

Microwave-Assisted Synthesis of Transition-metal Oxide Nanoparticles

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1 Introduction

Transition-metal oxides, such as manganese, cobalt, nickel and iron, have attracted increasing attention owing to their potential applications in high-performance electrodes, catalysts, magnetic materials and battery devices. Over the past years great efforts have been paid for the microwave (MW)-assisted synthesis of transition-metal oxide nanoparticles [1,2], because the MW heating can provide generation of homogeneous nucleation sites as compared to the conventional heating. In this study we have demonstrated the MW-assisted rapid synthesis of magnetite (Fe_3O_4) and manganese oxide (MnO and Mn_3O_4) nanoparticles and characterized their structures using EXAFS measurements.

2 Experimental

In a typical experiment for the preparation of Fe_3O_4 nanoparticles, $\text{Fe}(\text{CH}_3\text{COO})_2$ (or $\text{Fe}(\text{acac})_3$) (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-dodecanol (50 ml) dissolving oleic acid (3 mmol) and trioctylphosphine oxide (TOPO, 1 mmol) was added to the solution. The solution was heated to 533 K, and kept at this temperature for 20 min (or 60 min) under MW irradiation. The MW reactor was a focused single-mode MW synthesis system (CEM Discover SP). The temperature and pressure was controlled by regulation of MW power output. After naturally cooling down to room temperature, the colloidal solutions were collected for the EXAFS measurements. For the preparation of manganese oxide nanoparticles, similar procedures were applied except the use of various manganese precursors such as $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ and $\text{Mn}(\text{COOH})_2 \cdot x\text{H}_2\text{O}$. The EXAFS measurements were carried out in a transmission mode at BL-9C. Data analysis was performed by REX2000 (Rigaku Co.).

3 Results and Discussion

Figure 1 shows the Fourier transforms (FTs) of the colloidal Fe_3O_4 nanoparticles and their reference compounds. Even after the shorter irradiation time of 20 min, FT spectra of the colloidal samples show the first peak assigned to Fe-O bond (around 1.5 Å) and the second peak assigned to Fe-Fe bond (around 2.6 Å and 3.1 Å), which are similar to those of Fe_3O_4 reference compound. This obviously indicates the formation of Fe_3O_4 nanoparticles coordinated by oleylamine, oleic acid, and TOPO molecules in 1-dodecanol. Furthermore, as shown in Fig. 2, the dependence of reaction condition (irradiation time, kinds of precursors, additives and solvents, and so on) on the structure of the manganese

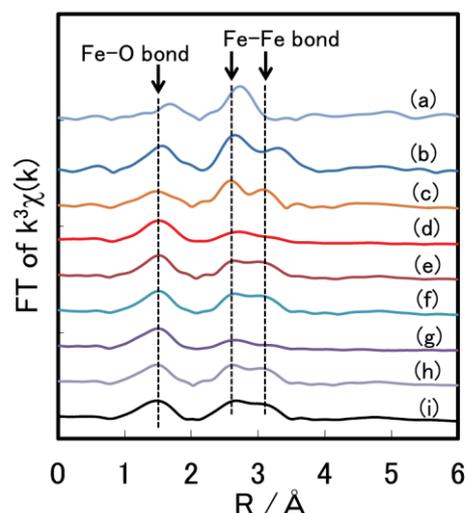


Fig. 1. Fourier transforms of Fe K-edge EXAFS spectra for (a) FeO powder, (b) Fe_2O_3 powder, (c) Fe_3O_4 powder, and those of the colloidal Fe_3O_4 nanoparticles prepared from $\text{Fe}(\text{CH}_3\text{COO})_2$ by MW irradiation of (d) 0 min, (e) 20 min, and (f) 60 min, and those of the colloidal Fe_3O_4 nanoparticles prepared from $\text{Fe}(\text{acac})_3$ by MW irradiation of (g) 0 min, (h) 20 min, and (i) 60 min.

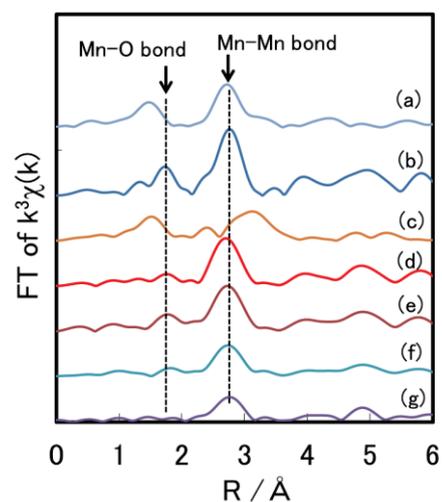


Fig. 2. Fourier transforms of Mn K-edge EXAFS spectra for (a) Mn_2O_3 powder, (b) MnO powder, (c) Mn_3O_4 powder, and those of the colloidal MnO nanoparticles prepared from $\text{Mn}(\text{CH}_3\text{COO})_2$ by MW irradiation of (d) 20 min and (e) 60 min, and those prepared from $\text{Mn}(\text{COOH})_2$ by MW irradiation of (f) 20 min and (g) 60 min.

oxide nanoparticles is also examined. The detailed analysis is in progress.

References

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- [2] Y. -J. Zhu et al., *Chem. Rev.* **2014**, *114*, 6462-6555.

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