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Continuous Flow Microwave-Assisted Synthesis of CoO and NiO Nanoparticles

Masafumi HARADA*, Mayuu KOGAI, and Yuuri TAKAHASHI
Department of Clothing Environmental Science, Faculty of Human Life and Environment,
Nara Women's University, Nara 630-8506, Japan

Introduction

Transition metal oxides, such as cobalt, nickel, and iron, have attracted increasing attention owing to their potential applications as catalysts, electrochromic films, magnetic materials and battery devices. In recent years there have been several developments in the synthesis of nanoparticles using the effective heating provided by microwave (MW) irradiation. Some research groups successfully made continuous flow MW reactor systems to scale up reactions and used them to conduct MW-assisted synthesis [1-3]. Herein we report on the synthesis for CoO and NiO nanoparticles under continuous flow MW irradiation and the characterization of their structures using EXAFS measurements.

Experimental

For the preparation of CoO nanoparticles, $Co(CH_3COO)_2{\cdot}4H_2O$ (1 mmol) and oleylamine (10 mmol) were mixed and heated in oil bath at 393 K for 30 min. After cooling to room temperature, 1-octanol (or 1-dodecanol) (50 ml) dissolving oleic acid (3 mmol) and trioctylphosphine oxide (TOPO, 1 mmol) was added to the solution. The solution was heated to 463 K (in the case of 1-octanol) or 533 K (in the case of 1-dodecanol), and kept at this temperature for 20 min by MW heating. The MW oven was a focused single-mode MW synthesis system (Discover SP, CEM Corp.). The temperature was controlled by automatic adjusting of MW power. When the continuous flow system operated, the reagent mixture flew to the reactor vessel inside the MW, where it was irradiated. After naturally cooling down to room temperature, the colloidal solutions were collected for the EXAFS measurements. For the preparation of NiO nanoparticles, similar procedures were applied except the use of $Ni(CH_3COO)_2{\cdot}4H_2O$. The EXAFS measurements were carried out in a transmission mode at BL-9C. Data analysis was performed by REX2000 (Rigaku Co.).

Results and Discussion

Figure 1 shows the Fourier transforms (FTs) of the colloidal CoO nanoparticles and their reference compounds (CoO and $Co(CH_3COO)_2$ powder). Even after MW irradiation of 20 min, FT spectra of the colloidal samples are similar to those of CoO powder. This obviously indicates the formation of CoO nanoparticles. The obtained structural parameters are listed in Table 1. The dependence of reaction condition (irradiation time, starting compound, additives, solvent, etc.) on the structure of the CoO and NiO nanoparticles is also examined. The detailed analysis is in progress.

Table 1. Structural parameters from EXAFS analysis for the colloidal dispersions of CoO nanparticles prepared by means of MW irradiation.

Sample	bond	C.N	r / Å	dE / eV	DW / Å
20 min irradiation	Co-O	4.5	2.13	7.13	0.113
in 1-octanol	Co-Co	11.8	3.02	-2.79	0.091
20 min irradiation	Co-O	3.3	2.08	0.48	0.072
in 1-dodecanol	Co-Co	11.3	3.01	-2.07	0.079

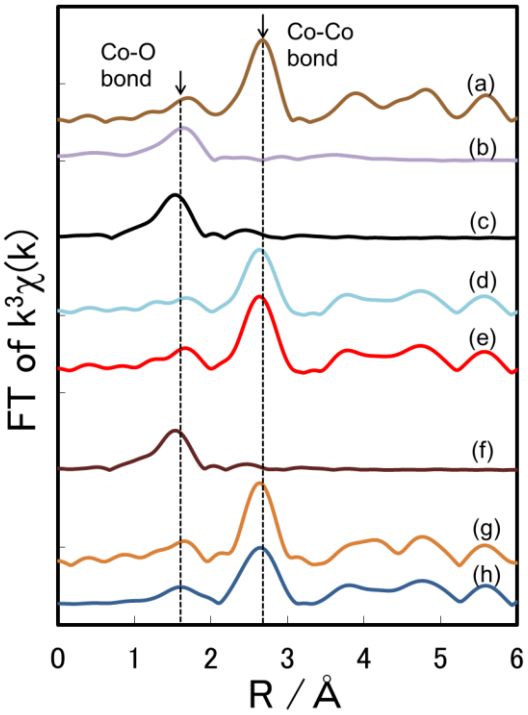

Fig. 1. Fourier transforms of Co K-edge EXAFS spectra for (a) CoO powder, (b) $Co(CH_3COO)_2{\cdot}4H2O$ powder, and those of the colloidal CoO nanoparticles prepared in 1-octanol by MW irradiation of (c) 0 min, (d) 20 min, and (e) 60 min, and those of the colloidal CoO nanoparticles prepared in 1-dodecanol by MW irradiation of (f) 0 min, (g) 20 min, and (h) 60 min.

References

[1] D. Damm et al., *Org. Process Res. Dev.* **2010**, *14*, 215.
[2] S. Horikoshi et al., *Nanoscale.* **2010**, *2*, 1441.
[3] Y. Groisman and A. Gedanken, *J. Phys. Chem. C* **2008**, *112*, 8802.
*harada@cc.nara-wu.ac.jp