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Synthesis of Cu Nanoparticles Prepared by Using Thermal Decomposition of Cu-oleate Complex

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In order to obtain well-dispersed Cu nanoparticles, we synthesized Cu nanoparticles by using thermal decomposition of Cu-oleate complex, which was prepared by the reaction with $CuCl_2$ and sodium oleate in aqueous condition. The resulting well-dispersed Cu nanoparticles were synthesized by autoclave. TEM image showed well-dispersed Cu nanoparticles with diameter of 8.9 ± 1.3 nm. EDX spectrum and XRD peaks of the nanoparticles showed the highly crystalline nature of the Cu structures. The decomposition of Cu-oleate complex was analyzed with TGA and the crystallization of Cu nanoparticles was observed with XRD. UV-Vis absorption spectrum of Cu nanoparticles is also observed.

Keywords: Cu nanoparticle; Cu-oleate complex; thermal decomposition

INTRODUCTION

Ultrafine particles of semiconductors and metals are of wide interest nowadays as they exhibit novel dimension-dependent properties, which lead to a variety of technological applications [1–4]. Mono and bimetallic particles in the nanosize regime find extensive applications

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in catalysis, since with reduced size, surface area increases leading to enhanced catalytic activity [5]. Various routes are available for the synthesis of capped metal nanoparticles [6]. These methods are based on reduction process of precursor metal ions that include chemical reduction using different reducing agent, photoreduction, sonochemical and radiolytic methods [7–10]. Cu nanoparticles attracted considerable attention because of their catalytic, optical, and conducting properties [11–13]. Their synthesis has been achieved via various routes, including radiation methods, microemulsion techniques, supercritical techniques, sonochemical reduction, laser ablation, metal vapor synthesis, vacuum vapor deposition, chemical reduction, etc. [14–16]. To avoid oxidation, these methods were usually performed in non-aqueous media, at low precursor concentration, and under an inert atmosphere. Using soluble polymers or surfactants as capping agents to prepare Cu nanoparticles in aqueous solutions is attractive because organic solvents are not used and the corresponding pollutants are absent. However, until now, only few works have been done because Cu is easily oxidized [17]. In this paper, Cu nanoparticles are synthesized by using thermal decomposition method of Cu-oleate complex. This method has the advantages of dispersibility in organic solvent and reduction stability because of oleate coating on the surface. The merits of inorganic antibiotic materials is superior to that of organic antibiotic materials in durability, heat resistant, toxicity, selectivity and so on. The usefulness of copper as an antimicrobial agent has been known for a long time. It is an effective agent with low toxicity, which is especially important in the topical antibacterial treatment [18]. Our final purpose is that Cu nanoparticles is applied to life environment as antibiotic materials. In the first place, we introduce new synthetic method of Cu nanoparticles prepared by using thermal decomposition of Cu-oleate complex.

EXPERIMENTALS

Synthesis of Cu Nanoparticles

Copper chloride ($CuCl_2$, 99+%) and sodium oleate (98%) were purchased from Aldrich Chemical Co. and used without further purification. The aqueous solutions contained 1 M sodium oleate were stirred at 20°C for 2 hrs and then 1 M copper chloride solution was added into oleate solution. After filtering and drying, it was transferred into the pyrex tube and immediately treated by heating to 295°C at 2°C/min (0.3 torr) for 2 hrs and then cooled at room temperature. Monodispersed Cu nanoparticles were obtained. Structural characterization of the product was done with transmission electron microscopy (TEM), energy dispersive

X-ray (EDX) and X-ray powder diffraction (XRD) instruments. Optical property of Cu nanoparticles was studied with UV-vis spectroscopy. The decomposition of Cu-oleate complex was analyzed with Thermogravimetric Analysis (TGA) and the crystallization process was studied with XRD.

Analysis

TEM examinations of the samples were carried out on a HITACHI H-7500 (low-resolution) and a JEOL JEM 2010 (high-resolution) TEM. TEM samples were prepared on the 400 mesh copper grid coated with carbon. The structure of synthesized nanoparticles was analyzed with XRD (Philips X'pert-MPD system) with a Cu Kα radiation source ($\lambda = 0.154056$ nm). Optical absorption band was measured with UV-vis spectroscope (HITACHIU-2001). EDX and TGA study of the sample were carried out on a Scanning Electron Microscope HITACHI S-2400 and PERKIN-ELMER TGA 7, respectively.

RESULTS AND DISCUSSION

The decomposition path of the Cu-oleate complex was studied by TGA analysis. Figure 1 shows weight loss of copper-oleate complex during heat treatment under air flow. Very strong endothermic peaks were

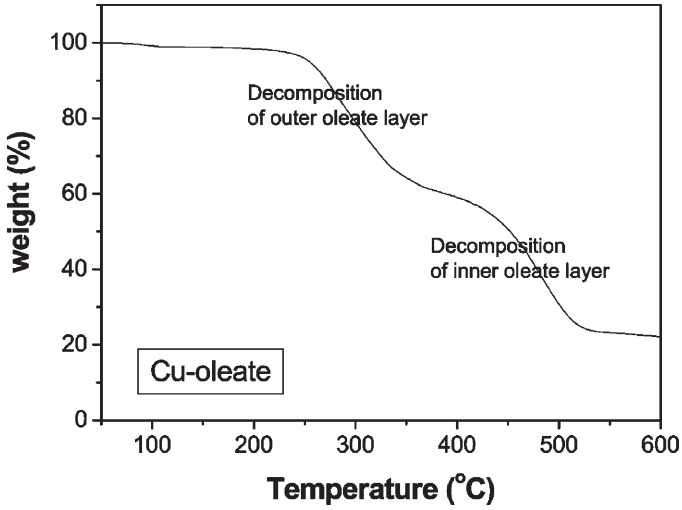

FIGURE 1 TGA curve of copper-oleate complex during heat treatment under air flow.

observed at 290°C and 580°C. The peaks are related to the evaporation of oleate molecules formed by the decomposition of copper-oleate. The first and second weight loss steps in the TGA curve might be

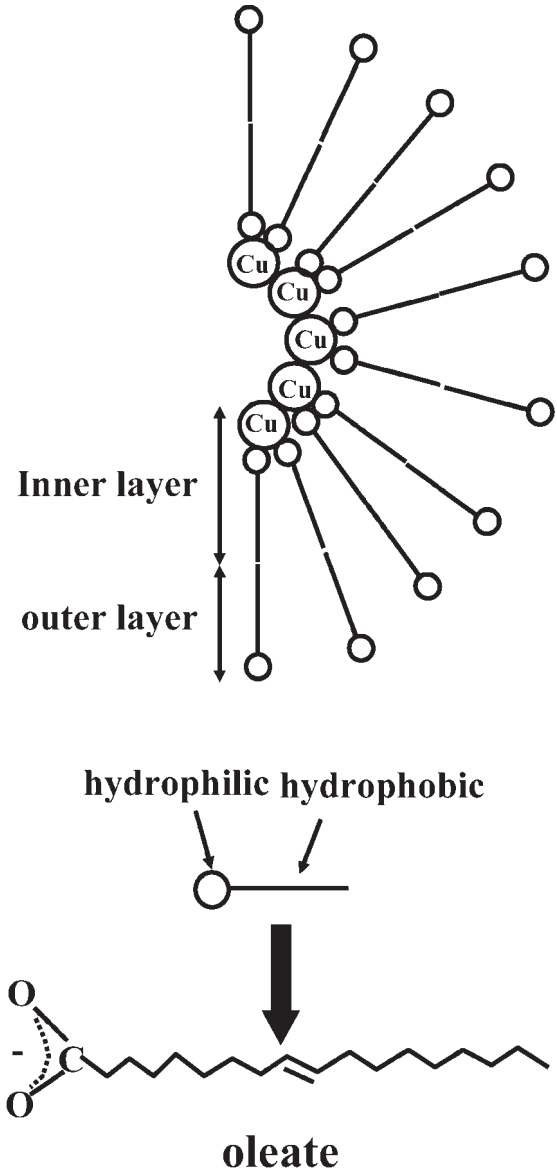

FIGURE 2 The formation of inner and outer layer of Cu-oleate complex.

attributed to the releases of the outer and inner oleate layers, respectively. Figure 2 shows the formation of inner and outer layer of Cu-oleate complex. Similar suggestion also has been proposed by Nikoobakht and El-sayed [19]. In this study, we used sodium oleate as capping agents to protect oxidation of Cu nanoparticles because oleate has a C_{18} (oleic) tail with a cis-double bond in the middle, forming a kink. Such kinks have been postulated as necessary for effective stabilization, and indeed stearic acid ($CH_3(CH_2)_{16}COOH$) with no double-bond in its C_{18} tail, cannot stabilize suspensions [20]. Figure 3 illustrates the XRD pattern of aging of copper-oleate complex at 300°C. The signature of copper has been observed in the aging of copper-oleate complex at 300°C. Peaks are very sharp due to the high nanocrystalline nature of copper. Figure 3 shows three peaks at 2θ values of 43.3°, 50.4°, and 74.1° corresponding to (111), (200), and (220) planes of copper, respectively. (JCPDS, copper file no. 04-0836). No impurity peak is observed in the X-ray diffraction pattern. Figure 4 is TEM images of monodispersed nanocrystallite of copper. Most of the copper nanoparticles are spherical. The mean size of copper nanoparticle was determined as 8.9 nm with a standard deviation 1.3 nm. This shows that the copper nanoparticles have very narrow size distribution. The lattice of Cu nanoparticle is shown in Figure 5. The lattice spacing in the HRTEM image of 1.99 Å is consistent with the distance for (111) lattice spacing in Cu. The size of this nanoparticle is about 8 nm. The EDX spectra of copper nanoparticles were excited by an electron beam (20 kV). Peaks for the elements of Cu were observed. There is no

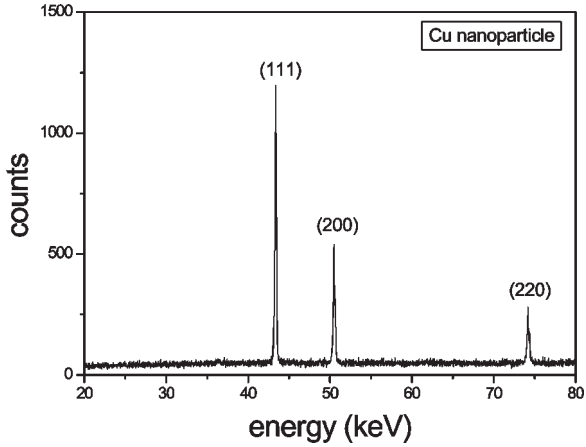

FIGURE 3 X-ray diffraction pattern (Cu Kα-radiation) of copper-oleate complex at 300°C.

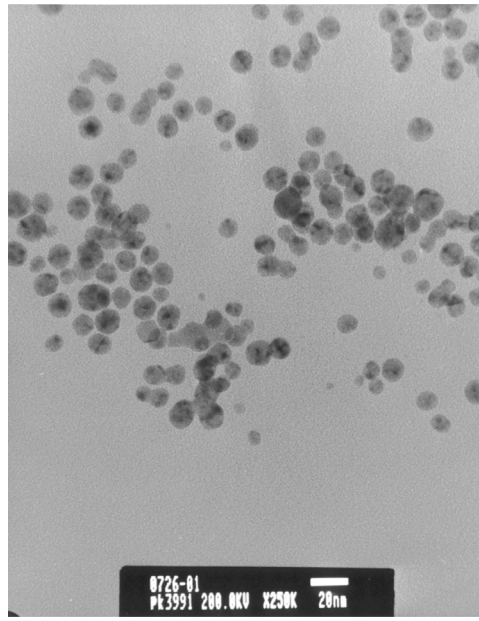

FIGURE 4 Transmission electron micrographs of copper nanoparticles. The particle size is determined as 8.9 ± 1.3 nm.

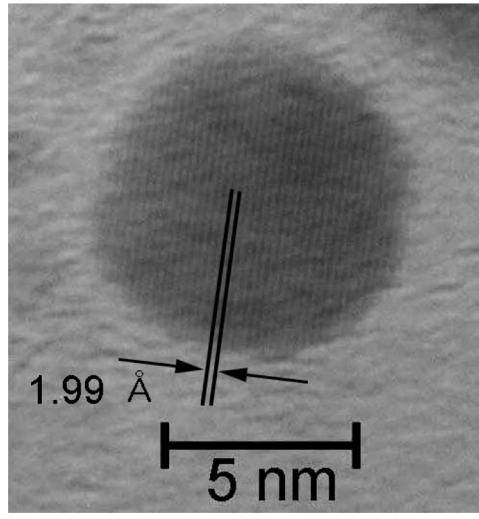

FIGURE 5 The lattice pattern of Cu nanoparticles.

impurity atom in the nanoparticles except copper atom. Accordingly, from the EDX spectra we could confirm that the nanoparticles in TEM images are pure copper. Cu nanoparticles display an optical absorption band peaked at 587 nm (~3 eV), typical absorption at metallic Cu nanoparticle, due to the surface plasmon resonance (SPR) [21]. Although the conduction and valence bands of semiconductors are separated by a well-defined band gap, metal nanoparticles have close-lying bands and electrons move quite freely. The free electrons give rise to a surface plasmon absorption band on the surface of metal nanoparticles, which depends on both the particle size and chemical surroundings [22,23].

CONCLUSIONS

A new synthetic method has been introduced to produce monodispersed copper nanoparticle using thermal decomposition of Cu-oleate complex, which was prepared by the reaction of $CuCl_2$ with sodium oleate in water solution. We also introduce that no extra inert gases protecting the oxidation of Cu nanoparticles were necessary. By TGA measurement, thermal decomposition of Cu-oleate complex was observed at 295°C. Transmission electron micrographs show that spherical copper nanoparticles (8.9 ± 1.3 nm) are prepared. This work is easily extended to other metals and to alloys of two or more metals. And this method can be easily increased scale up for industrial purpose.

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