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著者	Kawasaki Hideya, Kosaka Yuka, Myoujin Yuki, Narushima Takashi, Yonezawa Tetsu, Arakawa Ryuichi
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COMMUNICATION

Microwave-assisted polyol synthesis of copper nanocrystals without using additional protective agents†Hideya Kawasaki,^{*a} Yuka Kosaka,^a Yuki Myoujin,^a Takashi Narushima,^b Tetsu Yonezawa^b and Ryuichi Arakawa^a

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We report the synthesis of 2 nm copper nanocrystals (Cu NCs) via a microwave-assisted polyol method without using additional protective and reducing agents. The Cu NCs are oxidation resistant and exhibit photoluminescence and highly stable properties in a colloidal dispersion.

Metal nanocrystals (NCs) and metal nanoclusters with sizes less than 3 nm have attracted considerable attention in many areas of physics, chemistry, materials science, and bioscience because their physico-chemical properties differ from those of larger metallic nanoparticles. Recently, extensive studies have been focused on gold (Au) and silver (Ag) with sizes less than 3 nm because of their relative ease of synthesis through chemical reduction of their salts in solutions.¹ In particular, metal nanoclusters with sizes of about 1 nm show various interesting molecular-like features such as discrete electronic states and size-dependent fluorescence.¹ Copper (Cu) is highly conductive, quite inexpensive, and widely used in industries. Cu NCs (<3 nm in size) are suitable for use in printed electronics and catalytic materials because these NCs exhibit high catalytic properties and can be annealed at low temperatures to form low-resistance conductive films. However, Cu nanoparticles, thus far obtained *via* chemical reduction, are generally 10–100 nm in size.^{2–11} Compared to the extensive studies on Au and Ag NCs, very few attempts have been made to synthesize Cu NCs less than 3 nm in size.^{12–17} This is because single-nanosized Cu inherently suffers from unstable colloidal dispersion of its particles and easy surface oxidation on exposure to air.⁷ It is widely believed that the use of strongly bonded protective agents or template structures is essential for the solution synthesis of Cu NCs,^{12–17} but the use of strongly bonded protective agents may cause the surface deactivation of Cu NCs. More recently, we have developed a preparation

method for platinum (Pt) and palladium (Pd) nanoclusters without using additional protective agents for the highly active catalyst.¹⁸

Herein, we report the synthesis of fluorescent Cu NCs of approximately 2 nm in size *via* microwave-assisted polyol synthesis. Interestingly, we were able to synthesize the Cu NCs without using additional protective and reducing agents; further, the use of a non-aqueous solvent as the reaction medium minimizes the oxidation of the Cu surface. The resulting Cu NCs were highly resistant to oxidation and exhibited photoluminescence and highly stable properties in a colloidal dispersion.

As in a typical synthesis, 2 mL of ethylene glycol solution containing 38 mM CuCl₂ was mixed with 2 mL of ethylene glycol solution containing 0.5 M NaOH in a glass tube by magnetic stirring for 10 min. The solution mixture was placed in a microwave oven and was vigorously stirred for 30 min at a reaction temperature of 185 °C under a N₂ atmosphere. As the solution mixture underwent a reaction, its colour changed from light blue to light brown within a few minutes. The schematic diagram to illustrate the process of the preparation of these Cu NCs is shown in Fig. S1 of ESI.† After the reaction, 1 mL of HCl aqueous solution (1 M) was mixed with the resultant solution. The Cu NCs were extracted into the diethyl ether phase and were dried using a rotary evaporator at a low temperature of 30 °C. The dried Cu NCs, thus obtained, could be dispersed again in various solvents (*i.e.* ethylene glycol, *N,N*-dimethylformamide, ethanol, and water).

Transmission electron microscopy (TEM) images of the dried Cu NCs showed that the average size of the NC was 2.3 ± 0.25 nm (Fig. 1). The TEM image exhibited distinct and non-aggregated nanoparticles, in spite of being synthesized from dried Cu NCs. The high-magnification TEM images of Cu NCs showed that the crystal lattice fringes are 0.2 nm apart, which agrees with the *d* value of the (111) planes of the metallic Cu crystal (ESI†, Fig. S2). Dynamic light scattering (DLS) measurements of the Cu NCs indicated the presence of non-aggregated Cu NCs having a size of less than 2 nm (ESI†, Fig. S3). The TEM images and DLS results indicate the formation of Cu NCs having a size of approximately 2 nm *via* microwave-assisted polyol synthesis without using additional protective and reducing agents.

^a Department of Chemistry and Materials Engineering, Faculty of Chemistry, Materials and Bioengineering, Kansai University, 3-3-35 Yamate-cho, Suita-shi, Osaka 564-8680, Japan. E-mail: hkawa@kansai-u.ac.jp

^b Division of Materials Science and Engineering, Faculty of Engineering, Hokkaido University, Kita13, Nishi8, Kita-ku, Sapporo, Hokkaido 060-8628, Japan

† Electronic supplementary information (ESI) available: UV-visible absorption spectra of Cu NCs at different reaction temperatures and with additional amounts of NaOH, DLS, LDI-MS results of Cu NCs. See DOI: 10.1039/c1cc12346g

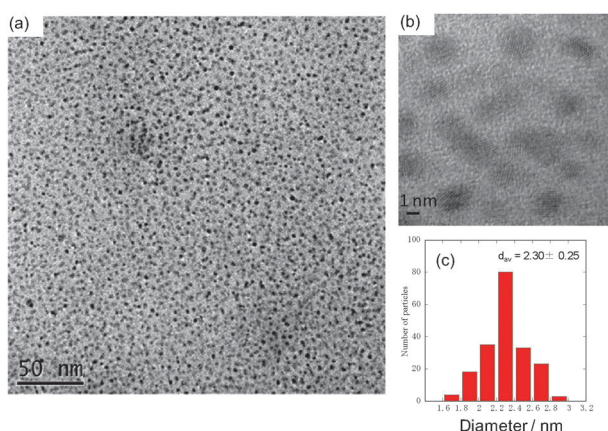


Fig. 1 (a) Low magnification TEM image of Cu NCs from the dried samples, (b) high magnification TEM image of Cu NCs, and (c) the histogram of particle sizes.

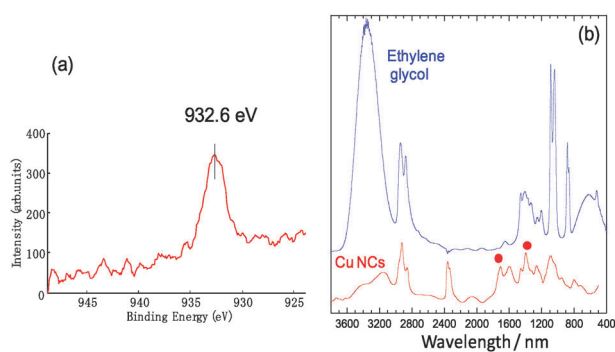


Fig. 2 (a) XPS spectrum of dried Cu NCs and (b) IR spectra of dried Cu NCs and ethylene glycol.

The oxidation state of the dried Cu NCs was investigated through X-ray photoelectron spectroscopy (XPS) (Fig. 2a). The Cu $2P_{3/2}$ peak (932.6 eV) is predominantly attributed to zero-valent copper, consistent with the peak (~ 932.4 eV) obtained in a previous report, attributed to zero-valent Cu NCs of approximately 2 nm in size.¹⁶ Interestingly, a previously reported peak (~ 934 eV), associated with CuO obtained from the Cu surface oxidation, was not observed in our study. Further, the infrared (IR) spectra of the dried Cu NCs showed no adsorption peak associated with the Cu–O stretches around 630 cm^{-1} (Fig. 2b).⁷ The XPS and IR spectra of the Cu NCs indicate suppression of the surface oxidation of Cu NCs even three months after the synthesis of the Cu NCs. It should be noted that the Fourier transform (FT)-IR spectra of the Cu NCs showed characteristic absorption peaks of aldehydes and ketones at 1707 cm^{-1} and 1395 cm^{-1} , respectively (denoted by closed circles in Fig. 2b); these peaks indicate that ethylene glycol is oxidized during the reduction of CuCl_2 . The oxidation of ethylene glycol also results in the decrease in the absorption intensity of OH groups around $3000\text{--}3600\text{ cm}^{-1}$.

Very recently, it was reported that Cu NCs (or Cu nanoclusters) with sizes less than 3 nm show molecular-like properties such as well-defined UV-vis absorption and photoluminescence.^{12,13,15} Such molecular-like properties were also observed for the Cu NCs synthesized in this study. Fig. 3a shows the UV-vis spectrum of Cu NCs in ethanol, with three absorption bands

at 212 nm, 231 nm, and 275 nm. These absorption bands are nearly consistent with those of other Cu NCs synthesized using different protective agents, at 212 nm, 231 nm, and 296 nm.¹³ No localized surface plasmon peak was observed around 550 nm for the Cu NCs, which supports the theory that Cu NCs less than 3 nm in size were synthesized.¹⁹ The Cu NCs in ethanol show a blue emission at 475 nm under 350 nm excitation (Fig. 3b). The blue fluorescence was observed for Cu NCs in various solvents such as ethylene glycol, *N,N*-dimethylformamide, ethanol, and water (Fig. 3a). The absolute quantum yield (QY) for the photoluminescence of Cu NCs in an ethylene glycol solution was 0.65%. The fluorescence and UV-vis absorption spectra of Cu NCs remained constant even 21 days after synthesis (ESI†, Fig. S4), indicating the stable properties of Cu NCs. The matrix-assisted laser desorption/ionization mass spectrometry (MALDI-MS) of the Cu NCs showed the characteristic negative ion peaks of Cu at m/z 607 with copper isotopic distribution of a mass difference of 2 Da. The ion peaks (m/z 607) can be assigned to atomic nanocrystals of $[\text{Cu}_9 + \text{Cl}]^-$ (ESI†, Fig. S5). The photoluminescence may be ascribed to the subnanometre-sized Cu nanoclusters as well as the Cu NCs with sizes of about 2 nm.

High reaction temperatures ($\sim 185\text{ }^\circ\text{C}$) and the addition of NaOH were essential to the microwave-assisted polyol synthesis of Cu NCs done in this study; the reaction did not proceed at a low temperature of $160\text{ }^\circ\text{C}$ even with the addition of NaOH. Further, in the absence of NaOH, the Cu NCs did not form even at $185\text{ }^\circ\text{C}$ (ESI†, Fig. S6). The high concentration of NaOH helps both the formation of $[\text{Cu}(\text{OH})_4]^{2-}$ and $[\text{Cu}(\text{OCH}_2\text{CH}_2\text{O})_2]^{2-}$, and also causes the dehydration of ethylene glycol to aldehyde at high temperatures.^{3,8,9} The resultant aldehyde can reduce Cu_2O to metallic Cu at high reaction temperatures of more than $165\text{ }^\circ\text{C}$.⁹ However, previous polyol synthesis of Cu nanoparticles in the absence of protective agents yielded large particle sizes of the order of a few hundred nanometres, and the agglomeration was more intense, even under the optimal reaction conditions of high concentration of NaOH and high reaction temperatures.⁹ Even though the previous microwave-assisted polyol synthesis of Cu nanoparticles was improved to produce smaller Cu nanoparticles, the nanoparticles sizes were still in the range of $10\text{--}50\text{ nm}$,^{4,10} which is much larger than the Cu NCs of approximately 2 nm in size.

To understand how the Cu NCs formed by the present microwave-assisted polyol synthesis are highly stable in colloidal dispersion and are oxidation resistant, it is beneficial to examine the surface organic layers of the Cu NCs. Thus, we investigate the Cu NCs extracted into the diethyl ether phase *via* MALDI-MS. Surprisingly, the MALDI-MS of Cu NCs revealed a group of peaks around m/z 1400. The groups of ion peaks have repeat units of 44 Da equivalent to a unit of ethylene oxide; hence, the peaks can be assigned to poly(ethylene glycol)s (PEGs) (Fig. 3c). This assignment implies that ethoxylation of ethylene glycol occurs during the reduction of CuCl_2 in the microwave-assisted polyol synthesis of Cu NCs, leading to the production of PEGs. Although the mechanism of ethoxylation in the polyol process is currently not clear, ethoxylation of ethylene glycol may progress with the assistance of the alkaline catalysts of NaOH

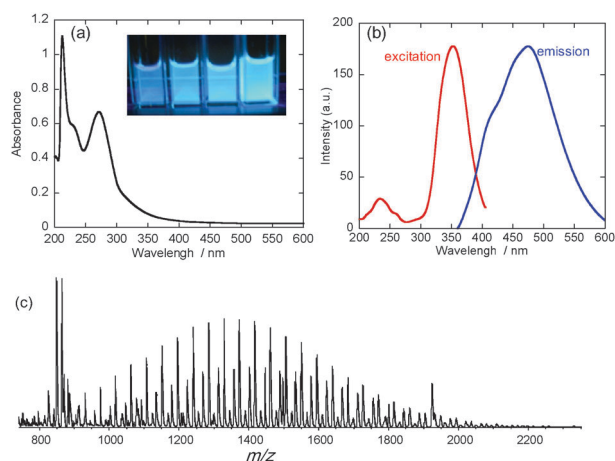


Fig. 3 (a) UV-vis spectrum of Cu NCs in ethanol. Photographs showing photoluminescent Cu NCs under UV light in water, ethanol, *N,N*-dimethylformamide, and ethylene glycol (left-to-right). (b) Excitation (red curve, $\lambda_{em} = 475$ nm) and emission (blue curve, $\lambda_{ex} = 355$ nm) spectra of Cu NCs in ethanol. (c) MALDI-MS spectrum of PEGs-stabilized Cu NCs.

and copper catalysts at a temperature of 185 °C.²⁰ The resultant PEGs can be adsorbed on the surface of Cu NCs, restricting the excessive growth and surface oxidation of the NCs.

In summary, we established a simple approach for synthesizing Cu NCs with sizes less than 3 nm with blue fluorescence *via* microwave-assisted polyol synthesis without using additional protective agents. The as-prepared Cu NCs can be extracted into the volatile diethyl ether phase. As a result, dried Cu NCs can be easily obtained by evaporation of the solvent at low temperatures, and re-dispersion of the dried Cu NCs is possible in various polar solvents. The synthesis of Cu NCs along with the ethoxylation reaction of ethylene glycol resulted in the formation of Cu NCs that are highly stable in a colloidal dispersion, because of the PEGs, and the suppression of the surface oxidation of Cu NCs.

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