

FACILE AND GREEN SYNTHESIS OF STABLE AQUEOUS DISPERSIONS OF NARROWLY DISTRIBUTED COPPER NANOPARTICLES

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Copper nanoparticles (Cu NPs) without aggregation and oxidation in solvents are highly desired in the fields of antibiosis, electronics, lubrication, heat transfer, etc. Here, we facilely prepared ~ 3 nm Cu NPs with narrow size distribution in water at a low temperature of 45 °C under ambient atmosphere, using L-ascorbic acid and cetyltrimethylammonium bromide (CTAB) as a reductant and a capping agent, respectively. The size and shape of the Cu NPs can be controlled by changing the reaction time, molar ratio of L-ascorbic acid to copper chloride, and concentration of CTAB. In addition, the Cu NP aqueous dispersions showed good stability after one month of storage under ambient atmosphere because of their great resistance against aggregation and oxidation. This study opens a facile and green way to prepare stable Cu NP aqueous dispersions for their practical applications.

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1. Introduction

Metal nanoparticles (NPs) have attracted considerable attention owing to their unique biological, electric, magnetic, optical and catalytic properties, which are different from those of bulk metals [1-5]. In particular, copper (Cu) NPs exhibit extraordinary properties and have potential applications in a few fields, such as antibiosis [6-9], thermal transfer [10-12], electronics [13], catalysis [14-16], optics [17-18], and lubrication [19-20].

The methods for preparing Cu NPs are classified into three main types: liquid phase method [3-4, 21], gas phase method [22-23], and solid phase method [24-25], which are based on the chemical reduction of Cu ions in liquids, the homogeneous nucleation of Cu in gas phase and subsequent coagulation during cooling process, and the size reduction of bulk Cu, respectively. It is more proper to prepare Cu NPs by the liquid phase method rather than the solid phase and gas phase methods, because of its excellent features in simple facilities, low temperature, the high purity and small size of the Cu NPs, etc [26-27].

Most of the synthesis of the Cu NPs in liquid phase involve the use of strong reducing

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reagents, such as hydrazine [28-29], sodium borohydride [30-31] and sodium hypophosphite [32]. To prevent the surface oxidation of the Cu NPs, the reaction solutions are carefully protected under inert gases, and a few organic solvents, such as ethylene glycol [33], dimethylether [34-35] and tetrahydrofuran [34-35], are usually used as reaction mediums. Silica [24] and various organic capping agents, such as cetyltrimethylammonium bromide (CTAB) [10, 28], polyvinylpyrrolidone (PVP) [36-37], and polyallylamine (PAAM) [4, 38], are also coated on the surfaces of the Cu NPs to prevent their oxidation as well as agglomeration.

Cu NP dispersions and inks still present considerable chemical challenges, though the great progress on their preparations [3, 39-41]. The Cu NPs in solvents more intend to agglomerate than NPs from other metals, for instance well-known gold colloids, due to the lower surface charges [3, 10, 40]. Cu NPs are also more chemically active than gold and silver NPs, which leads them to be more easily oxidized, especially in water [3, 42-43]. Novel methods for preparing stable Cu NP dispersions are still highly desired [40, 44-45].

Herein, we develop a facile method to obtain a ~ 3 nm Cu NP aqueous dispersion by heating a solution of Cu salt in the presence of L-ascorbic acid and CTAB at a low temperature of 45 °C. It is also a green method due to the use of L-ascorbic acid and water as a mild reductant and a solvent, respectively, as well as the preparation under ambient atmosphere without the protection of inert gas. In addition, the Cu NP dispersion showed good stability after one month of storage under ambient atmosphere, because of the great resistance against aggregation and oxidation.

2. Experimental details

2.1. Materials and chemicals

L-ascorbic acid, CTAB and copper chloride dihydrate ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$) were purchased from Sigma-Aldrich. Deionized water was obtained from a Barnstead E-pure water purification system.

2.2. Synthesis of Cu NP aqueous dispersions

A typical synthesis procedure was described as follows. First, 25 mL of 0.06 M CuCl_2 and 0.01 M CTAB aqueous solution and 25 mL of 0.8 M L-ascorbic acid and 0.01 M CTAB aqueous solution were prepared with the assistance of ultrasonication and stirring. After that they were mixed and then heated at 45 °C for 28–48 hours under violent magnetic stirring. The mixed solution containing 0.4 M L-ascorbic acid, 0.03 M CuCl_2 and 0.01 M CTAB turned from green/light brown to red, which indicated the generation of Cu NPs. The pure Cu NP aqueous dispersions were obtained by centrifugation at 10,000 rpm for 3 times and dialysis for 1 hour using a dialysis membrane to remove excessive CuCl_2 , CTAB and L-ascorbic acid. The size and shape of the Cu NPs were controlled by changing reaction time and the concentrations of the raw materials.

2.3. Characterizations

Transmission electron microscope (TEM) images were obtained using a JEOL 3011. The TEM specimens were prepared by dripping a drop of Cu NP solution onto a carbon-coated Cu or gold grid and allowing it to dry in air. The selected area electron diffraction (SAED) patterns of the Cu NPs were taken using the carbon-coated gold grids. The average diameters of the Cu NPs were calculated by counting the NPs in the TEM images. Optical photographs were taken by a Nikon

Coolpix L820 digital camera. UV-Vis absorbance spectra were obtained using an 8453 UV-Vis Chem Station spectrophotometer (Agilent Technologies, USA).

3. Results and discussion

3.1. The effect of reaction time on Cu NPs

L-ascorbic acid is a mild reductant and can reduce metal ions, such as Pt^{4+} , Au^{3+} , Cu^{2+} and Ag^+ [36]. Here, we easily prepared Cu NPs with various reaction time (Fig. 1), because of the high reducing activity of L-ascorbic acid even at the low temperature of 45 °C. With the increasing reaction time from 28 to 48 hours, the average size of the NPs increased slowly from 2.3 ± 0.27 to 3.3 ± 0.38 nm (Fig. 1A-F). The NPs were also discrete and mostly spherical with narrow size distributions. High-resolution TEM revealed that the lattice spacing of the NPs was 0.21 nm, which corresponded very well to the spacing of (111) lattice planes in face-centered cubic (FCC) Cu (Fig. 1G). The SAED pattern further showed that the first, second, third and fourth diffraction rings (from center to outermost) corresponded to the lattice spacing of 0.21, 0.18, 0.13 and 0.11 nm, respectively (Fig. 1H). This sequence was consistent with the lattice planes of (111), (200), (220), and (311) in metallic FCC Cu. The UV-Vis absorbance spectra were further used to characterize the Cu NPs (Fig. 1I). The surface plasmon peak of Cu NPs has been reported to appear at ~ 570 nm [46]. However, when the particle size is decreased to < 4 nm, the distinctive plasmon peak is known to be broadened with lower intensity and replaced by a featureless absorbance, which increases monotonically towards higher energies [47-49]. When increasing the reaction time, the absorbance peak of the Cu NPs broadened and varied from 420 to 450 nm with a red-shift rather than at ~ 570 nm, indicating the existence of smaller Cu NPs with the size of < 4 nm that was consistent with Fig. 1A-C [50-53]. Cumulatively these findings confirmed that the as-synthesized NPs were made from small-sized metallic Cu rather than from Cu oxides.

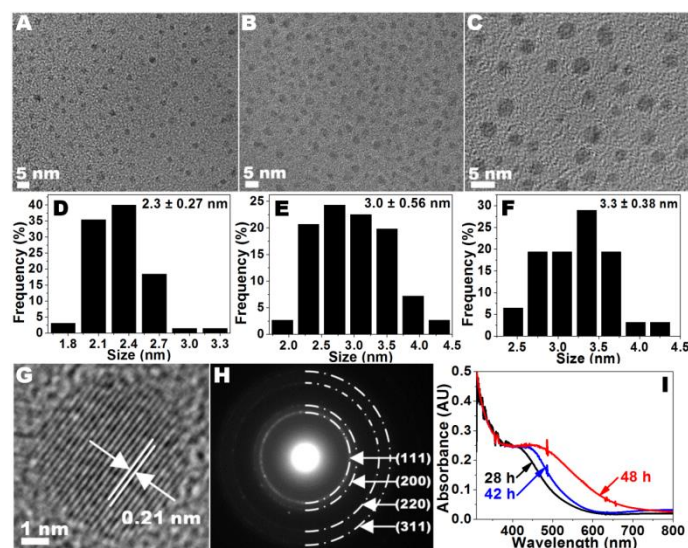


Fig. 1. (A-C) TEM images, (D-F) corresponding size distribution histograms, and (I) UV-Vis absorbance spectra of Cu NPs synthesized at 45 °C for (A, D) 28, (B, E) 42, and (C, F) 48 hours using 0.03 M CuCl_2 , 0.4 M L-ascorbic acid and 0.01 M CTAB solution. (G-H) showed the high-resolution TEM image of a Cu NP and selected area electron diffraction pattern of the Cu NPs corresponding to (B).

3.2. The effect of CTAB on Cu NPs

Besides resisting against aggregation and oxidation, Cu NPs should be capable of subsequent assembly process for electronic devices [49, 54-56]. Unlike silica and other organic capping agents, CTAB is a more labile surface ligand that is conducive to subsequent assembly, though its long hydrocarbon chain can hinder interparticle electron transport [57]. Here, we prepared Cu NPs using CTAB as capping agent (Fig. 2). Without the use of CTAB, the Cu NPs showed an average size of 9.6 ± 1.48 nm and a wide size distribution range of 4–18 nm with a little agglomeration, and not all the Cu NPs were spherical (Fig. 2A and D). However, when the CTAB concentration was 0.005 M, the size distribution of the Cu NPs became narrow with a smaller average size of 5.1 ± 1.21 nm and the Cu NPs became much more spherical and discrete (Fig. 2B and E). When increasing the concentration of CTAB to 0.01 M, the average size of the Cu NPs decreased to 3.3 ± 0.38 nm (Fig. 2C and F). The electron-deficient ammonium nitrogen groups of CTAB easily coordinated with the Cu NPs whose surfaces usually bore negative charges because of their electrical attraction [5]. Therefore, with the increase of CTAB concentration, the NPs were wrapped with more CTAB, the growth of the NPs was restricted by electrostatic and steric forces, and the size of the NPs decreased [28, 39]. CTAB not only prevented the agglomeration of the Cu NPs but also changed the shape and size of the Cu NPs [39], which was also proven in the growth of other metal NPs [58-60].

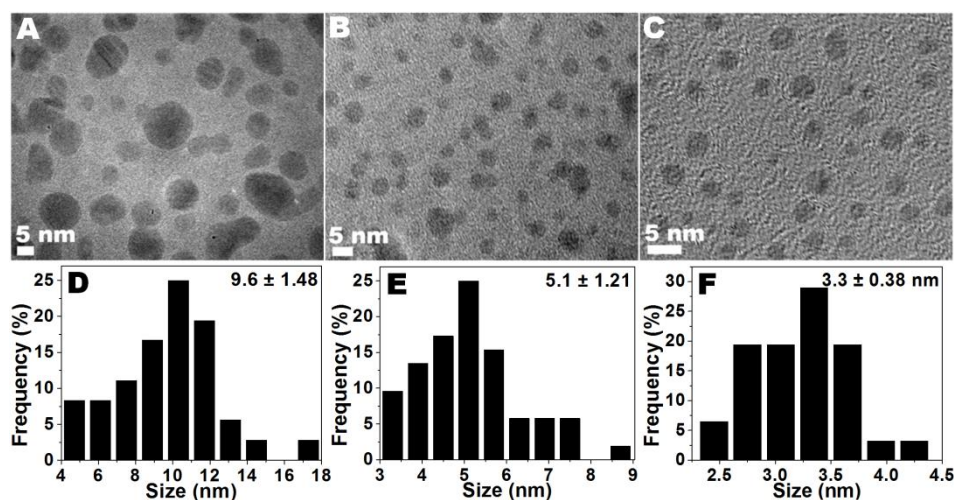


Fig. 2. (A-C) TEM images, and (D-F) corresponding size distribution histograms of the Cu NPs synthesized at 45 °C for 48 hours using (A, D) 0, (B, E) 0.005, and (C, F) 0.01 M CTAB solutions (CuCl_2 : 0.03 M, L-ascorbic acid: 0.4 M).

3.3. The effect of L-ascorbic acid on Cu NPs

We also investigated the effect of the molar ratio of L-ascorbic acid to CuCl_2 on the growth of Cu NPs (Fig. 3). With the same CuCl_2 concentration of 0.03 M, when increasing the concentration of L-ascorbic acid from 0.1 to 0.4 M, the average size of the Cu NPs decreased from 4.6 ± 0.89 to 2.3 ± 0.27 nm, and the size distribution became narrow. Because of the increase of the reductant concentration, the ability to reduce Cu^{2+} to $\text{Cu}(0)$ was enhanced, more nuclei were generated, and smaller Cu NPs more easily formed with the same reaction temperature and time [27].

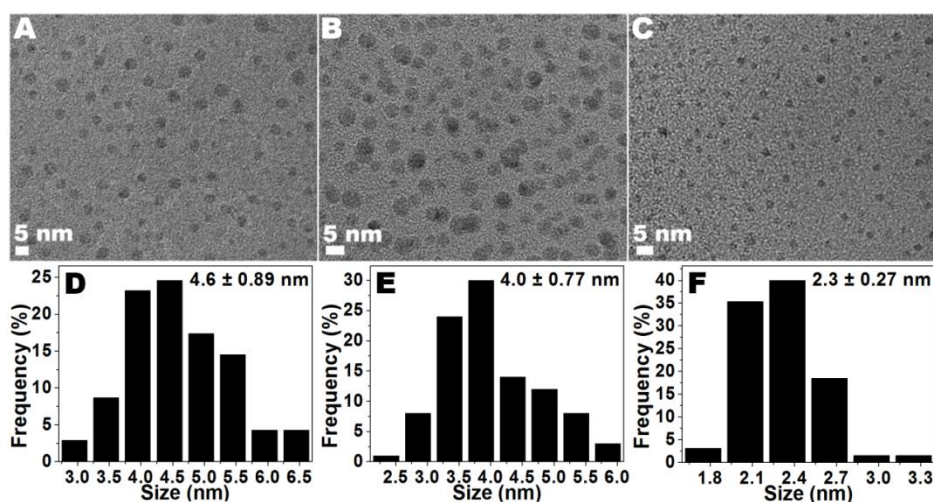


Fig. 3. (A-C) TEM images and (D-F) corresponding size distribution histograms of the Cu NPs synthesized at 45 °C for 42 hours using (A, D) 0.1, (B, E) 0.2, and (C, F) 0.4 M L-ascorbic acid solutions (CuCl_2 : 0.03 M, CTAB: 0.01 M).

3.4. The stability of Cu NPs in water

We further discussed the stability of the as-synthesized Cu NP aqueous dispersions by optical photography (Fig. 4A-B). The original and diluted Cu NP aqueous dispersions were red and yellow-orange, respectively, and displayed no indication of sedimentation or oxidation after one month of storage under ambient atmosphere condition (Fig. 4a-b). After adding NaOH solution into CuCl_2 solution, a few flocculates generated and the solution became less transparent due to the formation of $\text{Cu}(\text{OH})_2$ (Fig. 4e). However, after the injection of NaOH, the diluted Cu NP dispersion still remained the same color and no sediment was observed (Fig. 4c), which further indicated the good stability and dispersity of the Cu NPs in water. This should be ascribed to the use of L-ascorbic acid and CTAB, which formed stabilized coating shells on the surfaces of the Cu NPs, thus, effectively preventing the oxidation and aggregation of the Cu NPs [5, 39, 50]. Moreover, the diluted Cu NP dispersion changed from yellow-orange to colorless after the injection of HCl (Fig. 4d), which should be ascribed to the more chemical activity of nanoscaled Cu than bulk Cu.

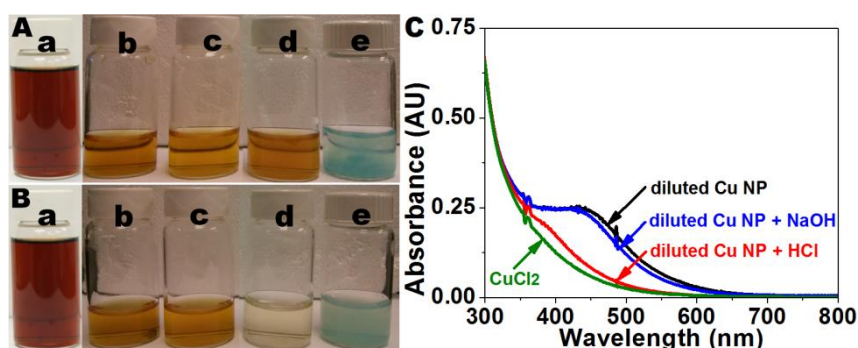


Fig. 4. Photographs of the (a) original Cu NP solution, diluted Cu NP solutions with one-tenth of the original Cu concentration after dripping (b) 0 and 0.5 mL of 0.1 M (c) NaOH and (d) HCl solutions, and (e) 0.03 M CuCl_2 solution after dripping 0.5 mL 0.1 M NaOH solution, after (A) one hour and (B) one month of storage under ambient atmosphere, and (C) their corresponding UV-Vis absorbance spectra after one month of storage under ambient atmosphere. The Cu NPs were prepared using 0.03 M CuCl_2 , 0.4 M L-ascorbic acid and 0.01 M CTAB solution at 45 °C for 42 hours.

The UV-Vis absorbance spectra were further taken to investigate the stability of the Cu NPs in water (Fig. 4C). The Cu NP dispersion showed a broad surface plasmon peak at ~ 440 nm. When adding NaOH solution into the NP dispersion, the position and shape of the absorbance peak remained almost unchanged, indicating the stability of the Cu NPs that agreed with Fig. 4A-B. However, when adding HCl solution into the NP dispersion, the absorbance peak of the Cu NPs disappeared behaving more like that of the CuCl_2 solution, which further proved the chemical activity of the Cu NPs that agreed with Fig. 4A-B.

4. Conclusions

A facile and green chemical reduction method was developed to obtain small-sized Cu NPs with narrow size distribution in water. The size and shape of the Cu NPs were controlled by changing the reaction time, molar ratio of L-ascorbic acid to CuCl_2 , and concentration of CTAB. In particular, the Cu NP aqueous dispersions were stable after one month of storage under ambient atmosphere. This study opens a way to prepare stable Cu NP aqueous dispersions for their potential applications in antibiosis, electronics, optics, etc.

Acknowledgments

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