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Boosting Sodium Storage of Titanium Oxide through Homojunction Design

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Sodium-ion batteries are regarded as the energy storage of choice for large-scale applications due to their ample resource and low cost. However, their practical application has been largely retarded by the lack of efficient and stable anodes capable of storing a large amount of Na⁺ ions reversibly. In this work, we introduce the concept of homojunction into the design of sodium anodes by growing TiO₂ nanowires composed of both anatase and bronze intimately interwoven. The interplay between the two phases brings abundant boundaries and

interfaces, which drastically increase the storage sites and facilitate the transport of Na⁺ ions. As a result, it reveals robust Na⁺ storage, affording a capability of 140 mAhg⁻¹ at a high rate of 20 C and retaining 85% of the initial capacity after 3000 cycles at 5 C. Furthermore, the practice of TiO₂ homojunction has been explored by pairing it with Na₃V₂(PO₄)₂O₂F cathode, thereby demonstrating the potential of designing homojunction as a promising materials strategy in rechargeable batteries.

Introduction

Sodium-ion batteries (SIBs) have become a strong competitor for next-generation energy storage batteries due to their abundant resources and low cost.^[1–4] The development of anode materials with high capacity, robust rate, and long lifespan is one of the keys to promoting the development of SIBs.^[5–7] As a promising anode material, titanium oxide (TiO₂) has attracted extensive attention because of its nontoxicity, potentially high capacity, and suitable working voltage (0.7 V vs. Na/Na⁺).^[8,9] However, TiO₂ is a typical semiconductor with a large band gap (~3.2 eV), resulting in poor electrical conduction.^[10,11]

To improve the electrochemical performance of TiO₂, several strategies have been reported such as constructing nanostructures,^[12,13] incorporating carbon matrix,^[14–16] introducing lattice defects,^[17,18] and doping of exotic elements.^[19,20] These strategies help to mitigate the conduction issue, thus raising the electrochemical Na⁺ storage performance. Despite their effectiveness, these strategies face some new challenges in practice. For instance, nanostructures usually show a low tap density,^[21] while carbon coating only addresses the interparticle conduction issue.^[22,23] Previously, our group has architected free-standing nanoarrays of TiO₂, enabling a remarkable

improvement in electrochemical performance.^[24,25] This is because these arrays feature a large accessible surface, short ion-transport path, and robust electrical connection between electrode and substrate.^[2,26,27] Nonetheless, the massive fabrication of TiO₂ architectures remains a grand challenge.

Another solution to this issue is to design a heterostructure of TiO₂ such as TiO₂@SnS₂^[28] and TiO₂@SnO₂.^[29] In the heterostructure, an electric field is often built in the interphase due to the difference in Fermi level between two components. The built-in electric field could speed the transport of charge carriers.^[30,31] However, heterostructures have to address the issues of lattice mismatch, lattice distortion, and phase separation.^[32,33] As a result, many TiO₂ heterostructures still exhibit insufficient capacity levels and poor rate performance.

An alternative solution is to design homojunction to enhance the electrochemical Na⁺ storage in TiO₂. A homojunction refers to a semiconductor interface that shares a similar semiconductor material but has a different structure or doping level.^[34] Homojunction features rich phase boundaries that offer freeway for rapid ion transport and active sites for Na⁺ storage.^[33,35,36] In recent years, homojunction design has been extensively used in fields such as photoelectrocatalysis,^[37,38] and solar cells.^[39,40] However, its exploration in rechargeable batteries is relatively rare.

Herein, we propose the design of TiO₂ homojunction of anatase and bronze (hereafter designated TiO₂(A/B)) to boost the electrochemical Na⁺ storage in TiO₂. TiO₂ exhibits versatile crystal structures; among them, anatase and bronze are two more exciting phases suitable for Na⁺ intercalation and storage because of their open structure and multiple diffusion channels.^[8,41] When the two phases are brought to contact, the charge redistribution will take place in the homojunction deriving from the Fermi level difference and result in a driving force to accelerate the ion diffusion.^[42,43] Meanwhile, the rich interfaces between them will provide more active sites for ion storage.^[35,44] Significantly, the TiO₂ homojunction exhibits an excellent rate capability of 140 mAhg⁻¹ at 20 C (1 C =

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335 mA g⁻¹) and sustains 85% of the capacity after 3000 cycles at 5 C, outperforming the single-phase and many recently reported TiO₂ anodes. In addition, the full cell of TiO₂(A/B)//Na₃V₂(PO₄)O₂F realizes an energy density of 160 Wh kg⁻¹, thereby demonstrating its great potential in practical sodium batteries for renewable and grid energy.

Results and Discussion

TiO₂ homojunction can be prepared through a two-step process, as illustrated in Figure 1(a). In the first step, commercial TiO₂ powder was hydrothermally treated with NaOH solution at 160 °C for 24 h. Upon this process, Ti–O–Ti bonds would be broken and Na₂Ti₃O₇ nanowires were generated.^[45] Afterward, these nanowires were immersed in an acidic solution for ion exchange, giving rise to H₂Ti₃O₇ nanowires (Figure S1). In the second step, as-prepared H₂Ti₃O₇ nanowires were vacuum dried and then annealed at a certain temperature (500, 600, and 700 °C) for 4 hours to give the final product. Interestingly, TiO₂ homojunction (TiO₂(A/B)) can be fabricated at a temperature of 600 °C. At heating temperatures of 500 and 700 °C, the final product is dominated by TiO₂ bronze (TiO₂(B)) and anatase (TiO₂(A)), respectively. Here we focus on the TiO₂(A/B) product, which was characterized by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Clearly, TiO₂(A/B) is composed of uniform nanowires, ~3 μm in length and ~100 nm in diameter (Figure 1b and c). The SEM images of TiO₂(A) and TiO₂(B) are also showed in Figure S2. High-resolution TEM imaging reveals two distinct phases in TiO₂(A/B) (Figures 1d and S3). The *d*-spacings of 0.298 and 0.300 nm correspond to the (111) and (40 $\bar{1}$) planes of the bronze phase, respectively. Meanwhile, the *d*-spacing of 0.189 nm well agrees with the distance of the (200) plane of anatase. The interwoven phases in a single nanowire afford abundant interphase and boundaries for Na⁺ transport and accommodation.^[44,46] Hence,

it is expected that TiO₂(A/B) would exhibit improved electrochemical performance for Na⁺ storage.

The temperature-dependent structure evolution was studied by X-ray diffraction (XRD) and Raman spectroscopy. As Figure 2(a) shows, different crystal structures of TiO₂ will be produced at varied annealing temperatures. The product is primarily composed of the bronze phase at 500 °C, and of anatase at 700 °C. At an intermediate temperature of 600 °C, both bronze and anatase are present. If we extend the heating duration at 600 °C, more bronze will transform to anatase (Figure S4a). This result suggests that 600 °C might be a critical temperature where the phase evolution between bronze and anatase can be realized. This trend of structure evolution is also verified by Raman spectroscopy (Figures 2b and S4b). Importantly, the vibration bands at 123 and 144 cm⁻¹ are the characteristic band of bronze and anatase, respectively. Based on this Raman feature, the contents of anatase in the three products of TiO₂(B), TiO₂(A/B), and TiO₂(A) are identified as 7%, 24%, and 100%, respectively (see details in Figures S4c, d and S5).^[47] In addition, the chemical states of TiO₂(A/B) are verified by X-ray photoelectron spectroscopy (XPS, Figures S6, and 2c, d). The core-level spectrum of Ti 2p displays two strong peaks at 458.4 eV and 464.1 eV, confirming the presence of Ti⁴⁺.^[25] The peaks of 529.7 eV and 531.1 eV for O 1s can be assigned to O–Ti and OH–Ti, respectively.^[48]

2032 coin cells were assembled to illustrate the effectiveness of this homojunction design. Figure 3(a) shows cyclic voltammetry (CV) curves of TiO₂(A/B) electrodes measured in the voltage range of 0.1 to 2.5 V at the sweep rate of 0.2 mV s⁻¹. The first cathodic scan shows a large irreversible peak in the range of 0.6–1.0 V, which can be attributed to the formation of solid-electrolyte interphase (SEI).^[15,16,49] In the following cycles, TiO₂(A/B) shows a pair of broad peaks at 0.80/0.82 V, representing the charge transfer between Ti⁴⁺ and Ti³⁺ accompanied by the intercalation and deintercalation of Na⁺ ions. Figure 3(b) exhibits the galvanostatic charge and dis-

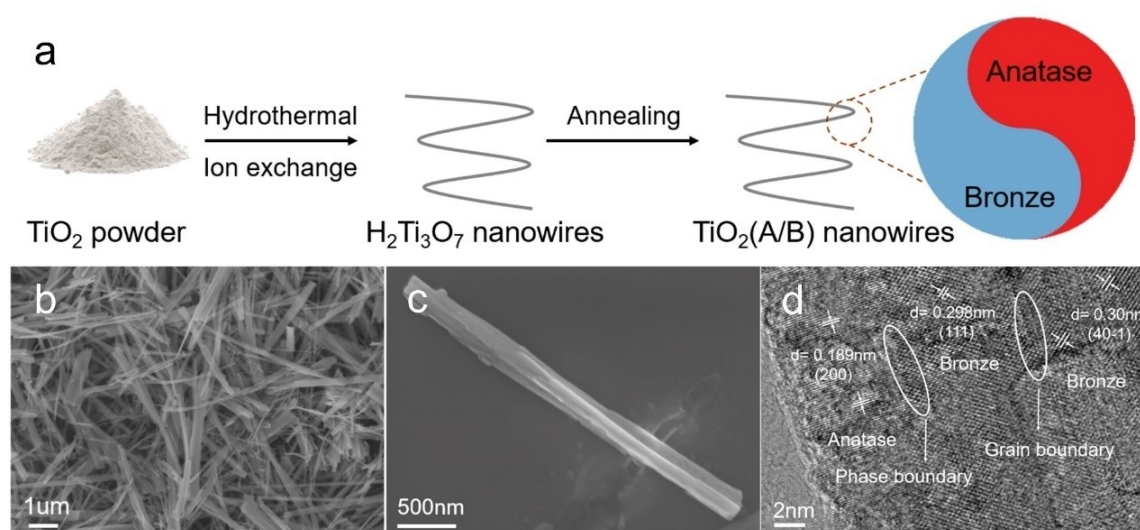


Figure 1. Synthesis and characterization of TiO₂(A/B) nanowires. a) Schematic illustrating the growth of TiO₂(A/B) nanowires. b) and c) SEM images of TiO₂(A/B). d) TEM image of TiO₂(A/B), showing the presence of rich phase boundaries.

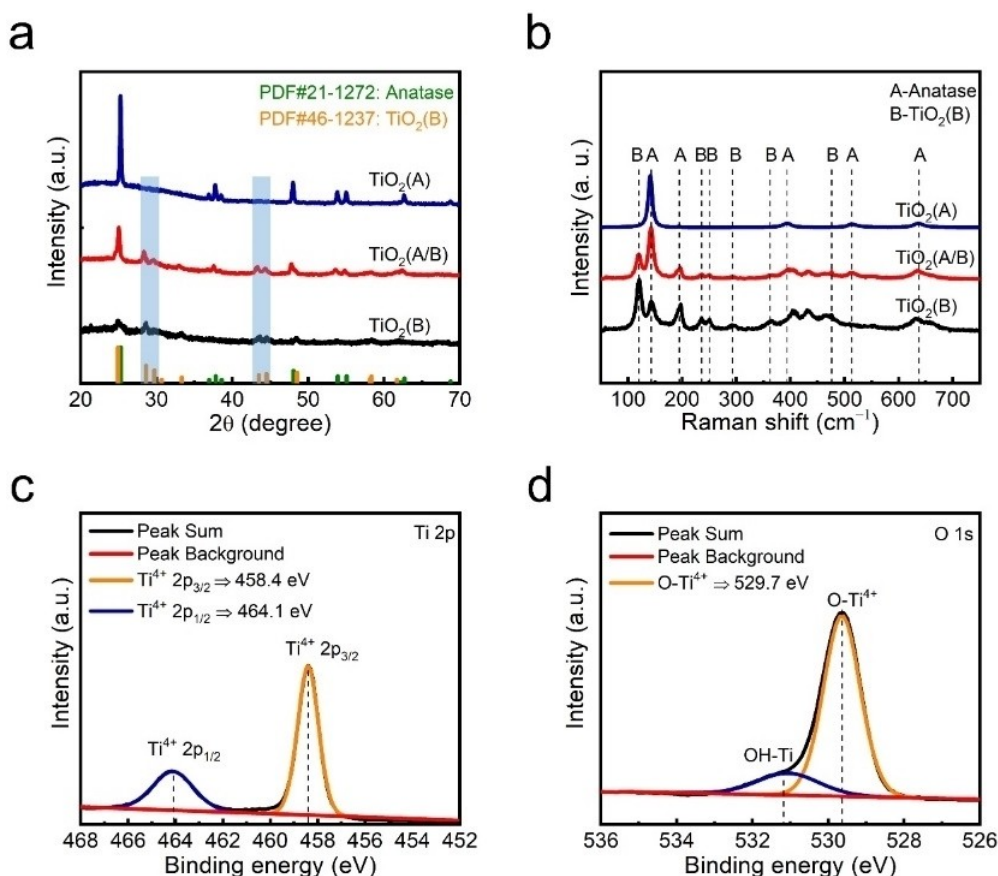


Figure 2. Structure and chemical composition of $\text{TiO}_2(\text{A/B})$. a) XRD patterns and b) Raman spectra of three TiO_2 nanowire products. Core-level XPS spectra of c) Ti 2p and d) O 1s of $\text{TiO}_2(\text{A/B})$.

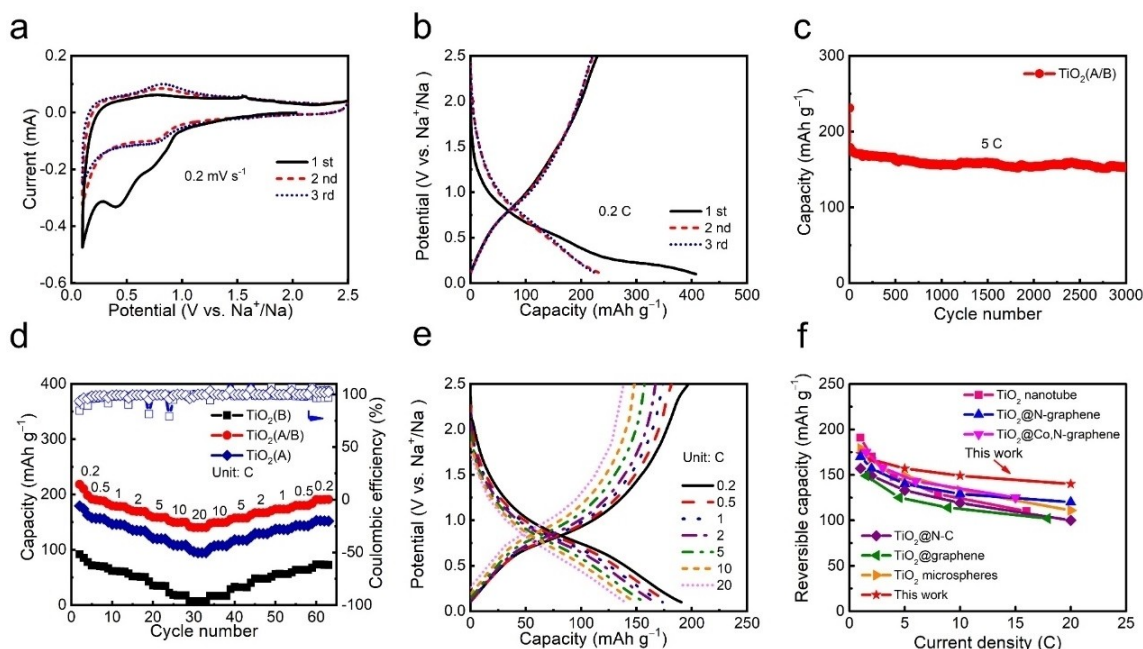


Figure 3. Electrochemical Na^+ storage performance of $\text{TiO}_2(\text{A/B})$. a) Initial CV curves at a rate of 0.2 mV s^{-1} . b) Initial galvanostatic curves. c) Cycling performance of $\text{TiO}_2(\text{A/B})$. d) Comparison of rate capability of three TiO_2 nanowire products. e) Galvanostatic profiles of $\text{TiO}_2(\text{A/B})$ at various current rates. f) Comparison of rate capability of $\text{TiO}_2(\text{A/B})$ with recently reported TiO_2 -based electrodes.

charge curves of $\text{TiO}_2(\text{A/B})$ at a rate of 0.2 C ($1 \text{ C} = 335 \text{ mA g}^{-1}$). $\text{TiO}_2(\text{A/B})$ delivers a reversible (charge) capacity of 230 mAh g^{-1} in the first charge. The initial Coulombic efficiency is 56.2%, as a result of the formation of SEI and irreversible trapping of Na^+ ions. SEM-EDS is conducted to confirm the irreversible trapping of Na^+ ions in Figure S7. In the subsequent cycles, the reversible capacity remains unchanged, but the Coulombic efficiency markedly increases to 95% and beyond. Similarly, the Coulombic efficiency of $\text{TiO}_2(\text{A})$ and $\text{TiO}_2(\text{B})$ are 53.6% and 33.6%, respectively (Figure S8). The homojunction is electrochemically stable (Figure 3c). At a high rate of 5 C, $\text{TiO}_2(\text{A/B})$ maintains a capacity of 162 mAh g^{-1} after 500 cycles and retains 152 mAh g^{-1} after 3000 cycles. The capacity decay is as low as 0.005% per cycle (Figure S9).

For three samples, $\text{TiO}_2(\text{A})$ is electrochemically active toward Na^+ while $\text{TiO}_2(\text{B})$ is almost not. However, $\text{TiO}_2(\text{A/B})$ exhibits a capacity superior to $\text{TiO}_2(\text{A})$ although it consists of $\text{TiO}_2(\text{B})$. Even with different content of $\text{TiO}_2(\text{B})$, $\text{TiO}_2(\text{A/B})$ shows accordingly high activity (Figure S10). This result indicates that the design of homojunction brings substantial augment in the capacity, as a direct result of grain and phase boundaries. These boundaries supply not only additional sites for Na^+ accommodation but also freeway for rapid ion travel.^[35,50,51] As shown in Figure 3(d and e), $\text{TiO}_2(\text{A/B})$ affords desodiation capacities of 199, 181, 173, 167, 157, 149, and 140 mAh g^{-1} at 0.2, 0.5, 1, 2, 5, 10 and 20 C, respectively, which are consistently higher than those of $\text{TiO}_2(\text{A})$ and $\text{TiO}_2(\text{B})$. In addition, such a rate capability is superior to many recently reported TiO_2 anodes (Figure 3f and Table S1).^[13,16,49,50,52,53]

To unravel the kinetic feature of $\text{TiO}_2(\text{A/B})$, CV scans at various rates have been implemented (Figure 4). Significantly,

when the rate increases from 0.2 to 1.0 mV s^{-1} , the CV curve reveals a redox pair at 0.80/0.82 V without evident distortion, reflecting vigorous reversibility upon Na^+ storage. The character reflects a pseudocapacitive behavior for Na^+ storage, as observed previously,^[24,54,55] and further enables higher sweep rates up to 50 mV s^{-1} . To quantitatively assess the kinetic robustness of $\text{TiO}_2(\text{A/B})$, we plot the CV peak current (i_p) versus scan rate (v) logarithmically in Figure 4(c). The slope (b) of the fitted line determines the kinetic feature of electrochemical reactions. A b value of 1 indicates a capacitive process, while a b value of 0.5 suggests a diffusion-controlled process. As both b values in the cathodic and anodic processes are greater than 0.9, the sodium storage process can be regarded a pseudocapacitive reaction. Using the Trasatti methodology [Eq. (1)], we can quantitatively determine the capacitive and diffusion-controlled contribution separately.^[56]

$$Q = Q_s + Q_b = Q_s + kv^{-1/2} \quad (1)$$

where Q , Q_s , and Q_b are the total charge storage, the surface charge contribution, and the bulk diffusion contribution, respectively. Figure 4(d–f) shows that Q_s dominates the total capacity in the electrode reaction. The ratio of Q_s increases from 79.5% at 0.2 mV s^{-1} to 89.6% at 1.0 mV s^{-1} , larger than that of $\text{TiO}_2(\text{B})$ and $\text{TiO}_2(\text{A})$ (Figure S11). This can be attributed to the rich grain boundaries of $\text{TiO}_2(\text{A/B})$ that provide a large portion of interphase for Na^+ storage.

The kinetic feature of $\text{TiO}_2(\text{A/B})$ is also measured by the galvanostatic intermittent titration technique (GITT) and electrochemical impedance spectroscopy (EIS) (Figure S12). $\text{TiO}_2(\text{A/B})$ shows a better dynamic behavior in both GITT and

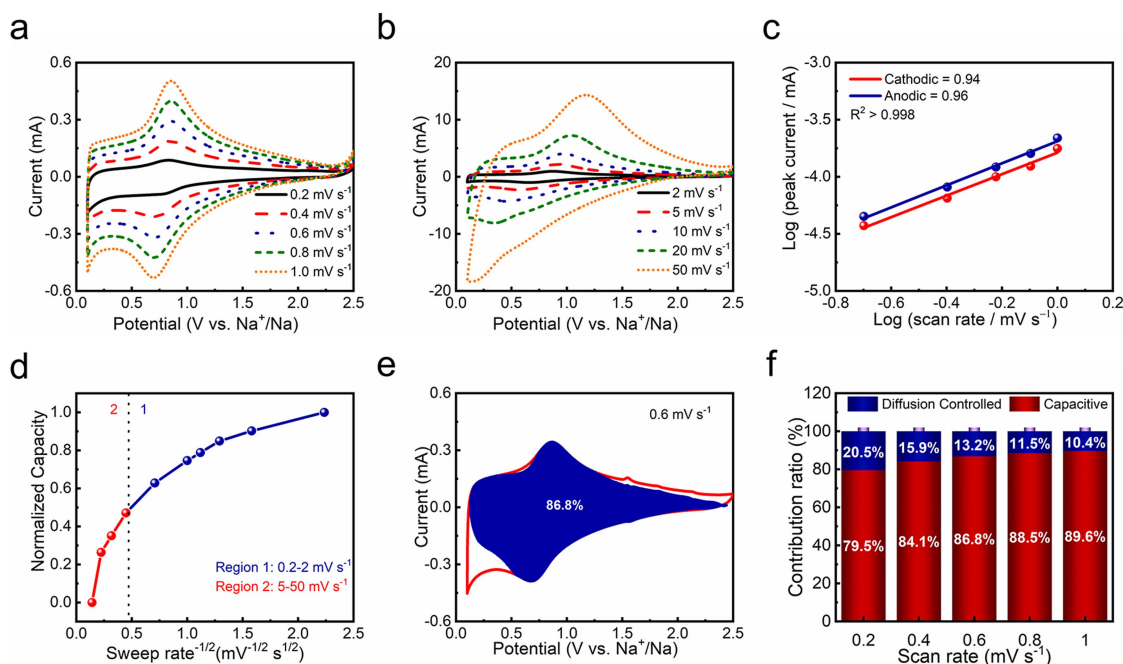


Figure 4. Kinetic analysis of $\text{TiO}_2(\text{A/B})$ by CV tests. CV curves at various sweep rates a) $0.2\text{--}1.0 \text{ mV s}^{-1}$ and b) $2.0\text{--}50.0 \text{ mV s}^{-1}$. c) Relationship between the peak currents and the potential sweep rates. d) The normalized capacity versus the reciprocal square root of the sweep rates. e) Capacitive contribution measured at a sweep rate of 0.6 mV s^{-1} . f) Ratio of capacitive against the diffusion-controlled capacity at different sweep rates.

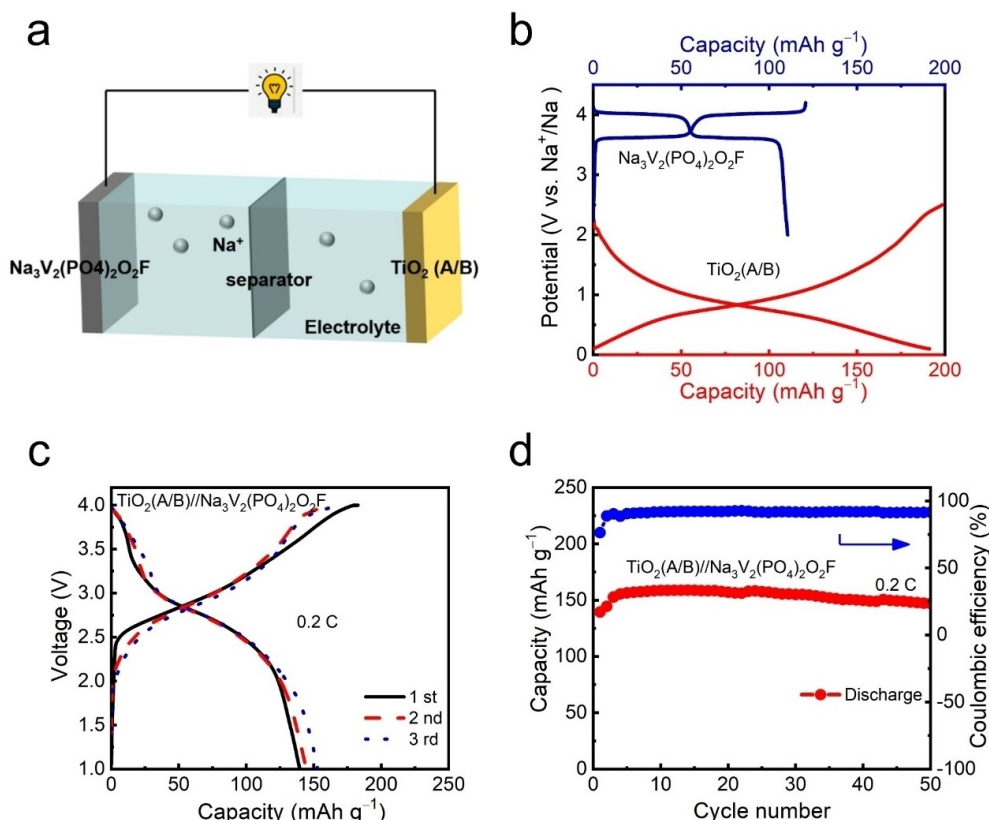


Figure 5. Electrochemical performance of $\text{TiO}_2(\text{A/B})//\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{O}_2\text{F}$ full cell. a) A scheme of the full cell. b) Galvanostatic curves of $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{O}_2\text{F}$ cathode (blue) and $\text{TiO}_2(\text{A/B})$ anode (red) half cells. c) Galvanostatic curves of a full cell for the initial three cycles at 0.2 C. d) Cycling performance of the full cell. The capacity in panels (c, d) is based on the anode.

EIS results, again confirming the efficacy of constructing homojunctions. The improved kinetic feature may result from the rich grain boundaries, which reduce activation barrier and thus accelerate ion transport.^[36]

The band gaps of three samples are investigated by UV-visible spectroscopy (Figure S13a and b). The samples show similar spectra, with the absorption edge located at 400 nm.^[35,42] As the Fermi levels of anatase and bronze have differences,^[42,43] charges will be distributed on both sides of the interface between anatase and bronze, leading to an internal electric field that could accelerate the transport and charge carriers.^[35,36,57] The conductivity of three samples shown in Figure S13(c) confirms this trend.

To demonstrate the potential of homojunction in practical batteries, $\text{TiO}_2(\text{A/B})//\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{O}_2\text{F}$ full cells were assembled and electrochemically evaluated. $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{O}_2\text{F}$ is a commercial product (Neware), showing a reversible capacity of 104 mAh g^{-1} and excellent stability (Figure S14). A mass ratio of 1.7:1 has been carefully adjusted to match the positive and negative capacities. Figure 5 shows the electrochemical performance of the full cell, which affords a capacity of 150 mAh g^{-1} with an average voltage of 2.7 V. Based on the mass of cathode and anode, the specific energy is calculated to be 160 Wh kg^{-1} . A fully charged cell can light up an LED array, thereby demonstrating its potential in practical applications (Figure S15).

Conclusion

In conclusion, we have demonstrated the design and fabrication of $\text{TiO}_2(\text{A/B})$ homojunction using a simple hydrothermal reaction followed by an annealing process. The composition ratio of anatase and bronze can be easily adjusted by annealing temperature and time. The $\text{TiO}_2(\text{A/B})$ homojunction brings rich interphases and active sites for Na^+ storage, leading to a marked improvement in electrochemical performance. $\text{TiO}_2(\text{A/B})$ supplies an excellent rate capability of 140 mAh g^{-1} at 20 C and a stable capacity of 152 mAh g^{-1} at 5 C after 3000 cycles, with a capacity decay as low as 0.005% per cycle. In addition, the full cell of $\text{TiO}_2(\text{A/B})//\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{O}_2\text{F}$ exhibits specific energy of 160 Wh kg^{-1} . This work demonstrates the potential of homojunction design in sodium batteries, which would find more applications in the engineering of electrode materials for rechargeable systems.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords: electrochemical performance · homojunction · sodium-ion batteries · titanium dioxide

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