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Short communication

One-step decomposition of basic carbonates into single-phase crystalline metallic oxides nanoparticle by ultrasonic wave-assisted ball milling technology

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Abstract

CuO and NiO nanoparticles were successfully prepared by means of solid–liquid reaction ball milling assisted by ultrasonic wave at relative low temperature, using basic cupric carbonate (BCC) and basic nickel carbonate (BNC) as the raw materials. The phases and particle size of the as-milled products were characterized by X-ray diffraction and TEM, respectively. Under mechanical force coupled with ultrasonic wave, BCC and BNC were directly decomposed into CuO and NiO nanoparticles, respectively. By the comparison of the as-milled products with and without the help of ultrasonic wave, it is found that ultrasonic wave is a key factor in promoting the decomposition of BCC and BNC. Furthermore, the mechanism of the decomposition reaction assisted by ultrasonic wave was discussed.

Keywords: Oxidate nanoparticles; Ultrasonic wave; Reaction ball milling; Phase transition

1. Introduction

Nano-sized oxides of transition metals (TM) are of great interest because of their unique physical and chemical properties different from the bulk counterparts, and have many important applications in catalysis, gas sensors, magnetic materials, battery cathodes, electronics, solar energy transformation, semiconductor etc. [1–7]. In recent years, the preparation and properties of nanoparticles of transition metal oxides, such as copper and nickel, has been a focus topic and many familiar methods have been developed [8–20]. However, all currently available methods are limited. For example, toward the precipitation method, it requires a relatively complicated process and is affected by precipitation agent, pH, temperature and solution concentration, solid-state method and the microemulsion are not mature in technology. Moreover, nearly all these methods need to use copper salt and nickel salt as the raw materials to prepare corresponding oxides by adding expensive agents. No elaborate literature about nanoparticles prepared by the direct decomposition of basic copper/nickel carbonate without any other additives are reported up to now [21–24].

In this paper, we successfully prepared CuO and NiO nanoparticles by one-step reaction via solid–liquid reaction ball milling assisted by ultrasonic wave developed by authors' group [25]. No catalyzer, dispersant or other organic solvents are added in this technique, which may be considered as a potential approach for mass production of metal oxides nanoparticles.

2. Experimental details

All of the chemical reagents used in this experiment were of analytical grade. The raw materials (BCC and BNC) were milled in a solid–liquid reaction ball milling device assisted by ultrasonic wave (Fig. 1) in an atmosphere of distilled water (1000 mL). The mass ratio of stainless steel balls (diameter 10 mm) to reactant was 50:1, the rotation speed of stirrer was 235 rpm, ultrasonic intensity and vibration frequency was 1.13 W/cm^2 and 40 kHz, respectively. After a certain time interval, the as-milled products were taken out, filtered, and dried at 50 °C for 24 h. The phase constitute and the microstructures of the as-milled products were analyzed by

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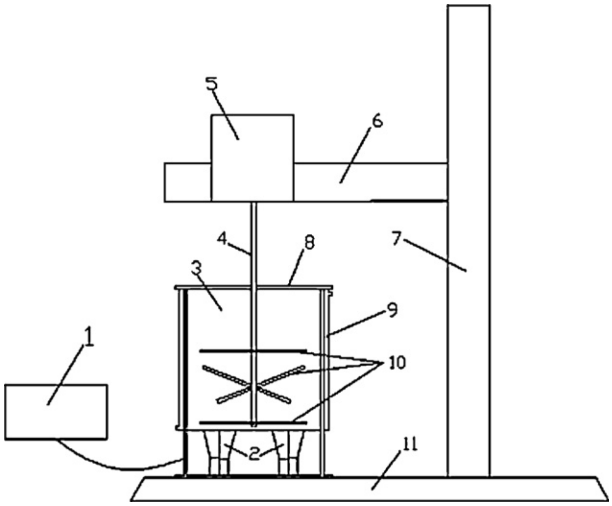

Fig. 1. Schematic diagram for solid–liquid reaction ball-mill equipment under ultrasonic wave. 1—ultrasonic generator; 2—energy conversion device; 3—milling tank; 4—drive shaft; 5—motor; 6—horizon beam; 7—vertical beam; 8—cover; 9—recycled water; 10—raker stirrer; 11—bed plate.

X-ray diffraction (XRD, D-5000) and transmission electron microscopy (TEM, JEM-3010), respectively.

3. Experimental results

Fig. 2 shows the XRD patterns of BCC milled for different durations, using aqueous ball milling with or without ultrasonic wave. The results show that BCC was not decomposed after milled for 10 h. After milling for 15 h, the diffraction peaks of BCC are greatly broadened and weakened, indicating a substantial grain refinement. At the same time, CuO phase appears. With further milling, the diffraction intensities of CuO increase gradually. After milling for 35 h, single phase CuO with a well developed XRD pattern is obtained, indicating that BCC has completely decomposed into CuO. For comparison, the case without ultrasonic wave assistance is also plotted in the same figure. It is seen that BCC cannot decompose into CuO without ultrasonic wave assistance even when milling time is extended to 80 h. The XRD patterns of BNC milled for different times with or without the ultrasonic wave assistance are given in Fig. 3. Very similarly, the ultrasonic wave assistance can make BNC completely transform into single phase NiO after 40 h milling, while such a transformation does not occur under the condition without ultrasonic wave. These results indicate that ultrasonic wave plays a very important role in the decomposition of BCC into CuO.

TEM images of the 35 h-milled BCC and the 40 h-milled BNC are shown in Fig. 4, respectively. The average particle sizes of CuO and NiO obtained are about 30 nm and 25 nm, respectively, with the smallest being 10 nm. Most of the particles are spherical, with good dispersancy, except for tiny agglomeration of some extremely small products.

4. Analysis and discussion

Generally, BCC is stable in room temperature, but when heated to 220 °C, it will decompose into CuO, H_2O and CO_2 by one-step reaction

$$CuCO_3Cu(OH)_2 \rightarrow 2CuO + H_2O + CO_2\uparrow \quad (1)$$

This has been confirmed by Koga and his coworkers [26] in the studies of the thermal decomposition of BCC. However, for BNC, the thermal decomposition is a two-step behavior as the following reactions (at 300 °C)[27]:

$$NiCO_3{\cdot}2Ni(OH)_2{\cdot}4H_2O \rightarrow NiCO_3{\cdot}2Ni(OH)_2 + 4H_2O \quad (2)$$

$$NiCO_3{\cdot}2Ni(OH)_2 \rightarrow 3NiO + CO_2 + 2H_2O \quad (3)$$

Present work shows that mechanical force and ultrasonic wave promote these chemical reactions and lead to the formation of oxides.

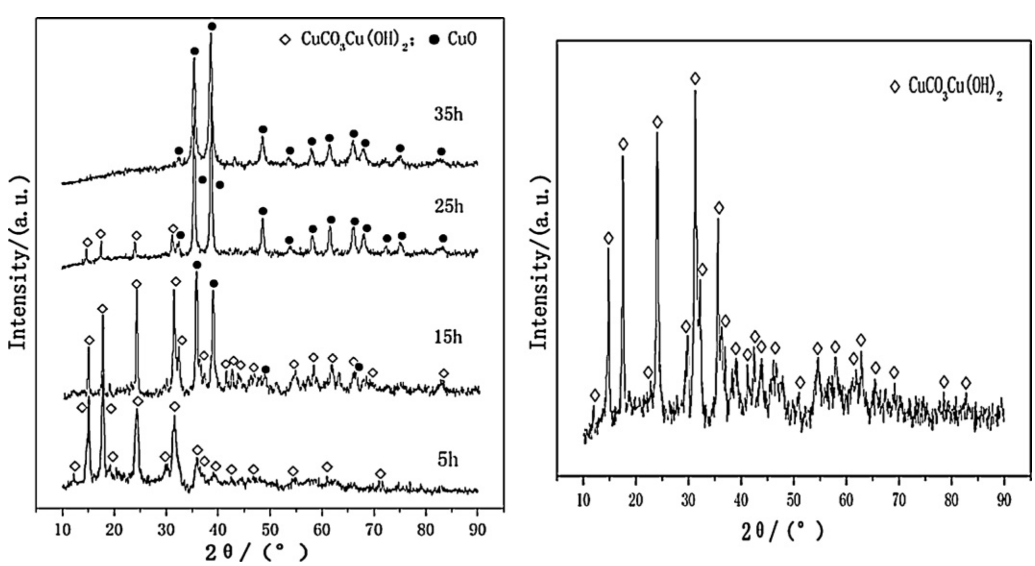

Fig. 2. X-ray diffraction patterns of BCC milled in different conditions. (a) Milled with ultrasonic wave for 5–35 h; (b) milled without ultrasonic wave for 80 h.

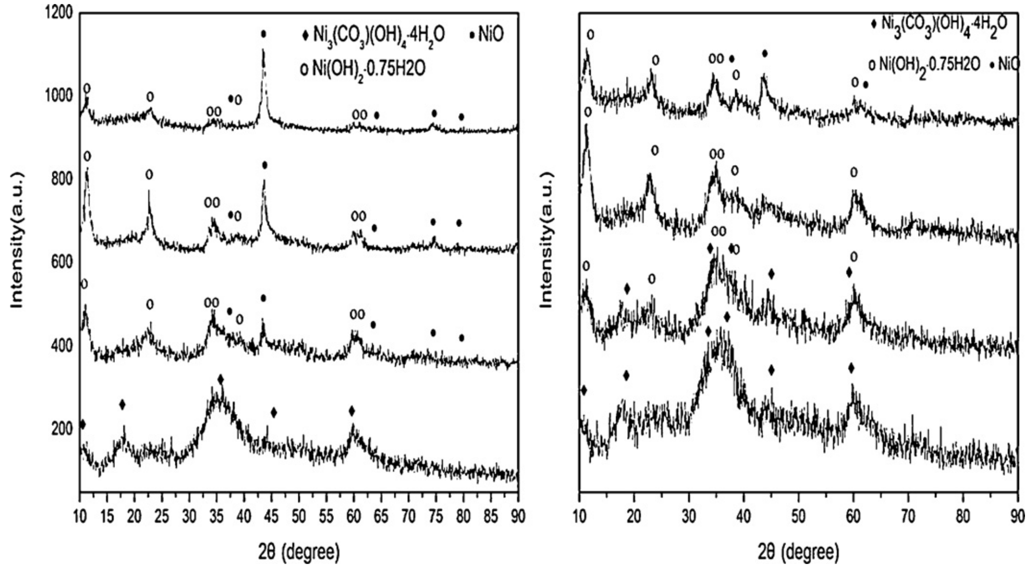

Fig. 3. X-ray diffraction patterns of BNC milled in different conditions. (a) Milled with ultrasonic wave; (b) milled without ultrasonic wave.

4.1. Impaction–abrasion behavior in the ball-milling process

As shown in Fig. 5, the whole process of decomposition reaction, accompanied by the mechanical force in an aqueous solution, is divided into the steps as follows:

$$\text{collision} \rightarrow \text{abrasion} \rightarrow \text{mechanical force-induced decomposition} \rightarrow \text{re-collision} \rightarrow \cdots$$

This process continuously repeats itself until the raw materials are completely decomposed.

Based on the principle of mechanochemistry [28], the continuous collision and abrasion by stainless steel balls can induce the decomposition reactions of carbonate. The reaction products, CuO and NiO, peeled off from the surfaces of raw materials can immediately enter into the solution to form ultrafine particles. The fresh surfaces of BNC with higher surface activity and energy can accelerate the reaction process. Based on this, the reaction can continuously go on. Therefore, mechanical milling could trigger the reactions which cannot be carried out using the conventional methods.

4.2. Effect of ultrasonic wave on ball-milling process

In addition to aqueous ball milling, present work shows that ultrasonic wave is crucial for the formation of transition metal oxides. Since the reaction proceeds in water, the reaction temperature unlikely exceeds 100 °C, which is much lower than that required for the thermal decomposition of BCC and BNC (220 °C and 300°C, respectively). The ultrasonic wave appears to be able to substantially reduce the onset temperature of

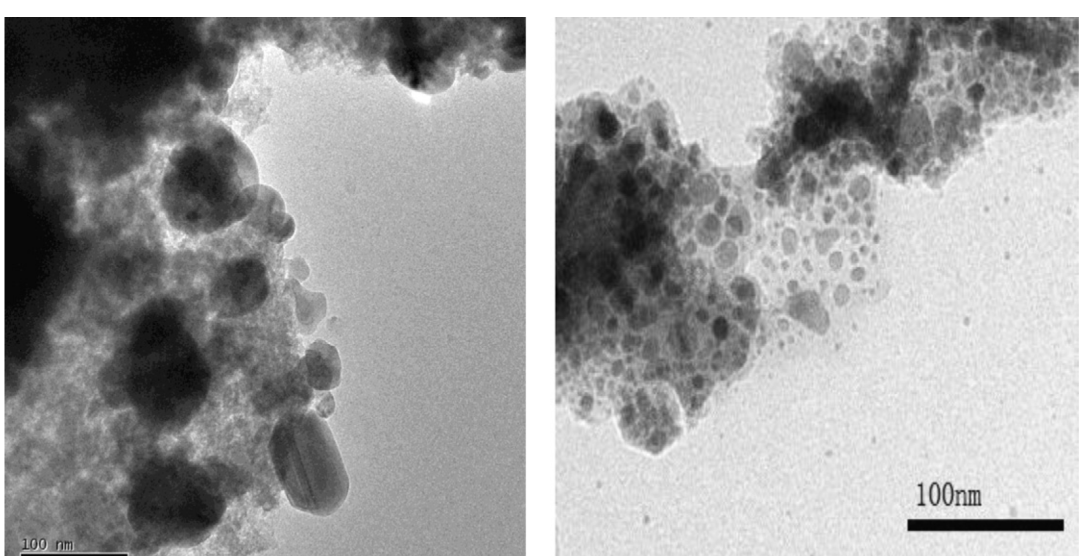

Fig. 4. TEM images of raw materials milled with ultrasonic waves in a certain time. (a) BCC milled under ultrasonic wave for 35 h; (b) BNC milled under ultrasonic wave for 40 h.

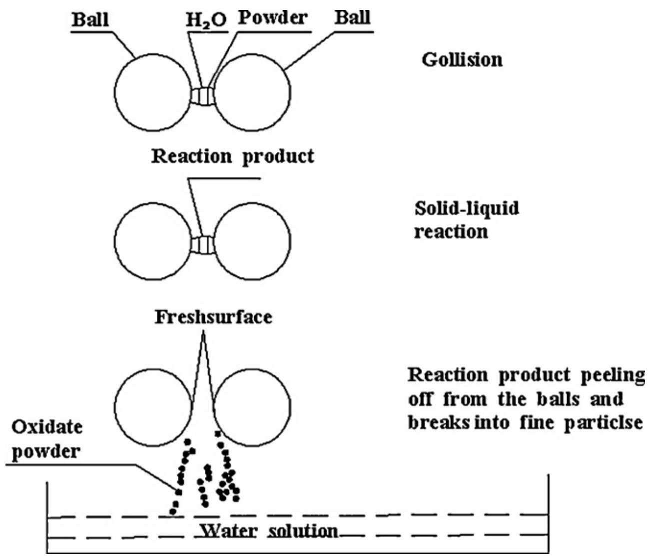

Fig. 5. The formation mechanism for the nanoparticles.

decomposition. Generally, the cavitations caused by the chemical and mechanical effect of ultrasound can result in the formation, growth, and implosive collapse of bubbles in a liquid [29]. Due to ultrasound wave effects, bubbles can continually absorb energy in the process of compression and expansion cycles. When the cavities implode, the gases as well as the vapors inside them are compressed, and generate intense heat. As a result, the local temperature of the liquid surrounding the cavity raises and a local hot spot is created. K.S. Suslick suggested that when cavitations occur in a liquid near an extended solid surface, the cavity implosion substantially differs from the ideally symmetrical spherical implosion observed in liquid-only systems [30]. The presence of the solid particles may distort the pressure produced by ultrasound field. Cavity implosion near the surfaces of particles will become markedly asymmetric. This can generate a toward-surface jet of liquid with speeds of roughly 400 km/h [29]. Such an effect, integrated with the shock waves produced by cavity implosion, will further erode solid surfaces, remove nonreactive coatings and break brittle powders and therefore reactions are facilitated. Furthermore, the formed local hot spots could cause localized highly concentrated $H^{\bullet}$ and $OH^{\bullet}$ free radicals by which the supercritical water and H_2O_2 form by the sonolysis of H_2O, the pH value of solution decrease and the solution gradually approaches to be neutral [25], forming a aqueous solution environment more suitable for the product of CuO and NiO. In addition, the oxides peeled off from the particles can be rapidly dispersed in the solution, due to coupling effects of ultrasonic wave and mechanical force. Cavitations and ball milling can effectively suppresses the grain growth of the formed oxides, and simultaneously stop the agglomeration of particles. This is the reason why ultrafine transition metal oxides are obtained by ultrasonic-assisted ball milling.

5. Conclusions

By using the solid–liquid reaction ball milling assisted by ultrasonic wave, single-phase nanocrystalline CuO and NiO were successfully synthesized by one-step decomposed reaction. Our results show that ultrasonic wave is a key factor in promoting the decomposition of BCC and BNC in the process of ball milling. And combining mechanochemistry and sonochemistry for obtained nano-scale particles, this new approach may low-cost and environmentally friendly.

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