figure 6(c) of the case of particles synthesized from CuSO$_4$ solution with additive ethanol (solution #2). These results indicate that the composition of the particles is almost the same and is expected to be consisting of CuO and Cu$_2$O. The particles attached on the core particles are expected to be Cu$_2$O particles.

Next, we analyzed urchin-like NPs synthesized by X-ray radiolysis with ethylene glycol (solution #5) by EDX spectroscopy. Figure 14 indicates that both the outshoot and core consisted of cupric oxide. The outshoot seems to contain a higher proportion of carbon C than the core. The micro-Raman spectra of these particles synthesized from solution with ethylene glycol (solution #5) are shown in Figure 15. Unfortunately, the particles were burned after the micro-Raman spectroscopy was measured as shown in the inset of Figure 15. Comparing the spectrum in Figure 15 with the other spectra depicted in Figures 6, 9, and 12, we found that the obtained spectrum is expected to be derived from the composite consisting of CuO and Cu$_2$O.

We investigate the dependence of the deposited particle size on the kinds of additive alcohol. Here, to simplify the estimation of particle size, we evaluated the maximum length of the synthesized particles because their shapes were various and diversified. The probability densities of the particles
synthesized from X-ray radiolysis with (a) methanol, (b) ethanol, (c) 2-propanol, and (d) ethylene glycol are plotted on a function of particle length in Figures 16(a)–16(d), respectively. The synthesized particles under the X-ray irradiation time of 5 min with various additives are similar in size. The result indicates that the irradiation time of 5 min is long enough to complete the series of nucleation, growth, and aggregation of particles which began and proceeded under
the competition of LaMer process [66] and DLVO interaction [67, 68]. Figure 17 shows the dependence of the synthesized particle length on the kinds of alcohol. It seems that the particle length increases with the order: methanol, ethanol, 2-propanol, and ethylene glycol. The trend of synthesis of particles is derived from the radical activity of alcohol, being consistent with the previous studies [65]. On the basis of the high-resolution SEM, TEM, and micro-Raman spectroscopy, we confirmed the synthesis of not only Cu particles but also higher-order aggregates consisting of cupric oxide and copper particles from liquid solution under X-ray irradiation.

As cupric oxide and copper particles are receiving considerable interest due to potential uses as anodes lithium ion cells, gas sensors, and p-type semiconductor materials, this X-ray irradiation method can provide a novel additive manufacturing process [69–71] for the devices and systems such as solar cells and plasmonic sensor in μTAS. In addition, this study sheds light on developing a three-dimensional printing with both metal and resin as a novel Lithographie Galvanomformung Abformung (LIGA) process [72].

4. Conclusion

The present work demonstrates that Cu/cupric oxide particles can be obtained by irradiating a CuSO₄ solution containing alcohol with SR. The synthesized cubic, cuboctahedral, and octahedral NPs aggregate to form higher-order nano/microstructures. High-resolution SEM, TEM, and micro-Raman spectroscopy analyses demonstrated that the core particles consisted of Cu₂O, CuO, and Cu₄O₂, while the particles attached to the core particles were copper. The additive alcohol helps the copper ions to reduce the copper colloids, cupric oxide particles, and Cu/cupric oxide aggregates. Two potential issues have arisen: (a) the synthetic process including the nucleation and formation of particles from the liquid solution by X-ray irradiation with/without ethanol or other alcohols and (b) the coagulation of the Cu/cupric oxide particles. These issues are worthy of further investigation.

The direct X-ray irradiation using an SR source can provide an alternative route to explore the novel physical mechanism of liquid/solid interlayer reaction process from the liquid phase. The higher-order nano/microstructure consisting of metallic particles and metal oxides particles offer an opportunity to conveniently and directly induce catalysis and probe surface enhanced Raman scattering. Particularly, cupric oxide particles have attracted much attention for application of gas sensor and solar cell. This one-step direct deposition process can be used in new devices such as “Lab-on-a-chip” and “μTAS: micron-Total-Analysis-System” applications for chemical and environmental analyses. In
Figure 14: EDX spectra of the red squared areas (a) and (b) on the synthesized particles observed in Figure 13(d).

Figure 15: Micro-Raman spectrum of the particle aggregate synthesized from CuSO₄ solution mixed with ethylene glycol (solution #5). The inset photographs display the green laser position on the measurement area. Indexes were taken from the following Raman spectrum patterns: Cu₂O, CuO, and Cu₄O₃ [38, 39].
addition, the development of this technique combined with the microfluidic chip enables integrating three-dimensional printing which can fabricate micro- or nanoscale structure consisting of metal and resin.

**Competing Interests**

The authors declare that they have no competing interests.

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**Figure 16:** Probability densities of the particles synthesized CuSO₄ mixed with (a) methanol, (b) ethanol, (c) 2-propanol, and (d) ethylene glycol, respectively, revealing the particle length distributions.
Particle length (µm)

Figure 17: Additive alcohol dependence of synthesized particle length. Met., Eth., 2-Pro., and Et.-gly. correspond to methanol, ethanol, 2-propanol, and ethylene glycol, respectively.

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