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X-ray absorption reveals surface structure of titanium dioxide nanoparticles

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The structures of TiO₂ nanoparticles with a 19 Å diameter have been probed using Ti K-edge XANES, revealing severe distortions in Ti site environments compared to those octahedral Ti sites in bulk anatase. The distorted Ti sites are likely to adopt a penta-coordinate square pyramid geometry due to the truncation of the lattice. Upon binding ascorbic acid on the surfaces of the 19 Å particles, the octahedral Ti site observed in the bulk TiO₂ is largely restored. This discovery shows that the distortions in TiO₂ lattice are mainly located on the surface of the particles. The distorted Ti surface sites are responsible for the binding with other small molecules, which is often a prerequisite in surface chemistry.

KEYWORDS XANES, XAFS, nanoparticles, titanium dioxide, semiconductor.

1. Introduction

Titanium dioxide (TiO₂) nanoparticles have been playing an increasing role in photocatalysis and environmental remediation in recent years due to its unique chemical properties that differ from the bulk (Stafford et al., 1996; Klabunde et al., 1996). Photoillumination of TiO₂ nanoparticles with photon energies higher than the band gap (3.2 eV) creates electron-hole (e/h) pairs which consequently lead to photocatalytic reduction/oxidation processes in the surrounding media. Extensive efforts have been made to enhance the reaction efficiencies by (1) reducing the activation barriers for redox reactions and (2) broadening the absorption spectra of the nanoparticles to the visible region. Attaching small molecules on the nanoparticle surfaces has been shown to accomplish one or both effectively (Rajh et al., 1996; Thurnauer et al., 1997). However, the structural origins of the unique properties of TiO₂ nanoparticles with and without the surface adsorbers are not completely clear. In our previous work, we conducted XAFS studies at Ti K-edge on fundamental structural aspects of TiO₂ nanoparticles with different sizes ranging from 30 to 500 Å in diameter, and identified the photocatalytic reaction products when heavy metal ions were attached to the surface of the nanoparticles (Chen et al., 1997). We observed an increase in the intensity of a pre-edge peak as well as a downshift of the peak position as the nanoparticle size got smaller, e.g. < 50 Å. These results suggested distortions at Ti sites in smaller TiO₂ nanoparticles based on previous XANES results on the tetrahedral Ti sites of dispersed titanate in silicate substrate (Greegor et al., 1983). More recently, comprehensive studies of Ti site coordinations in various Ti-bearing glasses by Farges et al. (1996a, 1996a, 1997b) at the Ti K-edge discovered correlations between the coordination numbers of Ti sites with the pre-edge

peak intensities and peak positions. Their results indicated that as the coordination number of the Ti site increases from 4 to 6, the pre-edge intensity decreases and the energy of the peak increases by approximately 0.9 eV for each additional coordinating oxygen atom, starting from around 4969.6 eV for the tetrahedral Ti site. In this paper, we present our recent XAFS study at the Ti K-edge on TiO₂ nanoparticles of 19 Å diameter without and with ascorbic acid. Based on our experimental results, as well as the results by Farges et al. (1997), surface distortion of the Ti sites in small nanoparticles and its implication to the surface binding and photocatalytic activities will be discussed.

2. Experimental

TiO₂ nanoparticles were made according to a method presented elsewhere (Rajh et al., 1992). The sizes of the nanoparticles are quite uniform with about 10% variation determined by TEM. The samples for X-ray absorption experiments were solutions with approximately 0.01M Ti concentration. Nanoparticle samples with ascorbic acid were made by adding the excess of the surface adsorbers. The XAFS sample was sealed between two Mylar windows and with a rubber spacer.

XAFS measurements at the Ti K-edge at 4.966 KeV were made at X19A, National Synchrotron Light Source (NSLS), Brookhaven National Laboratory using a Si(311) crystal in the monochromator with an energy resolution of about 1eV and with a detune of 60% for the higher harmonic rejection. A Lytle detector was used with a helium gas flow through the sample chamber and Ar gas through the detector chamber. Twenty or more scans were collected for each solution sample (both 19 and 500 Å particles) and 5 scans for the solid samples. EXAFS analysis was conducted with procedures presented elsewhere and k^3 -weighting was used in Fourier Transform ranging from 2.5-10 Å⁻¹. A powder anatase sample was used as a reference where Ti sites are octahedral with an average first shell Ti-O distance of 1.95 Å (two Ti-O bonds are 1.96 Å and the other four are 1.94 Å).

3. Results and Discussion

Figure 1 shows the XANES region of the spectra for 19 Å nanoparticles with and without ascorbic acid, along with the

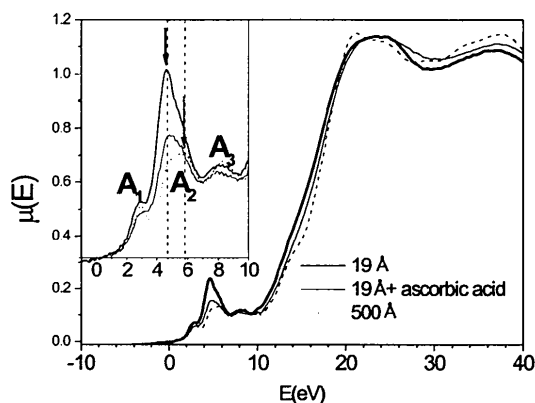


Figure 1
XANES spectra of TiO₂ nanoparticles. A₁, A₂, and A₃ are the pre-edge peaks. The middle peak intensity was used to calibrate the coordination numbers of Ti atoms.

spectrum for the 500 Å nanoparticles in water. The effect of adding ascorbic acid on the XANES spectrum for 500 Å nanoparticles is very little, thus the spectrum is omitted. The origins of three pre-edge peaks, A_1 , A_2 and A_3 have been discussed in the literature and summarized in the paper by Farges et al. (1997). According to the studies carried out by Farges et al. (1997), the correlation between the middle peak intensity and the energy position with the coordination numbers of Ti exists. In 500 Å TiO_2 particles, Ti sites are coordinated to the six nearest O atoms with an octahedral geometry except for 2.5% of these Ti sites that are on the surface. In addition, the XAFS spectrum is very similar to that of anatase. Thus, we used this spectrum as a reference of the bulk. However, the middle peak of the three pre-edge peaks in 19 Å nanoparticles in aqueous solution has an enhanced amplitude compared to that in 500 Å TiO_2 nanoparticles. The energy difference of the peak positions is about 0.9 eV, just like that between six- and five-coordinate Ti in glasses (Farges et al., 1996, 1997). This implies the presence of five coordinate Ti sites for 19 Å particles in solution.

Also shown in Figure 1, the middle peak of the pre-edge features is reduced in intensity and is largely recovered to what has been observed in the bulk anatase when ascorbic acid is adsorbed on the surfaces of 19 Å nanoparticles. This is very strong evidence showing that the distortions are mainly located on the surfaces in small TiO_2 nanoparticles. Changes in the surface structures can also be demonstrated in Figure 2 by Fourier transform EXAFS and data analysis. Figure 2(a) indicates that the nearest Ti-O bonds in 19 Å particles are shortened compared to 500 Å particles, and the amplitude of the first shell peak increases when ascorbic acid is added. Table 1 presents two important structural changes in 19 Å nanoparticles compared to those in 500 Å nanoparticles: (1) the first-shell Ti-O bond distances become shorter, and (2) the first-shell coordination number is smaller. The one-shell fits using 500 Å particles in water ($r_{Ti-O} = 1.96$ Å and $n = 6$) gave the first shell Ti-O distance and coordination number of 1.94 Å and 4.6 in 19 Å particles, and 1.94 Å and 5.8 in 19 Å particles with ascorbic acid. In addition, two Ti-O distances are needed in order to get satisfactory fits for the first-shell in 19 Å particles that would give two distances of 1.77 and 1.95±0.03 Å in 19 Å particles and 1.83 and 1.99±0.03 Å with the ascorbic acid. The corresponding coordination numbers are 3.5 and 0.4±1 without ascorbic acid, and 4.0 and 1.0±1 with ascorbic acid showing an increase of the coordination number for the shorter Ti-O bonds.

The structural parameters for the 19 Å TiO_2 nanoparticles and the XANES results reveal the existence of surface Ti sites with five coordinating O atoms similar to those in Ti-containing glasses where one of the Ti-O bonds has a double bond character. The four-coordinate Ti site is less likely present based on the amplitude and the position changes of the pre-edge peak. The most plausible cause of the distortions is from the truncation of neighboring Ti and O atoms due to the curvature of small spherical particles. The unit cell dimension of anatase is $3.785 \times 3.785 \times 9.514$ Å³, thus only 5 or 2 unit cell lengths are contained in 19 Å particles, where about 66% of the TiO_2 units are on the surface. According to Farges et al. (1997), the average relative pre-edge peak height for a penta-coordinated Ti is three times that of a hexa-coordinated counterpart. In the case of 19 Å particles, the middle pre-edge peak height is about 1.8 times that of 500 Å particles. This can be translated to about 70% of penta-coordinated Ti sites, which is close to 66% from the calculation. This implies that 13% of the total Ti-O bonds should be the

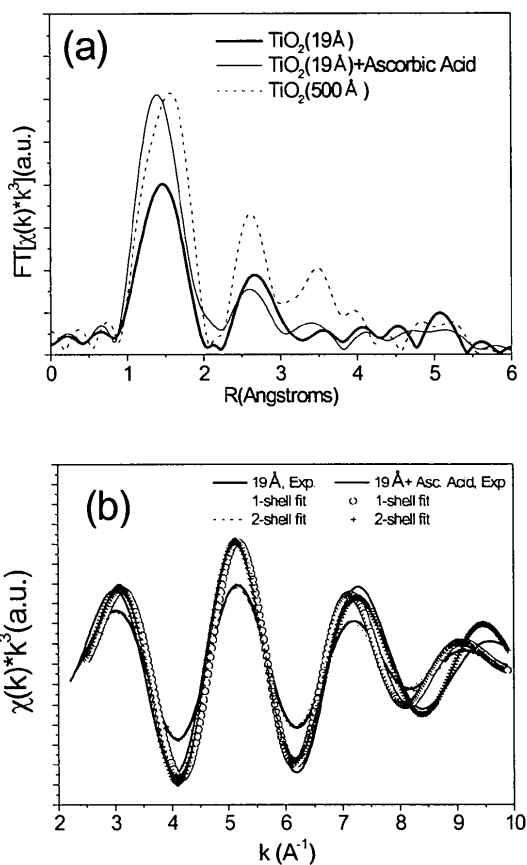


Figure 2
EXAFS spectra of TiO_2 nanoparticles. (a) Fourier transform EXAFS and (b) first shell fits.

Table 1
Structures of TiO_2 Colloids in Water (290K)

Diameter (Å)	N	R(Å)	$\Delta\sigma^2(\text{Å}^2)$
500*	6.0±1	1.96±0.02	0.0004
19 (1-shell)	4.6±1	1.94±0.03	0.014
19 (2-shell)	3.5±1	1.96±0.03	-0.0008
	0.4±0.2	1.79±0.03	-0.013
19 w/asc. acid (1-shell)	5.8±1	1.94±0.03	0.012
19 w/asc. acid (2-shell)	4.0±1	1.99±0.03	-0.003
	1.0±1	1.83±0.03	-0.012

*Powder of 500 Å diameter particles was used as the reference.

shorter ones, agreeing with our results. When ascorbic acid is added, the shorter Ti-O double bond can bind with two hydroxyl oxygen atoms on the five member ring, forming two single Ti-O (C) bonds. Some Ti sites may remain penta-coordinated due to the steric hindrance of the bound ascorbic acid molecules on the surface. The two Ti-O distances in 19 Å particles with ascorbic acid from the fitting result appear longer than their counterparts

without ascorbic acid, reflecting the change from the shorter Ti-O double bond to two single bonds connecting ascorbic acid. The fact that the overall coordination number increases when adding acid confirms this assumption.

4. Conclusion

The XAFS studies revealed that small nanoparticles of TiO₂ colloids display distortions in surface Ti sites from the octahedral geometry in the bulk. This distortion is due to truncation of the neighboring Ti and O atoms due to the large curvature in small TiO₂ particles. Based on the studies by Farges et al. (1997), the distortions are likely a penta-coordinate square pyramid with one double Ti-O bond. Binding ascorbic acid to the 19 Å diameter TiO₂ nanoparticle surfaces results in partial restoration of the octahedral Ti environment. Therefore, our study indicates that the distortions of Ti sites in small nanoparticles are mainly located on the surface. Due to the distortion, the surface sites become more active in binding functional groups of molecules and show enhanced catalytic activity. This study provides a structural origin for the unique chemistry of the small semiconductor nanoparticles, and a guide for the rational design of semiconductor catalysts.

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