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Full Length Research Paper

Mechanochemical route to synthesize Co_3O_4/CuO composite nanopowders

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Co_3O_4/CuO composite nanopowders have been successfully synthesized by heating the precursor obtained via a mechanochemical reaction. The precursor and the nanopowders were characterized using thermogravimetric (TG), X-ray diffraction (XRD) and transmission electron spectroscopy (TEM). Subsequent thermal treatment of the precursor at 550-700 ℃ in air for 2 h resulted in the formation of Co_3O_4/CuO nanopowders with an average crystal size of about 25-50 nm, varying with the calcination temperature. The mechanism of nanocrystallite growth is primarily investigated. The morphology of the synthesized Co_3O_4/CuO nanopowders is in irregular polyhedron shape and the mechanism of NaCl used as diluent have been analyzed. The mechanochemical route is a novel, cheap and convenient technique suitable for large-scale synthesis of composite nanomaterials.

Keywords: Composite nanopowders; Co_3O_4/CuO; Mechanochemical reaction; Nanocrystallite growth.

INTRODUCTION

Transition metal oxides have been widely investigated due to their potential applications in many technological fields, such as catalysis, batteries, magnetic materials, gas sensor and solar energy conversion [Petitto and Langell, 2005; Radwan et al, 2003; Wojciechowska et al, 2006; Choi et al, 2004; Pillai and Deevi, 2006; Raveau, 2005; Gruyters, 2002; Wang et al 2004; Zaki, 2005; Wang et al, 2005]. Researches are being carried out to improve their efficiency to the maximum possible extent. Principally two strategies were adopted: changes in preparation methods and/or addition of another dopant [Radwan et al, 2003]. Mixed oxides of transition metals are capable of mutual interactions, leading to the formation of complex structure. The catalytic activity of mixed oxide systems is usually higher than that of their individual oxide components [Wojciechowska et al, 2006]. A great deal of fundamental research has been carried out on mixed oxides [Choi et al, 2004; Pillai and Deevi, 2006].

Cupric oxide (CuO), a narrow band-gap and p-type semiconductor, is an important material for a variety of practical applications and cobalt oxide (Co_3O_4), a spinel-type oxide and also p-type semiconductor, has very attractive electrocatalytic properties for many important reactions [Lia et al, 2005; Yin, et al. 2005]. Co_3O_4 and CuO nanoparticles have been respectively prepared by several methods and copper-cobalt-based catalysts (the spinel $CuCo_2O_4$ and $Cu_xCo_{3-x}O_4$) have been investigated [He et al, 2004; Ye et al, 1999; Singh et al, 2000.], but no report has focused on the preparation of Co_3O_4/CuO (p-p type) nanopowders. Mechanochemical processing is a novel method for the production of nanosized materials, where well-separated nanoparticles can be produced (Fores et al, 2001).

Recently, a wide variety of nanosized oxides have been synthesized by mechanochemical route, including CdO, Co_3O_4, CeO_2, In_2O_3, Cu/Al_2O_3 and Fe_2O_3/SnO_2 [Yang et al, 2004; Lu and Fang, 2006; Hwang and Lee, 2005; Galatsis et al, 2003.]. Mechanochemical synthesis is particularly suitable for large-scale production because of its simple process and low cost. This paper first reports the synthesis of Co_3O_4/CuO composite nanopowders via mechano-chemical route.

EXPERIMENTAL DETAILS

The starting materials were AR-grade $CoCl_2 \cdot 6H_2O$, $CuCl_2 \cdot 2H_2O$,

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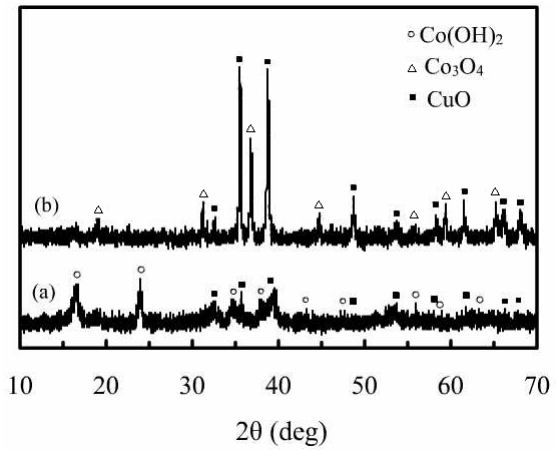

Figure 1. XRD patterns of the $InCl_3 \cdot 4H_2O+CuCl_2 \cdot 2H_2O+NaOH$ powder mixture. (a) The precursor and (b) after calcination of the precursor at 600℃ for 2h.

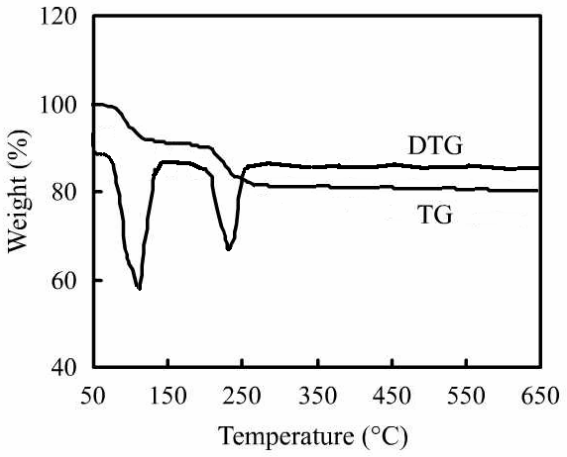

Figure 2. TG-DTG curves of the precursor.

NaOH and NaCl. NaCl was used as a diluent and added to the starting powder. 70 wt.% CuO in the nanopowders is first determined in order to calculate the amount of the reactants. 5.00 g $CuCl_2 \cdot 2H_2O$, 2.96 g $CoCl_2 \cdot 6H_2O$, 3.34 g NaOH and 5.5 g NaCl were mixed and milled at ambient temperature in an agate mortar until the color of the as-milled powder kept unchanged. The reaction started immediately during the mixing process, accompanying the emission of water vapor from the system for exothermic effect of the reaction. Then the as-milled powder was dispersed in a 90W SK2200LH ultrasonic bath for 15 min, thoroughly washed with distilled water until no Cl^- anions could be detected in the solution with $AgNO_3$ solution (0.10 mol/l) and dried at 100 ℃ for 2 h in air to form the nanoparticle precursor. The precursor was heated at 600 ℃ for 2 h in air in a porcelain crucible to form the black Co_3O_4/CuO nanopowders.

Thermogravimetric and differential thermogravimetric (TG/DTG) analysis of the precursor were performed in air atmosphere using a WCT-2 thermal analyzer with heating rate of 10 ℃/min. The precursor and nanopowders were examined by X-ray diffraction (XRD) (Rigaku, D/max-γA, CuKα radiation). The morphology of the nanopowders was obtained using transmission electron microscopy (TEM, JEM-200CX), using an accelerating voltage of 200 kV. The average crystal size (*D*) of the sample was calculated from the Scherrer's formula according to the half-width of the diffraction peak.

RESULTS AND DISCUSSION

Analysis of the synthesis reaction

During the mixing, the reaction was observed to be very fast, the color of the mixture changed frequently and remained black finally. Figure 1 shows the XRD patterns of the as-milled powders. After about 30min milling of the mixture and subsequently washed with distilled water, the CuO fine particles have been directly produced and the peaks of $Co(OH)_2$ are also evident. From the XRD profiles, it can be deduced that CuO is directly formed during the milling of the starting materials. Consequently, the solid-state diffusion is accelerated by the milling. Besides the CuO peaks, a new peak associated with Co_3O_4 was observed in the pattern of the sample after calcination of the precursor at 600℃ for 2 h, so the whole reaction equation can be written as below:

$$CoCl_2 \cdot 6H_2O + CuCl_2 \cdot 2H_2O + 4NaOH \xrightarrow{xNaCl} Co(OH)_2 + CuO + (4+x)NaCl + 10H_2O \quad (1)$$

$$6Co(OH)_2 + CuO + O_2 \xrightarrow{600°C} 2Co_3O_4 + CuO + 6H_2O \quad (2)$$

TG-DTG analysis of the precursor

Figure 2 shows the TG-DTG curves of the precursor in air. There are two obvious endothermic peaks at about 120℃ and 240℃, respectively. The first peak is attributed to the evaporation of surface water and the second one is due to the decomposition of structural water. It can be seen from the TG curve, there are two processes of the weight loss at about 60-120℃ and 200-250℃, corresponding to 10.3% and 6.9% weight loss, respectively. It is interesting to find that the second weight loss (6.9%) is consistent with the calculated result (6.3%) of the separation of H_2O from the precursor $Co(OH)_2$, which indicates that the second endothermic peak is corresponding to the decomposition of $Co(OH)_2$. The results agree with those in XRD patterns of Figure 1.

Morphology of nanopowders

Figure 3 shows the TEM image of the Co_3O_4/CuO nanopowders after calcination at 700ºC in air for 2h. The average particle size of the as-prepared nanopowders is less than 50nm, which agrees well with the results that

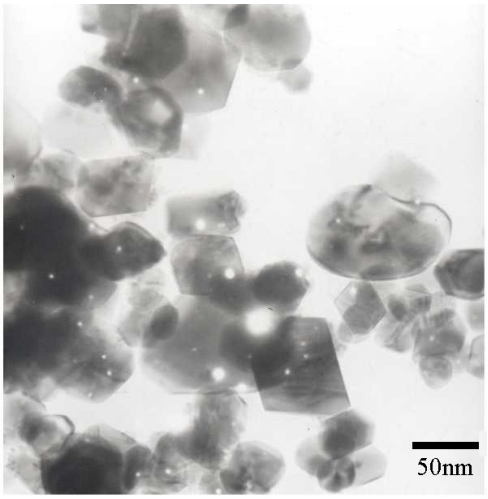

Figure 3. TEM images of the Co_3O_4/CuO nanopowders after calcination at 700ºC in air for 2 h.

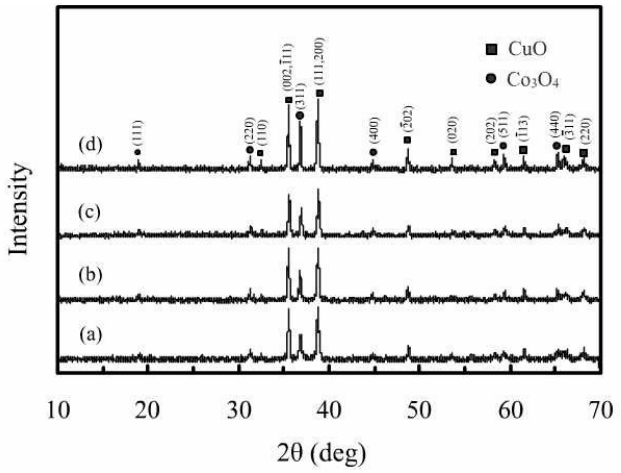

Figure 4. XRD patterns of Co_3O_4/CuO nanopowders at different calcination temperatures (a) 550℃; (b) 600℃; (c) 650℃ and (d) 700℃.

are calculated based on XRD analysis. Figure 3 indicates that the Co_3O_4/CuO nanopowders are mainly in irregular polyhedron shape and well-dispersed. The irregular polyhedron shape of the nanopowders may be caused by the characters of the solid-state reaction, which can only take place on the interface of reactions. The growth of the nanoparticles varies in the different direction because the density and components are not homogeneous around the particles during the reaction (Thostenson et al, 2005).

Effect of the calcination temperature

XRD patterns of the as-synthesized samples have been analyzed to investigate the phase structure in relation to

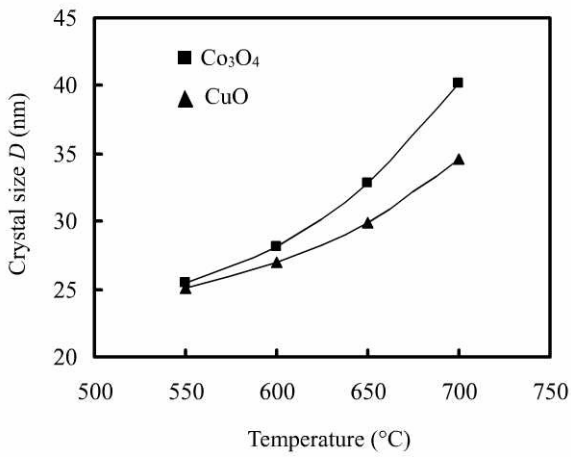

Figure 5. Effect of the calcination temperature on the average crystal size of CuO and In_2O_3 of nanopowders.

the calcination temperature. Figure 4 shows the XRD patterns of Co_3O_4/CuO nanopowders after heat-treated at 550-700℃ in air for 2 h. The results suggest that all the diffraction peaks can be readily indexed to the monoclinic structure of CuO in agreement with the literature (JCPDS 05-0661) and Co_3O_4 with cubic structure (JCPDS 43-1003). The peak intensities of the CuO and Co_3O_4 increased with increasing the calcination temperature, indicating a high degree of crystallization and the growth of nanocrystallites.

The average crystal sizes of the as-synthesized Co_3O_4/CuO nanopowders were calculated based on the Scherrer's formula. Figure 5 shows a plot of the XRD crystal size of CuO and Co_3O_4 as a function of calcination temperature. The crystal size of Co_3O_4 increased rapidly from about 25 nm at 550℃ to 42 nm at 700℃, while that of CuO increased correspondingly slowly. The *D* values reach approximately 25 and 35 nm at 550℃ and 700℃, respectively. This is directly related to the crystallization of nanoparticles. The result also indicates that the effect of the calcination temperature exists in the Co_3O_4/CuO composite nanopowders.

Straight lines of ln*D* against 1/*T* (Figure 6) are plotted according to the Scott equation given below under the condition of homogeneous growth of nanocrystallites, (Scott, 1983), which approximately describes the crystal growth during annealing:

$$D=Cexp(-E/RT) \quad (3)$$

where *C* is a constant, *E* is the activation energy, *R* is the gas constant, and *T* is the absolute temperature. There exists a good linear relationship. The *E* value was calculated from the slope of the straight line as *E*=14.04 kJ/mol and 20.10 kJ/mol for CuO and Co_3O_4, respectively. It shows that the calcination temperature

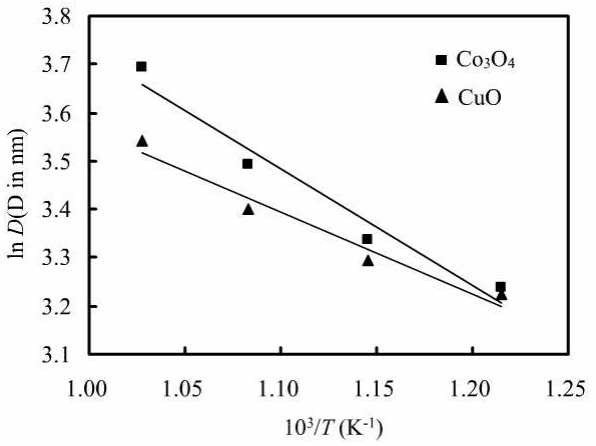

Figure 6. Plots of ln*D* against 1/*T* according to the Eq. (3).

has a more remarkable effect on the growth of nanocrystallites. Co_3O_4 nanoparticles are a little more easily affected by thermal treatment than CuO, which can be observed from Figure 5.

Mechanism of the diluent

In this experiment, NaCl is used as diluent during the process of preparation the Co_3O_4/CuO composite nanopowders. As shown in Figure 6, the individual particles are found to be well-dispersed without serious aggregates. This fact indicates that the presence of NaCl in the synthesized powder can inhibit particle agglomeration. Wiley and Kaner have suggested that the formation of salt provided an effective driving force for the formation of small particle (Yang et al, 2004). It can be concluded that the growth of the particles is inhibited by the addition of NaCl as diluent into the starting powder, due to the following reasons: (i) the formed NaCl tends to cover the reactant surface and hamper the further reaction, reducing the reaction volume between the reactant particles, leading to a decrease in reaction rate and the rate of heat generation; (ii) the diluent absorbs some of the collision energy during milling, reducing the energy transferring into the reactants, and (iii) the diluent absorbs heat generated by the reaction, reducing the temperature reached during milling. As a diluent material, NaCl has often been used because of its inert nature and excellent milling ability (Hwang and Lee, 2005). Recently, the influence of inert salts diluent on the morphology and particle size distribution of powders has attracted much attention because of many of its practical uses in synthesis of nanocrystalline particles with desirable characteristics, including very fine size, narrow size distribution, single crystal particle, high purity and good chemical homogeneity [Wiley and Kaner 1992; Li et al, 2005].

CONCLUSIONS

Mechanochemical reaction of $CoCl_2 \cdot 6H_2O$, $CuCl_2 \cdot 2H_2O$ and NaOH resulted in the formation of a precursor during milling with NaCl as a diluent, which was then heated to produce Co_3O_4/CuO composite nanopowders. The morphology of the synthesized Co_3O_4/CuO nanopowders are in irregular polyhedron shape. The XRD crystal size of the Co_3O_4/CuO nanopowders rapidly increased with increasing calcination temperature. The crystal size varied from 25 to 50 nm at 550–700℃. The activation energies of Co_3O_4/CuO nanocrystallite growth during thermal treatment were calculated to be 14.04 kJ/mol for CuO and 20.10 kJ/mol for Co_3O_4, respectively. The calcination temperature has a prominent effect on the nanocrystallite growth. The synthesized Co_3O_4/CuO nanopowders are promising for the advanced functional materials.

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