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Size effect on the lattice parameters of nanocrystalline anatase

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Crystallite size dependence on the lattice parameters of nanocrystalline anatase was examined by x-ray diffraction pattern analysis, x-ray photoelectron spectroscopy (XPS), and Raman spectroscopy. The lattice parameter *a* increased while the parameter *c* decreased with reducing crystallite sizes. However, the cell volume increased with decreasing crystallite size indicating an overall expansion due to confinement effect. The observed shift in E_g Raman mode (at 144 cm^{-1}) was in accordance with an empirical phonon confinement model while no substoichiometric titania could be detected by XPS. It was concluded that the lattice expansion was purely due to electrostatic relaxation as a result of size confinement. © *2009 American Institute of Physics*.
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Nanocrystalline ceramic powders have received attention during the past two decades for their unique and size dependent mechanical, electronic, ionic, thermal, optical, and catalytic properties. Size dependence of physical properties in the nanosize regime arises primarily due to the high surface area to volume ratio and confinement effects. Crystallite size reduction to nanocrystalline levels results in changes in lattice dimensions which, in turn determines the band structure and, therefore, physical properties of the material. There have been many theoretical and experimental studies on the size dependence of lattice dimensions of metals as well as compounds. Expansion in lattice parameters have been observed with decreasing crystallite sizes in many nanocrystalline oxides such as CeO_2,[1] Fe_2O_3,[2] MgO,[3] TiO_2 (rutile),[4] and ZrO_2.[5] On the other hand, the reduction in lattice parameters, primarily due to high surface curvature effects, have been observed in many metals and nonoxide nanocrystalline particles such as Au,[6] Ag,[7] Pt,[8] Si,[9] ZnS, and CdSe.[10,11] By far, the reports on nanocrystalline anatase titania have suggested contradictory effects. In some cases, contraction in lattice parameter with reducing crystallite sizes,[12,13] a behavior typical of metal, was observed while others reported expansion in lattice dimension with reducing crystallite sizes in the nanocrystalline regime.[14] In this letter we report a nonlinear expansion in lattice parameters of highly pure nanocrystalline anatase powders synthesized by a chemical vapor synthesis (CVS) route.[15] The observations were well-supported by an earlier reported mechanism for lattice expansion in pure rutile nanocrystals.[4]

Nanocrystalline anatase titania was synthesized in a completely vapor phase by CVS. Different crystallite sizes were obtained by varying the process parameters during CVS. Characterization by x-ray diffraction in a panalytical (X'Pert-PRO) machine was carried out with Cu Kα radiation using a step size of 0.02 and collection time of 15–20 s. Rietveld analysis of x-ray diffraction (XRD) patterns were performed using the general structure analysis system (GSAS) software suite.[16] In all cases, minor rutile phase (when present) was also included in pattern refinement and a reasonably good reliability factor (based on weighted profile, R_{wp}) value of less than 0.07 was obtained. Crystallite sizes were calculated from scaling factors and profile parameters of a pseudo-Voigt profile of type-III. The profile parameter, *LX* was used to calculate the crystallite size using the modified formula given by[16]

$$d_{XRD} = \frac{3600\lambda}{\pi^2(LX)}, \tag{1}$$

where d_{XRD} is the crystallite size and λ the wavelength of the x-ray radiation (1.5417 Å). A commercial refinement package TOPAS® was also used for analyzing the data pertaining to some of the samples to check the consistency and reproducibility of the results obtained from GSAS and the two were found to be in reasonably good agreement.

The lattice parameters *a* and *c* estimated from Rietveld analysis of the XRD patterns, are depicted as a function of crystallite size in Fig. 1. Earlier studies showed an approximately linear variation in lattice parameter *a* of CeO_2 (fluorite structure) and $BaTiO_3$ (perovskite structure) with the reciprocal of the crystallite size.[1] In the current study, the lattice parameter *a* of nanocrystalline anatase increased while at the same time the parameter *c* decreased with decreasing crystallite sizes. This observation was in accordance with the

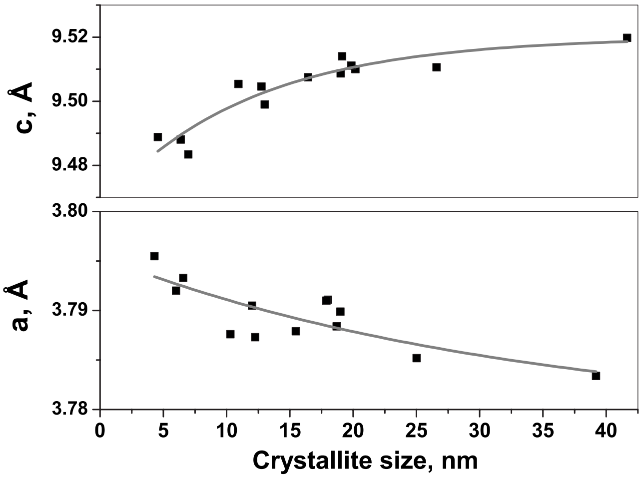

FIG. 1. Effect of crystallite size on the lattice parameters *a* and *c* of anatase.

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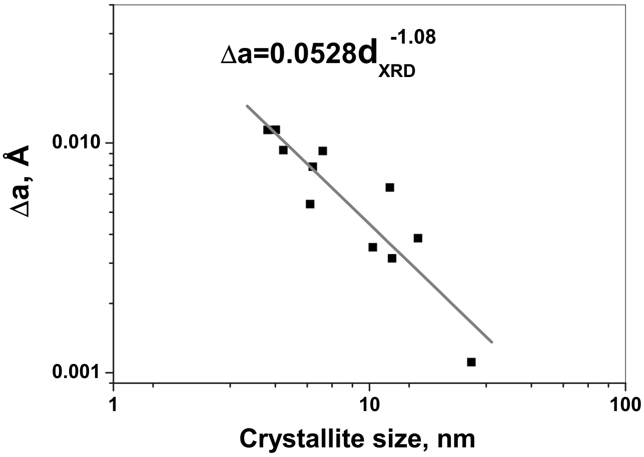

FIG. 2. Crystallite size dependency of change in the lattice parameter, a.

earlier report on $BaTiO_3$.[1] The change in lattice parameter (Δa) varied with the crystallite size according to the relation $\Delta a = 0.00528D^{-1.08}$ (Fig. 2). This was similar to the observation of Tsunekawa *et al.*,[1] where the lattice parameter change (Δa) in CeO_2 nanoparticle was reported to follow a relation $\Delta a = 0.0234D^{-1.06}$ with particle size D and Δa in nanometer. The cell volume (V) was found to increase linearly with $1/D$ as reported earlier in the case of rutile[4] (Fig. 3). The cell volume size dependence was adequately described by:

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

where V_0 is the unit cell volume for an infinitely large crystal and A is a constant. A V_0 value of about 136.14 Å^3 was obtained which is very close to the actual unit cell volume (136.25 Å^3, ICSD-9852) observed in case of large crystals. The observed expansion in cell volume with reducing crystallite size was in accordance with the suggestion of Li *et al.*[4] and was attributed to the presence of a larger number of dangling bonds in smaller crystals. Presence of dangling bonds resulted in the adsorption of water molecules on the surface which was confirmed by x-ray photoelectron spectroscopy (XPS) studies (see later). The adsorbed water molecules resulted in distortion around the Ti atoms at the surface. In turn, this displaced the Ti atoms toward the coordinated oxygen atoms producing parallel surface defect dipoles. The magnitude of the negative pressure due to the repulsive interaction between these dipoles exceeded the positive pressure due to surface curvature effect, resulting in a net negative pressure causing an expansion in lattice volume. The effect of this negative pressure reduces with increase in particle size due to reduced number of dangling bonds per unit volume. Beyond a critical size, D_c, the lattice volume will become close to that of bulk anatase, V_o. The critical crystallite size, D_c was given by[4]

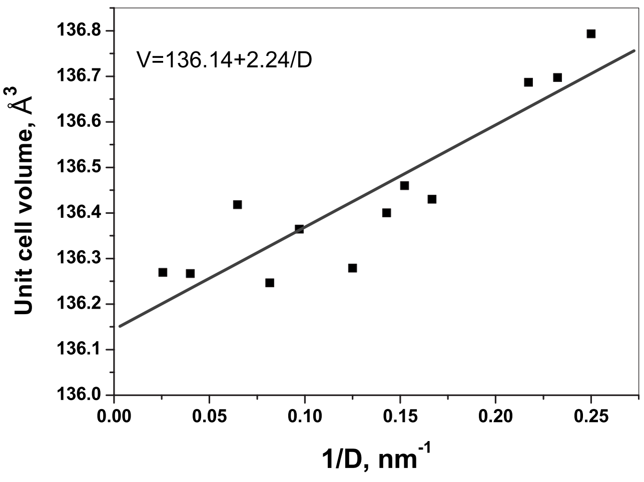

FIG. 3. Crystallite size dependence of unit cell volume of anatase.

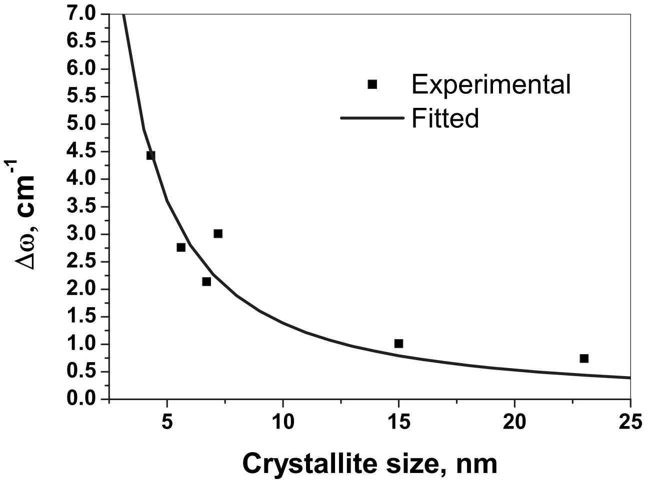

FIG. 4. Shift in 144 cm^{-1} peak in Raman spectra of nanocrystalline anatase powders.

$$D_c = \frac{(V - V_o)\,.\,D}{(V_c - V_o)}. \tag{3}$$

A critical diameter D_c of about 25 nm was obtained. This was close to the value of 28 nm below which significant shift in the E_g peak at 144 cm^{-1} in Raman spectra has been observed due to confinement effects.[17] Additionally, the observed shift in the 144 cm^{-1} peak agreed well with an empirical confinement model (Fig. 4) described by[18,19]

$$\Delta\omega = -A\left(\frac{a}{D}\right)^{\gamma}, \tag{4}$$

where $\Delta\omega$ is the peak shift, a is the lattice parameter, D is crystallite size, and γ is a constant. γ is typically around one for two-dimensional layered structures like graphite, boron nitride, and boehmite and close to 1.5 for three-dimensional structures like Si and GaAs.[18] In the present case, the experimental data gave $\gamma = 1.38$ which is close to 1.44 obtained for three-dimensional Si structure.[19,20] In the x-ray photoelectron spectrum of nanocrystalline anatase, Ti 2p doublet, shown in Fig. 5, consisted of $2p_{1/2}$ peak (at E_B of 459.6 eV) and $2p_{3/2}$ peak (at E_B of 465.31 eV) corresponding to the Ti^{4+} species in O–Ti–O bonding.[21] A separation of about 5.71 eV between $2p_{1/2}$ and $2p_{3/2}$ compared well with the 5.70 eV reported in literature for pure titania.[22] The O1s region (Fig. 6) was composed of two peaks at about 530.9 and 532.1 eV corresponding to oxygen in O–Ti–O and chemisorbed –OH group, respectively.[23,24] Further, no additional Ti2p emissions that could be assigned to reduced Ti in substoichiometric TiO_{2-x} (such as Ti^{3+} or Ti^{2+}) were detected by XPS. Additionally, in the electron paramagnetic resonance (EPR) spectrum of the 5 nm sized anatase, no Ti^{3+} could be observed. Because of the high sensitivity of EPR (≤ 0.1 at. %) it could be concluded

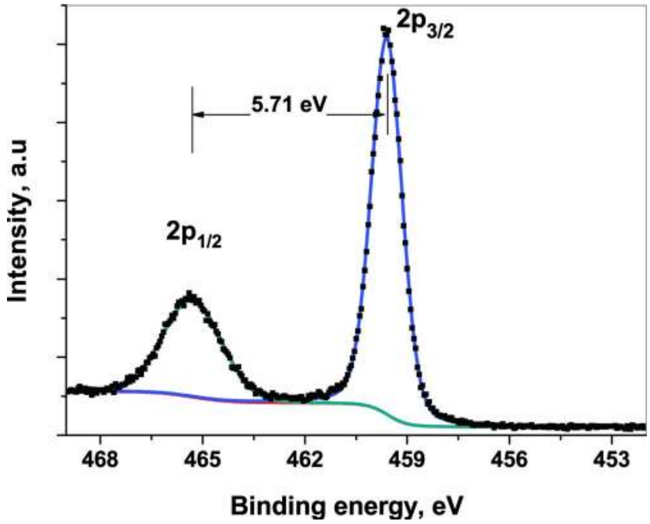

FIG. 5. (Color online) XPS Ti2p spectrum of nanocrystalline anatase having crystallite size 7 nm.

that the amount of Ti^{3+} or Ti^{2+}, if present, would be insignificant.

Earlier, it has been proposed that lattice expansion in oxides took place at reduced crystallite sizes mainly due to reduced ionic valencies resulting in decreased electrostatic force.[1,25] Perebeinos *et al.*[26] proposed a model based on electrostatic energy minimization and showed from calculations as well as experimental results that in both CeO_2 and $BaTiO_3$, Δa increased linearly with decreasing crystallite size. The earlier observed contraction in unit cell volume of anatase was attributed to a positive pressure due to surface hydration.[13] On the other hand, an increase in the nanocrystalline anatase lattice volume was explained in terms of the presence of oxygen vacancies.[14] Similar observations had been earlier reported in case of nanocrystalline ceria.[1] In the present study an overall expansion in lattice dimension (unit cell volume) was observed with decreased crystallite sizes. However, no substoichiometric titania or oxygen vacancy could be detected by XPS or EPR. Although, some amount of adsorbed –OH was observed in XPS, this was probably not sufficient to generate a significant positive pressure. Additionally, the shift in the 144 cm^{-1} peak in Raman spectra agreed reasonably well with an empirical confinement model. This along with XPS and EPR results confirmed that the lattice expansion arose purely from the confinement effects as significant oxygen vacancies were not present. This is in contrast with earlier reports where presence of oxygen vacancies was attributed to be the reason for the observed lattice expansion in CeO_2 (Ref. 1) and TiO_2.[14] In a nanocrystalline anatase crystallite progressively larger fractions of under-coordinated Ti atoms near the surface would result in the shifting of Ti atoms toward the coordinated oxygen atoms at the surface.[4] Therefore, the long range repulsive interaction arising from these under-coordinated Ti atoms would result in a net negative pressure and, in turn, a net expansion in unit cell volume.

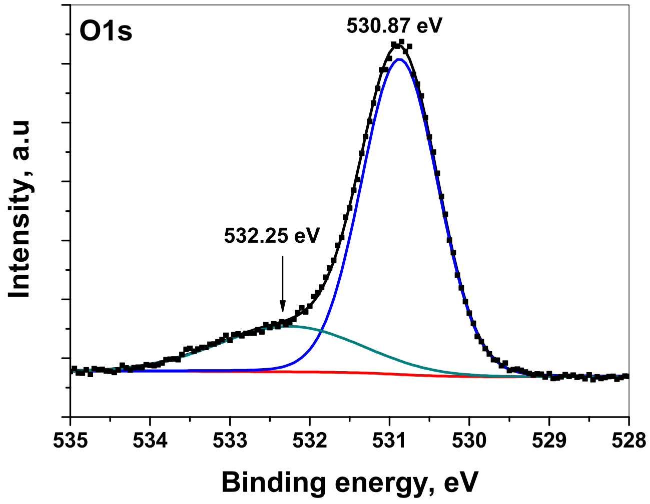

FIG. 6. (Color online) XPS O1s spectrum of nanocrystalline anatase having crystallite size 7 nm.

[1] S. Tsunekawa, K. Ishikawa, Z.-Q. Li, Y. Kawazoe, and A. Kasuya, Phys. Rev. Lett. **85**, 3440 (2000).
[2] P. Ayyub, V. R. Palkar, S. Chattopadhayay, and M. Multani, Phys. Rev. B **51** 6135 (1995).
[3] A. Cimino, P. Porta, and M. Valigi, J. Am. Ceram. Soc. **49**, 152 (1966).
[4] G. Li, J. Boerio-Goates, and B. F. Woodfield, Appl. Phys. Lett. **85**, 2059 (2004).
[5] H. K. Schmid, J. Am. Ceram. Soc. **70**, 367 (1987).
[6] J. S. Vermaak and D. K. Wisdorf, J. Phys. Chem. **72**, 4150 (1968).
[7] H. J. Wasserman and J. S. Vermaak, Surf. Sci. **22**, 164 (1970).
[8] H. J. Wasserman and J. S. Vermaak, Surf. Sci. **32**, 168 (1972).
[9] D. K. Yu, R. Q. Zhang, and S. T. Lee, Phys. Rev. B **65**, 245417 (2002).
[10] J.-Y. Zhang, X.-Y. Wang, M. Xiao, L. Qu, and X. Peng, Appl. Phys. Lett. **81**, 2076 (2002).
[11] S. N. Sarangi and S. N. Sahu, Physica E **23**, 159 (2004).
[12] A. M. Tonejc, I. Djerdj, and A. Tonejc, Mater. Sci. Eng., C **19**, 85 (2002).
[13] G. Li, L. Li, J. Boerio-Goates, and B. F. Woodfield, J. Am. Chem. Soc. **127**, 8659 (2005).
[14] V. Swamy, D. Menzies, and B. C. Muddle, Appl. Phys. Lett. **88**, 243103 (2006).
[15] I. Ahmad Md and S. S. Bhattacharya, J. Phys. D **41**, 155313 (2008).
[16] A. C. Larson and R. B. Von Dreele, "General Structure Analysis System (GSAS)" Los Alamos National Laboratory LAUR Report No. 86–748 (2004).
[17] A. Li Bassi, D. Cattaneo, V. Russo, C. E. Bottani, E. Barborini, T. Mazza, P. Piseri, P. Milani, F. O. Ernst, K. Wegner, and S. E. Pratsinis, J. Appl. Phys. **98**, 074305 (2005).
[18] C. J. Doss and R. Zallen, Phys. Rev. B **48**, 15626 (1993).
[19] K. R. Zhu, M. S. Zhang, Q. Chen, and Z. Yin, Phys. Lett. A **340**, 220 (2005).
[20] J. Zi, H. Buescher, C. Falter, W. Ludwig, K. Zhang, and X. Xie, Appl. Phys. Lett. **69**, 200 (1996).
[21] E. L. Bullock, L. Patthey, and S. G. Steinemann, Surf. Sci. **352**, 504 (1996).
[22] G. Liu, W. Jaegermann, J. He, V. Sundström, and L. Sun, J. Phys. Chem. B **106**, 5814 (2002).
[23] D. Chen, D. Yang, Q. Wang, and Z. Jiang, Ind. Eng. Chem. Res. **45**, 4110 (2006).
[24] N. Lu, X. Quan, J. Y. Li, S. Chen, H. T. Yu, and G. H. Chen, J. Phys. Chem. C **111**, 11836 (2007).
[25] H. Cordatos, D. Ford, and R. J. Gorte, J. Phys. Chem. **100**, 18128 (1996).
[26] V. Perebeinos, S.-W. Chanb, and F. Zhang, Solid State Commun. **123**, 295 (2002).