Synthesis and Characterization of Water Soluble Fluorescent Copper Nanoparticles

Ji Soo Yu, Sung Hun Kim, Minh Tan Man, and Hong Seok Lee*
Department of Physics, Research Institute of Physics and Chemistry, Chonbuk National University, Jeonju 54896, Republic of Korea

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Abstract The electrostatic interaction between emerging quantum-confined nanostructures with plasmonic structures is crucial for future biological applications. Water-soluble green fluorescent copper nanoparticles (Cu-NPs) were fabricated. We demonstrate that L-ascorbic acid is considered as a key to precisely control small Cu-NPs and the capability of the surface ligands, while cetyltrimethylammonium bromide is used as a stabilizing agent controls the particle growth, and stabilizes the nanoparticles. Water-soluble green fluorescent Cu-NPs are tunable through modification of the reaction periods.

Keywords: Nanoparticles, Copper, Reducing agent, Fluorescence, Plasmonic band

I. Introduction

To date, fluorescent metal nanoparticles are attracting a great deal of research attention in many areas of nanotechnology. One of the most potential metal nanoparticles is copper nanoparticles (Cu-NPs), which have been studied intensively due to their peculiar surface plasmon resonance occurring in the range of visible light [1-3]. Likewise, other noble and non-noble metals, such as Au, Ag, Pt, and Bi, showed that their fluorescence spectra are normally extremely low quantum yield $10^{-10}$ because of the efficient nonradiative decay and the absence of energy gap. Cu-NPs become molecular-like, and discrete states with strong fluorescence can be observed due to their sub-nanometer cluster size resulting from the success of synthesizing the water-soluble Cu-NPs [4,5]. There are many synthetic methods which have been used to synthesize fluorescent Cu-NPs, which can be classified into four categories: (1) direct reduction of copper precursors, or a bottom-up approach, including metal vapor synthesis [6], radiation techniques [7,8], microemulsion methods [9,10], sonochemical techniques [11,12], thermal decompositions [13], and chemical reductions [14]; (2) bringing the size of metal nanocluster up to dots or low one-dimensional nanostructures; and (3) use of cluster groups self-assembled by means of dynamic reduction reactions including stable clusters and other highly reactive species [15,16]. One of the as-prepared nanoclusters have been formed, they must be controlled as well to keep them coherent with the host carboxyl/thiol-terminated ligands [17]. One of those synthetic strategies is the bottom-up approach which has been more commonly used. The copper precursors are first treated with appropriate co-ordinated groups, followed by reduction of metal ions into solution through reducing agents via wet chemical processes.

In this work, we report a simple approach, using cetyltrimethylammonium bromide (CTAB) as a ligand protecting and reducing agent is L-ascorbic acid, for the preparation of fluorescent copper metallic nanoparticles from copper (II) chloride dehydrate solution. The reaction periods play a key to precisely control small Cu-NPs and the capability of the surface ligands. These Cu-NPs exhibited strong fluorescence at 520 nm. The Cu-NPs are expected to be a suitable alternative and play an important role the field of biological labels and environmental remediation.

II. Experiments

Copper (II) chloride dehydrate (CuCl$_2$·2H$_2$O), L-ascorbic acid (vitamin C-98%), and CTAB were purchased from Duksan Ltd. Double-distilled water was used for preparing the aqueous solutions. All chemicals were used without further purification. The synthesis of homogeneous and stable Cu-NPs was achieved by the reduction of copper (II) chloride with ascorbic acid in the presence of the cationic surfactant by the following method: 0.1 mM of copper (II) chloride dehydrate was stirred with 50 mL of double-distilled water at room temperature to form blue solution of copper chloride. Copper (II) chloride solution was slowly added dropwise to the reducing solution of 10 mL ascorbic acid (0.1 M) under rapid stirring (350 rpm) at room...
temperature. The blue solution of copper chloride turned transparent color. After this was added 10 mL of CTAB (0.025 M) solution as a stabilizing agent. These mixtures were kept at 80°C for different reaction periods. During the reduction process, the color solution of the colloidal suspension gradually changed from transparent to yellow brown with a number of the reaction periods, indicating the synthesis of the Cu-NPs. The reduction process and copper nanoparticle growth process were completed after 23 hours. The schematic diagram of the redox process of the ascorbic acid and copper ion was shown Fig. 1. Finally, the prepared samples were purified by adding ethanol to recrystallize the cluster and then thoroughly separated for 3 times by centrifuging at at 10,000 rpm for 15 min.. After that, the purified Cu-NPs were dried under vacuum overnight and then collected.

### III. Results and Discussion

The copper (II) chloride solution became colorless when L-ascorbic acid was added, then gradually turned to slight-green, yellow and finally yellow brown in 23 hours, as shown in Fig. 2(a). The appearance of a yellow color followed by yellow brown color indicated the formation of the fine Cu-NPs from L-ascorbic acid assisted reduction. The fluorescence of the Cu-NPs solution under irradiation of UV lamp 365 nm is shown in Fig. 2(b). Display fluorescence of the Cu-NPs solution changed from blue emission to green emission band having the increasing reaction period. Under strictly inert conditions, fluorescent copper clusters were obtained by using very low percentages of the reducing agent and reaction time. The copper cluster size increases with the increasing of the reaction periods and, at the same time, the plasmonic band emerges at green emission band. These fluorescent Cu-NPs exhibit considerable potential in preparing very tiny metal nanoclusters.

UV-Visible absorbance spectroscopy has proved to be a very useful technique for studying metal nanoparticles because the peak position and shapes are sensitive to particle size. We investigated the effect of the reaction time on the synthesis of the Cu-NPs by UV-Visible spectrophotometer, as shown in Fig. 3. The absorption peak is increasingly broadening with an increasing reaction time. The time dependent growth of the Cu-NPs under 1.5 hours, the peak absorptions are not observed, and the edge absorption bands are smaller than 400 nm of wavelength. These absorption bands are related to the aqueous Cu(II) cations, and can be assigned to the ligand-to-metal charge transfer transition. When increasing reaction period, a red-shift in the absorption bands at 440-460 nm is obtained that can be associated with the formation of copper clusters [5].

Furthermore, fluorescence spectra, one of the most important properties of the Cu-NPs show in Fig. 4, are using an excitation wavelength of 405 nm. It was noticed that fluorescence intensity as function time dependent

![Figure 1. Schematic diagram of the redox process of the ascorbic acid and copper ion.](image)

![Figure 2. (a) Time evolution photographs for the formation of the Cu nanoparticles. (b) Color of the Cu nanoparticles under UV lamp 365 nm.](image)

![Figure 3. UV-Visible absorbance spectra for the Cu nanoparticles at different reaction periods.](image)
growth of the Cu-NPs, the emission intensity was enhanced at 520 nm, due to formation of the Cu-NPs and stable nanoparticles. The fluorescent intensities of these Cu-NPs solutions robustly relate with their absorption spectra, i.e. the reaction periods.

The emission bands of the Cu-NPs originate from metal-centered (Cu $3d^{10}$ to $2sp$) interband transitions, ligand-metal charge-transfer transitions, or the electronic transitions between the highest occupied molecular orbital state and the lowest unoccupied molecular orbital state [5]. The rapid formation of Cu-NPs for 1.5-hour reactions, at the same time, all present species present include the ascorbic acid, Cu(II), chloride, Cu(I) ions, and dehydroascorbic acid that come to equilibrium, under synthesis conditions, and are then directed to the products by chloride complexation of Cu(I) ions. The resulting fluorescent Cu-NPs solutions are not observed. Assisted by adding CTAB, more effective capping agents are taken place due to electrostatic interactions between negatively charged carboxyl groups of L-ascorbic acids and the positively charged CTAB cations, and then formed smaller Cu nanoparticles, which in turn, the Cu-NPs exhibited strong fluorescence at 520 nm. These ultra small sizes promise to offer great opportunities for biological labels, energy transfer pairs, and light emitting sources in nanoscale optoelectronics.

The crystalline structure of Cu-NPs was further confirmed by X-ray diffraction measurements, as shown in Fig. 5. The broad peaks of the QDs manifested the distinguishing feature of small particle size and the cubic lattice structure. There are three main peaks at $2\theta = 43.35^\circ$, 50.50$^\circ$, and 74.16$^\circ$, which correspond to (111), (200), and (220), indicate cubic lattice structure of Cu (JCPDS file No. 03-065-9026). No characteristic peaks were observed for the absence of Cu$_2$O and CuO. Thus, it was found that Cu(II) ions were reduced completely to Cu(0) by reducing agent of L-ascorbic acid.

IV. Conclusions

The copper nanoparticles in an aqueous medium have been synthesized using ascorbic acid as a reducing agent via the chemical reduction process. CTAB which is used as a stabilizing agent controls the particle growth, and stabilizes the nanoparticles. Water-soluble green fluorescent Cu-NPs are tunable through modification of the reaction periods. The green fluorescent Cu-NPs promise great opportunities for biological labels, energy transfer pairs, and light emitting sources in optoelectronic devices.

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