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Synthesis of claw-like CuO and its catalytic activity in the thermal decomposition of ammonium perchlorate

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Claw-like CuO was prepared by solution process at 100 °C simply by using copper nitrate and hexamethylenetetramine for 3 h. The structure and morphology of resulting CuO powders were characterized by X-ray diffraction, scanning electron microscopy and transmission electron microscopy. CuO nanocrystals were studied as an additive for promoting the thermal decomposition of ammonium perchlorate. With the addition of the claw-like CuO nanocrystals, thermal decomposition temperature of ammonium perchlorate decreased. CuO nanocrystals showed catalytic activity on the decomposition of ammonium perchlorate.

Key words: *nanostructure; crystal growth; chemical synthesis; catalytic activity*

1. Introduction

In recent years, the research into the shape control of various nanostructures has been widely developed because of their morphology dependent properties. Such research concentrated not only on metal and semiconductor nanostructures but also on transitional metal oxide nanostructures. Copper oxide (CuO), as an important oxide of transitional metal with a narrow band gap ($E_g = 1.2$ eV), has been extensively studied because of its importance for fundamental investigations and practical applications such as heterogeneous catalysts [1–3], gas sensors [4], and electrode materials [5, 6]. It is also a promising material for fabricating solar cells [7], due to its photoconductive and photochemical properties. Because of the practical reasons mentioned above, the synthesis of nanostructured CuO has also attracted considerable attention. To this end, various techniques have been used including precursor thermal decomposition [8], hydrothermal methods [9–11], solid-phase methods [12], wet-chemical methods

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[7, 13], hydrolysis route [14], electrochemical methods [15], template-free solution route [16], and chemical deposition method [17].

Up to now, there have been many reports about the preparation of CuO nanostructures such as nanorods [6, 7, 13], nanowires [12, 18], nanosheets [19] nanoparticles [20], nanoplatelets [11], nanowhiskers [21], nanoribbons [13], Other than morphologies of CuO structures, some complex structures of CuO have also been reported in the literature, such as flower-like [14, 17], sheaf-like [22], dendrite-like [9], doughnut-like [8], and sphere-like structures [4, 23]. However, the obtained morphology (claw, flower,) in these reports is limited.

In this paper, a simple chemical precipitation method is employed to synthesize CuO nanostructures in the presence of aqueous solution of hexamethylenetetramine. Without using templates, surfactants or additives, this route is capable of synthesizing a variety of complex CuO structures, including claw-like structures, and multilayer flower-like ones. These structures consist of nanometer-sized CuO crystals self-organized into micrometer-sized flower-like with a hierarchical architecture. The influence of reaction time on morphology of the CuO nanostructure is examined. In addition, the catalytic effect of the as-synthesized CuO was studied in this paper. The claw-like CuO nanostructures showed effective catalytic activity on the decomposition of ammonium perchlorate.

2. Experimental

Synthesis of samples. Copper nitrate ($Cu(NO_3)_2 \cdot 3H_2O$), hexamethylenetetramine (HMTA, $C_6H_{12}N_4$) were all analytical reagents. In a typical procedure, 3.62 g of $Cu(NO_3)_2 \cdot 3H_2O$ was dissolved in 150 cm^3 of deionized water under stirring. Then, 0.05 M aqueous solution of hexamethylenetetramine was added into the above solution under constant stirring at room temperature, forming a blue aqueous solution with pH equal to 5.0. The obtained solution was then heated and refluxed with continuous stirring at 100 °C for 3 h in a three-necked refluxing pot. During refluxing, the temperature of the solution was controlled by manually adjustable thermocouple. After cooling to room temperature, the products were filtered, washed with deionized water and ethanol for several times, and finally dried in ambient environment. The product was labelled as sample A. Reaction time extended to 5 h, other conditions kept unchanged, the product was labelled as sample B.

Characterization of samples. The morphologies of products were determined by scanning electron microscopy (SEM, JSM-6480A), equipped with EDS (energy dispersive spectroscopy), and transmission electron microscopy (TEM, Philips CM 200 FEG, 160 kV). The structure and crystal phases were characterized by power X-ray diffraction (XRD) with CuK_α radiation, wavelength λ = 1.54178 Å (Rigaku D/Max-IIIA).The study of the thermal behaviour of the CuO nanocrystals was carried out with an STA 409 PC thermal analyzer at the heating rate of 10 °C·min^{-1} from 35 °C to 450 °C under argon atmosphere and under ambient atmospheric pressure. The quality and composition of the synthesized flower-shaped CuO nanostructures were characterized by the Fourier transform infrared (FT-IR) spectroscopy in the range of 400–4000 cm^{-1}.

Catalytic activity measurements. The catalytic activities of claw-like CuO nanostructures in the thermal decomposition of AP were studied by TG technique using the STA 409 PC thermal analyzer at the heating rate of 10 °C·min^{-1} in an Argon atmosphere over the temperature range of 35–450 °C. In this experiment, the CuO powders and NH_4ClO_4 were thoroughly mixed in the mass proportion of 2:98 to prepare the target samples for thermal decomposition analyses. A total sample mass of 3.0 mg was used in all runs. In this work, open alumina crucibles were employed for all runs in order to eliminate possible catalytic impacts from noble metals.

3. Results and discussion

In Figure 1, typical XRD patterns for the sample series are shown. XRD patterns of the samples thus obtained matched well the standard data for bulk CuO, while no impurity peaks from secondary phase of Cu_2O or Cu were detected. In addition, the EDS (Fig. 2c) spectrum reveals that the atomic ratio of Cu to O is equal to 1:1. Therefore, it is obvious that the sample is composed of pure monoclinic phase CuO which is consistent with the XRD pattern.

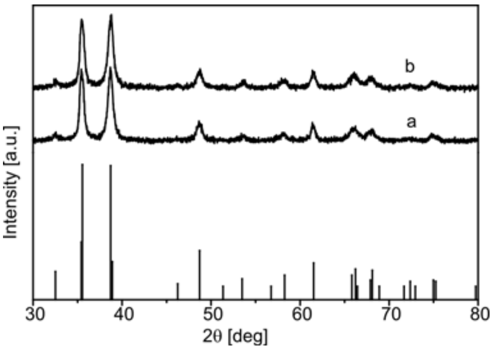
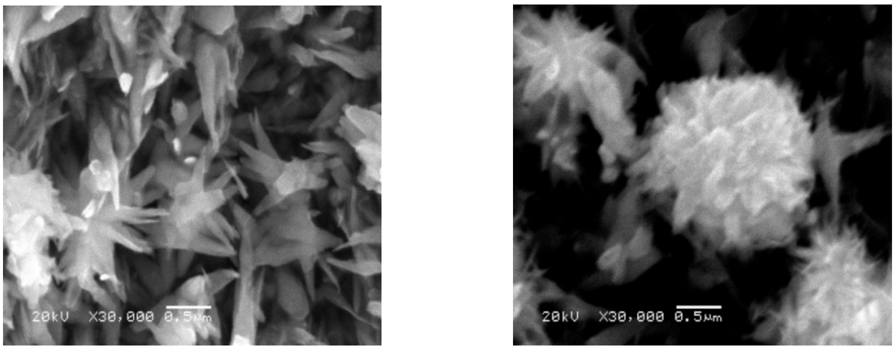


Fig. 1. XRD pattern of the CuO nanostructures; with reaction time 3 h (curve a) and 5 h (curve b); vertical lines represent the standard diffraction data of CuO from JPCDS file

The particle size and morphology of CuO nanocrystals were investigated using SEM (Fig. 2) and TEM (Fig. 3).

First, we briefly summarized the preparation conditions that yielded pure phase CuO nanocrystals with various reaction times. When CuO nanocrystals were prepared in solution at 100 °C simply by using copper nitrate and hexamethylenetetramine (HMTA) for 3 h, the morphologies of claw-like CuO nanocrystals with uniform shape and size were obtained on a large scale (Fig. 2a).



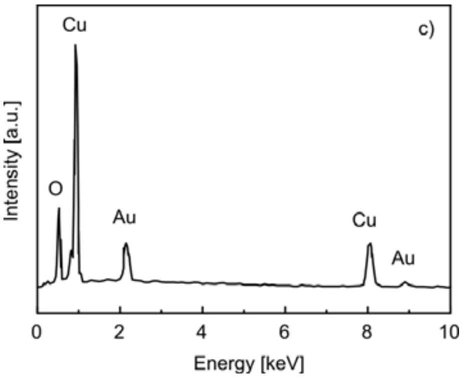


Fig. 2. SEM images of CuO nanostructures:
a) claw-like, b) flower-like, c) EDS of the sample A

When the reaction time extended to 5 h, the morphologies of CuO flower-like structures were investigated (Fig. 2b). Further structure characterization was carried out by the TEM equipped with the FFT setup. Figures 3a–c show the low magnification TEM images of the claw-like CuO nanocrystals, flower-like structures and building blocks. The lattice fringes can be easily observed from the HRTEM image. The lattice fringe corresponding to (110) (d = 0.25 nm) crystallographic planes of CuO is presented in Fig. 3d, which is consistent with the Fourier diffractogram shown in the inset. In addition, the crystal plane spacing (d = 0.25 nm) was calculated in the Gatan Digital Micrograph and the photos were disposed by the Adobe Photoshop Image.

The quality and compositions of the synthesized CuO structures, shown in Fig. 4, were characterized by the Fourier transform infrared (FTIR) spectroscopy in the range of 400–4000 cm^{-1}. Several bands appeared in the FTIR spectrum of the as-grown sample. The presence of a weak absorption at 3444 cm^{-1} is caused by the stretching vibration of the adsorbed water and surface hydroxyls. No infrared active modes from Cu_2O were detected. The absorption bands at 1673 cm^{-1} are bending vibrational modes of combined water molecules. The appearance of a weak and small absorption peak at 2339 cm^{-1} could be ascribed to CO_2 present in air. Absorption bands observed at 490, 433 cm^{-1} are characteristic of Cu–O vibrational modes. The absorption band at 1412 cm^{-1} was also found in the spectrum which was attributed to the presence of CH plane bending vibrations.

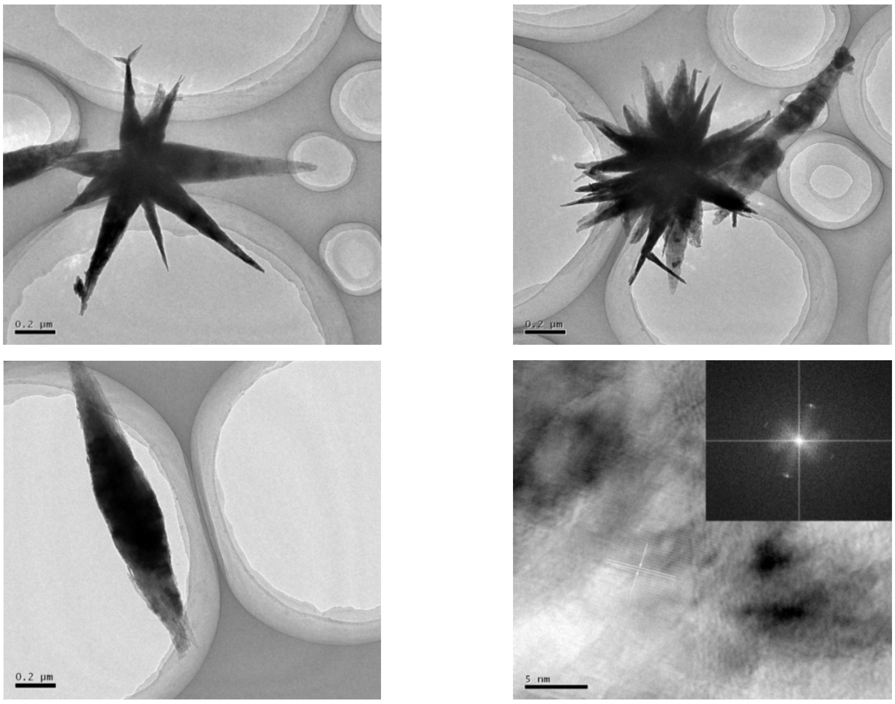


Fig. 3. Low magnification TEM image of CuO nanostructures: a) claw-like, b) flower-like, c) low magnification TEM image of primary building units, d) HRTEM image of sample A showing the difference between two lattice fringes being ca. 0.252 nm using a Gatan Digital Micrograph. Corresponding FFT pattern (inset) is consistent with the HRTEM observation

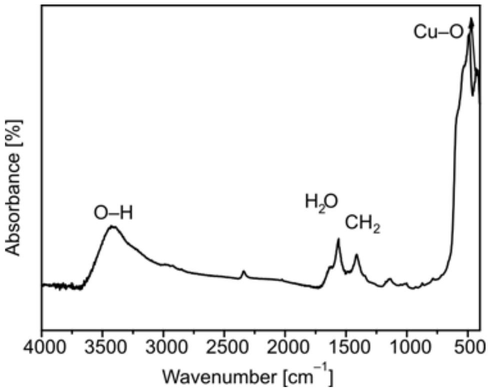


Fig. 4. FT–IR spectrum of the as-obtained final product A

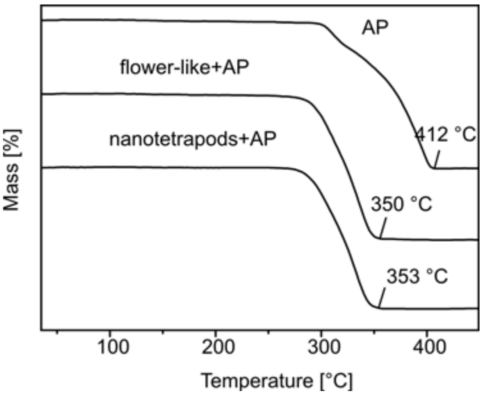


Fig. 5. TG curves for pure AP, mixtures of AP with addition of CuO nancrystals by the solution process in reaction times of 3 h and 5 h

To study the catalytic properties of the as-prepared CuO nanocrystals, the thermal-decomposition of the mixture of as-prepared CuO and NH_4ClO_4 was studied. Figure 5 shows TG curves for pure AP and mixtures of AP with CuO nanostructures. The decomposition of pure AP generally extends from 322 to 412 °C. Addition of CuO nanostructures in AP led to a significant reduction of the ending decomposition temperature, to 350 °C and 353 °C, respectively.

4. Conclusion

Claw-like or flower-like morphologies of CuO have been synthesized in a large-quantity via simple solution process at low temperature of 100 °C without the use of any complex instruments and reagents. The morphologies and crystallization of the as-prepared CuO were mainly determined by the molar ratio of hexamethylenetetramine ($C_6H_{12}N_4$) to $Cu(NO_3)_2$, reaction temperature and reaction time. The detailed structural investigations revealed that the as-grown products are nanocrystalline pure CuO possessing a monoclinic structure. The products show an effective catalytic activity on the decomposition of NH_4ClO_4. With the addition of nanocrystalline CuO, the temperature of thermal decomposition of AP decreased.

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