

Shape-Controlled Synthesis of Copper Colloids with a Simple Chemical Route

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The new electrical and optical properties of nanomaterials depend sensitively on both size and shape, which are of both fundamental and technological interest. This paper introduces a simple chemical method to produce copper particles, which has the ability to shape the particle without using any capping agent or template. In our synthetic procedure, the reactant concentration and temperature exerted a strong influence on the shape of the copper particles. At low reactant concentrations, the particles were cubic; at high reactant concentrations, obtained particles were spherical. The number of hollow particles greatly increased when the synthesis was performed at low temperature. We also synthesized a copper cubic ring at lower temperature, and it has been rarely reported. The absorption spectrum of hollow particles showed obvious red shifts, which suggests the possible assembly of novel optical materials.

1. Introduction

The shapes of metal or semiconductor colloidal particles have received much attention in recent years, due to their strong effects on the physical and chemical properties of materials.^{1–6} For example, studies on the plasma resonance of individual colloidal silver nanoparticles show that triangular, pentagonal, and spherical particles are able to display red, green, and blue colors, respectively, under optical microscopy.⁷ Metallic nanorods such as gold⁸ or silver⁹ exhibit anisotropic optical properties directly related to their aspect ratios. In the same way, the luminescence of CdSe nanorods,¹⁰ and the magnetic properties of maghemite,¹¹ and nickel¹² or cobalt¹³ nanorods, are also markedly affected by shape. In addition, hollow structures could offer some advantages over solid structures, due to their relatively low densities.¹⁴

Copper particles have been widely studied because of their roles in electronics, catalysts, resins, and thermal conducting.^{15,16} Various preparation methods to ultrafine Cu have been reported. Recently, Pileni¹⁷ et al. controlled size and shape of Cu nanoparticles with a diameter from 3 to 13 nm using reverse micelles. Sun¹⁸ et al. synthesized stable metallic copper nanoparticles with a diameter of 50–60 nm protected by bis-(ethylhexyl)hydrogen phosphate (HDEHP) in the organic phase. Rosenband¹⁹ et al. prepared the submicrometer copper powders by low-temperature pyrolysis of their formate salts in inert atmosphere. Zhu²⁰ et al. synthesized hollow Cu spheres and wormlike Cu nanorods that consist of nanoparticles in diameter about 10 nm by reducing $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ with $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$ in ethylene glycol under microwave irradiation. Yet, until now, it has been rarely reported for shape-controlled synthesis of submicrometer copper colloids.

In this paper, we describe a chemical procedure to produce copper particles with different shapes and narrow size distribution. Such materials were obtained by direct precipitation from homogeneous solutions in the presence of reducing agents. Our method differed from the previous chemical approach on the

following points: (i) the processing of our experiment was very convenient, as we used only copper(II) cation and the reducing agent hydrazine, without any capping agent; (ii) hollow copper spheres were synthesized in this “one-step” process without any template, and the production was uniform in size; and (iii) cubic copper particles were obtained in the same process by changing the reactant concentrations. We first synthesized a copper ring in this work. These copper particles with various morphologies could be used in a variety of areas, including catalysis, electronics, photonics, and new functional device assembly. Hollow spheres also have potentially wide applications, such as controlled release capsules of various substance (e.g., drugs, cosmetics, dyes, and inks), artificial cells, catalysts, and lightweight structural materials, because of their low density, large specific area, mechanical and thermal stability, and surface permeability.^{21,22}

2. Experimental Section

2.1. Preparation of Copper Particles. All of the chemical reagents used in this experiment were analytical grade. Copper particles were synthesized as follows: A 45 mL aqueous solution containing 0.43 mM CuCl_2 was prepared. Next, N_2H_4 solution was added dropwise into the CuCl_2 solution under constant stirring. The molar ratio of N_2H_4 and CuCl_2 was 20. The blue solution turned yellow, indicating the formation of copper particles. Throughout the experiment, the temperature was kept at 308 K. The aqueous suspension was dropped onto copper grids for TEM and HRTEM analysis. The products obtained were washed thoroughly with redistilled water and dried in a vacuum oven at 323 K for 4 h.

2.2. Characterization of Samples. The TEM images were obtained on a JEM-200CX transmission electron microscope. HRTEM images and SAED patterns were obtained on a JEOL-2010 electron microscope. They were both operated at 200 kV. The scanning electron microscopy (SEM) images were obtained using a FEI field emission microscope (SIRION) operated at 10 kV. The powder XRD analysis was performed using a Rigaku (Japan) D/max-RB X-ray diffractometer with graphite monochromatized Cu $K\alpha$ radiation ($\lambda = 1.5418$ nm). Absorption

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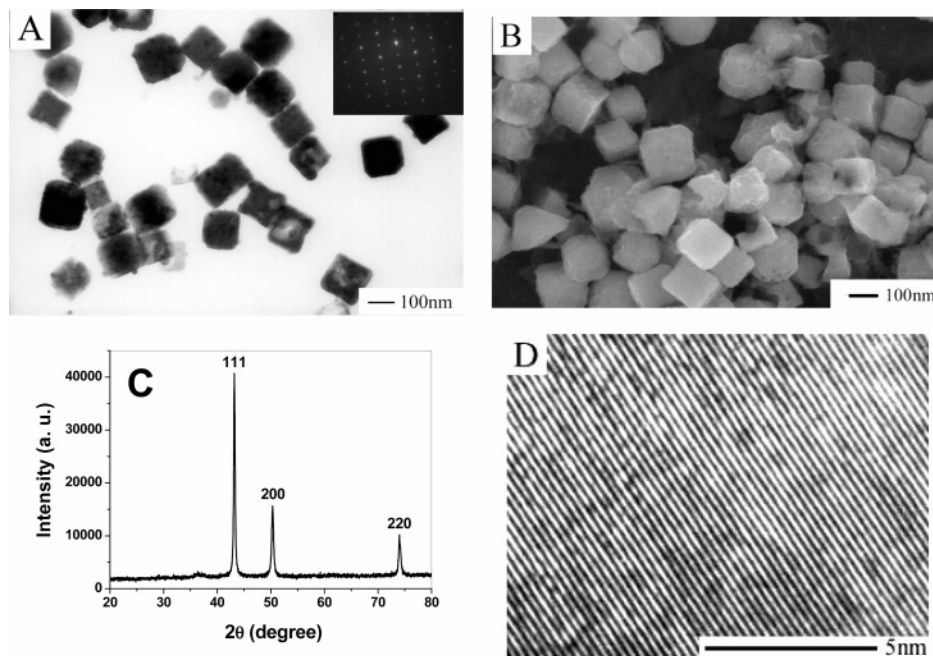


Figure 1. (A, B) TEM and SEM images of copper particles synthesized in low reactant concentration (0.15 mM). The inset shows the selected-area electron diffraction (SAED) pattern obtained by focusing the electron beam on a cubic copper particle. (C) An XRD pattern of copper particles. (D) A HRTEM image of one part of a cubic particle, indicating its crystal structure.

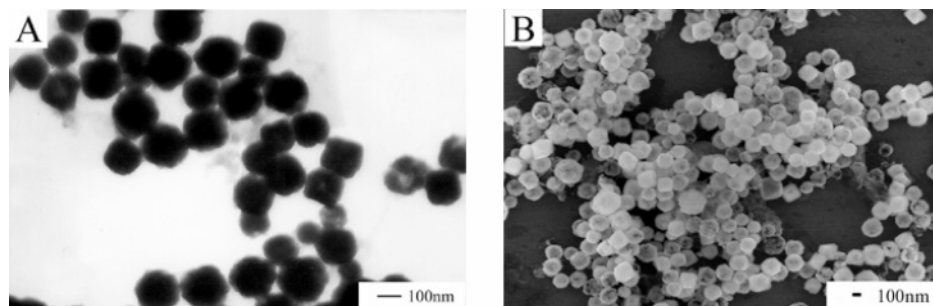


Figure 2. (A, B) TEM and SEM images of copper particles synthesized in high reactant concentration (0.62 mM).

spectra were recorded using a Hitachi U-2001 diode array spectrophotometer at 1 cm path length.

3. Results and Discussion

The morphology of the product depended strongly on the reactant concentration. When the initial reactant concentration was lower than 0.2 mM, cubic particles were the major products; when the reactant concentration was higher than 0.4 mM, spherical particles were the major products. The TEM image of the copper particles obtained with low reactant concentration (0.15 mM) is shown in Figure 1A. These cubic particles exhibited nearly identical morphologies and had a mean edge length of 155 nm. The SEM (Figure 1B) shows that these cubic particles had rough surfaces and were possibly composed of smaller particles. Furthermore, the highly crystalline nature of the copper particles was confirmed by selected area electron diffraction (SAED) measurement (the inset of Figure 1A). Figure 1C shows an X-ray diffraction (XRD) pattern of the particles. The peaks in our samples followed those observed in the standard material [Joint Committee on Powder Diffraction Studies (JCPDS) File No. 04-0836], which revealed that the material was crystalline copper. HRTEM image (Figure 1D) shows the fine structure for one part of a cubic particle. We chose a broken particle because a cubic particle was too thick

to be analyzed. In this picture, the crystal lattice fringes are spaced 0.208 nm apart, which agreed with the d value of the (111) planes of the copper crystal.

Figure 2 shows TEM and SEM images of copper particles obtained with high reactant concentrations (0.62 mM). These were well monodispersed particles, which were weakly agglomerated and uniformly spherical in shape. The mean size of the particles was 178 nm. The SEM (Figure 2B) shows that spherical particles also had rough surfaces. SAED measurement revealed that the spherical copper particles were crystal (this SAED was similar to Figure 1A).

Another factor influencing the morphology of particles was the temperature. To clearly elucidate this process, samples obtained at different temperatures were studied carefully (Figure 3). These particles were produced in a high reactant concentration; the reaction temperatures were 278 K (Figure 3A), 298 K (Figure 3C), and 318 K (Figure 3E), respectively. Figure 3A gives a TEM image of the product. As a characteristic feature of this product, the central portion of each Cu particle was lighter than the surrounding edges, indicating the formation of a hollow structure with a shell thinner than the escape depth of electrons,²³ which was further shown by the SEM image in Figure 3B. These particles were aggregates of small particles, and some particles' edges were incomplete. The latter phenomena could be ex-

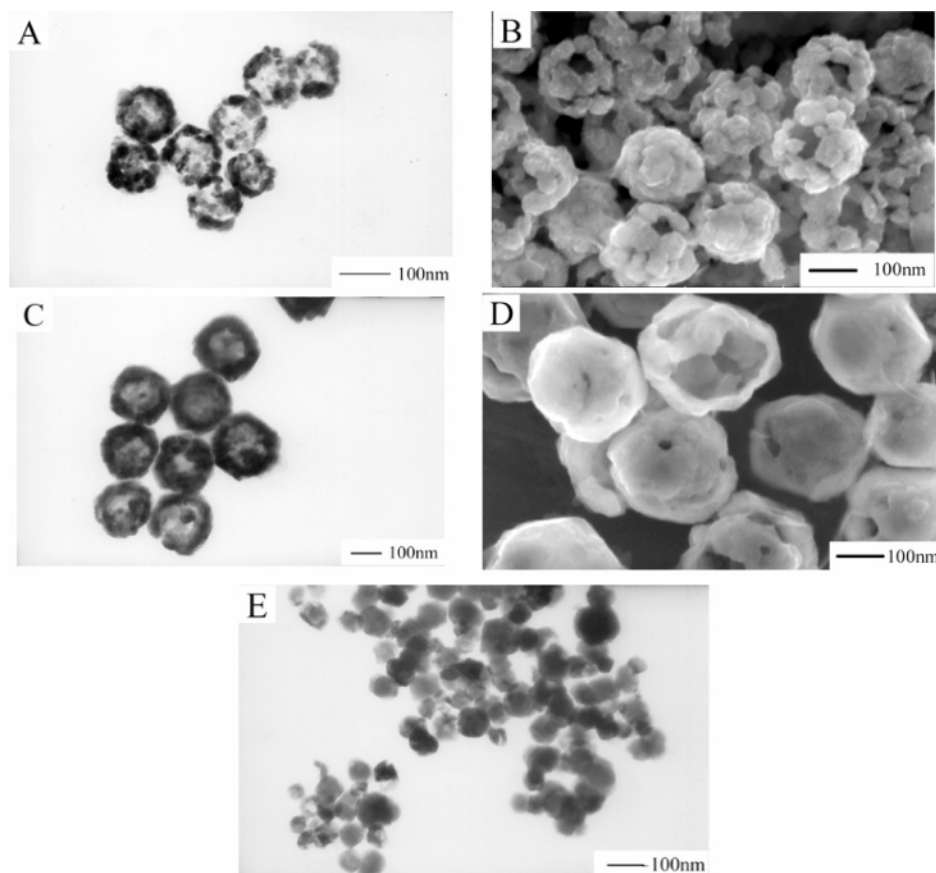


Figure 3. TEM and SEM images of copper particles, synthesized in high reactant concentration. The reaction temperatures were (A, B) 278 K, (C, D) 298 K, and (E) 318 K.

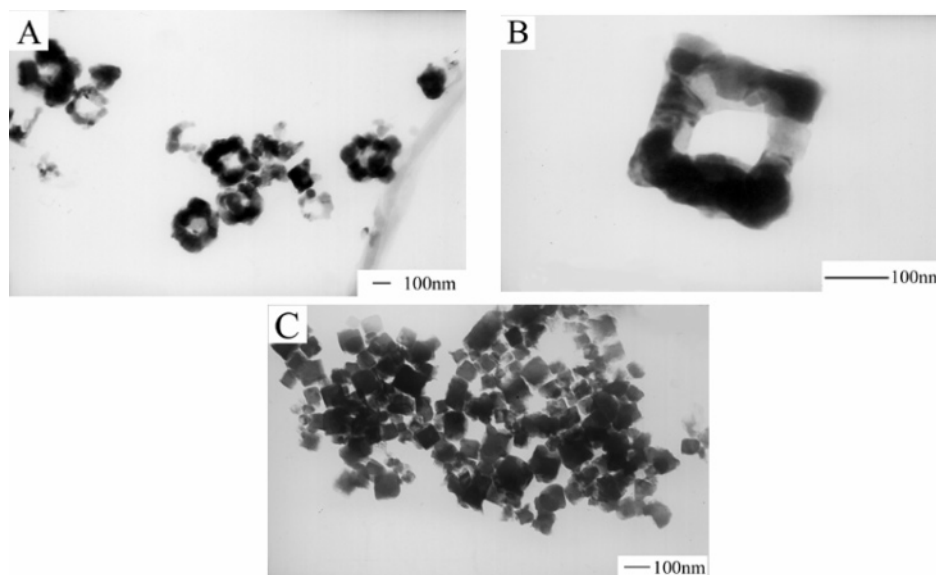


Figure 4. TEM images of copper particles, synthesized in low reactant concentration. The reaction temperatures were (A, B) 278 K and (C) 318 K.

plained by the low temperature. Figure 3C and 3D shows the images of these copper particles obtained at a higher temperature. Both thickness and density of the copper shell increased with temperature. Broken spheres were occasionally observed. A partly broken sphere can be clearly observed in the high-magnification SEM image. Figure 3D shows that these particles were hollow. However, when the temperature was raised, the number of monodispersed copper particles decreased, possibly

because of a faster reaction rate. Particles were not only less uniform in size, but also aggregated (Figure 3E).

We found some rings in the samples synthesized in low reactant concentration and low temperature (278 K) (Figure 4A). The central portions of these particles were lighter than their edges and the same as the background. A cubic ring particle formed by smaller particles can be clearly observed in the high-magnification TEM image in Figure 4B. When the temperature

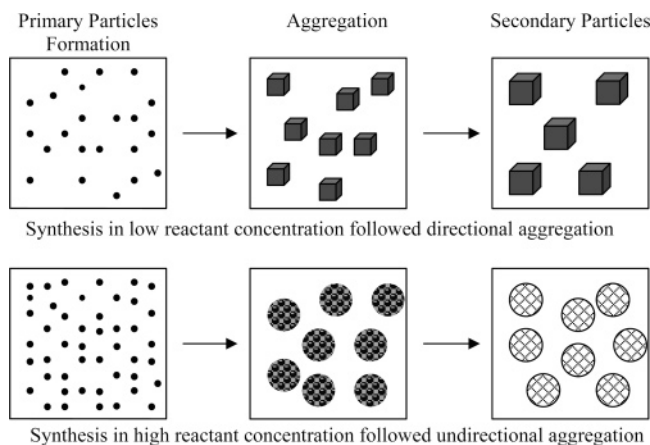


Figure 5. Schematic representation of the formation mechanism of monodispersed particles by aggregation of small particles.

increased (318 K), the monodispersity of these copper particles decreased, but their shapes were maintained (Figure 4C).

The above experimental results show that copper particles are composed of small aggregate particles. The reactant concentration influence on the morphology of the copper particles may be due to the different aggregation processes at different concentrations. When Cu particles were synthesized in low reactant concentrations, few primary particles were formed, and the rate of aggregation was low. The growth of nanocrystal may follow the typical crystal habit. Usually, the surface energies associated with different crystallographic planes are different, and a general sequence may hold, $\gamma_{\{111\}} < \gamma_{\{100\}} < \gamma_{\{110\}}$.²⁴ So the nanocrystal tends to have the higher growth rate along the $\langle 111 \rangle$ direction. On the other hand, the absorption of ions played an important role in the aggregation process, which was directional.²⁵ Murphy²⁶ concluded that the preferential absorption in solution of molecules or ions to different crystal faces directs the growth of particles into various shapes by controlling the growth rates along different crystal axes. It is commonly accepted that the shape of an fcc nanocrystal is mainly determined by the ratio (R) of the growth rate along the $\langle 100 \rangle$ versus the $\langle 111 \rangle$ direction.²⁷ The perfect cubes bounded by the less stable $\{100\}$ planes will be formed when R is reduced to 0.58. In our experiments, it is believed that the selective interaction between ions and various crystallographic planes of fcc copper could greatly reduce the growth rate along the $\langle 100 \rangle$ direction and/or enhance the growth rate along the $\langle 111 \rangle$ direction, and thus reduce R . Eventually, the $\{111\}$ facets were eliminated because of their higher growth rate, and the $\{100\}$ facets remained because they have the lower growth rate. Therefore, the cubic secondary particles were formed in low reactant concentrations.

When the reactant concentration increased, aggregation was performed at a higher rate. The aggregation rate was sharply increased, and the relative growth rate difference of different surfaces completely diminished. After a burst of nucleation, the primary particles may aggregate into secondary particles through a homogeneous aggregation. This aggregation process (Figure 5), in which spherical particles were formed, was named an undirectional aggregation.^{25,28} The influence of temperature on the morphology of the copper particles is not yet understood. Further studies are being made of the mechanism of such shape-controlled reactions.

UV-vis absorption spectra of the suspension of these copper particles, synthesized in high reactant concentration, were recorded to investigate their optical properties (Figure 6). As seen from curve A in Figure 6, copper particles have a broad

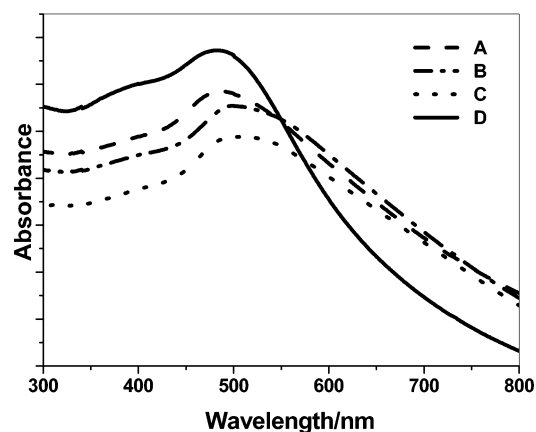


Figure 6. UV-vis spectra of copper particles synthesized in high reactant concentration. The reaction temperatures were (A) 318 K, (B) 298 K, (C) 288 K, and (D) 278 K.

absorption at 400–500 nm. For the suspension of hollow particles, the absorption (curve B in Figure 6) shows obvious red shifts. The shift in peak location was attributed to the cavity that affected the local dielectric environment of the particles. The absorption peak shifted slightly to a longer wavelength with falling temperature (curve C in Figure 6). This shift in peak position might have been caused by the decrease in wall thickness for the particles.²⁹ When the copper particles were produced at a lower temperature, a remarkable blue shift in peak was observed, indicating that hollow particles with an incomplete shell, as well as some small particles, were formed (curve D in Figure 6). The UV-vis investigation indicated that the hollow spheres showed broad absorption in the visible region. These spheres could be useful in the investigation of various optical phenomena, as novel supported photocatalysts, or as candidates for photonic crystals.³⁰

4. Conclusions

In conclusion, the novelty of this one-step chemical method for the generation of particles lies in its simplicity and ability to shape the particle without using any capping agent or template. The reactant concentration and temperature exerted a strong influence on the shape of the copper particles in our synthetic procedure. The particles were cubic at low reactant concentrations, and obtained particles were spherical at high reactant concentrations. The number of hollow particles greatly increased when the synthesis was performed at a low temperature. We first synthesized a copper cubic ring at a lower temperature. The absorption spectrum of hollow particles showed obvious red shifts, and the tuning of these materials' absorption peaks could offer the prospect of the assembly of a novel functional device.

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