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**Investigation of Amorphous to Crystalline Phase Transition of Sodium Titanate by X-ray
Absorption Spectroscopy and Scanning Transmission X-ray Microscopy**

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Abstract

Nanostructured sodium titanate has great potential for various applications, such as sodium-ion batteries, photocatalysts and waste treatment. Understanding of the phase transition mechanism in sodium titanate upon post annealing is fundamentally important in order to tune the structure, morphology, and property for targeted applications. In this work, we adopted amorphous sodium titanate grown on carbon nanotubes by an atomic layer deposition technique as a reference, and used X-ray absorption spectroscopy (XAS) and scanning transmission X-ray microscopy (STXM) as well as high-temperature *in-situ* X-ray diffraction (XRD) technique to elucidate the phase transition mechanism of sodium titanate from amorphous to crystalline upon annealing from 25 °C to 900 °C. XAS and XRD analysis disclosed that anatase TiO₂ first formed in the matrix of amorphous sodium titanate at 500 °C, and then recrystallized into Na_{0.23}TiO₂ at 700 °C and 900 °C. XAS studies also revealed the Ti atoms in sodium titanate were oxidized during annealing process, and reached an oxidation state about 3.8+ for Na_{0.23}TiO₂. The elevated annealing temperature increased the coordination number of Ti atoms and the crystallinity of sodium titanate. STXM chemical map provided spatial information and visualized evidence on the phase transition among amorphous sodium titanate, anatase TiO₂, and Na_{0.23}TiO₂ in the samples annealed at intermediate temperatures (500 °C and 700 °C). This work provides a comprehensive understanding on the evolution of sodium titanate, in terms of crystal structure, electronic structure, chemical environment, and morphology, under different post annealing conditions.

Keywords: sodium titanate, phase transition, X-ray absorption spectroscopy, scanning transmission X-ray microscopy

1. Introduction

Nanostructured alkaline titanates have received considerable interest because of their potential applications in sodium-ion batteries,¹⁻³ photocatalysts,⁴⁻⁵ and cation exchangers in the treatment of radioactive liquid waste.⁶ For example, sodium titanate (such as NaTiO_2 , $\text{Na}_2\text{Ti}_3\text{O}_7$ and $\text{Na}_2\text{Ti}_6\text{O}_{12}$) has been recently reported to show reversible Na^+ storage capability, and thus was promising low-voltage anode material for sodium-ion batteries.¹⁻³ Amorphous sodium titanate grown on carbon nanotubes maintained a discharge capacity of 100 mAh g^{-1} for 1,500 cycles in sodium-ion batteries, due to the unique core/shell structure that facilitated fast Na^+ and e^- transport during charge and discharge process.⁷ Nanosizing sodium titanate has been proven as an effective approach to improve Na^+ storage capacity in sodium-ion batteries, due to the reduced transport length for both Na^+ and e^- .³ Therefore, it is critically important to control the morphology, phase, and structure of nanostructured sodium titanate, in order to optimize their performance in targeted applications.

Alkaline hydrothermal (HT) method has been intensively used to prepare sodium titanate nanostructure. This method involves the treatment of crystalline TiO_2 in a concentrated aqueous NaOH solution under a HT condition at relatively low temperatures.⁸⁻¹⁰ The preparation conditions (reaction temperature, duration, and post treatment) might result in HT-derived sodium titanate with different compositions, crystal structures (bititanate $[\text{Na}_x\text{Ti}_{2-x}\text{O}_4(\text{OH})]$, trititanates $[\text{Na}_x\text{Ti}_{2-x}\text{Ti}_3\text{O}_7]$,^{11,12} and morphologies (nanotube, nanoribbon, nanosheet, and nanorod).⁸⁻¹² Nevertheless, the correlation between preparation conditions and properties of sodium titanate is still ambiguous in literatures, and no general rule is applicable to all cases so far. Another challenge is the discrepancy in the phase transition behavior of the HT-derived

sodium titanate during post treatment.¹³⁻¹⁵ For example, Zhu and co-workers found that NaHTi_3O_7 nanotubes synthesized by the HT method underwent a gradual degradation at 300 °C and 500 °C respectively, and finally transformed into $\text{Na}_2\text{Ti}_6\text{O}_{13}$ nanorods after heat treatment at 700 °C.¹³ The phase transition mechanism was explained by the release of structural water in the interlayer space in order for sodium titanate to take more stable configuration with low energy.¹³ Another work by Sun and Li¹⁴ found that titanate nanotubes changed to $\text{Na}_2\text{Ti}_9\text{O}_{19}$ during the thermal treatment at 600 °C, which then transformed into a mixture of $\text{Na}_2\text{Ti}_6\text{O}_{13}$ and anatase TiO_2 at 850 °C. *In-situ* Raman analysis revealed that titanate nanotubes transformed to anatase TiO_2 at 550 °C, which recrystallized into $\text{Na}_2\text{Ti}_6\text{O}_{13}$ and $\text{Na}_2\text{Ti}_3\text{O}_7$ at 800 °C.¹⁵ Nevertheless, the phase transition mechanism remains controversial, and might be related to the chemical composition of different titanates made under different operating conditions and possible impurity residual as a result of incomplete removal during washing process. Therefore, it is highly desirable to use sodium titanate sample with controlled composition and free of impurity, in order to establish an ideal reference for phase transition behavior study. Moreover, many previous work employed traditional X-ray techniques, such as X-ray diffraction (XRD), X-ray Raman scattering spectroscopy, as main tools to investigate the phase transition in titanates. These techniques collect averaged structure and phase information on a macroscopic level, and provide limited information on the phase transition on a microscopic level.

In this work, we adopted sodium titanate prepared by an atomic layer deposition (ALD) technique as a prototype for phase transition investigation.⁷ Different from the HT approach, ALD deposits sodium titanate in a layer-by-layer manner, by using self-limiting and saturated surface reactions.⁷ The composition of sodium titanate can be precisely controlled by adjusting

the ALD subcycles of $\text{NaO}^t\text{bu-H}_2\text{O}$ and $\text{TTIP-H}_2\text{O}$.⁷ The complete ligand exchange reactions in ALD processes avoid the introduction of impurities in sodium titanate. Therefore, sodium titanate deposited by ALD presents an excellent candidate for the purpose of phase transition study. In addition to traditional XRD techniques, X-ray absorption spectroscopy (XAS) is used as a powerful tool to investigate the electronic and crystal structure of sodium titanate subject to post annealing, because it is sensitive to materials with and without long-range order.^{16,17} In particular, X-ray absorption near-edge spectroscopy (XANES) provides local structure and bonding information, such as oxidation state, coordination, and local symmetry, of the absorbing atom, while extended X-ray absorption fine structure (EXAFS) yields information about the interatomic distance and near neighbor coordination number.¹⁶ Moreover, scanning transmission X-ray microscopy (STXM) is used to track the phase evolution and distribution in sodium titanate under different annealing temperature. STXM developed using undulator based third-generation synchrotron light source provides an exceptional capability for probing the electronic structure and chemical speciation of an individual nanostructure with a nanoscale spatial resolution.¹⁸ It can deliver combined information of XAS and X-ray microscopy, with a spectral and spatial resolution of 0.05 eV and 30 nm, respectively,¹⁹ and therefore is ideal for elucidating the phase transition mechanism of sodium titanate herein.

2. Experimental

2.1 Preparation of sodium titanates

Sodium titanate was deposited on carbon nanotubes (CNTs) at 225 °C in a Savannah 100 ALD system (Ultratech/Cambridge Inc., USA) by following an ALD recipe developed previously.⁷ In brief, sodium tert-butoxide (NaO^tBu), titanium(IV) isopropoxide (TTIP), and distilled water

(H₂O) were used as as ALD precursors. The source temperatures for NaO^tBu and TTIP were 185 °C and 85 °C, respectively. These presursors were introduced sequentially into ALD chamber in the order of NaO^tBu-H₂O-TTIP-H₂O (one ALD cycle), with complete N₂ gas purging prior to each precursor. Sodium titanate was deposited on CNTs by simply repeating the above ALD cycle.

2.2 Characterizations

High-temperature *in-situ* X-ray diffraction (XRD) measurement (Bruker D8 Advance, Cu - K α X-ray source) was performed on sodium titanate/CNTs at 25 °C (as-deposited state), 500 °C, 700 °C, and 900 °C, respectively. At each temperature, the sample was annealed for 1h before the XRD pattern was measured. *In-situ* XRD measurement (23°-27°, scan step of 0.02° per second) was further conducted on another sample at 900 °C with annealing time up to 300 min until the complete phase transition from anatase TiO₂ to crystalline Na_{0.23}TiO₂. The samples for morphology and structure characterization were obtained by heat treatment of sodium titanate/CNTs for 1h in air at 500 °C, 700 °C, and 900 °C, which hereafter are denoted as NTO-500, NTO-700, and NTO-900, respectively. The as-deposited sodium titanate on CNTs is designated as NTO-25. The morphology of the samples were observed by field-emission scanning electron microscope (SEM, Hitachi S4800) and transmission electron microscope (TEM, Hitachi 7000). X-ray absorption near-edge spectroscopy (XANES) and extended X-ray absorption fine structure (EXAFS) measurment was performed at the Canadian Light Source (CLS) on the Spherical Grating Monochromator (SGM) beamline for Ti L_{3,2}-edge spectrum and on the hard X-ray microanalysis beamline with a premirror-double crystal monochromator-post mirror configuration using Si (111) crystal and Rh mirror for Ti K-edge spectra. STXM measurement was conducted at the soft X-ray spectromicroscopy (SM) beamline at CLS, which

is equipped with a 25 nm outermost-zone zone plate (CXRO, Berkeley Lab). The diffraction-limited spatial resolution for this zone plate is 30 nm. Image sequence (stack) scans over a range of photon energies were acquired for the same sample region at the Ti $L_{3,2}$ -edge. Detailed information about STXM sample preparation, data acquisition, and data analysis can be found elsewhere.^{16,19}

3. Results and Discussion

Figure 1. (a) XRD patterns of sodium titanates at 25 °C (as-deposited) and *in-situ* annealed at 500 °C, 700 °C, and 900 °C in air; (b) series of XRD patterns recorded *in situ* during the annealing of sodium titanate in air at 900 °C for different annealing time; crystal structure of (c) $\text{Na}_{0.23}\text{TiO}_2$ (JCPDS No. 22-1404) and (d) anatase TiO_2 (JCPDS No. 02-0387) (red: oxygen; blue: titanium; green: sodium; blue polyhedron: Ti – O octahedra). (Partial XRD data in Figure 1a and 1b were adapted from ref. [7] with permission from the Royal Society of Chemistry).

Sodium titanate was deposited on carbon nanotubes (CNTs) at 225 °C by using an ALD process reported previously.⁷ The XRD pattern of sodium titanate on CNTs (**Figure 1a**, 25°C) exhibits only three diffraction peaks at 25°, 38°, and 48° originating from CNTs (JCPDS No. 08-0415), suggesting long-range disordered structure of sodium titanate at the as-deposited state. High-

temperature *in-situ* XRD measurement was performed on the sodium titanate/CNTs in air, in order to track the phase evolution from amorphous to crystalline sodium titanate. During the *in-situ* XRD measurement process, the sample was annealed for 1 h at each temperature (500 °C, 700 °C, and 900 °C), before an *in-situ* XRD measurement was made between 10° and 50° at a scanning rate of 0.02° per second. As shown in Figure 1, the XRD pattern of sodium titanate annealed at 500 °C is dominated by diffraction peaks from anatase TiO₂ (JCPDS No. 02-0387), with several weak peaks assignable to monoclinic Na_{0.23}TiO₂ (JCPDS No. 22-1404). The diffraction peaks of CNTs disappear in the sample annealed at 500 °C, due to the combustion of CNTs in air. Once the temperature is elevated to 700 °C, the peak intensity of anatase TiO₂ decreases while that of monoclinic Na_{0.23}TiO₂ increases, disclosing the gradual phase transition from the former to the latter. At 900 °C, the sodium titanate is mainly composed of monoclinic Na_{0.23}TiO₂, with the presence of minor diffraction peaks belonging to anatase TiO₂ (Figure 1). Another *in-situ* XRD measurement was conducted as a function of annealing time on sodium titanate at 900 °C, in order to find out the time needed to obtain pure monoclinic Na_{0.23}TiO₂. As illustrated in Figure 1b, the (101) peak of anatase TiO₂ gradually decreases in the intensity, while the (110) peak of monoclinic Na_{0.23}TiO₂ undergoes the opposite trend, with the increase of annealing time. It is found that 300-minute annealing is needed to complete the phase transition from anatase TiO₂ to monoclinic Na_{0.23}TiO₂. The XRD results in Figure 1 suggest that an intermediate anatase TiO₂ is formed in amorphous sodium titanate at a low temperature (500 °C), and recrystallizes to Na_{0.23}TiO₂ at temperatures higher than 700 °C. The fact that anatase TiO₂ first forms in sodium titanate at relative low temperatures suggests the lower nucleation and growth energy of anatase TiO₂ than Na_{0.23}TiO₂ (their crystalline structures are illustrated in Figure 1c and 1d).

Figure 2. Morphology evolution of sodium titanate (a) as-deposited (25 °C), annealed at (b) 500 °C, (c) 700 °C, and (d) 900 °C in air, corresponding to the XRD patterns in Figure 1a. The scale bars in (a-d) represent 200 nm.

Morphology evolution of sodium titanate with annealing temperature is examined by using SEM, and the typical images are illustrated in **Figure 2**. At the as-deposited state, the sodium titanate is uniformly covered on the surface of CNTs, forming a sodium titanate/CNTs shell/core structure (Figure 2a). Annealing at 500 °C leads to the burning of CNTs in sodium titanate/CNTs, creating hollow tubular structure (Figure 2b). Meanwhile, the hollow sodium titanate starts to collapse locally at 500 °C (as highlighted in the Figure 2b), and totally breaks into nanoparticles with size of 20-50 nm at 700 °C (Figure 2c). Further annealing at 900 °C results in the growth of these nanoparticles into 100-150 nm, as shown in Figure 2d. Figure 2 presents that with the increase of annealing temperature, sodium titanate evolves from shell/core structure to hollow structure, and finally nanoparticles.

Figure 3. (a) Ti L_{3,2}-edge in total electron yield (TEY), (b) Ti K-edge, (c) pre-edge region of Ti K-edge, and (d) R space XANES spectra of the as-deposited sodium titanate (NTO-25), and sodium titanate annealed at 500 °C (NTO-500), 700 °C (NTO-700), and 900 °C (NTO-900), in comparison to anatase TiO₂.

XANES and EXAFS techniques are used to examine the chemical environment, electronic structure, interatomic distance, and near neighbor coordination number of sodium titanate during the phase transition. Figure 3 depicts the Ti L_{3,2}-edge (in total electron field (TEY) mode) and Ti K-edge XANES spectra of the as-deposited sodium titanate and sodium titanate annealed at 500 °C, 700 °C, and 900 °C. Ti L_{3,2}-edge spectra in fluorescence yield (FLY) (Figure SI-1) and TEY mode the same spectral features. FLY gives bulk-sensitive information whereas TEY is surface sensitive. From Ti L_{3,2}-edge spectra in Figure 3a we can see that there are a couple of

weak pre-edge shoulder peaks (marked as p_1 and p_2) at 458.5 eV and 460.0 eV, followed by two series of strong resonances denoted as a, b, and c, d, for the apparent L_3 and L_2 edges, respectively. These spectral features are typical indication of Ti atoms in the distorted TiO_6 octahedral structure.^{20,21} In general, p_1 and p_2 at the pre-edge can be attributed to core hole-d electron coupling; peaks a, b at the Ti L_3 -edge are assigned to dipole excitation from Ti $2p_{3/2}$ state to t_{2g} and e_g unoccupied states, respectively; c and d peaks at Ti L_2 -edge to electronic transition from Ti $2p_{1/2}$ states to t_{2g} and e_g unoccupied states, respectively.^{16,17,20,21} For NTO-25, the Ti $L_{3,2}$ -edge spectrum shows broadening feature compared to anatase TiO_2 and NTO 900, reflecting the highly disordered and amorphous character in the as-deposited sodium titanate (NTO-25).^{21,22} Moreover, the a and b peaks for NTO-25 shift to a lower energy with 0.2 eV compared to those of anatase TiO_2 (Table SI-1), suggesting the reduction of Ti^{4+} in amorphous sodium titanate due to the introduction of Na ions.²² Turning our attention to NTO-500, the pre-edge peaks (p_1 and p_2) and L_3 -edge peaks (a and b) become more intense and well-resolved in contrast to NTO-25, and the splitting of b peak into b_1 and b_2 peaks can be clearly identified. The a and b peaks of NTO-500 and NTO-900 shift to energy positions higher than those of NTO-25, but slightly lower than anatase TiO_2 (~ 0.1 eV), indicating the oxidation of Ti atoms in amorphous sodium titanate during the annealing process (Table SI-1). The relative intensity ratio of b_1/b_2 peaks is the spectral fingerprint of different types of TiO_2 ($I_{b_1}/I_{b_2} > 1$ for anatase TiO_2 , $I_{b_1}/I_{b_2} < 1$ for rutile TiO_2), and it has been well documented by experiment and theory.^{16,20} In Figure 3a, the intensity ratio and position of b_1 and b_2 peaks for NTO-500 follow a similar trend as those for anatase TiO_2 , indicating the formation of anatase TiO_2 structure in NTO-500 (in agreement with the XRD finding in Figure 1a). It is noteworthy that I_{b_1}/I_{b_2} of NTO-500 is relatively lower than that of anatase TiO_2 , and the Ti L_3 -edge spectrum of NTO-500 bears the

broadening feature of NTO-25. This comparison suggests that amorphous sodium titanate still remains in NTO-500. Therefore, NTO-500 mainly consists of anatase TiO_2 and amorphous sodium titanate. For NTO-900, the Ti L_2 -edge and L_3 -edge peaks show narrowed feature, revealing a high crystallinity of sodium titanate annealed at 900 °C. Moreover, the absence of b peak splitting indicates that there is no significant tetragonal distortion in NTO-900,¹⁷ due to the incorporation of Na ions in the monoclinic $\text{Na}_{0.23}\text{TiO}_2$ structure. Another notable difference between NTO-900 and NTO-500 as well as anatase TiO_2 is the relative lower intensity ratio of a/b peak at L_3 -edge, which is reflective of the smaller crystal field in NTO-900 than in the latters.^{17,21} The relative intensity of the L_3 -edge doublets a and b peaks is related to the strength of the crystal field. In general, the larger the crystal field, the more intense the peak a relative to peak b.¹⁷ Ti $L_{3,2}$ -edge spectra analysis complements the finding on the phase transition pathway of sodium titanate from *in-situ* XRD characterization. It also reveals that the oxidation state of Ti atoms was lower than 4+ in amorphous sodium titanate, and then slightly increased during subsequent annealing process. In addition, Ti $L_{3,2}$ -edge spectra analysis discloses the reduced tetragonal distortion in NTO-900 compared with anatase TiO_2 as a result of their structural difference (Figures 1c, and 1d).

Ti K-edge feature is highly sensitive to local bonding environment of the targeted element, thus providing diagnostic information on the crystal structure and oxidation state.^{23,24} Therefore, Ti K-edge XANES analysis was further conducted on amorphous sodium titanate, NTO-500, NTO-700, and NTO-900. The results are presented in Figure 3b. All the Ti K-edge spectra show typical pre-edge feature and the white line.²³⁻²⁶ The edge region in the absorption spectra provides clear information on the environment geometry and electronic structure of the

absorption atom.^{23,24} In Figure 3b, the edge position (the peak maximum of the first derivative function) of Ti-K edge spectra are determined to be 4978.9 eV for NTO-25, 4979.1 eV for NTO-500, NTO-700 and NTO-900, and 4979.2 eV for anatase TiO₂ (as compared in Table SI-1). The relative lower edge position of NTO-25 than anatase TiO₂ is indicative of the oxidation state of Ti atoms lower than 4+ in the former, consistent with the conclusion drawn from Ti L_{3,2}-edge spectra analysis (Figure 3a). The white line of NTO-900 has a slightly lower energy than anatase TiO₂, due to a nominal Ti oxidation state of ~ 3.8+ in crystalline Na_{0.23}TiO₂. It should be pointed out that in addition to the oxidation state, the change in Ti-O bond distance and crystal structure can also affect the edge position of Ti K-edge.²³ In Figure 3c, the characteristic pre-edge peaks (marked as A, B, C, and D) between 4965 eV and 4973 eV arise from quadrupole transition and hybridization of p and d orbitals of the Ti atom and surrounding neighbors.²³⁻²⁶ Although the interpretation of these pre-edge peaks is still ambiguous in literatures, the spectral difference among anatase TiO₂ and sodium titanates in the pre-edge region still can act as a reference for identifying titanate structure in future. All the samples show one peak A at 4968.8 eV, which is assigned to the quadrupole transition of 1s to t_{2g} states of octahedral TiO₆.^{22,23} The relative intensity ratio between peak B and peak C is much higher in sodium titanate than in anatase TiO₂. The strongest peak B located at 4970.9 eV appears to be a typical feature of sodium titanate, and has been detected previously in sodium titanate nanoribbons. The peak D of sodium titanate is nearly the same as anatase TiO₂, and is attributable to the transition to e_g band state.^{22,23} Fourier transformations (FT) of extended X-ray absorption fine structure (EXAFS) spectra of sodium titanate are shown in Figure 3d. The change in the coordination number of Ti atoms can be clearly observed in the FTs of Ti K-edge EXAFS (in R-space). In Figure 3d the peaks located at about 1.6 Å and 2.5 Å correspond to Ti-O and Ti-Ti coordination shells,

275 respectively.²² The relative intensity tracks the coordination number and Debye-Waller factor
276 (disorder). Any static disorder will reduce the amplitude. All sodium titanates exhibit similar
277 EXAFS oscillations in the low R-region. But, noticeable higher magnitude is observed in the
278 sodium titanate annealed at a higher temperature, revealing a higher coordination number and/or
279 Debye-Waller factor on average of Ti atoms and hence an increase of crystallinity among them.²²
280 Moreover, NTO-900 exhibits a slightly larger R interatomic distance of Ti-O bond than the
281 others, probably due to the insertion of Na ions in the atomic structure, as seen in the crystal
282 structure of $\text{Na}_{0.23}\text{TiO}_2$ (Figure 1c). From Figure 3, it can be concluded that the elevated
283 annealing temperature increases the coordination number of Ti atoms and the crystallinity of
284 sodium titanate, and causes a slight increase in the Ti oxidation state.

285
286 **Figure 4.** (a) STXM optical density image of NTO-500 (the image was averaged from all
287 stack images at the Ti $L_{3,2}$ -edge); (b) Ti $L_{3,2}$ -edge XANES spectra extracted from different ROIs
288 in (a) and together with an average spectrum (sum) of these ROIs in comparison with the TEY
289 spectra of anatase TiO_2 , NTO-25, and NTO-900; STXM chemical maps of Ti in (c) anatase TiO_2 ,

(d) amorphous sodium titanate, and (e) composite map of Ti in anatase TiO_2 (red) and amorphous sodium titanate (blue) (green is holy carbon). The scale bars in (a, c, d, and e) represent 500 nm.

XANES analysis provides averaged spectroscopic information about the whole sample of sodium titanate, and no microscopic information could be extracted. In contrast, STXM measures absolute absorption of the specimen in transmission mode by using a nano-sized X-ray beam, and is a powerful technique to extract spectromicroscopic information on chemical map and corresponding absorption spectroscopic feature of an interested nanostructure.^{27,28} Therefore, STXM is adopted to analyze the phase and chemical distribution in NTO-500 and NTO-700, which have mixed phases of amorphous sodium titante, anatase TiO_2 and/or crystalline $\text{Na}_{0.23}\text{TiO}_2$. Figure 4a shows a STXM optical density image of NTO-500 recorded at the Ti $L_{3,2}$ -edge (see corresponding TEM image of the same region in Figure SI-2a). Ti $L_{3,2}$ -edge XANES spectra collected from the region of interest (ROI) marked in the STXM optical density image (Figure 4a) are shown in Figure 4b and compared with those of amorphous sodium titante (NTO-25), anatase TiO_2 , and crystalline $\text{Na}_{0.23}\text{TiO}_2$ (NTO-900). The Ti $L_{3,2}$ -edge XANES spectra from ROI-1, ROI-2, and ROI-3 show a distinct feature of energy splitting of b_1 and b_2 peaks, which is the same as observed in the Ti $L_{3,2}$ -edge spectrum of NTO-500 in Figure 3a. the energy positions of b_1 and b_2 peaks are aligned with those of anatase TiO_2 , revealing the dominance of anatase TiO_2 -like structure in ROI-1, ROI-2, and ROI-3. For ROI-4, ROI-5, ROI-6, and ROI-7, the Ti $L_{3,2}$ -edge XANES spectra exhibit broadened feature in the b peak, with a hardly noticable b_2 at the Ti L_3 -edge, which is about 0.2 eV lower than that of $\text{Na}_{0.23}\text{TiO}_2$, but in agreement well with that of amorphous sodium titanate. Therefore, the region of ROI-4, ROI-5, ROI-6, and ROI-7 is mainly composed of disordered sodium titanate. STXM chemical maps of anatase TiO_2 and

amorphous sodium titanate in NTO-500 are displayed in Figure 4c and 4d, respectively. While anatase TiO_2 mainly exists in the region of ROI-1, ROI-2, and ROI-3, a trace amount of anatase TiO_2 appears in ROI-6 and ROI-7 (Figure 4c). The distribution of amorphous sodium titanate in this sample is opposite to anatase TiO_2 (Figure 4d). Figure 4e presents the composite map of amorphous sodium titanate (blue) and anatase TiO_2 (red) in NTO-500. It is evident that both phases coexist in the region of ROI-3, while anatase TiO_2 begins to nucleate in the regions marked by white arrows. The TEM image of the same region (Figure SI-1a) indicates that the tubular structure collapse in ROI-1, ROI-2, and ROI-3, but maintain its shape in ROI-4, ROI-5, ROI-6. The STXM chemical map in Figure 4 clearly shows that the nucleation and growth of anatase TiO_2 are non-uniform in the local region of NTO-500, and preferably occurs in the collapsed structure.

Figure 5. (a) STXM optical density image of NTO-700 (the image was averaged from all stack images at the Ti $L_{3,2}$ -edge); (b) Ti $L_{3,2}$ -edge XANES spectra extracted from different ROIs in (a) and together with an average spectrum (sum) of these ROIs in comparison with the TEY spectra of anatase TiO_2 , NTO-25, and NTO-900; STXM chemical mappings of Ti in (c)

crystalline $\text{Na}_{0.23}\text{TiO}_2$, (d) anatase TiO_2 , and (e) overlap of Ti in crystalline $\text{Na}_{0.23}\text{TiO}_2$ (green) and anatase TiO_2 (red). The scale bars in (a, c, d, and e) represent 200 nm.

The STXM optical density image of NTO-500 recorded at the Ti $L_{3,2}$ -edge is illustrated in Figure 5a. Ti $L_{3,2}$ -edge XANES spectrum collected from ROI-1 (Figure 5b) exhibits a well-resolved b peak at the Ti L_3 -edge, and the intensity ratio of the splitted b_1/b_2 peaks is close to that of anatase TiO_2 . In contrast, the Ti $L_{3,2}$ -edge spectra extracted from other ROIs show similarity as $\text{Na}_{0.23}\text{TiO}_2$ (NTO-900), and the energy position of b peak is about 0.2 eV higher than that of amorphous sodium titanate (NTO-25). Chemical maps in Figures 5c and 5d present that $\text{Na}_{0.23}\text{TiO}_2$ and anatase TiO_2 are distributed across the whole region of NTO-700. The overlapping chemical map in Figure 5e show the mixed distribution of $\text{Na}_{0.23}\text{TiO}_2$ (green) and anatase TiO_2 (red), between which the boundary can be identified. The STXM analysis in Figure 4 and Figure 5 allow us to visualize the nanoscale phase distribution in sodium titanates at different annealing temperatures.

The detailed analysis by combining *in-situ* XRD, SEM, XAS, and STXM techniques reveal the phase transition pathway of amorphous to crystalline sodium titanate with annealing temperature. Sodium titanate grown on CNTs shows highly disordered structure at the as-deposited state. At a relative low temperature (500 °C), anatase TiO_2 first nucleates and grows in the amorphous sodium titanate, preferably in the collapsed region. With the increase of temperature to 700 °C, anatase TiO_2 recrystallizes into $\text{Na}_{0.23}\text{TiO}_2$ by reacting with sodium in the structure. TiO_2 to $\text{Na}_{0.23}\text{TiO}_2$ phase transition is relatively slow, and complete in 300 min at 900 °C. Anatase TiO_2 phase is stable even at 900 °C, and does not change to rutile TiO_2 phase as generally observed in

pure TiO_2 system.²⁹ While the influence of alkaline ions on the phase transition temperature of anatase TiO_2 to rutile TiO_2 is still in debate and totally opposite conclusions have been drawn, our work suggests that the introduction of Na^+ and sodium titanate improves the thermal stability of anatase TiO_2 and therefore increases the phase transition temperature of anatase TiO_2 to rutile TiO_2 .

Conclusions

The phase transition mechanism of sodium titanate upon annealing was elucidated by using *in-situ* XRD, SEM, XANES, and STXM characterizations. Amorphous sodium titanate was stable at room temperature and crystallized into anatase TiO_2 at low annealing temperatures. Anatase TiO_2 was found to recrystallize into monoclinic $\text{Na}_{0.23}\text{TiO}_2$ at 900 °C. STXM chemical mapping revealed that nucleation and growth of anatase TiO_2 was non-uniform in the matrix of amorphous sodium titanate at 500 °C, while the phase transition from anatase TiO_2 into $\text{Na}_{0.23}\text{TiO}_2$ occurred in the whole structure at 700 °C. Moreover, Ti $L_{3,2}$ -edge and K-edge XANES studies revealed that Ti oxidation state in sodium titanate increased during the annealing process.

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References

- (1) Senguttuvan, P.; Rousse, G.; Seznec, V.; Tarascon, J.-M.; Palacin, M.R. *Chem. Mater.* **2011**, 23, 4109. DOI: [10.1021/cm202076g](https://doi.org/10.1021/cm202076g)
- (2) Wu, D.; Li, X.; Xu, B.; Twu, N.; Liu, L.; Ceder, G. *Energy Environ. Sci.* **2015**, 8, 195. DOI: [10.1039/C4EE03045A](https://doi.org/10.1039/C4EE03045A)
- (3) Pan, H.; Lu, X.; Yu, X.; Hu, Y.-S.; Li, H.; Yang, X.-Q.; Chen, L. *Adv. Energy Mater.* **2013**, 3, 1186. DOI: [10.1002/aenm.201300139](https://doi.org/10.1002/aenm.201300139)
- (4) Štengl, V.; Bakardjieva, S.; Šubrt, J.; Večerníková, E.; Szatmary, L.; Klementová, M.; Balek, V. *Appl. Catal. B-Environ.* **2006**, 63, 20. DOI: [10.1016/j.apcatb.2005.09.006](https://doi.org/10.1016/j.apcatb.2005.09.006)
- (5) Song, H.; Jiang, H.; Liu, T.; Liu, X.; Meng, G. *Mater. Res. Bull.* **2007**, 42, 334. DOI: [10.1016/j.materresbull.2006.05.025](https://doi.org/10.1016/j.materresbull.2006.05.025)
- (6) El-Naggar, I.M.; Mowafy, E.-A.; Ali, I.M.; Aly, H.F. *J. Int. Adsorp. Soc.* **2002**, 8, 225. DOI: [10.1023/A:1021212617839](https://doi.org/10.1023/A:1021212617839)
- (7) Liu J.; Banis, M.N.; Xiao, B.; Sun, Q.; Lushington, A.; Li, R.; Guo, J.; Sham, T.-K.; X. Sun. *J. Mater. Chem. A* **2015**, 3, 24281. DOI: [10.1039/C5TA08435K](https://doi.org/10.1039/C5TA08435K)

- 397 (8) Li, M.-J.; Chi, Z.-Y.; Wu, Y.-C. *J. Am. Ceram. Soc.* **2012**, *95*, 3297. DOI: [10.1111/j.1551-](https://doi.org/10.1111/j.1551-2916.2012.05330.x)
398 [2916.2012.05330.x](https://doi.org/10.1111/j.1551-2916.2012.05330.x)
- 399 (9) Zárate, R.A.; Fuentes, S.; Wiff, J.P.; Fuenzalida, V.M.; Cabrera, A.L. *J. Phys. Chem. Solids*
400 **2017**, *68*, 628. DOI: [10.1016/j.jpcs.2007.02.011](https://doi.org/10.1016/j.jpcs.2007.02.011)
- 401 (10) Viana, B.C.; Ferreira, O.P.; Filho, A.G.S.; Filho, J.M.; Alves, O.L. *J. Braz. Chem. Soc.*
402 **2009**, *20*, 167. DOI: <http://dx.doi.org/10.1590/S0103-50532009000100025>
- 403 (11) Tsai, C.C.; Teng, H. *Chem. Mater.* **2006**, *18*, 367. DOI: [10.1021/cm0518527](https://doi.org/10.1021/cm0518527)
- 404 (12) Yang, J.; Jin, Z.; Wang, X.; Li, W.; Zhang, J.; Zhang, S.; Guo, X.; Zhang, Z. *Dalton*
405 *Trans.* **2003**, *20*, 3898. DOI: [10.1039/B305585J](https://doi.org/10.1039/B305585J)
- 406 (13) Zhu, K.R.; Yuan, Y.; Zhang, M.S.; Hong, J.M.; Deng, T.; Yin, Z. *Solid State Commun.*
407 **2007**, *144*, 450. DOI: [10.1016/j.ssc.2007.09.015](https://doi.org/10.1016/j.ssc.2007.09.015)
- 408 (14) Sun, X.; Li, Y. *Chem. Eur. J.* **2003**, *9*, 2229. DOI: [10.1002/chem.200204394](https://doi.org/10.1002/chem.200204394)
- 409 (15) Papp, S.; Korosi, L.; Meynen, V.; Cool, P.; Vansant, E.F.; Dekany, I. *J. Solid State Chem.*
410 **2005**, *178*, 1614. DOI: [10.1016/j.jssc.2005.03.001](https://doi.org/10.1016/j.jssc.2005.03.001)
- 411 (16) Li, J.; Wang, Z.; Zhao, A.; Wang, J.; Song, Y.; Sham, T.-K. *J. Phys. Chem. C.* **2015**, *119*,
412 17848. DOI: [10.1021/acs.jpcc.5b04276](https://doi.org/10.1021/acs.jpcc.5b04276)
- 413 (17) Zhou, J.G.; Fang, H.T.; Maley, J.M.; Murphy, M.W.; Peter Ko J.Y.; Cutler, J.N.;
414 Sammynaiken, R.; Sham, T.-K.; Liu, M.; Li, F. *J. Mater. Chem.* **2009**, *19*, 6804. DOI:
415 [10.1039/B909225K](https://doi.org/10.1039/B909225K)
- 416 (18) Pearson, A.L.; Chao, W.L.; Denbeaux, G.; Eimuller, T.; Fischer, P.; Johnson, L.; Koehler,
417 M.; Larabell, C.; Le Gros, M.; Yager, D.; Attwood, D.T. *Proc. SPIE* **2000**, *4146*, 54. DOI:
418 [10.1117/12.406672](https://doi.org/10.1117/12.406672)

- 419 (19) Wang, Z.Q.; Wang, W.; Sham, T.K.; Yang, S.G. *Nanoscale* **2014**, *6*, 9783. DOI:
420 [10.1039/C4NR02231A](https://doi.org/10.1039/C4NR02231A)
- 421 (20) Henderson, G.S.; Liu, X.; Fleet, M.E. *Phys. Chem. Minerals* **2002**, *29*, 32. DOI:
422 [10.1007/s002690100208](https://doi.org/10.1007/s002690100208)
- 423 (21) Kucheyev, S.O.; van Buuren, T.; Baumann, T.F.; Satcher, J.H.; Willey, T.M.;
424 Meulenberg, R.W.; Felter, T.E.; Poco, J.F.; Gammon, S.A.; Terminello, L.J. *Phys. Rev. B*
425 **2004**, *69*, 245102. DOI: [10.1103/PhysRevB.69.245102](https://doi.org/10.1103/PhysRevB.69.245102)
- 426 (22) Wang, D.; Liu, J.; Sun, X.; Sham, T.-K. *J. Mater. Chem. A* **2015**, *3*, 412. DOI:
427 [10.1039/C4TA04873C](https://doi.org/10.1039/C4TA04873C)
- 428 (23) Wagemaker, M.; Lützenkirchen-Hecht, D.; van Well, A.A.; Frahm, R. *J. Phys. Chem. B*
429 **2004**, *108*, 12456. DOI: [10.1021/jp048567f](https://doi.org/10.1021/jp048567f)
- 430 (24) Borghols, W.J.H.; Lützenkirchen-Hecht, D.; Haake, U.; van Eck, E.R.H.; Muldera, F.M.;
431 Wagemaker, M. *Phys. Chem. Chem. Phys.* **2009**, *11*, 5742. DOI: [10.1039/B823142G](https://doi.org/10.1039/B823142G)
- 432 (25) Nakahira, A.; Kubo, T.; Numako, C. *Appl. Mater. Interfaces* **2010**, *2*, 2611. DOI:
433 [10.1021/am1004442](https://doi.org/10.1021/am1004442)
- 434 (26) Avansi, Jr. W.; Arenal, R.; de Mendoca, V.R.; Ribeiro, C.; Longo, E. *CrystEngComm*
435 **2014**, *16*, 5021. DOI: [10.1039/C3CE42356E](https://doi.org/10.1039/C3CE42356E)
- 436 (27) Zhou, J.G.; Wang, J.; Liu, Hao.; Banis, M.N.; Sun, X.; Sham, T.-K. *J. Phys. Chem. Lett.*
437 **2010**, *1*, 1709. DOI: [10.1021/jz100376v](https://doi.org/10.1021/jz100376v)
- 438 (28) Wang, J.; Zhou, J.; Hu, Y.; Regier, T. *Energy Environ. Sci.* **2013**, *6*, 926. DOI:
439 [10.1039/C2EE23844F](https://doi.org/10.1039/C2EE23844F)
- 440 (29) Hanaor, D.A.H.; Sorrell, C.C. *J. Mater. Sci.* **2011**, *46*, 855. DOI: [10.1007/s10853-010-](https://doi.org/10.1007/s10853-010-5113-0)
441 [5113-0](https://doi.org/10.1007/s10853-010-5113-0)

Graphical Abstract