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Modulation of Crystal Surface and Lattice by Doping: Achieving Ultrafast Metal-Ion Insertion in Anatase TiO₂

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ABSTRACT

We report that an ultrafast kinetics of reversible metal-ion insertion can be realized in anatase titanium dioxide (TiO₂). Niobium ions (Nb⁵⁺) were carefully chosen to dope and drive anatase TiO₂ into very thin nanosheets standing perpendicularly onto transparent conductive electrode (TCE) and simultaneously construct TiO₂ with an ion-conducting surface together with expanded ion diffusion channels, which enabled ultrafast metal ions diffusion across the electrolyte/solid interface and into the bulk of TiO₂. To demonstrate the superior metal-ion insertion rate, the electrochromic features induced by ion intercalation were examined, which exhibited the best color switching speed of 4.82 s for coloration and 0.91 s for bleaching among all reported nano-sized TiO₂ devices. When performed as the anode for the secondary battery, the modified TiO₂ was capable to deliver a highly reversible capacity of 61.2 mAh/g at an ultrahigh specific current rate of 60 C (10.2 A/g). This fast metal-ion insertion behavior was systematically investigated by the well-controlled electrochemical approaches, which quantitatively

revealed both the enhanced surface kinetics and bulk ion diffusion rate. Our study could provide a facile methodology to modulate the ion diffusion kinetics for metal oxides.

KEYWORDS: TiO₂ nanosheets, doping modulation, lattice expansion, surface kinetics, metal-ion diffusion

INTRODUCTION

Constructing metal oxides with appropriate and tunable interlayer lattice capable of facilitating fast ion intercalation is an enabling methodology for energy storage and electrochromic applications,¹⁻⁵ e.g., it had been demonstrated that pre-intercalating the host metal oxide with alkali metal ions could produce a stable interlayer expansion, which prevented destructive collapse of lattice layers and allowed the metal ions to diffuse more freely.⁶ For rechargeable battery applications, except for some low-valence metal oxides which usually provide the capacity relying on the conversion reaction, specified metal oxides such as TiO₂ and MnO₂ are typically intercalation-type anode materials, which provide a reversible intercalation capacitance relying on repeated insertion/extraction of ions from electrolyte and simultaneously, reduction/oxidation of host materials by electrons passing through the back-side current collector.⁷⁻⁹ Consequently, the metal oxides could be colored due to the reduction process together with metal-ion insertion under a decreasing bias and then return to their original color by extracting metal ions with reversing bias.^{10, 11} Thus, on account of the performance of the intercalation-type electrochromic devices or energy storages, both coloring speed and power capability greatly depend on the rate of ion movement in the electrode material.^{7, 8} Hence, how to boost an ultrafast ion insertion rate regarding to the limitation of solid-state diffusion is a crucial challenge for the development of intercalation-type related devices.¹²

To build up an active material possessing a desirable ion-insertion rate, strategies to ameliorate the metal oxides are usually focused on: (i) architectural design with a favorable electronic and/or ionic transporting

direction as well as reduction in the path length over which the metal ions and electrons have to travel,^{13, 14} and (ii) improvement of charge transfer at the surface¹⁵ and charge transport in the bulk.¹⁶ A rapid ion transport across the interface between electrolyte and the host material has also been demonstrated as an important factor to promote the rate capability of device, e.g., a fast ion migration across the interface into the host material could be achieved by building an inherent ion-conducting surface on the host material.¹⁷ However, for most of the preparation method of the host metal oxide materials, it usually requires a high temperature annealing process at last to solidify the structure, which will make the arrangement of the atoms in the crystal relax to its thermodynamically stable state and thus the lattice space could be closely packed. Additionally, materials with broad ionic transport pathways and stable crystalline structures could even realize the pseudocapacitive current characteristics based on the bulk intercalation.¹⁸⁻²⁰

Herein, we present a methodology to modulate the metal oxide with suitable interlayer lattice spacing and kinetically favorable surface, which are capable of synergistically facilitating the ion insertion rate. Titanium oxide (TiO_2), a typical intercalation-type metal oxide^{21, 22} but suffered from slow ion diffusion, was selected as the prototype. Anatase TiO_2 with sheet-appearance was synthesized by blocking the {001} facets with F^- capping agent²³ on fluorine-doped tin oxide (FTO) substrate. To boost a fast ion-insertion rate in this material, niobium ions (Nb^{5+}) were used to further drive TiO_2 into very thin nanosheets (denoted as NSs) which stand perpendicularly to the substrate. Notably, Nb^{5+} was carefully selected to expand interlayer lattice spaces while retaining the phase and structure of TiO_2 owing to its larger but still comparable ionic radius (64 pm) to that of titanium ion (Ti^{4+} , 60.5 pm) and excellent solubility in anatase.^{24, 25} Besides, it has been reported the Nb dopant could enhance the conductivity of TiO_2 ,²⁶ and the electrode constructed by niobium oxide is capable of performing a fast ion-intercalation,^{19, 27} which makes Nb ion as an ideal dopant to build up an ion-conducting layer on TiO_2 surface. The modified TiO_2 NSs electrodes exhibit the state-of-the-art color switching speed compared to all reported nano-sized TiO_2 electrochromic devices, and deliver a highly reversible Li^+ storage capacity of 61.2 mAh/g at an ultrahigh specific current rate of 60 C (c.a. 10.2 A/g) when used as a secondary battery.

RESULTS AND DISCUSSION

The structural design of TiO_2 NSs electrode for the purpose of fast ion-insertion is illustrated in **Figure 1a**. **Figure S1** shows the field-emission scanning electron microscope (FESEM) images of pristine TiO_2 and Nb-doped TiO_2 NSs prepared by solvothermal method under different reaction time. It was observed that without Nb modification, the as-prepared TiO_2 densely stacked together along the [001] direction, possibly owing to the formation of hydrogen bond network among the hydroxyl groups of alcohol (used as solvent),²⁸ thereby leading to TiO_2 nucleation on the surface (**Figure S1a-c**). On the contrary, Nb doping could reduce the grain coarsening (**Figure S1d-f**) due to the diminished surface ionic oxygen mobility,²⁹ and further stabilized the surface energy of {001} facets.³⁰ The separation of individual nanosheet could greatly benefit the efficiency of ion insertion into the TiO_2 crystal because the exposed {001} facets of anatase are highly accessible for inserting metal ions (e.g., Li^+) owing to their invariant strain properties³¹ and thermodynamic favorability.^{32, 33} It was also found that increase in Nb ions concentration made the nanosheets grow thinner in terms of length-curtailment along [001] direction and split apart from each other (**Figure S2a-f**). Ultrathin TiO_2 nanosheets doped with 15 % of Nb (denoted as TiO_2 (15 % Nb)-NSs) reach an average sheet thickness of ~10 nm and film thickness of ~1 μm , where the nanosheets stand separately and perpendicularly on the FTO substrate (**Figure 1b-d**). A Nb/Ti composition ratio of ~16.1 % (**Figure S2g**) was measured by energy-dispersive X-ray (EDX) spectroscopy, which matches well with the atomic ratio in the precursor solution.

Figure 1. Structural features of TiO_2 (15 % Nb)-NSs. (a) Structural design of TiO_2 nanostructures for bifunctional smart windows. (b) FESEM images showing that TiO_2 (15 % Nb)-NSs are uniformly grown on the FTO substrate, and the thickness of individual nanosheet is estimated to be around 10 nm (inset image). (c & d), Cross-sectional FESEM images showing that individual nanosheet independently stands on the FTO substrate with a film thickness of ca. 900 nm.

The transmission electron microscope (TEM) and high-resolution TEM images of TiO_2 (15 % Nb)-NSs (shown in **Figure 2a & b**, respectively) reveal enlarged atomic spacing of $d_{(200)} = d_{(020)} = 0.21$ nm (compared with JCPDS # 21-1272, where $d_{(200)} = 0.189$ nm) with the two crystal planes interlaced with each other at an angle of 90° , identifying $\{001\}$ facets as the main exposed surface of nanosheets. The elemental chemical states of Ti and Nb on the surface of TiO_2 (15 % Nb)-NSs were determined to be Ti^{4+}

and Nb^{5+} by X-ray photoelectron spectroscopy (XPS), as shown in **Figure S3a & b**. Noteworthily, a new doublet, which was attributed to the chemical state of Ti^{3+} , emerged after Ar^+ etching for 1 min (**Figure S3c**). This observation could be ascribed to the charge compensation due to the incorporation of Nb^{5+} ions into TiO_2 crystal, thus leading to the donation of electrons into TiO_2 and resulting in valence state reduction from Ti^{4+} to Ti^{3+} .^{30, 34-36} Consistently, Nb^{4+} was also observed after 1 min Ar^+ etching (**Figure S3d**). The doping amount of Nb ions was estimated to be 49 % on the surface and 40 % after Ar^+ etching for 1 min by XPS. Based on the EDX mapping and XPS results, it is reasonable to disclose that Nb dopant is continuously distributed from a high concentration on the outermost surface to a moderate concentration in the bulk of TiO_2 (15 % Nb)-NSs. Meanwhile, XRD patterns reveal a pure anatase phase for TiO_2 (15 % Nb)-NSs without any notable impurity such as Nb_2O_5 , indicating a high solubility of Nb ions into the TiO_2 crystal (**Figure 1c**). The strong (004) peak intensity was indicative of {001} facets dominated structure. Moreover, a significant peak shift towards lower diffraction angle as well as peak broadening were observed, which were attributable to lattice expansion and crystallite size reduction, respectively. The lattice expansion of Nb-doped TiO_2 observed in the XRD pattern is ascribed to the fact of (i) the larger ionic radius of foreign Nb^{5+} (0.64 Å) as compared to that of host Ti^{4+} (0.605 Å) on TiO_2 surface, and (ii) the existence of Ti^{3+} (0.67 Å) and Nb^{4+} (0.68 Å) in the bulk of TiO_2 NSs by means of charge compensation. The X-ray absorption spectra (XAS) of Ti K edge were further acquired to clarify the Nb doping effect on TiO_2 . The X-ray absorption near edge structure (XANES) spectra exhibited three featured pre-edge peaks (A_1 , A_2 , and A_3) of anatase in an octahedral TiO_6 geometry (**Figure 2d**), where A_1 peak is assigned to the exciton band or $1s$ to $1t_{1g}$ transition, and the origins of A_2 and A_3 peaks can be attributed to the $1s$ to $2t_{2g}$ and $1s$ to $3e_g$ transitions, respectively.^{37, 38} It is noted that the oxidation state of Ti ion in TiO_2 (15 % Nb)-NSs is slightly lower than that in TiO_2 (0 % Nb)-NSs, which could be attributed to the existence of Ti^{3+} in the bulk induced by Nb doping. The Fourier transforms ranging from 4 to 14 k wavevector (**Figure S4**) of extended X-ray absorption fine structure (EXAFS) spectra were performed following the standard procedures without phase correction. **Figure 2e** shows similar 1st-shell of Ti to neighboring O atom distance of ~ 1.56 Å for both TiO_2 (15 % Nb)-NSs and TiO_2 (0 % Nb)-NSs, while the

2nd shell of Ti-Ti distance and 3rd shell of Ti-O distance of TiO₂ (15 % Nb)-NSs are obviously elongated as compared to that of TiO₂ (0 % Nb)-NSs, indicative of the expanded lattice spacing in Nb-modified TiO₂. Therefore, a desirable atomic distribution of Nb dopant from a high concentration on the surface, which is expected to construct an ion-conductive interface, to a moderate concentration in the bulk together with an expanded lattice space of TiO₂ is successfully achieved.

Figure 2. Lattice interlayer expansion of TiO₂ (15 % Nb)-NSs. (a) TEM and (b) HRTEM images of TiO₂ (15 % Nb)-NSs with {200} and {020} facets interlaced at an angle of 90°, indicating an exposed {001} facet on the sheets. (c) XRD patterns of a. TiO₂(0 % Nb)-NSs and b. TiO₂ (15 % Nb)-NSs. The obvious peak shift, peak broadening, and amplified (004) diffraction for TiO₂ (15 % Nb)-NSs evidence the success substitution of Ti with Nb dopant. (d) Normalized ex-situ Ti K-edge XANES spectra. From which, we could determine that the Ti valence state was slightly reduced after Nb doping. (e) Ti K-edge EXAFS

spectra, for TiO_2 (0 % Nb)-NSs, the 1st shell Ti-O distance is estimated as 1.56 Å, and the 2nd shell Ti-Ti distance and 3rd shell Ti-O distance are around 2.38 Å and 2.77 Å, respectively. It is worthy noting that the interatomic distances are shorter than the actual values³⁸ owing to the fact that Fourier transform (F. T.) spectra were not phase-corrected.

Ultrathin Nb modified TiO_2 -NSs standing perpendicularly on TCE could be promising for electrochromic devices owing to their high surface areas accessible for electrolyte from both sides and low possibility of light reflection. As electrochromic devices, the electrochemical insertion of ions into TiO_2 largely creates reduced titanium states (Ti^{3+}), which changes the color of TiO_2 due to the polaron absorption by electrons localized at Ti^{3+} ,³⁹ while the color change is reversible after ion removal.⁴⁰ Meanwhile, the insertion of Li^+ ions into TiO_2 crystals could dynamically modulate the anatase lattice and the surface plasmon resonance.⁴¹ The TiO_2 NSs with 15 % Nb doping was then chosen for the following demonstration due to its optimum thin nanosheet structure (**Figure S2**) and the best current response speed (**Figure S5**). For comparison, pure anatase TiO_2 nanosheets (TiO_2 -NSs) with exposed {001} facets individually standing on FTO were also synthesized by hydrothermal method (**Figure S6**). **Figure 3a** shows the optical transmittance at bleached state (T_b) of TiO_2 (15 % Nb)-NSs, which exceeds up to 80 % in the wavelength range from 450 to 750 nm covering the majority of the visible light region, indicating the maintenance of high transparency owing to the ultrathin NSs structure, whereas pristine TiO_2 -NSs electrode are opaque. Upon charging, 40 % of the optical transmittance at colored state (T_c) remains in the visible range, which is consistent with the observed deep blue color. The corresponding electrochromic properties of TiO_2 (15 % Nb)-NSs were probed by monitoring the optical transmittance at a wavelength of 685 nm in response to an applied voltage. As shown in **Figure S7a**, a fast and stable color switching was observed for TiO_2 (15 % Nb)-NSs electrode, while TiO_2 -NSs electrode exhibited sluggish electrochromic responses (**Figure S7d & e**). The measured switching time (defined as the time required to reach 80 % of the full response) is 4.82 s for coloration and 0.91 s for bleaching in TiO_2 (15 % Nb)-NSs electrode (**Figure 3b**), which is significantly faster than all the other reported nano-sized TiO_2 electrochromic devices (**Table S1**). **Figure**

3c displays the relationship between the in situ optical density (OD), where $OD = \log(T_b/T_c)$, and the intercalation charge density during the coloration process in the 1st cycle. The coloration efficiency (CE) defined as the variation in OD per unit area charge density (ΔQ), where ΔQ is the inserted charge through the electrode during the coloring period ($0 \rightarrow 60$ s), was calculated to be as high as 29.39 cm²/C. The cycling durability testing as shown in **Figure 3d** reveals a stable optical switching with a CE of 21.69 cm²/C at the 30th cycle (**Figure S7b & c**), manifesting the superior Li⁺ insertion/extraction kinetics. Meanwhile, the lithium ion battery performance was also estimated when the TiO₂ (15 % Nb)-NSs was employed as the anode. As shown in **Figure 3e**, the TiO₂ (15 % Nb)-NSs showed high Coulombic efficiency of 90 %, 93 %, and 99.7 % at 1 C (c.a. 170 mA/g), respectively, for the first three cycles. Meanwhile, the outstanding reversible cycling performance even at an ultrahigh current rate of 60 C, evidencing the fast reversible Li⁺ insertion/extraction behavior (**Figure 3f**).

Figure 3. Electrochemical performances of TiO_2 (15 % Nb)-NSs. (a) Optical transmittance spectra of the TiO_2 (15 % Nb)-NSs electrode in bleached and colored states. (b) Enlarged one switching cycle indicating rapid switching coloration and bleaching. Inserts are the digital photographs of the TiO_2 (15 % Nb)-NSs electrode in bleached and colored states. (c) Plot of OD versus charge density for the measurement of coloration efficiency (CE), which reveals an outstanding CE as high as $29.39 \text{ cm}^2/\text{C}$ for TiO_2 (15 % Nb)-NSs electrode at the 1st cycle. (d) Electrochromic cycling demonstrating a stable cycling performance of TiO_2 (15 % Nb)-NSs electrode. (e) Charge and discharge curves of TiO_2 (15 % Nb)-NSs electrode for

lithium ion storage at a high current rate of 1 C. (f) Cycling performance of TiO₂ (15 % Nb)-NSs and TiO₂-NSs electrode at various current rates. The comparison indicates a superior power rate performance of Nb-doped TiO₂ electrode.

To reveal the enhancement of the structural modification towards metal-ion insertion, the reversible metal ion insertion properties in Nb-doped TiO₂ nanosheets were studied by cyclic voltammetry (CV). **Figure 4a** shows the typical cyclic voltammogram curves with one pair of redox peaks representing reversible Li⁺ intercalation of TiO₂. The smaller anodic-to-cathodic peak splitting potential (ΔE_p) as well as the larger area under the CV curve for TiO₂ (15 % Nb)-NSs at a scan rate of 0.2 mV/s compared to TiO₂-NSs indicate a faster metal ion insertion kinetics in TiO₂ (15 % Nb)-NSs. The CV peak current (I_p) obeys the power-law relationship with scan rate (v)⁴² as shown in **Figure S8a**:

$$I_p = av^b$$

where I_p is the peak current, a and b are adjustable parameters, and the value of b can be determined from the slope of the plot of $\log I_p$ vs. $\log v$. There are two well-defined conditions depending on the value of b : (i) if b is 0.5, the current is controlled by semi-infinite linear solid-state diffusion, which is indicative of a faradaic insertion/extraction process in the bulk, and (ii) if b is 1.0, it represents a surface-limited capacitive response, where the current is controlled by faradaic pseudocapacitance and/or nonfaradaic double-layer effect.⁴³ At scan rates ranging from 0.2 to 20 mV/s, the value of b was estimated to be ~ 0.5 for TiO₂-NSs during anodic and cathodic processes (**Figure 4b**), implying that the Li⁺ insertion into TiO₂-NSs is controlled by solid-state diffusion, while larger b -values (0.64 and 0.58 in cathodic and anodic processes, respectively) of TiO₂ (15 % Nb)-NSs suggest a shift of Li⁺ insertion towards the pseudocapacitive behavior (**Figure 4c**).⁴⁴ It is clear to see that for TiO₂ (15 % Nb)-NSs electrode, parts of the cathodic and anodic current are contributed by the capacitive effect where two pseudocapacitive current peaks can be distinguished at 1.52 V and 2.25 V during cathodic and anodic processes, respectively.

Figure 4. Electrochemical measurements for the kinetic analysis of TiO₂ (15 % Nb)-NSs and TiO₂-NSs.

(a) Cyclic voltammogram curves at 0.2 mV/s, demonstrating faster ion insertion kinetics for TiO₂ (15 % Nb)-NSs as compared to TiO₂-NSs. (b) Determination of parameter b from the peak anodic and cathodic currents. (c) Estimation of capacitive contribution to the current response. Deconvolution of capacitive and insertion current at a fixed potential via: $I(V) = k_1 v + k_2 v^{1/2}$, where $I(V)$ is the voltage dependent current, and v is the scanning rate. In this equation, $k_1 v$ and $k_2 v^{1/2}$ correspond to the current contributions from capacitive effect and the diffusion controlled insertion process, respectively. (d) The plot of I_p versus $v^{1/2}$ from which diffusion coefficient of Li⁺ (D_{Li}) in the host material can be estimated from the slope. (e) The plots of $\ln[I_p]$ versus $(E_p - E_0)$ which are used to determine the standard rate constant of charge transfer

(k_0) and charge transfer coefficient (α). (f) Step charge curves revealing the variation of current versus time. It shows that the Nb modified TiO₂ nanosheets permit faster Li⁺ insertion, exhibiting a faster current declining as compared to that of pure TiO₂.

To quantitatively compare Li⁺ ions diffusion in both TiO₂ samples with/without Nb doping, physical kinetic parameters of Li⁺ insertion/extraction were calculated from the CV curves at various scanning rates (**Figure S8a**). These calculated values can offer a fair comparison because the geometrical influence such as surface roughness and thickness of different TiO₂ samples could be eliminated due to the fact that auto-correction can be realized by the physical parameters (surface area, A , diffusion path length, l , etc.) used in the equations. The rate constant of charge transfer (k_0) and charge transfer coefficient (α) were estimated by fitting the linear relation of anodic I_p as a function of the peak potential (E_p) at various scan rates (**Figure 4d**). Meanwhile, I_p also linearly scales with the square root of the scan rate (**Figure 4e**), from which the diffusion coefficient of Li⁺ (D_{Li}) could be obtained by fitting the slope of the linear relation. The details of calculation are described in Supplementary information, and the results are listed in **Table 1**.

Table 1. Kinetic parameters of Li⁺ diffusion in different TiO₂ samples. CV and PITT refer to cyclic voltammetry and potentiostatic intermittent titration technique, respectively.

	TiO ₂ (15 % Nb)-NSs	TiO ₂ -NSs
Rate constant, k_0 (CV) [cm/s]	1.17×10^{-9}	7.82×10^{-10}
Charge transfer coefficient, α (CV)	0.221	0.159
Diff. coefficient, D_{Li} (CV) [cm²/s]	4.68×10^{-15}	1.86×10^{-15}
Diff. coefficient, D_{Li} (PITT) [cm²/s]	2.1×10^{-12}	7.0×10^{-13}
Biot number, B (PITT)	2.7×10^{-5}	1.7×10^{-2}

The smaller values of α and k_0 for TiO₂-NSs indicate that the Li⁺ ion extraction at the surface of un-doped anatase is more sluggish as compared to that of Nb-doped TiO₂, showing a faster Li⁺ ion transport at the

electrode/electrolyte interface for TiO_2 (15 % Nb)-NSs. It is indicative of successful construction of ion conductive layers on Nb doped TiO_2 , where the surface is heavily doped with Nb ions. Furthermore, TiO_2 (15 % Nb)-NSs also possess larger D_{Li} , which is about 2.5 times that of pristine TiO_2 -NSs, illustrating a better Li^+ ion mobility in the bulk with moderate Nb doping concentration as well. To doubly verify enhancement of Li^+ diffusion in Nb-doped TiO_2 lattice, potentiostatic intermittent titration technique (PITT)⁴⁵ was further employed to determine the D_{Li} . Typically, the kinetic information of Li^+ insertion can be assessed by observing the trend of current variation as a function of time through introducing a small potential-step excitation. **Figure 4f** shows the plot of the natural logarithm of the current vs. time. By fitting the slope and intercept with the PITT equations (see the supporting information for the experimental details), D_{Li} and electrochemical Biot number (B) can thus be estimated. Biot number represents the ratio of diffusion resistance to the resistance of surface reaction.⁴⁶ A smaller Biot number indicates a larger surface reaction (e.g., charge transfer) resistance, i.e., a faster Li^+ insertion rate in the bulk. The estimated D_{Li} and B (Table 1), again, confirmed faster mobility of Li^+ in Nb-doped TiO_2 NSs.

It should be noted that the calculated D_{Li} by PITT method is 2~3 orders of magnitude larger than that obtained from CV method. The discrepancy can be attributed to the different charging conditions for the PITT and CV measurements. The anodic peak in CV represents Li^+ extraction from fully charged host material to concentrated electrolyte, while in the PITT method, the negative value of potential-step variation drives Li^+ insertion from concentrated electrolyte into the empty host material. Nevertheless, the improvement of Li^+ diffusion in Nb-doped TiO_2 can still be concluded from the ratio of $D_{\text{Li},\text{TiO}_2\text{ (15 % Nb)-NSs}}$ to $D_{\text{Li},\text{TiO}_2\text{-NSs}}$, which is around 2.5 and 3 estimated from the CV method and PITT approach, respectively. Furthermore, the improvement in ion transport kinetics on the surface of Nb-doped TiO_2 can also be evidenced based on the ratio of $k_{0,\text{TiO}_2\text{ (15 % Nb)-NSs}}$ to $k_{0,\text{TiO}_2\text{-NSs}}$, which is determined to be around 1.5. As a result, the significantly enhanced electrochemical performances of TiO_2 (15 % Nb)-NSs as compared to pristine TiO_2 -NSs are resulted from the synergistic contributions of faster bulk Li^+ diffusion in the direction parallel to the principal normal vector of the surface (i.e.,

perpendicular to the {001} facet) as well as ameliorated interfacial ion transport kinetics. It should be emphasized that the magnitude of the obtained physical parameters including α , k_0 , and D_{Li} for Nb-doped TiO_2 seems similar to those of TiO_2 as reported in the literature.^{32, 42, 47, 48} This discrepancy should be ascribed to the fact that in literature studies, the electrodes containing active materials, polymer binders and large amounts of conductive additives were applied during the electrochemical testing, which could remarkably influence the data interpretation. Besides improved metal-ion diffusion, niobium doping could also increase the electrical conductivity of TiO_2 (**Figure S8b**), which is beneficial for the metal-ion insertion in TiO_2 .

CONCLUSION

In summary, we have demonstrated a superior performance of rapid ion-insertion rate based on a modified TiO_2 nanostructure electrode. We used Nb^{5+} to drive TiO_2 nanostructure into ultrathin NSs and expedite reversible Li^+ insertion properties by simultaneously constructing ion-conducting layers on the surface and expanding ion-diffusion channels in the bulk. We believe that this transition metal doping strategy could provide a generic approach to modulate kinetic properties of a large variety of host metal oxides toward reversible insertion of metal ions (e.g., reversible Al^{3+} insertion has been demonstrated in **Figure S8c**), leading to enhanced electrochromic performances and energy storages with high energy density and fast rate capability.

METHODES

Synthesis. In a typical synthesis of TiO_2 (x % Nb) nanosheets where $x = 0-20$, 0.0254 g of $NbCl_5$ (99 %, Merck) was added into 15 mL of anhydrous ethanol, followed by adding 80 μ L of hydrofluoric acid (50 %, Sigma-Aldrich). The mixture was stirred for 5 min before adding 160 μ L of titanium butoxide (97 %, Sigma-Aldrich). After stirring for another 5 min, the mixture was transferred to a Teflon-lined stainless steel autoclave (volume = 50 ml). two pieces of FTO substrates ($F:SnO_2$, Tec 15, 10 Ω /, Hartford Glass Company), ultrasonically cleaned for 30 min in a mixed solution of deionized (DI) water, acetone, and 2-

propanol with volume ratios of 1 : 1 : 1, were placed at an angle against the wall of the Teflon-liner with the conducting side facing down. The solvothermal reaction was conducted in an electric oven at 200 °C for 24 h. Pristine anatase TiO₂ nanosheets (TiO₂-NSs) were grown on FTO substrate according to a literature method⁴⁹ with slight modifications: briefly, 0.4 mL of titanium (IV) butoxide and 0.2 g of ammonium hexafluorotitanate were mixed with 25 mL of 5 M hydrochloric acid, and then the mixture was sealed in a Teflon-lined stainless steel autoclave (volume = 50 ml) with two pieces of FTO substrates placed at an angle against the wall inside, and heated at 180 °C for 5 h. Finally, after reaction, all samples were washed with DI water for several times followed by calcining at 450 °C for 2 h under air atmosphere.

Characterization. The crystallographic information was examined using X-ray diffraction with Cu K α irradiation (λ = 1.5406 Å). The compositional information was probed via X-ray photoelectron spectroscopy (XPS, ESCALAB 250) with Al K α mono chromatid flood. The morphology was revealed via field emission scanning electron microscopy (FESEM, JSM-6700F) and transmission electron microscopy (TEM, JEM-2100). X-ray absorption spectroscopy (XAS) measurements were conducted by employing synchrotron radiation light source at 16A beam line from the National Synchrotron Radiation Research Center (NSRRC), Taiwan. The measurements were made at Ti K-edge (4966 eV) at room temperature. X-ray absorption data were analyzed according to the universal standards, including pre-edge and post-edge background subtraction, normalization with respect to edge-jumping height, and Fourier transformation with k^3 weighting yet without phase correction. For the electrochromic contrast measurements, TiO₂-FTO with a confined active area of $1 \times 1.8 \text{ cm}^2$ was used as working electrode, platinum foil as counter electrode, Ag/Ag⁺ as the reference electrode, and the electrolyte was 1M LiClO₄ (99% anhydrous, Sigma-Aldrich) in propylene carbonate (Sigma-Aldrich), which were sealed in a quartz cell connected with a potentiostat. The electrochromic performance was measured by the optical transmittance (UV-vis spectrophotometer, Cary 4000) in response to an applied 0 V vs. Ag/Ag⁺ (organic reference, 0.457 V vs. NHE) for bleaching period and -2 V vs. Ag/Ag⁺ for coloring period. The electrochemical characterization was carried out in an argon-filled glove box using a three-electrode

configuration cell and Bio-Logic VMP3 potentiostat. The FTO substrate with a confined active area of $1 \times 1 \text{ cm}^2$ was directly used as the working electrode. Lithium foil (Sigma-Aldrich) was used as the counter and reference electrode, and the electrolyte was 1M LiClO_4 (99% anhydrous, Sigma-Aldrich) in propylene carbonate (Sigma-Aldrich). For the lithium ion battery test, the theoretical capacity of 170 mAh/g for TiO_2 is adopted, and the loading amount of TiO_2 (15 % Nb)-NSs on FTO was estimated as $\sim 0.2 \text{ mg cm}^{-2}$ by measuring the active material scraped from the substrate.

ASSOCIATED CONTENT

Supporting information

Supporting information is available in the online version of the paper. Reprints and permissions information is available online at <http://pubs.acs.org>. Correspondence and requests for materials should be addressed to B.L.

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Notes

The Authors declare no competing financial interest.

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