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Preparation and characterization of CuO nanoparticles with different morphology through a simple quick-precipitation method in DMAC–water mixed solvent

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ABSTRACT

In this paper, highly dispersed copper oxide (CuO) nanoparticles have been successfully prepared in DMAC–water mixed solvent by a quick-precipitation method. The as-prepared CuO nanoparticles were characterized by high-resolution transmission electron microscopy (HRTEM) and X-ray diffraction (XRD). Several kinds of CuO particles with different shapes were obtained including panicle-like, spherical-like, spindle-like and rod-like CuO particles. The effects of processing parameters on the size and shape of CuO particles such as the volume ratio of DMAC and water, the adding temperature of NaOH and the molar ratio of Cu^{2+} and OH^- were investigated. It is found that higher volume ratio of DMAC and water, higher adding temperature of NaOH and higher molar ratio of Cu^{2+} and OH^- result in smaller size of CuO particles. The nucleation and growth kinetic of the resulting CuO particles were also discussed.

1. Introduction

Copper (II) oxide (CuO) nanoparticles have emerged as potentially powerful materials in various technological applications such as catalysis, magnetic storage media, batteries, solar energy conversion, gas sensing and field emission [1–4]. Size and shape controlled synthesis of CuO nanoparticles has received considerable attention because the physical and chemical properties of nanostructure materials are strongly related not only to their sizes but also to their shapes [5]. In the past decades, different methods have been proposed to synthesize CuO nanoparticles with different sizes and shapes, such as thermal oxidation [6], electrodeposition [7], hydrothermal treatment [8], high-temperature combustion [9], gas-phase oxidation [10] and quick-precipitation [11]. Among these methods, hydrothermal and quick-precipitation are important for their safety and environment friendly [12], and quick-precipitation is especially more attractive due to simple operation, ease of mass production and cost-effectiveness. Zhu et al. [11] prepared CuO nanoparticles with different shapes by a quick-precipitation method. The latest research results show that reaction solvent has a great influence on the size and shape of the obtained product. Many metal oxide including ZrO_2 [13], TiO_2 [14] and CeO_2 [15] with different sizes and shapes have been successfully synthesized in oil–water mixed solvent. Kumar et al. [16] developed a new sonochemical method to prepare CuO spherical nanoparticles in DMF–water mixed solvent. However, expensive ultrasonic equipment and severe reaction conditions were needed in this method.

In the current paper, well-dispersed CuO nanoparticles with controllable size and morphology were prepared in oil–water mixed solvent by a simple quick-precipitation method. In the preparation process, N,N-Dimethylacetamide (DMAC) was chosen to serve as oil. The efforts were focused on the size and shape of the obtained CuO nanoparticles varied with the processing parameters including the volume ratio of DMAC and water, the adding temperature of NaOH and the molar ratio of Cu^{2+} and OH^-. The formation mechanism was also discussed.

2. Experimental

2.1. Preparation

All of the reactants were of analytical grade, bought from Shanghai Chem. Comp. Ltd. and were used without further purification. In a typical experimental procedure, 6 mmol $Cu(NO_3)_2\cdot 3H_2O$ was dissolved in 40 ml DMAC. The solution was added into a round-bottom flask equipped with a refluxing device and kept at 100 °C with vigorous stirring. Then 20 ml NaOH solution prepared by dissolving 12 mmol solid NaOH (platelets) in DMAC–water mixed solvent was rapidly added into $Cu(NO_3)_2$ solution, where a large amount of black precipitate was simultaneously produced and maintained at the crystallization temperature for 10 min. The precipitate was then heated at 110 °C for another 10 min. After being cooled to room temperature, the black precipitate was collected, washed with distilled water and absolute ethanol several times to remove the impurities, and dried in air at room temperature.

2.2. Characterization

XRD patterns of the as-prepared products were recorded on a Bruker D8 Advance X-ray diffractometer equipped with graphite monochromatized Cu Kα ($\lambda = 0.1542$ nm), using a scanning rate of 0.02°/s in 2θ ranges from 20° to 80°. HRTEM

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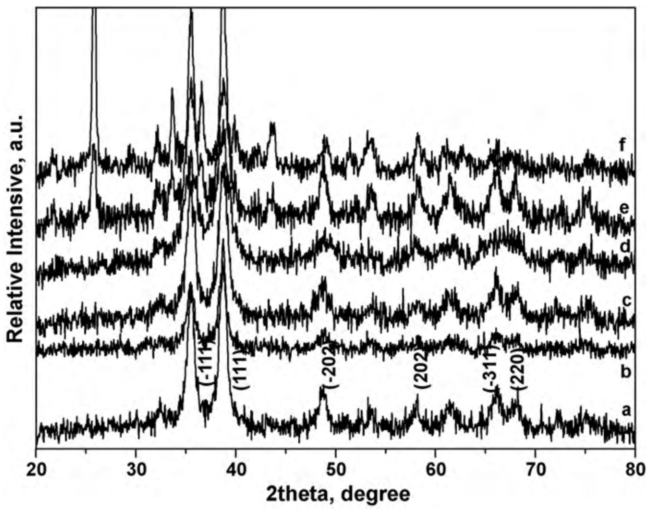

Fig. 1. XRD patterns of CuO prepared at different volume ratios of DMAC/water. (a) 1/5; (b) 1/1; (c) 2/1; (d) 5/1; (e) 7/1; (f) 11/1.

images of the products were obtained on a JEOL-2100 high-resolution transmission electron microscope, employing an accelerating voltage of 200 kV.

3. Results and discussion

3.1. Effect of the volume ratio of DMAC and water

The volume ratio of the mixed solvent has an important influence on final product. To investigate the effect of the volume ratio of DMAC and water on the phase and morphology of the product, the products were prepared at six volume ratios of DMAC and water, including 1:5, 1:1, 2:1, 5:1, 7:1 and 11:1, respectively. The XRD patterns of the obtained products are shown in Fig. 1. As shown in Fig. 1a–d, the characteristic peaks located at $2\theta = 35.57^\circ$, 38.74°, 48.76°, 58.35°, 66.28° and 68.13° are assigned to the (1 1 1), (−1 1 1), (−2 0 2), (2 0 2), (−3 1 1), and (2 2 0) crystal planes, respectively. They are well consistent with the JCPDS card files no. 48-1548, indicating the formation of monoclinic phase. The broadening of the peaks indicates the small size of the products. It is very clear that the width of characteristic peaks broadens with the increase of volume ratio of DMAC and water, which indicates the formation of smaller CuO particles. Actually, the average sizes of the CuO nanoparticles prepared at the volume ratio of 1:5, 1:1, 2:1 and 5:1, are estimated to be 11.2 nm, 10.0 nm, 9.0 nm and 6.7 nm, respectively, according to the Scherrer equation. However, further increasing the volume ratio to 7:1 and 11:1, the diffraction peaks located at $2\theta = 25.84^\circ$, 33.58°, and 36.56° clearly indicates the existence of impurities (see Fig. 1e and f). It is noted that the reaction could not be initiated in pure DMAC solvent, because NaOH is difficult to dissolve in DMAC solvent. Therefore, excessive DMAC amount will lead to the incomplete reaction.

Fig. 2 illustrates the HRTEM images of CuO nanoparticles prepared at volume ratio of DMAC and water of 1:5 and 5:1, respectively. It is found that the volume ratio of mixed solvent has an important influence on the shape and size of CuO nanoparticles. As can be seen from Fig. 2a, panicle-like CuO nanoparticles with diameters of 30 nm and lengths of 150 nm were formed at volume ratio of 1:5. Detailed analysis of the HRTEM image (the inset of Fig. 2a) reveals that each panicle-shaped particle is composed of interconnected spherical-shaped crystallites with diameters of 10 nm or so, which agrees well with that calculated from the XRD pattern. However, spherical-shaped CuO particles with narrow size distribution and high dispersion were prepared at volume ratio of 5:1. The size of the obtained CuO particles is in the range of 5–6 nm (see Fig. 2b) which is in good agreement with that estimated by Scherrer equation from the XRD pattern.

3.2. Effect of the adding temperature of NaOH

The adding temperature of NaOH is also an important factor on the morphology of the product. The products were prepared at adding temperatures of NaOH of 20 °C, 55 °C, 100 °C and 140 °C, respectively, under otherwise identical conditions. The XRD patterns of the as-prepared CuO nanoparticles are shown in Fig. 3. It can be seen that all the diffraction peaks belong exclusively to the CuO monoclinic phase (JCPDS 48-1548). The average sizes of the CuO nanoparticles prepared at adding temperatures of 20 °C, 55 °C, 100 °C, and 140 °C, are estimated to be 11.0 nm, 9.0 nm, 6.7 nm and 8.7 nm, respectively, according to the Scherrer equation.

Fig. 4 illustrates the HRTEM images of CuO nanostructures prepared at different adding temperatures of NaOH. As can be seen from Fig. 4a, spindly nanoparticles with lengths of 1 μm and diameters of 20 nm were prepared by adding NaOH at 25 °C. Detailed analysis of the HRTEM image (the inset of Fig. 4a) reveals that each spindly particle is composed of interconnected elliptical-like crystallites with diameters of 10 nm, which agrees with that calculated from the XRD pattern. As the adding temperature increased, the shape and size of final products are changed greatly. Well-separated and spherical-like nanoparticles with diameters of 5–6 nm can be achieved at the adding temperature 100 °C (see Fig. 2b). It is clear that the adding temperature of NaOH plays an important role in the formation of CuO nanoparticles.

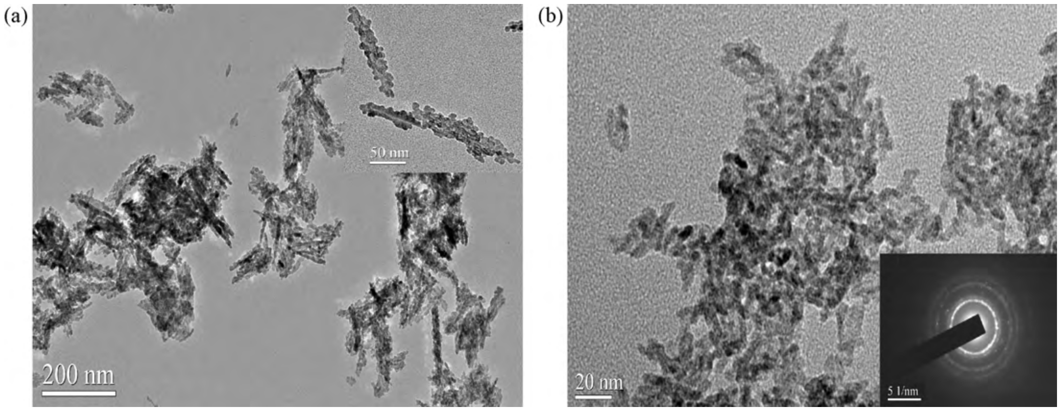

Fig. 2. HRTEM images of CuO prepared at different volume ratio of DMAC/water. (a) 1/5; (b) 5/1.

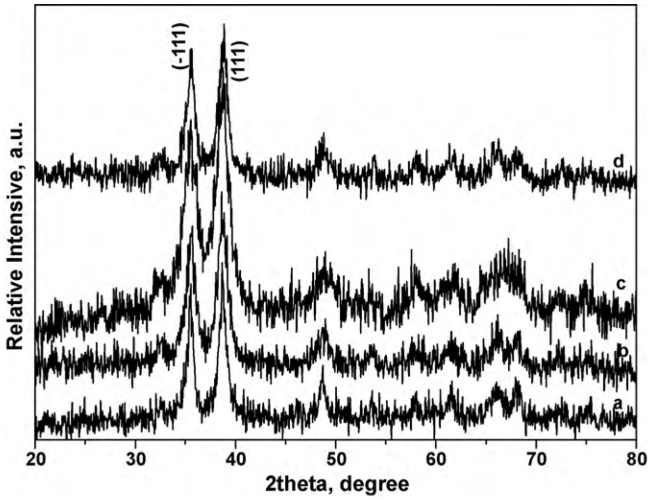

Fig. 3. XRD patterns of CuO prepared at different adding temperatures of NaOH. (a) 20 °C; (b) 55 °C; (c) 100 °C; (d) 140 °C.

3.3. *Effect of the molar ratio of Cu^{2+} and OH^-*

The molar ratio of Cu^{2+} and OH^- could influence the final product. When the molar ratio of Cu^{2+} and OH^- is 1:1, the diffraction peaks indicate that the final product is not pure CuO (see Fig. 5a). Pure monoclinic and spherical-like CuO nanoparticles with diameters of 5–6 nm were obtained at the molar ratio of 1:2 (see Fig. 5b and Fig. 2b). Further changing the molar ratio to 1:4 and 1:5, the crystal phases are all monoclinic (see Fig. 5c and d). Fig. 6a shows rod-like nanoparticles with 10 nm in width and 50 nm in length at the molar ratio of 1:4. Similar shaped but larger nanoparticles of 8 nm in width and 100 nm in length were obtained at the molar ratio of 1:5 (see Fig. 6b). The above facts clearly show that the molar ratio of Cu^{2+} and OH^- affects the morphology of the products.

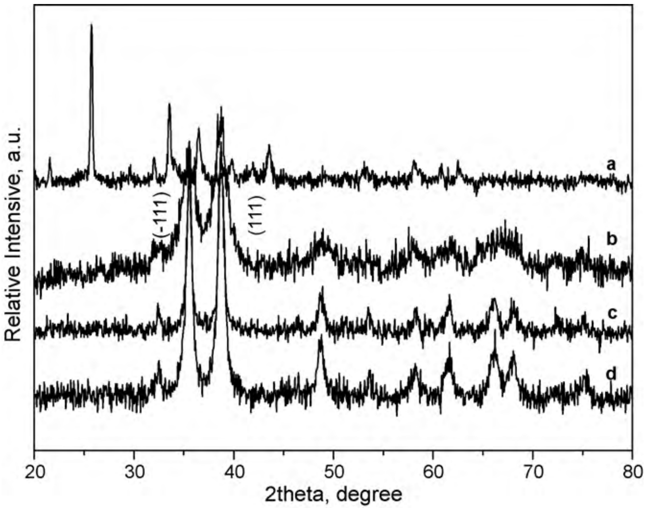

Fig. 5. XRD patterns of CuO prepared at different molar ratio of Cu^{2+}/OH^-. (a) 1:1; (b) 1:2; (c) 1:4; (d) 1:5.

3.4. *Mechanism*

The growth mechanism of different shapes of CuO crystals can be explained with the hypothesis of growth unit [17,18]. Based on the anionic coordinative polyhedral theoretical model, it consid-

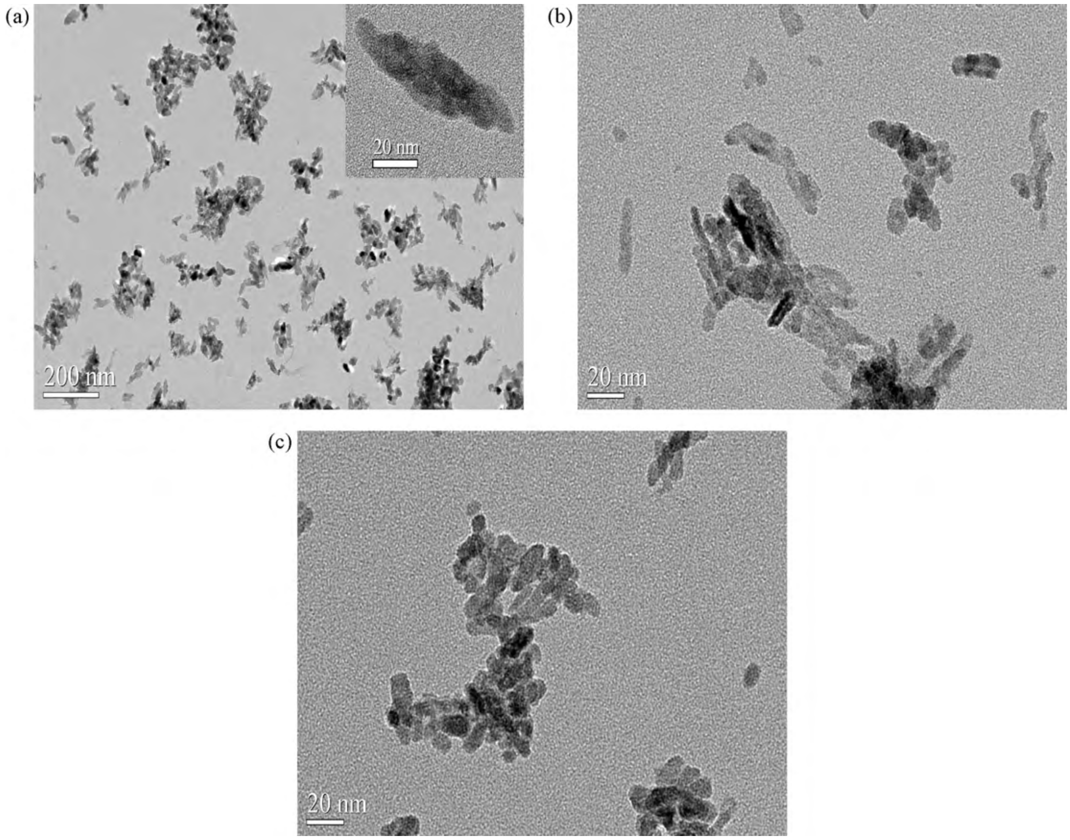

Fig. 4. HRTEM images of CuO prepared at different adding temperature of NaOH. (a) 20 °C; (b) 55 °C; (c) 140 °C.

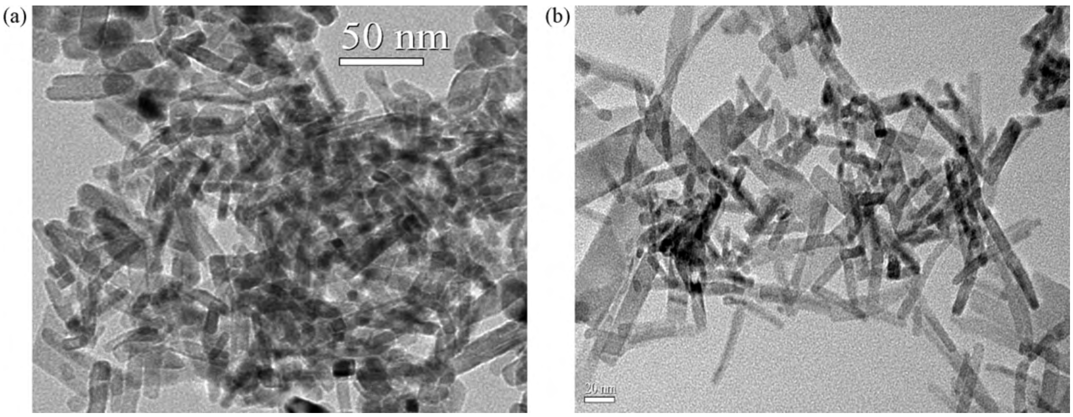

Fig. 6. HRTEM images of CuO prepared at different molar ratios of Cu^{2+}/OH^-. (a) 1:4; (b) 1:5.

ers that cations exist in the form of complex whose ligands are OH^- ions in aqueous solution, and the complex whose coordination numbers are equal to that of the crystal formed is called a growth unit. It is considered that the coordination number of Cu^{2+} ion generally keeps six in aqueous solutions. As a result, the growth units are expected to be $Cu(OH)_6{}^{4-}$ of coordinating octahedron in the NaOH solution. Four OH^- ligands are located at the equatorial position (square plane) of the octahedron while the other two OH^- at its axis. The two axial binding energies are lower than the four equatorial ones. So, the two axial OH^- ligands are easily replaced and dehydrated to form anisotropic CuO nanoparticles.

Being a polar aprotic solvent, DMAC is soluble in the aqueous medium. Introduction of DMAC into the system will change the system's viscosity and surface tension which will in turn affect the kinetics of the crystal growth. Accordingly, there will be a site competition for the cation (Cu^{2+}). Given that DMAC is more bulky, this competition for binding sites in the interfacial region will supposedly bring complications that will disrupt the directional growth as hypothesized by the above-mentioned theoretical model. The formation of panicle-like at volume ratio of DMAC and water of 1:5 (see Fig. 2a) particles and spherical-like at volume ratio of DMAC and water of 5:1 (see Fig. 2b) particles illustrates nicely the growth course of CuO nanoparticles.

The reaction temperature is another key factor for the growth of the CuO nanoparticles. At low temperatures, there is a possibility of formation of hydrogen bonds by the $Cu(OH)_6{}^{4-}$ complex which would be broken at high temperatures. That is, at low temperatures the complex is stabilized by intermolecular hydrogen bonds. It is speculated that the directional growth would be inhibited by formation of these hydrogen bonds [19–21]. The complicated association of hydrogen bonds could result in coarse aggregation of elliptical-shaped CuO crystallites to form spindly products (see Fig. 4a). As the temperatures increased, more and more hydrogen bonds were destroyed, and the growth units of $Cu(OH)_6{}^{4-}$ were exhausted rapidly, the aggregation growth of crystallites was effectively inhibited. So, the high disperse spherical-like nanoparticles were formed at 100 °C. For comparison, the CuO nanoparticles were prepared by adding NaOH at 55 °C. The HRTEM analysis of the products shows that it consists of nanorod particles in excess of 40 nm in diameter (see Fig. 4b), which is in good agreement with that estimated by our hypothesis. Interestingly, when the adding temperatures further increased to 140 °C, the average size of the spherical-like nanoparticles increased to 20 nm (see Fig. 4c). This is possible because the free energy of particles is high enough at the higher temperature of system, which leads to promote the motion transmissibility and probability of collision, the aggregation of intermolecular is induced.

In the present system, the molar ratio of Cu^{2+} and OH^- also influences the final product. The suitable amount of OH^- firstly combined with Cu^{2+} to form CuO precipitates, then, the precipitates are surrounded by excessive OH^- ligands, probably "OH^- ions residue" might form hydrogen bonds by interconnection. These hydrogen bonds between crystal domains in turn accelerated the rate of aggregation and promoted a one-dimensional aggregation to produce rod-like nanoparticles that are highly elongated along the *c*-axis. When the molar ratio of Cu^{2+} and OH^- is 1:5, excessive hydrogen bonds induce orderly aggregation growth of spherical-like CuO crystallites to form rod-like products (see Fig. 6b). The results confirmed our speculation. Further study on the influence of the molar ratio of Cu^{2+} and OH^- will be more interesting.

4. Conclusions

Highly dispersed CuO nanoparticles with different size and morphology can be successfully prepared in DMAC–water mixed solvent by a quick-precipitation method. The nucleation and growth kinetic of as-prepared CuO particles can be tuned by varying the processing parameters including the volume ratio of DMAC and water, the adding temperature of NaOH, and the molar ratio of Cu^{2+} and OH^-. The spherical, panicle-like and rod-like CuO nanoparticles could be formed by regulating these parameters without any additional surfactants. It is found that higher volume ratio of DMAC and water, higher adding temperature of NaOH and higher molar ratio of Cu^{2+} and OH^- result in smaller particle size of CuO nanoparticles.

Acknowledgements

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