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微波辅助水热法制备花状氧化铜

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摘要: 以硝酸铜为铜源,氨水为碱源,通过微波辅助水热法制备了花状 CuO 微纳米材料。制备过程中没有使用表面活性剂或离子液体等软模板剂。利用 X-射线衍射、电子能谱、场发射扫描电镜以及高分辨透射电镜表征了产物的物相和形貌。对照实验显示碱源对产物形貌有着很大的影响。通过时间演化实验研究了花状 CuO 的生长过程。结果显示反应过程经历了 $Cu_2(OH)_3NO_3$ 和 $Cu(OH)_2$ 两种中间产物。

关键词: 氧化铜, 花状, 微波水热法
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Microwave-Assisted Hydrothermal Preparation of Flower-Like CuO

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Abstract: The flower-like CuO was prepared via a simple, rapid, microwave-assisted hydrothermal process, using $Cu(NO_3)_2 \cdot 6H_2O$ as the copper source and ammonia solution as the alkali source. No soft template such as surfactant or ionic liquid was used in the preparation. The phases and morphologies of the as-prepared products were characterized by using powder X-ray diffraction (XRD), energy dispersive X-ray spectroscopy (EDS), field emission scanning electron microscopy (FE-SEM) and high resolution transmission electron microscopy (HRTEM). The controlled experiments showed that the morphologies were influenced greatly by the alkali source. The time-dependent experiments were performed to study the crystal growth process. The results also showed that the intermediates of $Cu_2(OH)_3NO_3$ and $Cu(OH)_2$ were involved in the reaction.

Key words: CuO; flower-like; microwave-assisted hydrothermal

Copper oxide (CuO), a typical narrow p-type semiconductor with a band gap of 1.2 eV [1-2], has attracted a great deal of attention because of its potential technological applications in heterogeneous catalysts, gas sensors, lithium ion electrode materials, solar cells, photocatalysts, and so on[3-5]. Up to now, CuO nanomaterials with different morphologies have been prepared by several methods, including thermal oxidation, electrochemical method, sonochemical method, hydrothermal/solvothermal method, etc[6-10].

Recently, microwave has been widely used in organic synthesis and nanomaterials preparation. Compared to the traditional heating, microwave heating is simple, rapid, uniform, efficient, economical, and environmentally friendly. So far, several studies have been performed on the

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preparation of CuO nanomaterials via the microwave-assisted solution-phase process. Several kinds of morphologies such as nanoparticles, nanoleaves, nanosheets, nanowhiskers, nanorods, chrysanthemum-like, flower-like, and sea urchin-like have been prepared by microwave-assisted solution-phase process [11-15]. The surfactants or the ionic liquids were usually used to prepare the flower-like CuO hierarchical nano-/microstructures [16-19]. The use of soft template usually pollutes the sample and the post-processing is tedious. In the present paper, we report the preparation of flower-like CuO nanomaterials via a 1 min microwave-assisted hydrothermal process without the use of any surfactants or ionic liquids. The effect of the alkali source on the morphologies has been studied. The crystal growth process of as-prepared CuO is suggested.

1 Experimental

All reagents were purchased from Shanghai Chemical Company and used without further purification. All samples were prepared in a microwave system (2.45 GHz, Discover S-Class, CEM) equipped with in situ magnetic stirring. The exposure time and temperature were programmed. The automatic temperature-control system allowed continuous monitoring and control of the internal temperature of the reaction system (1 ℃). The preset profile (desired time and temperature) was followed automatically by continuously adjusting the applied microwave power.

In a typical preparation procedure, $Cu(NO_3)_2 \cdot 6H_2O$ (1.0 mmol, AR) was dissolved in H_2O (9.5 mL). Then 0.5 mL ammonia solution (30%) was added dropwise to the above solution under continuous stirring. The color of the solution gradually changed from light blue to dark blue. The reaction solution was stirred at room temperature for 10 minutes and then transferred to a 35 mL round-bottom flask. After treating the mixture at 150 ℃ for 1 min under microwave irradiation, it was cooled to room temperature rapidly by compressed air. The product was collected, washed with deionized water and absolute ethanol, and dried in air at 60 ℃ for 6 h. Other experiments were also conducted under different conditions such as using different alkali sources (NaOH, urea) while the other reaction conditions were kept the same.

The products were characterized by X-ray powder diffraction (XRD) with a Bruker D8 Advance Powder X-ray Diffractometer, equipped with graphite monochromatized Cu $K\alpha$ radiation (λ=0.154 06 nm), employing a scanning rate of 4°·min^{-1}, in the 2θ range from 10° to 70°. The operation voltage and current were maintained at 40 kV and 30 mA, respectively. FE-SEM images and EDS were measured on a Hitachi S-4800 field emission scanning electron microanalyser employing an operating voltage of 5 kV or 25 kV. TEM images were obtained on a JEM-200CX transmission electronic microscope, employing an accelerating voltage of 200 kV.

2 Results and discussion

Fig.1a shows the XRD pattern of the product prepared in the typical procedure. All diffraction

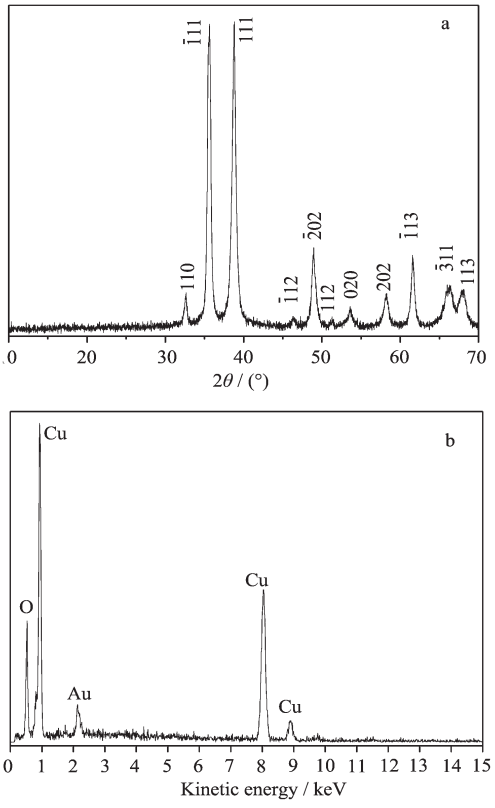


Fig.1 XRD patterns (a) and the EDS spectrum (b) of the product prepared in a typical experiment

peaks could be indexed to the monoclinic phase of CuO by comparison with the data from PDF card No. 65-2309. No peaks of any other phases or impurities are detected. Fig.1b is the EDS spectrum of a typical sample. The peaks of Cu and O are found. No impurities peaks are detected except Au, which is due to the gold plating.

Fig.2a is the low magnified FE-SEM image of the sample obtained in the typical procedure, indicating that the product is flower-like particles with diameters ranging from 2 to 3 μm. The magnified FE-SEM images (Fig.2b and 2c) show the CuO flower is constructed by the triangular sheets. In the HRTEM image (Fig.2d) taken from the edge of the individual microstructure, the (110) planes are marked, with the spacing of the adjacent lattice planes of 0.278 nm, which is very close to the theoretical value of 0.275 nm.

The alkali source was an important influence factor on the morphologies [20]. Fig.3 shows the morphologies of the products prepared using urea and NaOH as the alkali source. Fig.3a and b show that the product is platy flower-like particles with diameters ranging from 2.5 to 3.5 μm. Fig.3c is the magnified FE-SEM image of the platy flower-like particles, exhibiting that the assembly units are the same with those of the product prepared in the typical procedure. Fig.3d and e are the FE-SEM images of the CuO nanoparticles prepared using NaOH as the alkali source. The images show that the product is leaf-like nanosheets with widths in the range of 200~650 nm and lengths in the range of 3~4 μm. The smaller nanosheets with ca. 20 nm thickness are perpendicular to the leaf-like nanosheets. No self-assembled nanostructures are obtained. The possible reason could be that the NaOH has the stronger basicity.

The temperature does not greatly influence the morphology of the product. When the reaction is carried out at 120 ℃ for 1 min, the reaction rate is still fast and the product is flower-like CuO particles (Fig.4a and c). With the further decrease of the reaction temperature to 80 ℃, the product is also the flower-like particles (Fig. 4b and d). But the formation is slow compared with that obtained at 150 and 120 ℃.

In order to study the crystal growth process, the time-dependent controlled experiments were performed. As the high reaction temperature would result in the fast formation of CuO, the crystal growth process could not be detected at 150 ℃ in the typical procedure. In controlled experiments, lower reaction temperature (80 ℃) was adopted to decrease the

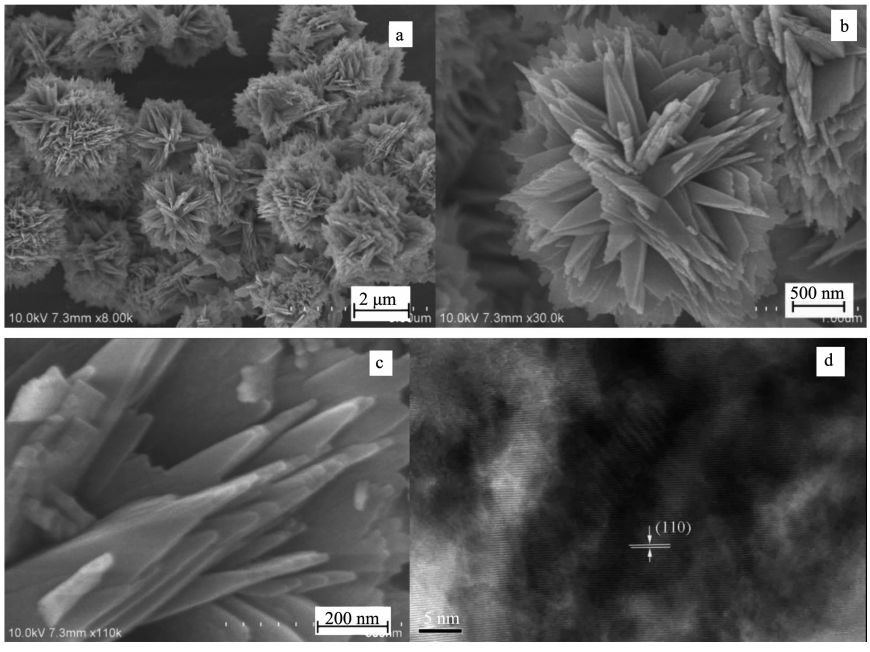


Fig.2　FE-SEM and HRTEM images of the sample prepared in a typical experiment

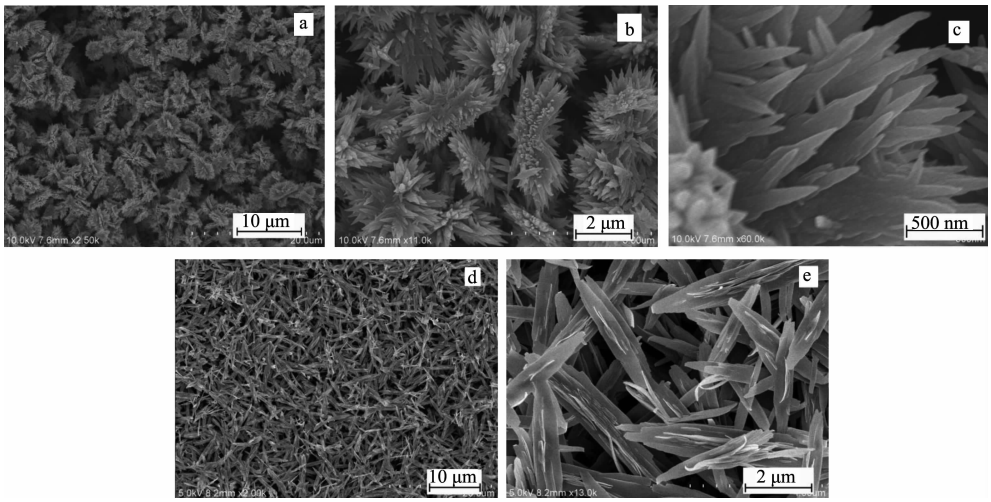


Fig.3 FE-SEM images of the products prepared using urea (a, b and c) and NaOH (d and e) as the alkali source

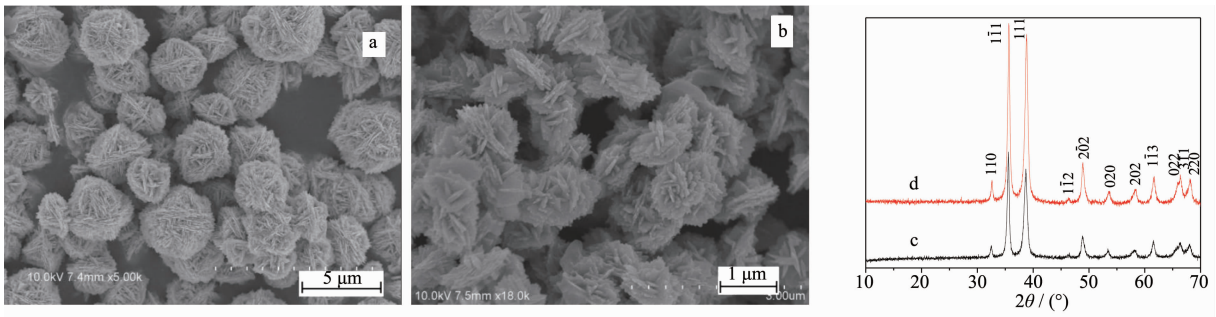


Fig.4 FE-SEM images and XRD patterns of the products prepared at (a)(c) 120 ℃ for 1 min and (b) (d) 80 ℃ for 10 min

reaction rate to investigate the crystal growth behaviors. When the reaction time was 30s at 80 ℃, the product was nanowires with 25~40 nm in width and several microns in length (Fig.5a). The XRD pattern (Fig.5d) shows that the product is a mixture of $Cu_2(OH)_3NO_3$ (monoclinic phase, PDF No. 14-0687) and CuO (monoclinic phase, PDF No. 65-2309). When the reaction time is extended to 1 min, some flower-like particles appear and the major product is still nanowires (Fig.5b). Correspondingly, the phase of the product is changed (Fig.5e). The monoclinic phase of $Cu_2(OH)_3NO_3$ disappears and the product is a mixture of $Cu(OH)_2$ (orthorhombic phase, PDF No. 80-0656) and CuO (monoclinic phase, PDF No. 65-2309). Further extending the reaction time to 3 min, the nanowires disappear. The flower-like particles and nanowires bundles coexist in the product (Fig.5c). The product is CuO entirely and all of the impurities disappear (Fig.5f). When the reaction time is 10 min, the product is entirely the flower-like particles and the phase of monoclinic CuO had been maintained (Fig.4b and 4d). The experimental phenomenon shows that a typical Oswald ripening process is involved in the process from 3 min to 10 min. The possible reactions could be described as follows:

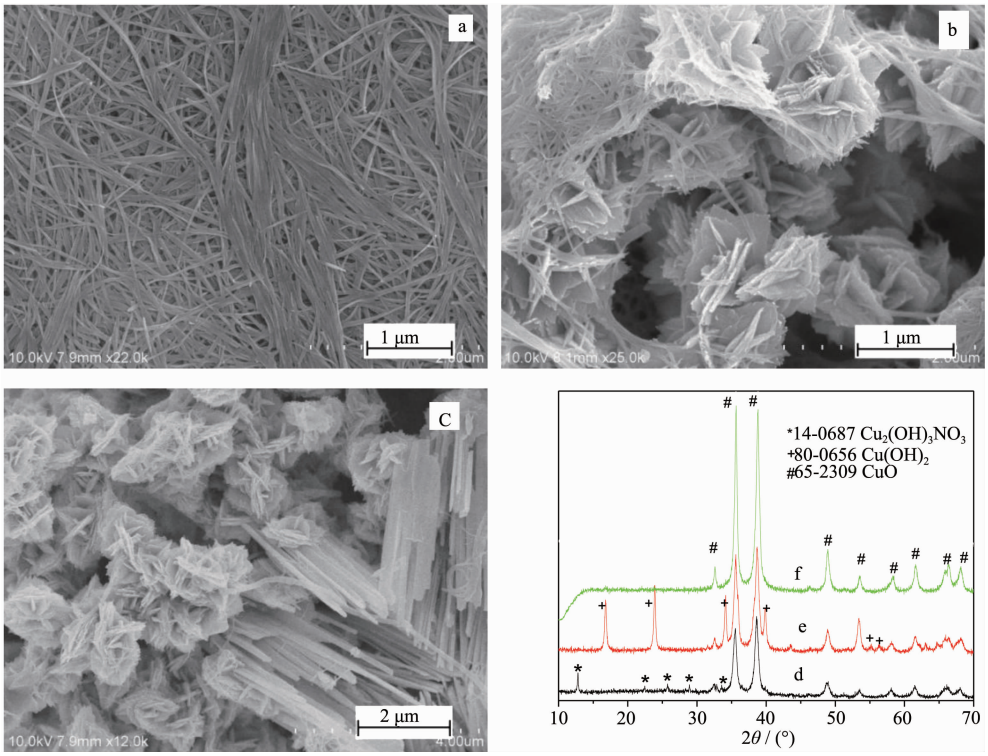
$$Cu(II)+NO_3^-+OH^- \longrightarrow Cu_2(OH)_3NO_3\downarrow \quad (\mathbf{1})$$

$$Cu_2(OH)_3NO_3+OH^- \longrightarrow Cu(OH)_2\downarrow \quad (\mathbf{2})$$

$$Cu(OH)_2 \longrightarrow CuO\downarrow \quad (\mathbf{3})$$

$$Cu_2(OH)_3NO_3 \longrightarrow CuO\downarrow +HNO_3+H_2O \quad (\mathbf{4})$$

Firstly, Cu^{2+} cation can coordinate with ammonia to form the $[Cu(NH_3)_4]^{2+}$ complex ions[21]. Subsequently, $[Cu(NH_3)_4]^{2+}$ complex ions can react with OH^- and NO_3^- to form the intermediate $Cu_2(OH)_3NO_3$(eq.**1**). The $Cu_2(OH)_3NO_3$ has the botallackite-type layer structures [22]. Two Cu^{2+} cations have the different coordination and chemical environments. In the alkaline condition, $Cu_2(OH)_3NO_3$ can react with OH^- to form 1D $Cu(OH)_2$ (eq.**2**) [23]. Thirdly, $Cu(OH)_2$ can decompose to produce CuO under the microwave-assisted hydrothermal condition (eq.**3**).



(a) (d) 30 s, (b)(e) 1 min, and (c)(f) 3 min

Fig.5　FE-SEM images and XRD patterns of the products prepared at 80 ℃ for different periods of time

Simultaneously, the $Cu_2(OH)_3NO_3$ might decompose to produce CuO directly (eq.**4**)[24].

3　Conclusions

In summary, we have prepared flower-like CuO via a simple microwave-assisted hydrothermal process. The results show that the alkali source could significantly influence the morphologies of the products. When ammonia or urea was used as the alkali source, the assembled flower-like nanostructures were obtained. When NaOH is used the products are leaf-like nanosheets. The formation process of flower-like CuO shows that intermediates of $Cu_2(OH)_3NO_3$ and $Cu(OH)_2$ are involved in the reaction.

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