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Synthesis of magnetite nanoparticles in W/O microemulsion

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Nanoparticles of magnetite have great potential for several applications in different areas such as recording material, pigment, biomedical and bioengineering, etc. [1–3]. Conventional techniques for preparation of magnetite (Fe_3O_4) nanoparticles include bulk precipitation [4], spray-drying [5], microwave hydrothermal method [6], etc. But most of the above methods have trouble with controlling precisely the size and the size distribution of the particles prepared. Recently, a new method for preparation of nanoparticles by utilizing the water cores of water-of-oil (W/O) microemulsions has been adopted for the synthesis of magnetic nanoparticles [7–10]. By using this method the particle size can be controlled easily.

In this letter we report a new microemulsion method to synthesize the magnetite nanoparticles. In this method we used a single microemulsion as reaction mediator in this method. To our knowledge it is the first time that the magnetite is produced by this single microemulsion system. It costs much less than other microemulsion methods. From the transmission electron microscopy (TEM) image, it can be seen that the the particle size distributions are consistently narrow and the shape of the particle is approximately spherical.

The procedure for magnetite preparation was described as follows. Water was distilled before use. The purity of all materials used in this study is more than 99%. Ferric chloride hexahydrate ($FeCl_3·6H_2O$) and ferrous chloride tetrahydrate ($FeCl_2·4H_2O$) are used as iron sources. In W/O microemulsion, sodium hydroxide (NaOH), which was dissolved in water, served

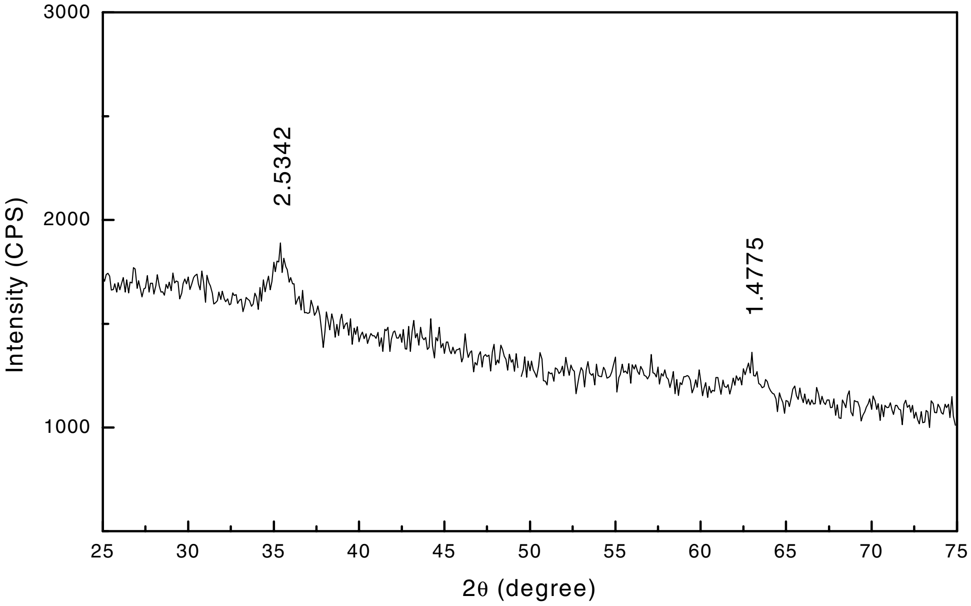

Figure 1 XRD of the dried magnetite powder, measured at room temperature.

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TABLE I The partial composition of the microemulsion system

	Microemulsion	Volume fraction
Aqueous phase	NaOH solution	0.05
Cosurfactant	Ethanol	0.27
Oil phase	Toluene	0.68

as dispersed phase, toluene served as oil phase, the sodium dodecyle benzene sulphonate (DBS) served as surfactant, and ethanol served as cosurfactant. The microemulsion was prepared by solubilizing NaOH solution into DBS/ethanol/toluene system. In the aqueous phase, the concentration of NaOH is 4.0 mol/L, and in oil phase (toluene) the concentration of DBS is 0.4 mol/L. The rest of the composition of the microemulsion system is presented in Table I.

Ferric and ferrous salts ($FeCl_3$ and $FeCl_2$) with molar ratio (2:1) were made into a mixed solution. Then in a nonoxidation environment this mixture in a certain volume was dropped into the microemulsion prepared by the above method with vigorous stirring at the same time. As the salts solution was added into the microemulsion, the mixed system turned black immediately. After the mixed system was stirred for 0.5 h and left standing for 5 h, a two layer system was formed. The upper layer was black in color and the bottom layer was discarded with a separation funnel. The magnetite was removed from the upper layer by a magnetic separation technique and washed for several times with a mixed solution of 1:1 ethanol/water. Thus the magnetite particles are obtained.

Phase analysis of the powders which had been dried at 323 K in a vacuum environment for 24 h, was carried out by powder X-ray diffraction (XRD) on a Japanese Rigaku D/max-3B fine-powder diffractometer at room temperature using Cu K_α radiation at 40 kV and 20 mA. The XRD pattern of the sample is shown in Fig. 1. In this figure, the two most intense diffraction peaks are at $2\theta = 35.4^\circ$ with d value of 2.5342 Å and $2\theta = 62.9^\circ$ and d value of 1.4775 Å respectively, which is similar to the diffraction pattern of standard Fe_3O_4. Because the diffraction lines become broader and smaller than that of the bulk counterparts owing to the small size of the particles, weak peaks can not be distinguished from the background noise [10]. It indicated that the major component of the sample is most probably Fe_3O_4.

Fourier transform infrared spectroscopy (FTIR) measurement of the dried powders was carried out on a Fourier transform infrared spectrometer (German BRUKE EQUINO55). All the spectra were recorded in the range 500–4000 cm^{-1} (wavenumber). The FTIR spectrum is provided in Fig. 2. The absorption band at 583.11 cm^{-1} in the spectrum is the characteristic of Fe_3O_4 [11]. An absorption band at 1632.80 cm^{-1} may be ascribed to the presence of the water molecules [12]. From the above analyses, we can conclude that the constituent of the sample was Fe_3O_4.

The diameter and the morphology of the magnetite particles, which were dispersed in water, were studied by transmission electron microscopy (TEM) on a Hitachi H-8100 transmission electron microscope. TEM image of the magnetite particles is presented in Fig. 3. The photograph indicates the magnetite synthesized by as-presented method has a narrow and uniform size distribution with an average diameter of 10 nm. In addition, from this picture, it can be seen that the shape of the samples is approximately spherical. This reflects the shape and the size range of the water droplet in the microemulsion, where the particles are formed [13]. Thus the W/O microemulsion method employed in this study provides a novel promising synthesis method to achieve the monodispersed and narrowly-distributed magnetite nanoparticles.

The magnetization measurement of the dried powders was carried out at room temperature on a vibration sample magnetometer (TM-VSM 2050 HGC). The hysteresis loop was presented with applied field of 10 K (oe). The hysteresis loop is shown in Fig. 4. The value of the saturation magnetization (M_s) is 33.48 emu/g, the value of the remnant magnetization (M_r) is 1.21 emu/g

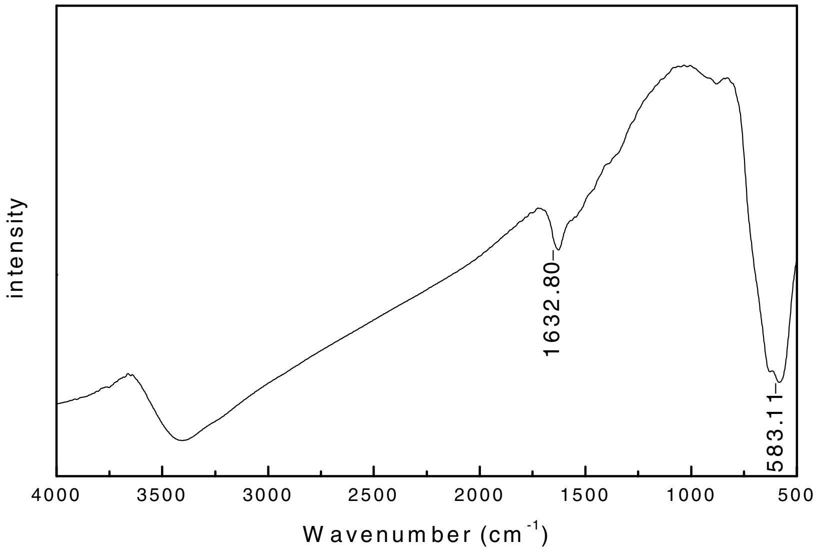

Figure 2 FTIR spectrum of the dried powder.

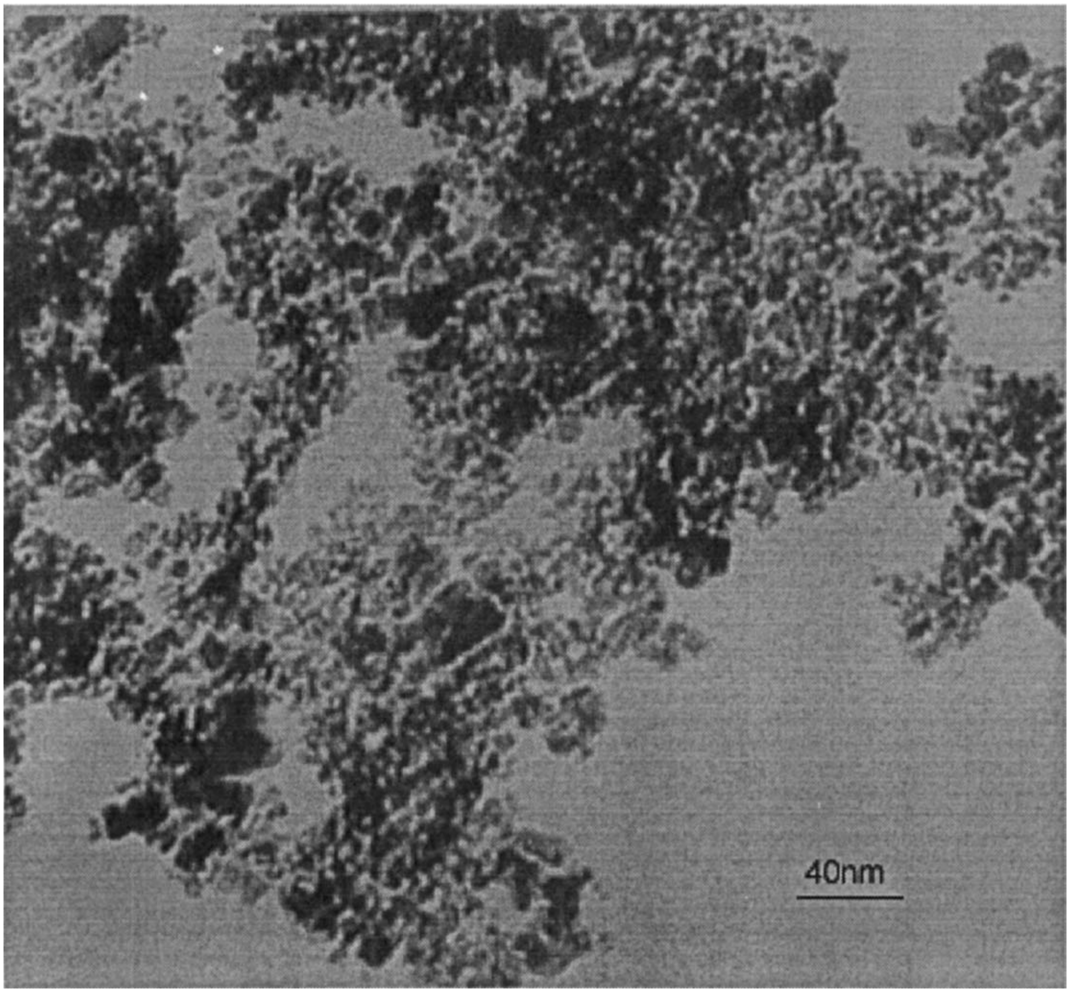

Figure 3 TEM image of the magnetite particles dispersed in water.

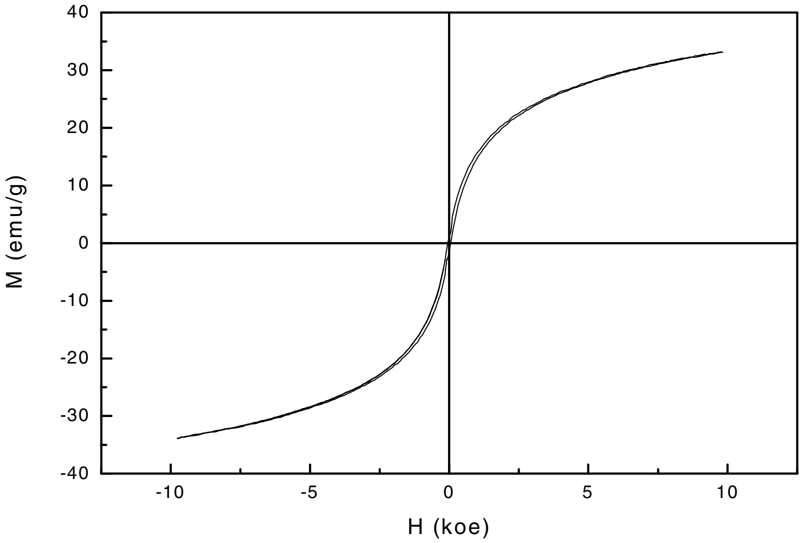

Figure 4 Magnetic hysteresis of the magnetite particles, measured at room temperature.

and the coercivity (H_c) approximately is zero oe. It shows that the magnetite synthesized by the microemulsion method has quite low coercivity and remnant magnetization but high saturation magnetization value, which indicates the sample has perfect superparamagnetism.

Thermogravimetric analysis (TGA) was studied using 7 Series Thermal Analysis System (Perkin-Elmer) in the temperature range from 493 to 923 K in an argon atmosphere. Thermogravity analysis (TGA) is shown in Fig. 5. According to the curve, the Curie temperature T_c of the sample determined by the intersection of angent line at largest slope with the flat bottom is 860 K which is higher than that of the bulk counterparts [14]. This indicates the change in magnetic structure of the magnetite nanoparticles [15]. In application,

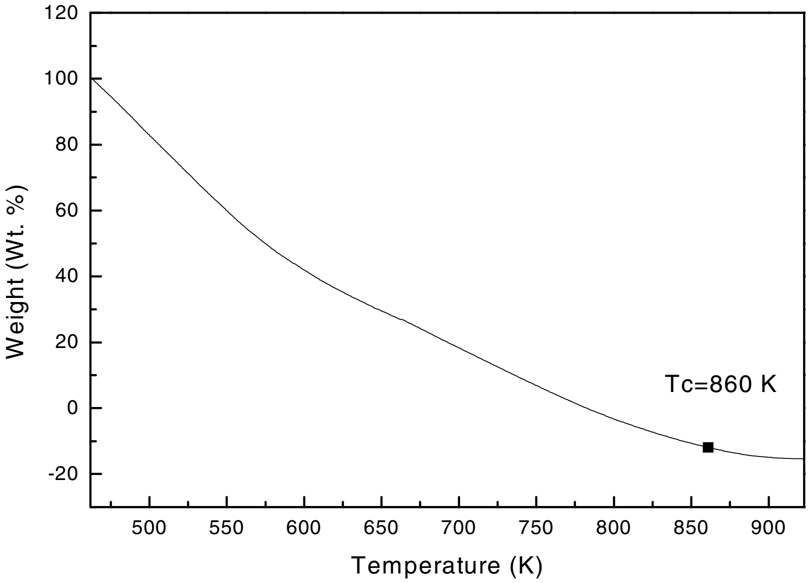

Figure 5 Thermogravity analysis TGA of magnetite particles.

nanosized magnetite particles with perfect superparamagnetism and high Curie temperature are desirable material used as a high-density recording media [16].

In summary, the magnetite nanoparticles have been successfully synthesized by using a new single microemulsion method. The structure and composition of particles are characterized by XRD and FTIR, which shows the sample is composed of magnetite. TEM image shows the magnetite particles have an average diameter of 10 nm and in the shape of quasisphere. The magnetic measurement showed the magnetite nanoparticles have perfect superparamagnetism and high Curie temperature T_c value of 860 K. It is demonstrated that the new method provided is a very effective way to synthesize magnetite nanoparticles.

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