

TiO₂ bunched hierarchical structure with effective enhancement in sodium storage behaviors

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Abstract

Bronze phase TiO₂ [TiO₂(B)] has great research potential for sodium storage since it has a higher theoretical capacity and ion mobility compared with other phases of TiO₂. In this case, preparing porous TiO₂(B) nanosheets, which can provide abundant sodium insertion channels, is the most effective way to improve transport kinetics. Here, we use the strong one-dimensional TiO₂ nanowires as the matrix for stringing these nanosheets together through a simple solvothermal method to build a bunched hierarchical structure [TiO₂(B)-BH], which has fast pseudocapacitance behavior, high structural stability, and effective ion/electron transport. With the superiorities of this structure design, TiO₂(B)-BH has a higher capacity (131 vs. 70 mAh g⁻¹ [TiO₂-NWs] at 0.5 C). And it is worth mentioning that the reversible capacity of up to 500 cycles can still be maintained at 85 mAh g⁻¹ at a high rate of 10 C. Meanwhile, we also further analyzed the sodium storage mechanism through the ex-situ X-ray powder diffraction test, which proved the high structural stability of TiO₂(B)-BH in the process of sodiumization/de-sodiumization. This strategy of uniformly integrating nanosheets into a matrix can also be extended to preparing electrode material structures of other energy devices.

KEYWORDS

hierarchical, porous, sodium-ion batteries, TiO₂ bronze phase nanosheets

1 | INTRODUCTION

In the 1980s, lithium-ion batteries (LIBs) and sodium-ion batteries (SIBs) were proposed simultaneously.^{1,2} So far, LIB is still regarded as the most potential energy storage battery. Stimulated by Sony's successful commercialization in the 1990s, its application density in energy storage power stations and electric vehicles (EV) has increased. However, compared with the lithium content, sodium

resources are more abundant and extensive.³ In addition, when considering electrochemical principles similar to LIB, SIB may be more privileged than other energy storage batteries.^{4,5} Not surprisingly, SIB has grown rapidly in recent decades.

However, due to concerns about the high ionization potential and radius of sodium ions, there is a great need to develop suitable electrode materials for sodium-ion batteries. For the anode material, it is divided into three

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types according to its charge and discharge mechanism. Alloying/dealloying materials, such as Sn,^{6,7} Sb,^{8–10} and P,^{11–13} generally have serious volume changes in the process of sodiumization and de-sodiumization, which can easily lead to follow-up pulverization, endangering battery safety. The initial Coulombic efficiency of the conversion reaction electrode will be very low, and there will be a higher potential hysteresis.^{14,15} The electrode material of the insertion/extraction reaction type is still the researcher's favorite. As a classic candidate for insertion, titanium-based anode materials have attracted great attention from the scientific community.^{16–18}

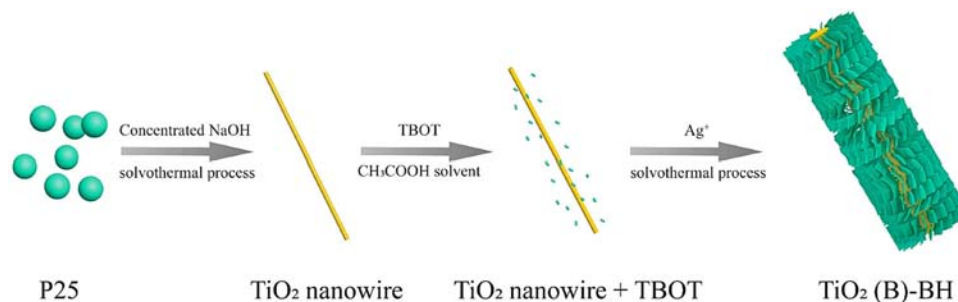
For titanium dioxide (TiO₂), it is one of the most potential SIB candidate materials due to its rich content, nonpolluting nature, stability, and safety.¹⁹ Thanks to its own pseudo-capacitance behavior, TiO₂ has nice sodium storage performance.^{20–22} However, TiO₂ is a semiconductor that cannot be used well in the negative electrode of sodium ion batteries.²³ Among the polymorphs of titanium dioxide, TiO₂(B) can provide more insertion sites and diffusion paths by its open-channel framework. The fast pseudo-capacitance sodiumization/desodiumization behavior leads to an increase in the maximum theoretical capacity to 335 mAh g⁻¹.^{24,25} The calculation results by Dawson and Robertson showed that TiO₂(B) is more suitable for Na⁺ ion intercalation than anatase and rutile TiO₂.²⁶ Legrain et al. showed that TiO₂(B) can reduce the formation energy of Na⁺ insertion defects compared with anatase and rutile TiO₂, which is consistent with the former research.²⁷ However, the inherent shortcomings still reduce the potential of TiO₂(B) as an anode material for SIBs.^{28,29} In addition, TiO₂(B) is not stable, and it is easy to generate a stable phase through irreversible phase transition during the sodiumization/desodiumization process,³⁰ resulting in poor cycle stability. Moreover, due to low thermodynamic stability, TiO₂(B) nanosheets will agglomerate into a powder state during deep cycles, which will reduce the conductivity and cycle stability of the electrode. Therefore, improving the long-term cycling stability of TiO₂(B) nanosheets is important for their application in SIBs.

In this article, we use a self-assembly strategy to integrate TiO₂(B) nanosheets on a one-dimensional (1D) nanowire matrix to build a TiO₂ bunchy hierarchical structure. This structure prevents the nanosheets from crushing, agglomerating, or peeling off during repeated sodiumization/de-sodiumization processes, thereby improving the structural stability of the entire hierarchical system. A vast number of micro-TiO₂(B) nanosheets provide a wide electrode/electrolyte interface contact area, which promotes rapid charge transfer and pseudocapacitance manners. This synthesis strategy effectively improves the capacity (131 mAh g⁻¹) and rate performance (92 mAh g⁻¹ at 3350 mA g⁻¹) of the TiO₂ anode material in SIB, showing a huge practical application potential.

2 | RESULTS AND DISCUSSION

Here, a simple hydrothermal method of 1D TiO₂ nanowires prepared with Ag cations as a medium was used to build this structure. The schematic process was shown in Scheme 1. The TiO₂ nanowires prepared were used as the basis, which is essential for constructing the structure. If TiO₂ nanowires are not added, TiO₂(B) nanosheets will self-stack into spheres by adding Ag⁺ (Figure S1B). In the above process, different amounts of Ag⁺ will also cause the morphology of the product to be different (Figure S2). This difference may have an impact on the performance of the battery.

As shown in the scanning electron microscope (SEM) image (Figure 1A,B), the elongated structure of one-dimensional TiO₂ nanowires supports the growth of densely packed ultra-thin nanosheets. The mechanism of sodium ion deintercalation and transport caused by its surface morphology is shown in Figure 1C. Many porous nanosheets grow around the belt to form a 3D hierarchical structure. On the basis of using the intercalation and deintercalation mechanism to store sodium ions, the structure also provides a channel for sodium ions, which improves the sodium storage performance of the battery. Transmission electron microscopy (TEM) images further



SCHEME 1 Illustration of the preparation of the TiO₂(B)-BH

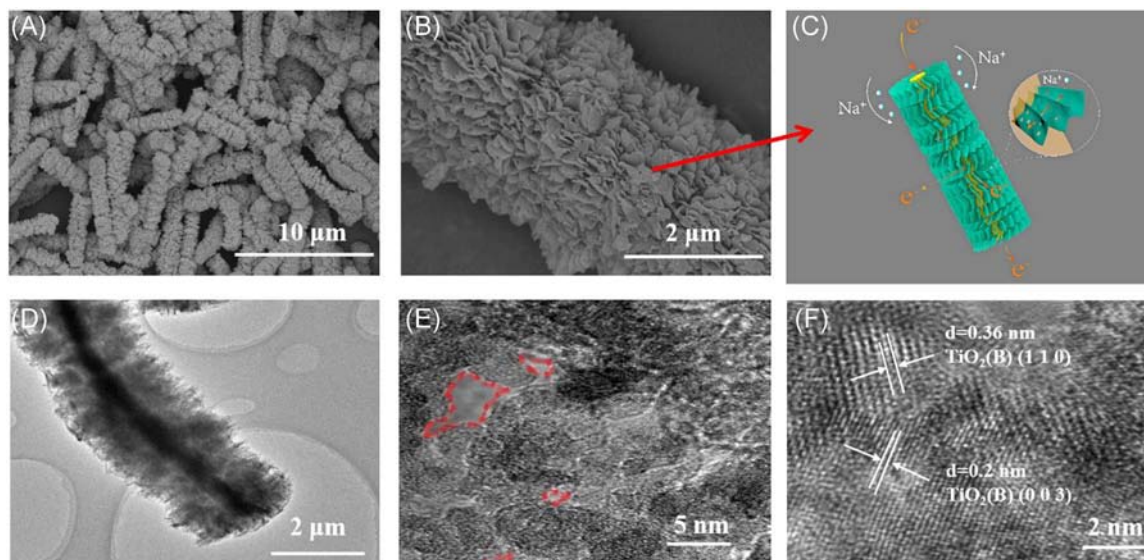


FIGURE 1 (A,B) SEM images of $\text{TiO}_2(\text{B})\text{-BH}$. (C) $\text{TiO}_2(\text{B})\text{-BH}$ sodium ion transmission path diagram. (D) TEM image of $\text{TiO}_2(\text{B})\text{-BH}$. (E,F) HRTEM images of TiO_2 nanosheets over the surface of $\text{TiO}_2(\text{B})\text{-BH}$. HRTEM, high-resolution transmission electron microscopy; SEM, scanning electron microscope; TEM, transmission electron microscopy

clarify the $\text{TiO}_2(\text{B})\text{-BH}$ in detail, and it can be seen that a 1D nucleus exists in the center (Figure 1D). The size of the center is the same as that of the added TiO_2 nanowires; we can say TiO_2 nanowires effectively string the porous nanosheets together. The important thing is that the thickness of the integrated TiO_2 nanosheets ($>1 \mu\text{m}$) on the 1D TiO_2 nanowires, which is much larger than the thickness of the thin TiO_2 layer ($<100 \text{ nm}$) in the previous report.^{31,32} Taking into account the 0–2.5 V safe operating window, thicker layers can increase the loading rate and the usage rate of the active material (TiO_2) in the electrode. The high-resolution transmission electron microscopy (HRTEM) image (Figure 1E) shows that the $\text{TiO}_2(\text{B})$ nanosheets have about 5 nm nanopores (marked with red lines). In Figure 1E, the lattice fringes of the nanosheets can be clearly observed, indicating that the crystal structure is clear. EDS shows that oxygen and titanium are uniformly distributed in $\text{TiO}_2(\text{B})\text{-BH}$ (Figure S3). It can be seen in Figure S4 that there is still a small amount of Ag^+ on $\text{TiO}_2(\text{B})\text{-BH}$, and Ag^+ promotes the conduction of electrons, expands the layer spacing of $\text{TiO}_2(\text{B})$ nanosheets, and provides more sodium storage space for the material.³³

In addition, X-ray powder diffraction (XRD) analysis was performed on the structure of the material, as shown in Figure 2A. The synthesized $\text{TiO}_2(\text{B})\text{-BH}$ has a monoclinic B-phase structure and the space group is C2/m . In the test results, the highest diffraction peak appears at 25° , which corresponds to the (110) plane. The result is completely consistent with the PDF card of $\text{TiO}_2(\text{B})$ (JCPDS 046-1238), which is in good agreement with the HRTEM

observation. All the results show that we have obtained the $\text{TiO}_2(\text{B})\text{-BH}$ by stringing a large number of $\text{TiO}_2(\text{B})$ nanosheets on the nanowires. The adsorption isotherm is shown in Figure 2B. The curve shows the presence of nanopores in the material, which is formed mainly by the stacking of nanosheets.³⁴ According to the Barrett-Joyner-Halenda pore size distribution diagram, the pore size on the nanosheet is about 5–7 nm, which corresponds to the TEM observation. $\text{TiO}_2(\text{B})\text{-BH}$ has a high specific surface area ($198 \text{ m}^2 \text{ g}^{-1}$) and pore volume ($0.80 \text{ cm}^3 \text{ g}^{-1}$). Moreover, the gap between nanosheets is larger, which can be verified by the differentiated pore distributions and TEM images. As we all know, a larger specific surface area provides a wider electrode/electrolyte interface which can reduce interface resistance and accelerate sodium ion diffusion, thereby improving the rate performance of SIBs. In this case, $\text{TiO}_2(\text{B})\text{-BH}$ has shown broad prospects at a high rate as SIB anode material.

We assembled $\text{TiO}_2(\text{B})\text{-BH}$ into Na half-cells and conducted a series of electrochemical tests. Figure 3A shows the cyclic voltammetry curve of the battery between 0 and 2.5 V during the first three cycles. The position of the reduction peak in the first circle is approximately 0.5 V because of the formation of a stable solid electrolyte interphase (SEI) and the irreversible decomposition of the electrolyte.^{35,36} It is also possible that Na^+ is irreversibly inserted into the structural defect crystals of TiO_2 .³⁷ In the next two scans, the position of the reduction peak is around 0.76 V, and the position of the oxidation peak is around 0.84 V, which proves that there is a reversible reduction/oxidation process between Ti^{4+} and Ti^{3+} . Obviously, there

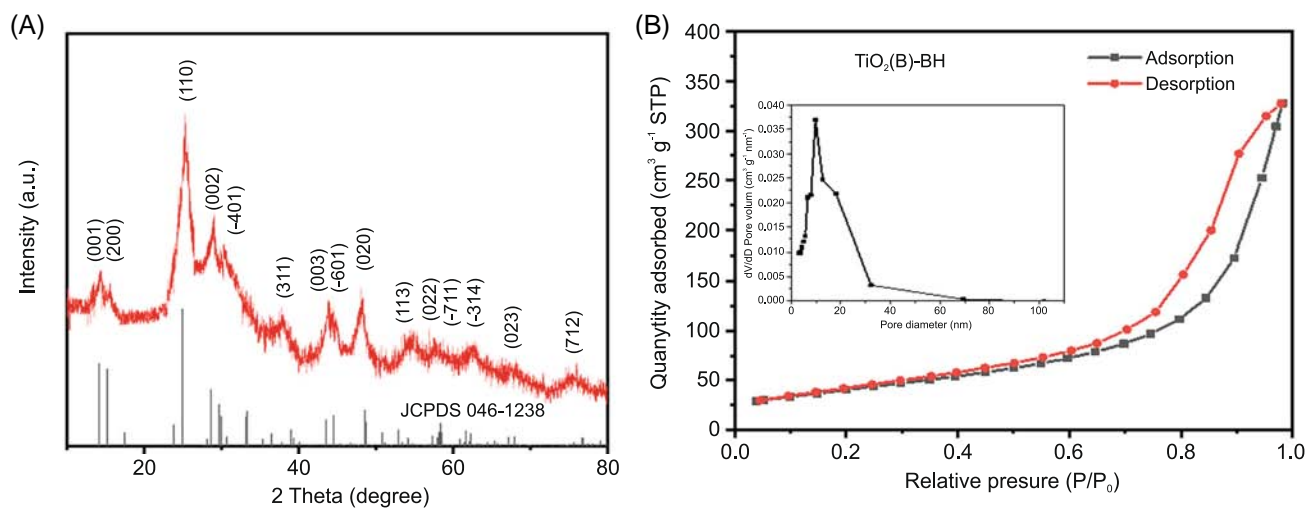


FIGURE 2 (A) XRD pattern of $\text{TiO}_2(\text{B})\text{-BH}$ and standard JCPDS card of $\text{TiO}_2(\text{B})$; (B) adsorption–desorption isotherms of $\text{TiO}_2(\text{B})\text{-BH}$ (inset is corresponding pore size distribution curves). XRD, X-ray powder diffraction

is a lower deviation between the redox peaks in the $\text{TiO}_2(\text{B})\text{-BH}$ electrode (voltage deviation between the anode peak and the cathode peak ($\Delta E = 0.08 \text{ V}$)) and obvious peak intensity were observed, indicating the structural design improved the kinetics of the $\text{TiO}_2(\text{B})$ anode. Figure 3B shows the galvanostatic discharge–charge curve of the battery in the 0–2.5 V potential window at a current density of 0.5 C. The wide plateau during discharge and charging of 0.6–0.9 V is caused by the reversible insertion/deintercalation of Na^+ . The plateau period of the first five turns of the discharge curve is the highest among all the curves, which agrees well with the cyclic voltammetry (CV) result. The initial Coulombic efficiency of the $\text{TiO}_2(\text{B})\text{-BH}$ electrode at 0.5 C is 41.2% because of the loss of sodium ions resulting from the formation of the SEI film. After the 50th and 100th cycles, there is no significant difference in the charge–discharge curve of the battery. It indicates that the electrode has high cycle stability during long-term operation. After 100 cycles, the $\text{TiO}_2(\text{B})\text{-BH}$ anode can maintain a high specific capacity of 131 mAh g^{-1} (Figure 3C). The low initial Coulombic capacity loss is mainly ascribed to the interfacial reaction between electrolyte and the active substance on/in $\text{TiO}_2(\text{B})$, such as inevitable oxygen, water or active impurity. Unlike lithium-ion batteries, the Coulombic efficiency is basically stable at about 100% after 10 cycles. The instability of the curve in the first 50 cycles may be due to the unevenness of the sodium foil and the activation of the porous electrode. For the $\text{TiO}_2\text{-NWs}$ electrode, its initial capacity value is 115.5 mAh g^{-1} at 0.5 C. After 100 discharge–charge cycles, the specific capacity drops rapidly and finally remains at 70 mAh g^{-1} . The $\text{TiO}_2(\text{B})\text{-BH}$ also shows good rate performance from 0.2 to 10 C. As shown in Figure 3D, it can be clearly seen that the SIB of the $\text{TiO}_2(\text{B})\text{-BH}$ electrode has a high specific capacity at each rate,

which shows that the unique advantage of the bunchy hierarchical structure. It can transmit electrons more effectively, and the ion adsorption/diffusion kinetics is improved. At the same time, we also made a comparison in electrochemical performance with $\text{TiO}_2(\text{B})\text{-nanosphere}$ and P25 (Figure S4). Obviously, the specific capacity of $\text{TiO}_2(\text{B})\text{-nanosphere}$ and P25 is also much lower than that of $\text{TiO}_2(\text{B})\text{-BH}$, proving the contribution of this structure to high capacity. To further study the cycle stability of the sample as an anode material for SIBs, $\text{TiO}_2(\text{B})\text{-BH}$ was run for 500 cycles at a high current density of 10 C, and it still showed the capacity of 85 mAh g^{-1} . In particular, the Coulombic efficiency climbed to 98% after 30 cycles, and the specific capacity remained basically unchanged. Compared with the sodium storage capacity of bronze and anatase titanium dioxide in other works (Table S1), the $\text{TiO}_2(\text{B})\text{-BH}$ electrode prepared in this study has good cycle performance and longevity due to its unique structure.

To deeply study the good rate performance of the $\text{TiO}_2(\text{B})\text{-BH}$ anode, we studied the reaction kinetics through altering scan rate of CV tests. In Figure 4A,B, we can see that CV curves under different scan rates show similar shapes and broad peaks. Figure 4C,D shows the $\log(i)$ and $\log(v)$ graphs of the reduction peak and the oxidation peak of the $\text{TiO}_2(\text{B})\text{-BH}$ electrode in the scan rate range of 0.2–1.2 mV s^{-1} . The current shows a relationship related to the scan rate³⁸:

$$i = av^b \quad (1)$$

The b -value of 0.5 represents a diffusion-controlled process, whereas the b -value of 1 represents a capacitance-controlled process. For the reduction and oxidation peaks, the b values of the $\text{TiO}_2(\text{B})\text{-BH}$ electrode are 0.76971 and

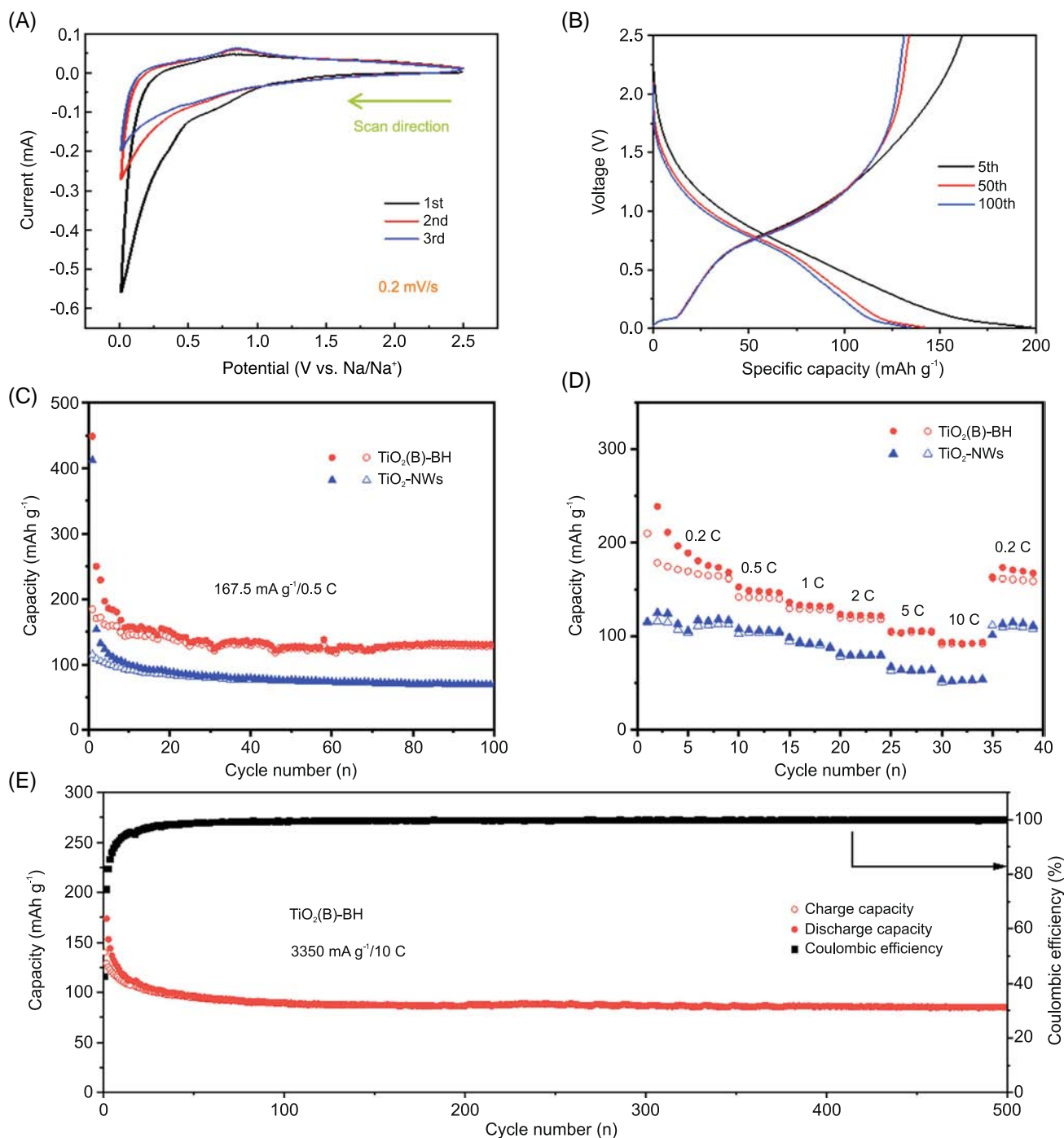


FIGURE 3 (A) CV curve of $\text{TiO}_2(\text{B})\text{-BH}$ at the scan rate of 0.2 mV s^{-1} for the first, second, and third cycles; (B) charge and discharge curve at 0.5 C ; (C) $\text{TiO}_2(\text{B})\text{-BH}$ electrode cycle performance at 0.5 C (167.5 mA g^{-1}); (D) rate performance; and (E) long-term cycle performance at a rate of 10 C . CV, Cyclic Voltammetry

0.93231, respectively, which indicates that the sodium storage process is mainly a surface capacitance effect. In addition, we can also quantify the contribution rate of diffusion and capacitance by the following equation^{39,40}:

$$i(V) = k_1 v + k_2 v^{1/2}. \quad (2)$$

In Equation 2, $k_1 v$ and $k_2 v^{1/2}$ correspond to the current contributions from the surface capacitive effects and the diffusion-controlled intercalation process, respectively. Thus, by determining k_1 and k_2 , we are able to quantify, at specific potentials, the fraction of the current due to each of these contributions.

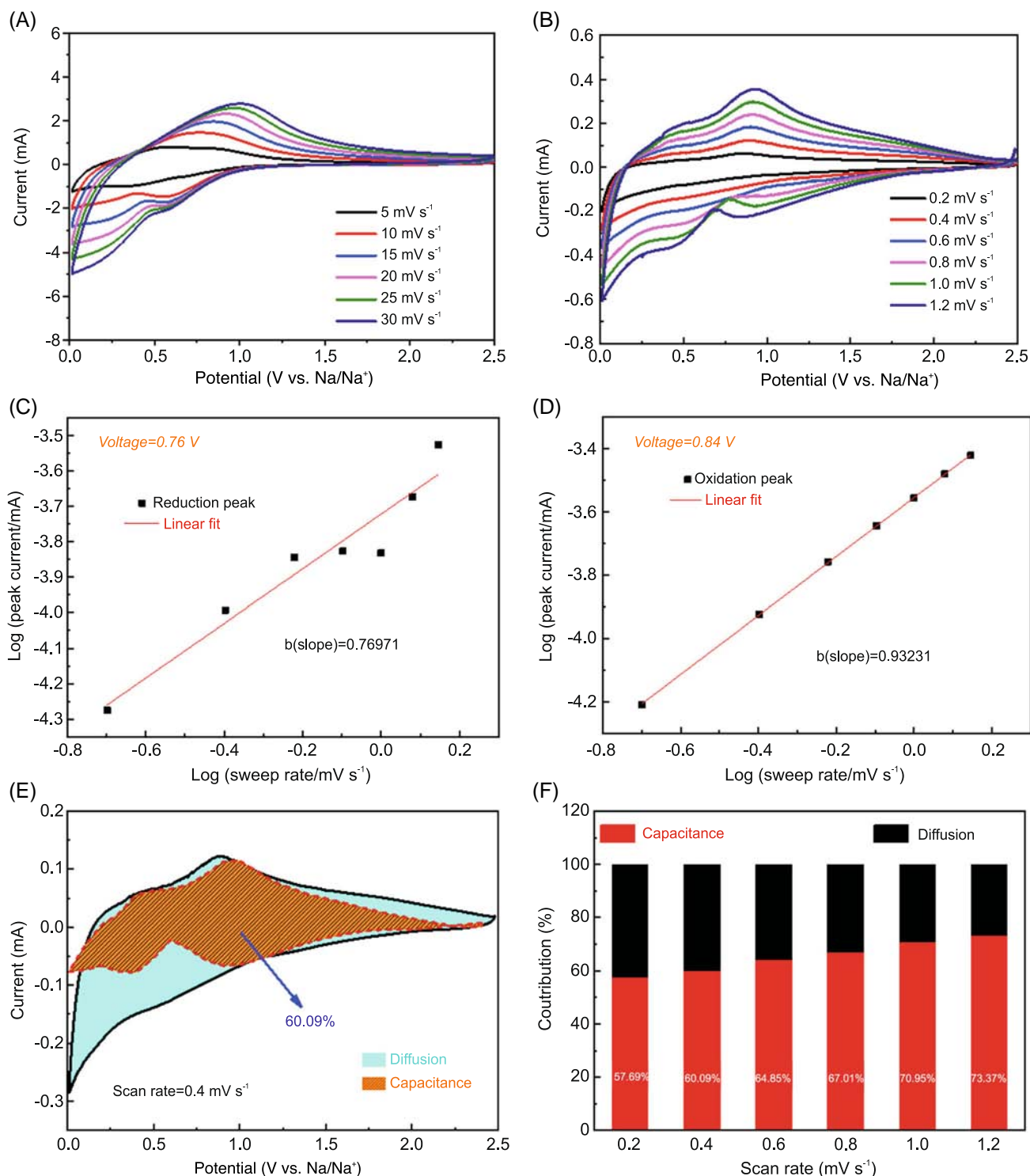


FIGURE 4 Sodium storage kinetics for the TiO₂(B)-BH electrode. (A) CV curves at different scan rates of 5–30 mV s⁻¹. (B) CV curves over the scan rate range of 0.2–1.2 mV s⁻¹. (C,D) *b*-value analysis using the relationship between the peak current and the scan rate. (E) Separation of the capacitive (shaded region) and diffusion currents in the TiO₂(B)-BH electrode at the scan rate of 0.4 mV s⁻¹. (F) Contribution ratio of the capacitive and diffusion-controlled charges at different scan rates. CV, Cyclic Voltammetry

As shown in Figures 4E, 69.0% of the total charge corresponds to the “capacitance” contribution at 0.4 mV s⁻¹. The remaining part corresponds to the charge controlled by diffusion, which almost occurs in the peak

voltage. It represents the oxidation–reduction reaction between Ti⁴⁺/Ti³⁺.⁴¹ We can also calculate the contribution of capacitance and diffusion at other scan rates by using the equations mentioned above. At a scan rate

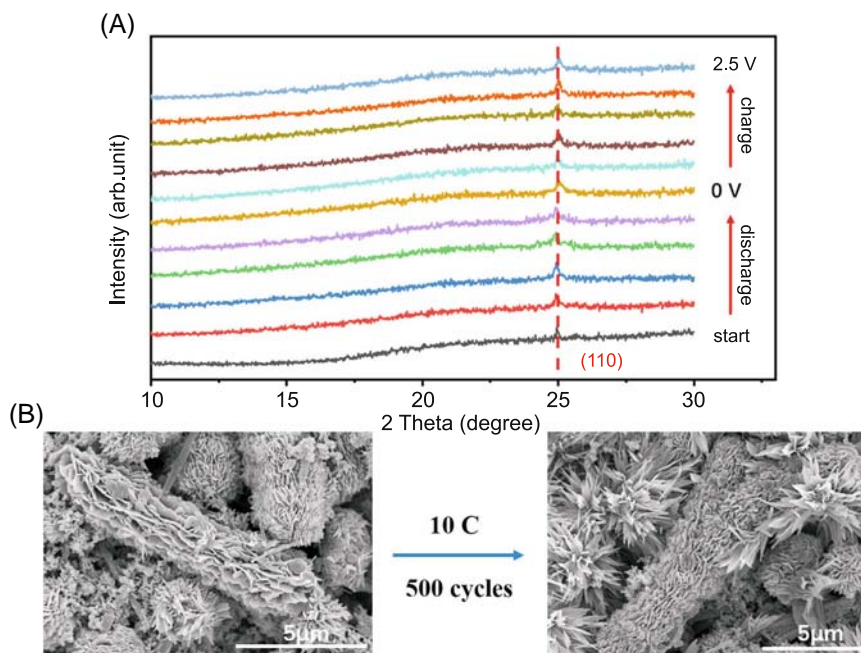
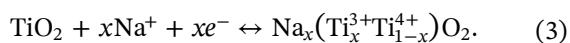


FIGURE 5 (A) Ex situ XRD patterns of $\text{TiO}_2(\text{B})\text{-BH}$ anode during the first cycle with a constant current of 0.2 C rate. (B) SEM images of initial $\text{TiO}_2(\text{B})\text{-BH}$ and that after 500 cycles. SEM, scanning electron microscope; XRD, X-ray powder diffraction

of 0.6 mV s^{-1} (Figure 4F), the capacitance contribution rate of the $\text{TiO}_2(\text{B})\text{-BH}$ electrode reaches 64.85%. As the scan rate increases, the contribution rate of the capacitance gradually rises. Therefore, we can infer that the high capacitance contribution rate can significantly improve the rate and cycle performance of the electrode. This pseudo-capacitance effect is caused by the high specific surface area of the $\text{TiO}_2(\text{B})\text{-BH}$, that is, hole defects in the ordered nanosheets around the titanium oxide nanowires, the spacing between the nanosheets, and the interface between the nanosheets and the nanowires.

We performed an ex-situ XRD analysis on $\text{TiO}_2(\text{B})\text{-BH}$ to have a deeper understanding of the sodium storage mechanism. As shown in Figure 5A, the (110) characteristic peak at about 25° (2θ) shifts slightly to the left due to the expansion of the crystal lattice during the initial discharge process. It indicates the reaction is not conversion of TiO_2 to Ti metal, but is the electrochemical reduction of $\text{Ti}^{4+/3+}$.^{36,42} This corresponds to the position of the oxidation peak (0.84 V) and the reduction peak (0.76 V) in the 2nd and 3rd cycles in Figure 3A,B. During the charging process, the detachment of sodium ions causes the structure to shrink, and the characteristic peaks return to their original positions. The reaction equations between sodium and TiO_2 are as follows:⁴¹



The results show that the structure of this bunched hierarchical structure has a very good effect on the reversible insertion of sodium ions into the main structure of the electrode material. The structure and morphology of $\text{TiO}_2(\text{B})\text{-BH}$ after 500 cycles are shown in Figure 5B. The volume of $\text{TiO}_2(\text{B})$ nanosheets is reduced and partly falls off during charging and discharging, but $\text{TiO}_2(\text{B})\text{-BH}$ can still maintain the bunched hierarchical structure during the continuous sodiumization/de-sodiumization process due to the 1D nanowires as the core is not destroyed. It indicates that $\text{TiO}_2(\text{B})\text{-BH}$ maintains a high degree of structural stability during the sodium insertion/extraction process.

3 | CONCLUSIONS

In summary, we built $\text{TiO}_2(\text{B})\text{-BH}$ by stringing porous $\text{TiO}_2(\text{B})$ nanosheets on TiO_2 nanowires to gain high capacity and good recyclability of SIB. The core is a 1D nanowire, which occupies a very small solid volume in the bunched hierarchical structure, resulting in a shortened electron/ion path. In addition, this structure reduces the volume expansion during charging and discharging, and thereby $\text{TiO}_2(\text{B})\text{-BH}$ has very high stability. $\text{TiO}_2(\text{B})\text{-BH}$ can achieve a high reversible capacity (131 mAh g^{-1} at 0.5 C) and good rate performance (92 mAh g^{-1} at 10 C). In addition, the reversible capacity

of sodium-ion batteries can be maintained at 85 mAh g⁻¹ even after 500 cycles at 10 C. This integrated strategy of nanoscale construction can also be used in the structure design of materials for LIBs, Mg-ion batteries, lithium-sulfur batteries, supercapacitors, and so on.

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CONFLICT OF INTEREST

The authors declare no conflict of interest.

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SUPPORTING INFORMATION

Additional supporting information may be found in the online version of the article at the publisher's website.

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