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Nanocrystals in compression: unexpected structural phase transition and amorphization due to surface impurities†

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We report an unprecedented surface doping-driven anomaly in the compression behaviors of nanocrystals demonstrating that the change of surface chemistry can lead to an interior bulk structure change in nanoparticles. In the synchrotron-based X-ray diffraction experiments, titania nanocrystals with low concentration yttrium dopants at the surface are found to be less compressible than undoped titania nanocrystals. More surprisingly, an unexpected $\text{TiO}_2(\text{II})$ phase ($\alpha\text{-PbO}_2$ type) is induced and obvious anisotropy is observed in the compression of yttrium-doped TiO_2 , in sharp contrast to the compression behavior of undoped TiO_2 . In addition, the undoped brookite nanocrystals remain with the same structure up to 30 GPa, whereas the yttrium-doped brookite amorphizes above 20 GPa. The abnormal structural evolution observed in yttrium-doped TiO_2 does not agree with the reported phase stability of nano titania polymorphs, thus suggesting that the physical properties of the interior of nanocrystals can be controlled by the surface, providing an unconventional and new degree of freedom in search for nanocrystals with novel tunable properties that can trigger applications in multiple areas of industry and provoke more related basic science research.

Introduction

Large surface-to-volume ratios and quantum confinement effects result in many unique physical and chemical properties of nanomaterials, such as ductility, strain-rate sensitivity, and chemical reactivity.¹ By means of the high free energy state of their interface and surface, nanomaterials have advanced many critical technologies in superconductors, catalysis, biology, energy storage, and information technology.^{1,3} Over decades, exploring the unique properties of nanomaterials has attracted a great deal of interest and has been the main research motivation for nanomaterials science and engineering.

Since a large fraction of atoms are on the surfaces, nanoparticles are often distinctive from their bulk counterparts. Previous efforts have been intuitively focused on tuning the surface structure by exterior environments, including water,⁴ surface stress,⁵ ionic salts,⁶ organic molecules,⁶ and nanoparticle

aggregation states.⁷ However, an intriguing out-of-the-box strategy would be to explore whether the bulk atomic arrangement in nanoparticles can be affected by the surface environments. Controlling the bulk properties of nanomaterials *via* surface environments is indeed far more than needed because this offers not only a relatively less explored approach for controlling material functions, but also a good opportunity for uncovering the fundamental physical and chemical mechanisms that control the bulk properties by just a small fraction of surface atoms. Therefore, in this article, using titania as an exploratory platform, we investigate the role of the surface state in the compression behavior of the host nanocrystals for exploring the correlation between the surface and bulk interior of the nanoparticles.

Titania is one of the most important inorganic materials and a well-studied model material. It has applications in many areas such as electrochemical dye solar cells, (photo)catalysts and so on.⁸ Nano-sized TiO₂ has many polymorphs that include rutile, anatase, brookite, fluorite, columbite, baddeleyite, and amorphous structures.⁹⁻¹¹ The thermodynamic properties of various nano-sized TiO₂ phases have been studied intensively based on both computational modeling and experimental investigations, from which it can be concluded that the phase stability is significantly affected by various system variables, such as temperature, pressure, particle dimension, morphology, and solution composition.^{3,7,12-14} Thus, if a rare polymorph can be stabilized by an easily achieved surface environment state such as surface impurity, it should provide an innovative approach to develop materials with tunable properties and unusual functions that can trigger applications in multiple areas of industry and provoke related basic science research.

Experimental

Undoped and yttrium doped TiO₂ nanocrystals were prepared using the sol-gel route, as described in detail in our previous work.^{12,13} A field-emission

transmission electron microscope (FEI Tecnai™ G2 20 TEM) was used to investigate the size distribution of undoped and yttrium doped TiO₂ samples. In our TEM measurements, the dispersed materials in ethanol were dropped onto holey carbon grids with a Cu support. EDX experiments were also performed here using the embedded function in a transmission electron microscope. Infrared spectroscopy experiments were performed at the U2A beamline, National Synchrotron Light Source (NSLS), Brookhaven National Laboratory (BNL). A symmetric DAC with a pair of 300 μm culets was used to generate a high pressure. A metal gasket was pre-indented to 50 μm in thickness, and then a hole with a diameter of 120 μm was laser-drilled to serve as the sample chamber. Pre-compressed powders and a ruby ball with a diameter of 10 μm were loaded in the chamber. The pressure was determined by the ruby luminescence method.¹⁵ DAC high-pressure angle-dispersive XRD experiments were carried out at the 12.2.2 beamline, Advanced Light Source (ALS), Lawrence Berkeley National Laboratory (LBNL), and at the 16BMD beamline, Advanced Photon Source (APS), Argonne National Laboratory (ANL). A focused monochromatic beam with a diameter about 25 μm and wavelength of 0.6199 Å or 0.4959 Å was used for the diffraction experiments. A Mar345 image plate was used to record the Debye diffraction rings of the samples. The 2D scattering images were integrated into 1D data within fit2d and the XRD patterns were fitted with refinement through the GSAS program package.¹⁶ High-pressure Raman spectroscopy measurements were conducted with a Renishaw Raman spectrometer and a 532 nm excitation laser. A 4 : 1 methanol-ethanol mixture was used as the pressure-transmitting medium.

Results and discussion

For this study, we used nano-TiO₂ with low concentration surface impurities of yttrium. Before compression, a spectrum of techniques including transmission electron microscopy (TEM), energy dispersive X-ray spectrometry (EDX), synchrotron X-ray diffraction (XRD), Raman spectra, and infrared (IR) spectroscopy, were performed to investigate the as-synthesized samples and the yttrium doped samples that were annealed at 400 °C for 2 h in air beforehand ([Fig. 1](#)).

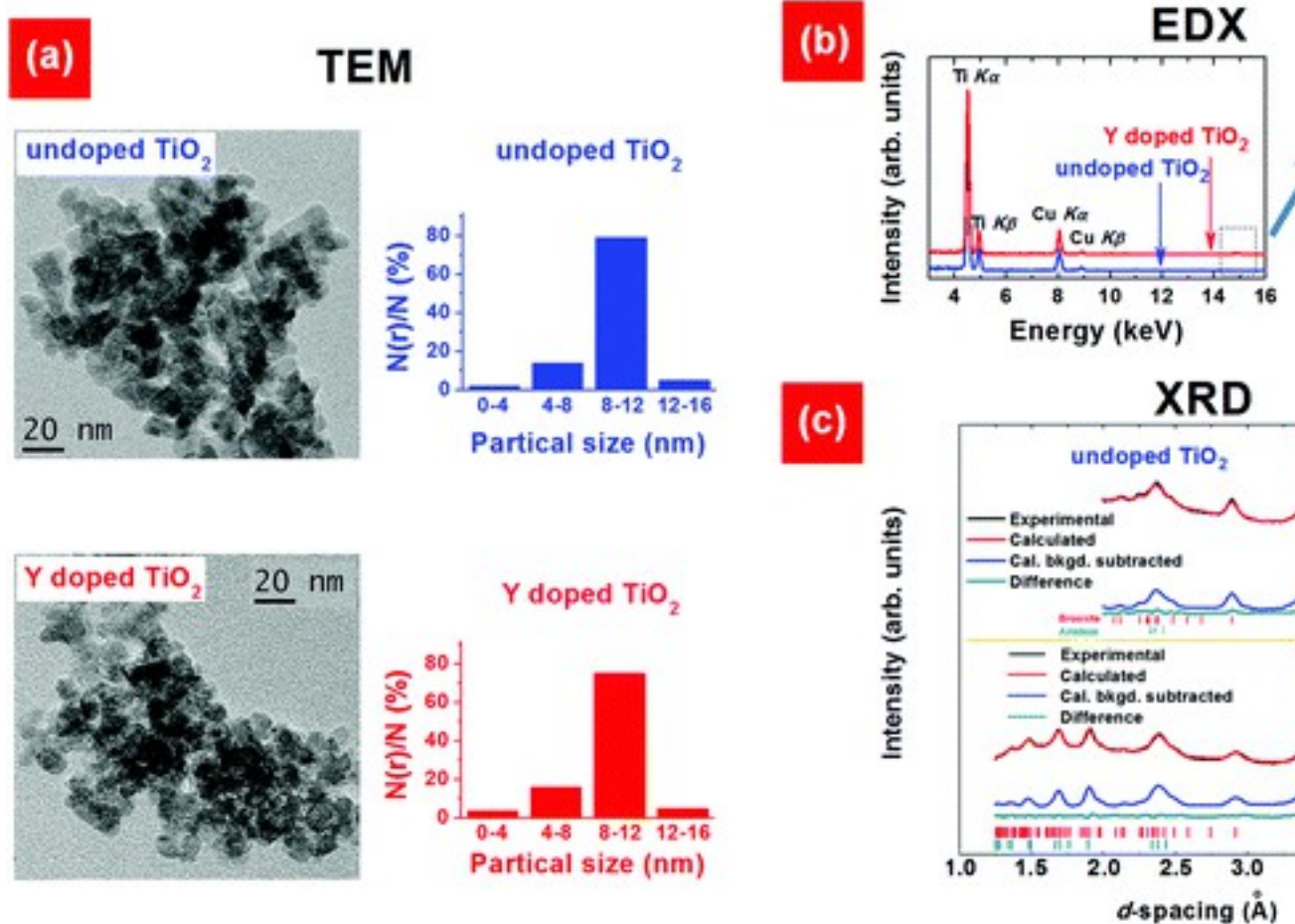


Fig. 1 Characterization of undoped and yttrium doped TiO_2 nanoparticles before compression. (a) TEM examining size distributions of both undoped and Y doped samples. The particle sizes fall in the narrow range of 8–12 nm, percentage of 79% and 75% for undoped TiO_2 and yttrium doped TiO_2 , respectively. (b) An Y : Ti atomic ratio of doped sample based on the EDX estimation. The detected Cu signal originates from the Cu TEM support (see ESI). The results of synchrotron XRD experiments indicate the mixed phases of brookite and anatase in both samples. The percentage of brookite in undoped and doped samples before compression is $\sim 66\%$ and $\sim 70\%$, respectively. Anatase is indicated by dark green ‘|’; the pink ones represent the brookite diffraction positions. The calculated spectra from the GSAS software package are given for comparison.

To examine the potential size effects in our doped and undoped samples, we used TEM imaging ([Fig. 1\(a\)](#)) to determine the average particle sizes of the TiO_2 nanoparticles. The TEM analysis of more than 100 undoped TiO_2 nanoparticles gave an average grain size of ~ 10 nm, almost the same as that of the yttrium doped samples ([Fig. 1\(a\)](#)). Moreover, both undoped and doped TiO_2 nanoparticles have nearly the same particle size distributions. Therefore, the contribution of the size effect to the observed property difference of the samples in this study is negligible.

EDX microanalyses confirm the presence of the yttrium impurities ($\sim 1\%$ atomic number percentage) ([Fig. 1\(b\)](#)). A previous study showed that yttrium existed in dispersed atoms on the TiO_2 surface.¹⁴ Although yttrium forms yttrium–oxygen clusters on the surfaces of the doped nanoparticles, it does not change the host phase state significantly under ambient conditions. The synchrotron XRD results indicate that brookite (*Pbca*) and anatase (*I4₁/amd*) phases coexist in both the undoped and yttrium doped samples ([Fig. 1\(c\)](#)). Characteristic XRD peaks of Y_2O_3 are not detected from yttrium doped samples due to the very small fraction of surface yttrium atoms. Also, Raman and IR spectroscopy measurements (see ESI Fig. S1 and S2†) show no major differences in the optical properties of the yttrium doped samples and the undoped samples, further supporting that yttrium is not incorporated into the nanoparticle interior but forms Y–O–Ti clusters at the particle surface.

In the high pressure synchrotron XRD experiments, obviously different compression behaviors of yttrium doped and undoped TiO_2 nanocrystals were observed. [Fig. 2\(a\) and \(b\)](#) show the pressure dependent XRD patterns for yttrium doped TiO_2 and several GSAS refinements at selected high pressures, respectively. Based on a series of GSAS refinement results, it has been found that at low pressures a $\text{TiO}_2(\text{II})$ phase ($\alpha\text{-PbO}_2$ structure, *Pbcn* space group³) is induced in yttrium doped TiO_2 samples, which can also be easily demonstrated from the (112) characteristic peaks of the $\text{TiO}_2(\text{II})$ phase highlighted in the green dash box in [Fig. 2\(a\)](#). In addition, for pressures higher than 11.4 GPa, the strength of a group of peaks (highlighted in the blue dash box, [Fig. 2\(a\)](#)) is obviously lower than that at lower pressures (highlighted in the red dash box, [Fig. 2\(a\)](#)), indicating the disappearance of a parent phase. Our further GSAS refinements concluded that the induced $\text{TiO}_2(\text{II})$ phase coexists with other two parent phases brookite and anatase, and this multi-phase structure persisted up to 11.4 GPa in compression,

above which the three phases merged into the two phases of brookite and $\text{TiO}_2(\text{II})$, followed by an amorphization state above 20 GPa suggested by the disappearance of Bragg diffraction peaks.

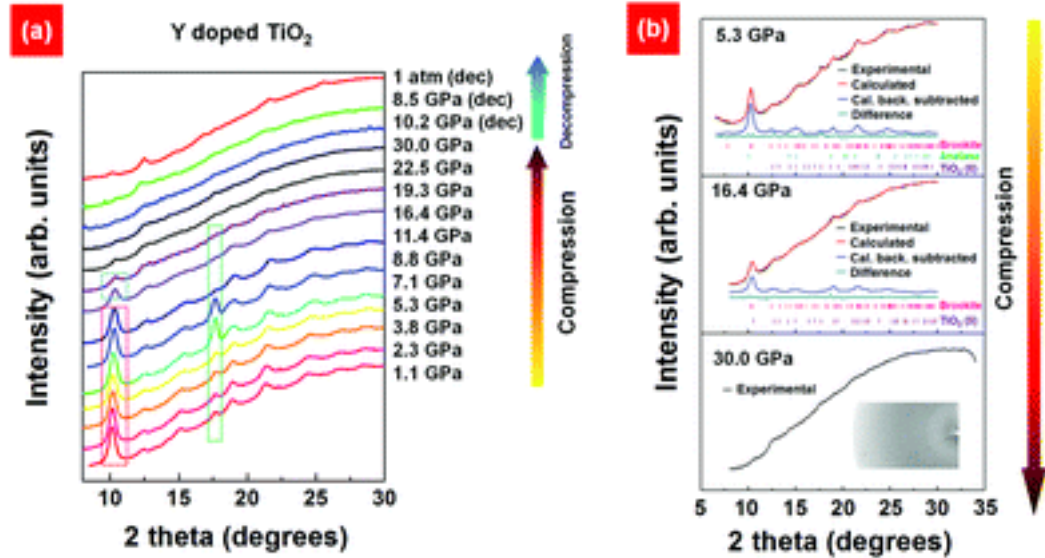


Fig. 2 *In situ* high pressure XRD characterization for yttrium doped TiO_2 nanoparticles. (a) Pressure dependent XRD patterns in compression up to 30 GPa and in decompression down to 1 atm. (b) Selected GSAS Rietveld pressure XRD at the low and high pressure phases in compression. Anatase reflections are indicated by dark green, purple ones represent the brookite and $\text{TiO}_2(\text{II})$ diffraction positions, respectively. Insets clearly show the absence of diffraction rings in the yttrium doped samples at 30 GPa.

The modification effect of surface doping on the surface energy should be considered for understanding the appearance of an unexpected $\text{TiO}_2(\text{II})$ phase. The phase stability of nano titania polymorphs was demonstrated to be particle size dependent associated with surface free energy, and consequently the $\text{TiO}_2(\text{II})$ phase was believed to be thermodynamically stable only for crystallites with sizes >50 nm at $P > 5$ GPa.¹⁷ Thus, such a rare titania polymorph should not exist in small-sized particles at very low pressures. As shown in Fig. 1(a), the average size of our samples is only ~ 10 nm, and the surface energy of the nanoparticles in these samples should be much higher than that of 50 nm sized particles if the difference in the surface states is not considered, as would be inferred from the size-dependence of the surface energy of anatase.¹⁸ It has been shown that there is a ~ 0.2 J

m^{-2} difference in the surface free energy between undoped titania of 10 nm and 35 nm.¹⁸ However, such a gap can be filled by surface state modification since surface adsorption generally lowers substrate surface energy.³ For the present system, a previous investigation has shown that the surface energy of the yttrium doped anatase nanoparticles is $\sim 0.94 \text{ J m}^{-2}$,¹⁴ much lower than the value of the undoped one (2.1 J m^{-2}).¹⁹ This is consistent with the lower lattice energy of Y_2O_3 ($6353.5 \text{ kJ mol}^{-1}$) compared to that of TiO_2 ($12\,150 \text{ kJ mol}^{-1}$), which can lead to lower surface energy for titania faces terminated by yttrium vs. titanium sites coordinated by 6 oxygen atoms.²⁰ Thus, the significantly lowered surface free energy due to yttrium doping plays the same role in reducing the total system energy as particle growth in the phase stability of the $\text{TiO}_2(\text{II})$ phase in compression.

The pressure-driven structural evolution and phase transitions of yttrium doped titania are strongly contrasted to the compression behavior of undoped samples. The pressure dependent XRD patterns for undoped TiO_2 and several GSAS refinements at selected high pressures are given in [Fig. 3\(a\) and \(b\)](#), respectively. The significant decrease in the peak strength above 14.5 GPa (highlighted in the blue and red boxes in [Fig. 3\(a\)](#)) suggests a phase transition, which has been further demonstrated to be a gradual anatase $\rightarrow$ brookite phase transition around 12–15 GPa by GSAS refinements. The brookite phase maintains stability up to the highest applied pressure in this investigation, ~ 30 GPa. The anatase $\rightarrow$ brookite phase transition at this pressure was not experimentally detected in titania nanoparticles with the pure anatase phase.^{17,21} Previous investigations revealed that nanocrystalline brookite could develop at some $\{112\}$ twin surfaces of anatase, where nucleation of brookite initiated due to the fact that the $\{112\}$ twin surfaces contain a unit cell of brookite,²² then the anatase $\rightarrow$ brookite phase transition observed in the present study can be

explained by the existence of many brookite nucleation sites induced by the large phase ratio of brookite in the mixed-phase.

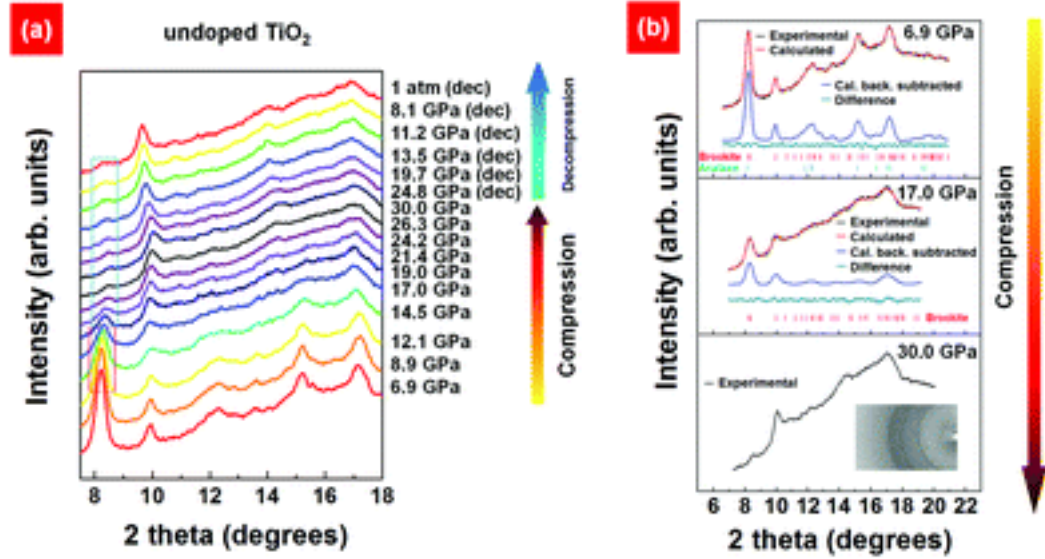


Fig. 3 *In situ* high pressure XRD characterization for undoped TiO₂ nanoparticles. (a) Pressure dependent angle diffraction patterns in compression up to 30 GPa and in decompression down to 1 atm. (b) Selected GSAS Rietveld pressure XRD at the low and high pressure phases in compression. Anatase and brookite reflections are indicated by 'A', respectively. Insets clearly show the presence of crystalline diffraction rings in the undoped samples at 30 GPa.

Another interesting observation is the pressure induced amorphization (PIA) in the yttrium doped sample occurring at ~19.3 GPa in compression. This finding indicates that the surface doping promotes the PIA. The PIA is attributed to the fact that in the doped samples the Y-O clusters increase the degree of disorder of the particle surface since the elongated Y-O bonds modify the local structures.¹⁴ The Y-O clusters could be the precursor of the amorphousness and induce the fluctuation in the structure and/or atom concentration, promoting the high-density driven-frustration of stable packing of the crystal, and then the PIA is thermodynamically favored at high pressures. By comparing the XRD patterns before compression (see Fig. 1(c)) and after decompression (see Fig. 2(a) and 3(a)) for both yttrium doped and undoped TiO₂ nanocrystals, it can be concluded that the phase transitions are irreversible in high pressure compression, while reversible in low pressure compression confirmed by *in situ* high pressure Raman results (see ESI Fig.

S3†). The phase transitions in compression and decompression for yttrium doped and undoped TiO₂ are summarized in Fig. 4(a) and (b), respectively.

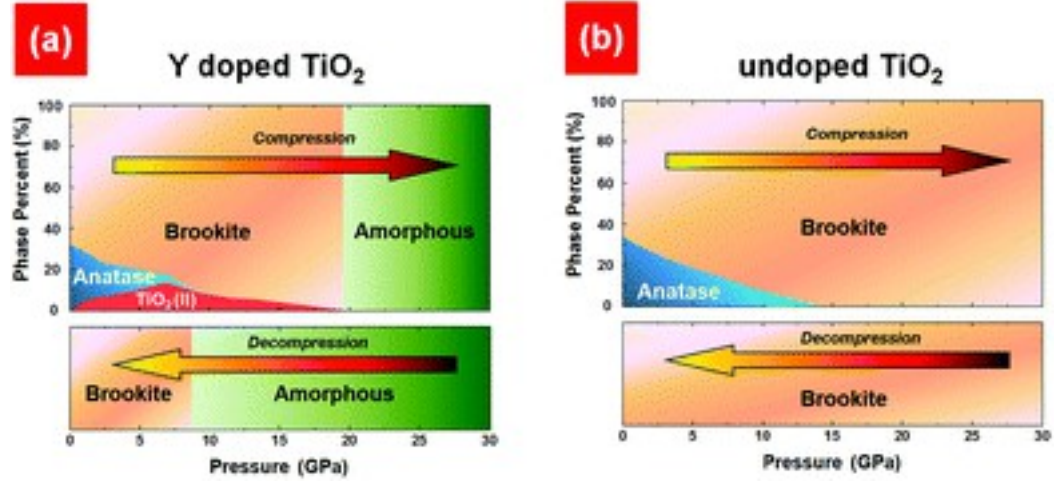


Fig. 4 Summary of the pressure–structure relationship for undoped and yttrium doped TiO₂ nanoparticles investigated. (a) and (b) show the high pressure structural evolution for yttrium doped and undoped TiO₂ nanoparticles, respectively. As pressure increases, anatase → brookite phase transition occurs in both samples, which is reversible at low pressures (confirmed by high pressure Raman spectra, see ESI Fig. S3†) but irreversible at high pressures. In addition, pressure induced amorphization was only observed in the yttrium doped sample, which is partly reversible.

In the high pressure experiments, obvious anisotropy in compressibility was observed in yttrium doped TiO₂ nanocrystals (Fig. 5). As shown in Fig. 5(a) and (b), the Bragg diffraction (112) reflection of the TiO₂(II) phase exhibited a maximum value in the peak intensity at 7.1 GPa, as also seen from the phase content evolution of TiO₂(II) obtained by GSAS refinements. The full width at half maximum (FWHM) of the peak of TiO₂(II) was found to be significantly broadened on increasing pressure (see Fig. 5(c)), indicating pressure-induced amorphization in nanocrystals (summarized in Fig. 4(a)). In addition, the TiO₂(II) (112) peak shifted very slightly with the pressure (Fig. 5(a) and (d)), indicating that the *d*-spacing decreased little in compression, which seems unusual. The *d*-spacing of TiO₂(II) (orthorhombic) can be calculated from

$$\frac{1}{d_{(112)}^2} = \frac{1}{a^2} + \frac{1}{b^2} + \frac{4}{c^2}$$

here a , b , and c are the three lattice parameters. Considering the relatively unchanged $d_{(112)}$, we infer that in compression, the three lattice parameters changed such that the right side of [eqn \(1\)](#) coincidentally remained almost unchanged. Refinements of XRD data yield changes of the unit cell parameters along all three directions are shown in [Fig. 5\(e\)](#). The lattice parameter c of the $\text{TiO}_2(\text{II})$ phase expanded $\sim 1.2\%$, whereas the parameters a and b contracted $\sim 3\%$ and $\sim 1.4\%$, respectively. Such a difference in the incompressibility in a , b , and c suggests the anisotropic compression behavior of $\text{TiO}_2(\text{II})$ nanoparticles. This can be understood by the inherent $\text{TiO}_2(\text{II})$ structure, in which the $\{001\}$ plane is more closely packed than the $\{100\}$ and $\{010\}$ planes, which can be directly described by [Fig. 6](#). By fitting the experimental data with the Birch relation,²³ as shown in [Fig. 5\(f\)](#), the bulk modulus of the nano-sized $\text{TiO}_2(\text{II})$ phase, 319 GPa, was obtained. It is $\sim 20\%$ higher than that of bulk $\text{TiO}_2(\text{II})$ (253–258 GPa),^{24,25} which can be attributed to the surface tension effects and dislocation behavior. For our ~ 10 nm sized nanocrystals, the surface to volume ratio is definitely much higher than bulk materials which can induce strong surface tension effects and then significantly increases the measured elastic modulus.²⁶ In addition, it has been experimentally demonstrated that the bulk modulus of nanocrystalline titania has a maximum at a particle size of 15 nm,²⁷ slightly higher than our samples. Such a size-dependent elasticity of nanocrystalline titania was believed to be inherently correlated with the dislocation density, which can be understood by elastic stiffening conferred by the dislocation network increase as the size decreases until the particles become too small (less than few nanometers) to sustain high dislocation concentrations.²⁷

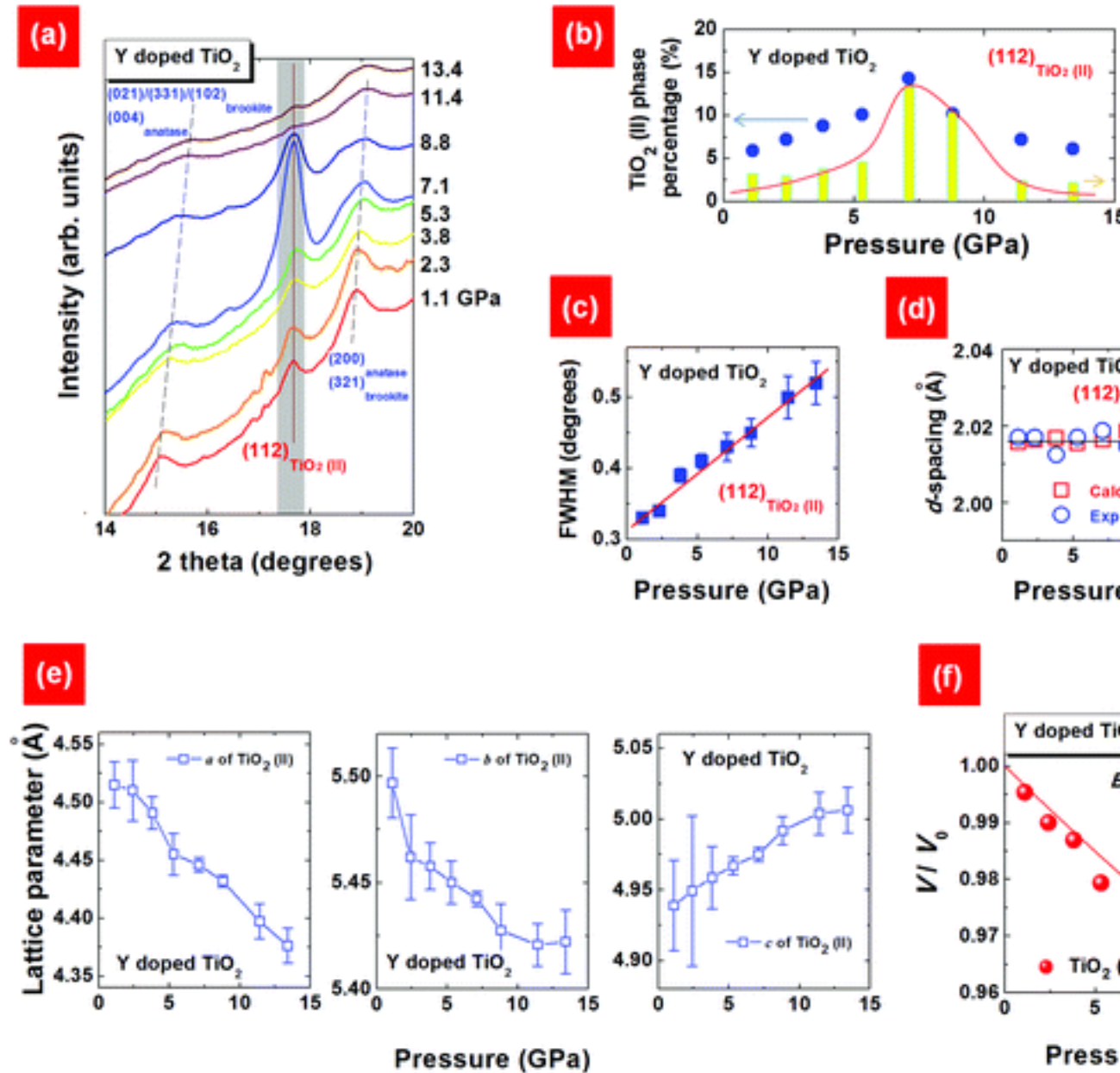


Fig. 5 High pressure TiO₂(II) phase in yttrium doped TiO₂ nanoparticles. (a) The representative diffraction pattern of TiO₂(II) in compression. Compared with other peaks, the (112) peak of the TiO₂(II) phase shifts much less upon compression, indicating an anisotropic compression behavior. (b) Pressure dependence of normalized intensity of the peak (112) of TiO₂(II) phase. (c) Percentage of the TiO₂(II) phase percentage obtained from the GSAS refinement. (d) Obvious increase in the full width at half maximum of the peak (112) suggests the pressure-induced amorphization in the nanocrystals. Using GSAS Rietveld refinement of the diffraction reflections, including TiO₂(II) (112) of yttrium doped nanocrystals (d). Then, the lattice parameters were obtained (e). The low XRD intensities at higher pressures do not allow for reliable structure refinement. (f) Lower volume of yttrium doped titania, indicated by a higher bulk modulus of 319 GPa. The bulk modulus B_0 was obtained by fitting the data to the Birch-Murnaghan equation of state.

$$P(V) = \frac{3}{2} \left[B_0 \left(\frac{V_0}{V} \right)^{\frac{7}{3}} - \left(\frac{V_0}{V} \right)^{\frac{5}{3}} \right] \left\{ 1 + \frac{3}{4} (B' - 4) \left[\left(\frac{V_0}{V} \right)^{\frac{2}{3}} - 1 \right] \right\}$$

with the Birch relation

, where we assume

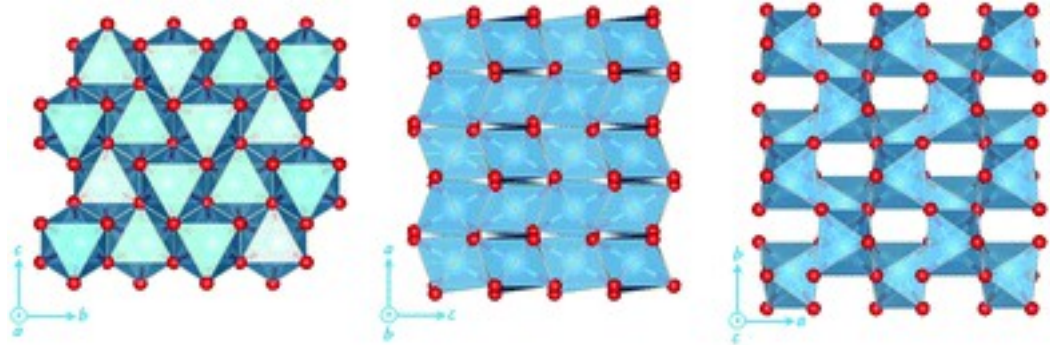


Fig. 6 Structure of the $\text{TiO}_2(\text{II})$ phase viewed along the (100), (010), (001) directions.

Surface doping also leads to an increase in the bulk modulus of the parent brookite phase. Based on the results of refinements on brookite for both yttrium and undoped samples, lattice constants, volume compressibility, and bulk moduli were obtained, as shown in [Fig. 7\(a\) and \(b\)](#). The bulk modulus of yttrium doped brookite was found to be 256 GPa, ~18% higher than that of undoped brookite (217 GPa), which could be attributed to surface doping. It is known that the density of bulk brookite $\sim 4.133 \text{ g cm}^{-3}$ is lower than that of the bulk $\text{TiO}_2(\text{II})$ phase, $\sim 4.336 \text{ g cm}^{-3}$.²³ Such a difference was also confirmed in the present investigation, as shown in ESI Fig. S4,[†] from which one can see for yttrium doped nanoparticles that the density of the induced $\text{TiO}_2(\text{II})$ phase is always higher than that of the brookite parent phase at all measured pressures. In addition, considering the PIA occurred in yttrium doped titania, the surface shell will get stiffer due to the low density amorphous to high density amorphous transformation (LDA $\rightarrow$ HDA) under compression compared to the nanocrystalline core.^{17,28} Consequently, the pressure induced states with high densities, $\text{TiO}_2(\text{II})$ and/or HDA, could support more applied pressures and cause a so-called “nano arching effect”,²⁸ and then lower the core pressure for titania grains with low density.

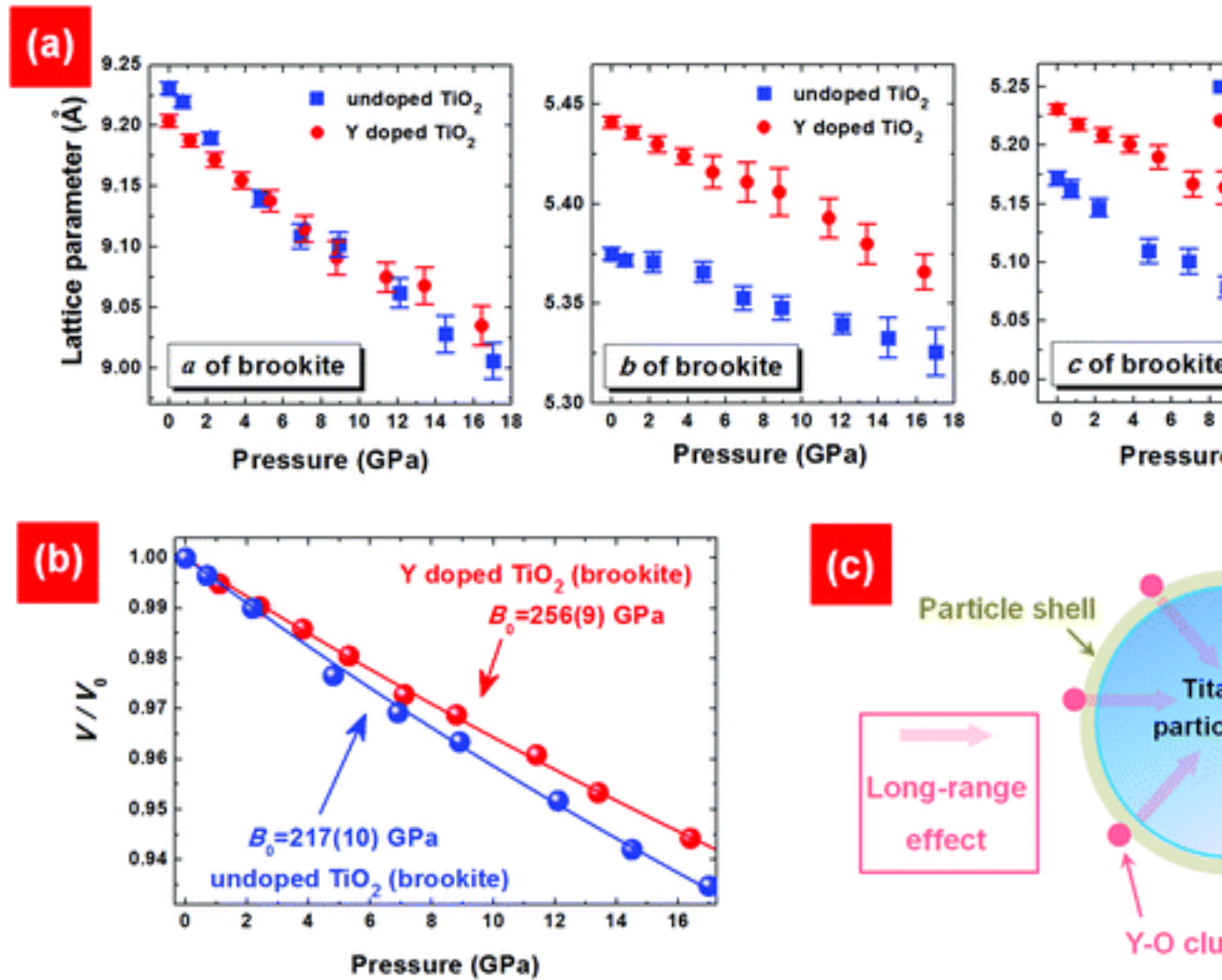


Fig. 7 Parent brookite phase in yttrium doped and undoped TiO₂ nanoparticles at pressures. (a) Pressure-dependent lattice parameters of the brookite phase of undoped and yttrium doped TiO₂ nanoparticles. (b) Relative unit cell volume of doped (red) and undoped (blue) samples as a function of pressure. The solid lines are the fitted results according to the Birch equation of state, from which one can obtain the higher bulk modulus ($\sim 256(9)$ GPa) of the doped sample and the undoped sample, $\sim 217(10)$ GPa. (c) Schematic of yttrium-doped titania nano brookite particles.

Conclusions

In summary, we demonstrate that the low concentrations of impure ions that are chemically bonded on the surface of TiO₂ nanoparticles dominate many structural anomalies as exemplified by the pressure-induced formation of an un-reported TiO₂(II) phase and a PIA, where the former is associated with the reduced surface free energy, while the latter is attributed to the amorphous precursor replaced by the Y-O clusters. In addition, strong anisotropic characteristics and mechanical stiffening were also observed due to the modification of the surface environment for nanoparticles. This study addresses the questions of what and how the structural anomaly is triggered by surface impurities at the nanoscale, which is significant in quest for

controlling the interior from the surface of nanocrystals through a relatively long-range interaction as described in [Fig. 7\(c\)](#) schematically. The structure and potential use of nanoparticles seem to be more complicated than previously expected as evidenced by the critical role of surface doping reported herein. In addition, previous investigations have confirmed that doped TiO₂ with various doping concentrations exhibit distinct structural and functional properties.²⁹ Thus, to further understand the surface modified effect, the influence of the doping concentration on the structure stability of nanocrystals under high pressure should be carried out in the near future. Our work provides a basis to interpret pressure effects on the physical properties of surface modified nanocrystals and we suggest the observed phenomenon as a new degree of freedom in the search for nanocrystals with a novel compression response that is particularly attractive in light of the understanding of solid state physics and chemistry.

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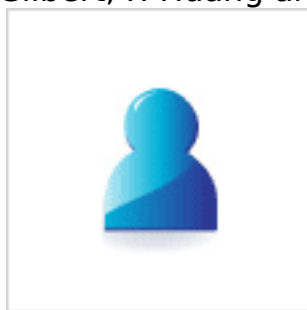
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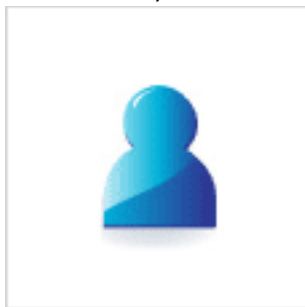
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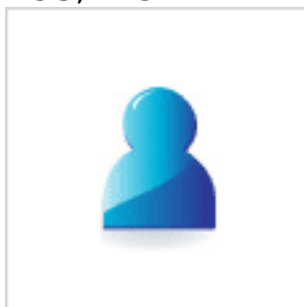
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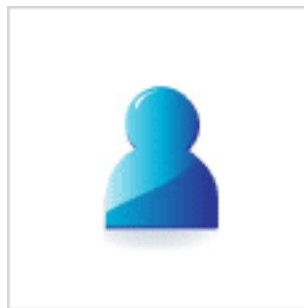


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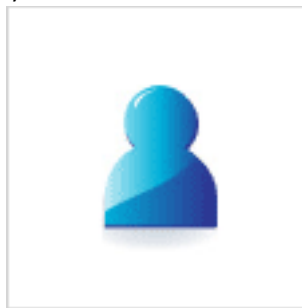
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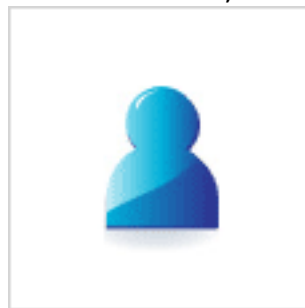
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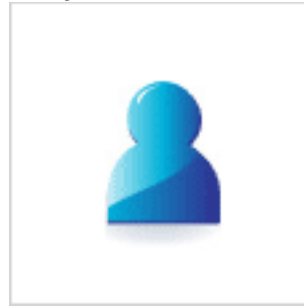
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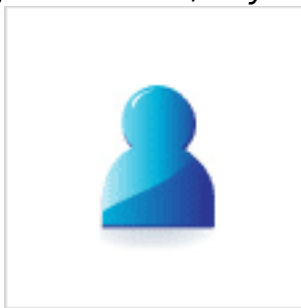
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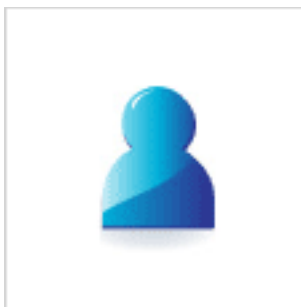
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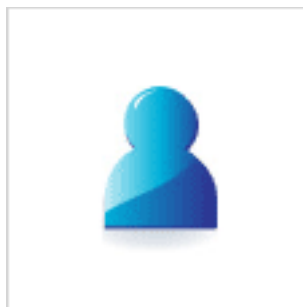
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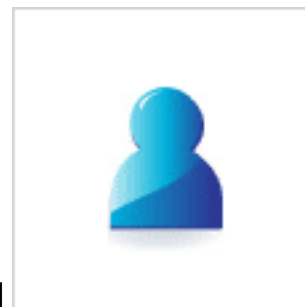


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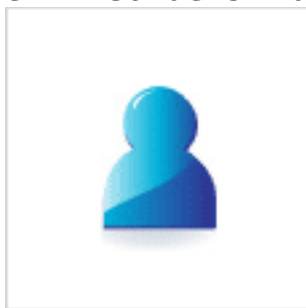


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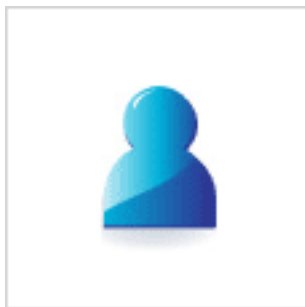
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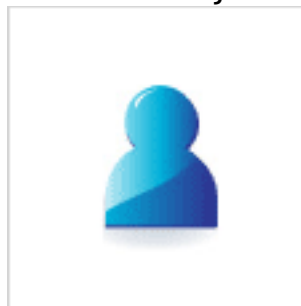
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