

Preparation of Metal Oxide Nanoparticles from Metal Powders

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Abstract

A one-step solid state reaction between a chemical precursor and hydroxide was employed to prepare metal oxide nanoparticles. After synthesis, the products were characterized by using XRD, SEM and TEM. It was proved that the one-step solid state reaction could produce CuO and ZnO nanoparticles. Estimation of particle sizes by using TEM and XRD indicates that the synthesized CuO particles are smaller than 30 nm.

Keywords: Metal oxide, nanoparticles, synthesis.

1. Introduction

Cupric oxide (CuO) is widely used as a catalyst due to its high activity and selectivity in oxidation and reduction reactions [1]. It can be used as a single catalyst, such as, for carbon monoxide oxidation [2] and for lactic acid production from glucose under hydrothermal conditions [3]. CuO can be used as a co-catalyst with various oxides for different applications. Co-catalysts of CuO with ZnO were used for methanol formation [1], for phenol oxidation in water [4] and for carbon monoxide oxidation [5]. In this article, we propose a simple route for preparation of metal oxide nanoparticles using a one-step solid state reaction.

2. Experimental procedure

In the one-step solid state reaction, each precursors ($\text{Cu}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$, $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot x\text{H}_2\text{O}$, $\text{Zn}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$ and $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot x\text{H}_2\text{O}$) was ground with hydroxide pellets, with mole ratio (1:2) until reaction completion. For the synthesis routes using copper compounds as precursors, precipitations were filtered and cleaned with deionized water and 95% ethanol for removal of excessive alkaline solution. Finally, the synthesized metal oxide nanoparticles were dried at 100°C for several hours. Using zinc compounds as precursors, nanoparticles of products were separated from solution by

centrifugal separation. The synthesized metal oxide nanoparticles were characterized by using X-ray diffraction (XRD). Morphology and particle size of metal oxide nanoparticles were observed by scanning electron microscopy (SEM). Particle size and shape and electron diffraction pattern were investigated by using transmission electron microscopy (TEM).

3. Results and discussion

3.1 XRD of synthesized powders

Synthesized powders obtained when different metal compounds were used as starting materials are given in Table 1. From the table, using copper compounds as precursors can produce 70% of products. This indicates that using copper compounds as raw materials are successful for production of CuO nanoparticles. Whereas using zinc compounds to react with NaOH seems to be unsuccessful for production of ZnO nanoparticles in term of product yield.

Table 1 Product yields of different precursors

Precursor	% yield
$\text{Cu}(\text{NO}_3)_2$	72.57
$\text{Cu}(\text{CH}_3\text{COO})_2$	70.06
$\text{Zn}(\text{NO}_3)_2$	Low
$\text{Zn}(\text{CH}_3\text{COO})_2$	0.00

XRD patterns of CuO and ZnO particles are given in Fig. 1. The synthesized CuO powders showed broad XRD peaks whereas the synthesized ZnO powders showed narrower peaks. The XRD lines of the synthesized CuO nanoparticles are in a good agreement with those of the tenorite (JCPDS Card No. 48-1548) and with those of the CuO nanoparticles synthesized by other routes [1, 2, 5]. Similarly the XRD lines of the synthesized ZnO powders matched exactly with XRD database of ZnO compound. Broad nature of XRD peaks indicates that the synthesized CuO crystallite sizes lie in the nanometer size.

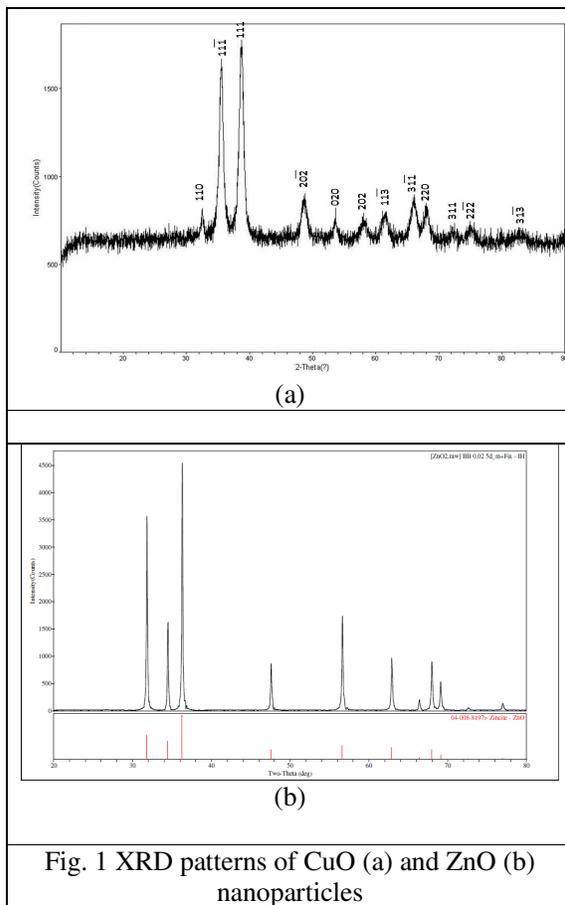
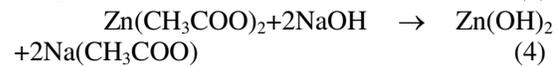
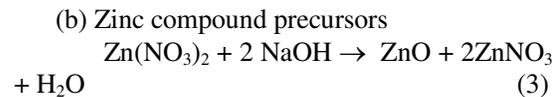
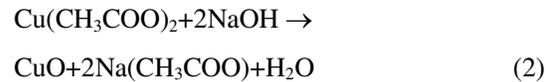
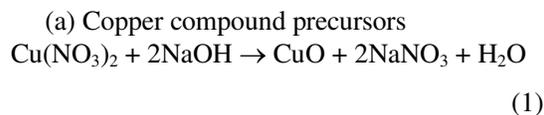


Fig. 1 XRD patterns of CuO (a) and ZnO (b) nanoparticles

3.2 Reactions of precursors with NaOH

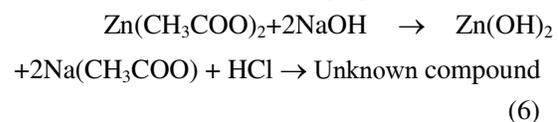
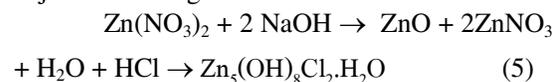
The synthesis routes employed in this research can be represented by using Equations (1) to (4).



The equations are simple chemistry. According to Table 1 and XRD results, metal oxide nanoparticles can be produced according to Equations (1) to (3) only. Since there were no precipitates observed when $\text{Zn}(\text{CH}_3\text{COO})_2$ was used as a raw material, the reaction given by Equation (4) was reasonable.

According to Table 1, low yields of ZnO nanoparticles attracted our attention. One important reason may be due to the fact that ZnO nanoparticles are soluble in strong base solution. In order to increase yields of ZnO nanoparticles, pH values of the products were adjusted using hydrochloric acid (HCl). Higher amounts of powder products were obtained by pH adjustment. However, XRD patterns of the HCl-adjusted products (Fig. 2) were not ZnO nanoparticles.

(c) Zinc compound precursors plus pH adjustment using HCl



3.3 Powder particle size

Based on the principle stating that the width of XRD peaks increases as the sizes of the crystalline domains (crystallites) that diffract the x-rays decreases [6, 7], broad nature of XRD peaks indicate that the synthesized CuO crystallite sizes lie in the nanometer size. Given in Table 2 is the particle measurement by using the Scherrer formula:

$$d = \frac{0.9\lambda}{B \cos \theta}$$
 (7)

where d is the average crystallite size, λ is the wavelength of X-ray, B is the full width at the half maximum at diffraction angle θ (in radian).

The results of particle measurement by using XRD peak data indicate that the synthesized

CuO crystallite sizes are less than 20 nm.

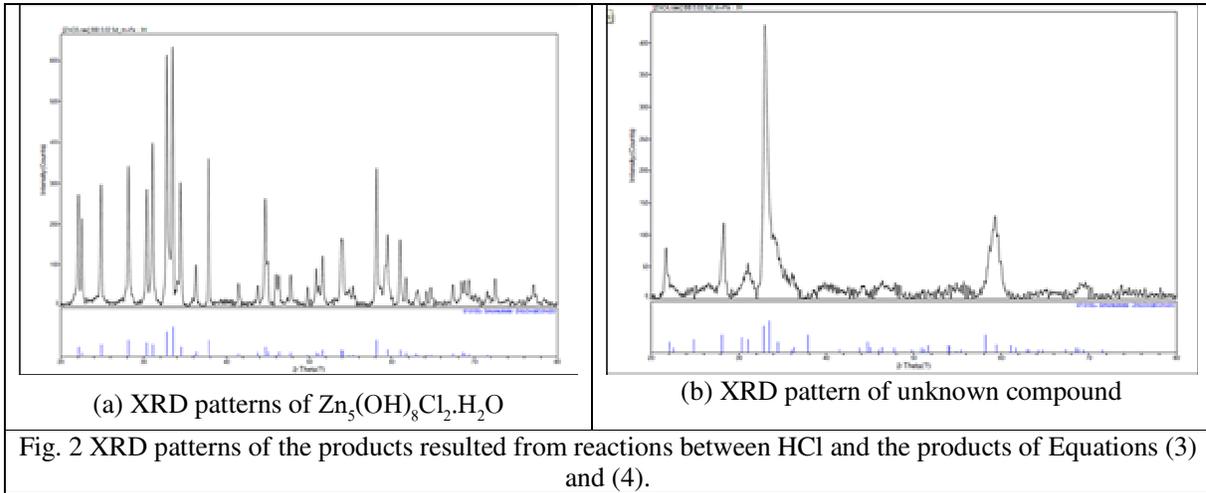
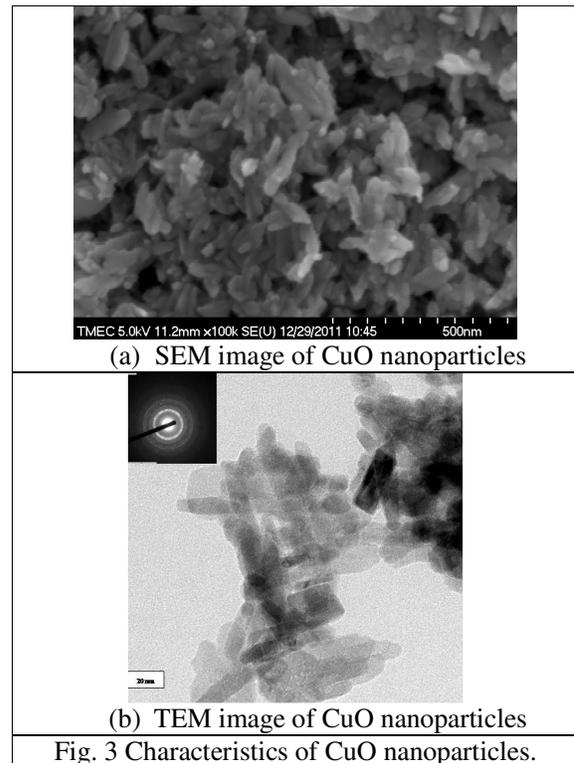


Table 2 Metal oxide particle sizes determined by TEM and XRD

CuO from	Particle size by TEM (nm)		Particle size by XRD (nm)
	Width	Length	
$Cu(NO_3)_2 \cdot 3H_2O$	8.75 ± 1.94	29.29 ± 4.00	14.12 ± 1.83
$Cu(CH_3COO)_2 \cdot H_2O$	10.60 ± 3.15	11.17 ± 1.29	7.59 ± 1.58
$Zn(NO_3)_2$	Not measured	Not measured	50.00 ± 1.65

3.4 Micrographs of CuO nanoparticles

Fine nanoparticle agglomeration resulted in formation of micron-sized porous particles is shown in Fig. 3(a). The TEM image (Fig. 3(b)) not only confirms that the synthesized CuO particles are nanoparticles it also confirms the surface morphology of the synthesized CuO nanoparticle aggregates observed by SEM. The SAED patterns (the insets of Fig. 3(b)) show a ring pattern nature because the selected area is large and it covers a lot of CuO particles. Estimation of particle sizes by using TEM and XRD indicates that the synthesized CuO particles are smaller than 30 nm.



4. Conclusions

The one-step solid state reaction between a chemical precursor and hydroxide could produce metal oxide nanoparticles. However, yields of metal oxide nanoparticles depend on chemistry of precursors and the products themselves. Using copper compounds as raw materials can produce satisfactory yields of CuO nanoparticles. Whereas using zinc compounds as raw materials, the one-step solid state reaction is not successful. Estimation of powder particle sizes by using TEM and XRD indicates that the synthesized CuO powders has particle sizes smaller than 30 nm.

5. Acknowledgement

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6. References

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