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Interfacial Lattice Strain-Driven Generation of Oxygen Vacancies in Aerobic-Annealed TiO₂(B) Electrode

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Abstract

Oxygen vacancies play crucial roles in defining physical and chemical properties of materials to enhance the performances in electronics, solar cells, catalysis, sensors, energy conversion and storage. Conventional approaches to incorporate oxygen defects mainly rely on reducing oxygen partial pressure for the removal of product to change equilibrium position. However, directly affecting reactants to shift the reaction towards generating oxygen vacancies is lacking and to fill this blank in synthetic methodology is very challenging. Here we

demonstrated a strategy to create oxygen vacancies through making reaction energetically more favorable via applying interfacial strain on reactant by coating, using $\text{TiO}_2(\text{B})$ as model system. Geometrical phase analysis and density functional theory simulations verified the formation energy of oxygen vacancies was largely decreased under external strain. Benefited from these, the obtained oxygen-deficient $\text{TiO}_2(\text{B})$ exhibited impressively high level of capacitive charge storage, e.g. $\sim 53\%$ at 0.5 mV/s , far surpassing $\sim 31\%$ of unmodified counterpart. Meanwhile, the modified electrode showed significantly enhanced rate-capability delivering a capacity of 112 mAh g^{-1} at 20 C ($\sim 6.7 \text{ A g}^{-1}$), $\sim 30\%$ higher than air-annealed TiO_2 and comparable to vacuum-calcined TiO_2 . This work heralds a new paradigm of mechanical manipulation of materials through interfacial control for rational defect engineering.

The introduction of oxygen vacancies to tune geometric and electronic structure as well as chemical properties of materials is widely adopted in electronics, catalysis, solar cells, sensors, energy conversion and storage.^[1] In terms of energy storage, incorporating oxygen vacancies into electrode materials has been demonstrated as an effective strategy to enhance pseudocapacitive charge storage, which is a desired faradaic process with extremely rapid kinetics for various high-power energy storage applications, e.g. electric vehicles.^[2] Extensive efforts have been devoted into developing various methods for the generation of oxygen vacancies without altering the bulk structure, which could be mainly classified in two types.^[3] The most widely-used one is heat treatment in vacuum furnace.^[4] Since the formation reaction of oxygen vacancies (V_o) from oxides (e.g. TiO_2) by releasing oxygen gas (O_2) can be described using the following equation:^[5]

high vacuum ($\sim 10^{-5}$ - 10^{-6} mbar) largely reduces the partial pressure of oxygen, causing the equilibrium to shift towards the direction of the generation of oxygen vacancies according to Le Chatelier's principle (**Scheme 1a**). The other approach to make the forward reaction favorable is utilizing highly reductive agent (e.g. H_2) as a promoter to facilitate the escape of oxygen in the form of water.^[6] These conventional strategies mainly focus on adopting anaerobic conditions for the removal of O_2 product to move the reaction equilibrium towards the formation of oxygen vacancies. However, affecting the reactant to favor the generation of oxygen vacancies is still lacking and how to fill this blank in synthetic methodology is still a great challenge.

Our hypothesis is that modifying solid reactant could change the equilibrium concentration to generate more oxygen vacancies, which should not rely on oxygen-deficient environment. The spontaneity of the reaction is determined by the change in Gibbs free energy of the process (ΔG) according to the second law in chemical thermodynamics Eq. (2).

$$\Delta G = G(TiO_{2-x}) - G(TiO_2) + \frac{1}{2}xG(O_2) \quad (2)$$

The more decreased ΔG between products and reactants, the more thermodynamically favorable the oxygen vacancy formation reaction is (Scheme 1b). The thermodynamically shifted Gibbs free energy of oxygen vacancy formation can be defined as a function of epitaxial strain (η) and temperature (T) according to the following relationship in the quasi-harmonic approximation Eq. (3),^[7]

$$\Delta G = \Delta E(\eta) + \Delta F(\eta, T) + \frac{1}{2}x\mu_o(T) \quad (3)$$

where ΔE account for the zero-temperature contributions to the free energy and ΔF represents the thermal contributions to the free energy. To achieve a decreased value of ΔG and make the oxygen vacancy formation reaction energetically favorable, the key lies in applying lattice strain on the corresponding crystal (Scheme 1c).

Guided by these, we designed metal oxide heterostructures, at which interfacial strain was probably produced by the uneven volumetric shrinkage during the crystallization process, using TiO_2 as a model system (Scheme 1d). This generated interfacial strain realized the introduction of oxygen defects through simple heat treatment at 300 °C in air, rather than traditionally relying on anaerobic reducing atmosphere. Geometrical phase analysis and numerical simulations based on density functional theory (DFT) corroborated the formation energy of oxygen vacancies in TiO_2 was largely decreased under the generated interfacial strain. Benefited from this, the prepared TiO_2 -Nb electrode was oxygen-deficient and exhibited significantly enhanced ratio of pseudocapacitive contribution to the total capacity, typically, ~53% at a scanning speed of 0.5 mV/s, superior to the unmodified counterpart (~31%). Meanwhile, the rate capability of the modified electrode was significantly improved with a delivered capacity of 112 mAh g⁻¹ at 20 C (~6.7 A g⁻¹), which was ~30% higher than unmodified TiO_2 and comparable to the conventional vacuum annealed TiO_2 . This work provides new design and insights for the incorporation of oxygen vacancies via mechanical manipulation for electrode materials, endowing batteries with greatly enhanced capacitive charge storage for high-power applications.

In a typical experiment, titanium oxide hydrate (H- TiO_2) nanofibers were first synthesized through a hydrothermal method according to the modified literature procedure and further used as core materials for subsequent surface coating with oxides (Figure S1).^[8] The final products of bare and modified TiO_2 were obtained after thermal treatment at 300 °C in air and denoted as TiO_2 and TiO_2 -M, respectively. Taking TiO_2 and TiO_2 -Nb as examples, it's hard to distinguish the morphological difference in low-magnification (<10 K) scanning electron microscopy (SEM) and transmission electron microscopy (TEM), eliminating the possible effect of large size change on the electrochemical performance (Figure S2, S3). From the high resolution TEM (HRTEM) image of TiO_2 -Nb, a thin coating layer without discernable lattice fringe was observed on the surface of nanofibers (**Figure 1a**), indicating

the amorphous nature of the shell. To study the chemical composition of the coating, several nanofibers have been randomly picked (Figure 1b) and examined by chemical mapping in scanning TEM (STEM). As depicted in Figure 1c-1e, element Ti and O dispersed evenly in each fiber, while Nb was mainly identified in the surface layers, well consistent with the desired TiO₂-Nb₂O₅ core-shell structure. Meanwhile, X-ray photoelectron spectroscopy (XPS) was conducted to examine the change of surface compositions before and after coating (Figure 1f, g, S4). The typical photoelectron peaks locate at 459.0 and 464.7 eV are indexed as Ti 2p_{3/2} and Ti 2p_{1/2}. New emerged peaks at 207.3 and 210.2 eV of TiO₂-Nb should be correlated to Nb 3d_{5/2} and Nb 3d_{3/2}, confirming the presence of niobium oxide in the topmost layers.^[9] X-ray diffraction (XRD) was further performed to investigate the crystal structures of TiO₂ and TiO₂-Nb. Both patterns displayed the characteristic diffraction peaks of bronze phase TiO₂(B) (PDF#46-1237) and no new emerged peaks for TiO₂-Nb, which are in good agreement with the amorphous property of Nb₂O₅ coating (Figure 1h, S5). In addition, X-ray absorption near edge structure (XANES) were further carried out to investigate the local environment of Ti. As revealed by the Ti XANES spectra in Figure 1i and S6, TiO₂-Nb exhibited nearly identical features as the bare TiO₂, suggesting that no bulk doping was happened after coating and the formation of oxygen vacancies was not because of the isovalent doping.

In order to measure and map the strain at the TiO₂ and Nb₂O₅ interface, HRTEM image of the crystallized TiO₂-Nb after post-treatment was analyzed by using geometric phase analysis (GPA) method.^[10] As presented in **Figure 2a, 2b**, tensile strain was observed on TiO₂ nanofibers near the interface, which should be aroused by the uneven volumetric shrinkage between TiO₂ core and Nb₂O₅ shell. To evaluate the impact of interfacial lattice strain on the properties of TiO₂, ultraviolet–visible spectroscopy was carried out. As shown in Figure 2c, the absorption peak of the TiO₂-Nb show slightly red shift compared to bare TiO₂, which was observed on other oxide modified samples including TiO₂-Fe, TiO₂-Zr and TiO₂-V. To probe

oxygen vacancies in these samples, electron paramagnetic resonance (EPR) analysis was performed, a powerful technique for characterizing the magnetic properties of defect centers at an atomic scale.^[11] As depicted by in Figure 2d, there is a strong peak emerged at the g value of 2.003 for TiO₂-M samples that can be attributed to the oxygen vacancies on the surface,^[12] while no discernable signal can be observed for bare TiO₂. Then XPS spectra of O 1s for bare and modified TiO₂ were further studied in detail. As revealed in Figure 2e, the typical absorption peak at ~530.2 eV should be indexed as lattice oxygen. Besides this, a new shoulder peak emerged at ~532.0 eV for the TiO₂-M samples, which was correlated to oxygen vacancies.^[13] Based on the area of these two peaks, the normalized ratio of oxygen vacancies in the surface was calculated in Figure 2f, indicating the successful introduction of oxygen vacancies after modification. In addition, four-point probe resistivity measurements revealed the electrical conductivity was enhanced after metal oxide coating, which served as another good indicator for the incorporation of oxygen vacancies (Figure 2g). In addition, considering transition metals with varied valence state exhibit very different effects on the formation of oxygen vacancies, this introduction of oxygen vacancy may not be aroused by the surface energy change.^[14] Notably, the depth of generated oxygen vacancies might be several atomic layers under interfacial strain according to the literature.^[15]

To correlate the formation of oxygen vacancy with the presence of lattice strain, density functional theory (DFT) calculations of TiO₂ had been performed. The stoichiometric TiO₂(B) (110) surface was used with a vacuum layer to avoid virtual interaction and the relaxed crystal structure was depicted in **Figure 3a**. An energy favorable oxygen position was selected to investigate the formation energy of oxygen vacancy (ΔE_{V_o}) under different strain from 0 to 3% along the x, y and z directions according to Eq. (S1) (Figure 3b).^[16] As displayed in Figure 3c, the energy barrier for the generation of oxygen vacancy was largely lowered with the increased lattice strain. For instance, as the lattice strain increased up to 2%, the oxygen vacancy formation energy was significantly decreased by ~1.1 eV in the surface of

TiO₂, resulting in a reduced value of ΔG . Since the concentration of oxygen-deficient TiO_{2-x} as a function of ΔG per mole in the standard state can be described quantitatively by the following relationship Eq. (4),

$$[TiO_{2-x}] = \frac{K[TiO_2]}{[O_2]^{\frac{1}{2}x}} = \frac{[TiO_2]}{[O_2]^{\frac{1}{2}x}} \exp\left(-\frac{\Delta G}{RT}\right) \quad (4)$$

where K is equilibrium constant, [A] represents the concentration of A (A = TiO₂, TiO_{2-x} and O₂), R is the gas constant and T means the temperature in Kelvin, the decreased value of ΔG after applying the lattice strain brings the exponential growth of concentration for oxygen vacancy. All these further corroborated that the lattice strain at the interface facilitated the generation of oxygen vacancies.

Considering the introduction of oxygen vacancies has been demonstrated an effective approach to enhance the pseudocapacitive charge storage property of electrode materials,^[17] cyclic voltammetry was performed on TiO₂ and TiO₂-Nb at varied sweep rate to characterize the charge storage mechanism (**Figure 4a, 4b, S7**). Based on the relationship between the current (*i*) and the sweep rate (*v*) followed, $i = av^b$,^[18] *b* = 0.5 indicates the diffusion-controlled process and *b*=1 represents the capacitive processes. As shown in Figure 4c, the calculated *b* values of TiO₂ and TiO₂-Nb are 0.60 and 0.80, respectively, signifying a combination of capacitor-like and diffusion-controlled behaviors. But higher capacitive contributions from fast near-surface activities is achieved after Nb₂O₅ coating and similar improvement is also emerged on other oxide modified samples, indicating the enhancement is originated from oxygen defects. To analyze the level of pseudocapacitive charge storage in detail, the fraction of current could be calculated by determining *k*₁ and *k*₂ at specific potentials (Figure S8) according to the relationship Eq. (S2-S5).^[19] As displayed by the typical results in Figure 4d, the ratio of capacitor-like charge storage in total capacity of electrode is impressively enhanced by ~20% after metal oxide coating, which should be attributed to the introduction of oxygen vacancies. All above results demonstrated our

1 approach well realized the incorporation of oxygen vacancies under heat treatment in air, not
2 relying on traditionally anaerobic conditions.

3 To investigate the effect of oxygen vacancies on electrochemical performance, coin
4 cells were fabricated using lithium metal as anode and TiO_2 or $\text{TiO}_2\text{-Nb}$ as cathode. As shown
5 by the typical galvanostatic discharging/charging curves between 1.0 and 3.0 V vs Li^+/Li
6 (Figure S9), the sloping discharging potential profile and no distinguishable flat plateau at
7 ~ 1.8 V verify the pure phase of $\text{TiO}_2(\text{B})$. Two electrodes deliver a comparable capacity of 230
8 $\text{mAh}\cdot\text{g}^{-1}$ at a low rate of 0.2 C ($1\text{C}=140\text{ mA}\cdot\text{g}^{-1}$), but at high rates, the electrochemical
9 performance of $\text{TiO}_2\text{-Nb}$ far surpasses the unmodified counterpart (Figure 4e). Taking 20 C
10 ($\sim 6.7\text{ A g}^{-1}$) as an example, $\text{TiO}_2\text{-Nb}$ can still deliver a capacity of 112 mAh g^{-1} , which is
11 $\sim 30\%$ higher than unmodified TiO_2 . These superior rate performances are comparable to
12 traditional vacuum annealed TiO_2 ($\text{TiO}_2\text{-vac}$). Since Nb_2O_5 can be also used for lithium
13 storage, the electrochemical performance of blank Nb_2O_5 and $\text{TiO}_2\text{-Nb}$ with varied coating
14 amount was carefully investigated for control experiments. As displayed in Figure S10, blank
15 Nb_2O_5 can only deliver a capacity less than 150 $\text{mAh}\cdot\text{g}^{-1}$ at 0.2 C and the capacity fades very
16 fast probably due to poor electronic conductivity, which is much worse than that of $\text{TiO}_2(\text{B})$.
17 Meanwhile, the rate capability of $\text{TiO}_2\text{-Nb}$ decreases with the increased amount of Nb_2O_5
18 coating from 1wt% to 10wt%. Therefore, the improved electrochemical performance of $\text{TiO}_2\text{-}$
19 Nb , compared to bare TiO_2 , should be attributed to the incorporation of oxygen vacancies
20 rather than coating materials itself. Moreover, this enhanced rate performance is not at the
21 cost of cycle life and $\text{TiO}_2\text{-Nb}$ still maintained a capacity retention larger than 80% after 4000
22 cycles (Figure 4f). In addition, the feasibility of oxygen vacancies for electrode towards full
23 cell application is affirmed by coupling with LiCoO_2 (LCO) cathode (Figure S11). The
24 improved rate capability of LCO/ $\text{TiO}_2\text{-Nb}$ full cell should be originated from the anode side
25 attributed to the introduction of oxygen vacancies.

In summary, using TiO_2 as model system, we demonstrated an effective approach to incorporate oxygen vacancies under aerobic atmosphere through generated interfacial lattice strain by oxide coating. DFT theoretic simulations verified the interfacial strain largely decreased the energy barrier for the formation of oxygen vacancies. The introduction of oxygen defects brought electrode significantly enhanced pseudocapacitive charge storage properties, which accounted for ~53% of the total capacity of $\text{TiO}_2\text{-Nb}$ at a scanning speed of 0.5 mV/s, superior to ~31 % of unmodified counterpart. In addition, the obtained oxygen-deficient electrode showed significantly enhanced rate capability with a delivered capacity of 112 mAh g^{-1} at 20 C (~6.7 A g^{-1}), ~30% higher than unmodified TiO_2 . This exploration of innovative strategy for the introduction of oxygen vacancies into electrode materials based on aerobic-annealing process not only fills in the blank of synthetic methodology, but also possesses promising application to industry.

Supporting Information

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

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Scheme 1. Current efforts and the proposed strategy for the introduction of oxygen defects based on aerobic-annealing process. (a) Schematic illustration of conventional approach to remove O_2 to shift the equilibrium. (b) Schematic diagrams of affecting reactant to make the formation reaction of oxygen vacancies more energetically favorable. (c) The more negative ΔG associated with oxygen vacancies formation under epitaxial strain (η) at a constant temperature. (d) The proposed approach to construct oxide heterostructures for the introduction of interfacial lattice strain based on uneven volumetric shrinkage, promoting the generation of oxygen vacancies.

Figure 1. (a) TEM image of TiO₂-Nb. (b) STEM image and (c-e) elemental mapping of titanium (c), oxygen (d) and niobium (e). (f-g) XPS spectra of Nb 3d (g) and Ti 2p (h) of unmodified and modified samples. (h) XRD patterns of TiO₂, TiO₂-Nb and standard TiO₂(B). (i) Ti-edge XANES of TiO₂ and TiO₂-Nb. The same Ti-edge XANES of both samples indicates that the formation of oxygen vacancies is not because of isovalent doping.

Figure 2. (a) TEM image of $\text{TiO}_2\text{-Nb}$ and (b) the corresponding strain mapping of $\text{TiO}_2\text{-Nb}$ interfaces from GPA analysis. Dashed lines mark the $\text{TiO}_2/\text{Nb}_2\text{O}_5$ interface. (c) UV-Vis and (d) EPR spectra of TiO_2 , $\text{TiO}_2\text{-Nb}$, $\text{TiO}_2\text{-Fe}$, $\text{TiO}_2\text{-Zr}$ and $\text{TiO}_2\text{-V}$. (e) O 1s XPS spectra and (f) normalized atomic ratio of surface oxygen vacancies on TiO_2 , $\text{TiO}_2\text{-Nb}$, $\text{TiO}_2\text{-Fe}$, $\text{TiO}_2\text{-Zr}$ and $\text{TiO}_2\text{-V}$. (g) Electrical conductivity of TiO_2 , $\text{TiO}_2\text{-Nb}$, $\text{TiO}_2\text{-Fe}$, $\text{TiO}_2\text{-Zr}$ and $\text{TiO}_2\text{-V}$ at room temperature.

Figure 3. (a-b) Crystal structures of relaxed $\text{TiO}_2(\text{B})$ (110) surfaces without (a) and with (b) one oxygen vacancy (marked with a red dotted hollow circle). (c) The calculated formation energy of oxygen vacancy under various strain rates.

Figure 4. (a-b) Cyclic voltammetry study on TiO_2 (a) and TiO_2 -Nb (b) at varied sweep rates from 0.1 to 1 mV/s . (c) Calculated b value of TiO_2 and TiO_2 -M. (d) The ratio of capacitive contribution to total capacity of TiO_2 and TiO_2 -M. (e) Rate performance of TiO_2 , TiO_2 -M and TiO_2 -vac. (f) Cycling performance of TiO_2 and TiO_2 -Nb at 10 C.

An atmosphere-independent approach to incorporate oxygen vacancies into electrode is developed via applying interfacial lattice strain by oxide coating, using $\text{TiO}_2(\text{B})$ as a model system. The obtained oxygen-deficient electrode shows significantly enhanced pseudocapacitive charge storage and high rate capability, making this strategy very promising for high power energy storage applications.

Keyword: oxygen vacancy, interfacial lattice strain, aerobic-annealing, pseudocapacitive charge storage, lithium-ion batteries

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Interfacial Lattice Strain-Driven Generation of Oxygen Vacancies in Aerobic-Annealed $\text{TiO}_2(\text{B})$ Electrode