Surfaces and interfaces of ferroelectric oxides exhibit enhanced functionality, and therefore serve as a platform for novel nano and quantum technologies. Experimental and theoretical challenges associated with examining the subtle electro-chemo-mechanical balance at metal-oxide surfaces have hindered the understanding and control of their structure and behavior. Here, combined are advanced electron-microscopy and first-principles thermodynamics methods to reveal the atomic-scale chemical and crystallographic structure of the surface of the seminal ferroelectric BaTiO$_3$. It is shown that the surface is composed of a native $<$2 nm thick TiO$_x$ rock-salt layer in epitaxial registry with the BaTiO$_3$. Using electron-beam irradiation, artificial TiO$_x$ sites with sub-nanometer resolution are successfully patterned, by inducing Ba escape. Therefore, this work offers electro-chemo-mechanical insights into ferroelectric surface behavior in addition to a method for scalable high-resolution beam-induced chemical lithography for selectively driving surface phase transitions, and thereby functionalizing metal-oxide surfaces.

1. Introduction

The ability of oxides to endure extreme mechanical, chemical, and thermal conditions has been intriguing for researchers from a broad range of disciplines, e.g., earth science, nuclear engineering, space technology, and dental care.[1–3] Subtle electro-chemo-mechanical balance at complex-oxide surfaces and interfaces allows the formation of phases with structural and functional characteristics that differ from the bulk.[4–6] The unique electric and magnetic properties of such phases arise from their divergence from stoichiometry, leading to variations in oxidation states of the participating ions. Hence, functional-oxide surfaces and interfaces constitute a rich platform for novel phases that are attractive for high-performance miniaturized electronic devices[7,8] as well as for chemical catalyses.[9]

Because ferroelectric oxides comprise regions with varying crystallographic and electric polarization orientations, there has been a growing interest in their outer surface and domain wall functionality, which is expressed as enhanced conductivity,[10–12] magnetism,[4] and even superconductivity.[13] The chemical origin of such a functional behavior is typically attributed to either oxygen vacancy delocalization and are attractive for, e.g., nano lithography[19–23] and catalysis,[9,24–27] have remained elusive. Specifically, the longstanding challenge in understanding how the surface mediates between the absence of electric and mechanical fields in the vacuum and the polarization, and strain in the bulk is not merely experimental or theoretical, but even conceptual.[28] Hence, computational methods that were developed to explain the electro-chemical[29] and electro-mechanical[30] atomic-scale interactions in ferroelectrics have been adopted to describe experimental observations of the surface behavior. For example, Tsurumi et al.[31,32] combined dielectric measurements and density functional theory (DFT) calculations to demonstrate that nanoparticles (NPs) of the seminal nontoxic ferroelectric, BaTiO$_3$, organize in a core–shell structure that helps release strain. These authors suggested that the unit cells at the shell (a few nanometers thick) assume a cubic structure that helps mediate between the tetragonal symmetry of the core and the vacuum. Likewise, a collaborative experimental (scanning tunnelling microscopy)–computational (DFT thermodynamics) study demonstrated the stability of various titanium-oxide terminations during surface reconstruction in BaTiO$_3$.[33] By contrast, although transition electron microscopy (TEM) provides us with significant input regarding domain wall structure and functionality at the atomic scale,[34–40] such TEM characterization of the surface is lacking. Consequently, experimental or theoretical data regarding the surface formation and dynamics or even the surface structure, are absent.
2. Results and Discussion

Combining advanced and conventional electron-microscopy techniques for structural, chemical, and oxidation-state analyses with computational methods, we looked at the native chemical, ionic, and crystallographic structure of BaTiO$_3$ in ≈50 nm particles. Moreover, by increasing the dose exposure we used the electron beam to excite the surface, allowing us to image its real-time dynamics. Such particles are, on the one hand, large enough to be considered bulk-like,[31] while, on the other hand, they are thin enough to allow atomic-resolution TEM imaging. We demonstrate that the native surface of the tetragonal BaTiO$_3$ crystal is composed of a nonstoichiometric (i.e., high defect concentration) nearly cubic titanium oxide phase (TiO$_x$, x ≈ 1). We also show that by increasing the dose exposure of the material to the electron beam, the electron beam can be used for chemical patterning with sub-nanometer controllability. That is, using the electron beam as a source for exerting localized electric field and heat, we induced Ba escape contactless and expanded the native TiO$_x$ phase by will with nearly atomic resolution on the cost of the bulk BaTiO$_3$. Our imaging methods allowed us not only to realize the Ba escape mechanism, but also to quantify the process.

To reveal the structure near the native surface, we imaged with high-resolution TEM (HRTEM) the particles from both {100} and {110} zone axes (ZAs) as seen in Figure 1a–f, respectively. We also performed high-angle annular dark-field imaging scanning transmission electron microscopy (HAADF-STEM) from these ZAs (Figure 1c,g), in which the brightness of each atomic column is proportional to the atomic weight squared ($Z^2$), allowing us to deduce the chemical structure near the surface. The electron micrographs clearly show a difference between the bulk tetragonal BaTiO$_3$ unit cells and a ~1-nm thick terrace-like epitaxial structure of different chemical and crystallographic footprints. The HAADF images (Figure 1c,g) indicate that although columns of both Ti and Ba appear clearly in the bulk region (oxygen atoms are too light to be detected in these images), the surface region contains only Ti columns and no Ba. A careful look at the surface in the HRTEM images, where the oxygen columns can be detected, reveals neighboring columns with different contrast only from {110} ZA (Figure 1e–h) and not from the {100} ZA (Figure 1a–d). Combining the information from the HAADF-STEM and HRTEM methods suggests that the columns are composed of alternating Ti-O columns that can be observed separately only from {110} ZA. Likewise, the interatomic distance is similar for both ZAs (eliminating the possibility of rutile or anatase structures). Therefore, we can conclude confidently that the native surface of the BaTiO$_3$ is a rock-salt-like titanium oxide. This conclusion is in agreement with our measurement of the Ti–Ti interatomic distance at the interface (2.09 ± 0.005 Å, see Figure 1b,f), which is substantially smaller than in BaTiO$_3$ (3.99–4.04 Å[41]) and is in agreement with the 4.18 Å lattice parameter of TiO$_4$[42] (we should note that this value is much smaller than, e.g., the 5.54 Å lattice parameter of BaO).

To support our chemical analysis, we used a novel microscopy system that allows us to perform atomic-resolution

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**Figure 1.** Epitaxial TiO surface layer in BaTiO$_3$ crystals. a) HRTEM of the BaTiO$_3$ surface from a [010] ZA. b) A closer look at the area highlighted in (a) shows the rock-salt structure of the TiO surface as well as the epitaxial registry of the TiO surface on the perovskite BaTiO$_3$ crystal. c) HAADF image from a similar ZA (of a different grain). d) Schematic illustration of the [100] nonstoichiometric TiO$_x$ surface–BaTiO$_3$ bulk native structure. The complementary e) large-scale and f) closer-look HRTEM images as well as an g) HAADF image taken from the {110} ZA show the BaTiO$_3$ crystal and rock-salt TiO from a perpendicular orientation. h) Schematic illustration of the {110} nonstoichiometric TiO$_x$ surface–BaTiO$_3$ bulk native structure. The border between the bulk BaTiO$_3$ and the TiO surface is highlighted (orange lines in a, c, e, and g), while the location of Ba, Ti, and O atoms is designated in (b) and (f).
electron-diffraction X-ray spectroscopy (EDX) mapping simultaneously with HAADF imaging at the same region. Figure 2 shows such cross-identification of the Ba, Ti, and oxygen columns. Likewise, to further support our structural analysis, we used integrated differential phase contrast (iDPC) imaging, which is a method that has recently been developed for mapping the location of individual atomic columns with very high accuracy (also simultaneously with the HAADF and EDX imaging). In iDPC, the contrast is proportional to the atomic weight \((Z)\), allowing for high detectability of heavy and light atoms alike (see the Experimental Section for more details about the iDPC and EDX imaging). Figure 2h shows the iDPC signal from a small area near the surface (same area as in Figure 1c), verifying the exact location of the rock-salt-like Ti\(\times\) atomic columns (as well as of the perovskite BaTiO\(_3\) structure of the bulk).

We should note that the universality of the existence of a native Ti\(\times\) layer at the surface of BaTiO\(_3\) was confirmed by a large-area panoramic view (see Figure 3), while the appearance of a Ti\(\times\) surface was observed in all the different BaTiO\(_3\) crystals we examined (>50 different crystals), including the five different particles that are presented in this paper. These crystals arrived from different sources and were prepared by different methods (see the Experimental Section). Moreover, revisiting existing literature (e.g., Figure 5 from Zhu et al.\([45]\)), we believe that the Ti\(\times\) surface has been observed previously, but the chemical and crystallographic structures have not yet been identified, probably due to the lack of the novel imaging methods that have been used in the current study. Finally, the thickness of the native Ti\(\times\) surface layer which is \(\approx 1\) nm suggests that there are only one to three monolayers, and hence this observation is in agreement with the previous observations of titanium-oxide termination in BaTiO\(_3\)\([33]\) which typically cannot determine the exact structure of the inner layers.

The deviation from TiO stoichiometry in a rock-salt structure (Ti\(\times\) with \(1.3 > x > 0.7\)) leads to high defect concentration.\([46]\) Using the 3D nature of TEM imaging, we identified three types of defects at the very thin native surface: stacking fault, twinning, and vacancies. These defects appear clearly in Figure 4. Moreover, using electron energy-loss spectroscopy (EELS) signals, we were able to identify the chemical shift\([47]\) of the Ti peaks between the ions at the bulk and the ions at the surface. This shift corresponds to the variations in the Ti oxidation.

Figure 2. Cross-chemical and-structural analysis of the BaTiO\(_3\) crystal and Ti\(\times\) surface. a) HAADF image of the BaTiO\(_3\) crystal and its surface. b) Atomic-scale chemical mapping (EDX) showing higher Ti concentration and lower Ba concentration at the surface (here, the signal is not of an instantaneous beam detection. Rather, the signal is integrating over a large time, hence deteriorating the imaging stability and the spatial resolution. See individual barium, titanium, and oxygen EDX mapping in Figure SI1, Supporting Information). c) High-accuracy location mapping (iDPC) of the same area demonstrates the oxygen–titanium rock-salt structure of the Ti\(\times\) surface. Simultaneous high-resolution chemical analysis of the d) barium, e) titanium, and f) oxygen EDX signals as well as the combined chemical analysis g) and high-precision location mapping (iDPC) are given as a reference. The areas in (a) from which the surface and bulk images were taken are highlighted, while the HAADF image of the same surface area is given in Figure 1c.

Figure 3. Long-range presence of the native epitaxial Ti\(\times\) surface of a BaTiO\(_3\) crystal. High-precision atomic-scale mapping (iDPC) of the native Ti\(\times\) surface over a long range (1–2 nm layer at the surface). The panoramic image is composed of four iDPC images.
The reduction in oxidation state from Ti\textsuperscript{4+} and L\textsubscript{3} energy of the Ti ions show a chemical shift that corresponds to the peaks related to the Ba or to the O ions, a closer look (inset) at the L\textsubscript{2} were taken is given as a reference). Although no change was observed in the Ti\textsuperscript{4+} in rock-salt structure TiO surface.\cite{47–49}

Figure 4. Defects in the native TiO\textsubscript{x} surface. Highlighted (red arrows) crystallographic defects in the TiO surface at the areas presented a) in Figure 1a and b) in Figure 1d.

state, while no shift was observed in either the Ba or O peaks. Figure 5 shows that the position of the Ti cation peaks recorded from the bulk BaTiO\textsubscript{3} corresponds to Ti\textsuperscript{4+}. However, the signal recorded from the surface demonstrates that the peak shifts toward lower energies, indicating on the existence of Ti\textsuperscript{2+}, as expected from the TEM imaging.\cite{47–49}

The experimental identification of a TiO epitaxial surface for native BaTiO\textsubscript{3} indicates that TiO is a stable phase on the BaTiO\textsubscript{3} surface. Because the stability of heterogenous thin films depends strongly on the interfacial interactions and cannot be directly predicted from their bulk stability, we performed ab initio DFT calculations to determine the stability of different surfaces on BaTiO\textsubscript{3} and to derive the stability map of this interface. To cover a large span of possible surface phases, we include all phases in the Ba-Ti-O\textsubscript{2} ternary system found in the ternary region on the phase diagram. This ternary region evolves from the bulk BaTiO\textsubscript{3} to the areas presented a) in Figure 1a and b) in Figure 1d. These results are in close agreement with our experimental measurements, while our prediction of the TiO–Ti\textsubscript{4}O\textsubscript{5} interplay is that the TiO\textsubscript{2} layer closest to the BaTiO\textsubscript{3} lattice plane. A consequence is confirmed by comparing the lattice mismatch from their bulk states, where Ti\textsubscript{4}O\textsubscript{5} has 5.0% lattice mismatch and TiO has 3.5% lattice mismatch. Second, Ti\textsubscript{4}O\textsubscript{5} has a stronger interaction with the BaTiO\textsubscript{3} (001) lattice plane. A consequence is that the TiO\textsubscript{2} layer closest to the BaTiO\textsubscript{3} (e.g., the native TiO\textsubscript{2}) is Ti\textsubscript{4}O\textsubscript{5}, while subsequent layers of TiO may be induced. These results are in close agreement with our experimental measurements, while our prediction of the TiO–Ti\textsubscript{4}O\textsubscript{5} interplay

$E_{f} = E_{BTO,i} - E_{BTO}$ \hspace{1cm} (1)

where $E_{BTO,i}$ is the total energy of BaTiO\textsubscript{3} with $P_{i}$ phases on the surface, and $E_{BTO}$ is the energy of the bare BaTiO\textsubscript{3} crystal. A phase is considered stable if none of the decomposition paths is spontaneous, i.e., when for any other three phases $P_{i}$, $P_{k}$, and $P_{l}$ that satisfy Equation (2)

$P_{i} \rightarrow n_{i}P_{j} + n_{k}P_{k} + n_{l}P_{l}$ \hspace{1cm} (2)

where $n_{i}$, $n_{k}$, and $n_{l}$ are stoichiometric numbers, the following inequality holds in Equation (3)

$E_{i} \leq n_{i}E_{f,i} + n_{k}E_{f,k} + n_{l}E_{f,l}$ \hspace{1cm} (3)

where energies are calculated from Equation (1). Similarly, two phases $P_{i}$ and $P_{j}$ could coexist if, for any other two phases $P_{k}$ and $P_{l}$, as given in Equation (4)

$P_{i} + n_{i}P_{j} \rightarrow n_{k}P_{k} + n_{l}P_{l}$ \hspace{1cm} (4)

$P_{i}$ and $P_{j}$ have lower energy, as shown in Equation (5)

$E_{i} + n_{i}E_{f,i} \leq n_{k}E_{f,k} + n_{l}E_{f,l}$ \hspace{1cm} (5)

Figure 5. Chemical shift between the bulk and surface Ti binding energies in BaTiO\textsubscript{3}. A comparison between the EELS signals from the bulk and from the surface (HAADF image of the areas from which the EELS signals were taken is given as a reference). Although no change was observed in the picks related to the Ba or to the O ions, a closer look (inset) at the L\textsubscript{2} and L\textsubscript{3} energies of the Ti ions show a chemical shift that corresponds to the reduction in oxidation state from Ti\textsuperscript{4+} in the perovskite BaTiO\textsubscript{3} bulk toward the Ti\textsuperscript{2+} in rock-salt structure TiO surface.\cite{47–49}

Figure 6 shows that based on this method (more computational details can be found in the Supporting Information), we not only show the stability of the native TiO\textsubscript{x} layer, but we also predict that a thicker layer may also be stable, while the stoichiometry (x) varies with the film thickness. This effect can be seen in the difference between the ternary diagrams of two atomic monolayers (Figure 6a) and four atomic monolayers (Figure 6c) of TiO\textsubscript{x} on the BaTiO\textsubscript{3} surface. We think that introducing external excitations in the experimental conditions discussed here (i.e., TEM), a removal of oxygen from the system can be induced, driving it down from the point of BaTiO\textsubscript{3} into a ternary region on the phase diagram. This ternary region evolves from BaTiO\textsubscript{3} to BaTiO\textsubscript{2} to BaTiO\textsubscript{2} when increasing thickness of overlayers, suggesting that Ti\textsubscript{4}O\textsubscript{5} is the stable composition for the thinner TiO\textsubscript{x} layer (Figure 6a,b), while TiO is also stable for thicker layers (Figure 6c,d).

These results allow us to draw two main conclusions regarding the observed surface overlayers. First, TiO incurs less lattice mismatch penalty compared with Ti\textsubscript{4}O\textsubscript{5} because the relative stability of TiO increases for thicker TiO layers. This conclusion is confirmed by comparing the lattice mismatch from their bulk states, where Ti\textsubscript{4}O\textsubscript{5} has 5.0% lattice mismatch and TiO has 3.5% lattice mismatch. Second, Ti\textsubscript{4}O\textsubscript{5} has a stronger interaction with the BaTiO\textsubscript{3} (001) lattice plane. A consequence is that the TiO\textsubscript{2} layer closest to the BaTiO\textsubscript{3} (e.g., the native TiO\textsubscript{2}) is Ti\textsubscript{4}O\textsubscript{5}, while subsequent layers of TiO may be induced. These results are in close agreement with our experimental measurements, while our prediction of the TiO–Ti\textsubscript{4}O\textsubscript{5} interplay
may also explain the observations of high defect concentration (Figure 4). Finally, these calculations allow us to predict that introducing external excitations to the BaTiO₃-TiOₓ system may favor controlled growth of the pseudo-cubic TiOₓ (Ti₄O₅–TiO) near the native TiOₓ surface. We should note that Ti is smaller than Ba and hence presumably we expect that the growth of the surface will include barium oxide formation rather than titanium oxide formation. However, Ba ions do not have many intermediate oxidation states and tend to be stable only as Ba²⁺. Hence, as soon as the surface becomes suboxide, barium oxide would become unstable. On the other hand, Ti has a broader range of oxidation-state stability and can even be stable as Ti³⁺, e.g., in Ti₂O₃. This analysis is in agreement also with previous studies regarding BaTiO₃ surface termination that show that under reducing conditions (i.e., when oxygen atoms are driven away), the Ba also goes away, leaving a Ti-rich level.[33]

Following the prediction that exciting the system can grow the TiOₓ phase, we used the electron-beam irradiation as a contactless source for such excitations at a length scale that is determined by the beam size. Because we knew that TEM imaging does not affect the surface, the attempts to excite the surface included increase of the electron-beam doses with respect to the doses that are used for TEM imaging. Figure 7a–d shows the growth of the TiOₓ surface on the expense of BaTiO₃ as a function of electron-beam irradiation time over a large area. Calculating carefully (see the Experimental Section and Figure SI3, Adv. Funct. Mater. 2019, 1902549).
Supporting Information) the irradiation of the HRTEM electron beam, the dose was 0.003 nA nm$^{-2}$. The growth of the TiO$_x$ surface as a function of dose exposure is clearly observed at the images. We should note that for very long exposure times, we can confidently assume that the TiO$_x$ grew significantly also at the direction parallel to the beam and not only perpendicular to the surface, so that a distinction between the bulk BaTiO$_3$ and the TiO$_x$ surface is not so clear any more (see Figure 7d). Thanks to the accurate EDX measurements we were able to quantify the rate of Ba escape (Figure 7f,g), i.e., the dynamic BaTiO$_3$-to-TiO$_x$ transition under a constant electron-beam irradiation. Here, the dose was much higher than that in the TEM imaging: 80 nA nm$^{-2}$ at 200 keV (see the Experimental Section and Figure S13 in the Supporting Information for further details regarding the dose calculation), so that the Ba escape process was also much faster. Given the above theoretical analysis regarding the Ba escape, we can deduce that the electron-beam irradiation lowers the oxidation state of the metal atoms, so that to become more stable, there must be less oxygen atoms around them. This state of oxygen deficiency would favor Ba escape over Ti escape, even though the Ba atoms are larger.

We then wanted to examine whether such chemical patterning can be performed also at higher resolution, using a smaller beam size. Video S1 in the Supporting Information and Figure 8 show real-time TiO$_x$ patterning in sub-nanometer resolution as imaged with iDPC (obtained simultaneously with the EDX characterization). Here, the higher currents accelerate the formation of the TiO$_x$ layer as expected. The dynamics of the high-resolution TiO$_x$ patterning shows that the process involves intermediate formation of an amorphous state (see Video S1 in the Supporting Information and Figure 8), while the ability to tune the beam parameters with high accuracy (energy and spatial resolution) allows us to control the TiO$_x$ patterning.

We should note that the dose window for TiO$_x$ patterning is rather narrow as, on the one hand, the energy should be higher than a certain threshold value that induces Ba escape. On the other hand, larger doses are too violent and might also evaporate the Ti and O ions from the surface, i.e., etch away the entire BaTiO$_3$ (here, such high doses correspond to electron-beam irradiation of $\geq$270 nA nm$^{-2}$ at 200 keV even for short periods of time, as can be seen in Video S4, Supporting Information). We should also note that as opposed to the quantitative EDX data (Figure 7e,f), the EDX imaging is an integration of an accumulated signal, allowing us to increase the signal-to-noise ratio above an imaging-relevant threshold. Hence, EDX imaging of the surface, where the material is rather thin and produces even weaker signals, requires large integration time. Given the fluctuation in STEM (thermal, electromagnetic, etc.), the long integration time gives rise to reduction in the spatial resolution. Such a decrease in the EDX imaging resolution is seen, e.g., in the case of Figure 2b. Moreover, if the exposure time is too long, the beam might also induce chemical and structural changes (e.g., amorphization and Ba escape), reducing the imaging resolution even further. Yet, the quantitative data (e.g., Figure 7e,f) can be evaluated accurately even as a function of time, because it is based on spatial integration rather than on time integration.

3. Conclusion

Our results can explain previous observations of a Ti-rich surface in BaTiO$_3$ crystals,[51] while the observed dynamic growth of the TiO layer under the electron beam supports earlier predictions of Ba escape from the BaTiO$_3$ surface,[33,45] giving rise to enhanced surface reactivity.[52] The existence of cation escape mechanisms near the surface, including as a consequence of electron-beam irradiation[53] as well as the effects of these mechanisms on enhanced surface reactivity has been reported recently in other ferroelectrics.[54] However, the exact phases of these surfaces have not been predicted or determined experimentally. Hence, we encourage future examination of the generality of the TiO$_x$ surface formation in other Ti-based ferroelectric oxides. It is possible that the presence of the cubic TiO (or TiO$_4$) at the surface is in agreement with the hypothesis of Tsurumi et al., who suggest that the surface of the tetragonal
ferroelectric must be cubic, for stabilizing the polar-matter - air discontinuity. Nevertheless, we see that the cubic surface is not the BaTiO$_3$ ferroelectric, but rather it is a chemically distinct phase, TiO, which can also be grown by will.

Although the combined chemical-structural TEM analysis method provided here is advantageous for characterizing free crystallites, the sample preparation required for thin film or bulk crystal characterization might not be as ideal. That is, the lamella preparation is usually destructive and comprises damaging and contamination due to ion bombarding. Therefore, we should note that although our computational data do not distinguish between the different geometries, we encourage further experiments along the line of our cross chemical-crystallographic approach for examining the atomic-scale surface structure of bulk crystals and thin films. Such studies will potentially allow determining how general our findings are, when bearing in mind, e.g., that using other methods, the surface structure of BaTiO$_3$ thin films has been characterized sometimes as a monolayer of a Ti-O phase[@012] and sometimes as a BaO structure.[@013] Obviously, other surface structures can be formed when the BaTiO$_3$ is interfacing other heteroepitaxial engineered layers[@014] rather than the vacuum (e.g., as in the case of engineered vortex structures that have garnered much interest recently).

Similar to mechanical mediation between the bulk and the vacuum, we would like to suggest a possible electric mediation between the ferroelectric crystal and the vacuum. Although the observed high defect concentration may be explained partially by the co-existence of TiO and Ti$_2$O$_5$, we would like to raise the possibility that the observed high defect concentration may be explained partially between the ferroelectric crystal and the vacuum. Although the vacuum, we would like to suggest a possible electric mediation between the ferroelectric crystal and the vacuum. Although the vacuum, we would like to suggest a possible electric mediation between the ferroelectric crystal and the vacuum. Although the vacuum, we would like to suggest a possible electric mediation between the ferroelectric crystal and the vacuum. Although the vacuum, we would like to suggest a possible electric mediation between the ferroelectric crystal and the vacuum. Although the vacuum, we would like to suggest a possible electric mediation between the ferroelectric crystal and the vacuum.

4. Experimental Section

Commercially available BaTiO$_3$ NP (99.9% purity spherical particles, purchased from US Research Nanomaterials, Inc.) as well as particles from collaboration with Prof. Yoed Tsur (Technion not presented in this work) were used. The NPs were suspended in ethanol and sprayed on an amorphous carbon-Cu grid by introducing high pressure N$_2$, allowing the individual NPs to be spread evenly on the grid.

All in situ irradiation experiments and imaging in this work was done using double-corrected Titan Themis G2 300 (FEI/Thermo Fisher) HRTEM with sub-angstrom resolution. Both TEM and STEM images were taken with 300–200 keV acceleration voltage, with medium-low monochromated current of 2–0.1 nA depending on using HRTEM or HRSTEM mode. No manipulation had been conducted to the images.

In order to investigate the surface of BTO NPs, different TEM methods were used. Structural analysis was performed by high-resolution observations. Atomic-scale chemical mapping was done by Dual-X detector: EDX detector, drift correction was applied. Accurate positions of the heavy elements and Z contrast analysis were performed using HAADF. Accurate position and Z contrast analysis of the light elements were performed using four quadrants detectors for the novel HRSTEM (iDPC (HRSTEM)/STEM) technique. Flux calculations were done as follows. For the HRTEM: the measured screen current was divided by the beam size (the beam was steady and larger than the CCD camera, with 30–50 nm diameter). For HRSTEM (or iDPC): the measured screen current was divided by the pixel size (the beam scanned the sample and its diameter was smaller than the pixel size: 0.04–0.02 nm with 512 × 512 pixels for EDX/HAADF mapping and 0.008–0.004 nm with 2048 × 2048 pixels for iDPC/HAADF images). See Figure S13 in the Supporting Information for further details. It should be noted that during the initial alignment of the system for finding the desired ZA, the particles were exposed to some irradiation. Based on Figure 7, this exposure was estimated to be negligible, in particular for HRSTEM modes, where the area examined was mostly different than the area used for the alignment. Yet, in some cases, minor contribution of the beam to enhance the native layer was possible.

The advantage of using simultaneously HAADF and iDPC was the complementary information which was provided. The HAADF was very sensitive to atomic mass and less affected by nonuniform thickness in the sample. However, the contrast in the HAADF images was proportional to $Z^2$. Therefore, when imaging together light with heavy elements by HAADF, the light elements were usually invisible.

The iDPC-STEM technique was sensitive to the electrostatic potential of the atoms, and the contrast in images was relative to Z. Using the iDPC technique drastically improved the detectability of light elements among heavy elements in the same image.

Computational and modeling: for detailed explanations regarding the methods used for the modeling and computational analysis presented in this work please refer to the relevant Section in the Supporting Information and references therein.[@015,63–68]

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest
The authors declare no conflict of interest.

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