



Synthesis of Cu nanoparticles by chemical reduction method

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Abstract: Cu nanoparticles (CuNPs) have been synthesized through an easy route by chemical reduction at room temperature. The Cu^{2+} ions were reduced and stabilized with sodium borohydride and polyvinylpyrrolidone, respectively. The effect of the variation of the reducing agent/precursor-salt (RA/PS) ratio on the size and morphology of the CuNPs was evaluated. The synthesized material was studied by ultraviolet–visible (UV–Vis) spectroscopy, X-ray diffraction (XRD), scanning electron microscopy (SEM), and transmission electron microscopy (TEM). The UV–Vis spectra showed a CuNPs plasmon peak at 569 nm and another peak belonging to Cu_2O at 485 nm. XRD analysis showed the fcc-Cu phase with a small amount of fcc- Cu_2O compound. SEM and TEM studies displayed that small semispherical CuNPs of approximately 7 nm were obtained at the RA/PS ratio of 2.6. The excess of polyvinylpyrrolidone stabilizer played an essential role in preventing CuNPs oxidation. On the other side, Cu_2O polyhedral particles with larger sizes up to 150 nm were identified in the RA/PS ratio range of 2.0–1.84. In addition, Cu_2O particles having star morphologies with quantum confinement at their tips were obtained at the RA/PS ratio of 1.66.

Key words: Cu nanoparticles; NaBH_4 ; chemical reduction; polyvinylpyrrolidone stabilization; Cu_2O

1 Introduction

In recent years, interest in the controlled synthesis of new nanomaterials has increased dramatically due to their wide range of applications in various areas of technology. However, the development of metal particles for nanoelectronic devices is affected by their instability and reactivity [1]. For example, synthesis of pure copper nanoparticles (CuNPs) is rare unless entire procedure is carried out in an inert atmosphere [2,3]. Although many synthesis processes of CuNPs report the use of a controlled atmosphere, they still obtain a mixture of Cu and Cu_2O [4]. Therefore, the synthesis of stable Cu nanoparticles remains a challenge.

Several methods have been used to synthesize CuNPs, such as chemical reduction [5], electroreduction process [6], polyol method [7], laser ablation [8] and microwave irradiation [9]. Chemical reduction is one of the most feasible methods for the synthesis of nanoparticles and offers potential advantages, such as rapid and low-cost processing, and controlled particle size. For example, copper nanoparticles have been reported using L-ascorbic acid as reducing and capping

agent in aqueous medium [10]. Regularly, surfactants such as polyvinylpyrrolidone (PVP) [11–13], cetyltrimethyl-ammonium bromide (CTAB) [12] and sodium dodecyl sulfate (SDS) [11] are used to prevent growth and control oxidation. CuNPs have applications in catalysis [14,10], antibacterial agents [15], solar cells [16], nanodevices, nanoelectronics, and nanosensors. In addition, copper is an important material because it has high electrical, optical and thermal properties.

In the present investigation, CuNPs were synthesized using a chemical reduction method. For this propose, sodium borohydride was used due to its high reducing capacity and polyvinylpyrrolidone for growth control, agglomeration, and avoiding oxidation. Although the most stable form of copper is copper oxide, it was possible to prevent the oxidation of CuNPs without the control of any atmosphere due to the excess of PVP used.

2 Experimental

Materials used for the synthesis of copper nanoparticles (CuNPs) are J. T. Baker-brand copper

chloride ($\text{CuCl}_2 \cdot \text{H}_2\text{O}$), sodium borohydride (NaBH_4), and polyvinylpyrrolidone (PVP) acquired from Sigma–Aldrich.

2.1 Synthesis of CuNPs

The synthesis of CuNPs was achieved through the reduction of $\text{CuCl}_2 \cdot \text{H}_2\text{O}$ with NaBH_4 in the presence of PVP. The reaction was carried out under magnetic stirring at room temperature. To synthesize the nanoparticles, initially, a dilution of 10 mL (5.6, 7.3, 7.9, 8.8 mol/L) of precursor salt, 7.7 mL (14.6 mol/L) of reducing agent, and 35 mL (0.9 mol/L) of surfactant were prepared separately. Subsequently, the reaction dilutions were made by adding the reducing agent and the surfactant agent to the precursor salt. From the above, a ratio of reducing agent to precursor salt (RA/PS) equal to 2.6, 2.0, 1.84 and 1.66 was deduced. When the reaction was carried out, the color of the solution changed to black and gradually to brown, characteristic of the formation of copper nanoparticles. After the synthesis, the solution obtained was stored at 10 °C for its subsequent characterization.

2.2 Structural characterization

The characterization of the solids synthesized was done by transmission electron microscopy (TEM) in a Phillips Tecnai F–20 microscope, whose filament is a field emission and works at a voltage of 200 keV. The analytical techniques used were a bright field and a high resolution. For the scanning electron microscopy (SEM), a JEOL JSM–7600F FEG-SEM microscope was used. The structural characterization was performed on a Bruker D8 ADVANCE DAVINCI diffractometer. The UV–Vis analysis was used to identify the presence of particles by absorption bands with a UV–Vis spectrophotometer Beckman Du–20.

3 Results and discussion

3.1 UV–Vis and XRD analyses

Figure 1(a) shows the results obtained after the chemical reduction of the sample with the higher RA/PS ratio (2.6) used in this work. A typical band of the surface plasmon resonance of CuNPs situated at 569 nm was observed. Also, a small peak of SPR, indicating the presence of Cu_2O particles, was also found at 485 nm. The partial oxidation of the particles comes from their direct contact with the air, which is in agreement with previous works [17]. However, in this case, considering the differences in the intensity of both bands, the amount of CuNPs phase is higher compared to that of Cu_2O .

The X-ray diffraction technique was used to extend structural characterization. Figure 1(b) shows the XRD pattern of the as-synthesized powder, indicating a

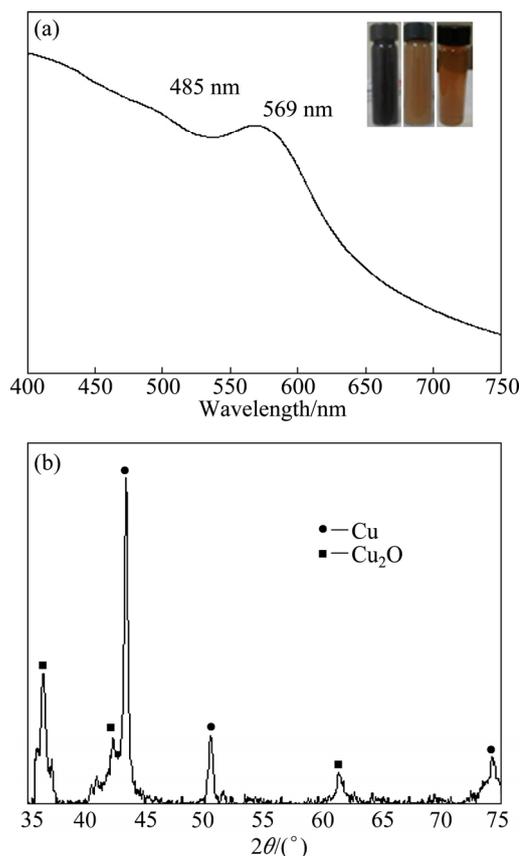


Fig. 1 UV–Vis spectrum of CuNPs synthesized for RA/PS ratio equal to 2.6 (a) and XRD pattern of obtained solids (b)

mixture of phases derived from the chemical reduction of Cu^{2+} ions with NaBH_4 as a reducing agent and PVP as a surface stabilizer. A higher intensity of the (111) fcc-CuNPs diffraction peak in comparison to the (111) fcc- Cu_2O particles indicates that more was obtained in the CuNPs crystalline phase. In order to quantify the percentage of Cu and Cu_2O , the relative intensities of the Cu (111) peak and the Cu_2O (111) peak were used, as outlined in Eq. (1) [18]:

$$\varphi(\text{CuNPs}) = \frac{I_{111}(\text{Cu}_2\text{O})}{I_{111}(\text{Cu}_2\text{O}) + I_{111}(\text{Cu})} \quad (1)$$

By using this technique, the CuNPs volume fraction of the as-synthesized sample was determined to be 72%. This result confirms that the present method has produced a large percentage of the CuNPs in comparison of the Cu_2O phase. These results are in good agreement with the UV–Vis technique.

3.2 SEM studies

Figures 2(a) and (b) show a couple of scanning electron microscopy (SEM) images that illustrate the nano-solids formed after the chemical reduction of CuCl_2 . As seen in Fig. 2(a), a significant amount of NP was prepared to indicate a good yield for the synthesis of the

reaction. Furthermore, judging from the backscattered image in Fig. 2(b), we can appreciate semispherical and polyhedral particles that have *Z*-contrast differences.

Semispherical particles are observed with a light-gray contrast and polyhedral particles with a medium-gray contrast. These results and their combination with XRD analyses show that the semispherical particles correspond to Cu, whereas the polyhedral morphologies correspond to Cu₂O particles. The oxygen in the air reacts with Cu, oxidizing the material and modifying its morphology. The larger amount of copper nanoparticles observed compared to some previous works [5,13] may be related to the use of the excess of surface agent PVP, which achieved good stabilization of the Cu nanoparticles, retarding their oxidation.

An EDS chemical analysis (Fig. 2(c)) of the sample

indicated the presence of Cu and O, confirming the chemical composition of the products. These findings are in good agreement with the previous characterization techniques.

3.3 TEM investigations

The CuNPs and Cu₂O particles were also observed by transmission electron microscopy (TEM). Figures 3(a) and (b) display a couple of bright-field TEM images taken from the Cu and Cu₂O particles, respectively. It can be seen that the Cu particles are semispherical in shape with narrow particle size distribution.

The average particle size, as determined by TEM micrographs, is 7 nm; whereas the polyhedral oxide particles have larger sizes up to 150 nm (Fig. 3(c)). Three typical HRTEM images of the CuNPs are shown in

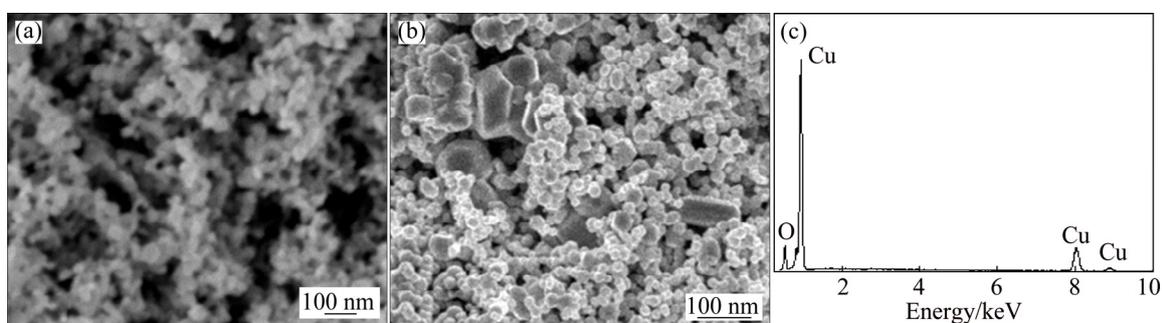


Fig. 2 SEM images of synthesized particles using RA/PS ratio of 2.6: (a) Semispherical CuNPs with average size of 7 nm; (b) Cu₂O polyhedral particles with 150 nm in size; (c) Chemical analysis result of synthesized solids

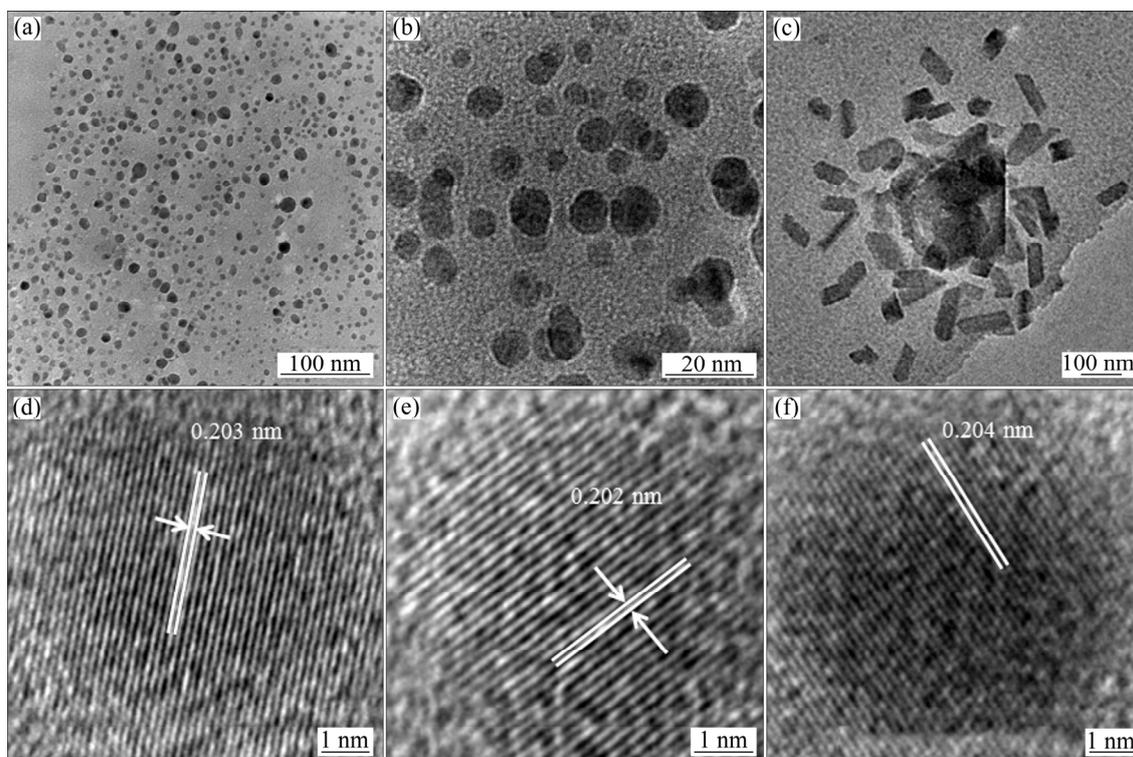


Fig. 3 TEM images of semispherical CuNPs (a, b), TEM micrograph of Cu₂O polyhedral particles (c) and HRTEM images showing inter-spacing distances that correspond to Cu cubic structure (d–f)

Figs. 3(d–f). The interlayer distances correspond to 0.203, 0.202, and 0.204 nm, respectively, that belong to the (111) crystallographic planes of the fcc-Cu.

Previous results showed that small particles were obtained at the ratio of reducing agent /precursor salt concentration (RA/PS) equaling 2.6. However, for low ratio of RA/PS, the average particle size of the products substantially increased. For example, Figures 4(a) and (b) show the morphology of the Cu_2O particles for the RA/PS ratios of 2.0 and 1.84, respectively. It is found that particles have star morphology, and the average particle sizes are around 0.5 μm . As the RA/PS ratio decreased even more (1.66), the particles turn to semispherical morphologies. Under these conditions, the average particle size is near 2 μm (Fig. 4(c)). Figure 4(d) shows a chemical analysis of solids illustrated in Fig. 4(c), in which the copper with higher intensity is observed, followed by oxygen with a lower intensity; this indicates that the composition of the material obtained is Cu_2O .

Figure 5 shows high-magnification TEM images of the Cu_2O products. Figures 5(a) and (b) display bright-field and HAADF-TEM micrographs, of the star-shaped

morphology. As can be observed, the tips of the star have sizes near the nanometric scale. Besides, some of them have sharp-tip type termination while others have a square shape.

This type of growth is due to the high amount of reduced copper ions that grow along with preferential directions. However, with the relative increases in the precursor salt (lower RA/PS ratio), the size of the products increased by the material saturation around the branch of the stars, giving spherical morphologies, as shown in Fig. 5(c).

HRTEM observations taken from one branch of the star-shape Cu_2O morphology demonstrated their crystal structure, as shown in Fig. 5(d). The image indicates that the branch has an interlayer distance of 0.25 nm, which is in agreement with the (111) crystallographic planes of the cubic Cu_2O phase. These results indicate that for high RA/PS ratios (2.6), the main product was CuNPs. As the RA/PS ratio decreased, the composition of the Cu_2O particles changed, firstly with star-shaped morphology with RA/PS ratio of 2.0 and 1.84 and then to semispherical particles with RA/PS ratio of 1.66.

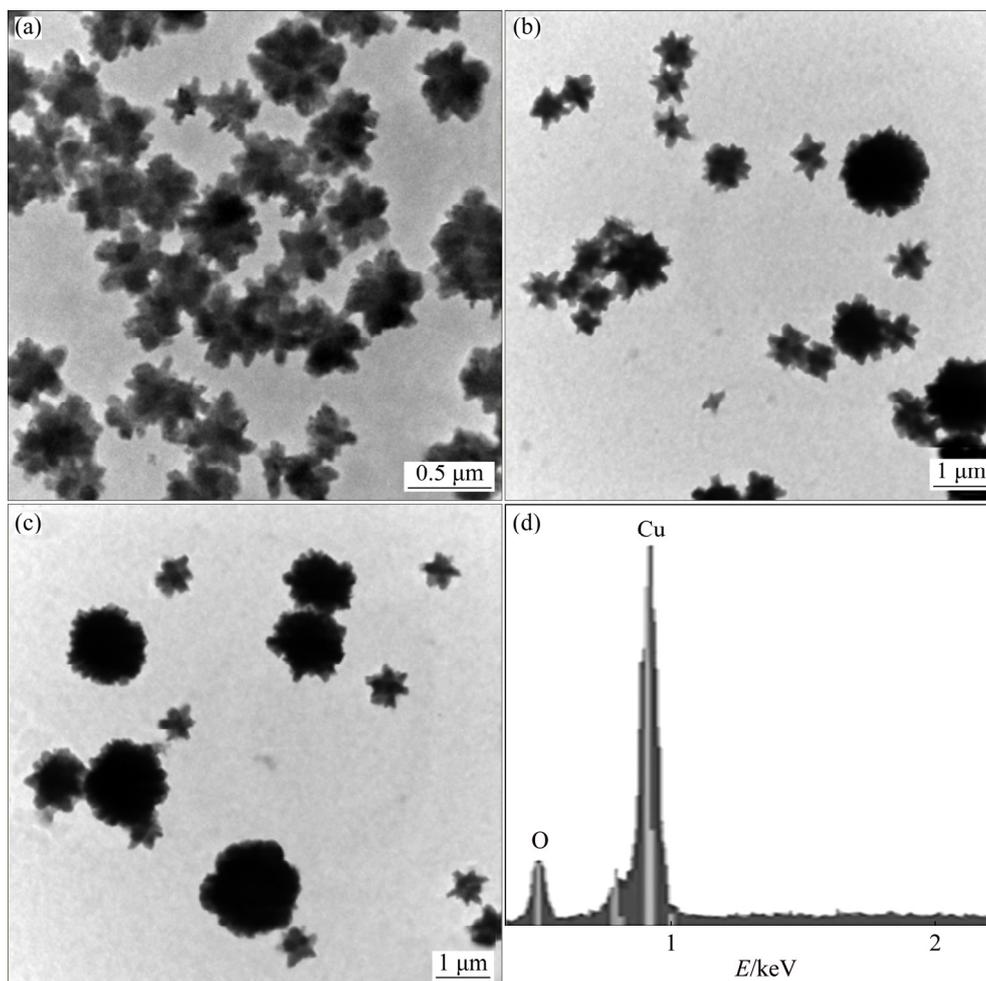


Fig. 4 SEM micrographs of Cu_2O particles synthesized with RA/PS ratio equal to 2 (a), 1.84 (b) and 1.66 (c), respectively, and chemical analysis result of particles (d)

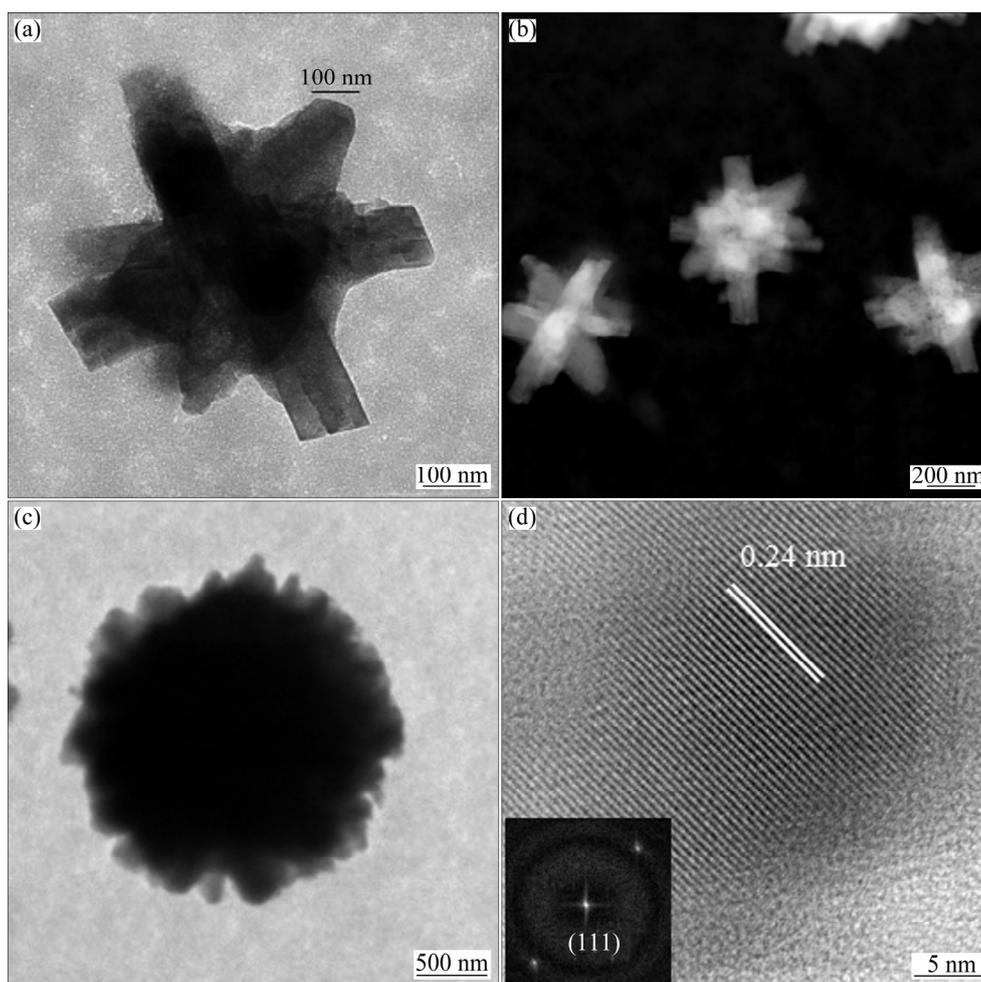


Fig. 5 Bright-field TEM (a) and HAADF-TEM (b) micrographs corresponding to Cu_2O particles synthesized with RA/PS ratio equal to 2, bright-field TEM image of Cu_2O particles synthesized with RA/PS ratio of 1.66 (c), and high-resolution images corresponding to (111) crystallographic planes of Cu_2O cubic phase (d)

4 Conclusions

(1) CuNPs with small amounts of the copper oxide (Cu_2O) were synthesized with NaBH_4 as a reducing agent and PVP as a stabilizer.

(2) SEM micrographs illustrate that CuNPs have a semispherical morphology, while Cu_2O particles have a polyhedral shape. EDS chemical analysis confirmed the presence of Cu and O in the reduction of products.

(3) The UV–Vis and XRD analyses confirmed the formation of CuNPs and small amounts of Cu_2O particles with a concentration ratio for reducing agent/precursor salt of 2.6.

(4) TEM analysis determined that the average particle size of CuNPs was 7 nm; whereas the polyhedral oxide particles have larger sizes up to 150 nm. Besides, bigger Cu_2O particles having star morphology and quantum confinement at the tips were obtained at lower RA/PS ratio (2.0).

(5) The excess of stabilizer used has a remarkable effect on the size of the copper nanoparticles as well as their oxidation.

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化学还原法合成 Cu 纳米粒子

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摘要: 通过室温化学还原合成 Cu 纳米粒子(CuNPs)。采用硼氢化钠还原 Cu²⁺离子,并用聚乙烯吡咯烷酮进行稳定化处理。考察还原剂/前驱体盐 (RA/PS) 比值的变化对 CuNPs 粒径和形貌的影响。利用紫外-可见光谱(UV-Vis)、X 射线衍射(XRD)、扫描电镜(SEM)和透射电镜(TEM)对合成的材料进行表征。UV-Vis 光谱显示, 569 nm 处存在一 CuNPs 的等离激元峰; 另一峰位于 485 nm 处, 为 Cu₂O 的特征峰。XRD 分析表明, 合成的材料为 fcc-Cu 相, 并含有少量的 fcc-Cu₂O 化合物。SEM 和 TEM 研究显示, 当 RA/PS 比值为 2.6 时, 得到粒径约 7 nm 的半球形 CuNPs 微粒。过量的聚乙烯吡咯烷酮稳定剂对于防止 CuNPs 的氧化至关重要。另一方面, 当 RA/PS 比在 2.0~1.84 范围内时, 获得较大粒径的多面体形 Cu₂O 颗粒, 最大粒径可达 150 nm。此外, 在 RA/PS 比为 1.66 时, 得到在其尖端具有量子限域效应的星形 Cu₂O 粒子。

关键词: 铜纳米粒子; NaBH₄; 化学还原; 聚乙烯吡咯烷酮稳定化; 星形 Cu₂O

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