Crystallographic and Magnetic Properties of Iron Oxide Nanoparticles for Applications in Biomedicine

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Magnetic nanoparticles have been investigated for use as biomedical purposes for several years. For biomedical applications the use of particles that present superparamagnetic behavior at room temperature is preferred [1-4]. To control the magnetic materials by magnetic field is essential locate particle to the suitable destination on feeding by injection. In order to use them properly, the particles should be nano size. However there are many difficulties in applications, because there is lack of identifications in nano magnetic properties. In our studies, structural and magnetic properties of iron oxide nanoparticles were investigated by XRD, VSM, TEM, and Mössbauer spectroscopy. At 13 K, hyperfine fields of γ Fe₂O₃ were 516 kOe and 490 kOe, that of Fe₃O₄ were 517 kOe and 482 kOe. The saturation magnetizations were 21.42 emu/g and 39.42 emu/g. The particle size of powders is 5~19 nm.

Key words: Iron oxide, Mössbauer, Applications in Biomedicine, Nanoparticles

1. Introduction

Magnetic nanoparticles offer some attractive possibilities n biomedicine. First, they have controllable sizes ranging from a few nanometers up to tens of nanometers. Second, the nanoparticles are magnetic, which means that they obey Coulomb's law, and can be manipulated by an external magnetic field [5].

Magnetic oxide nanoparticles, such as iron oxides and ferrite, are becoming increasingly important for biomedical applications such as hyperthermia, tissue engineering, and lrug delivery, etc. Magnetically guided devices have found biomedical application in diagnostic and therapeutic areas n both animal and human subjects [6].

Iron oxide magnetic nanoparticles tend to be both paramagnetic and superparamagnetic, with particles approximately 19 nm being classed as the latter. In most cases superparamagnetic particles (usually Fe₂O₃ and Fe₃O₄) are of interest for biomedical applications, as they do not retain any magnetism after removal of the nagnetic field [7]. However, routine medical applications are not known until now, and there is a demand for more

profound understanding of the magnetic properties to render it reliable for tumor therapy of human beings [8, 9]. And the control by magnetic field is essential locate particle to the suitable destination on feeding by injection.

In this paper, magnetic properties of iron oxide nanoparticles were investigated by XRD, VSM, TEM, and Mössbauer spectroscopy. The aim of the present investigation is to offer the information of iron oxide nanoparticles in structural and magnetic properties for biomedical applications.

2. Experimental Procedures

Magnetic iron oxide nanoparticles with different particle size were prepared by a sol-gel reaction. The reaction was carried out utilizing a sol-gel reaction inside reverse micelles and followed crystallization by reflux [10]. Appropriate portion of [Fe(CO)₅] was dissolved in hot-surfactant solution [11].

The crystal structure was measured using a x-ray diffractometer with a $CuK\alpha$ radiation source, and magnetic properties were measured using a vibrating sample magnetometer. Mössbauer spectra were investigated in the temperature range from 15 to 415 K using a conventional spectrometer with a ^{57}Co source in Rh matrix, and isomer

shift values were reported with respect to the Fe metal.

3. Results and Discussion

The crystalline properties of synthesized samples of fine particles of iron oxides were investigated by XRD, in Fig. 1. It is considered that the phase of samples are maghemite (γ Fe₂O₃) or magnetite (Fe₃O₄), because the crystal structure of them is spinel. Also, the considerable line broadening of the diffraction peak of sample I suggest that the size of the particles is relatively very small. Therefore, the kind of iron oxide nanoparticles is difficult to distinguish.

Figure 2 and Fig. 3 show some of the Mössbauer spectra of iron oxide samples measured at room temperature and 13 K. The Mössbauer spectrum of sample I and sample II at room temperature show superparamagnetic phase (doublet line), but that of sample III shows two-six line sub-patterns of typical magnetite. At 13 K, the spectra of all samples show two-six line patters, isomer shifts of sample I and II are in the ranges of 0.26~0.35 mm/s relative to Fe metal, which means that the ionic state of irons with respect to the two sites is ferric (Fe³⁺). Isomer shift of sample III is 0.83 mm/s and 0.33 mm/s relative to Fe metal that means ferrous (Fe²⁺) and ferric (Fe³⁺).

Magnetite (Fe₃O₄; [Fe³⁺]_{tel}[Fe²⁺Fe³⁺]_{oct}O₄) is a common magnetic iron oxide that has a cubic inverse spinel structure and the electrons can hop between Fe²⁺ and Fe³⁺ ions in the octahedral sites at room temperature [12]. Maghemite (γ -Fe₂O₃) is the completely oxidized form of magnetite. It also contains iron in tetrahedral A and

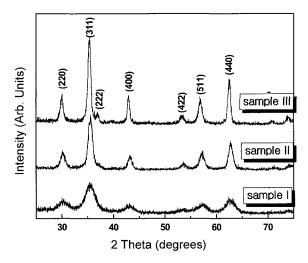


Fig. 1. XRD patterns of iron oxide nanoparticles. The crystal structure of sample I~sample III were spinel structure, but the kind of iron oxide materials cannot be distinguished.

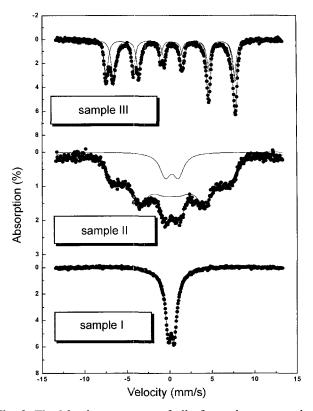


Fig. 2. The Mössbauer spectra of all of samples measured at room temperature.

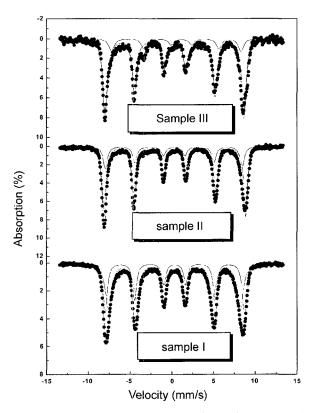


Fig. 3. The Mössbauer spectra of all of samples measured at 13 K.

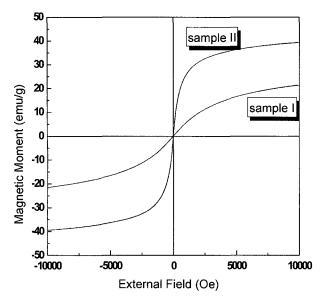


Fig. 4. Hysteresis loops of sample I and sample II. The particle size of sample I is 5 nm and that of sample II is 11 nm. The hysteresis loop of sample I shows nearly superparamagnetic property.

octahedral B sites, but there are vacancies (usually in the octahedral positions) to compensate for the increased positive charge and the two sites in maghemite have almost the same hyperfine field [13]. At 13 K, hyperfine fields of sample I were 516 kOe and 490 kOe, that of sample II were 527 kOe and 509 kOe, and that of sample III were 517 kOe and 482 kOe. So we can regard sample 1 and II as maghemite (γ -Fe₂O₃) and sample III as magnetite (Fe₃O₄).

In addition, the hysteresis loops of sample I and II were measured by a vibrating sample magnetometer (VSM, Lakeshore, Model 7300) in the maximum applied field of 0 kOe at room temperature, in Fig. 4. The saturation magnetizations M_S of sample I and sample II were 21.4 emu/g and 39.4 emu/g, and coercivities H_C were 10.9 Oe and 7.8 Oe at room temperature. For biomedicine application, such as hyperthermia, drug delivery system (DDS), and so on, magnetic fluid carrier should not lump for the smooth circulation of the blood and should not be sharp for the prevention of a hurt. Therefore, they should be superparamagnetic and have the spherical shape.

The sample I have the superparamagnetic property and the sample II have a little superparamagnetic property at toom temperature. However, sample II have the possibility of the lump in the applied field and the ferri-magnetism of maghemite (γ Fe₂O₃).

4. Conclusion

Iron oxide nanoparticles with different diameters have been prepared and their structural and magnetic properties have been investigated by XRD, VSM, TEM, and Mössbauer spectroscopy.

Sample I and II are the maghemite phase (γ -Fe₂O₃) and sample III is the magnetite phase (Fe₃O₄). The particle size of the iron oxide nanoparticles is in the range of 5~19 nm by TEM. From the results of VSM and Mössbauer spectrum, sample II and III are ferri-magnetic phase, but sample I have superparamagnetic phase at room temperature. It is considered that sample I is available for biomedicine application such as hyperthermia and drug delivery system as a magnetic fluid carrier.

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