

Facile Synthesis of $\text{Co}_3\text{O}_4/\text{CoO}$ Nanoparticles by Thermal Treatment of Ball-Milled Precursors

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Abstract $\text{Co}_3\text{O}_4/\text{CoO}$ nanoparticles have been synthesized by a simple method which is based on the ball-milling and calcination of cobalt acetate and citric acid. The samples were characterized using X-ray diffraction, transmission electron microscope, and Fourier transform infrared spectroscopy. The results show that Co_3O_4 nanoparticles with an average particle size of ~ 40 nm can be obtained by calcination of ball-milled precursors at relatively low temperature (350°C) for 3 hours. It should be noted that it is possible to control the size of Co_3O_4 particles by calcination temperature, calcination time and also by ball-milling duration using this method. Meanwhile, the pure CoO nanoparticles were obtained successfully by thermal decomposition of Co_3O_4 at 950°C and quickly quenching to liquid nitrogen.

Keywords Cobalt oxides · Nanoparticles · Ball mill · X-ray diffraction

1 Introduction

Nanostructure materials have attracted considerable interest in recent years due to their interesting properties. Among these materials, researches on fundamental properties and practical applications of transition-metal oxides are attracting much attention [1–4]. Cobalt oxides, CoO and Co_3O_4

are of the versatile materials among the transition-metal oxides that are stable in the natural environment [5, 6]. Through last years, much effort has been directed to the synthesis and investigation of properties of CoO and Co_3O_4 nanostructures due to their potential applications [7–9].

Co_3O_4 is the thermodynamically stable form of cobalt oxide under atmospheric air below 1164 K, while above this temperature Co_3O_4 is decomposed into CoO [10]. At room temperature Co_3O_4 is a normal spinel [11], and it has many potential applications in catalysts, gas sensors, solar energy absorbers and magnetic materials [12–15]. Recently several methods have been developed for the preparation of Co_3O_4 , such as hydrothermal, combustion, ultrasonic-assisted and microwave-assisted hydrothermal [16–19].

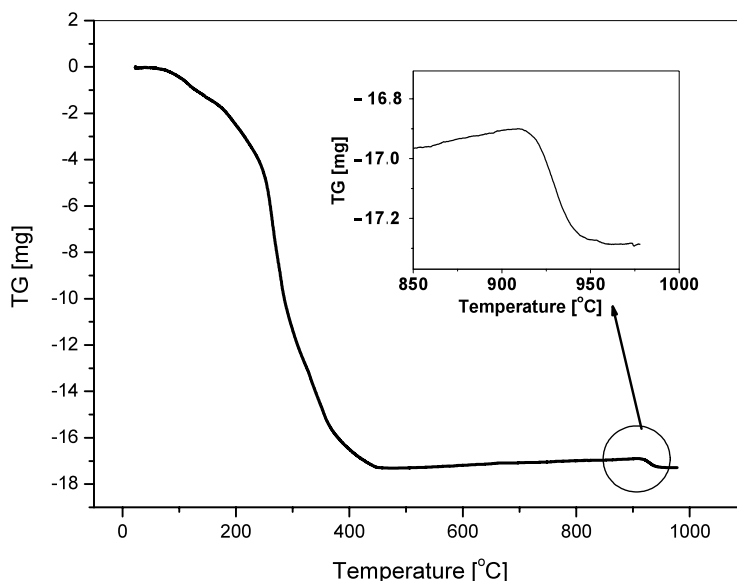
On the other hand, CoO crystallizes in the rock salt structure and it has potential applications in many fields as gas sensors, anodes of lithium batteries, magnetoresistant read heads and pigment [20–22]. Although there are a few reports on the synthesis of CoO in the bulk form, this compound is difficult to obtain in pure form by simple methods, often being contaminated with Co_3O_4 and Co metal. Yin and Wang [23] have shown that decomposition of $\text{Co}_2(\text{CO})_8$ in toluene in the presence of the surfactant Na(AOT) at 130°C in air results in CoO nanocrystals mixed with Co_3O_4 and Co. Ye et al. [24] have prepared CoO nanoparticles by esterification reaction under solvothermal conditions. Ghosh et al. [25] synthesized pure CoO nanoparticles by the decomposition of Co (II) cupferronate in decalin at 270°C under solvothermal conditions. Very recently, Guo et al. [26] have prepared CoO particles using CoCl_2 solution via a spray roasting method.

In this paper, a simple synthesis method, different from those mentioned above, is proposed. We will report on the synthesis method of Co_3O_4 and CoO nanoparticles, via solid-state ball-milling and calcination of acetate precursors

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Fig. 1 TG curve of ball-milled precursors in air



and citric acid. We have used the same method for the preparation of MnFe_2O_4 spinel ferrite nanoparticles [27].

2 Experimental

All chemicals (analytical grade reagents) were purchased from Merck Company and used as received without further purification. The starting materials were cobalt acetate tetrahydrate ($\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$), and citric acid ($\text{C}_6\text{H}_8\text{O}_7$). The synthesis process of Co_3O_4 nanoparticles is as follows: cobalt acetate and citric acid powders were mixed by a 1:1 molar ratio. The powders were milled in a planetary ball mill under air atmosphere for 1 hour. The ball-milled powder was calcined in air at 350°C for 3 hours to obtain Co_3O_4 nanoparticles (sample S1). In order to prepare CoO nanoparticles, the ball-milled powders were calcined in air at 950°C and quenched quickly from 950°C to room temperature (sample S2) and liquid nitrogen (sample S3).

The crystal structure of samples were analyzed, using X-ray diffractometer (Philips EXPERT MPD) with $\text{Cu-}k\alpha$ ($\lambda = 0.154 \text{ nm}$) radiation. The morphology of the samples was characterized by a transmission electron microscope (TEM) (LEO model 912 AB). The composition quality of the synthesized material was characterized by Fourier transform infrared spectroscopy (FT-IR, JASCO, 680 Plus) in the mid-infrared range ($400\text{--}4000 \text{ cm}^{-1}$).

3 Results and Discussion

We have studied the oxidation behavior of ball-milled precursors by thermogravimetry. Figure 1 shows the TG profile of the ball-milled precursors versus temperature. The initial

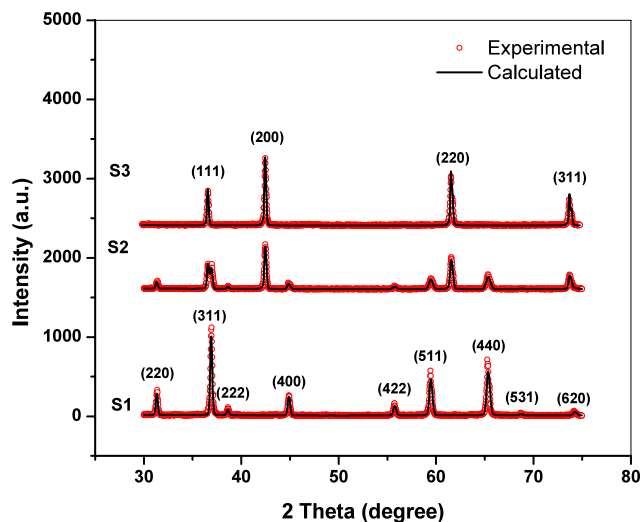


Fig. 2 X-ray diffraction patterns of samples S1, S2 and S3

weight loss observed in the $30\text{--}170^\circ\text{C}$ temperature range is related to the removal of absorbed water. The second weight loss started at 250°C temperature can be attributed to decomposition of cobalt citrate to Co_3O_4 . It seems that the third stage weight loss occurs at high temperature (920°C) and is related to the decomposition of Co_3O_4 to CoO.

Figure 2 shows the XRD patterns of the samples at room temperature. The XRD data is analyzed with Rietveld refinement using the FULLPROF software and Pseudo-Voigt function. It is found that the sample S1 is a single-phase Co_3O_4 spinel, without any noticeable trace of impurity phases such as CoO or Co. Also, the lattice parameter of the sample S1 was obtained by the Rietveld analysis of the XRD data by using the FULLPROF software. The estimated lattice constant of 8.075 \AA is in agreement with earlier works

[26]. We believe that it is possible to control the size of particles by calcination temperature, calcination time and also by ball-milling duration using this method. Recently, Tang et al. [11] have shown that the CoO may be obtained by thermal decomposition of Co_3O_4 at 950°C . Therefore the ball-milled powders were calcined in air at 950°C for 3 hours. In order to avoid oxidation of the as-prepared CoO nanoparticles into Co_3O_4 , the sample was quenched from 950°C to room temperature very quickly. As can be seen from the Rietveld refinement of sample S2, two phases were identified for this sample, namely Co_3O_4 and CoO. We propose that the surface of the as-prepared CoO nanoparticles oxidized to Co_3O_4 during the cooling from high temperature to room temperature. The surface oxidation of CoO nanoparticles to Co_3O_4 has been investigated by Soriano et al. [28]. They showed that the surface of CoO nanoparticles appears oxidized up to Co_3O_4 and annealing in ultra-high vacuum reduces the surface of the nanoparticles to the CoO. It seems that oxidation of the nanoparticles surface is very fast. Therefore we managed an experimental set-up by

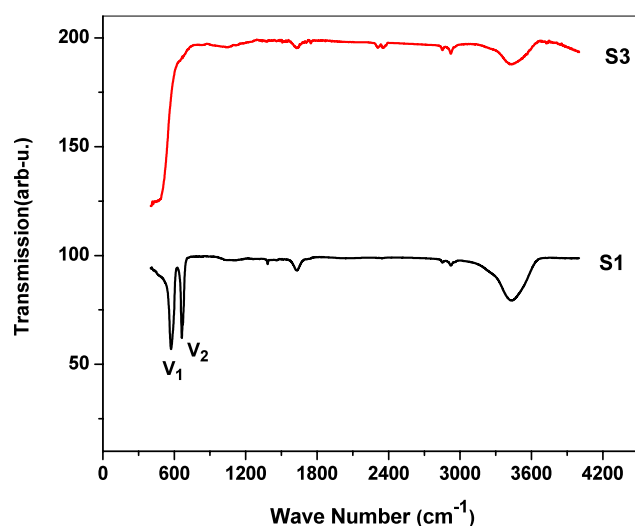


Fig. 3 FTIR spectrum of samples S1 and S3

which the calcined sample at 950°C was quickly quenched to liquid nitrogen (sample S3). The XRD result in Fig. 2 shows that the sample S3 contains pure CoO phase. The estimated lattice constant of 4.26 \AA is in agreement with earlier works [26]. It seems that the rapid cooling of the powders to liquid nitrogen (77 K) has not given opportunity to as-prepared CoO nanoparticles to be oxidized to the Co_3O_4 phase.

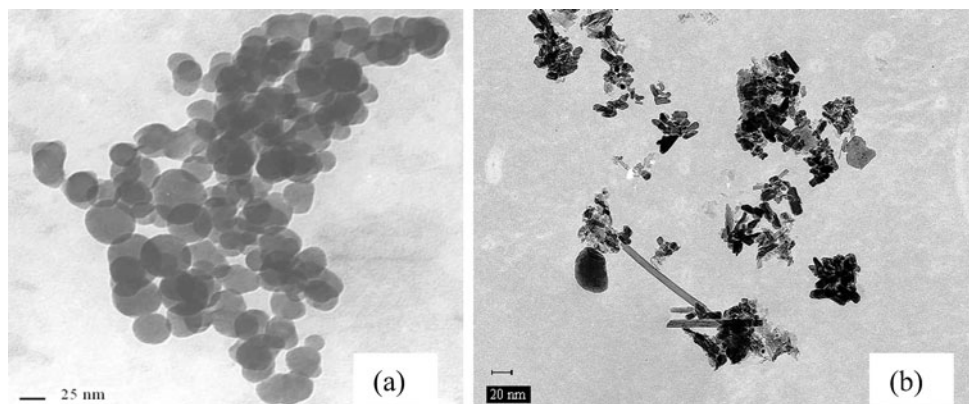
Figure 3 shows the FTIR spectrum of the samples S1 and S3. It can be seen two absorption bands in 578 cm^{-1} (ν_1) and 662 cm^{-1} (ν_2) in the FTIR spectrum of sample S1. The first band (ν_1) is associated with the Co^{3+} vibration in the octahedral hole and second band (ν_2) is attributed to the Co^{2+} vibration in the tetrahedral hole [29], which confirms the formation of the Co_3O_4 spinel. In the FTIR spectrum of sample S3, the (ν_1) and (ν_2) peaks disappeared and broad band at 450 cm^{-1} appeared, because of the formation of cubic CoO.

Figure 4 shows the typical TEM micrographs of samples S1 and S3. As Fig. 3(a) shows, the uniform spherical shape nanoparticles with average particle size of 40 nm are well distributed with some agglomeration occurring. Figure 3(b) shows that the as-prepared CoO powders consist of two parts: small nanoparticles and nanorods.

4 Conclusion

$\text{Co}_3\text{O}_4/\text{CoO}$ nanoparticles have been successfully synthesized by a ball-milling and calcination of cobalt acetate and citric acid. This method is more cost-efficient and could be used in a mass production process. The results show that Co_3O_4 nanoparticles with average particle size of $40\text{--}50 \text{ nm}$ can be obtained by calcination of ball-milled precursors at relatively low temperature (350°C) for 3 hours. Meanwhile, the pure CoO nanoparticles were obtained successfully by thermal decomposition of Co_3O_4 at 950°C and quickly quenching to liquid nitrogen.

Fig. 4 TEM micrographs of samples: (a) S1 and (b) S3



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