

New approach for preparation of ultrafine Cu particles and shell/core compounds of Cu/CuO and Cu/Cu₂O

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Recently, the research of nanoparticles of Cu and its compounds has been considered to be of both fundamental and practical importance. Cu-based compositions, such as Cu/ZnO [1] and Cu/Zn/Al₂O₃ [2] have wide applications as high active catalysts in a multitude of industrial processes. Many reports are available about the synthesis of Cu nanoparticles, including the microemulsion method [3], the irradiation method [4], the reduction method [5, 6], the ion beam deposition [7], the ion implantation method [8] and so on. However, many present methods are not perfect. They also have some common weak points that should be improved, for example they are not environment friendly or not suitable for large-scale production.

Our basic experimental strategy in this paper is to find a simple and controllable method for preparation of nanosized Cu and its compounds. The quench as a conventional method to cool metals or plastics has been employed to control compositions of products from CuO reaction in a special medium. Precursor Cu₂CO₃(OH)₂ obtained through deposition reaction of Cu(NO₃)₂ and Na₂CO₃, was calcined at a series of high temperatures. However, we chose n-butanol as a medium to cool CuO particles instead of air, water or other media. Thus, the particles of Cu, CuO/Cu or Cu₂O/Cu could be selectively generated, which depended largely on the calcination temperatures of Cu₂CO₃(OH)₂.

200 ml 0.5 M Cu(NO₃)₂ was chosen as the copper providing material, and the solution containing 0.5 M Na₂CO₃ was added to the former, which was vigorously stirred at room temperature. The deposit was filtered, rinsed with distilled water several times and dried. Then the obtained precursor Cu₂CO₃(OH)₂ was calcined at temperatures ranging from 200 °C to 600 °C for about 2.5 hrs. Importantly, we used remaining heat of calcinations to undertake following reactions. The moment of CuO powder was taken from Muffle furnace, it was carefully spread into n-butanol. The reaction was very drastic and the dark powder turned to red instantly. Then the product was rinsed with absolute alcohol several times and dried under vacuum.

Fig. 1 shows the XRD patterns for specimens obtained at different preheated temperatures. When the CuO powder at 200 °C was spread into n-butanol, the powder color after the quench was unchangeable and its XRD pattern also shows that the powder is all CuO.

The quenched product from CuO treated at 300 °C was still in dark, but the XRD pattern has given other peaks. These new peaks are attributed to the diffraction of copper and their intensity grows gradually with the increment of the treatment temperatures. In the cases of other three quench processes the red products could be found. While the quenched powder related to 500 °C has indicated a pure Cu phase. Finally, the peak of Cu₂O appears corresponded to precursor preheated at 600 °C. Above-mentioned color change depends on Cu or Cu₂O content (see Table I) as well as nanomaterial optical property, which makes ultrafine metallic crystallite dark or black.

In order to determine the amount of phase A(CuO) and B(Cu₂O) in the specimen, we applied the internal standard method [9]. A know amount the standard substance S(NaCl) is mixed with a know amount of the original specimen to form a new mixture. If the volume fraction of phase A is C_A in the original specimen and C'_A in the new mixture and C_S is the volume fraction of the standard in the new mixture. Then the equation is given by

$$I_{\alpha} = \frac{K C_{\alpha}}{\mu_m}$$

Where I_{α} is the intensity of the diffracted beam; C_{α} is the volume fraction of the α phase in the mixture; μ_m is the linear absorption coefficient for the mixture; K is a constant.

For a particular reflection from phase A can be written as

$$I_A = \frac{K_1 C'_A}{\mu_m} \quad (1)$$

and that from the standard as

$$I_S = \frac{K_2 C_S}{\mu_m} \quad (2)$$

then, dividing Eq. (1) by Eq. (2) gives

$$\frac{I_A}{I_S} = \frac{K_1 C'_A}{K_2 C_S} = \frac{K_1}{K_2} \frac{\rho_S}{\rho_A W_S} W'_A = \frac{K_1}{K_2} \frac{\rho_S(1 - W_S)}{\rho_A W_S} W_A \quad (3)$$

Since K_1 , K_2 , ρ_S and ρ_A are all constants, W_A is the weight fraction of phase A in the mixture and W_S as a

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TABLE I The content of Cu, CuO and Cu₂O calculated through XRD patterns

Temperature	W _A	W _B	W _C
200 °C	100	0	0
300 °C	56.44	0	43.56
400 °C	12.68	0	87.20
500 °C	0	0	100
600 °C	0	4.24	95.76

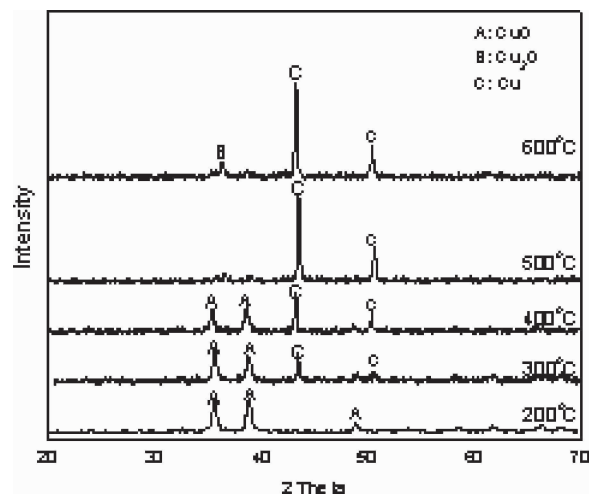


Figure 1 XRD patterns of products of quenching a series of CuO powder obtained by precursor calcinations at 200 °C to 600 °C.

constant is kept at 50% in all the composite specimens, the Eq. (3) can be rewritten as

$$\frac{I_A}{I_S} = K_A W_A \quad (4)$$

Therefore, the intensity ratio of a peak from phase A and a peak from the standard S varies linearly with the weight fraction of phase A in the original specimen.

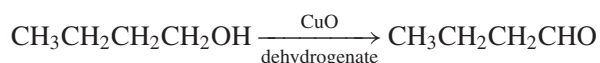
We prepare the CuO and Cu₂O according to reference [10, 11], then use the monophase CuO and Cu₂O to determine the value of K_A and K_B (A: CuO, B: Cu₂O). According to the Eq. (4), the value of K_A and K_B is 2.02 and 21.75 respectively. Knowing the relative intensity of the strongest peak of A, B, S and

the value of K_A , K_B , we calculated the weight fraction of phase A(CuO) and B(Cu₂O). So the content of phase A(CuO), B(Cu₂O) in the specimen can be calculated and the content of C(Cu) can also be obtained by Eq. (5).

$$W_C = 1 - W_A - W_B \quad (5)$$

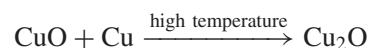
The results are listed in the Table I.

We also investigated the mechanism of these reactions. When CuO particles treated at more than 300 °C were spread into n-butanol to cool, the redox reaction occurred. CuO could be reduced to metal Cu and hydroxyl group of n-butanol was oxidized to aldehyde group.



This assumption could be confirmed by Tollens reagent. After adding residual quench liquid to Ag(NH₃)₄OH solution, the formation of fine Ag particles could be seen immediately. Obviously, above reaction occurred at the CuO/ n-butanol interface, implying that residual CuO was coated by generated Cu.

Furthermore, for the CuO treated at 600 °C, firstly the outside of the particles was reduced to Cu. But inside heat could raise a reaction between Cu and inside CuO according to following process



The thermodynamical judgment of this reaction takes the form

$$\Delta_r G^\theta = \Delta_r H^\theta - T \Delta_r S^\theta$$

Gibbs Free Energy of this reaction achieves -26.2 kJ/mol, indicating the reaction can spontaneously occur at high temperature. So we suggest that there has been a shell/core structure for Cu/Cu₂O composite.

The SEM observations in Fig. 2 reveal that the morphology of Cu/Cu₂O is quiet different from CuO particles obtained from the calcination at 600 °C. In

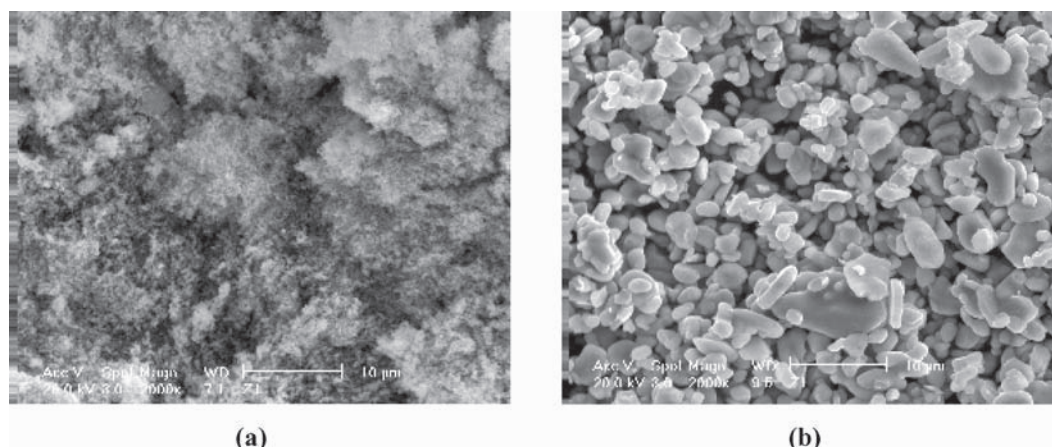


Figure 2 SEM images (a) CuO particles obtained by precursor calcination at 600 °C; (b) quenched product of (a): Cu/Cu₂O shell/core particles.

Fig. 2b we can see that the shell/core particles coated by metal Cu are homogenous and have clear interfaces.

So far the pyrolysis of inorganic and organic compounds has been extensively used for nanomaterials preparation. In this paper, we extend this method to the production of more advanced and complicated nanomaterials, for example Cu/CuO and Cu/Cu₂O with shell/core structure. The heat from pyrolysis step can be reused to promote and control following reactions, and residual organic liquid can also be separated and collected. So we propose that our contribution has established potential capability not only on laboratorial scale but also on a large scale.

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