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Abstract

α-Fe_2O_3 nanoparticles coated by sodium dodecyl/benzene sulphonic were prepared using a micro-emulsion method in the system of water/toluene. An obvious photoluminescence was observed. The luminescence intensities increase as the treatment temperature was increased and the treatment time was extended. Mechanisms for these effects are discussed.

1. Introduction

Recently, the study of nanoparticles have received increasing attention [1, 2]. Reduction of the particle size to the nanometer range is accompanied by altered electrical, magnetic, electro-optical and chemical properties. Usually, these special properties are caused by the changes of the band structure with decrease of the particle size, which is usually called the quantum-confinement effect [3]. However, as a larger fraction of the atoms in the particles comprises surface atoms, the surface layer has a significant influence on the properties of these nanoparticles. For example, as the transition metal oxides such as α-Fe_2O_3 (hematite) have a small exciton Bohr radius, the changes of their band structure caused by the decrease of the particle size is not evident compared to those for other semiconductor nanoparticles. But, the surface effect became predominant in determining the properties of the nanosize Fe_2O_3 particles. Some new phenomena, such as the increase of the absorption coefficient, the appearance of photoluminescence and the enhancement of the third-order susceptibility at different treatment temperatures, are observed for this system. We have observed for the first time a nonlinear optical enhancement for α-Fe_2O_3 nanoparticles coated with a layer of organic molecules and the effects of this surface modification on the Mössbauer spectra of ^{57}Fe in Fe_2O_3 nanoparticles [4].

For hematite (α-Fe_2O_3), because the d-electron transition is localized, no luminescence could be detected. But, if the particles were coated with polar organic molecules, the condition is quite different for nanosize particles due to the effect of the coordinating molecules on the particle surface. An obvious photoluminescence was observed and the luminescence intensities were observed to increase as the treatment temperature was increased and the treating time extended. This paper is directed to the photoluminescence properties of the coated α-Fe_2O_3 nanoparticles and relevant mechanisms for producing these properties are discussed.

2. Preparation of hematite samples

α-Fe_2O_3 nanoparticles were prepared in a reversed micelle of micro-emulsion: 0.01 $mol\,dm^{-1}$

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$FeCl_2$ solution, sodium dodecyl benzene sulphonate (DBS) and organic solvent benzene were mixed to form an emulsion, then ferric hydroxide precipitated by dilution with sodium hydroxide to yield particles coated with DBS in the organic phase. Finally, the red ferric oxide toluene organosol was refluxed for different temperatures and different times. From this, α-Fe_2O_3 organosol was obtained for several treatment temperatures. The average size of the α-Fe_2O_3 particles, as measured by the TEM method, is about 21 Å.

3. Experimental results and discussion

The absorption spectra of α-Fe_2O_3 particles were recorded with a Shimadzu UV 365 spectrophotometer, and the absorption of the coated α-Fe_2O_3 particle organosol increased as the treatment temperature was increased. Fig. 1 shows the photoluminescence spectra of α-Fe_2O_3 particles for excitation at 488 nm, as three spectral curves a, b and c for the three different treatment temperatures listed in Table 1. Photoluminescence was observed only for coated α-Fe_2O_3 particles at the higher treatment temperatures and was not observed for bare α-Fe_2O_3 particles. As the treatment temperature was increased, the maximum photoluminescence intensity increased correspondingly.

For the absorption spectrum of the bulk hematite, the absorption above 400 nm is usually attributed to d–d transitions. Absorption lower than 400 nm was attributed to a charge transfer electronic process by Marusak et al. early in 1980 [5]. However, the criteria are quite different for nanosize particles, where the large surface-to-volume ratio produces a lot of lattice defects on the particle surface and the bonding molecules on the surface may result in changes of the electronic structure of the whole particle. Due to the lower symmetry and coordination number on the surface, the Fe^{3+} charge near to the surface of the bare particle in hydrosol may coordinate with the OH or $(OH)_2$ radicals during the synthesis process. But once the Fe_2O_3 particle is coated with a layer of DBS molecules, the OH or $(OH)_2$ radicals are replaced by DBS ions and the chemical reactions between –OH –$(OH)_2$ radicals and DBS ions increase with the treatment temperature. Typically, some OH or $(OH)_2$ radicals coordinating on the Fe^{3+} near the surface were removed in the form of water during the heat treatment process, which led to the changes of such groups as (–OH–Fe–SO_3–PH) and (–$(OH)_2$–Fe–SO_3–PH) to (–0–Fe–SO_3–PH).

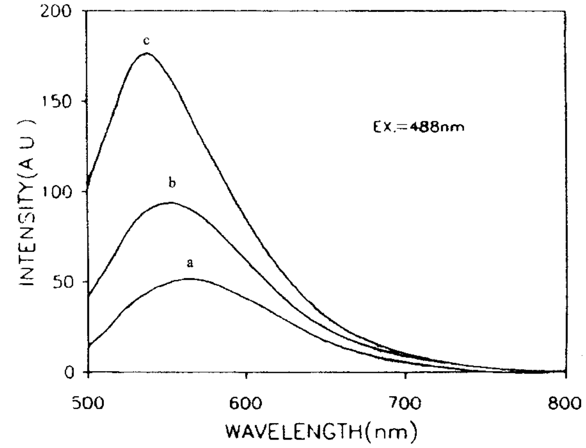

Fig. 1. Photoluminescence spectra of the α-Fe_2O_3 nanoparticles excited by the 488 nm line of an Ar^+ laser. The spectra a, b and c correspond to treatment temperatures of 110°C for 1 h, 110°C for 3 h and 140°C for 3 h, respectively.

Table 1
The data obtained from Mössbauer spectroscopy at different heating treatment conditions. Both the isomer shifts (DIS) and the quadrupole shifts (DQS) are in units of mm s^{-1}. The additional labels i and s stand for inside and surface, respectively

Sample label	DISi (mm s^{-1})	DQSi (mm s^{-1})	DISs (mm s^{-1})	DQSs (mm s^{-1})	Treatment temperature (°C)	Treatment time (h)
a	0.59955	0.559646	0.557062	1.02566	110	1
b	0.49146	0.559215	0.47499	1.08068	110	3
c	0.44727	0.62524	0.43219	1.03376	140	3

Because O^{2-} has the ability of attracting electrons more strongly than either $(OH)^-$ or $(OH)_2^{2-}$ radicals, while the –SO–PH radical has a strong ability of repelling electrons, the electronegativity of the oxygen is increased while the ligand ($-SO_3-PH$) present on the surface increased proportionally during the treatment. Thus, the refluxing process resulted in an enhancement of the surface electro-field gradient. It is the electro-field gradient that increases the 3d–4sp coupling, and the probability of 4s or 4p population and electron delocalization was enhanced correspondingly. It is suggested that, apart from the localized d–d transition near the band edge, other states such as 4s or 4p may be involved in the band-edge transitions as a result of the heat treatment and cause an increase in the absorption coefficient. This is the reason why the absorption coefficient and photoluminescence intensity increases as the treatment temperature increases and treating times are lengthened.

In order to understand the surface modification's influence on the properties of α-Fe_2O_3 nanoparticles better, ^{57}Fe Mössbauer spectra of α-Fe_2O_3 nanoparticles coated with organic molecules were measured. The room temperature Mössbauer spectra of the three samples listed in Table 1 are shown in Fig. 2. Because the size of the α-Fe_2O_3 particles was so small, the spectra of all samples consist of only the quadrupole-split central line and the behavior is completely superparamagnetic. The Mössbauer spectra parameters of the three samples, derived from computer fittings, are given in Table 1. Because the particles were coated with a strong polar organic molecule (DBS), the chemical environment of the Fe nuclei on the surface of the particle differs significantly from that inside the particles. So each experimental spectrum was fitted by two spectra: One corresponds to the surface Fe nuclei and the other corresponds to the Fe nuclei in the core of the particle. From Table 1, it can be seen that the isomer shifts DISs and DISi, which correspond to Fe on the surface and Fe in the particle's core decrease as the treatment temperature is raised and the treatment time is lengthened. These results imply that the electron density (electronegativity) around the Fe increases during the treatment process due to the strong polar molecules coated on the particle's surface. On the other hand, the quadrupole splitting DQS of the Fe nuclei, as well as the electric field gradient, increases during the heat treatment process, as shown in Table 1.

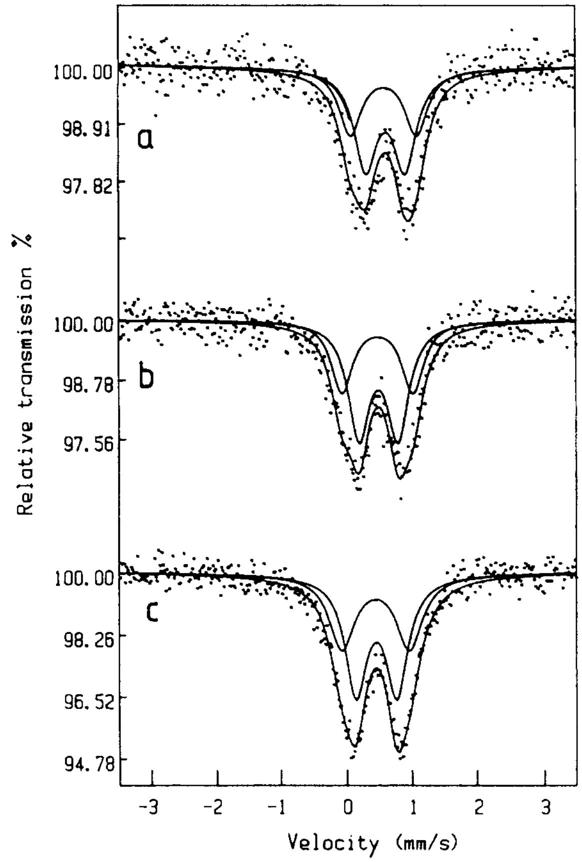

Fig. 2. Mössbauer spectra of coated α-Fe_2O_3 nanoparticle powder. The spectra a, b and c correspond to the three samples detailed in Fig. 1.

Fig. 3 shows photoluminescence spectra of coated α-Fe_2O_3 nanoparticle organosol (sample 3) for different excitation wavelengths. The red shift of the emission peak can be observed with the increase of the excitation wavelength, but gradually becomes no longer apparent around 520 nm. This proves that the emission around 520 nm is band-edge emission. Considering the large Stokes shift of the emission peak compared with the excitation line, we attribute the emission to bound-exciton emission, as observed for other typical semiconductor nanoparticles. As we know that d–d transitions

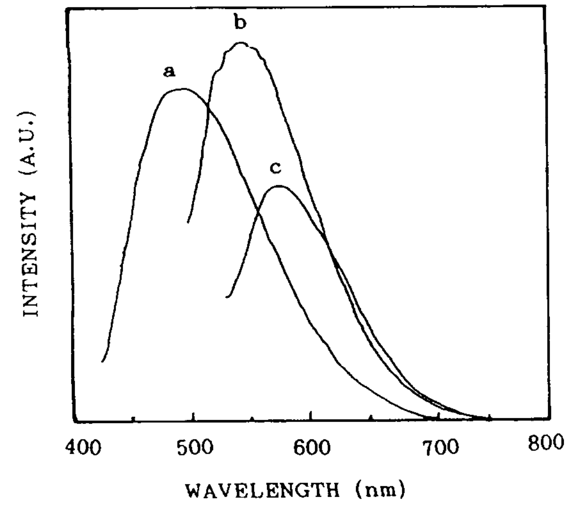

Fig. 3. The photoluminescence spectra of coated α-Fe_2O_3 nanoparticles at different excitation wavelengths: (a) 400 nm excitation; (b) 480 nm excitation; (c) 520 nm excitation.

are spin-forbidden, this special photon luminescence phenomena provides further proof for the involvement of another state, which is necessarily involved in a spin-allowed transition. From the existence of other bound-exciton emission, it can be proposed that the metal-like 4s state may possibly be involved in the transition.

4. Conclusion

The heat treatment of 2 nm coated α-Fe_2O_3 nanoparticle organosol led to structural changes of the α-Fe_2O_3 particles and an increase of the surface electro-field gradient, which results in the 3d–4s coupling, as well as the involvement of metal-like 4s states in the transition. Because of the delocalization of 4s electrons, the α-Fe_2O_3 nanoparticles behave like typical semiconductor nanoparticles. They show obvious quantum size effects and photoluminescence as well as properties of bound-exciton emission. On the other hand, the heat treatment can also result in the increase of the degree of crystallization, and the increase of this could reduce the probability of the nonradiative recombination for the charge carriers, which also contribute to the photoluminescence of treated nanoparticles.

Acknowledgements

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