Synthesis and Properties of Monodisperse Superparamagnetic $\text{Mg}_{0.8}\text{Mn}_{0.2}\text{Fe}_2\text{O}_4$ Nanoparticles Using Polyol Reflux Method

Sandip Sabale · Vishwajeet Khot · Vidhya Jadhav · Xiaoli Zhu · Yanhong Xu

Received: 17 February 2014 / Revised: 1 May 2014 / Published online: 26 September 2014
© The Chinese Society for Metals and Springer-Verlag Berlin Heidelberg 2014

Abstract Superparamagnetic monodisperse $\text{Mg}_{0.8}\text{Mn}_{0.2}\text{Fe}_2\text{O}_4$ nanoparticles have been successfully synthesized in liquid polyol at elevated temperature of 200 °C. Diethylene glycol (DEG) used here plays dual role in synthesis as it acts as reducing agent and alternatively coats the surface of nanoparticles while synthesis and thereby maintaining uniform size and dispersibility. Powder X-ray diffraction (XRD) and magnetic measurements showed that the sample is cubic spinel and superparamagnetic at room temperature. Raman spectra confirmed the formation of the $\text{Mg}_{0.8}\text{Mn}_{0.2}\text{Fe}_2\text{O}_4$ nanoparticles. The nanoparticles exhibit very good stability in water due to *in situ* coating with DEG molecules.

KEY WORDS: Magnetic materials; Chemical synthesis; Magnetic properties; Transmission electron microscopy (TEM); X-ray diffraction; $\text{Mg}_{0.8}\text{Mn}_{0.2}\text{Fe}_2\text{O}_4$ nanoparticles

1 Introduction

The synthesis of nanostructured magnetic materials has become an important area of research since such materials are attracting growing interest in technological applications of modern magnetic materials which reveal a range of fascinating phenomena. Properties of single nanostructures can be tailored to specific needs by varying size, composition, or morphology. In particular, the nanometer scale MFe_2O_4 ($M = \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}, \text{Cu}, \text{Zn}, \text{etc.}$) spinel ferrites

and their dispersions in various substances are among the most important magnetic materials which have been widely used for studies of nanomagnetism [1]. Magnesium–manganese ferrite nanoparticles (MFNs) are one of the most interesting soft magnetic materials. Due to their low coercivity and low eddy current (high resistivity), they have been extensively used in a number of electronic devices, especially for high-frequency applications (radio-frequency coils, transformer cores, *etc.*). The properties of the ferrite particles are influenced by the composition and the microstructure, which are sensitive to the preparation methodology. Many methods have been developed to prepare nanocrystalline soft ferrites; *e.g.*, combustion [2, 3], ceramic technique [4], coprecipitation [5], *etc.*

Very few studies are available on Mn–Mg by wet chemical method, and there is no report about the preparation and characterization of Mn–Mg ferrites by the polyol method. Polyol method [6, 7] using polyalcohol's (ethylene glycol and diethylene glycol) to reduce metal salts into particles was successfully used to prepare variety of non-aggregated inorganic compounds. The polyol often serves as reaction medium with high boiling point solvent and reducing agent, as well as stabilizer to control the particle

Available online at <http://link.springer.com/journal/40195>

S. Sabale (✉) · X. Zhu · Y. Xu
Laboratory of Biosensing Technology, School of Lifesciences,
Shanghai University, Shanghai 200444, China
e-mail: srsabale@gmail.com

S. Sabale · V. Khot · V. Jadhav
P. G. Department of Chemistry, Jaysingpur College, Jaysingpur
416101, India

V. Khot
Centre for Interdisciplinary Research, D. Y. Patil University,
Kolhapur 416006, India

growth and prevent interparticle aggregation. The advantage of this method is the possibility to control experimental conditions and easy scale-up [8].

In the present investigation, MFNs have been prepared by polyol method. Narrow size distribution can be easily obtained directly using this method. The structural, morphological, and magnetic properties of the obtained nanoparticles are characterized by X-ray, Raman spectroscopy, VSM, and TEM.

2 Experimental

All chemicals were purchased from Sigma Aldrich (Analytical grade and high degree purity) and used without further purification. Precursor salts, anhydrous $\text{Mn}(\text{NO}_3)_2$, $\text{Fe}(\text{NO}_3)_2$ and $\text{Mg}(\text{NO}_3)_2$ in an atomic ratio of 0.8:2:0.2 were added to 20 mL of DEG, and 3.6 g sodium acetate trihydrate was added to mixture. The mixture was then heated to boil (~ 473 K) for 3 h, which results in black precipitate. After cooling to the room temperature, the particles were separated from the supernatant by centrifugation, washed with ethanol:ethyl acetate, and re-dispersed in water. The powder was dried in air at 325 K for physico-chemical property measurements.

The phase identification of the sample was performed on Ragaku Miniflex X-ray diffractometer with CuK_α radiation ($\lambda = 0.15418$ nm). TEM image and the electron diffraction (ED) pattern were recorded on a JEOL-2010 transmission electron microscope at an accelerating voltage of 200 kV. Magnetic measurements were carried out using a vibrating sample magnetometer (VSM, Lakeshore 7404) with a maximum magnetic field of 1,500 kA/m. Particle size distribution (hydrodynamic diameter) was studied using NICOMP 380TM particle sizing system (Santa Barbara, CA). Raman spectra were obtained on a Renishaw RM1000 Raman spectroscopy (Ar-ion laser, 514.5 nm).

3 Results and Discussion

3.1 Structural Analysis

Figure 1 shows a typical XRD pattern of the $\text{Mg}_{0.8}\text{Mn}_{0.2}\text{Fe}_2\text{O}_4$ obtained by a refluxing process in diethylene glycol. It is found that all diffraction peaks can be perfectly indexed to the cubic spinel structure, and no characteristic peaks of the impurities are detected in the XRD pattern [2, 3]. The broadening of the diffraction peaks distinctly indicates the nanocrystalline nature of the materials. The calculated average crystallite size, D_{XRD} , of the product was (11 ± 2) nm.

Fig. 1 XRD pattern of $\text{Mg}_{0.8}\text{Mn}_{0.2}\text{Fe}_2\text{O}_4$ nanoparticles synthesized by polyol synthesis

3.2 Morphology and Size Analysis

The morphology and particle size determined by TEM (Fig. 2a) indicate that the ferrite particles are quasi-spherical with the average size of (10 ± 2) nm. Some agglomeration is observed from the micrographs, which may be due to the sample preparation. Size estimated from TEM micrographs agrees well with the crystallite size estimated from XRD pattern [(11 ± 2) nm], which may reveal nearly single crystalline character of $\text{Mg}_{0.8}\text{Mn}_{0.2}\text{Fe}_2\text{O}_4$ nanoparticles. The ED rings corresponding to $\text{Mg}_{0.8}\text{Mn}_{0.2}\text{Fe}_2\text{O}_4$ (Fig. 2a, inset) are indexed as (220), (311), (400), (422), and (511) reflections of cubic spinel structure.

Dynamic light scattering (DLS) is commonly used for the particle size determination. The particle size is defined as the size of a hypothetical hard sphere that diffuses in the same fashion as that of the NPs being measured. The result is reported as a mean particle size and homogeneity of the size distribution. The particle size distribution obtained from DLS is given in Fig. 2b. The result shows that hydrodynamic diameters of the particles are in the range of 40–95 nm (polydispersity index 0.17) with a narrow distribution [9]. The mean hydrodynamic diameter of $\text{Mg}_{0.8}\text{Mn}_{0.2}\text{Fe}_2\text{O}_4$ is (61.1 ± 9) nm, indicating that the particles are monodisperse in nature. Diethylene glycol (DEG) plays an important role in the formation of the spinel phase. As a good capping agent with two hydroxyl groups, DEG can hold free metal ions tightly in the solution. With the addition of NaAc into the solution, CH_3COO^- is attracted to the vicinity of the metal ions, assisting in the DEG-mediated conversion of metal salts into spinel phase sample under reaction temperature of 200 °C [10–12].

Fig. 2 **a** TEM image (inset SAED pattern), **b** DLS spectra of $\text{Mg}_{0.8}\text{Mn}_{0.2}\text{Fe}_2\text{O}_4$ nanoparticles synthesized by polyol

Fig. 3 **a** Thermogravimetric graph, **b** Raman spectra of $\text{Mg}_{0.8}\text{Mn}_{0.2}\text{Fe}_2\text{O}_4$ nanoparticles

3.3 Thermogravimetric and Raman Analysis

The presence of polyol ligands on the surface of the magnetite nanoparticles is supported by TG measurement. Figure 3a shows the TG curve of the nanoparticles indicating a two-stage for weight loss in the temperature ranges of 25–70 and 70–294 °C. In the first step, slight amount of the weight loss corresponded to evaporation of adsorbed water and ethanol or ethyl acetate. The second step

represents the most significant weight loss which could be attributed to the removal of residual DEG in the sample of which the boiling point is around 290 °C. The total weight loss of the sample is around 11% which yields the product up to 89%. The sample attains stability above 300 °C.

Raman spectrum of the as-prepared sample is shown in Fig. 3b. $\text{Mg}_{0.8}\text{Mn}_{0.2}\text{Fe}_2\text{O}_4$ ferrite has a cubic spinel structure that belongs to the space group $Oh7$ ($Fd3m$). The group theory predicts the following modes in spinel [13]:

Fig. 4 **a** M–H curve at 300 and 10 K, **b** M–T curve of $\text{Mg}_{0.8}\text{Mn}_{0.2}\text{Fe}_2\text{O}_4$ nanoparticles

$$\Gamma = A_{1g}^{(R)} + E_g^{(R)} + F_{1g}^{(in)} + 3F_{2g}^{(R)} + A_{2u}^{(in)} + 2E_u^{(in)} + 4F_{1u}^{(IR)} + 2F_{2u}^{(in)},$$

where $^{(R)}$, $^{(IR)}$ and $^{(in)}$ represent Raman-active vibrations, infrared-active vibration, and inactive modes, respectively. As for $\text{Mg}_{0.8}\text{Mn}_{0.2}\text{Fe}_2\text{O}_4$ ferrite, there are five Raman-active modes ($A_{1g} + E_g + 3F_{2g}$) and four infrared-active modes ($4F_{1u}$).

All five Raman modes are observed at ambient conditions in this study, as shown in Fig. 3b. The modes at 533 and 691 cm^{-1} are attributed to the characteristics of the tetrahedral sites; other peaks at 225, 325 and 469 cm^{-1} correspond to the characteristics of the octahedral sites, which are consistent with the previously reported studies [14, 15]. These results further confirm the formation of $\text{Mg}_{0.8}\text{Mn}_{0.2}\text{Fe}_2\text{O}_4$ nanoparticles.

3.4 Magnetic Measurements

Magnetization measurements were performed on the powders under the applied field of ± 1500 kA/m (Fig. 4). The sample is cooled from room temperature to 10 K without any external magnetic field (zero field cooled, ZFC), and the magnetization is recorded while warming the sample at an applied field of 8 kA/m. The magnetization initially increases as the temperature increases from 10 K and then starts to decrease after reaching a maximum value. Such temperature-dependent magnetization, with a broad maximum in the ZFC magnetization, is a characteristic feature of superparamagnetism, and the temperature at which maxima are obtained is called blocking temperature. In the case of FC procedure, magnetization

monotonically increases as the temperature decreases. The divergence of FC and ZFC curves below blocking temperature T_B is attributed to the existence of magnetic anisotropy barriers. Thus, the resulting nanoparticles can be considered as magnetic single domains with a blocking temperature T_B around 100 K.

For $\text{Mg}_{0.8}\text{Mn}_{0.2}\text{Fe}_2\text{O}_4$ particles of 10-nm size, the blocking temperature is obtained at 38 K, when magnetization is recorded at 8 kA/m [8]. It is known that the fine particles are easier to be thermally activated to overcome the magnetic anisotropy [16]. When the nanoparticle size is smaller than the superparamagnetic critical size, above the blocking temperature, the hysteresis behavior vanishes and the magnetization direction of the particles simply follows the direction of the applied magnetic field. For the $\text{Mg}_{0.8}\text{Mn}_{0.2}\text{Fe}_2\text{O}_4$ ferrite, the absence of hysteresis, immeasurable remanence and coercivity, and the non-attainment of saturation at a high applied magnetic field of 1,500 kA/m indicate the presence of superparamagnetic behavior, which is attributed to the size of the equiaxial-shaped nanoparticles below the superparamagnetic critical size [10, 17].

4 Conclusions

Monodisperse $\text{Mg}_{0.8}\text{Mn}_{0.2}\text{Fe}_2\text{O}_4$ nanoparticles with size around 10 nm have been successfully prepared by one-step polyol synthesis. The nanoparticles are superparamagnetic at room temperature with their blocking temperature 38 K. The hydrodynamic diameter of these nanoparticles is found to be about 61 nm. Therefore, this improved polyol

synthesis may be useful in size-controlled, phase pure, and superparamagnetic nanoparticles synthesis of mixed ferrites for variety of technological and biomedical applications.

Acknowledgments One of the authors (Dr. Sandip Sabale) is thankful to Prof. Dr. Genxi Li, Dean, School of Life Sciences, Shanghai University, China for his valuable discussion. Author VMK acknowledges the Council of Scientific and Industrial Research, India for the award of senior research fellowship (File. 09/1077/(0001)/2012/EMR-1).

References

- [1] T.G. Altincekic, I. Boz, A. Baykal, S. Kazan, R. Topkaya, M.S. Toprak, *J. Alloys Compd.* **493**, 493 (2010)
- [2] V.M. Khot, A.B. Salunkhe, M.R. Phadatare, N.D. Thorat, S.H. Pawar, *J. Phys. D Appl. Phys.* **46**, 0553031 (2013)
- [3] M.A. Ahmed, *J. Magn. Magn. Mater.* **322**, 763 (2010)
- [4] M. Singh, S.P. Sud, *Mater. Sci. Eng. B* **83**, 180 (2001)
- [5] S.F. Mansour, *J. Magn. Magn. Mater.* **323**, 1735 (2011)
- [6] F. Fievet, J.P. Lagier, B. Blin, M. Beaudoin, *Solid State Ionics* **32**, 198 (1989)
- [7] C. Feldman, G.O. Jungk, *Angew. Chem. Int. Ed.* **40**, 359 (2001)
- [8] W. Cai, J. Wan, *J. Colloid Interface Sci.* **305**, 366 (2007)
- [9] E.J. Cho, H. Holback, K.C. Liu, S.A. Abouelmagd, J. Park, Y. Yeo, *Mol. Pharm.* **10**, 2093 (2013)
- [10] J. Jiang, *Mater. Lett.* **61**, 3239 (2007)
- [11] H. Deng, X. Li, Q. Peng, X. Wang, J. Chen, Y. Li, *Angew. Chem. Int. Ed.* **117**, 2842 (2005)
- [12] H. Hu, M. Mo, B. Yang, X. Zhang, Q. Li, W. Yu, Y. Qian, *J. Cryst. Growth* **258**, 106 (2003)
- [13] W.G. Fateley, F.R. Dollish, N.T. McDevitt, F.F. Bentley, *Infrared and Raman Selection Rules for Molecular and Lattice Vibrations: The Correlation Method* (Weily, New York, 1972), p. 169
- [14] T. Yu, Z.X. Shen, Y. Shi, J. Ding, *J. Phys. Condens. Matter* **14**, 613 (2002)
- [15] Y. Qu, H. Yang, N. Yang, Y. Fan, H. Zhu, G. Zou, *Mater. Lett.* **60**, 3548 (2006)
- [16] X. Cao, L. Gu, *Nanotechnology* **16**, 180 (2005)
- [17] C. Liu, B. Zou, A.J. Rondinone, Z.J. Zhang, *J. Am. Chem. Soc.* **122**, 6263 (2000)