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# $^{57}$Fe Mössbauer spectra study of coated $\alpha$-$Fe_2O_3$ nanoparticles

**Haosheng Fei**[1], **Mingyuan Gao**[2], **Xicheng Ai**[1], **Yangqiang Yang**[1], **Tieqiao Zhang**[1], **Jiacong Shen**[2]

[1]Department of Physics, Jilin University, Changchun, 130023, People's Republic of China
[2]Key Lab of Molecular Spectrum and Structure, Jilin University, Changchun, 130023,People's Republic of China
(Fax: + 86-431/892-3907)

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**Abstract.** Nano-sized $\alpha$-$Fe_2O_3$ particles coated with polar organic molecules have been studied using the Mössbauer spectroscopy method. The $\alpha$-$Fe_2O_3$ nanoparticles were prepared by the microemulsion method. The average particle size of the $Fe_2O_3$ particles is about 24 Å. Because the particle size is so small that the Mössbauer spectra of the $\alpha$-$Fe_2O_3$ samples only consist of a quadrupole-split central line. It was proved that the Isomer Shifts (DIS) and the Quadrupole Splitting (DQS) changed as the refluxing time prolongs and the refluxing temperature increases during the preparation of the $Fe_2O_3$ nanoparticles, which implied an enhancement of the surface electrofield gradient formed by the surface coated polar molecules during the refluxing process.

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Recently, the study of nanoparticles have received increasing attention [1–2]. Reducing of particle size to nanometer range is accompanied by altered electrical, magnetic, electrooptical and chemical properties. Usually, these special properties are caused by the changes of band structure with decrease of the particle size, which is usually called quantum-size effect [3]. On the other hand, the surface effect also play a very important role in controlling the special properties on the nanoparticles. It's known that a considerable number of atoms in particles exist on the particle surface which form the surface defects, so the influence of the particle surface on the properties of the particles can not be neglected in nanometer range. For the transition metal oxides, such as $\alpha$-$Fe_2O_3$ (hematite), it's exciton Bohr radius is very small, the changes of band structure caused by the decrease of the particle size is not evident compared to that of other semiconductor nanoparticles. The surface effect became predominant in determining the properties of the nano-sized $Fe_2O_3$ particles. We have firstly observed a nonlinear optical enhancement of $\alpha$-$Fe_2O_3$ nanoparticles coated with layer of organic molecules [4, 5]. In order to understand the surface influence on the optical properties of $\alpha$-$Fe_2O_3$ nanoparticles, $^{57}$Fe Mössbauer spectroscopy study of $\alpha$-$Fe_2O_3$ nanoparticles coated with organic molecules become necessary.

Hematite, $\alpha$-$Fe_2O_3$, is an antiferremagnetic compound, some Mössbauer spectra of $^{57}$Fe in $\alpha$-$Fe_2O_3$ have been studied. It has been proved by W. Kundig that when the particle size is less than 135 Å, the room-temperature spectrum only consists of a quadruple-split center line corresponding to superparamagnetic $\alpha$-$Fe_2O_3$ [6]. J.S. Jiang has also demonstrated the surface effect on the hyperfine field of $\alpha$-$Fe_2O_3$ [7]. Recently, F. Bodker shown that the magnetic anisotropy energy constant increase while the size of the particle decrease, presumably because of the influence of surface effects [8]. In the present paper, the Mössbauer spectroscopy study of the coated $\alpha$-$Fe_2O_3$ particles with polar molecular are reported, the effects of the surface modification on the Mössbauer spectra and the related properties of coated nanoparticles are discussed.

## 1 Experimental

$\alpha$-$Fe_2O_3$ nanoparticles organosol was prepared using microemulsion method in the system of water/toluene. 475 ml of water, 25 ml of 0.2 M aqueous $FeCl_3$ and 120 ml of toluene were poured into a beaker. This solution was stirred and sodium dodecyle benzene sulphonate (**DBS**) was added as a surfactant. By controlling a proper pH value (pH 4), a red $\alpha$-$Fe_2O_3$ nanoparticles organosol were obtained after further stirring. Then the organosol was divided into three parts and refluxed in different temperature for different time respectively. As a result of the refluxing process, a $\alpha$-$Fe_2O_3$ organosol was obtained, the treating conditions at different temperatures together with particle size are listed in Table 1. The average size of the $\alpha$-$Fe_2O_3$ particles measured by TEM method. The TEM photograph of sample **c** in Table 1 is presented as Fig. 1.

Figure 2 is the Histogram of particle size shown in Fig. 1. It presents a narrow particle size distribution.

$^{57}$Fe Mössbauer spectra were measured with an OXFORD MV-500 constant acceleration spectrometer at room temperature. The best Lorentzian fit to the experimental data was made by method of least squares. The electron diffraction image were obtained with a HITACHI H 8100.

**Table 1.** The heating treatment conditions for $Fe_2O_3$ nanoparticle organosol

| Number of sample | Treating temperature [°C] | Treating time [h] | Average particle size [Å] |
|---|---|---|---|
| a | 110 | 1 | 24.5 |
| b | 110 | 3 | 24 |
| c | 140 | 3 | 23.5 |

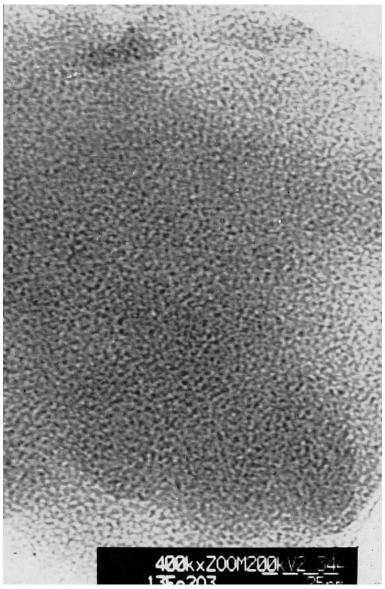

**Fig. 1.** TEM photograph (400 K) of α-$Fe_2O_3$ nanoparticles prepared by microemulsion method

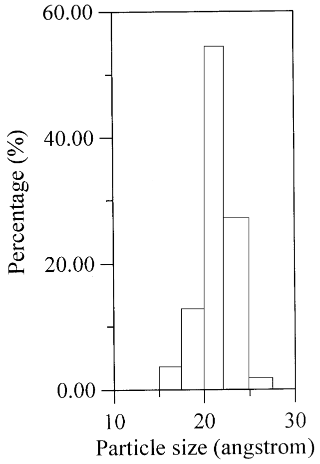

**Fig. 2.** Histogram of particle size shown in Fig. 1

## 2 Results and discussion

The room temperature Mössbauer spectra of three type of samples listed in Table 1 were shown in Fig. 3. Because the α-$Fe_2O_3$ particle size was so small that the spectra of all samples only consist of the quadrupole split central line and the behavior was completely superparamagnetic. The Mössbauer spectra parameters of three samples from computer fitting were given in Table 2. Because the particles were coated with strong polar organic molecules (DBS), the chemical environment of the Fe nuclear on the surface of the particle significantly differs from that inside the particles, so each experimental spectrum was fitted by

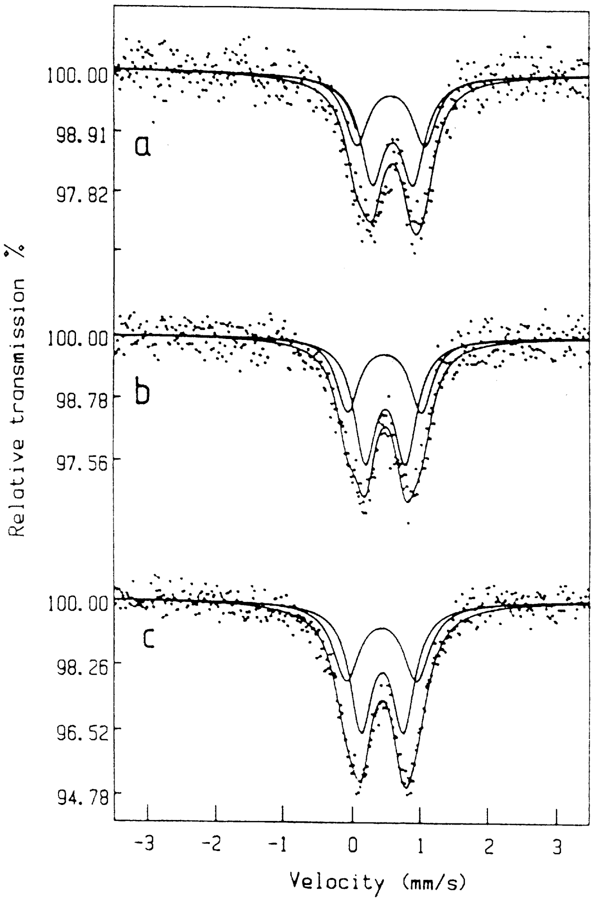

**Fig. 3a–c.** Mössbauer spectra of coated α-$Fe_2O_3$ nanoparticles powder samples. The spectrum **a**, **b**, **c** are correspondent to the samples **a**, **b** and **c** respectively

**Table 2.** The data obtained from the Mössbauer spectra

| Number of sample | DIS*i* [mm $s^{-1}$] | DQS*i* [mm $s^{-1}$] | DIS*s* [mm $s^{-1}$] | DQS*s* [m $s^{-1}$] |
|---|---|---|---|---|
| a | 0.5996 | 0.5865 | 0.5709 | 1.0273 |
| b | 0.4916 | 0.5937 | 0.4737 | 1.0634 |
| c | 0.4461 | 0.6459 | 0.4304 | 1.0903 |

IS: Isomer shift; DQS; Quadrupole shift
*i*, *s* stands for inside and surface respectively

two spectra. One corresponds to the surface Fe nuclear and the other corresponds to the Fe nuclear in the core of the particle. From Table 2, it can be seen that the isomer shifts **DIS*s*** and **DIS*i***, which is corresponding to Fe nuclear on surface and Fe particle core respectively, decrease as the treating temperature rises and the treating times prolongs. This results imply that the electron density (electronegativity) around Fe increases during the treating process. On the other hand, the quadrupole splitting (DQS) of Fe nuclear increases during the heating process, which demonstrated that the asymmetry of the electrofield around the Fe nuclear increased. All these changes can be attributed to the surface chemical structural changes and crystalline structural changes caused by the heating process.

For the naked ferric oxide particle, the $Fe^{3+}$ ions on or near the surface were coordinated by $-OH$ or $(OH)_2$ groups. But once the $Fe_2O_3$ particle is coated with one layer of DBS molecules by microemulsion method, $-OH$ and $(OH)_2$ groups will be substituted by DBS molecules. The heating treatment accelerated this reaction process. The combination between the DBS with the $Fe^{3+}$ after the heating treatment has been proved by Y. Zhang et al using IR method [9]. As a result, the $-OH$ or $(OH)_2$ groups coordinating on the $Fe^{3+}$ near the surface were replaced by DBS molecules and removed in the form of water. The changes of the surface coordinating groups resulted in a decrease of the DIS. On the other hand, the electronegativity of sulphonate is greatly larger than that of the $-OH$ or $(OH)_2$ groups, so the refluxing process also result in an enhancement of the surface electrofield gradient formed by the surface coated DBS molecules. The enhancement of the surface electrofield cause the increase of DQS as shown in Table 2.

It's well known that the heating process can induce the formation of a crystalline structure. The improvement of the crystalline degree will make the surface effect on the whole particle outstanding. Figure 4 presents the electron diffraction images of the samples treated at different conditions. The diffraction data of sample **c** (140 °C, 3 h) are listed in Table 3 with the corresponding data for standard $\alpha$-$Fe_2O_3$ given in parentheses. The results proved that sample **c** is of $\alpha$-$Fe_2O_3$ structure. Comparing the diffraction image of sample **c** with that of sample **a** and **b**, it can be seen that all the diffraction spots in image **c** are located on different diffraction rings of pure $\alpha$-$Fe_2O_3$ phase. This result proved that the heating process induced the formation of $\alpha$-$Fe_2O_3$ from ferric oxide. As seen from image **c**, the diffraction spots are sharper than that shown in the images of sample **a** and **b**. This result indicated that the crystalline degree was improved during the heating process. All these changes of surface chemical structure and crystalline structure make the surface effect of electrofield formed by the layer of DBS molecules more outstanding. Hence the increase of the DQS can be observed from Table 2. Other optical experiment results also provided strong proof for the enhancement of the surface electrofield formed by the DBS molecules during the heating treatment process [4, 5, 10].

Luminescence experiment results have proved that a increase of the intensity of the luminescence band located between 500~700 nm appeared during the heating treatment of the $Fe_2O_3$ nanoparticle organosol, the luminescence spectra are shown as Fig. 5. It's known that $\alpha$-$Fe_2O_3$ is a transition metal oxide semiconductor in which the *d* electron transition is localized and the direct transition of bandgap is dipole forbidden, so no luminescence could be detected. The luminescence phenomena of the surface coated $\alpha$-$Fe_2O_3$ indicated that some other state of spin permission are involved in the transition, that is to say $3d$-$4s$ $4p$ orbit in surface coated $\alpha$-$Fe_2O_3$ nanoparticles can be coupled with each other. Two possible reasons may be responsible for such changes of such electronic states. One is the quantum size effect, the other is the surface effect. However no luminescence phenomena had ever been observed for the same size ferric oxide nanoparticle organosol. Hence the luminescence can only be caused by the surface effects. The increase of the

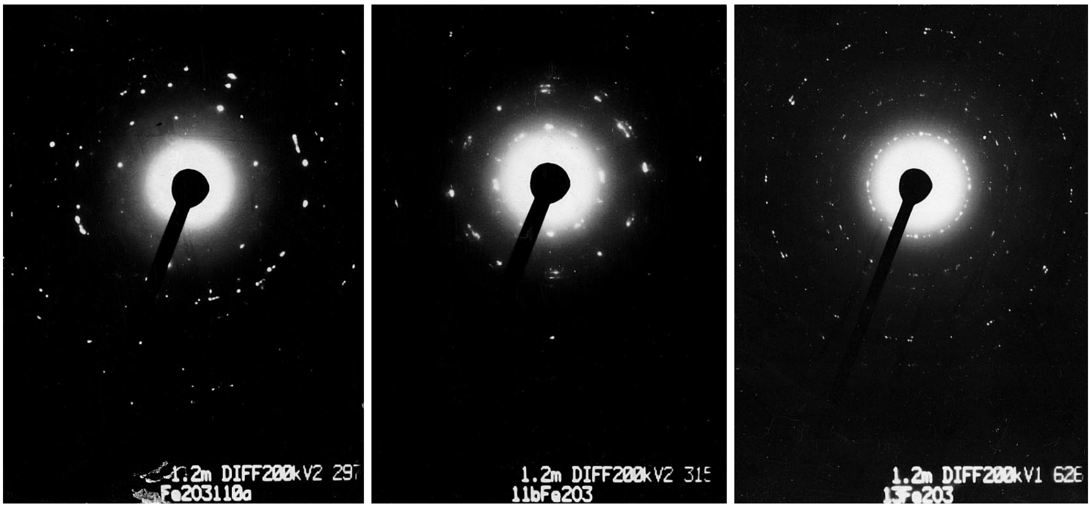

**Fig. 4.** Electron images of coated ferric oxide nanoparticles. The image in *left*, *middle* and *right* are correspondent to sample **a, b** and **c** listed in Table 1 respectively

**Table 3.** Diffraction data for $Fe_2O_3$ nanoparticles with corresponding data for standard $Fe_2O_3$ given in parentheses

| nd | d/Å (experiment results) | d/Å (standard values) |
|---|---|---|
| 1 | 4.46 | |
| 2 | 2.585 | 2.519 |
| 3 | 2.229 | 2.207 |
| 4 | 1.697 | 1.694 |
| 5 | 1.487 | 1.486 |
| 6 | 1.295 | 1.306 |
| 7 | 1.249 | 1.259 |
| 8 | 1.1053 | 1.1075 |

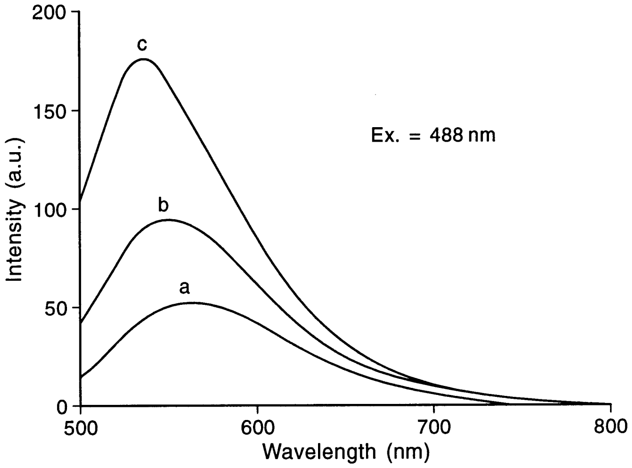

**Fig. 5.** Photoluminescence spectra of the $Fe_2O_3$ nanoparticle organosols. The spectrum *a*, *b*, and *c* correspondent to sample **a, b** and **c** listed in Table 1 respectively

luminescence intensity during the heating treatment process indicated that the surface electrofield increase correspondingly. This results coincide well with Mössbauer spectra analysis. More detail luminescence experiment results have been published elsewhere [10].

In conclusion, the Mössbauer spectra results prove that heating treatment of the surface coated ferric oxide nanoparticle resulted in an increase of the surface electrofield formed by the surface coating DBS. This may provide a prospective way to control the optical properties of $\alpha$-$Fe_2O_3$ nanoparticle materials.

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