

A Simple Microwave-Assisted Route to Prepare Black Cobalt, Co_3O_4 ¹

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Abstract—In this communication, we report a novel microwave-assisted decomposition reaction of cobalt nitrate hexahydrate, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. Using microwave processing (10 min, 2.45 GHz), phase-pure tricobalt tetroxide (black cobalt, Co_3O_4) was obtained. The compound was characterized by x-ray powder diffraction and infrared spectroscopy.

INTRODUCTION

Cobalt oxide, Co_3O_4 , is an interesting material among transition-metal oxides. Co_3O_4 is used as an active catalyst in air pollution monitoring [1]. It has been studied mainly for its optical, semiconducting, magnetic, and electrochemical properties, which render it attractive for solar photochemical applications [2–4] and electrochromic devices as a counter electrode [5]. Cobalt oxide has also many potential applications in nanomaterials science because of its particle size and surface effects [6]. Nanostructured materials have many potential applications for nanodevices such as nanorods, nanowires, nanofibers, and nanotubes [7, 8].

In recent years, to easily obtain black cobalt, Co_3O_4 , many methods have been developed. Most popular methods are sol–gel [9], spray pyrolysis [10], chemical vapor deposition [11], chemical precursor routes [12], electrochemical, sonochemical synthesis [13], and a simple reduction oxidation method [14]. However, a relatively high temperature is necessary in most of the above methods.

In order to have better control in the preparation of high-valence and pure cobalt oxides, we have adopted microwave-assisted decomposition of cobalt nitrate hexahydrate, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. Characterization of the synthesized tricobalt tetroxide, Co_3O_4 , includes x-ray powder diffraction (XRD) and FTIR measurements.

EXPERIMENTAL

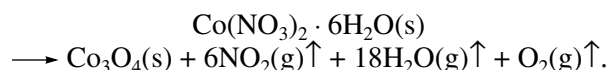
Sample preparation. Co_3O_4 was synthesized using microwave methods. As the starting material, we used high-purity $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Merck, 99.9% purity). The sample (5 g) was weighed and transferred to a crucible and exposed to microwave energy (2.45 GHz, 750 W) in a domestic-type microwave oven (Arçelik

MD560) for 10 min. At the end of the experiment, the sample was allowed to cool inside the oven. The resulting product was subjected to XRD and FTIR analyses.

Characterization techniques. The XRD data were collected using Philips X' Pert-Pro x-ray diffractometer with a position-sensitive detector, graphite monochromator, and $\text{CuK}\alpha$ radiation (40 kV, 20 mA, $\lambda = 1.54056 \text{ \AA}$). IR spectrum was obtained using a Perkin-Elmer BX-2 FTIR spectrometer in the $4000\text{--}400 \text{ cm}^{-1}$ region with sample as KBr discs.

RESULTS AND DISCUSSION

XRD study. The microwave-assisted decomposition reaction of cobalt nitrate hexahydrate, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, can be represented as follows:



During microwave irradiation, a decomposition reaction took place and caused NO_2 and O_2 gases to

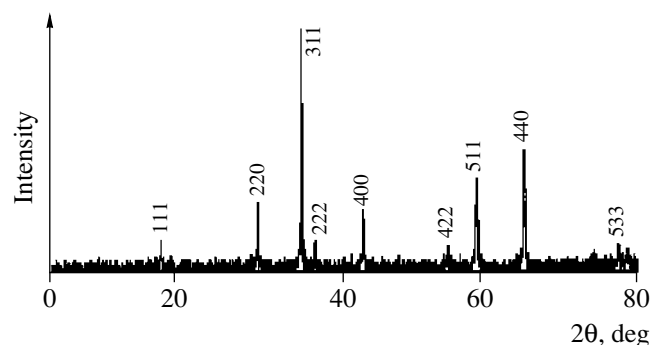


Fig. 1. XRD pattern of Co_3O_4 .

¹ This article was submitted by the authors in English.

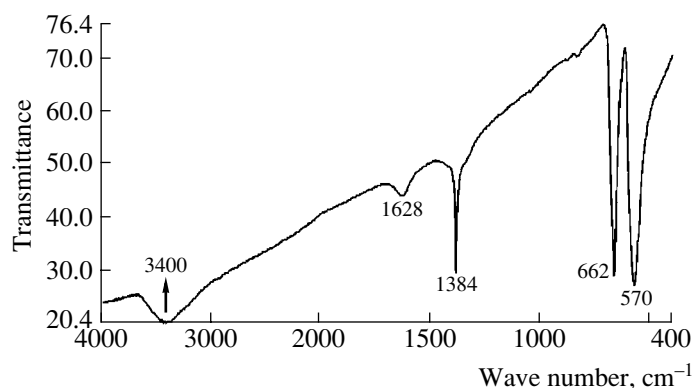


Fig. 2. FTIR spectrum of Co_3O_4 .

evolve. The color of the material changed from red to black.

The XRD pattern and data of the product are given in Fig. 1 and the table. The XRD peaks attest to the formation of black cobalt, Co_3O_4 , as a main and pure phase. All the experimental XRD peaks are in excellent agreement with those reported in the literature for Co_3O_4 (JCPDS card no. 01-1152).

FTIR study. Figure 2 shows that the Fourier transform IR spectra for the synthesized black cobalt, Co_3O_4 . The IR bands at 3400 and 1628 cm^{-1} may be due to moisture, and the band at 1384 cm^{-1} can be assigned to ν_1 vibrations of carbon dioxide molecules [15]. The IR spectrum displays two distinct and sharp bands at 570 (ν_1) and 662 (ν_2) cm^{-1} , which originate from the stretching vibrations of the metal–oxygen bond [16–18]. The ν_1 band is characteristic of OCo_3 vibrations (Co^{3+} in octahedral coordination), and the ν_2 band is attributable to $\text{Co}^{2+}\text{Co}^{3+}\text{O}_3$ (Co^{2+} in tetrahedral coordination) vibrations in the spinel lattice [19]. The

presence of these bands confirms the formation of phase-pure black cobalt, Co_3O_4 .

CONCLUSIONS

Black cobalt, Co_3O_4 , was synthesized successfully as a pure phase using microwave-assisted decomposition of cobalt nitrate hexahydrate, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. Compared to traditional methods, microwave synthesis has several advantages, including a considerably reduced processing time and energy saving. This method appears to be a good alternative for the synthesis of black cobalt, Co_3O_4 .

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REFERENCES

- Mergler, Y.J., Van Aalst, A., Van Delft, J., and Nieuwenhuys, B.E., *J. Catal.*, 1996, vol. 161, p. 310.
- Barrera, E., Gonzalez, I., and Viveros, T., *Sol. Energy Mater. Sol. Cell*, 1998, vol. 51, p. 69.
- Grangvist, C.G. and Eriksson, T.S., *Material Science for Solar Energy Conversion Systems*, Oxford: Pergamon, 1991.
- Duffie, J.A. and Beckman, W.A., *Solar Engineering of Thermal Process*, New York: Wiley, 1980.
- Burke, L.D., Lyons, M.E., and Murphy, O.J., *Electroanal. Chem.*, 1982, vol. 132, p. 247.
- Lewis, L.N., *Chem. Rev.*, 1993, vol. 93, p. 2693.
- Cavicchi, R.E. and Silsbe, R.H., *Phys. Rev. Lett.*, 1984, vol. 52, no. 16, p. 1435.
- Ball, P. and Li, G., *Nature (London)*, 1992, vol. 355, p. 761.

Observed and literature (JCPDS 01-1152) XRD data for Co_3O_4

I , %	d , Å	d_{obs} , Å	I_{obs} , %	hkl
8	4.68	4.67	10	1 1 1
20	2.86	2.85	23	2 2 0
100	2.43	2.43	100	3 1 1
6	2.34	2.32	10	2 2 2
13	2.02	2.01	20	4 0 0
4	1.65	1.64	5	4 2 2
25	1.56	1.55	30	5 1 1
30	1.43	1.42	44	4 0 0
2	1.24	1.24	6	5 3 3

9. Baydi, M.E., Poillerat, G., Rehspringer, J.-L., *et al.*, *J. Solid State Chem.*, 1994, vol. 109, p. 281.
10. Fujii, E., Torii, H., Tomozawa, A., *et al.*, *J. Mater. Sci.*, 1995, vol. 30, p. 6013.
11. Gautier, J.L., Rios, E., Gracia, M., *et al.*, *Thin Solid Films*, 1997, vol. 311, p. 51.
12. Furlanetto, G. and Formado, L., *J. Colloid Interface Sci.*, 1995, vol. 170, p. 169.
13. Koinuma, M., Hirae, T., and Matsumoto, Y., *J. Mater. Res.*, 1998, vol. 13, p. 837.
14. Yonghong, N., Xuewu, G., Zhicheng, Z., *et al.*, *Mater. Res. Bull.*, 2001, vol. 36, p. 2383.
15. Nakamoto, K., *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, New York: Wiley, 1986.
16. Lin, H.K., Chiu, H.C., Tsai, H.C., *et al.*, *Catal. Lett.*, 2003, vol. 88, p. 169.
17. Spencer, C. and Schroeder, D., *Phys. Rev. B: Condens. Matter*, 1974, vol. 9, p. 3658.
18. Andrushkevich, T., Borekov, G., Popovksii, V., *et al.*, *Kinet. Katal.*, 1968, vol. 6, p. 1244.
19. Christoskova, St.G., Stayonava, M., Georgieva, M., and Mehandjiev, D., *Mater. Chem. Phys.*, 1999, vol. 60, p. 39.

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