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Controllable Synthesis and Catalytic Property of Novel Copper Oxides (CuO and Cu_2O) Nanostructures

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Abstract: Copper oxides (CuO and Cu_2O) semiconductor micro- and nanostructures have been selectively synthesized using cupric nitrate trihydrate ($Cu(NO_3)_2{\cdot}3H_2O$), potassium biphthalate ($KHC_8H_4O_4$) and sodium hydroxide (NaOH) as starting materials in water solution by a simple hydrothermal method. The phase and morphology of the products could be controlled by changing the amount of sodium hydroxide and sodium potassium biphthalate. X-ray diffraction (XRD), field scanning electron microscopy (SEM) and Raman spectra (Raman) were used to characterize the products. It was found that oval-shaped CuO, CuO nanoplates and octahedral Cu_2O were prepared by adjusting the molar of the NaOH and $KHC_8H_4O_4$, meaning that NaOH and $KHC_8H_4O_4$ played an important role in the morphology and phase of the samples. The catalytic application in accelerating catalytic decomposition of ammonium perchlorate (AP) of the as-prepared samples was also investigated by means of differential scanning calorimetry (DSC). Compared with CuO (oval-shaped or plates), octahedral Cu_2O exhibited better catalysis on thermal decomposition of AP. The present work can afford some guidance for the rationally controllable synthesis of other catalytic materials.

Keywords: Electron Microscopy, Raman, Catalytic, Copper Oxides

1. Introduction

Nanostructured materials have received extensive attention due to their unusual properties and potential applications. It remains a great challenge to precisely control the size, morphology, and crystal structure of nanomaterials and thus to tailor their properties [1-3]. Many techniques and approaches have been developed to prepare various types of functional materials such as metals, metal oxides, and semiconductors. The hydrothermal method provides a promising way for the synthesis of crystalline materials due to its low cost, high efficiency and potential for large-scale production [4-7]. It not only can induce the formation of well-crystallized products at low temperatures, but also can control the phase, shape and size of the resultant products simply by adjusting the synthesis conditions such as composition of the solution, pH, temperature and duration, etc.

Copper oxides (CuO and Cu_2O) semiconductor nanomaterials have drawn considerable attention due to their potential applications in catalysts [8], gas sensors [9], optical material [10] and lithium ion electrode [11]. It is reported that the performance of semiconductor materials is closely related to their morphology, size and microstructures [12], etc. Therefore, synthesis of shape- and size-controlled copper oxides (CuO and Cu_2O) nanostructures is necessary to tailor their chemical and physical properties. Various copper oxides have been prepared via different methods [13-18]. Though the great progress in the synthesis of copper oxides was achieved, it is still a challenge to develop different strategies to achieve the synthesis of copper oxides nanostructures with controlled phase and morphology.

The hydrothermal method provides a promising way for the synthesis of crystalline materials due to its low cost, high efficiency and potential for large-scale production. It not only can induce the formation of well-crystallized products at low temperatures, but also can control the phase, shape and size of the resultant products simply by adjusting the synthesis conditions such as composition of the solution, pH, temperature and duration, etc. Herein, a simple hydrothermal method was demonstrated to synthesize CuO and Cu_2O nanomaterials with controlled morphology, and the detailed crystal structure and morphology were investigated.

Meanwhile, it is well known that the thermal decomposition characteristics of oxidizers in propellants can influence the combustion behavior of propellants, therefore copper oxides are usually used as additives for modifying the thermal properties of the oxidizers [19-21]. Ammonium perchlorate (AP) is the most common oxidizer for composite solid propellant and its thermal decomposition characteristics was widely investigate [22]. In this paper, the catalytic properties of as-prepared CuO and Cu_2O on the thermal decomposition of AP were also studied. The results will be meaningful for improving the combustion properties of composite solid propellants.

2. Experimental

All chemicals including cupric nitrate trihydrate ($Cu(NO_3)_2 \cdot 3H_2O$), potassium biphthalate ($KHC_8H_4O_4$), sodium hydroxide (NaOH) and ammonium perchlorate (AP) were analytically pure and were used as received without further purification. A typical synthesis of copper oxides nanostructure (octahedral Cu_2O) is as follows: Firstly, 6 mmol $Cu(NO_3)_2 \cdot 3H_2O$ and 6 mmol $KHC_8H_4O_4$ were dissolved in 50 mL distilled water and the solution was stirred at room temperature for 0.5 h. Then 6 mmol NaOH was added into the above solution with stirring for 20 min. Finally the mixed solution was transferred into a Teflon-lined autoclave of 80 mL capacity and was filled up to 85% of the total volume with deionized water. After being sealed and heated at 180°C for 12 h, the autoclave was cooled to room temperature naturally. The resulting products were collected by centrifugation, washed with distilled water and ethanol for several times, and finally dried in vacuum at 70°C for 6 h. A similar synthetic procedure was employed by adjusting the molar of the NaOH and $KHC_8H_4O_4$. The methods and products were listed in Table1.

The phase purity of the products was characterized by X-ray diffraction (XRD, German Bruker AXSD8 ADVANCE X-ray diffractometer) using a X-ray diffractometer with Cu KR radiation (λ=1.5418 Å). Scanning electron microscope (SEM) images were obtained on a Japan Hitachi S-4800 field emission scanning electron microscopy. Raman spectra of the samples were measured using a Britain Renishaw Invia Raman spectrometer with a solid-state laser (excitation at 532 nm, 35 mW) at room temperature in the range of 150-800 cm^{-1}. The thermal decomposition analysis was performed by employing differential scanning calorimetry (DSC) using Mettler DSC827e thermal analysis system covering a temperature range of 100~500°C under a flow gas of nitrogen. The sample mass used was about 2 mg and the mass percentage of catalyst to AP in the mixture was fixed at 2%.

Table 1. *The adopt method and its corresponding product.*

Sample	$Cu(NO_3)_2 \cdot 3H_2O$ (mmol)	$KHC_8H_4O_4$ (mmol)	NaOH (mmol)
Octahedral Cu_2O	6	6	6
The mixure of CuOand Cu_2O	6	6	12
CuO nanoplates	6	6	24
oval-shaped CuO	6	0.25	12

3. Results and Discussion

The XRD patterns of the as-prepared samples are shown in Fig. 1. The amount of NaOH was a key factor for the formation of copper oxides (CuO and Cu_2O) by keeping the other parameters unchanged. The cubic phase of Cu_2O in Fig. 1a (JCPDS No. 05-0667) was prepared in typical reaction condition (6 mmol $Cu(NO_3)_2 \cdot 3H_2O$, 6 mmol $KHC_8H_4O_4$ and 6 mmol NaOH). When the amount of NaOH was increased to 12 mmol, the mixture of CuO (JCPDS No. 05-0661) and Cu_2O (JCPDS No. 05-0667) was found in Fig. 1b. However, when the amount of NaOH was further increased to 24 mmol, pure monoclinic structure of CuO (JCPDS No. 05-0661) was obtained in Fig. 1c. In addition, pure CuO was also prepared (Fig. 1d) by adjusting the amount of $KHC_8H_4O_4$ (0.25mmol) while other parameters were kept just the same as that of the mixture. The strong and sharp peaks indicated that the as-obtained products were highly crystallized.

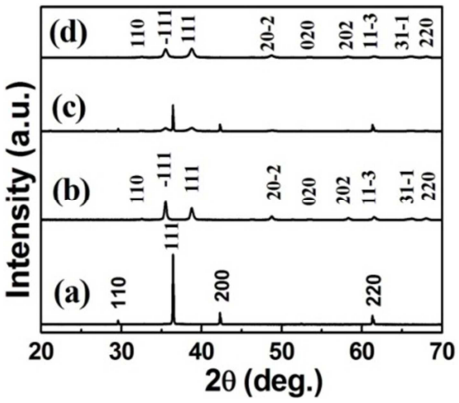

Fig. 1. *XRD patterns of the as-prepared samples under different reaction conditions (a) Cu_2O under typical experimental condition (6 mmol $Cu(NO_3)_2 \cdot 3H_2O$, 6 mmol $KHC_8H_4O_4$ and 6 mmol NaOH) (b) the mixture of CuO and Cu_2O (12 mmol NaOH) (c) CuO nanoplates (24 mmol NaOH) (d) CuO (6 mmol $Cu(NO_3)_2 \cdot 3H_2O$, 0.25 mmol $KHC_8H_4O_4$ and 12 mmol NaOH).*

The morphologies of the as-synthesized samples were characterized by SEM. It can be seen that monodispersed Cu_2O octahedron with diameters of about 20 μm was obtained in Fig. 2a under typical reaction condition (6 mmol $Cu(NO_3)_2 \cdot 3H_2O$, 6 mmol $KHC_8H_4O_4$ and 6 mmol NaOH). When the amount of NaOH was increased to 12 mmol, octahedral structures disappeared and the mixture of oval-shaped structures and nanowires was found in Fig. 2b. When the amount of NaOH was further increased to 24 mmol, uniform CuO nanoplates with a diameter of about 400 nm were obtained in Fig. 2c. Compared to the mixture morphology, uniform oval-like CuO (ca. 300 nm in size) assembling with tiny nanoparticles in Fig. 2d was also prepared by adjusting the amount of $KHC_8H_4O_4$ while other parameters were kept just the same as that of the mixture. It is well known that the properties of micro- and nano-sized colloidal particles formed by the precipitation from a homogeneous solution are highly sensitive to many factors such as pH, base and anion sources. We believe that the pH and $HC_8H_4O_4^-$ are responsible for the phase and morphologies of the as-prepared products. The $HC_8H_4O_4^-$ could form

Cu-$HC_8H_4O_4$ complexes by coordinating with Cu^{2+} cations with different pH values which can adjust the process of nucleation and growth. The similar process was reported by Yin et al [23].

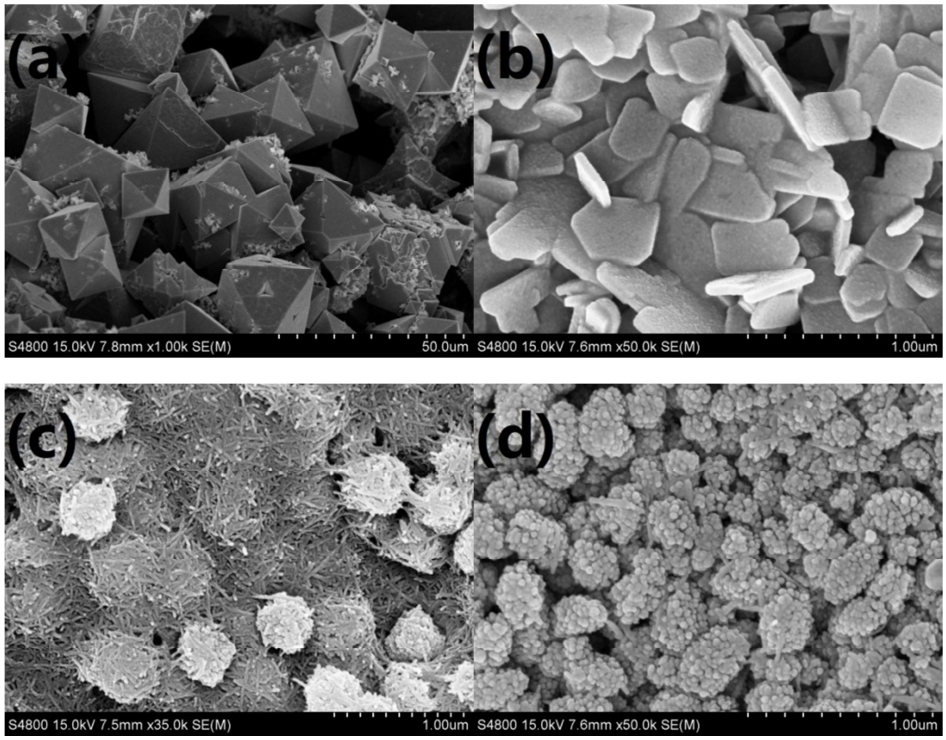

Fig. 2. *SEM images of the samples prepared under different reaction conditions (a) Cu_2O under typical experimental condition (6 mmol NaOH) (b) the mixure of CuO and Cu_2O (12 mmol NaOH) (c) CuO nanoplates (24 mmol NaOH) (d) oval-shaped CuO (6 mmol $Cu(NO_3)_2{\cdot}3H_2O$, 0.25 mmol $KHC_8H_4O_4$ and 12 mmol NaOH).*

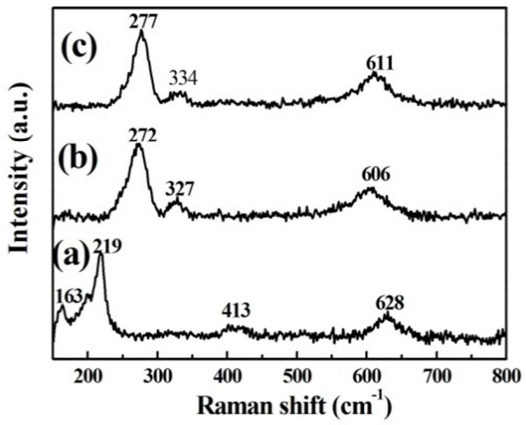

Fig. 3. *Raman spectra of (a) octahedral Cu_2O (b) oval-shaped CuO (c) CuO nanoplates.*

Raman spectroscopy is applied to determine the structure of metal oxides due to different Raman active vibrational modes. The Raman analysis of the as-prepared products further revealed the purity and structure of the as-prepared samples in Fig. 3. It can be seen that several peaks were found in Fig. 3a. According to early report [24], the strongest peak at about 219 cm^{-1} could be attributed to the second order overtones $2\Gamma_{12}$ and the other weaker peaks at 164 cm^{-1}, 413 cm^{-1} and 628 cm^{-1} correspond to Γ_{15} oxygen vacancies (LO), the fourth-order overtone $4\Gamma_{12}$ and the red-allowed mode $\Gamma_{15}^{(2)}$ (TO) phonon vibrations of Cu_2O [25]. In Fig 3b and 3c, similar Raman vibrational modes were obtained. Three Raman peaks at about 272 cm^{-1} (A_g mode), 327 cm^{-1} (B_g mode) and 606 cm^{-1} (B_g mode) were found, which are consistent with early report on CuO [26]. It can be concluded that CuO and Cu_2O were prepared by a facile hydrothermal method.

The catalytic activity of as-prepared samples was investigated via their performance in the thermal decomposition of AP at different heating rates from 10°C/min to 30°C/min.

Fig. 4 shows the DSC curves of pure AP and the mixture of AP with catalysts at 2% mass basis at a heating rate of 10°C/min. According to DSC curve of pure AP in Fig.4a, the first peak at 240.7°C is an endothermic peak, which is associated with a phase transition of AP from orthorhombic to cubic. The other two exothermic peaks at 298.5°C and 420.6°C were corresponded to the low-temperature decomposition (LTD) and high-temperature decomposition (HTD) processes respectively [27]. It can be found that adding catalysts to AP has little influence on the phase transition and LTD processes, but the HTD peak temperature evidently decreases with the addition of catalysts. Meanwhile, for the existence of catalysts, the thermal decomposition heat of 2% octahedral Cu_2O (1135.8 J/g, Fig. 4b), oval-shaped CuO (924.7 J/g, Fig. 4c) and CuO nanoplates (966.7 J/g, Fig. 4d) was obviously increased compared with the decomposition heat of pure AP (428.1 J/g).

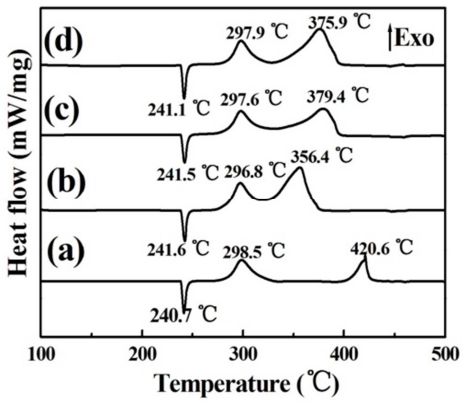

Fig. 4. DSC of (a) pure AP (b) AP+ octahedral Cu_2O (c) AP+ oval-shaped CuO (d) AP+CuO nanoplates.at a heating rate of 10°C/min.

The thermal decomposition analysis was also performed with a heating rate of 20°C/min and 30°C/min respectively, and the results can be found in Fig.5 and Fig.6. It can be seen that the CuO and Cu_2O can promote the thermal decomposition of AP with different heating rates, and octahedral Cu_2O exhibited better catalysis on the thermal decomposition of AP than that of CuO samples.

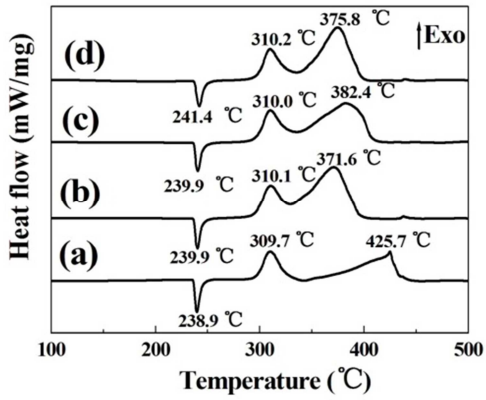

Fig. 5. DSC of (a) pure AP (b) AP+ octahedral Cu_2O (c) AP+ oval-shaped CuO (d) AP+CuO nanoplates.at a heating rate of 20°C/min.

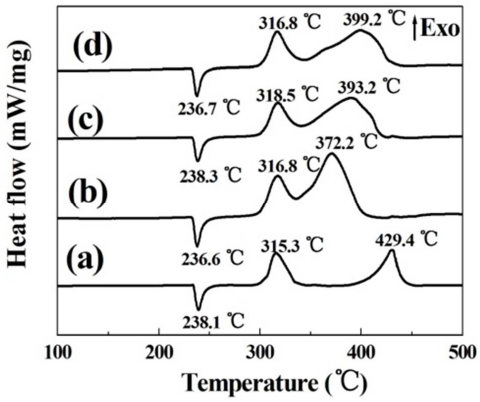

Fig. 6. DSC of (a) pure AP (b) AP+ octahedral Cu_2O (c) AP+ oval-shaped CuO (d) AP+CuO nanoplates.at a heating rate of 30°C/min.

Consequently, adding the as-prepared catalysts can decrease the decomposition temperature and increase the apparent heat release of AP. Compared with oval-shaped CuO or CuO nanoplates, octahedral Cu_2O exhibits better catalysis on the thermal decomposition of AP.

4. Conclusions

CuO and Cu_2O nanomaterials with different morphologies were obtained by a hydrothermal process and verified by XRD, SEM and Raman. Sodium hydroxide (NaOH) and potassium biphthalate played an important role in the morphology and phase of the as-prepared samples, which may offer a promising way to synthesize different morphologies and phase of other metal oxides. In addition, it was found that Cu_2O octahedron had better abilities to accelerate the thermal decomposition of ammonium perchlorate than other samples.

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