Atomistic Mechanisms of Ultralarge Bending Deformation of Single-Crystalline TiO$_2$-B Nanowires

Qiong Liu,$^a$ Yihan Nie,$^a$ Haifei Zhan,$^a$ Huaiyong Zhu,$^a$ Ziqi Sun,$^a$ John Bell,$^{a,b}$ Arixin Bo,$^{a,*}$ andYuantong Gu$^{a,*}$

$^a$School of Chemistry, Physics and Mechanical Engineering, Queensland University of Technology, GPO Box 2434, Brisbane, QLD 4001, Australia

$^b$School of Chemistry, Physics and Mechanical Engineering, University of Southern Queensland, 37 Sinnathamby Blvd, Springfield Central, Ipswich, QLD 4300, Australia

Abstract

Titanium dioxide (TiO$_2$) nanowires (NWs) are usually considered to be brittle semiconductor materials, which limits their use in strain-related applications, even though they are already widely applied in various fields. Based on observations using an in situ transmission electron microscopy (TEM) method, we find, for the first time, that individual crystalline TiO$_2$ NWs with a bronze phase (TiO$_2$-B) can exhibit an ultralarge elastic bending strain of up to 18.7%. Using an in situ atomic-scale study, the underlying mechanisms of the ultralarge bending deformation of TiO$_2$-B NWs under the <111>{100} system are revealed to be governed by lattice shear and rich dislocation movements; the lattice shearing is supported by numerical simulations. Locally, large-scale sheared lattices with a shear strain of up to 10.7% can be observed in a bent NW. It is believed that the large-scale lattice shearing deformation offers the NW the ability to absorb a large bending energy so that fast dislocation aggregation and propagation are avoided. Therefore, the TiO$_2$-B NWs can endure an ultralarge bending strain without crack formation or amorphization. However, it is found that the lattice-shear governed bending mechanism is not applied in the <010>{100} system. These results are able to provide more opportunities for the strain engineering of TiO$_2$ NWs and also help to promote the potential applications of TiO$_2$-NWs-based flexible devices.
Introduction

Titanium dioxide (TiO₂) has received tremendous attention in the past few decades due to its low toxicity, favorable chemical stability, cost-efficiency, and unique optical and electrical properties. In particular, crystalline TiO₂ nanowires (NWs) possess a large specific surface area and offer a direct electrical channel for electrons, making them excellent building blocks for use in energy harvesting, electronics, batteries, sensors, and biorelated systems. However, TiO₂ NWs are compelled to withstand mechanical strain when used in applications that involve deformation, such as nanoelectromechanical configurations. Under this circumstance, the elasticity and deformability of crystalline TiO₂ NWs plays an important role in maintaining the reliability and functionality of working systems. Thus, it is crucial to elucidate the mechanical behavior of crystalline TiO₂ NWs. Being a member of the ceramic material family, crystalline TiO₂ is considered brittle; however, previous reports show that brittle materials can endure large mechanical strains when their dimensions are reduced to the nanoscale, showing higher elasticity, or demonstrate brittle-to-ductile transition at room temperature. For instance, an ultralarge local tensile strain of up to 9% was demonstrated on diamond needles under fully reversible elastic deformation.

Typically, the enhanced elasticity of NWs compared to their bulk counterparts is usually attributed to the size effect (increased surface atom ratio), especially when the internal defects are scarce. On the other hand, due to the reduced material size, the differential of the defect quantity can result in fluctuating elastic moduli. More intriguingly, it is found that during the deformation of NWs, the aggregation of dislocations can be mitigated so that amorphization or crack formation in the NWs can be hindered even with a large elastic strain. In some other cases, mechanical energy can also be dissipated in strained lattices, which allows the NWs to withstand high-deformation. Nevertheless, the lattice shear accompanying deformation will be probably terminated by inelastic dislocation and/or other defect activities, such as twinning. Consequently, it is difficult to realize reversible lattice shear strain beyond 8%.

In terms of the mechanical characterization of TiO₂ NWs, previous research has mainly focused on studying the Young’s modulus and strength using scanning electron microscopy (SEM) or numerical investigation. Recently, we launched an atomic-scale study on the bending behaviors of individual anatase/bronze dual-phase TiO₂ NWs. Large bending deformation of anatase/bronze dual-phase TiO₂ NWs was found, which is due to the dislocation activity, phase transition, and small deformation twinning. However, the mechanical properties of single crystalline TiO₂ NWs at the atomic scale are still rather limited and unclear. Since TiO₂ possesses various single-crystalline structures (anatase, rutile, bronze, and brookite), the reveal of structural
evolution during deformation for single-crystalline TiO$_2$ NWs remains a challenge and requires an enormous effort.

In this paper, single-crystalline bronze TiO$_2$ (TiO$_2$-B) NWs are synthesized by a facile hydrothermal method. *In situ* bending tests for individual TiO$_2$-B NWs are carried out using transmission electron microscope (TEM) by using a colloidal thin film,$^{30}$ which particularly allows for atomically observing the lattice evolution during deformation. Intriguingly, a TiO$_2$-B NW can recover after experiencing an ultralarge elastic bending strain of up to approximately 18.7%. To the best of our knowledge, such a large value for elastic bending strain has not been experimentally reported for TiO$_2$-B NWs. Further atomic study shows that the ultralarge bending behavior of the TiO$_2$-B NWs is attributed to dislocation activities and lattice shear. On the one hand, Large-scale sheared lattices with a rather large shear strain of 10.7% can be observed in the $<111>\{100\}$ shear system with the bending strain of 9.5%. The lattice-shearing phenomenon is verified by subjecting TiO$_2$ NWs to bending deformation by molecular dynamics (MD) simulations. The large-scale sheared crystalline structure for the TiO$_2$-B NWs provides an effective approach to dissipate mechanical energy. On the other hand, however, it is found that the lattice-shear governed bending mechanism is not applied in the $<010>\{100\}$ system. Under the $<010>\{100\}$ system, large bending strain of 10% for a NW can be observed, which is only related to rich dislocation activities. The anisotropy of the bending mechanisms for TiO$_2$-B NWs may provide new insights for NW strain engineering.

**Methodology**

**Synthesis of TiO$_2$-B NWs.** Single-crystalline TiO$_2$-B NWs were synthesized by a hydrothermal method.$^{31}$ Typically, 2.4 g of TiO$_2$ P25 powder was added into 80 mL of 10 M NaOH aqueous solution and stirred vigorously for 1 h. Then, the precursory suspension was placed into a 120 mL Teflon-lined autoclave. The autoclave was sealed and kept at 200 °C for 48 h. The product was washed with dilute HCl solution (0.01 M) to obtain the protonated titanate NWs, and then washed by deionized water and ethanol several times until the pH value was reduced to ~7. After drying at 80 °C for 24 h, the product was annealed at 500 °C in atmosphere for 2 h in a muffle furnace.

**Characterization.** The crystalline phase of the sample was defined by the X-ray diffraction (XRD) pattern collected through a Philips PANalytical X’Spert pro diffractometer equipped with a graphite monochromator with Cu Kα radiation at 40 kV. The morphology was characterized by a field-emission SEM (JEOL JSM-7001F, Japan) and a TEM (JEOL 2100, Japan). High-resolution TEM (HRTEM) was used to analyze the crystalline structure.
**In situ bending tests.** In situ bending tests for individual TiO$_2$-B NWs were performed using a TEM with a ± 20° double-tilt holder following a reported method.$^{30,32,33}$ Briefly, a colloidal carbon film attached onto a TEM Cu grid was gently scratched by a sharp needle, where the as-prepared NWs were then scattered. An external mechanical force was applied to the NWs through irradiation of the colloidal film by an electron beam. The bending deformation was conducted at a low strain rate of approximately 10$^{-5}$/s. Direct electron beam irradiation of the NWs was avoided except during observation. When capturing images, the electron beam dose was kept around a level of approximately 3 × 10$^{19}$ e/(cm$^2$ s), which minimized the thermal effect.$^{34}$

**Geometric phase analysis.** The lattice strain mapping was conducted using the geometric phase analysis (GPA) method, which can map the strain distribution from HRTEM images.$^{25,35,36}$ This method is based on combining real-space and Fourier-space information. Two basis reciprocal lattice vectors are determined in the Fourier transform of a reference HRTEM image to calculate the phase images. Then, the distortion of the lattice can be calculated. The shear strain for a distorted lattice follows by numerical differentiation, $\varepsilon_{xy} = \frac{1}{2} \left( \frac{\partial u_x}{\partial y} + \frac{\partial u_y}{\partial x} \right)$.

**MD simulation methods.** The bending mechanisms of TiO$_2$-B NWs are further studied by MD simulations using the large-scale atomic/molecular massively parallel simulator (LAMMPS). The third-generation charge-optimized many body (COMB3) potential is used for the bending simulations.$^{37}$ The TiO$_2$-B NW model is constructed along the <010> axial direction (growth direction) with the length of 44 nm and the diameter of 6 nm. The simulated bending tests are performed in a quasi-static manner.$^{38,39}$ The bent NWs with the specific bending strains are initially generated by the codes, respectively. The bent NWs are constrained by the repulsive walls to maintain the bending deformation during energy minimization. The Hessian-free truncated Newton algorithm is adopted to find the configuration with the local minimum energy state. The force of each atom meets the tolerance of 1 × 10$^{-10}$ eV/Å after energy minimization.

**Results and discussion**

**Structural characterization**

The XRD pattern for the product is depicted in Figure 1a. All diffraction peaks are well assigned to monoclinic (C2/m) TiO$_2$-B (JCPDS 46-1237). Figure 1b shows the SEM image of the sample, from which the NWs are measured to be approximately several-micrometer long with a diameter ranging from 20 nm to 150 nm. A diameter larger than 150 nm leads to belt-like NWs. The morphology and crystalline structure of the NWs is further confirmed by TEM. Figure 1c shows a low-magnification TEM image of a typical NW with a diameter of ~80 nm. The selected area electron diffraction (SAED) pattern (inset, Figure 1d) for the NW displays a single set of diffraction
spots, which indicates the single-crystalline nature of the as-synthesized TiO$_2$-B NWs. The SAED pattern is indexed to the TiO$_2$ bronze phase viewed along the [001] zone axis, from which the NW growth direction can be defined along the <010> direction. The corresponding HRTEM image is shown in Figure 1d. The marked $d$-spacings of 0.59 nm and 0.36 nm are in good agreement with those for the (200) and (110) planes of TiO$_2$-B, respectively, with an angle of approximately 73° in between the two planes. The white dots are the projections of the TiO$_6$ octahedra. As shown in the schematic crystal structure of TiO$_2$-B viewed along the [001] direction (Figure 1e), TiO$_6$ octahedra build up zigzag strips along the [010] zone axis. The yellow dots that represent the TiO$_6$ in the box well illustrate the framed area in Figure 1d.

![Figure 1](image1.png)

**Figure 1.** The structural information of the as-prepared TiO$_2$-B NWs. (a) XRD pattern, (b) SEM image, (c) low-magnification TEM image, and (d) HRTEM image (inset: SAED pattern) of TiO$_2$-B NWs. (e) A schematic crystal structure of TiO$_2$-B viewed along the [001] direction. The blue balls and red balls represent Ti and O, respectively. Scale bar, 1 μm (b), 200 nm (c), 2 nm (d).

**In situ bending deformation**

An ultralarge elastic bending strain of the TiO$_2$-B NWs was revealed by in situ TEM bending tests. During the bending process, the NW might be tilted or rotated out of plane. To avoid this situation and ensure the accuracy of the observation, the viewing direction of the most strained segment was held constant by tilting the TEM holder. Figure 2a-e exhibits a continuous bending process for an individual NW with the diameter of ~100 nm. The local bending strain $\varepsilon_M$ was determined using the radius of the bending curvature $\rho$ and the formula, $\varepsilon_M = r/\rho$, as shown in the inset of Figure 2a. It is clearly seen that the radius of the bending curvature decreased gradually, corresponding to an increase in bending strain from 0.4% (Figure 2a) to an ultralarge value of 18.7% (Figure 2e). To be noted that the initial strain of the NW was induced by the shrinkage of the nearby broken colloidal carbon film under the irradiation of the electron beam.
when capturing the TEM images. The same situation also happened on the NWs in the following contents. After the NW was released, it snapped back immediately and showed a straightforward feature, as shown in Figure 2f. Neglectable residual inelastic strain was observed in the most strained segment (indicated by the white arrow), suggesting a large bending elasticity. However, it can be observed that the free segment in the circled area in Figure 2e had an apparent defocus feature, indicating the occurrence of bending out of plane of this segment. To rule out the possibility that the NW recovery from bending might be a visually straightening caused by rotating or tilting out of plane, the lengths of the segment between one end of the NW and a marker during bending and after releasing (dashed lines) were measured. As shown in Figures 2e and f, the lengths were measured to be nearly the same, which are 5.63 μm and 5.73 μm, respectively. The bending elasticity was also illustrated by the absence of residual strain in another NW (most strained segment indicated by the arrow) with a diameter of 110 nm before and after the release from the mechanical constraint (Figure S1). Generally, ceramic NWs that contain both ionic and covalent bonds tend to be fractured or decrystallized, which results from scarce dislocation slippage.\textsuperscript{16,40,41} Given that TiO$_2$ contains not only Ti-Ti ionic bonds but also Ti-O covalent bonds,\textsuperscript{28} it is speculated that the high Peierls potential can limit the dislocation slippage. Consequently, dislocations are most likely to aggregate under external loading, resulting in the formation of lattice disorder or cracks in TiO$_2$. However, the distinctive elastic bending behavior of individual TiO$_2$-B NWs deviates from the fundamental knowledge of the mechanical properties of most studied ceramic NWs.

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{figure2.png}
\caption{\textit{In situ} bending process of a TiO$_2$-B NW. (a-e) A series of low-magnification TEM images of a bent NW with bending strain increasing from 0.4\% to 18.7\%. (f) low-magnification TEM image of the NW after it was released. Inset shows the SAED pattern of the most strained area pointed by the arrow. The lengths of the segment between the end of the NW and the marker in (e) and (f) are denoted by $L$ and $L'$. Scale bar, 1.5 μm.}
\end{figure}

\textbf{Bending mechanisms}
When an NW is subjected to bending deformation, the strain distribution along the radial direction is not uniform. Theoretically, the stress near the tensile and compressive surfaces is always larger than that in the neutral part. Consequently, bending test is an effective method to study the strain-dependent structure evolution of one-dimensional (1D) nanostructures.\textsuperscript{17,41} To gain atomistic insight into mechanisms of the large-bending deformation of the TiO\textsubscript{2}-B NWs, \textit{in situ} TEM tests at the atomic scale were carried out. The \textit{in situ} observation of the dislocation activities in a bending TiO\textsubscript{2}-B NW with a diameter of ~29 nm viewed along the [0\overline{1}1] direction is shown in Figure 3. HRTEM images of the same region at the bottom of the NW that is framed in the corresponding low-magnification TEM images (Figure 3a and b) were taken at a time interval of approximately 300 s, respectively, with bending strain increased from 1.2\% to 2.4\%, as shown in Figure 3c and d. With a bending strain of 1.2\% (Figure 3c), three dislocations (marked by “\textbullet”) were observed in the viewing region, with one lying in (\overline{1}1\overline{1}) planes (“1”) and two in (100) planes (“2” and “3”). When the bending strain increased to 2.4\%, dislocation “1” moved down across several (100) planes; dislocation “3” moved away from the viewing region while dislocation “2” remained stationary. This indicates that at a low bending strain, the bending deformation of TiO\textsubscript{2}-B NWs are accompanied with dislocation motions.

\textbf{Figure 3.} In situ observation of dislocation movements during the bending deformation of the TiO\textsubscript{2}-B NW. Low-magnification TEM images of the NW with the bending strain of (a) 1.2\% and (b) 2.4\%. (c) and (d) are HRTEM images of the same framed region in (a) and (b), respectively. Scale bar, 200 nm in panels a and b; 5 nm in panels c and d.

To better observe and understand the large bending deformation, a thicker NW with a diameter of 90 nm was conducted the \textit{in situ} bending test. The bending process for the NW is shown in Figure 4a-c, with the bending strain increased from 3.4\% to 5.9\%, and then to 8.5\%. Figure 4d shows the enlarged TEM image captured from the marked square in Figure 4a, showing that the bending configuration is viewed along the [0\overline{1}1] direction. Figure 4e-g shows enlarged HRTEM images of three representative regions located at the compressive (“com”), central (“cen”), and tensile (“ten”) parts of the NW in Figure 4d, respectively. It can be seen from Figure 4e that
under the bending stain of 3.4%, the (1\bar{1}\bar{1}) planes near the compressive surface experience a slight lattice distortion, with an angle (defined as “\(\alpha\)”) of 83° between \{1\bar{1}\bar{1}\} planes and \{100\} planes. However, the value of \(\alpha\) increases to 86° in the central (Figure 4f) and tensile (Figure 4g) regions, corresponding to the lattice shear strain of \(~3\%\) along the \{1\bar{1}\bar{1}\} direction. The increased value of \(\alpha\) for the compressive surface to the tensile surface can also be observed when the bending strain increased to 5.9% (Figure 4h-j) and 8.5% (Figure 4k-m). Additionally, with increasing bending strain, the value of \(\alpha\) was increased from 83° to 87° (Figure 4h), and then to 93° (Figure 4k) in the “com” region; the value of \(\alpha\) increased from 86° (Figure 4g) to 88° (Figure 4j), and then to 96° (Figure 4m) in the “ten” region. The value of 96° corresponds to a rather large lattice shear strain of approximately 10.7%. It can be assumed that this large-scale lattice shearing offers an effective way to absorb the large bending energy in the NW so that it is relieved from the dislocation aggregation and the subsequent crack formation or amorphization. Meanwhile, the lattices observed in the HRTEM images are found to be further distorted with increasing bending strain, especially in the tensile region. Hence, there might be an inaccuracy in the value of \(\alpha\) for the whole framed area measured from a local region in the HRTEM image, where the \{100\} planes were severely distorted. To more precisely reveal the increase in the value of \(\alpha\) in a large-scale lattice frame, the corresponding FFT patterns for Figure 4e-m are displayed in Figure S2, from which the variation trend of \(\alpha\) can be observed explicitly and was found to coincide with the results from HRTEM results. By horizontal comparison, it is found that the lattice shear was enlarged gradually from the compressive surface to the tensile surface. This indicates that the shear stress along the \{1\bar{1}\bar{1}\} direction has a gradient in the radial direction (<100>). At a specific position, a larger lattice shear can be induced by the increasing bending strain as seen by vertical comparison. Bond distortions accompanied by dislocations often occur in strained ceramic materials, but this kind of large-scale sheared lattice structure has been seldom reported in ceramic NWs like TiO$_2$-B. To be noted that the dislocation motion still happened with the bending strain increasing, which is confirmed by the disappear of the two dislocations from Figure 4f to Figure 4i.
Figure 4. *In situ* observation of the lattice shear. (a-c) Low-magnification TEM images showing the bending process of an NW with bending strain increasing from 3.4% to 5.9%, and then to 8.5%, respectively. (d) Enlarged TEM image of the framed area in (a). (e-g) HRTEM images corresponding to the “com” (compressive, indicated by the red box), “cen” (central, indicated by the green box), and “ten” (tensile, indicated by the blue box) regions in (d), respectively. (h-j) and (k-m) HRTEM images corresponding to the same three regions as panel e-g under a bending strain of 5.9% and 8.5%, respectively. Scale bar, 500 nm (a-c), 30 nm (d), 2 nm (e-m).

To measure and map continuous strain fields in different parts of the NW under increasing bending strain, HRTEM images are further analyzed using GPA technique. GPA method is based on two nonlinear reciprocal lattice vectors (\( \mathbf{g} \)-vectors) determined from the reciprocal space information (FFT patterns) transformed from a HRTEM image. This method measures the lattice deformation with respect to a strain-free reference lattice. Generally, it is better to select two \( \mathbf{g} \)-vectors that are perpendicular to each other so that the orientation of each strain tensor can be visualized directly.\(^{42}\) However, in the reciprocal space viewed along the [0\( \bar{1} \)1] direction of a strain-free TiO\(_2\)-B NW, it is difficult to determine two orthogonal \( \mathbf{g} \)-vectors. Resourcefully, we select a strained lattice frame (a region at the compressive side of the NW under the bending strain of 8.5%) as the reference area where the (1\( \bar{1} \)\( \bar{1} \)) fringes are orthogonal to the (200) fringes, as Figure 5b and the lower panel of Figure 5c shown. Therefore, two orthogonal \( \mathbf{g} \)-vectors are expected to be determined. Figure 5d is the FFT pattern of the composite HRTEM image (Figure 5e) by merging
Figure 5a (a region at compressive side of the NW under the bending strain of 3.4%) and Figure 5b (reference region). As shown in Figure 5d, two sets of FFT spots are found, where two $\text{g}$-vectors are determined from the reciprocal space of the reference region. The framed area in Figure 5b is used to refine the $\text{g}$-vectors to map the strain fields more precisely. The lattice strain maps of three strain tensors, $\varepsilon_{xx}$, $\varepsilon_{yy}$, $\varepsilon_{xy}$, for a specific area under different bending strains are shown in Figure S3 and Figure S4. The color variation from blue to red corresponds to a change in strain values from -20% to 20%. In these cases, $\varepsilon_{xx}$ and $\varepsilon_{yy}$ reflect the strain change in (111) planes and (200) planes, respectively, while $\varepsilon_{xy}$ reveals the distribution of lattice shear strain.

The $\varepsilon_{xx}$ strain map of Figure 5e is shown in Figure 5f, where the red color indicates the increase of the (111) d-spacing compared to the reference region, which indicates about 10% decrease in (111) d-spacing in the compressive region of the NW with bending strain increasing from 3.4% to 8.5%. Figure 5j shows the $\varepsilon_{xx}$ strain map of a composite HRTEM image (Figure 5i) by merging the HRTEM images of the reference region and the tensile region under the bending strain of 8.5%. Except several small red regions caused by defects, this image shows no large-scale color variation, suggesting a minor increase (less than 3%) in (111) d-spacing from the compressive surface to the tensile surface of the NW. Figure 5g and k show the shear strain ($\varepsilon_{xy}$) maps for Figure 5e and i, respectively. The yellow regions in Figure 5g and the blue regions in Figure 5k indicate the increase of the shear strain with bending strain increasing from 3.4% to 8.5%. The quantitative shear strain values scanning along the lines in Figure 5g and k are extracted and shown in Figure 5h and l, respectively, where the average strain values are measured to be approximately 3% and 7%, respectively. The sum suggests that the shear strain is increased to around 10%, consistent with the shear angle analysis based on Figure 4.
Figure 5. Strain mapping of the NW under different bending strain using GPA technique. (a) HRTEM image under the bending strain of 3.4%. (b) HRTEM image under the bending strain of 8.5% serving as a reference for GPA analysis. (c) Upper panel and lower panel showing the FFT patterns of (a) and (b), respectively. (d) FFT pattern of (e) the composite HRTEM image by merging (a) and (b). (f) $\varepsilon_{xx}$ strain map, (g) $\varepsilon_{xy}$ (shear) strain map of (e). (h) Line graph of $\varepsilon_{xy}$ strain values along the line drawn in (g). (i) Composite HRTEM image by merging (b) and an area at tensile side of the NW under the bending strain of 8.5%. (j) $\varepsilon_{xx}$ strain map, (k) $\varepsilon_{xy}$ (shear) strain map of (i). (l) Line graph of $\varepsilon_{xy}$ strain values along the line drawn in (k). The color variation from blue to red in all strain maps indicates a change in strain values from -20% to 20%.

The bending process of the TiO$_2$-B NW was simulated by a MD method to gain deeper insight into the lattice shear. The NW (length: 44 nm; diameter: 6 nm) was viewed along the [01$\bar{1}$1] direction with the (100) planes being arc-shaped, which is consistent with the bending configuration of the NW shown in Figure 4. As shown in Figure 6a, the bending strain is increased from 0 to 10%, where no amorphization or fracture is found in the NW. Figure 6b-e illustrates the (01$\bar{1}$1) atomic structures of the same yellow-colored area in Figure 6a with a bending strain of 0, 2.5%, 5.0%, and 10.0%, respectively. As shown in the left panel of Figure 6b, a unit cell is marked with an angle of 83° in between its two edges that represent the (100) and (1$\bar{1}$1$\bar{1}$) planes, respectively. The value of this angle is in good agreement with the TEM results obtained for a strain-free NW. With increasing bending strain, the atomic configuration continues to evolve. To better observe
change in angle between the (100) and (111̅) planes, a parallelogram area with four Ti atoms (“A”, “B”, “C”, “D”) as its vertices is magnified and shown in the right panel of Figure 6b, where the “line AC” represents the (111̅) plane while the “line CD” represents the (100) plane. With increasing bending strain, the angle between “line AC” and “line CD” is increased from 83° (Figure 6b) to 87° (Figure 6c), 91° (Figure 6d), and 96° (Figure 6e). Ignoring the O atoms, the MD results illustrate that the Ti atoms lying in the (111̅) planes undergo a gradually increasing shearing displacement along the NW longitudinal direction with increasing bending strain, resulting in the shearing of (111̅) planes. These results are consistent with the aforementioned in situ TEM observation of the shearing of the (111̅) lattice plane along the [111] direction.

Figure 6. MD simulated bending tests for a TiO$_2$-B NW with a diameter and length of 6 nm and 44 nm, respectively. (a) The simulated bending process with increasing bending strain from 0 to 10%. (b-e) Atomic structures of the (01̅1) section for the same yellow-colored area in (a), corresponding to the bending strain of 0, 2.5%, 5.0%, and 10.0%, respectively. Blue balls: Ti; Red balls: O.

Lattice strain can significantly influence the mechanical properties of a material. Previously, large reversible lattice strains of 2-8% were reported for single-crystalline NWs with minor defects, which benefits from the limited inelastic evolution of lattice structure associated with dislocations, twinning and first-order phase transitions.$^{24,25}$ In Wang’s work, a continuous elastic shear strain with an ultralarge value of up to 34.6% was observed for Ni NWs, with deformation twinning and inelastic dislocation activities suppressed by confined stress. After the ultralarge lattice shear was terminated by the generation of dislocation/small angle boundaries, the lattice fully recovered.$^{25}$ Since the lattice shear strain greatly contributes to the large bending deformation of the TiO$_2$-B NWs, it is important to clarify the impact of dislocations on the lattice shear. Two HRTEM images captured close to the compressive surface of the NW are shown in Figure 7, withstanding bending strains of 5.9% and 8.5%, respectively. As shown in Figure 7a, two dislocations lying in the (111̅) planes were found in this region. Due to the generation of the two dislocations, the elastic energy
stored in the lattices was partially released to force the nearby (111) planes to recover from shearing. In the case of a bent NW under a bending strain of 8.5%, several dislocations in both the (111) and (100) planes can also be found (see Figure 7b). Due to the intervention of the dislocations, some shearing lattices can be partially recovered with a decrease in the value of $\alpha$ from 93° to 89°, or 87°. The results suggest that the shear strain for the (111) planes can be terminated or alleviated by the dislocations, but the overall radial distribution of the lattice shearing is still well preserved. It indicates that the large-scale sheared crystalline structure can endow the TiO$_2$-B NW with a capability to accommodate a large quantity of dislocations.

![Figure 7](image.png)

**Figure 7.** Observation of the influence of dislocations on lattice shear. HRTEM images of a region located near the compressive surface of a NW with a bending strain of (a) 5.9% and (b) 8.5%, respectively. Scale bar: 2 nm.

To verify whether the lattice shearing in TiO$_2$-B NWs can also happen in other bending configurations, atomic-level studies of the structural evolution of a NW viewed along the [001] direction were also carried out for a gradually increasing bending strain. Figure 8a-c shows the bending process of the TiO$_2$-B NW with bending strain increasing from 2.2% to 10.0%. Figure 8d-f shows the corresponding HRTEM images for the same framed region in Figure 8a-c, respectively. Initially, some dislocations lying in the (110) planes can be clearly observed in this area under a bending strain of 2.2%. It is clearly seen that the dislocation pattern evolved with increasing bending strain, indicating that dislocation nucleation and movement were active during the NW deformation. No dislocation aggregation was found in either the compressive or tensile sides of the NW, where strong strain fields are generated. Vigorous dislocation movement without aggregation should help mitigate the formation of cracks or amorphization in the TiO$_2$-B NWs. However, no lattice shearing deformation was observed under the $<010\{100}$ system during bending, indicating that the TiO$_2$-B NWs possess the anisotropy considering the lattice shearing deformation.
Figure 8. *In situ* TEM observation of bending behaviors of an individual TiO$_2$-B NW viewed along the [001] zone axis on the atomic scale. (a-c) Low-magnification TEM images showing the bending process of the NW with bending strain increasing from 2.2% to 5.0%, and then to 10.0%, respectively. (d-f) HRTEM images of the same framed in (a-c), respectively. Scale bar, 250 nm (a-c), 5 nm (d-f).

Conclusions

In summary, we have reported, for the first time, the large bending behavior of single-crystalline TiO$_2$-B NWs, with an ultralarge bending strain of 18.7% observed for individual NWs. During the bending deformation under the <111>{100} shearing system of the TiO$_2$-B NWs, a large lattice shear strain of up to 10.7% can be reached. *In situ* atomic-scale investigation found that under the <111>{100} shearing system, dislocation movement and the lattice shearing together account for the large bending deformation. Especially, large-scale lattice shearing provides the NW with an effective way to absorb large bending energy. However, the lattice shearing shows an anisotropy, which is not observed under the <010>{100} system. These results indicate that it is important to consider the impact of lattice shear on global bending behavior of NWs. Our results are also likely to provide more opportunities for strain engineering of TiO$_2$ NWs, and to help to promote potential applications of TiO$_2$-NW-based flexible devices.

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Supporting Information Available: Another case of elasticity. Lattice shear revealed by FFT patterns. Strain mapping results. This material is available free of charge via the Internet at http://pubs.acs.org.
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