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Preparation and Characterization of Flower-shaped CuO Nanostructures by Complex Precipitation Method

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Abstract

Flower-shaped CuO nanostructures have been prepared by complex precipitation method using $NH_3 \cdot H_2O$ as a complexing agent. The products were characterized in detail by combined means of X-ray diffraction (XRD), field-emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM), and Brunauer–Emmett–Teller N_2 adsorption-desorption analyses. Experimental results showed that the flower-shaped CuO nanostructures were composed of many coaxial CuO nanosheets in size of 3 μm in length and 61.61 nm in thickness. A detailed observation by TEM showed that the CuO nanosheets consisted of a large number of nanoparticles with the average size of about 40-70 nm and had porous structures with pore size of about 25.52 nm and surface area of 18.44 m^2/g. The formation mechanism of the flower-shaped CuO nanostructures was discussed.

Keywords: CuO; Flower-shaped; Nanosheets; Formation Mechanism

1 INTRODUCTION

Copper oxide (CuO) is an important p-type metal oxide semiconductor with a narrow band gap (1.2 eV). Due to its unique physical and chemical properties, nano-CuO has attracted considerable attention for its diverse applications as materials for catalysts [1], solar cells [2], optoelectronics devices [3], antibacterial materials [4], lithium batteries [5], and so on. Nano-CuO is also one of the most promising materials in the development of gas sensors because of its highly specific surface area and good electrochemical activity, and the nano-CuO based gas sensors have been extensively reported using for determination of H_2S [6,7], CO [8, 9], NO_x [10,11], ethanol [12,13], dopamine [14], nonenzymatic glucose [15], etc. In order to further enhance its performance in currently existing applications, extensive research efforts have been devoted to preparation of CuO with different morphologies due to their morphology dependent properties. So far, many CuO nanostructures and assemblies with varied morphologies have been obtained, such as nanofibers [16], nanoribbons [17], hollow [18], nanomorphs [19], dandelions [3], and flowers [20-29]. It is worth mentioning that nanoflowers, with current and possible applications in catalysis, gas sensors, antibacterial activity and lithium batteries, caused a definite interest to them [20]. For instance, Zaman and coworkers [28] reported that the flower-shaped CuO nanostructures with enhanced properties could be used to fabricate pH sensor and the CuO based pH sensor exhibited a linear electrochemical response within a wide pH range of 2-11. Mageshwari et al. [29] synthesized flower-shaped CuO nanostructures by reflux condensation method and they found that the flower-shaped CuO nanostructures could be used as an effective antimicrobial agent against pathogenic bacteria and fungi.

Due to their unique properties and wide applications, many research groups have paid more attentions to controlled preparation of the flower-shaped CuO nanostructures via different methods by investigating the experimental conditions and they found that the type of reactants, reaction time, temperature, pH value and surfactants played important roles in the formation of CuO nanostructures in different process [22-29]. For instance, Vaseem et al. [24] prepared the flower-shaped CuO nanostructures by solution process at 100 ^oC using copper nitrate, sodium hydroxide (NaOH), and hexamethylenetetramine (HMTA) for 3 hours without the use of any complex reagents.

They pointed that HMTA played a key role in the formation of flower-shaped morphologies. In addition to providing the OH^- ions to the solution, HMTA also acted as an effective shape-directing agent, which affected the flower-shaped morphology in a prominent way. According to the references above, it can be found that the CuO nanostructures with different morphologies can be prepared by changing the preparation method or the experimental conditions.

In the present study, flower-shaped CuO nanostructures were prepared by complex precipitation method using $NH_3 \cdot H_2O$ as a complexing agent without using any surfactant for controlling the crystal structure, such as cetyltrimethylammonium bromide (CTAB). The as-obtained CuO nanostructures were characterized by XRD, FESEM, TEM and BET. The formation mechanism of the flower-shaped CuO nanostructures was discussed.

2 EXPERIMENTAL

2.1 Materials

Copper nitrate ($Cu(NO_3)_2 \cdot 3H_2O$, 99 *wt*%), sodium hydroxide (NaOH, 96 *wt*%), ammonia ($NH_3 \cdot H_2O$, 25 *wt*%) and absolute ethanol (C_2H_5OH, 99.7%) were purchased from Kewei Company of Tianjin University. All the reagents were of analytical grade and were used without further purification.

2.2 Synthesis of Flower-shaped CuO Nanostructures

In a typical procedure, the flower-shaped CuO nanostructures have been prepared as follows: 3.025 g of $Cu(NO_3)_2 \cdot 3H_2O$ was added to 50 mL of distilled water under vigorous stir to form a homogeneous solution. Then, 8 mL of 25% $NH_3 \cdot H_2O$ was added to the above solution drop by drop under vigorous stirring and kept stirring for 30 min until a stable complex of $Cu(NO_3)_2$ and $NH_3 \cdot H_2O$ was formed (pH = 8). After that, 25 mL of 1.5 $mol \cdot L^{-1}$ NaOH solution was dropped slowly into the mixed solution (pH = 12) under vigorous stirring. After reaction, the obtained blue precipitate were washed several times with distilled water and then with ethanol, and dried in drying oven at 80 ^oC for 24 hours. Finally, the product was calcined in a furnace with an air atmosphere at 400 ^oC for 2 hours.

2.3Measurement and Characterization

The as-obtained samples were characterized using X-ray diffraction (XRD), which was carried out on a DX-2000 X-ray diffractometer equipped with a CuKa (λ=0.1542 nm) radiation tube operating at 40 kV and 25 mA. Transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HRTEM), and scanning electron microscope images were obtained by employing a FEI Tecnai G^2F20 transmission electron microscope and a 1530VP model field emission scanning electron microscope (FESEM). TEM samples were prepared by dispersing the as-obtained sample in ethanol by ultrasonic treatment, dropping it onto a carbon coated copper grid, and then drying it in air. All the measurements were performed at room temperature. Nitrogen adsorption-desorption measurements were performed at 77 K using 3H-2000PS1 (Beishide Instrument S&T (Beijing) Co., Ltd.) utilizing the Brunauer–Emmett–Teller (BET) method in the relative pressure range of 0.05-0.20 for the calculation of surface areas. The pore size distribution was calculated from the adsorption isotherm curves using the Barrett-Joyner-Halenda (BJH) method.

3 RESULTS AND DISCUSSIONS

3.1 XRD Analysis

The crystallinity of the product prepared by complex precipitation method using $NH_3 \cdot H_2O$ as a complexing agent was studied by XRD pattern, which is shown in Fig. 1 and compared with the Joint Committee on Powder Diffraction Standards (JCPDS) cards shown as bars at the below of the XRD pattern. In Fig. 1, all the reflection peaks of the products can be indexed to a monoclinic pure phase CuO in the standard data (JCPDS card number 48-1548). No diffraction peaks from any other impurities were detected. The strong and sharp diffraction peaks indicate that the product is crystallized.

The average crystallite sizes were estimated by the Scherrer's equation using the full width at half maximum

(FWHM) of the most intense peak ($11\bar{1}$). The Scherrer's equation (Eq. (1)) is described as follows:

$$D = 0.89\,\lambda / \beta \cos\theta \quad (1)$$

where D is the average crystallite size or particle size, λ is the X-ray wavelength (0.154056), θ is the Bragg angle and β is the full width at half-maximum (FWHM) of the peak. The calculation result shows that the average crystallite size of the as-obtained CuO, which was calculated from the full width at half-maximum of the peak ($11\bar{1}$) at 2θ = 35.590 ^{o}, was approximately 60.7 nm.

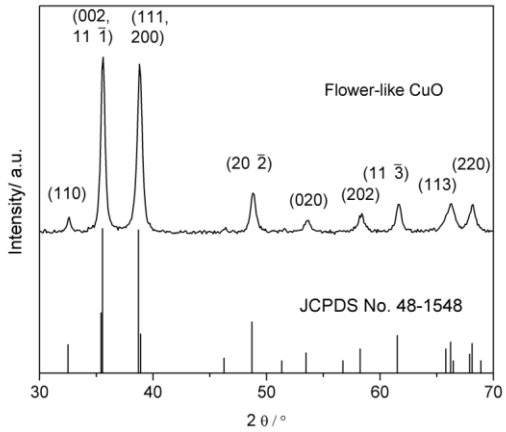


FIG. 1 XRD PATTERNS OF FLOWER-SHAPED CUO NANOSTRUCTURES. VERTICAL BAR IN BOTTOM LAYER DENOTES THE STANDARD DATA FOR CUO (JCPDS, NO. 48-1548)

3.2 SEM and TEM Analysis

The general morphologies of the as-prepared uniform flower-shaped CuO nanostructures prepared via complex precipitation method were examined by FESEM. A panoramic morphology of the CuO samples is displayed in Fig. 2a, indicating the high yield and uniformity. A magnified FESEM image showing the close observation of the CuO nanostructures is given in Fig. 2b. It can be found that the CuO samples show flower-shaped structures with the diameters in the range of about 3-5 μm, which are composed of a large number of coaxial nanosheets. Under the reported conditions, the CuO products are all in this morphology. A detailed view on a single flower-shaped CuO nanostructure can be observed from the high-magnification image (Fig. 2c and 2d), which shows that many bounds of coaxial CuO nanosheets cross connected with each other to form a flower-shaped structure. The further observation of CuO nanosheets are showed in Fig. 2e and 2f. It can be seen from Fig. 2e and 2f that the nanosheets with the length of about 3 μm and the thickness of about 61.61 nm are porous structures, which consist of a large number of CuO nanoparticles connected side by side.

The detailed structural characterization of the products was conducted by the transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM). A bound of nanosheets grown in the flower-shaped CuO nanostructures can be observed in the typical low-resolution TEM image of the products as shown in Fig. 3a, which demonstrates that the CuO nanosheets connected side by side are made up of a large number of nanoparticles. This result reveals the consistency with FE-SEM observations (Fig. 2d). It can be clearly observed from Fig. 3b that the average size of the CuO nanoparticles varies in the range of 40-60 nm, which are in good agreement with the calculated crystallite size of 60.7 nm in XRD pattern. Fig. 3c shows the high-resolution transmission electron microscopy (HRTEM) image of a CuO nanoparticle. The resolved fringes with a separation of 0.232 nm and 0.253 nm can be observed in Fig. 3d, which corresponds to the (111) and ($\underline{1}11$) planes of monoclinic CuO, respectively. These results indicated that the nanoparticles grew along [111] and [$\underline{1}11$] directions.

3.3 Surface Areas and Porosity

In order to to get more information about the flower-shaped CuO naostructures, N_2 adsorption- desorption analysis was performed and the results were shown in Fig. 4. The N_2 adsorption-desorption isotherm and the pore-size distribution confirmed the presence of porous structures of the products. The BET specific surface area of the flower-

shaped CuO is not large (about 18.44 m^2/g), which is mainly because that the pores are formed by the combination of CuO nanoparticles with the average size of about 60 nm. According to the BJH pore size distribution curve (Fig. 4b), the pore size of the CuO products is about 25.52 nm, which is consistent with the microscopy observations.

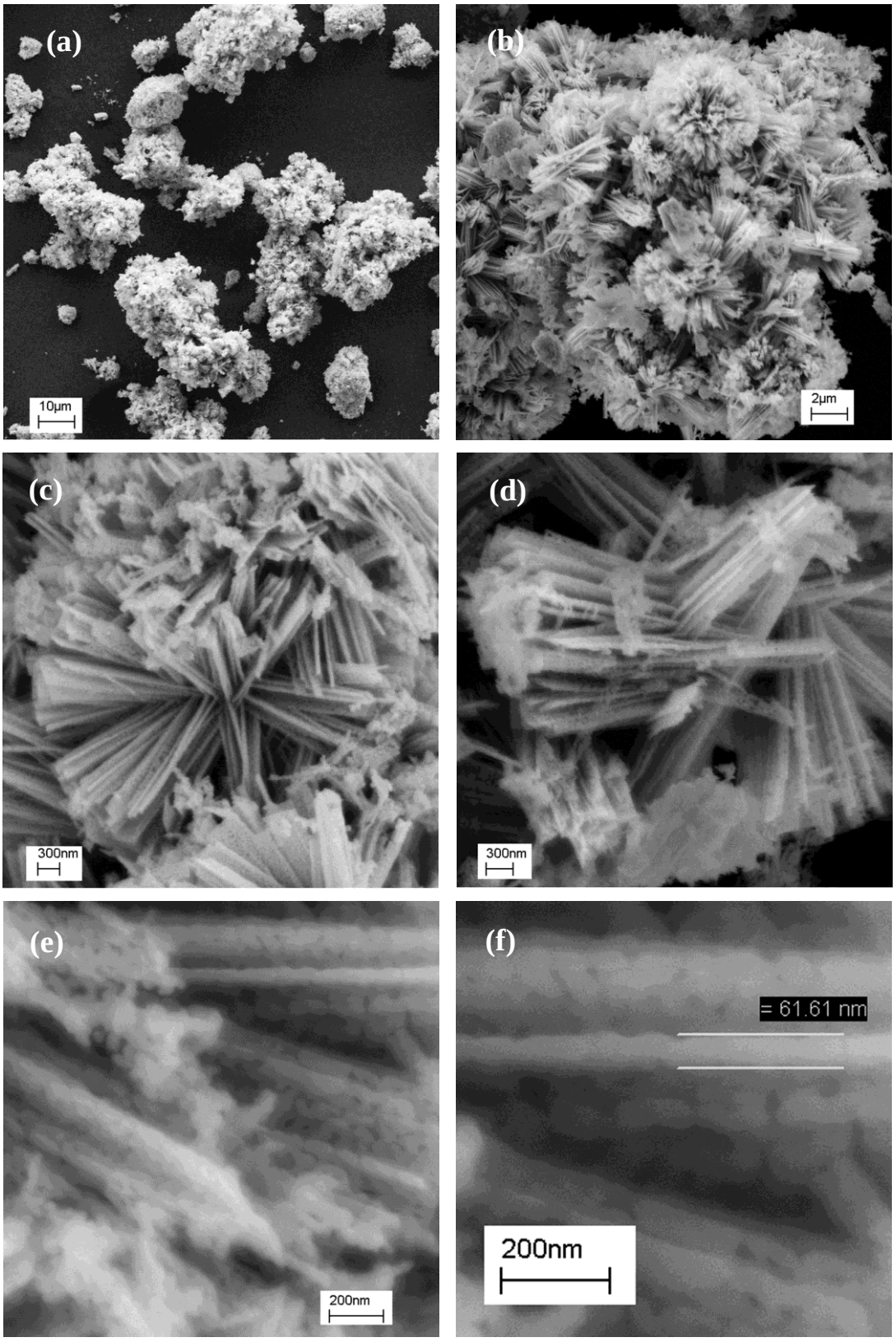


FIG. 2 FE-SEM IMAGES: THE LOWER MAGNIFICATION IMAGE (A, B) AND THE HIGHER MAGNIFICATION IMAGES(C, D, E, F) OF THE CUO SAMPLES OBTAINED BY COMPLEX PRECIPITATION METHOD.

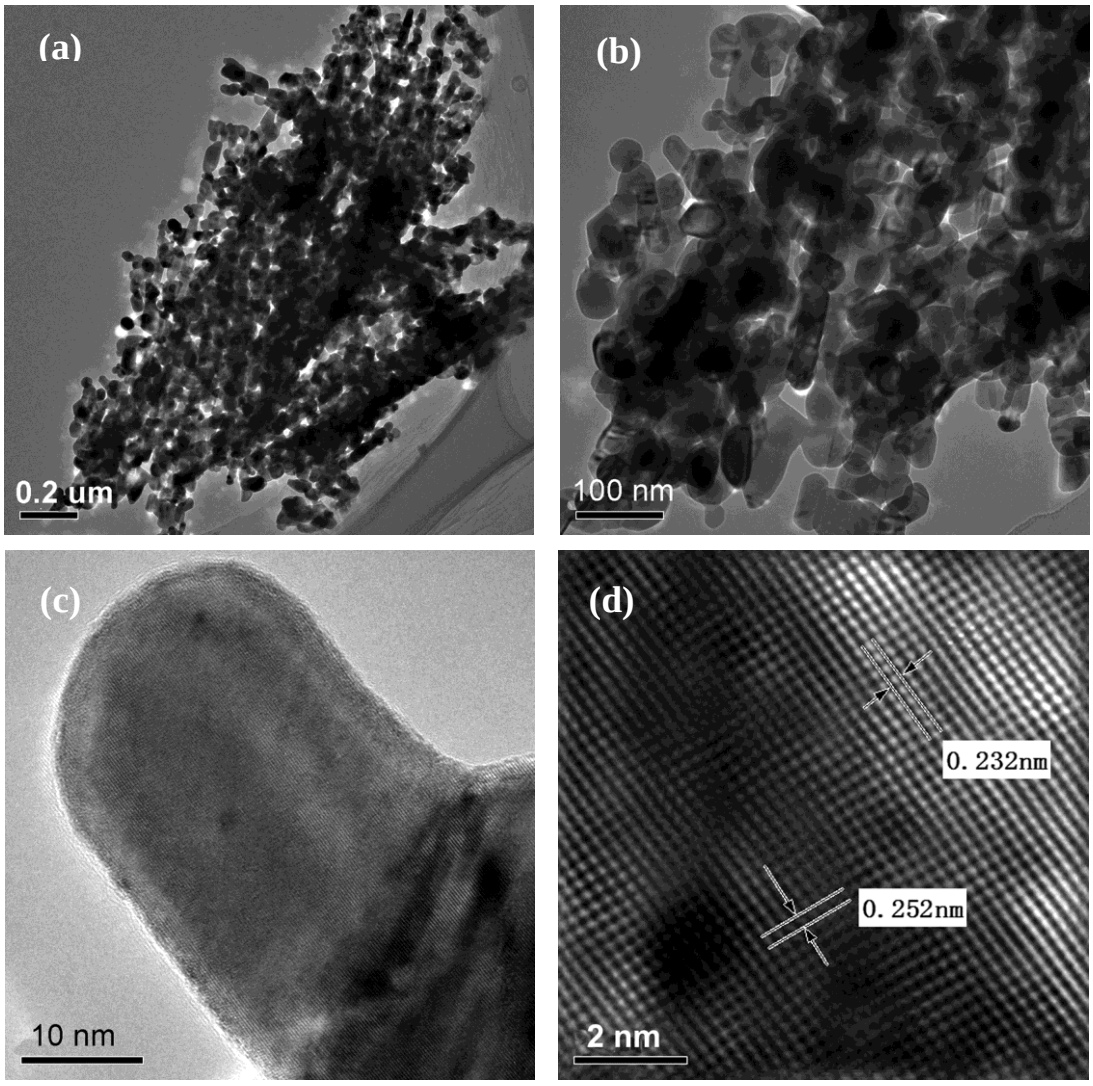


FIG. 3 LOW MAGNIFICATION TEM IMAGE (A, B) AND HRTEM IMAGE (C, D) OF THE FLOWER-SHAPED CUO NANOSTRUCTURES OBTAINED BY COMPLEX PRECIPITATION METHOD

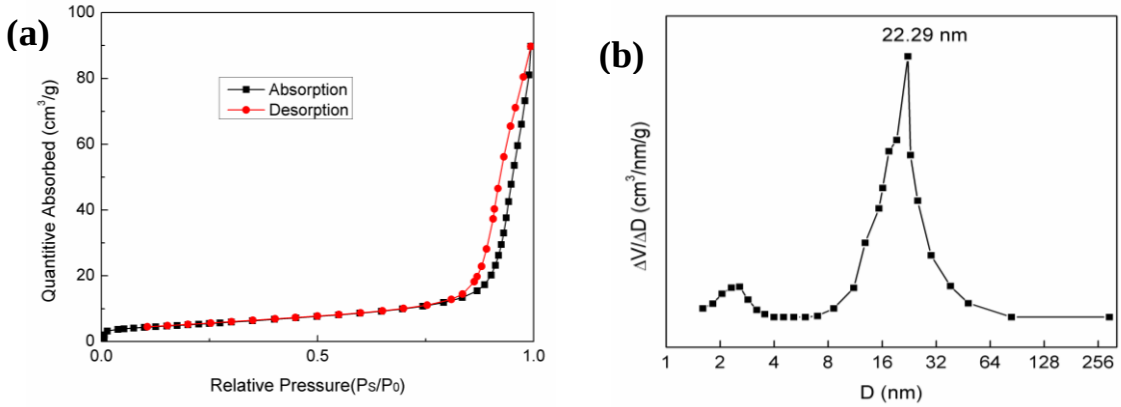


FIG. 4 BET N_2 ADSORPTION-DESORPTION ISOTHERM AND BJH PORE SIZE DISTRIBUTION OF THE FLOWER-SHAPED CUO PRODUCTS.

3.4 Formatiom Mechanism of the Flower-shaped CuO Nanostructures

During the past decade, many research groups have reported the preparation of flower-shaped CuO nanostructures and their growth mechanisms. For instance, Chu and co-workers [26] prepared hierarchical 3D flower-like CuO nanostructures and straw-like CuO nanostructures via reverse micro-emulsion method. They concluded that there

were four stages in the synthesis process: primary nanoparticles synthesis, oriented growth, ordered self-assembly, and crystal growth. They also found that the hierarchical 3D flower-shaped CuO nanostructures formed during the aging procedure rather than in reverse micelles. Sun et al. [27] demonstrated a one-pot water/ethanol solution-phase transformation of $Cu_2(NO_3)(OH)_3$ precursors into bi-component CuO hierarchical nanoflowers by a sequential in situ dissolution–precipitation process. The formation mechanism was described as follows: CuO seeds or clusters were generated in situ from dissolution of the $Cu_2(OH)_3NO_3$ nanoflowers at the initial dehydration stage; in order to minimize the overall energy of the reaction system, primary nanoparticles tended to aggregate rapidly; as time progressed, CuO nanoparticles were fused together to finally form the monoclinic CuO nanoflowers. They pointed that the CuO nanostructures with different morphologies could be controlled prepared by adjusting the volume ratio between water and ethanol. Zaman et al. [28] synthesized flower-shaped CuO nanostructures composed of thin leaves by a low-temperature chemical bath method. They described the growth mechanism of the CuO nanostructures as follows: a small amount of CuO nuclei formed firstly at the initial stage of the reaction; a new surface covered with ions would in turn attracted ions with opposite charges to cover the next surface; different CuO nanostructures formed by changing the pH of the solution. According to the above, we found that the formation mechanisms of the flower-shaped CuO structures reported in the literatures were different from each other due to the differences of preparation methods and reaction conditions. In the present study, we have prepared the flower-shaped CuO nanostructures by complex precipitation method using $NH_3{\cdot}H_2O$ as a complexing agent and NaOH as a precipitant. The reaction mechanism involved in the formation of the flower-shaped CuO nanostructures can be described as follow:

$$NH_3{\cdot}H_2O \rightarrow NH_4^+ + OH^- \quad (1)$$

$$[Cu(NH_3)_4]^{2+} + 2OH^- \rightarrow Cu(OH)_2 + 4NH_3 \quad (2)$$

$$Cu(OH)_2 \rightarrow CuO + H_2O \quad (3)$$

$NH_3{\cdot}H_2O$ played a key role in the formation of flower-shaped nanostructures, which not only acted as a complexing agent, but also provided the OH^- ions to the solution. According to the Eq. 1 and 2, it can be concluded that $Cu(NH_3)_4^{2+}$ was first formed when $NH_3{\cdot}H_2O$ was added into $Cu(NO_3)_2$ solution at the initial stage of the reaction. As the concentration of OH^- in the solution increased due to the slowly dropped addition of NaOH solution, $Cu(NH_3)_4^{2+}$ was reacted with OH^- and $Cu(OH)_2$ precipitate was obtained as the precursor. An oriented aggregation growth process might take place because of the electrostatic attraction during the formation of $Cu(OH)_2$ precipitate. Finally, the flower-shaped CuO nanostructures formed after an aging process. The formation of flower-like CuO nanostructures can be described as follows (as shown in Fig. 5):

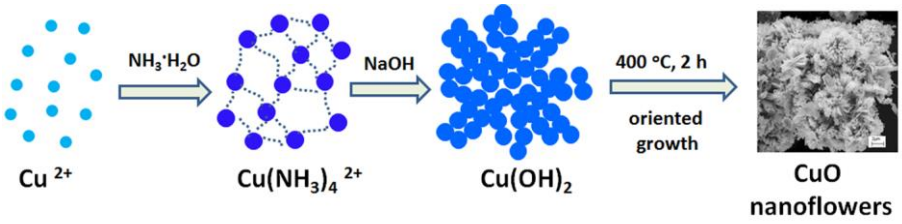


FIG.5 SCHEMATIC ILLUSTRATION OF THE FORMATION OF FLOWER-SHAPED CUO NANOSTRUCTURES

4 CONCLUSIONS

In this paper, flower-shaped CuO nanostructures have been prepared by complex precipitation method using $NH_3{\cdot}H_2O$ as a complexing agent. Experimental results showed that the flower-shaped CuO nanostructures were composed of many coaxial CuO nanosheets in size of 3 μm in length and 61.61 nm in thickness. A detailed observation by TEM showed that the CuO nanosheets consisted of a large number of nanoparticles with the average size of about 40-70 nm. The flower-shaped CuO structures show porous structures with the pore size of about 25.52 nm and a specific surface area of 18.44 m^2/g. $NH_3{\cdot}H_2O$ played a key role in the formation of the flower-shaped nanostructures, which not only acted as a complexing agent, but also provided the OH^- ions to the solution. The

flower-shaped CuO nanostructures obtained by complex precipitation method here can be used as materials for gas sensors, catalysts, and antimicrobial agent.

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