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A novel one-step method to synthesize copper nitrate hydroxide nanorings

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Abstract: With the purpose of searching for a convenient process to synthesize nanoparticles with special structure, a simple solid-state reaction in the presence of nonionic surfactant OP-10 at room temperature was adopted to prepare copper nitrate hydroxide ($Cu_2(OH)_3NO_3$) nanorings with an average internal diameter of 250 nm and average wall thickness of 100 nm. The formation of $Cu_2(OH)_3NO_3$ nanorings has a close relation with OP-10. Transmission electron microscopy(TEM), field emission scanning electron microscopy(FESEM), thermogravimetric analysis(TGA) and X-ray diffractometry(XRD) were used to characterize the obtained nanorings. The UV-Vis spectrum shows that the optical property of $Cu_2(OH)_3NO_3$ nanorings is similar to that of CuO or CuS. The synthesis method used here proves both simplicity and high efficiency.

Key words: copper nitrate hydroxide; solid-state reaction; nanorings

1 Introduction

Recently, there is a lot of research on nanometer-sized rings (nanorings). Many methods have been used to prepare nanorings[1−3]. However, most methods often need expensive apparatus and complicated process. Solid-state chemistry is a fast-developed science, enhanced by its numerous applications in the high-technology industries[4]. Over the past decades, solid-state reactions have been used to prepare considerable materials[5−6]. CAO et al[7] prepared pure and Nd-doped ZnO nanorods by simple low-heating solid-state chemical reaction of zinc acetate dihydrate and sodium hydroxide in the presence of sodium dodecyl sulfate (SDS) at room temperature. Their results indicate that the sensor based on 2% (molar fraction) Nd-doped ZnO nanorods presents much higher sensitivity, better selectivity and shorter response-recovery time to 100×10^{-6} ethanol vapor than the pure ZnO nanorods sensor. WU et al[8] synthesized nano-sized cerium-titanium pyrophosphates $Ce_{1-x}Ti_xP_2O_7$ by grinding a mixture of $Ce(SO_4)_2\cdot 4H_2O$, $Ti(SO_4)_2$, and $Na_4P_2O_7\cdot 10H_2O$ in the presence of surfactant PEG-400 at room temperature. Their results show that nano-sized $Ce_{1-x}Ti_xP_2O_7$ behaves as an excellent UV-shielding material. In their synthesis, the yield of various nanomaterials synthesized by the solid-state reaction is as high as nearly 100%. REN et al [9] also found a very high yield during large-scale synthesis of single-crystal alpha manganese sesquioxide nanowires via solid-state reaction method.

Copper nitrate hydroxide is a kind of intermediate of copper products and often used as pesticide, filler of gas sac, etc. It is a good additive. The study about copper nitrate hydroxide is very few and there is less report on the synthesis of nanorings by solid-state reaction at room temperature.

In this work, we adopted this simple one-step, solid-state reaction to prepare copper nitrate hydroxide nanorings in the presence of nonionic surfactant octyl phenyl poly (ethylene oxide)-10 (OP-10) at room temperature. This process was carried out in air.

2 Experimental

2.1 Synthesis

All reagents were used directly without further purification. In a typical synthesis, 0.79 g NH_4HCO_3 and

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2 mL OP-10 were mixed and ground for 10 min; then 2.42 g $Cu(NO_3)_2{\cdot}3H_2O$ was added and ground for another 30 min. The mixture was put aside in air at room temperature for about 4 h and then washed by distilled water at least three times. The final precipitation was dried in an oven at 60 ℃ for 6 h.

2.2 Characterization

Powder XRD patterns of as-synthesized samples were recorded on a Philips X'Pert PRO S X-ray diffractometer with Cu K_α irradiation (λ=1.541 874 Å). TEM images were observed on a Hitachi-H800 transmission electron microscope under 200 kV accelerating voltage. Field emission scanning electron microscopy(FESEM) images were observed on a JEOL JSM-6700F microanalyzer with 10 kV accelerating voltage. Thermogravimetric analysis(TGA) was performed with a Shimadzu TGA-50H instrument under a stream of air. The sample was heated from 40 to 600 ℃ at 10 ℃/min. Samples for ultraviolet–visible (UV-Vis) absorption were dispersed with absolute ethanol and recorded on an UV-2401 PC Shimadzu UV-Vis spectrophotometer.

3 Results and discussion

When the stoichiometric mixture of the starting reagents is ground, the following reaction occurs:

$$3NH_4HCO_3+2Cu(NO_3)_2 \xrightarrow{\text{OP-10}} Cu_2(OH)_3NO_3\downarrow+3NH_4NO_3+3CO_2\uparrow \quad (1)$$

3.1 XRD analysis of synthesized powders

The product was washed with distilled water at least three times to remove excessive NH_4HCO_3 and OP-10 after starting reagents were ground completely. The XRD pattern of the product is shown in Fig.1. It can be seen that the remainder is very pure. The main peaks of marked numbers can be indexed to the primitive monoclinic structure with cell parameters, a=5.605 Å, b= 6.087 Å, c=6.929 Å, β=94.48°, which are similar to the values in the standard card JCPDS file No.15-0014 ($Cu_2(OH)_3NO_3$).

3.2 Microscopic patterns of $Cu_2(OH)_3NO_3$

The TEM and FESEM images of the $Cu_2(OH)_3NO_3$ sample in Fig.2 reveal that the copper nitrate hydroxide powders consist of nanorings. These nanorings have a average internal diameter of 250 nm and average wall thickness of 100 nm. The FESEM images further show that the rings in TEM image are stacked one by one into cylinders. It cannot be seen and speculated how many rings are stacked into one cylinder. Every nanoring is not an single $Cu_2(OH)_3NO_3$ particle but made of small pieces of $Cu_2(OH)_3NO_3$ particles.

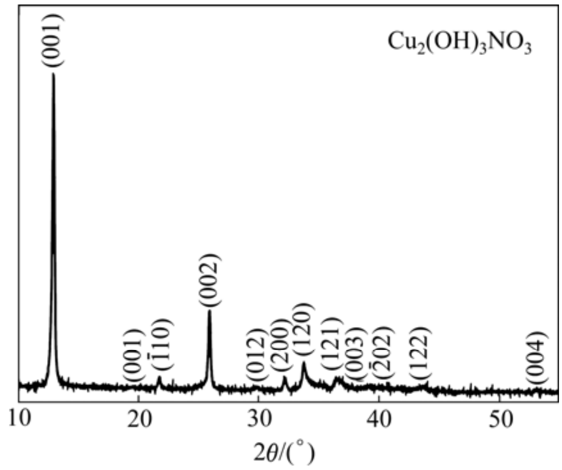

Fig.1 XRD pattern of prepared copper nitrate hydroxide nanorings

3.3 Decomposition of $Cu_2(OH)_3NO_3$

Fig.3 shows the result of thermogravimetric analysis of the product and the XRD pattern of the prepared sample after thermogravimetric analysis.

$Cu_2(OH)_3NO_3$ decomposes into CuO at 236−280 ℃ in Fig.3(a), which also can be proved from Fig.3(b). In Fig.3(b), the main peaks of marked numbers can be indexed to the end-centered monoclinic structure with cell parameters, a=4.683 Å, b=3.422 Å, c=5.128 Å, β=99.54°, which are similar to the values in the standard card JCPDS file No.72-0629 (CuO). So, when the sample is heated, the following reaction can occur:

$$4Cu_2(OH)_3NO_3 \xrightarrow{\text{High temperature}} 8CuO+6H_2O\uparrow+4NO_2\uparrow+O_2\uparrow \quad (2)$$

The initial mass loss of 0.4% (up to 236 ℃) is due to the evaporation of physically adsorbed water. Between 210 and 325 ℃, a mass loss of 32.70% is attributed to removal of H_2O (gas), NO_2 and O_2. The residual mass of 66.90% should be the CuO solid. The mass loss of 32.70% is very close to the theoretic value (33.60%) according to reaction (2). Therefore, reactions (1) and (2) proposed above are correct from TGA and XRD analysis.

3.4 UV-Vis spectrum analysis of $Cu_2(OH)_3NO_3$

Fig.4 shows UV-Vis spectrum of $Cu_2(OH)_3NO_3$ nanorings, which has a broad absorption peak whose center is at about 295 nm. This value is the same as that of CuO and CuS[10−11]. This indicates that the synthesized $Cu_2(OH)_3NO_3$ nanorings have similar optical property.

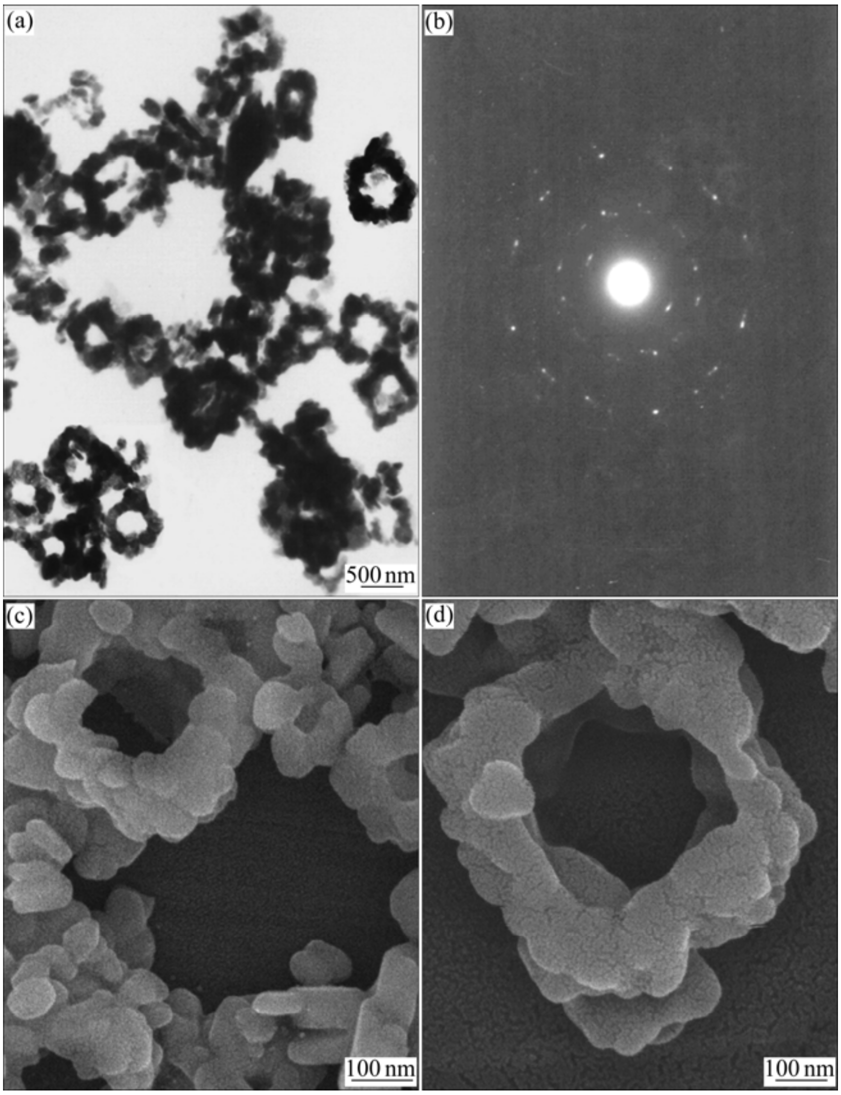

Fig.2 TEM image (a), selected area electron diffraction pattern (b) and FESEM images (c, d) of synthesized copper nitrate hydroxide

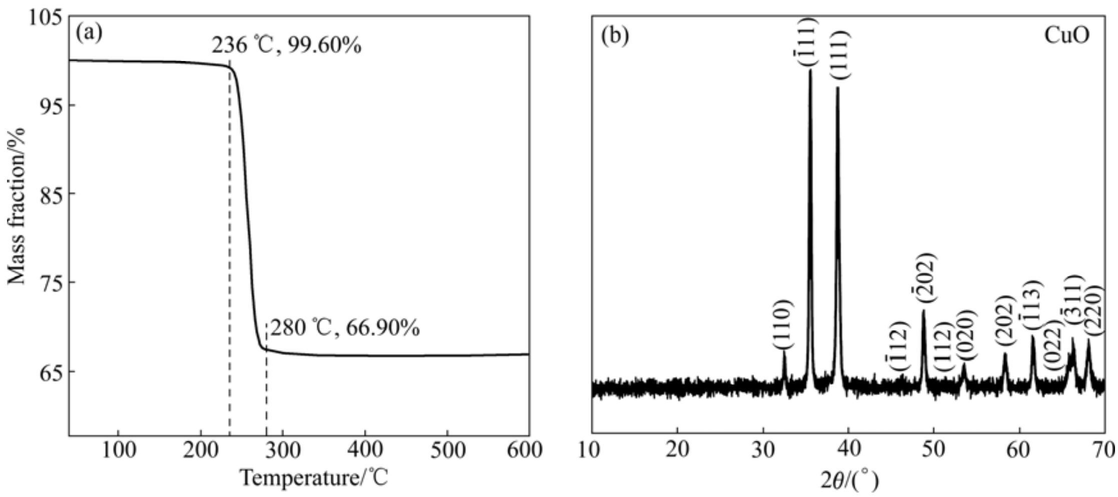

Fig.3 TGA plot (a) and XRD pattern (b) of $Cu_2(OH)_3NO_3$ nanorings after being heated at 600 ℃

3.5 Comparative experiments

But under similar experiment conditions except not using additives or using other surfactant, almost no nanorings could be found as shown in Fig.5. It can be

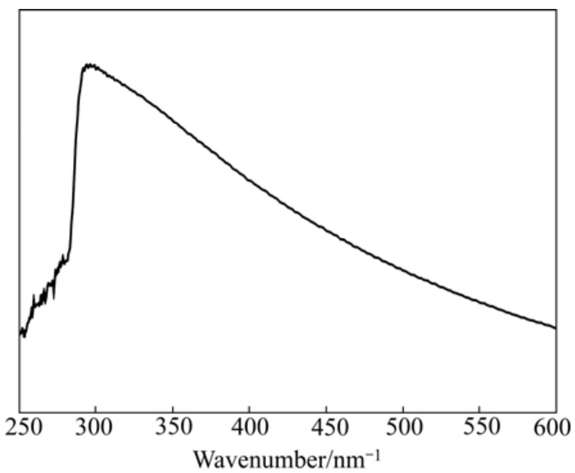

Fig.4 UV-Vis spectrum of $Cu_2(OH)_3NO_3$ nanorings

concluded that anionic surfactants are not beneficial to the formation of nanorings (Fig.5(b)). Maybe this is due to the strong interaction of the ions of reactants and anionic surfactant. While without any additive, only very few nanorings can form (Fig.5(a)).

3.6 Formation mechanism of $Cu_2(OH)_3NO_3$ nanorings

Dry hole formation mechanism was reported to explain the formation of nanorings[12−13]. Our system does not agree with this mechanism. The formation of a ring shape of copper nitrate hydroxide is speculated to be due to the interaction between OP-10 and metal ions and the distinct mechanism of solid-state reaction at room temperature[14−18].

When reagents and OP-10 were mixed and ground together, $Cu(NO_3)_2·3H_2O$ released Cu^{2+} in the microzone which formed under the action of coordinated water. OP-10 was favorable to form fine particles and make a 'shell' surrounding the particles to prevent them from aggregating to larger particles during grinding. The reason that the mixtures ground for 30 min were put aside was to make the nanoparticles nucleate better. Because Cu^{2+} was prone to form complex with OP-10 and the complexation stability constant between Cu^{2+} and OP-10 was less than the solubility product constant of $Cu_2(OH)_3NO_3$, $Cu_2(OH)_3NO_3$ formed mostly in the neighborhood of OP-10. It is the template role of OP-10 that forms ring structure. Further experimental work needs to explain the exact formation mechanism of nanorings. Fig.6 shows the schematic diagram of possible formation process.

4 Conclusions

In summary, a novel and facile process was developed to synthesize copper nitrate hydroxide nanorings. This facile one-step solid-state reaction gives nanorings potentially broad applications in the synthesis and the shape control of nanomaterials.

1) Solid-state reaction adopted here is not only easy to operate but also can be used to synthesize copious morphology of nano particles.

2) OP-10 plays a key role in the formation mechanism of synthesized $Cu_2(OH)_3NO_3$ nanorings.

3) The nanorings structure as a novel nanocavities can lead to novel device concepts and can be used as carrier of nanocatalysts applied in chemical industry.

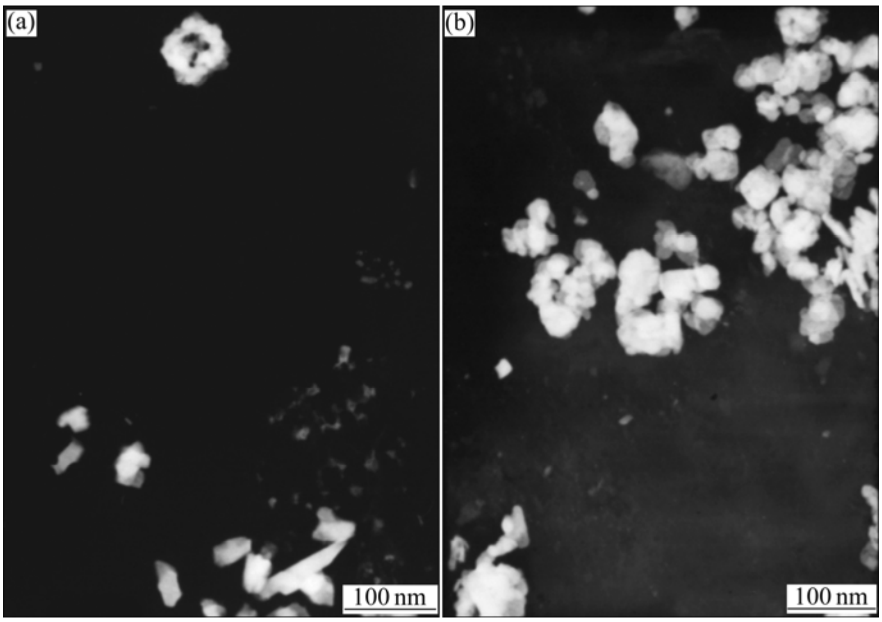

Fig.5 TEM images of synthesized products using NH_4HCO_3 and $Cu(NO_3)_2·3H_2O$: (a) Without any additive; (b) With surfactant sodium dodecyl sulfate(SDS)

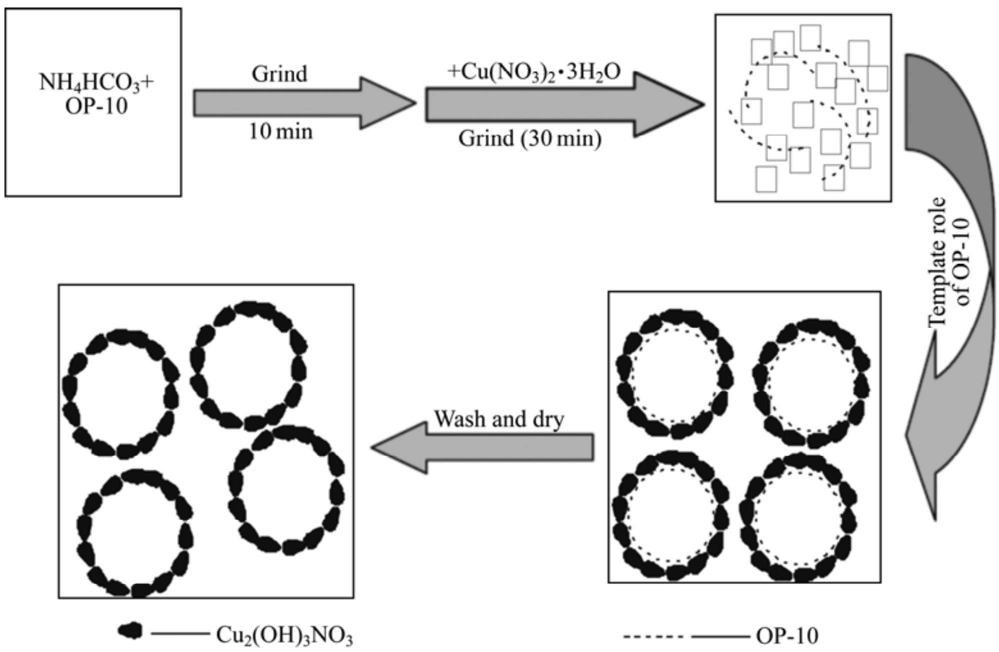

Fig.6 Schematic illustration of formation process of $Cu_2(OH)_3NO_3$ nanorings

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