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Growth and characterizations of magnetic nanoparticles under hydrothermal conditions: Reaction time and temperature

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ABSTRACT

Magnetic iron oxide nanoparticles with various sizes and magnetic properties were synthesized by using a hydrothermal method. The initial nanoparticles were obtained by co-precipitation of ferric and ferrous salts and then treated under a hydrothermal condition for 1–120 h at 160 °C. At reaction time of 12 h, further treatment on the particles was performed at 200 °C. The resultant nanoparticles were characterized by transmission electron microscopy (TEM), X-ray diffractometer (XRD) and vibrating sample magnetometer. The images obtained by TEM showed that the particles are around spherical in shape. The mean size of particles increased from 14 ± 4 nm to 74 ± 9 nm as the reaction time was increased from 1 h to 120 h. From the XRD patterns, high crystalline iron oxide nanoparticles were obtained with increasing reaction time and temperature. The saturation magnetizations obtained from magnetization curves were found to be rising from 74.9 to 93.5 emu/g that is consistent with the bulk value of the magnetite.

1. Introduction

Nanometer sized particles have been widely studied due to their widespread use in technological and biomedical application [1,2]. Magnetic properties of particles are highly related to the volume and temperature because this property arises from the collective interaction of atomic magnetic dipoles [3]. Bulk magnetic materials which have multidomain structures are composed of regions which have uniform magnetization because of the alignment of the magnetic moments, called magnetic domains, and the domains are separated by domain walls [4]. When the size of materials decreases to a certain critical value, the particles change from multidomain state to single domain state. And, the size of particles continues to decrease, the thermal energy leading to randomization of the magnetic dipoles in a short period of time [3,5]. These particles, called superparamagnetic nanoparticles, do not have permanent magnetic moment in the absence of an external field.

The most commonly used metal oxides are magnetite and maghemite due to their biocompatibility and high saturation magnetization M_s values [6,7]. Nano-sized ferrite particles can be obtained by various ways, such as hydrothermal method, co-precipitation method, microemulsion techniques and decomposition of organo-metalic compounds [8–15]. Co-precipitation has a simple synthesis route and can be prepared on a large scale of products [16–19]. Also, the hydrothermal method under study allows the synthesis of high-quality nanoparticles. In some cases, two techniques are used together to the purposed size and related magnetic properties. Furthermore, there has been limited number of studies on this field. Wu et al. [20] combined procedure of microemulsion and hydrothermal synthesis to prepare nanoparticles. Daou et al. [21] synthesized 39 nm magnetite particles by the coprecipitation method followed by hydrothermal treatment at 250 °C. To improve the magnetic properties of the produced magnetic nanoparticles the co-precipitation method can be performed under hydrothermal conditions. In the hydrothermal method, the reaction conditions, such as solvent, especially temperature and reaction time have important effects on the synthesis outcomes [22]. Therefore, the hydrothermal process together with co-precipiation was used for synthesis of magnetic iron oxide nanoparticles under study. By changing the reaction time and temperature crystalline iron oxide particles with different size and magnetic properties were generated.

2. Experimental

Ferrous chloride tetrahydrate ($FeCl_2 \cdot 4H_2O$ Merck > 99%) ferric chloride hexahydrate ($FeCl_3 \cdot 6H_2O$ Merck > 99%) salts and ammonium hydroxide (NH_4OH Merck, 25% of ammonia) were used for

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the synthesis of iron oxide nanoparticles. All chemicals were of reagent grade and used without further purification.

Superparamagnetic iron oxide nanoparticles were traditionally synthesized by coprecipitation of ferric and ferrous salts. 20.3 g (75 mmol) $FeCl_3 \cdot 6H_2O$ and 14.9 g (75 mmol) $FeCl_2 \cdot 4H_2O$ were dissolved into 50 ml distilled water. 50 ml of 25% ammonia was added to the salt solution under a stirring condition at 700 rpm. The stirring was continued for 2 min [23]. The mixture (15 ml) was put into a teflon-lined stainless autoclave and the autoclave was heated to 160 °C and was maintained at this temperature. At this temperature, the samples were kept at the reaction times of 1, 12, 24, 48, 92 and 120 h in an oven, respectively. Autoclave was naturally cooled to room temperature for each process and the precipitates were washed with distilled water and isolated under magnet. The final products were dried at 60 °C. A further sample for 12 h was treated at 200 °C for comparison reason.

Particle size and shape were determined from transmission electron microscopy using a HRTEM, FEI TECNAI G2 F30 model microscope. The samples were prepared by placing one drop of a dilute suspension of iron oxide nanoparticles in water on a carbon coated copper grid and water evaporated in air. The crystal structure of the samples was obtained using an X-ray diffractometer (X'pert Pro MPD) with an angle range from 20° to 80°. Magnetic measurement was performed with a vibration sample magnetometer (VSM, ADE EV9 Model). Magnetization curves were measured at room temperature in a maximum magnetic field of 20 kOe.

3. Results and discussion

The TEM images of the nanoparticles were taken to observe the morphology and the size of nanoparticles prepared under different reaction times (1–120 h). In Fig. 1, the images of samples S1 (1 h) and S6 (120 h) are mostly spherical in shape. However, few of the particles at sample S6 grew like rod and cube shapes; see Fig. 1(b). And, the mean sizes, d_{TEM}, of nanoparticles obtained from the TEM images for 1 h and 120 h were 14 ± 4 nm and 74 ± 9 nm, respectively. When the reaction time in the alkaline medium was increased, the particle size was observed to increase, and by looking at the standard deviations the particle size distribution broadened.

To characterize the crystallinity of samples, XRD measurements were carried out on the samples treated under different reaction times and temperatures. All peak positions at (220), (311), (222), (400), (422), (511), (440), (620) and (533) are consistent with the standard X-ray data for the magnetite (JCPDS no. 019-0629) or maghemite phase (JCPDS no. 039-1346) as seen in Figs. 2 and 3 for reaction time and temperature, respectively. Magnetite has a cubic structure and contains both Fe^{2+} and Fe^{3+} ions. Maghemite has similar structure of magnetite. The Fe^{2+} cations in nanoparticles are not thermodynamically stable in air and easily oxidized into Fe^{3+}. Maghemite has similar structure of magnetite. The Fe^{2+} cations in nanoparticles are not thermodynamically stable in air and easily oxidized into Fe^{3+}. Maghemite has only Fe^{3+}, such that the charge deficiency produced by the oxidation of ferrous ions is compensated by cation vacancies [1,24]. The pattern of magnetite and maghemite is almost identical. The crystal diameters, d_{XRD}, of the nanoparticles calculated from the broadened peak data using

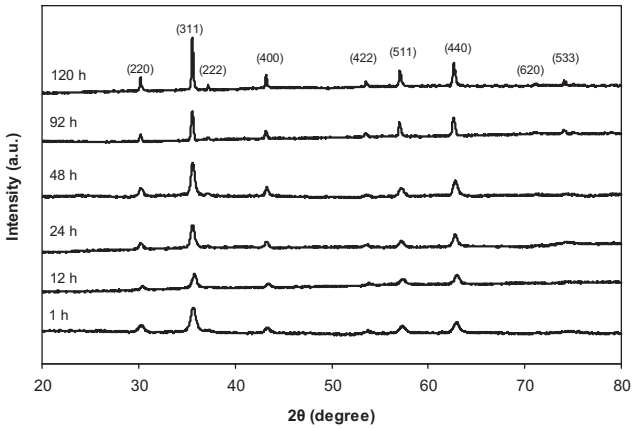

Fig. 2. The XRD patterns of iron oxide nanoparticles synthesized under different reaction times at 160 °C.

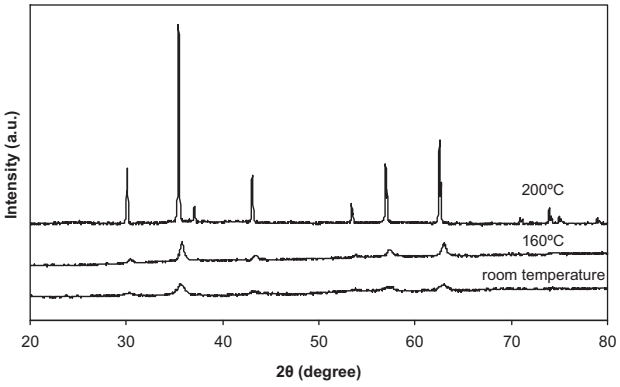

Fig. 3. The XRD patterns of iron oxide nanoparticles synthesized under different reaction temperatures.

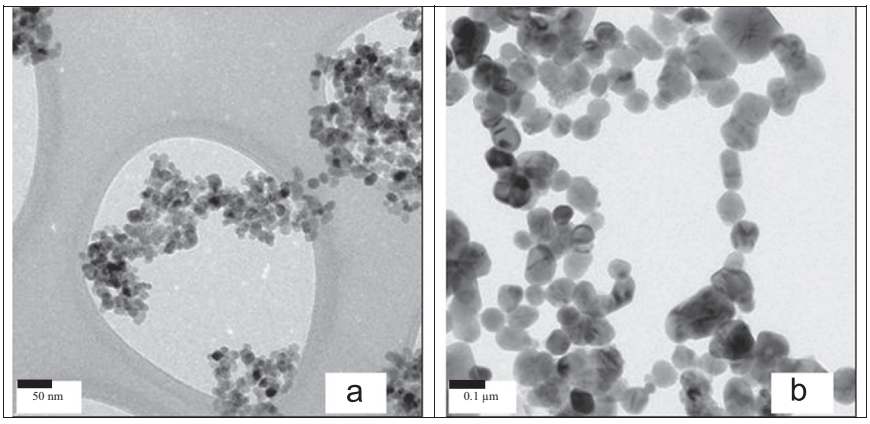

Fig. 1. The TEM images of nanoparticles synthesized at 160 °C for (a) 1 h and (b) 120 h.