Size effects in the Raman spectra of TiO$_2$ nanoparticles

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Abstract

To investigate the relationship between the particle size and the Raman bands of TiO$_2$ nanoparticles, two different size-selected samples of TiO$_2$ nanoparticles were investigated using transmission electron microscopy (TEM), X-ray absorption near edge structure (XANES), extended X-ray absorption fine structure (EXAFS), and Raman spectroscopy. Analysis of the XANES spectra showed that the nanoparticles in both sample A (particle size $\sim$30 nm) and sample B (particle size $\sim$12 nm) have an anatase structure, and that there is no difference between the electronic structure of titanium atoms in TiO$_2$ nanoparticles and that of titanium atoms in bulk TiO$_2$. The EXAFS results indicate that a contraction effect occurs in the anatase TiO$_2$ nanoparticles. In the Raman spectra, both broadening and shifts of the Raman bands with decreasing particle diameter were observed. In this paper, these Raman shifts are attributed to the effects of decreasing particle size on the force constants and vibrational amplitudes of the nearest neighbor bonds.

Keywords: Raman spectra; TiO$_2$; Nanoparticles; X-ray absorption spectroscopy (XAS)

1. Introduction

Nanometer-sized materials have recently gained a considerable amount of attention because of their unique physical and chemical properties and their importance in technological applications [1,2]. Because of their large surface-to-volume ratios and quantum-size effect, their properties and structural stability are very different to those of their bulk counterparts [3–5]. A significant motivation of current research into nanometer-sized materials is the need to develop an understanding of the relationships between their structures and their properties. Despite the extensive research efforts in this area using various characterization techniques, such an understanding has still not been achieved.

Raman spectroscopy is a powerful method for the investigation of the structural properties of nanoparticles because the variations in Raman spectra with decreases in particle size can be easily detected. Although there is still some controversy as to what effects variation in particle size has on phonon modes and on the electron-phonon interaction [6,7], Raman studies of these materials are useful in two distinct ways. Firstly, it is possible to determine the size of nanoparticles from a measurement of the maximum of the low-frequency Raman band [8–10]. The frequency $\nu$ (in cm$^{-1}$) of the lowest-energy spherical mode of a free particle, corresponding to angular momentum $l = 0$, is given by [11,12]

$$\nu = \frac{0.7v_L}{d \times c}$$

where $v_L$ is the speed of the longitudinal sound waves, $c$ is the vacuum light velocity of sound, and $d$ is particle diameter. Secondly, this technique provides valuable information about the surface modes and thus about the effects of the finite size of the nanoparticles, because the surface modes become dominant as particle size decreases due to the increase in the surface-to-volume ratio, which means that new bands can be observed. For example, Campbell and Fauchet have reported that grain size effects produce large shifts and broadening of the Raman spectrum of silicon [13]. Palkar et al. studied the Raman spectra of Si-doped PbTiO$_3$ and reported that the broadening and shifts of the Raman bands of PbTiO$_3$ with increasing Si content can be attributed to an Si-induced finite size effect [14]. Zuo et al. obtained the Raman spectra of SnO$_2$ nanoparticles and reported that two new characteristic bands resulting from surface phonon modes are present when the particle diameter is less than 10 nm [15]. The dependence of Raman bands on particle size has also been observed for MgO, ZnO, CdS, and other nanoparticles [16–19].

In contrast to the above-mentioned results for SnO$_2$ nanoparticles, only band broadening and shifts of the Raman
bands in the spectra of TiO$_2$ nanoparticles with decreasing particle size have been observed, even though TiO$_2$ and SnO$_2$ possess the same crystal structure (tetragonal) [20–23]. Parker et al. have suggested that the observed variations in the Raman spectra with particle size are related to the oxygen stoichiometry of the TiO$_2$ nanoparticles and are not due to any internal stress or grain size effects [20]. However, the Raman results described above show that grain size effects do manifest within nanoparticles. Further, Luca et al. detected the presence of contracted Ti–O bonds in anatase TiO$_2$ nanoparticles using X-ray absorption spectroscopy (XAS) [24]. Toneje et al. reported that a dependence of the lattice parameter on grain size arises for anatase TiO$_2$ nanoparticles [25]. Clearly an improved understanding of the origin of the observed variation of Raman bands of TiO$_2$ nanoparticles with particle size is required.

The positions and widths of Raman bands of materials are related to their vibrational and structural properties. Thus, a better understanding of the Raman spectra of a material can be obtained by examining the local structure and electronic environment of its constituent atoms. XAS is known to provide valuable information about the local structure around atoms of interest [26,27]. The absorption peak features in the X-ray absorption near edge structure (XANES) can be used to extract useful structural parameters such as the oxidation states of the chemical species, site symmetry, and covalent bond strengths. Further, the study of extended X-ray absorption fine structure (EXAFS) is a powerful technique for the local structural analysis of short-range ordered compounds because it is very sensitive to the local atomic environment and does not depend on long-range order. Therefore, a combined analysis of Raman and XAS spectra can greatly enhance the understanding of the experimental results.

The objective of the present study is to elucidate the origin of the variations in the Raman bands of TiO$_2$ nanoparticles with particle size. To achieve this objective, two samples of size-selected TiO$_2$ nanoparticles were prepared and each of these samples was investigated using X-ray absorption spectroscopy and Raman spectroscopy. Both broadening and shifts of the Raman bands with decreasing particle diameter were observed. In this paper, we conclude that these Raman shifts are due to the effects of decreasing particle size on the force constants and vibrational amplitudes of the nearest neighbor bonds.

2. Experimental

TiO$_2$ nanoparticles were prepared via a hydrolysis method using titanium isopropoxide [Ti(OCH(CH$_3$)$_2$)$_4$, Aldrich, 99.999%] as the starting material without further purification. The Ti(OCH(CH$_3$)$_2$)$_4$ solution was added to 200 mL of 2-propanol at room temperature with vigorous stirring, and then 800 mL of deionized water was added to the solution. The reaction conditions were maintained for 1 h, which was assumed to be sufficient time for the reactions, hydrolysis, and particle formation to reach equilibrium. Sample A was obtained by heating the precipitated particles at 450 °C for 1 h. Sample B was obtained by adjusting the stirring rate of the original reaction mixture (i.e. Ti(OCH(CH$_3$)$_2$)$_4$ and 2-propanol) to 200 rpm, and the precipitated particles were dried with a freeze-drier. The TiO$_2$ nanoparticles of sample B were then obtained by heating the dried particles at 450 °C for 1 h.

TEM images were obtained using a Phillips CM20T/STEM Electron Microscope at an accelerating voltage of 200 kV. FT-Raman spectra were obtained at room temperature using a Bruker FRA 106/S FT-Raman spectrometer (Germany) equipped with an InGaAs detector. The radiation from an Nd-YAG laser (1.5 W) was used as the excitation source. Ti K-edge X-ray absorption spectra were recorded using the 7C beam line at the Pohang Light Source (PLS) with a ring current of 120–170 mA at 2.5 GeV. A Si(1 1 1) monochromator crystal was used with detuning to 85% in intensity to eliminate high-order harmonics. Data were collected in transmission mode using gas-filled ionization chambers as detectors. Energy calibration was carried out for all measurements using Ti foil placed in front of the third ion chamber, assigning the first inflection point to 4966 eV.

The measured X-ray absorption spectra below the pre-edge region were fitted to a straight line, and then the background contribution above the post-edge region, $\mu_0(E)$, was fitted to a high order polynomial (cubic spline). The fitted polynomials were extrapolated over the entire energy region and subtracted from the total absorption spectra. The absorption spectra with the background subtracted were normalized for the above energy region, $\gamma(E) = \{\mu(E) - \mu_0(E)\}/\mu_0(E)$. The normalized $k^3$-weighted EXAFS spectra, $k^3\gamma(k)$, were Fourier transformed to reveal the contribution of each bond pair to the Fourier transform (FT) peak.

3. Results and discussion

Fig. 1 shows the TEM images of the samples. It is obvious from these images that the samples are disperse, with an average particle size of ~30 nm for sample A, and ~12 nm for sample B. The particle sizes of samples A and B determined from the TEM images are in good agreement with the values obtained by applying the Scherrer equation to the XRD patterns (results not shown) [28]. The particle sizes of samples A and B determined from the TEM images are in good agreement with the values determined from the XRD analysis [29]. The TEM results show that size-selected samples of TiO$_2$ nanoparticles have been successfully prepared from the Ti(OCH(CH$_3$)$_2$)$_4$ precursor. To elucidate the variations in structure and electronic state of the titanium ions with decreasing particle size, XAS data were collected for the two samples of TiO$_2$ nanoparticles.

Absorption in the XANES region varies with the site symmetry, coordination, and the oxidation states of the
central atoms, so the XANES has been widely used to characterize various forms of TiO$_2$ [24,30–33]. A Ti K-edge XANES spectrum is usually divided into two regions. The region above approximately 4980 eV is assigned to the well-understood dipole-allowed 1s → np ($n \geq 4$) transitions; below 4980 eV lies the so-called pre-edge peaks. In previous studies of TiO$_2$ [24,31,32], four pre-edge peaks (usually labeled A$_1$, A$_2$, A$_3$, and B) were observed in the range 4960–4980 eV. Feature A$_2$ is sometimes observed as a weak shoulder on the low energy side of peak A$_3$, and requires good energy resolution to be observed. The pre-edge peak arises from transitions of electrons to bound excited electronic states, but this electronic excitation is strongly modulated by the surrounding atoms in the short to medium range (<100 absorbing atoms) [24]. Therefore the pre-edge region contains much potentially useful structural and electronic information, and is frequently used to elucidate the structure of TiO$_2$ powders in the Ti K-edge XANES spectrum.

Fig. 2 shows the Ti K-edge XANES spectra of the two samples of TiO$_2$ nanoparticles and of a reference material (anatase TiO$_2$, Aldrich, 99.9%). Based on previous band structure calculations [34,35], peaks A$_3$ and B in the Ti K-edge XANES spectra were assigned to 1s transitions to the t$_{2g}$ and e$_g$ bands, which do not have pure Ti d character because of the hybridization of Ti 3d and 4p orbitals on different sites in the conduction band region [24,33]. However, the assignment in the literature of the A$_1$ and A$_2$ transitions has not been unanimous. Parlebas et al. suggested that peak A$_1$ is essentially due to the quadruple transition to 3d states of t$_{2g}$ symmetry on the central atom, which are shifted down from their unperturbed position by the 1s core-hole potential (a type of excitonic mechanism) [32]. In contrast, Wu et al. based their assignment on multiple scattering calculations, and concluded that peaks A$_1$, A$_2$, A$_3$.
and A3 arise dominantly from the hybridization of 3d-4p orbitals, and reflect a different degree of hybridization with the central Ti 4p orbitals due to the different distance of the two Ti shells [33].

Because XANES measurements involve the excitation of electrons from core levels to partially filled and empty states, the peak positions and spectral features of the Ti K-edge XANES spectra will be affected not only by the oxidation state but also by other chemical features of Ti species, such as the structural symmetry and the covalent/ionic character of the bonds between Ti and neighboring atoms. In Fig. 2 it can be seen that the main features of the spectra of the TiO2 nanoparticles show no noticeable variation with decreases in particle size. This indicates that the nanoparticles in samples A and B have anatase structures, and that there is no change in the oxidation state of the titanium ions with decreasing particle size. However, when the particle size is decreased from 30 to 12 nm, the ratio of the intensity of A2 to that of A3 increases slightly. This increase can be attributed to the decrease in particle size. It is known that peak A2 arises predominantly from the surface structure of anatase particles [24]. As the particle size decreases, peak A2 becomes dominant due to the increase in the surface-to-volume ratio. These observations are also in good agreement with a recent study of the anatase Ti K-edge XANES [24]. Thus, our XANES results show that the nanoparticles in samples A and B have anatase structures, and that there is no difference between the oxidation state of the titanium ions in the nanoparticles and that of titanium ions in bulk TiO2.

When the particle size decreases to the nanometer scale, the structural properties of nanoparticles can become different to those of the bulk material. Bulk anatase has a tetragonal structure (space group I41/amd) containing 12 atoms per unit cell with lattice parameters a = 3.784 Å and c = 9.514 Å [36]. The Ti4+ ions are surrounded by six O2− (4 × Ti–O = 1.939 Å, 2 × Ti–O = 1.980 Å) at the corners of a slightly distorted octahedron, and each O2− is surrounded by three Ti4+ lying in a plane at the corners of an equilateral triangle. The anatase structure comprises two interpenetrating zigzag chains of edge-shared octahedra, which are linked to form a three-dimensional network of edge-shared octahedra. To elucidate the variation in the local structure around Ti atoms as a function of particle size, we carried out an EXAFS analysis.

Fig. 3 shows the EXAFS spectra of the anatase TiO2 nanoparticles and that of the reference material. The Fourier transforms alter the phase shift parameters, so the peak positions are shifted to values below those in the original spectrum. In the spectrum of the reference TiO2, the FT peak at ~1.6 Å is due to the single scattering path of Ti → O by six-coordinated oxygen nearest neighbors around the Ti atom. On the other hand, the two peaks in the range 2–4 Å are due to the single scattering path of Ti → Ti by neighboring Ti atoms. The magnitudes of the FT at ~2.7 and ~3.6 Å correspond to single scattering by the edge-shared octahedra and corner-shared octahedra respectively. The magnitudes of the FT above ~4.0 Å indicate the single and multiple scattering contributions. The general features of the spectra of the anatase TiO2 nanoparticles have a strong resemblance to those of the spectrum of the bulk, with a reduction in the magnitude of the FT peaks with decreasing particle size. It is also observed that the FT peaks in the range 2–4 Å are slightly shifted down compared to those of the reference material. The first observation can be explained in terms of the effects of decreasing particle size: because the surface-to-volume ratio and the number of distorted sites at the surface increase as the particle size decreases, a reduction in the magnitude of the FT peaks of
nanoparticles is generally observed \[37\]. The second observation suggests that the size-induced radial pressure of TiO$_2$ nanoparticles leads to a volume contraction as the particle size decreases. The next nearest neighbor (Ti–Ti) shells thus experience an increase in the mean square relative displacement (MSRD) with decreases in particle size, because the magnitude of the FT peak of a bond pair is inversely related to the Debye–Waller factor corresponding to the MSRD of the interatomic distance; similar observations have been reported for TiO$_2$ and CdS nanoparticles \[24,38\].

TiO$_2$ nanoparticles have frequently been investigated with Raman spectroscopy because of the unusual band broadening and shifts of Raman bands with decreasing particle size. However, there is no general agreement about the origin of the broadening and shifts of the Raman bands. In contrast, Xu et al. have tried to explain the variation in the Raman bands with a phonon confinement model \[23\]. On the basis of the Heisenberg uncertainty principle, the relationship between particle size and phonon position can be expressed as follows:

$$\Delta X \Delta P \geq \frac{\hbar^2}{4}$$

(2)

where $\Delta X$ is the particle size, $\Delta P$ is the phonon momentum distribution, and $\hbar$ is the reduced Planck’s constant. As the particle size decreases, the phonon is increasingly confined within the particle and the phonon momentum distribution increases. This broadening of the phonon momentum leads to a broadening of the scattered phonon momentum according to the law of conservation of momentum. This phonon dispersion causes asymmetric broadening and may lead to a shift of the Raman bands \[23\].

According to factor group analysis, anatase has six Raman active modes ($A_{1g} + 2B_{1g} + 3E_g$). The Raman spectrum of an anatase single crystal has been investigated by Ohsaka, who concluded that the six allowed modes appear at 144 cm$^{-1}$ ($E_g$), 197 cm$^{-1}$ ($E_g$), 399 cm$^{-1}$ ($B_{1g}$), 513 cm$^{-1}$ ($A_{1g}$), 519 cm$^{-1}$ ($B_{1g}$), and 639 cm$^{-1}$ ($E_g$) \[39\]. In this study, we assigned and interpreted the Raman bands of the TiO$_2$ nanoparticles using earlier results obtained for the bulk phase. Fig. 4 shows the Raman spectra of the two samples of TiO$_2$ nanoparticles and of the reference spectrum of anatase TiO$_2$. In order to see the differences between the spectra more clearly, the wavenumbers and the full-widths at half-maximum (FWHM) of the bands are given in Table 1.

The main features of the spectra of samples A and B are very similar to those of the reference TiO$_2$, which means that the anatase phases of the nanoparticles of samples A and B possess a certain degree of long-range order. Comparing the three Raman spectra, it is clear that the Raman bands shift towards higher wavenumber and their intensities relatively decrease as the particle size decreases. However, the band

<table>
<thead>
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<th>$E_g$ (cm$^{-1}$)</th>
<th>$E_g$ (cm$^{-1}$)</th>
<th>$B_{1g}$ (cm$^{-1}$)</th>
<th>$A_{1g}$ (cm$^{-1}$)</th>
<th>$E_g$ (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reference TiO$_2$</td>
<td>143 (8.61)</td>
<td>196 (4.28)</td>
<td>396 (18.34)</td>
<td>514 (21.93)</td>
<td>637 (23.36)</td>
</tr>
<tr>
<td>Sample A</td>
<td>144 (13.23)</td>
<td>196 (4.39)</td>
<td>396 (36.53)</td>
<td>515 (23.87)</td>
<td>638 (25.01)</td>
</tr>
<tr>
<td>Sample B</td>
<td>145 (11.31)</td>
<td>196 (9.14)</td>
<td>398 (24.20)</td>
<td>516 (30.68)</td>
<td>639 (31.73)</td>
</tr>
</tbody>
</table>
broadening is insignificant, and so is not considered further in this study. These observations cannot be explained in terms of changes in oxygen stoichiometry with decreasing particle size, because the XANES results show that there is no variation of the electronic structure around the Ti atoms. Thus, the observed shift is due to the effect of decreasing particle size on other properties of the nanoparticles. When the particle size decreases to the nanometer scale, two effects on the vibrational properties of these materials might occur. Firstly, a volume contraction occurs within the nanoparticles that is due to the size-induced radial pressure, which leads to increases in the force constants as a result of the decreases in the interatomic distances. In vibrational transitions, the wavenumber varies approximately in proportion to $k^{1/2}$, where $k$ is the force constant. Consequently, the Raman bands shift towards a higher wavenumber due to the increasing force constants. Secondly, the contraction effect induces decreases in the vibrational amplitudes of the nearest neighbor bonds due to the increase of the MSRD, which can be interpreted as a measure of the static disorder and thermal vibrational disorder of a material \cite{38,40}. This decrease in vibrational amplitude with decreasing particle size affects the intensity of the Raman bands. We conclude that the variation in the Raman spectra of TiO$_2$ nanoparticles is due to the effect of smaller particle size on the force constants and vibrational amplitudes of the nearest neighbor bonds.

4. Conclusion

The broadening and shifts of Raman bands of anatase TiO$_2$ nanoparticles with decreasing particle size were investigated using X-ray absorption spectroscopy and Raman spectroscopy. The XANES results show that the prepared 30 and 12 nm TiO$_2$ nanoparticles have an anatase structure, and that there is no difference between the oxidation state of the titanium ions in the nanoparticles and that of titanium ions in bulk TiO$_2$. The EXAFS results indicate that size-induced radial pressure in TiO$_2$ nanoparticles increases as the particle size decreases, and this results in a volume contraction. Additionally, the next nearest neighbor (Ti–Ti) shells are strongly influenced by decreases in the particle size, which produces increases in the mean square relative displacement (MSRD). Both broadening and shifts of the Raman bands were observed with decreasing particle diameter. The observed Raman shifts are thus due to the effects of decreasing particle size on the force constants and vibrational amplitudes of the nearest neighbor bonds.

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