Journal of Magnetism and Magnetic Materials 361 (2014) 249–254

Contents lists available at ScienceDirect

Journal of Magnetism and Magnetic Materials

journal homepage: www.elsevier.com/locate/jmmm

Use of triethylene glycol monobutyl ether in synthesis of iron oxide nanoparticles

Seda Beyaz [a], Fatmahan Ozel [b], Hakan Kockar [b,*], Taner Tanrisever [a]

[a] Department of Chemistry, Balikesir University, Balikesir 10145, Turkey
[b] Department of Physics, Balikesir University, Balıkesir 10145, Turkey

ARTICLE INFO

Article history:
Received 8 May 2013
Received in revised form
9 January 2014
Available online 21 February 2014

Keywords:
Magnetic material
Iron oxide
Nanostructure
Chemical synthesis

ABSTRACT

Superparamagnetic iron oxide nanoparticles were synthesized by thermal decomposition of iron–oleate complex using triethylene glycol monobutyl ether (TREGBE) as solvent for the first time for more mass of the nanoparticles. The effect of TREGBE on the properties of the nanoparticles was compared with that of 1-hexadecene. The impact of oleic acid concentration on the properties of the nanoparticles was also studied. On the use of TREGBE as compared with 1-hexadecene, the average crystal size reduced from 9.1 ± 2.1 to 8.2 ± 0.7 nm whereas the saturation magnetization (M_s) increased from 53.6 to 58.0 emu/g. Moreover, more products can be synthesized using TREGBE. Besides, the interactions between particle surfaces and TREGBE are weaker than that of 1-hexadecene according to gravimetric analysis results. X-ray diffraction analysis revealed that crystallinity and particle size scaled up with increasing oleic acid amount in TREGBE. The electron microscopy showed that dot-shaped particles turned into irregular particles with increasing amount of oleic acid molecules using TREGBE. The results disclosed that TREGBE is quite a suitable solvent to synthesize the superparamagnetic iron oxide nanoparticles with the desired size and M_s for more mass production at low temperature.

1. Introduction

Magnetic iron oxide nanoparticles (γFe_2O_3 and Fe_3O_4) have gained considerable attention in the past decade driven by their broad technological applications, including single-bit elements in high density magnetic data storage arrays [1], ferrofluids, magnetic refrigeration systems, photocatalysts, photoelectrodes, battery electrodes, magnetic inks for jet printing [2], contrast enhancement agents for magnetic resonance imaging [3], and magnetic carriers for drug targeting [4]. Among the synthesis methods of the iron oxide nanoparticles, thermal decomposition-based synthesis has proved a great success for the preparation of monodisperse nanoparticles [5–7]. This can also be done with high-temperature hydrolysis method [8,9]. This method is also suitable for mass production [10]. In thermal decomposition, many factors such as the nature of the precursor [11,12] and capping group [13], the concentration of precursor [14] and the decomposition temperature [10,15] affect the properties of the resulting particles. In some cases, a reducing or oxidizing agent may be required to obtain Fe(II) ion in the formation of magnetite. For instance, an alcohol is preferred in order to produce the partial reduction of the Fe^{3+} in case of iron (acetylacetonate) precursor [6]. In recent years, triethylene glycol molecules have been used for this purpose. In fact it has performed triple roles as a high-boiling solvent, reducing agent and stabilizer [16–18] which made this process easy to scale up for mass production. Generally, the polyol molecules are proposed for the preparation of easily reducible metals such as Pt, Ag, Au or Co [19]. However some metal oxide nanoparticles were also obtained by the polyol process [20] but the method is limited to polar precursors such as metal oxalate and metal acetates. The reducing agents are not required for iron–oleate complexes since a trace amount of CO, H_2, and carbon produced by the thermal decomposition of the complex is enough for the reduction of Fe^{3+} to Fe^{2+} [15]. But they can alter decomposition ratio of the complex and thus they can affect the product amount and particle size [10,15]. For instance, when the solvents with low boiling temperature such as hexadecene are used relatively poor decomposition occurs, resulting in less product and smaller particles [13].

This study presents a new solvent, triethylene glycol monobutyl ether (TREGBE; see Fig. 1), for mass production of iron oxide nanoparticles at low temperatures. The study investigated the properties of the resultant particles in TREGBE and compared them to those prepared in 1-hexadecene which has the same boiling

* Corresponding author. Tel.: +90 2666121278.
E-mail address: hkockar@balikesir.edu.tr (H. Kockar).

http://dx.doi.org/10.1016/j.jmmm.2014.02.032
0304-8853

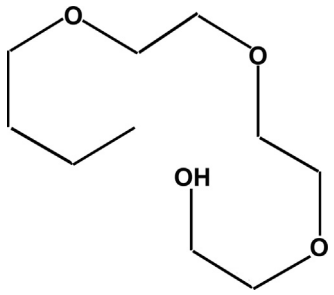

Fig. 1. Chemical structure of a TREGBE molecule.

point (280 °C). Besides, a series of nanoparticles were synthesized and characterized varying the concentration of oleic acid and the reaction time in the solvent of TREGBE. The results revealed that TREGBE provided higher magnetization and smaller particle size compared to 1-hexadecene probably due to its reducing character. Moreover, it is very suitable for mass production at low temperature, which provides efficient energy use for potential electronic and magnetic applications.

2. Experimental

The iron–oleate complex precursors were prepared using a published procedure [21]. In a typical experiment of this study, 2.7 g of $FeCl_3 \cdot 6H_2O$ (Merck, 99%) was dissolved in 50 mL of methanol (Merck, 99%) and then 3 equivalents oleic acid (Sigma-Aldrich, 99%) was added (9 mL) to the ferric salt. A solution with 1.2 g of NaOH (Merck, 99%) in 100 mL of methanol was dropped into this solution under magnetic stirring. The observed brown precipitate was washed with methanol 4–5 times and dried at 40 °C for 24 h.

By thermal decomposition of the iron–oleate complex, the magnetic iron oxide nanoparticles were synthesized in the different solvents with approximately the same boiling temperature: 1-hexadecene (Sigma-Aldrich, 92%) and TREGBE (Fluka, 70%). 0.9 g (1 mmol) of the iron–oleate complex and 10 mL of the chosen solvent were combined in a two-neck round-bottom reaction flask. The reaction mixture was then heated to about 274 °C using a temperature controller and with the temperature set at 300 °C it was refluxed for atleast 30 min. The initial reddish-brown color of the reaction solution turned brownish-black. The resultant solution was then cooled down to room temperature. In the use of 1-hexadecene solvent, a mixture of 10 mL of hexane (Merck, 95%) and 40 mL of acetone (Merck, 99%) was added to the reaction flask to precipitate the nanoparticles whereas the nanoparticles produced in TREGBE were precipitated by using water. All nanoparticles were separated under the magnet and washed 3 times by a mixture of hexane and acetone. After washing, they were collected using a magnet and dissolved in chloroform (Merck, 99%) to avoid aggregation in a liquid during storage time. All reaction conditions are listed in Table 1.

For the analysis of the Fourier transform infrared (IR) spectra, the samples dried by evaporating the chloroform were mixed with KBR powder and then recorded on a Perkin-Elmer spectrometer. X-ray diffraction (XRD) patterns were collected using a PANalytical's X'Pert PRO X-ray diffractometer system with a Cu-Kα source (1.54 Å). A high resolution transmission electron microscope (HRTEM, FEI TECNAI G^2 F30 model) with an accelerating voltage of 200 kV was used to obtain information of particle shape and size. Thermo-gravimetric analysis (TGA) was carried out using powder samples (~10 mg) with a heating rate of 10 °C/min using a Perkin-Elmer TG-DTA analyzer in air atmosphere up to 600 °C. Magnetic measurements were measured by a vibration sample magnetometer (VSM-ADE EV9 Model) at ±20 kOe. All measurements were carried out at room temperature.

Table 1
Synthesis conditions and results of the analysis.

Sample	Solvent type	Oleic acid (mL)	Reaction time (min)	HRTEM diameter (nm)	Crystallite size (nm)	M_s (emu/g)
H1	1-hexadecene	0	30	9.9 ± 2.0	9.1 ± 2.1	53.6
T1	TREGBE	0	30	8.6 ± 1.6	8.2 ± 0.7	58.0
T2	TREGBE	0.4	30	9.5 ± 1.7	8.5 ± 0.9	62.7
T3	TREGBE	0.9	30	9.2 ± 2.0	8.3 ± 0.8	68.2
T4	TREGBE	1.3	30	9.1 ± 2.2	8.4 ± 0.9	66.4
T5	TREGBE	2.2	30	11.4 ± 2.3	10.0 ± 0.2	31.6
T6	TREGBE	0.4	180	10.3 ± 1.6	9.0 ± 1.1	65.9

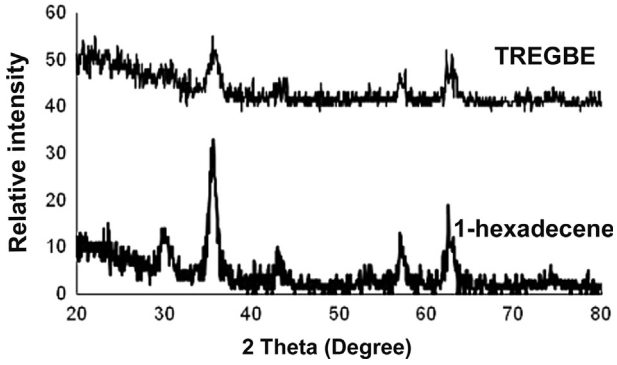

Fig. 2. XRD patterns of nanoparticles prepared in the 1-hexadecene solvent (sample H1) and TREGBE (sample T1).

3. Results and discussion

The properties of iron oxide nanoparticles prepared in the same experimental conditions but in different solvents, 1-hexadecene and TREGBE, were investigated comparatively. The effect of oleic acid amount on the properties of iron oxide nanoparticles prepared in TREGBE is discussed.

XRD patterns in Figs. 2–4 reveal a phase formation of magnetite or maghemite without contamination of other iron oxide phases. However, since their XRD patterns are very similar, it is difficult to distinguish the two phases simply from their XRD patterns.

The peak intensities in Fig. 2 indicate that the particles in 1-hexadecene have a higher crystallinity than the ones in TREGBE. This difference can be attributed to different mechanisms in the growth of crystals due to intervention of solvent molecules.

Fig. 3 presents a comparison of the XRD patterns of iron oxide nanoparticles prepared with various oleic acid concentrations. An increase was observed with addition of oleic acid in terms of crystallinity. Moreover, this trend is more pronounced at the highest oleic acid concentration (T5). Thus, it can be concluded that oleic acid causes the formation of more crystalline nanoparticles.

Average crystallite size of particles was calculated on the basis of the Scherrer equation [22] using the half maximum width of the intense peaks. For this, diffraction profile was fitted by a pseudo-Voight function [23] using the XFit program [24] and a line profile was obtained as shown in Fig. 4. The peaks used for size calculations were selected from those that have the best fit percentage. For example (220), (311), (511) and (440) peaks were used to calculate the average crystal size of T5 sample (see Fig. 4).