



Investigation of lattice distortion of Co_3O_4 nanoparticles prepared by a carbon-assisted method



Xiaogang Tong^a, Zhenyin Hai^a, Danfeng Cui^a, Libo Gao^a, Qiang Zhang^a, Hongyan Xu^b, Yating Ma^c,
Chenyang Xue^{a,*}, Jun Liu^{a,*}

^a Key Laboratory of Instrumentation Science and Dynamic Measurement of Ministry of Education, North University of China, Taiyuan, Shanxi 030051, China

^b School of Materials Science and Engineering, North University of China, Taiyuan, Shanxi 030051, China

^c School of Science, North University of China, Taiyuan, Shanxi 030051, China

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ABSTRACT

Cobalt oxide nanoparticles with spherical structures (~50 nm in diameter) were prepared by a carbon-assisted method using absorbent cotton as the carbon source and cobalt nitrate as the precursor. The phases, particle size, and lattice distortion of the samples obtained at different baking temperatures (200–600 °C) were characterized by X-ray diffraction. The results show that lattice expansion has taken place in the prepared samples. Furthermore, Fourier-transform infrared spectroscopy was used to analyze the phase evolution of Co_3O_4 , showing that CoCO_3 is the intermediate precursor. The best temperature (600 °C) for preparing Co_3O_4 nanoparticles was determined through analysis of the morphology and particle size of the samples using scanning electron microscopy and transmission electron microscopy.

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1. Introduction

Nanomaterials, especially the internal lattice and surface lattice of nanoparticles, will have a certain degree of lattice distortion. This type of lattice distortion breaks the lattice symmetry of the crystal in the local area, thus leading to localized states and material properties that are different from the intact lattice material, such as the decrease in Curie temperature [1], the change of conductivity [2], and the blue shift of the light absorption band [3]. With its special capabilities in magnetism, diffusivity, conductivity, chemical activity, and catalysis, the functional nanomaterial Co_3O_4 is widely used in the fields of magnetic materials, sensors, super capacitor, lithium ion batteries, electrode materials, and catalysis [4–9]. The physical and chemical properties of Co_3O_4 relate closely to the composition, size, and shape of the nanomaterial [10–12]; however, it is rare to see any report about the lattice distortion of nanomaterials.

This paper uses a carbon-assisted method using degreasing cotton as the carbon source, which has never been reported before, to prepare spherical Co_3O_4 nanoparticles. Because degreasing cotton is used as the carbon source, no by-product and contaminative gas is formed during calcination. Therefore, the cost is extremely low and it is

environmentally friendly. The whole process is simple and easy to handle. The lattice distortion of the sample was studied by X-ray diffraction (XRD).

2. Experimental

2.1. Sample preparation

A stable pink solution was obtained after 17.46 g of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was added to 20 mL deionized water and stirred vigorously for 10 min. To obtain a good dispersion of Co^{2+} on the surface of the degreasing cotton, 1.5 g of degreasing cotton was immersed into the pink solution and kept in an ultrasonic bath for 10 min. The treated degreasing cotton was collected and transferred into a quartz petri dish in the tube furnace (OTF-1200X-III, Hefei, China) and kept at 200 °C, 400 °C, and 600 °C for 2 h in air. The resultant samples designated as Co-C-200-2, Co-C-400-2, and Co-C-600-2 were obtained without any further processing.

2.2. Sample characterization

The crystal structure of the sample was performed using XRD (Bruker D8, $\lambda = 1.5406 \text{ \AA}$) in the 2θ of 10–80° with a scan rate of 10°/min and $\text{CuK}\alpha$ radiation of 40 kV. Fourier-transform infrared (FTIR) spectra of samples were recorded from KBr pellets in the range of 500–4000 cm^{-1} on an Avatar360 spectrometer. Scanning electron microscopy images

* Corresponding authors.

E-mail addresses: xuechenyang@nuc.edu.cn (C. Xue), Liuju@nuc.edu.cn (J. Liu).

were obtained on a Hitachi S-4800 scanning electron microscope. The particle shapes and sizes were characterized by transmission electron microscopy measurement (JEM-1200EX, JEOL) with a working voltage of 120 kV.

3. Results and discussion

3.1. Phase evolution analysis of Co_3O_4

Fig. 1 shows the XRD of the product after chemical reactions at different temperatures (200–600 °C) for 2 h, using $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ as the cobalt source. At 200 °C, when comparing the map and the PDF standard card (No. 78-209) at 2θ of 24.5, 42.2, and 54.0, it is evident that CoCO_3 is present in the product. When compared with the standard image (PDF No. 42-1467) of the cubic phase Co_3O_4 , it is evident that there is a Co_3O_4 phase present in the product. Therefore, at 200 °C, the precursor CoCO_3 is not able to transform into Co_3O_4 completely. At 400 °C, there is no obvious characteristic peak of the precursor. But we can still see some very small peaks of the precursor. It demonstrates that almost all the precursors are transformed into Co_3O_4 . At 600 °C, all the peaks correspond to the cubic phase Co_3O_4 . So the product is pure phase Co_3O_4 and all the CoCO_3 is completely transformed into Co_3O_4 . Through these comparisons of the XRD maps of the products obtained at different temperatures, it is obvious that as the temperature increases, the strength of the characteristic peaks enhances gradually and the half peak width becomes narrower and narrower, which indicates that the size of particles gradually increases. This proves that high temperature is conducive to the formation of Co_3O_4 crystals. The crystallization becomes more and more obvious, which corresponds with the study of Liu's group [13]. Obviously, temperature is a decisive condition in the formation of Co_3O_4 . Furthermore, we also observed broadening of the diffraction peaks. On the one hand, the broadening is caused by grain refinement; on the other hand, it is a result of lattice defects.

To further study the formation mechanism of Co_3O_4 , we used FTIR to analyze the different products formed (not being cleaned by deionized water and anhydrous ethanol), as shown in Fig. 2. The absorption peaks around 3425 and 1642 cm^{-1} belong to the stretching vibration and the flexural vibration, respectively, of the water–OH absorbed by the samples. The absorption peaks around 836 cm^{-1} belong to the characteristic absorption peaks of CO_3^{2-} [14], around 1317 cm^{-1} , the stretching vibration peaks of the C–O bond [15], and the strong absorption peaks at 658 and 570 cm^{-1} are the stretching vibrations of Co(III)-O and Co(II)-O , respectively. The analysis above proves that the products formed at 200 °C are mixtures of CoCO_3 and Co_3O_4 , and have almost completely turned into

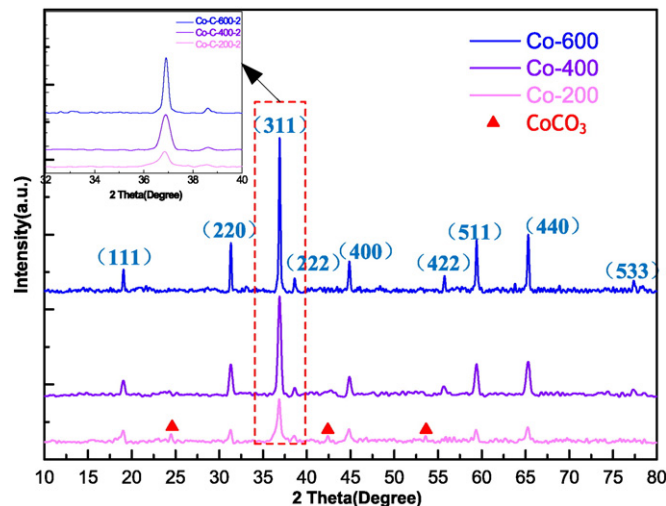


Fig. 1. The XRD map of the products in different temperatures (200–600 °C).

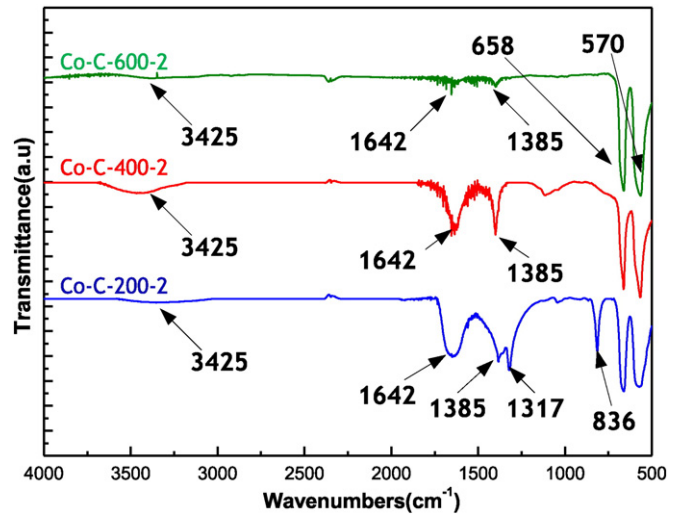
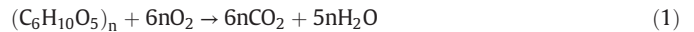


Fig. 2. The FTIR map of the products in different temperatures (200–600 °C).

CoCO_3 particles at 400 °C and 600 °C. In addition, the absorption peak at 1358 cm^{-1} belongs to the vibration of NO_3^- , which exists in the form of highly symmetric free ions [16]. It will not combine with Co^{2+} in the solid phase. The XRD map in Fig. 1 does not show the presence of Co^{2+} , which corresponds with the observations of Chen [17] at Shandong University.

According to the analyses above, we can confirm the mechanism of the carbon-assisted method using degreasing cotton as the carbon source. Under high-temperature conditions, degreasing cotton is burnt, releasing CO_2 . The CO_2 hydrolyzes to CO_3^{2-} , which combines with Co^{2+} forming the CoCO_3 precursor precipitate. The main reactions are:



Finally, CoCO_3 calcines in O_2 , obtaining the product Co_3O_4 :



The NO_3^- present in the chemical experiment does not participate in the reaction and the degreasing cotton plays an important role during the formation of the Co_3O_4 .

3.2. The impact of temperature on the microstructure of Co_3O_4

Fig. 3 shows the scanning electron microscopy and transmission electron microscopy images of the products obtained after 2 h at 200–600 °C using $\text{Co}(\text{NO}_3)_2$ as the Co source. The nanospheres in Fig. 3a are the precursors CoCO_3 . In Fig. 3b, it is clear that the samples are amorphous and there is no obvious sphere nanoparticles existing. The size of the particles is about 20 nm. Fig. 3c and d shows that the precursor microspheres have decomposed into Co_3O_4 nanoparticles with good dispersion. The particle size is about 30 nm and the shape of the particles is close to spherical. At 600 °C, the dispersion of Co_3O_4 is further improved, showing regular spheres, the size of which is around 50 nm (Fig. 3e and f). According to Fig. 3, the size and appearance of Co_3O_4 particles change as the temperature increases. The particles tend to be the shape of spheres; the size of the particles tends to be bigger as the calcination temperature increases, the range of which is from 20 to 50 nm. From Figs. 1 and 3, we can draw the conclusion that the best conditions for

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