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Evidence of linear lattice expansion and covalency enhancement in rutile TiO₂ nanocrystals

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Lattice variations and bonding characteristics in rutile TiO₂ nanocrystals were examined by x-ray diffraction and x-ray photoelectron spectroscopy. With a reduction in the physical dimensions, rutile TiO₂ nanocrystals show a linear lattice expansion and an anomalous covalency enhancement in apparent contradiction to the ionicity increase in BaTiO₃ and CuO nanocrystals as reported recently by S. Tsunekawa *et al.* [Phys. Rev. Lett. 2000, **85**, 3440] and V. R. Palkar *et al.* [Phys. Rev. B 1996, **53**, 2167]. A surface defect dipole model is proposed to explain these physical phenomena in terms of the strong interactions among the surface dipoles that produce an increased negative pressure. The covalency enhancement is interpreted according to the critical properties of the increased Ti—O bond lengths in the expanded lattice. © 2004 American Institute of Physics.
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Metal-oxide nanocrystals have potential for or demonstrated applications in many technologies including solar energy conversion, batteries, and ductile ceramics.¹ These materials have properties that are highly dependent on the physical dimensions or grain size. Extensive theoretical and experimental studies² have shown that the dimensional reduction into the nanoscale regime produces distinct properties from the bulk, which is thought to originate from phonon confinement, additional surface phonons, or tensile surface stresses. The reduction in grain size is also generally followed by certain variations in lattice parameters. From a solid-state physics viewpoint, the lattice dimensions directly determine the band structure and, consequently, the physical properties of the solids since the variations in lattice can lead to a significant shift of the Brillouin zone. Metal-insulator transitions observed in lower-dimensional solids are a good example, illustrating the importance of lattice modulations.³ However, the origin of size-induced changes in the lattice volume of metal-oxide nanocrystals is still not clearly understood.

In contrast with the lattice contraction in metal nanocrystals,⁴ most metal-oxide nanocrystals exhibit lattice expansion as the particle size is reduced.^{5,6} This is somewhat surprising since it is counter to general physical observations for small particles⁷ in which surface stresses cause small particles to compress. Tsunekawa *et al.*⁵ proposed that the lattice expansion in metal-oxide nanocrystals is due to the valence reduction such as from Ce⁴⁺ to the larger Ce³⁺ in CeO₂ nanocrystals, but Palkar *et al.*⁶ found that there was no oxygen loss as the particle size was reduced. Furthermore, in certain transition-metal oxides, it has also been reported⁶ that there is an ionicity increase as the particle size is reduced, which is explained on the basis of a pressure-induced covalency increase. This conclusion is questionable, since in certain solids that are primarily ionic in nature, ionicity enhancement occurs at high pressures.⁸ Rutile TiO₂ is a model

compound that shows approximately 63% ionic nature in the Ti—O bonding as deduced from the electronegativity values of Ti and O, and has a close structural link to high-pressure phases of many metal oxides including GeO₂,⁹ ZrO₂, and HfO₂¹⁰ as well as the low-pressure earth's mantle material, stishovite SiO₂.¹¹ Of its various analogues, rutile TiO₂ is among the few that can be stabilized at nanoscale sizes under ambient conditions with a typical size effect being demonstrated by a significant decrease in the transition pressure to a phase of PbO₂-type TiO₂.¹² This has also led to the possibility of finding more high-pressure polymorphs including α -PbO₂-type and baddeleyite-structured TiO₂. A precise determination of the size dependence of the lattice volumes and bonding characteristics of rutile TiO₂ nanocrystals is thus expected to improve our understanding on the nanophysics, size-related properties (e.g., quantum effects), and even certain geological processes.

In this letter, we report a linear lattice expansion as a function of particle size in rutile TiO₂ nanocrystals that demonstrates critical quantum-size effects.

Highly pure rutile nanoparticles were prepared by a hydrothermal method.¹³ X-ray diffraction (XRD) data of the rutile nanoparticles were measured at room temperature at a scan rate of 0.2° 2 θ /min. The lattice parameters for the samples were calculated by least-squares methods. The average grain size (D) was measured from the most intense XRD peak (110) using the Scherrer formula.¹³ The ionic characteristics were studied by determining the binding energies of the O 1s and Ti 2p electrons using x-ray photoelectron spectroscopy (XPS). The binding-energy data are calibrated with the C 1s signal at 284.6 eV.

XRD and TEM have already confirmed the formation of single-phase rutile TiO₂ nanocrystals in a rodlike shape.¹³ Figure 1 shows the main diffraction peak (110) on an expanded scale, where the broadening effects are clearly seen. The strain and particle size are two predominant factors controlling the broadenings of the diffraction peaks.¹⁴ The effective strain is calculated using the Williams and Hall theorem¹⁵

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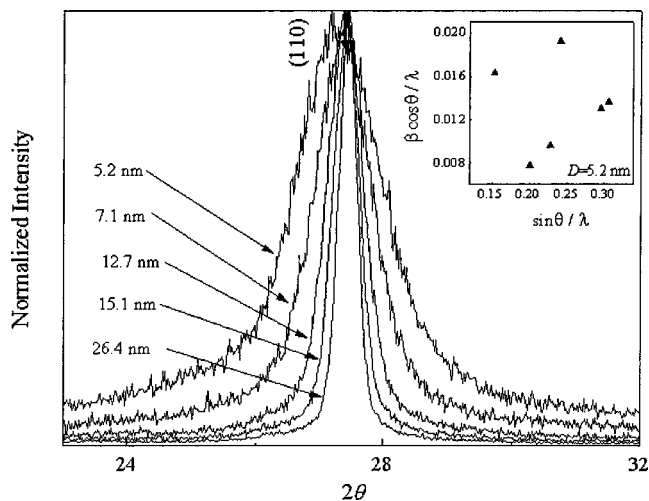


FIG. 1. Normalized diffraction peak (110) for rutile TiO₂ nanocrystals at the indicated grain sizes. Inset is the relationship between $(\beta \cos \theta)/\lambda$ and $(\sin \theta)/\lambda$.

$$\frac{\beta \cos \theta}{\lambda} = \frac{1}{D} + \frac{\eta \sin \theta}{\lambda}, \tag{1}$$

where β is the full width at half maximum (FWHM), θ is the diffraction angle, λ is the x-ray wavelength, D is the effective particle size, and η is the effective strain. A typical plot of $(\beta \cos \theta)/\lambda$ vs $(\sin \theta)/\lambda$ for six intense peaks of 5.2 nm rutile is shown in the inset of Fig. 1. The scattered data points strongly demonstrate the absence of any significant strain in our rutile TiO₂ nanocrystals. Consequently, the average grain size of the rutile nanocrystals was calculated using only the peak broadenings, which will be described in more detail elsewhere. Also indicated in Fig. 1, the (110) peak shows a significant shift towards lower diffraction angles as the particle size is reduced. This is associated with the lattice expansion and has already been found in CeO₂ nanocrystals containing dopants larger than Ce⁴⁺, such as Nd³⁺.¹⁶

Structural refinements using a least-squares method indicate the lattice volume of rutile TiO₂ nanocrystals increases monotonically with a reduction in grain size (D) (Fig. 2).

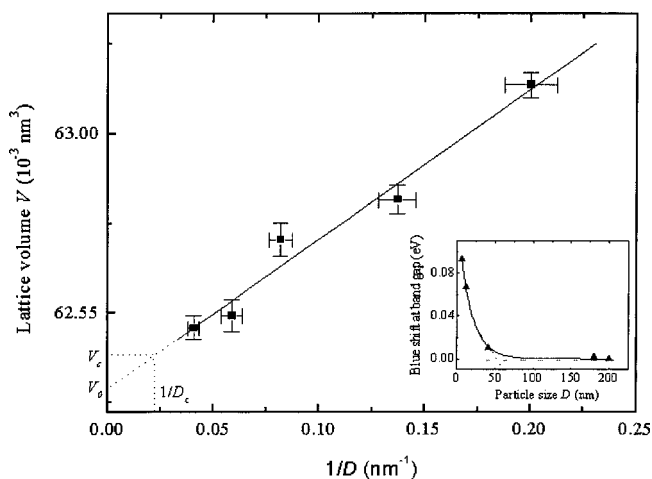


FIG. 2. Grain-size dependence of the lattice volume for rutile TiO₂ nanocrystals (■). Inset shows grain-size dependence of the blueshifts of the band gap compared with that of the bulk TiO₂ crystallites (▲) (see Ref. 22).

The lattice volume (V) size dependence was fitted to the following linear equation:

$$V = V_0 + \frac{A}{D}, \tag{2}$$

where $V_0 = 6.236 \times 10^{-2} \text{ nm}^3$ and $A = 3.75(0) \times 10^{-3} \text{ nm}^4$. The occurrence of a linear lattice expansion can be related to a negative interface pressure, but this is different from the positive surface pressure that is associated with the lattice contractions in metal nanocrystals with a predominant surface stress effect via $f_{rr} = \frac{1}{2} r \cdot p$ (where f_{rr} is the surface stress and p is the hydrostatic pressure due to the surface of radius r).⁴ Tsunekawa *et al.*⁵ and Ayyub *et al.*¹⁷ have proposed several reasons for the lattice expansions appearing in certain metal-oxide nanocrystals according to (i) the valence reduction as in CeO₂,⁵ and (ii) the unpaired electronic orbitals at the outer surface as in Fe₂O₃.¹⁷ However our XPS and EPR results do not show any evidence of Ti³⁺ or oxygen vacancies in our rutile TiO₂ nanocrystals. Here, we propose a surface defect dipole model to explain the negative pressure observed for the rutile nanocrystals.

Ideally, in the highly symmetric Ti—O₆ octahedra, the centers of positive and negative charges are located at the octahedral sites. However, rutile TiO₂ has been shown to have intrinsic polarization fields in the lattice.¹⁸ That is, the coordinated oxygen ions occupy positions where crystal electrical fields may occur causing the ions to become polarized.¹⁹ The titanium atoms are distributed with some amount of disorder at several sites adjacent to the octahedral sites due to the low-energy barrier between these sites.²⁰ Therefore, titanium atoms can move off the centers of the Ti—O₆ octahedra building blocks and form dipoles. Because of the smaller cell volume of the rutile lattice and two equivalent molecules for each cell, stronger interactions between dipoles of the Ti—O₆ octahedra can be expected, which most likely leads to a highly oriented array of dipoles with a directional character similar to those found in most titanate ferroelectrics and piezoelectrics.²¹

There are several factors that can considerably enhance the strength of the surface dipoles in rutile nanocrystals. With decreasing grain size, there will be a larger fraction of titanium atoms appearing on the surface with lower coordination compared with the six-fold coordinated Ti in the bulk phase. Consequently, surface titanium atoms will most likely show a significant increase in the number of dangling bonds, which could be compensated by the absorption of some reactive molecules, such as H₂O, by forming terminal hydration layers as was confirmed by our TGA-DSC and IR measurements (not shown), causing a significant distortion around the Ti ions. Consequently, the negative centers will show a significant downward shift towards the grain interior relative to the positive centers of the surface titanium atoms. This shift of the negative centers is expected to produce enhanced surface defect dipoles that are perpendicular to the outer surface of each rutile nanocrystal. The strong dipole-dipole interactions would lead to a roughly parallel array of the dipoles yielding larger defect dipoles on the surface layer of each nanocrystal. The strong repulsive interactions of the parallel surface defect dipoles account for the negative pressure on the rutile nanocrystals. Even though the nanocrystals may also show some positive pressure due to surface stresses as has been indicated in metal nanocrystals,⁴ for the present

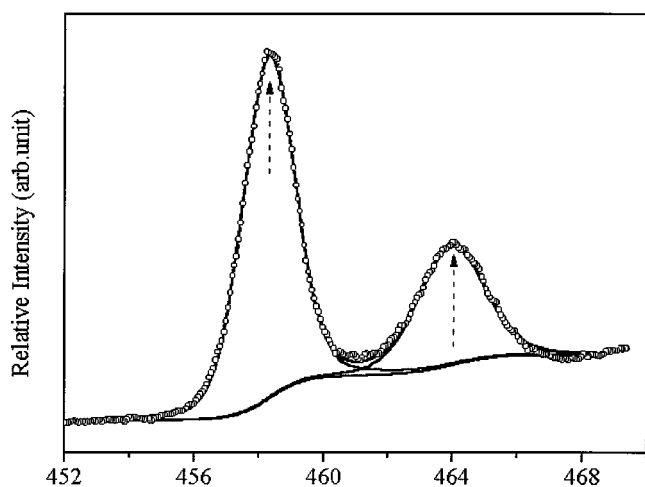


FIG. 3. XPS Ti $2p$ core-level spectra for 7.9 nm rutile nanocrystals.

rutile nanocrystals, the negative pressure is evidently much larger as the particle size is reduced below some critical dimension. The net negative pressure is the primary reason for rutile nanocrystals having a larger equilibrium volume than that of the bulk phase. Similar defect dipoles have been proposed on the grain surfaces of $\text{Ba}_4\text{Ti}_3\text{O}_{12}$ nanocrystals and $(\text{Ba}, \text{Sr})\text{TiO}_3$ -based oxides.²¹

Now let us return to our linear equation for lattice expansion in rutile nanocrystals. Equation (2) can be rewritten as follows:

$$V = V_0 + \frac{(V_c - V_0) \cdot D_c}{D}, \quad (3)$$

where $V_0 (= 6.236 \times 10^{-2} \text{ nm}^3)$ denotes an imaginary bulk lattice infinitely large and D_c and V_c are the critical particle size and lattice volume when the external forces from the surface dipoles and surface tension are balanced. As the particle size increases beyond D_c , the relative surface area and surface tension will become extremely small and the lattice volume at $D \geq D_c$ can be taken as a constant; that is, V_c will have a value much closer to the actual lattice volume of $6.243 \times 10^{-2} \text{ nm}^3$ for the bulk phase of rutile TiO_2 . If we assume this value for V_c , Eq. (3) will yield a critical size of $D_c = 54 \text{ nm}$. This critical size, obtained by our linear lattice expansion, is in excellent agreement with that of approximately 50 nm as determined by the photoluminescence method²² below which a significant blueshift is observed in the absorption spectra relative to those of bulk phases, indicating a quantum-size effect (see the inset of Fig. 2).

The lattice expansion in rutile nanocrystals is also associated with changes in the chemical bonding. The Ti $2p$ spectra of 7.9 nm rutile TiO_2 (Fig. 3) consist of well-defined Ti $2p_{1/2}$ and Ti $2p_{3/2}$ photoelectron signals that are located near 464 and 458 eV, respectively. No shoulders associated with Ti^{3+} or Ti^{2+} were observed at the lower energy sides. The spin-orbital splitting between these peaks is nearly constant at approximately 5.6 eV, which is comparable with the value of 5.74 eV for nanoporous anatase TiO_2 .²³ Taking the O $1s$ binding energy for the bulk oxygen species as a reference, the bonding energy difference (ΔE) between O $1s$ and Ti

$2p_{3/2}$ was calculated by fitting the photoelectron peaks. It was found that with decreasing particle size from 17.8 to 5.4 nm, ΔE decreased from 71.40(2) to 70.54(2) eV, which clearly indicates a decrease in the relative ionicity that has also been demonstrated by a nonempirical electronic-structure calculation.²⁴ The covalency enhancement is closely related to the change in the electronic transfer ability during the lattice expansion. The covalent Ti—O bond distance is 0.202 nm, which is nearly the same as that for the ionic Ti—O bond length (0.201 nm).⁵ The increased Ti—O bond lengths during the lattice expansion might provide a higher barrier for retarding the electronic transfer between Ti and O by reducing the ability to donate or accept electrons between Ti and O atoms.

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