Understanding the Orderliness of Atomic Arrangement toward Enhanced Sodium Storage

Min Zhou, Yang Xu, Junxiang Xiang, Chengliang Wang, Liying Liang, Liao Yong Wen, Yaoguo Fang, Yan Mi, and Yong Lei*

In response to the increased demands of available energy storage, sodium ion batteries (SIBs) appear as promising alternatives to widely used lithium ion batteries. However, because of large radius of Na ions, more complex requirements for the intrinsic properties raise the difficulties in finding a suitable material, in particularly for electrodes with intercalation mechanism. Concerning the principle of designing effective electrodes, the ordering of atomic arrangements should be at the heart in SIBs due to its significant influences on various electrochemical processes, such as ion absorption, ion diffusion, electron diffusion, etc. As proof-of-concept, the state-of-the art TiO2 electrodes with different orderliness of atomic arrangement are achieved through colloidal crystal template method assisted by low-temperature atomic layer deposition and post-heating treatment. The disordering at the surface is benefit for the contribution from surface processes, which is particularly significant to the electrode materials with poorer affinity of transporting ions. Meanwhile, the disordering in bulk results in better ion diffusion, but worse electron transport. Understanding this relationship between atomic orderliness and battery performance is of importance for extending the design principle to some traditional electrodes for highly effective energy storage.

1. Introduction

Owing to the dependence on the consumption of fossil fuel, more and more serious environmental issues prompt a strong demand of green energy storage with high efficiency.[1] Among numerous available alternative technologies, secondary lithium-ion battery (LIB) has been regarded as predominant power source for electronics and vehicles now.[2] However, the scarcity of lithium, safety, and cost form a potential obstacle for large-scale applications. Na, which is in the same series of alkali metal elements, possesses similar electrochemical properties with Li, but earth-abundance and low cost. So sodium-ion battery (SIB) becomes commercially competitive for with LIB.[3] Drawing inspiration from the similar rocking-chair mechanism with LIB, researchers has made rapid progress in identifying ideal electrodes, especially in the field of cathodes.[4] As for anodes, some state-of-the-art materials cannot accommodate the reversible intercalation of Na ions.[3] such as graphite.[6] The reasons mainly arise from the larger ionic radius of Na (1.02 Å) than Li (0.76 Å).[7] A higher ionization potential,[8] and preferable coordination in octahedral or prismatic site of Na ions.[9] More complex requirements for the intrinsic properties raise the difficulties in finding a suitable material, in particularly for electrodes with intercalation mechanism. A more open framework is favorable for acceptable mobility, otherwise, the (de-) sodiation processes could induce large distortions in the lattice that ultimately lead to pulverization of the electrode and the impending failure of batteries.[10]

Concerning the discovery and design of ideal electrodes, the ordering of atomic arrangements is at the heart in SIBs, because the resulting changes on storage mechanism,[11] surface state,[12] and type/volume of polyhedral sites[13] play a vital role on the important electrochemical processes, like electrical conductivity, ion absorption, ion insertion, ion diffusion, and so on. Disordered atomic arrangements with isotropic characteristics may form percolation pathways via some open active diffusion channels to facilitate ionic transport, while long-range ordered atomic arrangements have the primary electro-active species of choice, and narrow potential window required to achieve the capacities.[14,15] With regard to SIB field, the controversy about the ordering seems more obscure due to the large Na ions. Taking a typical electrode material, TiO2, as an example, Xiong et al. proposed that long-range ordered polymorphs (e.g., anatase, rutile) cannot support Na-ion intercalation at all because of higher sodium diffusion barrier.[12] But Su et al. found that anatase TiO2 have superior capacities than disordered amorphous TiO2.[16]

To reach a more accurate insight into the argument, a suitable platform is required for the systemic and scientific studies. Two factors of electrode design should be considered simultaneously. (1) The electrode should be tested without any conductive additive and polymeric binder, which will bring unclear changes on the electrical conductivity and surface state. (2) Morphological features of materials with different atomic
ordering should be identical to avoid extra influences from surface area, electron/ion diffusion length, and so on. Therefore, it is highly desirable to explore a strategy that is capable of achieving TiO$_2$ architectures with precise structure and atomic ordering tuning. The architectures with designed features must be stable during the tuning of the structural ordering. Inspired by above considerations and template confined method, we choose colloidal crystal templates\(^\text{[17,18]}\) and seek to realize the topological transformation from the templates using low-temperature atomic layer deposition (ALD) technique.\(^\text{[19]}\) The 3D ordered porous architecture is constructed directly on the conductive substrate with identical morphologic features according to the templates, such as pore size, packing type of particles. Meanwhile, the operation at low temperature holds the promise to assure the integrity and the unique of the architecture and the amorphous structural features with short-range ordered or disordered atomic arrangements. Subsequently, the ordering of atomic arrangements can be adjusted easily upon different heating treatment.

In this work, the state-of-the art electrodes in SIBs with different ordered degrees of atomic arrangement are achieved through colloidal crystal template method assisted by low-temperature ALD. Based on this platform, we correlate the battery performance with structural ordering. Different from previous reports in LIBs and SIBs, our results conclude that the disordering at the surface is benefit for the contribution from surface processes, which is particularly significant to the electrode materials with poorer affinity of transporting ions. But the more interrelations with electrolyte will decrease the long-term stability. Meanwhile, the disordering in bulk results in better ion diffusion, but worse electron transport. Understanding this relationship between atomic ordering degree and battery performance is of importance for systematically adjusting and finally extending the design principle to some traditional electrodes for highly effective energy storage.

### 2. Results and Discussions

The actualization of this tentative architecture is revealed in Figure 1a.\(^\text{[20]}\) Polystyrene spheres (PSs) are self-assembled to form colloidal crystal template directly on the conductive Ti foil. Then low-temperature ALD is employed as the infiltration technique to realize the complete topological transform from the templates. To ensure disordered nature and avoid the huge deformation above the PSs’ glass transition (98 °C), we choose 70 °C as the deposition temperature after optimization, and then the as-prepared intermediate is immersed into tetrahydrofuran (THF) for 48 h in ambient air to remove the template via dissolution. The featureless X-ray diffraction (XRD) pattern and Raman spectra of pristine sample in Figure 1b,c (red) indicates disordered atomic arrangement. Post-heating process has been regarded as a facile and straightforward procedure to change the order degree of atomic arrangement. Upon annealing at different temperatures, it is clearly seen from the XRD patterns in Figure 1b that the atoms become more ordered to form anatase TiO$_2$ (I41/amd) above 350 °C. As well known, XRD indicates the long-range order of materials and offers average structural information within several unit cells. Raman scattering as a local probe is more sensitive to local symmetry of materials\(^\text{[21]}\). The Raman modes of anatase TiO$_2$\(^\text{[22]}\) appear at the spectra of samples after annealing at 350 °C, where no peaks can be observed from pristine sample without annealing. The comparison indicates the long-range orderliness of atomic arrangement. Furthermore, two characteristic peaks in X-ray photoelectron spectroscopy (XPS) (458.6 and 464.4 eV) manifest that Ti ions are mainly presented as...
Ti$^{4+}$ in the lattice within all the samples instead of Ti$^{3+}$ or Ti$^{0}$.[23,24] As for the pristine sample after annealing at 250 °C, it is worth noting that although there are no peaks belonged to anatase TiO$_2$ appearing in the XRD pattern, but the obvious peak in Raman spectra proves that the atomic arrangement turns to be more ordered and form partial symmetry. In this sense, the TiO$_2$ architectures with different order degrees of atomic arrangements are well realized to validate this rational design. Considering that anatase structure is the most feasible matrix for the reversible intercalation of Na ions because of possible interstitial sites based on the stacking TiO$_6$ octahedraons and suitable paths for ion diffusion, we choose anatase as the reference with long-range order. For the purpose of visualized understanding, hereafter, as shown in Figure 1 b–d, the pristine sample without annealing is designated as sample with disordered (DO) atomic arrangement, whereas the samples after annealing at 350 °C are designated as samples with long-range ordered (LO) atomic arrangement. Similarly, we name the sample after annealing at 250 °C as partially ordered (PO) sample.

To further make sure the unique morphological features, we perform the observations from the scanning electron microscopic (SEM) images and transmission electron microscopic (TEM) images (Figure 2). The morphological features nearly keep the same upon different annealing temperatures. All the electron microscopic images demonstrate similar inverse opal morphology with high degree of hexagonal symmetry, which is completely transformed from colloidal crystal template using ≈500 nm PSs. More details seen from TEM images in Figure 2c,h,m confirm that the periodic packing of hollow spheres with unique diameter (≈500 nm) and wall thickness (≈20 nm) are connected with each other to make open channels that allow a continuous skeleton with a three-dimensionally interconnected pore system. Although LO, PO, and DO share nearly all the same geometrical characteristics, when carefully observing the SEM images at high magnification, we find that the surface of LO is much rougher than that of DO and PO, in compliance with the TEM results. This variation could be ascribed to the increased degree of atomic order and correspond to the formation of anatase crystalline particles as

Figure 2. Morphology characterizations of disordered (DO, a–e), partially ordered (PO, f–j) and long-range ordered (LO, k–o) TiO$_2$ architectures. a,b,f,g,k,l) Typical top-view SEM images corresponding inverse opal architecture at low and high magnifications. c,d,h,i,m,n) Typical TEM and HRTEM images in edge part. e,j) Typical SAED pattern of (c, h). o) Fast Fourier transform (FFT) image based on the lattice fringe in panel (n).
evidenced from the high-resolution TEM images. No discernible lattice fringe can be observed in DO and PO (Figure 2d,i), while we could find clear lattice fringe in LO that are assigned to (010) facet in anatase TiO$_2$. These results are in accord with above-mentioned conclusions from XRD and Raman analysis, together with the proofs from featureless selected area electron diffraction (SAED) pattern of DO (Figure 2e,j) and clear fast Fourier transform images of LO (Figure 2o).

To quantify the activity toward Na-ion storage, two-electrode coin cells with TiO$_2$-based working electrode and Na disk counter electrode are employed as a half-cell configuration. Since the interconnected porous architectures are fabricated directly on the conductive substrate, it is not necessary to add any conductive additive and polymeric binder, which may introduce uncertain influences to hinder the observations between atomic arrangement and SIB performance. Cyclic voltammetry (CV) are first recorded to elucidate the redox processes in host matrix with different degree of atomic ordering. Shown in Figure 3a are the CV curves of the 10th cycle at a sweep rate of 0.1 mV s$^{-1}$ in the potential range of 0.01–3.0 V (vs. Na/Na$^+$), where the curves of 1st and 5th cycles are illustrated in Figure S1 (Supporting Information). Regarding the CV curve of LO, a redox couple at 0.82 V (anodic) and 0.66 V (cathodic) indicates the reversible insertion/extraction of sodium.\[25\] In the case of DO and PO, no peaks appear over the entire potential range, indicating the wide distribution of redox events associated with broad energy dispersion of sodiation sites.

More information can be revealed from the voltage profiles to illustrate the electrochemistry of (de-)sodiation in the host. As shown in Figure 3b–d, we list the discharge voltage profiles of 1st, 2nd, 20th, and 50th cycles at 50 mA g$^{-1}$. Compared with the profiles among DO, PO and LO after different cycles, DO and PO exhibit a slope feature, while the plateau is more obvious in LO’s curves. These appearances further evidence the CV analysis of redox. More noteworthy, the initial discharge capacity of DO is 408.9 mA h g$^{-1}$, while the value turns to 218.2 mA h g$^{-1}$ after 50 cycles. In case of LO TiO$_2$, the specific capacities are 280.9 and 219.1 mA h g$^{-1}$. PO shows medium performance in both capacity and stability to bridge the electrochemical properties between DO and LO. These values represent the high specific capacity within various pure TiO$_2$ anodes as evidenced in Table S1 (Supporting Information)$^{[5,10,12,15,26]}$ and even higher or comparable to composite TiO$_2$ systems$^{[25,27,28]}$ implying that LO, PO and DO TiO$_2$ possess excellent ability of sodium storage.

To illuminate the effects of atomic ordering on sodium storage, the cycle stability at different charging/discharging current densities and rate performance of these half-cells are depicted in Figure 4. As a comparatively low current density, 50 mA g$^{-1}$, the specific capacities of DO and LO TiO$_2$ still remain 171 and 202.9 mA h g$^{-1}$ even upon 200 cycles (Figure 4a). Both the values stand out among numerous TiO$_2$-based electrodes in SIBs because of the long-term stability.$^{[5,12,16,25]}$ When carefully observing this segment, we find that DO possesses higher capacities at the initial several cycles, but suffers from a rapid fading of capacities. In other words, the stability of LO is comparatively better. The retention reaches 92.5% from 50 cycles to 200 cycles. However, with the charging/discharging current density increasing to 500 and 2000 mA g$^{-1}$ (Figure 4b,c), all DO, PO, and LO show the good

![Figure 3. a) The CV curves at a scan rate of 0.1 mV s$^{-1}$ in the potential range of 0.01–3.0 V of TiO$_2$ electrodes with different atomic ordering. b,c,d) Sodiation voltage profiles at 50 mA g$^{-1}$ of DO (b), PO (c), and LO (d).](image-url)
stabilities, implying that high-rate Na-ion insertion/extraction into the hosts is feasible. A close look at the capacities at high rates suggests better sodium storage of DO than LO. The comparison of rate performance in Figure 4d and Figure S3 (Supporting Information) further confirms the evolution of the specific capacities upon cycling. Overall, since Ti foil as the substrate contributes little to the final capacity (Figure S2, Supporting Information) and the morphology features keep unique, the striking differences in electrochemistry are completely attributed to the order degree of atomic arrangement.

Analysis of the cycling and rate performance of disordered, partially ordered and long-range ordered TiO2 allows us to draw the following conclusions: (1) All disordered, partially ordered, and long-range ordered TiO2 with periodic porous architectures are potential candidates for high performance SIB because of superior rate capacities and cycling stability, in particularly at high rates. (2) Disordered TiO2 shows better rate performance both in capacities and stability at high rates. (3) Long-range ordered TiO2 exhibits excellent long-term stability at low rate. (4) Partially ordered TiO2 possesses medium electrochemical performance between LO and DO. Hence, the degree of atomic order indeed plays a visible role on SIB performance.

In order to systemically understand why the degree of atomic order can influence the battery performance so much, an investigation of thermodynamics is helpful to gain insight to the feasibility and reversibility of the process. With regard to the sodium storage mechanism, according to the XRD patterns after long-term cycling in Figure S4 (Supporting Information), invisible peaks from Na2O, etc. or other extra products indicate a reversible Ti\(^4+\)/Ti\(^3+\) redox and Na-ion intercalation mechanism, being consistent with studies in previous literatures. The overall reaction can be written as

\[
\text{TiO}_2 + x\text{Na} \leftrightarrow \text{Na}_x\text{TiO}_2
\]

After simulation and structural optimization, the sodium storage in both disordered and long-range ordered TiO2 is possible up to one Na per TiO2 (i.e., \(x = 1\)), yielding the theoretical capacity as high as 335 mA h g\(^{-1}\). As shown in Figure 5a,b, because of the large radius, Na ions prefer to occupy interstitial octahedral positions. Fortunately, the volume of octahedral site in LO (anatase) is large enough for the accommodation. Meanwhile, disordered atomic arrangement in DO can create larger or smaller spatial sites than those in LO. On average, the thermodynamic ability for (de-)sodiation is similar between DO and LO in theory.

However, what is the possible origin of the gaps between the SIB performance of DO and LO? With the understanding in thermodynamics established, we turn our eyes on the kinetic factors. As well known, CV is a powerful approach to illuminate the electrochemical kinetics of the electrodes toward Na ions. Figure 6a,c,e displays the CV curves of DO, PO, and LO at various sweep rates from 0.1 to 5 mV s\(^{-1}\). Regarding to the contributions to total sodium storage, there are two typical types\([28,29]\): (1) the faradaic contribution from Na-ion intercalation; (2) the surface faradaic pseudocapacity and nonfaradaic double-layer capacity. Generally, we can infer the contributions of different mechanisms through CV analysis with the help of varying rates\([28,29]\)

\[
i = a \upsilon^b
\]

Therefore, by plotting log\((i)\) against log\((\upsilon)\), we can obtain \(b\)-value from the slopes. In general, \(b\)-value should be 0.5 if the sodium storage is dominated by bulk diffusion, whereas the \(b\)-value of 1.0 represents a pure capacitive process. The detailed
explanation can be found in the Supporting Information. As depicted in Figure 5b, the $b$-values of LO are larger than 0.95 over the wide potential range, which is close to 1, indicating the dominant surface storage mechanism. So does PO. As for LO, $b$-values are calculated based on the current at peak potential, because the diffusion process is most feasible at this region.\[28\]

Surveying from Figure 5d, the $b$-values of 0.89 and 0.90 are quantified for anodic and cathodic peaks, respectively. So even current at peak potential is mainly generated from surface contribution. Such results confirm that most sodium storage within DO, PO, and LO comes from the surface storage instead of bulk redox reaction between Ti$^{4+}$/Ti$^{3+}$, which is different with the mechanism in LIBs.\[18,31\]

Such an important result inspires us to first pay our attention on the detailed kinetic impacts from atomic arrangements at surface. When looking carefully into the cycling performance at 50 mA g$^{-1}$, it is easy to find that the specific capacities of DO and LO decrease along with cycles like most reported electrodes, however, when the charging/discharging current density increases to 500 mA g$^{-1}$, LO undergoes a self-improving process with 42 cycles to achieve the highest capacitance as shown in Figure 4b and Figure 7a, which tends to be prolonged with increased rates. If the current density further increases to 2000 mA g$^{-1}$, the self-improving process further extends to 160 cycles, whereas the capacities of DO suffer only 10-cycle self-improving. With regard to PO, the number of self-improving cycles is 41.

Several competing mechanisms might be used to explain the observed differences. Some studies conclude that the origin of the self-improving stage is attributed to the electrochemically driven phase transformation or continually formation of solid-electrolyte interphase (SEI) layer due to the exfoliation of active materials. Since the XRD patterns and SEM images after cycling (Figures S4 and S5, Supporting Information) prove the stable phase and overall integrity of complex porous architectures, so we can exclude possible influences from phase and morphology. Meanwhile, considering that the self-improving process appears at the initial stage of cycles, more possibilities are attributed to the influences of surface kinetics. A survey of literatures illustrates that similar variation can also be observed at fast cycling in LIBs\[12\] because of insufficient Li ions to support fast cycling. In the case of SIBs, larger radius leads to poorer affinity of Na ions to TiO$_2$ surface. It was previously observed that Li ions adsorb strongly on the surface of TiO$_2$ in aprotic electrolyte solutions, whereas no adsorption of Na ions can be found under the same conditions.\[32\]

So a relatively high concentration of Na ions need to be first established near the surface, then Na ions can concentrate at reduced Ti centers, and finally diffuse into the TiO$_2$ matrix. Insufficient ion availability near the surface can account for observed self-improvement of the capacities upon cycling at fast cycling. This understanding implies that dispersed atomic arrangement in DO possesses a surface with higher potential for Na-ion absorption, leading to more effective surface ion availability than that of long-range ordered TiO$_2$. This view can be evidenced from the much lower absorption energy of Na ions in propylene carbonate (PC) at disordered surface of DO as shown in Figure 7b.

Considering the similar morphology parameters, we contribute this enhanced absorption to the roughness on atomic level, where more potential defects induced by dispersed atomic arrangement, such as dangling bonds, enables stronger attraction of Na ions.\[13\] Moreover, the poorly defined atomic arrangement with thermodynamically metastable energetic state as compared to crystalline surface generates more open channels with enough volume for better penetration of Na ions, while some unexpected electronic states are expected to raise electric conductivity near the surface.\[14\] So low order degree of atomic arrangement at surface is helpful to voluntarily maintain a sufficient ion concentration near the surface for supporting the fast cycling in short time. That is why DO have shorter self-improving cycles and better rate capacities. To prove this hypothesis, electrochemical impedance spectra are conducted after different cycles (Figure S6, Supporting Information). As shown in Figure 7c, DO and PO shows much lower charge transfer resistance ($R_{ct}$) than LO, and the gap becomes larger and larger with increased cycles. Since all the sodium storage are limited by the surface capacitive process, $R_{ct}$ mainly depends on the charge transfer resistance related to the redox reaction across the electrode/electrolyte interface.\[35\] Smaller $R_{ct}$ suggests much easier reactions at surface. Therefore, the

Figure 5. Schematic simulation of atomic arrangement of a) disordered and b) long-range ordered TiO$_2$ (anatase) before and after Na-ion insertion.
Figure 6. Kinetics analysis of the electrochemical behaviors toward Na ions. a,c,e) CV curves at various sweep rates from 0.1 to 5 mV s\(^{-1}\) of DO (a), PO (c) and LO (e). b,d) \(b\)-values for DO and PO as a function of potential for anodic sweep. d) Determination of \(b\)-values for LO based on the anodic and cathodic current at peak potential.

Figure 7. Analysis of surface orderliness: a) The performance comparison among DO, PO, and LO of self-improving process. b) Absorption energy of Na ions in propylene carbonate (PC). c) Charge transfer resistance (\(R_{\text{ct}}\)) after different cycles.
disordering at the surface is indeed benefit for the contribution from surface processes, which contribute major capacities to the whole sodium storage.

Beside the surface reaction, bulk sodium storage is another important component. During this process, two vital kinetic factors should be considered: electron transport and ion diffusion. To obtain more insight into charge transport within the electrodes and the electrical contact at the current collector interface, we next check the resistance of DO, PO and LO. The resulting symmetrical and linear appearance of $I$–$V$ curves in Figure 8a displays the Ohmic contacts between the electrode and conductive substrate.[36] However, LO possesses smallest resistance throughout the whole matrix. Facile electron transport could be realized in long-range ordered TiO$_2$ rather than in disordered TiO$_2$. With respect to ion diffusion, as shown in Figure 5b, Na ions are favorable to occupy the octahedral sites in long-range ordered anatase TiO$_2$. For the purpose of ion diffusion, all the Na ions hop between the neighboring octahedral sites. They are forced to travel along the shared octahedron edges because of the strong electrostatic repulsion between Na and adjacent Ti drives.[37] Two Na-O$_6$ octahedrons will suffer distinct distortion to allow Na-ion hop between them, and thus the shared edge of the two octahedrons changes between 3.56 and 4.02 Å,[38] which causes huge energy barrier upon Na-ion diffusion. According to the simulation, if one Na can completely insert into anatase TiO$_2$, the lattice will suffer 32.23% expansion in volume (NaTiO$_2$ vs. TiO$_2$). However, disordered atomic arrangements offer a more open framework to facilitate ion transport and tolerance of the distortion during (de-)sodiation.

So the Na-ion diffusion is facilitated in disordered TiO$_2$ rather than long-range ordered TiO$_2$, which can be evidenced by the Na-ion diffusion coefficients ($D_{Na^+}$) after cycles as depicted in Figure 8b and Figure S7 (Supporting Information). The Na-ion diffusion in disordered TiO$_2$ is nearly 300-times than that in long-range ordered TiO$_2$ ($6.56 \times 10^{-10}$ cm$^2$ s$^{-1}$ vs. $2.11 \times 10^{-12}$ cm$^2$ s$^{-1}$). This variation may result from the difficult diffusion barrier of Na ions in long-range ordered matrix because of the requirements based on crystalline symmetry. More ratio of shortened Ti–O bond hinders mobility and increases the difficulties of diffusion in LO.

As electron diffusion coefficients are magnitudes higher than that of Na ions,[38] DO TiO$_2$ would only increase a smaller electron diffusion resistance but gain a large decrease of Na-ion diffusion resistance. Overall, the disordered atomic arrangement in bulk will prompt the contribution from Na-ion intercalation. So, DO shows comparatively high capacities at different rates, especially at initial stage.

Given these analysis, our results prove that the disordering at the surface is benefit for the faradaic contribution from surface processes, in particularly significant to the electrode materials with poorer affinity of transporting ions. The disordering in bulk results in better ion diffusion, but worse electron transport. As mentioned above, the disordered atomic arrangement at surface provides a roughness surface at atomic level, which can improve the attraction to Na ions. However, some side reactions with electrolyte may also become easier. Following this rule, strategies to further enhance the electrochemical sodium storage of TiO$_2$ should concentrate on the surface.
reconstruction and electrolyte choice to promote the long-term stability and rate performance. Though the relative study is beyond our present work, we are looking forward to more effort in these open questions in the near future.

3. Conclusion
As proof-of-concept, inverse opal TiO$_2$ electrodes are realized with controllable orderliness of atomic arrangement. With the help of low-temperature atomic layer deposition technique, identical morphologic features and stability against the temperatures allow a suitable platform for observing the influences from orderliness of atomic arrangement on sodium storage. As proved by the good rate performance and cycling stability, inverse opals with disordered, partially ordered and long-range ordered TiO$_2$ are promising candidates for high performance SIBs. The different electrochemical behaviors are attributed to the intrinsic atomic arrangement. According to the thermodynamics analysis, all the samples (DO, PO, LO) share similar ability for (de-) sodiation. However, the orderliness of atomic arrangement results in different kinetics barriers in various electrochemical processes. The disordering at the surface is beneficial for the contribution from surface processes, in particularly significant to the electrode materials with poorer affinity of transporting ions. The disordering in bulk results in better ion diffusion, but worse electron transport. The understanding of employing orderliness paradigm into electrode design provides a powerful design foundation for realizing efficient energy storage. Further engineering of atomic ordering on traditional materials is expected to stimulate more research interests in the development of sodium-ion batteries.

4. Experimental Section
Assembly of Colloidal Crystal Templates: The well-ordered colloidal crystal templates were fabricated by PSs directly on the conductive Ti foils, which have been cleaned under sonication by sequentially acetone, ethanol, and distilled water. Then, Ti foils were immersed vertically in the 0.5 wt% polystyrene latex at 60 °C. The drying of sample at very low speed under large moisture can prevent the occurrence of cracking.

Fabrication of Disordered, Partially Ordered, and Long-Range Ordered TiO$_2$ Architectures: In a typical procedure, disordered TiO$_2$ were fabricated by low-temperature atomic layer deposition on the surface of the colloidal crystal templates using a PicoSun SUNALETM R-150 ALD system (PicoSun, Finland) according to the following procedure. The reaction temperature was set as 70 °C after optimization, and TiCl$_4$ and H$_2$O were chosen as the precursors. TiCl$_4$ was purged for 0.1 s and purged for 10 s, followed by a 0.1 s pulse and 10 s purge of H$_2$O. This procedure was repeated for 600 cycles. Then, the as-prepared TiO$_2$ was formed by adding Na into the TiO$_2$ interspace and the structure was relaxed several times using dynamic simulation method before further geometry optimization.

Simulation of Atomic Arrangements before and after Na Intercalation: To create the DO-TiO$_2$ model, anatase-TiO$_2$ fragments were compacted into a cell fixing density of 4.23 g cm$^{-3}$ and total atoms of 48 O and 24 Ti. The Na inserted TiO$_2$ was formed by adding Na into the TiO$_2$ interspace and the structure was relaxed several times using dynamic simulation method before further geometry optimization. The Na inserted TiO$_2$ was formed by adding Na into the TiO$_2$ interspace and the structure was relaxed several times using dynamic simulation method before further geometry optimization.

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

Acknowledgements
This work was supported by a European Research Council Grant (Three-D Surface: 240144), Federal Ministry of Education and Research in Germany (BMBF: ZIK-3DNano-Device: 03Z1MN11) and German Research Foundation (DFG:LE 2249_4-1).

Received: February 28, 2016
Revised: April 30, 2016
Published online:


