Local atomic structures of hematite nanoparticles studied with XAFS

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Hematite nanoparticles which were coated, respectively, with sodium dodecyle benzene sulphonate (DBS) and cetyltrimethyl ammonium bromide (CTAB) were synthesized by using microemulsion method in the system of water/toluene. The particle size and shape were characterized with transmission electron microscopy (TEM). The TEM results show that the nanoparticles take the shape of sphere with diameter of 5.0 nm and 6.0 nm for modified DBS and CTAB respectively. The local atomic structures of these nanoparticles were probed by using XAFS technique. Fe-K absorption spectra were collected at beam line 4W1B of BSRF. The local atomic structure in DBS-coated hematite was found to be similar with that in bulk hematite except the anharmonicity increasing, but about 0.04 Å expansion of Fe-O bond length in CTAB-coated hematite. The interface/surface atomic configuration were compared and discussed.

Key Words: nanoparticle, XAFS, hematite, local atomic structures, surface/interface.

1. Introduction

Recently, there is great scientific interest in synthesis of α-Fe_2O_3 nanoparticles and the modifications of their size, morphology and property for their different application in the anticorrosion protective paints, magnetic oxide ceramics, gas sensor as well as in fundamental research in colloid and surface chemistry (Music, et al., 1997; Vollath, et al., 1997), microstructure (Borker, et al., 1994; Fei, et al., 1996; Peng, et al., 1994) and nonlinear optical properties (Ai, et al., 1994). All the peculiar properties of nanometer-sized material are duo to their high surface to volume ratio and quantity-size effect (Kubo, 1962; Ying, 1992). In this paper, two type of Fe_2O_3 nanoparticles coated, respectively, with Dodecyl benzene sulfonic (DBS) and cetytrimethyl ammonium bromide (CTAB) were synthesized. Using XAFS technique, we attempt to probe the local atomic structures on the surface of the nanoparticles and compare the influences of different activations on the surface structures. We expect that this is helpful for explaining the peculiar properties of these nanoparticle.

2. Experimental

Fe_2O_3 nanoparticles coated with DBS and CTAB were, respectively, synthesized using microemulation methods in the system of water/toluene. The samples were characterized using transmission electron microscopy (TEM). The averaged sizes of the DBS- and CTAB-coated Fe_2O_3 particles are 5.0 nm and 6.0 nm measured by TEM method.

The nanoparticles were homogeneously smeared on Scotch adhesive tape. More than 8 layers were folded to reach the optimum absorption thickness ($\Delta\mu d \approx 1.0$, d is the physical thickness of the sample). X-ray absorption spectra of Fe-K edge of bulk- and nano- Fe_2O_3 coated, respectively, with CTAB and DBS, were collected at ambient temperature with transmission mode on XAFS station (Beam line 4W1B) of Beijing Synchrotron Radiation Facility. The storage ring was run at 2.2 GeV with the electron current about 50 mA. High harmonics were eliminated by detuning the double crystal Si (111) monochromator. X-ray energy was calibrated by using the inflect point on the Cu-K absorption edge (8980.3 eV). Energy resolution at the Fe-K absorption edge is about 2 eV.

3. XAFS data analysis

The XAFS data were analyzed by using the common data-analysis method (Sayers & Bunker, 1988). XAFS functions were Fourier-transformed to R space with k^3 weight in the range of 2.7 to 14.4 Å. Fourier filters were performed in the range of 0.9 to 3.0 Å. Hanning windows were used in the Fourier transform and filter process. The Fourier-transform spectra and the near-neighbor coordination XAFS functions were, respectively, shown in Fig. 1 and 2.

The following XAFS formula (Bunker, 1983; Tranquada & Ingalls, 1983) was used to fit the experimental spectra:

$$\chi_j(k) = \frac{s_0^2 N_j}{kR_j^2} F_j(\pi, k) e^{-2k^2 \Delta\sigma_j^2} e^{-2R_j / \lambda_j} \sin(2kR_j + \phi_j + \Sigma_j)$$

And,

$$\Sigma_j = -4\frac{\Delta\sigma_j^2}{R_j}k - \frac{4}{3}\sigma_j^3 k^3$$

Here, σ_j^3 is the third cumulant. $\Delta\sigma_j^2 = \sigma_{uj}^2 - \sigma_{sj}^2$, subscripts u and s, respectively, stand for the unknown and reference samples. The fitting curves for the experimental XAFS function were also shown in Fig.2. Table 1 tabulated the fitting parameters.

4. Results and Discussion

In the data analysis, crystalline $LaFeO_3$ was chosen as the reference sample. The backscattering amplitude and phase shift of Fe-O bond were extracted with the following crystallographic data (Marezio & Dernier, 1971): N=6, R=2.006Å. The XAFS spectrum of bulk Fe_2O_3 was fitted by using two shells. For the

Table 1

Structural parameters of Fe-O coordination in bulk- and nanometer Fe_2O_3 coated, respectively with CTAB and DBS.

Fe_2O_3	α	β	N	R(Å)	$\Delta\sigma^2$ (Å^2)	σ^3(Å^3)	E_0(eV)
Bulk [1]	1.0	0.0	3.0±0.4	1.96±0.01	0.002 ±0.004	0.0000±0.0005	-0.8±1.0
			3.0±0.4	2.06±0.01	0.009 ±0.004	0.0003±0.0005	-0.8±1.0
CTAB [2]	0.44	0.56	5.2±0.4	2.04±0.01	0.003 ±0.004	0.0021±0.0005	6.9±1.0
DBS [2]	0.52	0.48	6.0±0.4	2.01±0.01	0.005 ±0.004	0.0012±0.0005	5.9±1.0

1. Here bulk stand for the bulk Fe_2O_3.
2. CTAB and DBS are, respectively, denoted the CTAB- and DBS-coated Fe_2O_3 nanoparticles. Here these parameters of the surface part are listed in this table. The parameters of the core part are the same as listed for the bulk Fe_2O_3.

nanoparticles of Fe_2O_3, they have still the space group of $R\bar{3}c$ as demonstrated by TEM results. Besides the CTAB or DBS activations, we suppose that these nanoparticles consist of two parts, i.e. the core part (α) and the surface part (β). The core parts still keep the same atomic structures as in bulk Fe_2O_3, while the surface parts are different and depend on the surfactant (CTAB or DBS). The mixed-phase and mixed-coordination XAFS formula (Lu & Wan, 1987) was used to fit the XAFS spectra of the CTAB- and DBS-coated Fe_2O_3 nanoparticles. The structural parameters obtained from bulk Fe_2O_3 were chosen to describe the core parts, these parameters, except the coordination number N_1 (=N_2), were fixed in the fitting. A single shell was used to describe the surface one that is for the following two reasons. One is that introducing another coordination shell will cause the parameter correlation. Another is that a single coordination shell is enough to describe the surface part as demonstrated by the fiiting results. Only six parameters were used in the fitting, i.e. the coordination number N_1 (=N_2) of the core part, the coordination number N_3, bond length R_3, Debye-Waller factor σ^2, energy shift E_0 and the third cumulant σ^3 of the surface shell. For the core part, the actual coordination numbers of the two shells are all 3 while the nominal coordination numbers of the two shells are 3α (=N_1) and 3α (=N_2) respectively. From the coordination number N_1 or N_2 obtained from XAFS analysis, the

content of the core part (α) can be obtained to be $N_1/3$, and the content (β) of surface part is 1-α. The actual coordination number at surface shell is expressed as N_s =N_3/β, here N_3 is the nominal coordination number of the surface part. All the parameters of bulk Fe_2O_3, CTAB and DBS-coated Fe_2O_3 nanoparticles are listed in Table 1.

From Table 1, we can found that the averaged bond lengths of Fe-O in the core part or in the bulk Fe_2O_3 are 1.999Å. The averaged bond-lengths of Fe-O in CATB-coated and DBS-coated nano-Fe_2O_3 are, respectively 2.023 and 2.003 Å. The Fe-O bond length (2.008Å) in the surface part of DBS-coated Fe_2O_3 nanoparticle is only slight larger than that in the core part. While in the CTAB-coated Fe_2O_3 nanoparticle, the Fe-O bond length (2.044Å) of the surface part is obviously larger than that of the core part. Although the Debye-Waller factor in these nanoparticles have no obviously increase corresponding to the bulk Fe_2O_3, the third cumulants have obviously increase in the
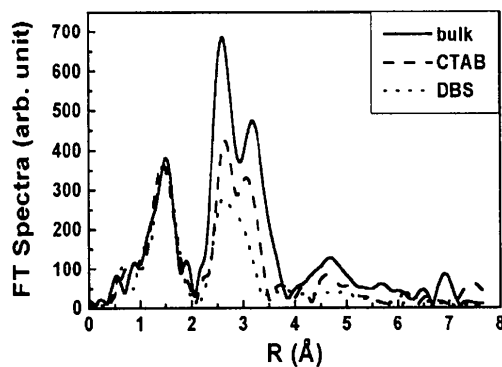
Figure 1
Fourier Transform spectra (k^3-weight) of Fe-K absorption in bulk Fe_2O_3 (solid line), CTAB-coated (dash line) and DBS-coated (dot line) Fe_2O_3 nanoparticles.
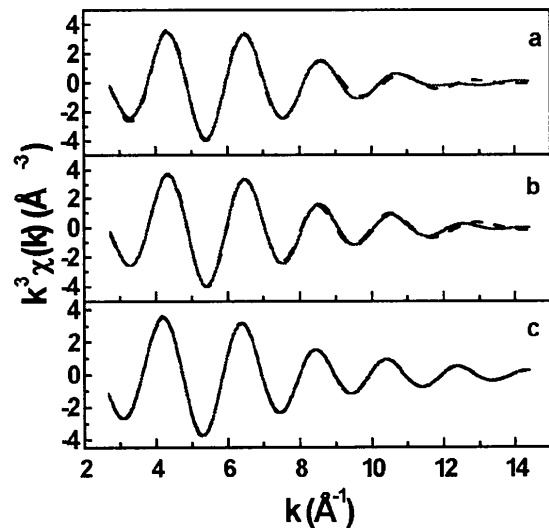
Figure 2
Experimental and Fitting XAFS spectra of Fe-O coordination in CTAB-coated Fe_2O_3 nanoparticles (a), DBS-coated Fe_2O_3 nanoparticles (b) and bulk Fe_2O_3 (c) (k^3-weight).

surface parts. It can also be found that CTAB-coated Fe_2O_3 nanoparticles have more anharmonic than DBS-coated ones. This can be summed as: Firstly, CATB group has larger spatial configuration than DBS group has, and leave more "gear clearance" in the interface between Fe_2O_3 nanoparticles and CATB; Secondly, CTAB is cation ligand and tends to attract the O anion, while DBS is anion ligand and tends to attract the Fe cation. At the surface part of the nanoparticles, the averaged coordination number around Fe in DBS-coated Fe_2O_3 tends to keep the value as in bulk Fe_2O_3, while tends to decrease in the CTAB-coated Fe_2O_3. Surfactant (CTAB or DBS) prevents the nanoparticles from growing, but because of the mismatch of the atomic structures between the surfactant and Fe_2O_3, there are much vacancies left in the interface between the surfactant and the Fe_2O_3 nanoparticles. All these demonstrate that the atomic vibrations are seriously limited by the surfactant, and the small particle-size results in the outstanding anharmonicity, however the surface/interface atomic structure of the nanoparticles are of order.

For the crystalline Fe_2O_3 nanoparticles, the core part is relatively stable and keeps the structures as in the bulk materials, while the surface parts present more anharmonicity. In this study, there are about 50% atoms locating in the core parts and 50% atoms locating in the surface parts for the CTAB-coated (~6 nm) and DBS-coated (~5 nm) Fe_2O_3 nanoparticles. Assuming the nanoparticles take the shape of sphere, the thickness of the surface part is about 0.7 nm in the CTAB-coated Fe_2O_3 nanoparticle and about 0.5 nm in the DBS-coated Fe_2O_3 nanoparticle. In fact, the anharmonicitie of the atom-pair distribution in these nanoparticles are gradually increasing from the core to the surface. XAFS technique shows us an averaged result. From this study, we recognize that the surface/interface of the nanoparticles coated with surfactant are quite order, but the anharmonicity of the atom-pair distribution increase dramatically.

5. Conclusion

The local atomic structures of Fe_2O_3 nanoparticles coated, respectively, with surfactant CTAB and DBS were studied with XAFS technique. It has been found that the surface/interface are quite order but with large anharmonicity. The contents of the surface/interface was evaluated to be about 50%. The thickness of

the surface/interface are about 0.7 and 0.5 nm, respectively, for the 6 nm CTAB-coated Fe_2O_3 particles and the 5 nm DBS-coated Fe_2O_3 particles. The bond length of Fe-O pair in surface of DBS-coated Fe_2O_3 is almost the same with the bulk materials and equals to 2.008 Å. but the Fe-O bond length is about 2.044 Å in CTAB-coated Fe_2O_3 case. Different surfactants show obviously different influence on the local atomic structures of the surface of the nanoparticles.

References

Ai, X. C., Fei, H. S. & Yang, Y. Q. (1994). J. Luminiscence, 61&62, 364 - 367.

Bodker, F., Morup, S. & Linderoth, S. (1994). Phys. Rev. Lett., 72, 282 - 285.

Bunker, G. (1983). Nucl. Instrum. Methods, 207, 437- 444.

Fei, H. S., Gao, M. Y., Ai, X. C., Yang, Y. Q., Zhang, T. Q. & Shen, J. C. (1996). Appl. Phys. A62, 525 - 528.

Kubo, R. (1962). J. Phys. Soc. Jpn., 17(5), 986 -1004.

Lu, K. & Wan, J. (1987). Phys. Rev. B35, 4497- 4499.

Marezio, M. & Dernier, P. D. (1971). Mat. Res. Bull., 6, 23 - 30.

Music, S., Czako-Nagy, I., Salaj-Obelic, I. & Ljubesic, N. (1997). Materials Letters, 32, 301 - 305.

Peng, Y., Wang, T., Zou, S. Y., Bu, W. & Zheng, L. D. (1994). Acta Physica Sinica, 43, 1208 -1216.

Sayers, D. E. & Bunker, B. A. (1988). X-ray Absorption: Principle, Applications and Techniques of EXAFS, SEXAFS and XANES, edited by D.C.Koningsberger and R. Prins, Chap. 6., New York: Wiley.

Tranquada, J. M. & Ingalls, R. (1983). Phys. Rev. B28, 3520 -3528.

Vollath, D., Szabo, D. V., Taylor, R. D. & Willis, J. O. (1997). J. Mater. Res., 12, 2175-2182.

Ying, J. Y. (1992). Materials Lett., 15, 180 - 185.