**TiO<sub>2</sub> Nanobelt@Co<sub>9</sub>S<sub>8</sub> Composites as Promising Anode Materials for Lithium and Sodium Ion Batteries**

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**Abstract:** TiO<sub>2</sub> anodes have attracted great attention due to their good cycling stability for lithium ion batteries and sodium ion batteries (LIBs and SIBs). Unfortunately, the low specific capacity and poor conductivity limit their practical application. The mixed phase TiO<sub>2</sub> nanobelt (ananase and TiO<sub>2</sub>-B) based Co<sub>9</sub>S<sub>8</sub> composites have been synthesized via the solvothermal reaction and subsequent calcination. During the formation process of hierarchical composites, glucose between TiO<sub>2</sub> nanobelts and Co<sub>9</sub>S<sub>8</sub> serves as a linker to increase the nucleation and growth of sulfides on the surface of TiO<sub>2</sub> nanobelts. As anode materials for LIBs and SIBs, the composites combine the advantages of TiO<sub>2</sub> nanobelts with those of Co<sub>9</sub>S<sub>8</sub> nanomaterials. The reversible specific capacity of TiO<sub>2</sub> nanobelt@Co<sub>9</sub>S<sub>8</sub> composites is up to 889 and 387 mAh·g<sup>−1</sup> after 100 cycles, respectively. The cooperation of excellent cycling stability of TiO<sub>2</sub> nanobelts and high capacities of Co<sub>9</sub>S<sub>8</sub> nanoparticles leads to the good electrochemical performances of TiO<sub>2</sub> nanobelt@Co<sub>9</sub>S<sub>8</sub> composites.

**Keywords:** TiO<sub>2</sub> nanobelt@Co<sub>9</sub>S<sub>8</sub>; mixed phases; cycling stability; lithium ion batteries (LIBs); sodium ion batteries (SIBs)

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### 1. Introduction

Lithium-ion batteries (LIBs), as one of the most important energy storage devices, have attracted extensive attention due to their advantages of high energy density and long cycle life [1,2]. However, the practical application of LIBs is still restricted especially in electrical devices and hybrid electric vehicles (HEV). Electrodes materials are key factors to affect the electrochemical performance for energy storages devices [3]. The commercial graphite anode for LIBs cannot meet the ever-increasing requirement owing to its low specific capacity (372 mAh·g<sup>−1</sup>) and the safety problems [4]. Therefore, more attention has been focused on designing new anode materials to replace graphite [5–10]. Among various transition metal oxides, Titanium dioxide (TiO<sub>2</sub>) has been considered as new anode materials for both LIBs and SIBs because of its low cost, environmental friendliness, high voltage platform, and long cycling stability [11–15].

One-dimensional (1D) TiO<sub>2</sub> nanomaterials such as nanowires, nanotubes, and nanorods have been investigated as anodes, which effectively improved the ionic and electronic transport properties compared to TiO<sub>2</sub> nanoparticles [16–19]. TiO<sub>2</sub> nanobelt is one of the potential candidates among these materials in energy storage fields [20,21]. However, the intrinsic low theoretical capacity of TiO<sub>2</sub> still...
limits its wide application. Thus, many effective methods have been adopted to increase its inherent low specific capacity. An efficient way is to hybridize TiO$_2$ with another active material with high capacity. The composites synthesized by TiO$_2$ and metal oxides or sulfides delivered excellent lithium storage performances [22–24]. For instance, the 3D electrode by assembling Fe$_2$O$_3$ hollow nanorods onto highly oriented TiO$_2$ nanotube arrays delivered a high capacity of over 600 mAh·cm$^{-2}$ at a current density of 100 mA·cm$^{-2}$ after 50 cycles [23]. Furthermore, the TiO$_2$@MoS$_2$ hybrid exhibited a reversible capacity of 710 mAh·g$^{-1}$ after 100 cycles at 100 mA·g$^{-1}$ [24]. Another common method is to change the crystal phases of TiO$_2$ to enhance its electrochemical performance. Very recently, TiO$_2$-B anode materials have attracted great interest for both LIBs and SIBs [25–28]. They presented better electrochemical performances than the other phases of TiO$_2$ due to their open tunnel structure and pseudocapacitive lithium storage properties [29,30]. Besides, it has been reported that the anatase/TiO$_2$-B coherent interfaces could contribute to additional lithium storage, leading to better electrochemical performances than single phase TiO$_2$ [31]. TiO$_2$-B related composites have also become the research focus for LIBs. For example, the hierarchical TiO$_2$-B nanowire@α-Fe$_2$O$_3$ composites exhibited better cycling stability than pure TiO$_2$-B [32]. In addition, the TiO$_2$-B nanoribbons anchored with NiO nanosheets as anode materials also displayed good cycling stability at a large rate of 5 C [33]. Cobalt sulfides as high capacity anodes have so many distinct advantages, such as the good conductivity, low electrode polarization and good thermal stability compared with transition metal oxides. However, to our knowledge, the composites of anatase/TiO$_2$-B nanobelt and cobalt sulfides have not been reported yet for both LIBs and SIBs.

In this paper, TiO$_2$ nanobelt@Co$_9$S$_8$ composites have been successfully obtained via a solvothermal reaction and high-temperature calcination process. The composites as anode materials for both LIBs and SIBs present good electrochemical performances, which is better than single TiO$_2$ nanobelts and Co$_9$S$_8$ nanoparticles. The high reversible capacity, good cycling stability and rate capability of TiO$_2$ nanobelt@Co$_9$S$_8$ composites are likely attributed to the synergistic effect of Co$_9$S$_8$ nanoparticles and anatase/TiO$_2$-B nanobelts.

2. Materials and Methods

2.1. Synthesis of mixed Phase TiO$_2$ Nanobelt@Co$_9$S$_8$ Composites

Mixed phase TiO$_2$ nanobelts were prepared by a previously reported method [34]. TiO$_2$ nanobelt@Co$_9$S$_8$ composites were synthesized via the following preparation procedure: First, 30 mg TiO$_2$ nanobelts glucose aqueous solution (25 mL, 0.05 M) was dispersed by ultrasonic treatment for 2 min. Then 1.5 mmol of cobalt acetate were added into this solution and stirred for another 20 min to form a homogeneous dispersion. After that, 4.5 mmol of thiourea in ethylene glycol (25 mL) was added into the above mixture. The obtained dispersion was transferred to a Teflon-lined stainless steel autoclave and then heated at 180 ºC for 10 h. After it was cooled to room temperature, the precipitate was collected, washed with deionized water and absolute alcohol thoroughly, and dried at 60 ºC for 12 h. Finally, the TiO$_2$ nanobelt@Co$_9$S$_8$ composites were obtained through annealing the precipitate at 650 ºC for 10 h under Ar/H$_2$ (5%) atmosphere. Co$_9$S$_8$ nanoparticles were also prepared according to the methods reported in previous paper [35].

2.2. Sample Characterization

X-ray diffraction (XRD) patterns were carried out by a Bruker D8 advanced X-ray diffractometer using monochromatic Cu Kα radiation (λ = 1.5418 Å). Transmission electron microscope (TEM) images and high-resolution transmission electron microscopy (HRTEM) images were achieved on a high-resolution transmission electron microscope (JEOL-2100, Akishima, Tokyo, Japan). Scanning electron microscope (SEM) images, mapping images, and energy dispersive spectrometer (EDS) spectrum were taken from a field-emission scanning electron microscope (FEI Nova 450, Hillsboro, OR, USA). Raman spectra were obtained on a MicroRaman spectrometer using a laser of 532 nm as
an excitation (LabRAM HR Evolution, Kyoto, Japan). Nitrogen sorption isotherm was examined on a Micromeritics ASAP2020HD88 gas sorptometer at 77.3 K (Micromeritics, Norcross, GA, USA).

2.3. Electrochemical Measurements

Electrochemical performances of various electrodes were evaluated by CR2032 coin cells. The working electrode was fabricated by coating a mixture of 70 wt % of active material, 20 wt % of acetylene black, and 10 wt % of binder CMC (carboxyl methyl cellulose) in deionized water on a clean copper foil. Then the obtained foil was dried in vacuum at 60 °C for 10 h. The resulting foil was roll-pressed and punched into discs with a diameter of 12 mm. The mass loading of active material is estimated to 1.0–1.5 mg·cm$^{-2}$. The coin cells were assembled in an Ar-filled glovebox. For LIBs, the lithium foil was used as the counter electrode, Celgard 2400 microporous polypropylene membrane as the separator, and a solution of 1 M LiPF$_6$ in ethylene carbonate (EC) and dimethyl carbonate (DMC) (1:1 v/v) as the organic electrolyte. For SIBs, the sodium foil was used as the counter electrode, glass fiber was used as the separator, and the electrolyte is a solution of 1 M NaClO$_4$ in EC and diethyl carbonate (DEC) (1:1 v/v) containing of 2 wt % fluoroethylene carbonate (FEC). Galvanostatic charge-discharge curves were acquired in a range of 0.01 to 3 V on the battery cyclers (Land CT2001A, Wuhan, China). Electrochemical impedance spectra (EIS) were carried out on an electrochemical workstation (AUTOLAB PGSTAT302N, Herisau, Switzerland) over a frequency range of 100 kHz to 0.01 Hz. Cyclic voltammetry (CV) curves were measured on an electrochemical workstation (CHI660E, Shanghai, China) over 0.01 to 3 V at a scanning rate of 0.1 mV s$^{-1}$. All the electrochemical tests were performed at 25 °C.

3. Results and Discussion

Figure 1 shows the preparation process of TiO$_2$ nanobelt@Co$_9$S$_8$ composites. Firstly, the mixed phase TiO$_2$ nanobelts were prepared via a three step chemical reaction and annealing [34]. Secondly, the intermediate products labeled as TiO$_2$ nanobelt@Co$_x$S$_y$ were obtained by a solvothermal reaction, using mixed phase TiO$_2$ nanobelts as growth templates and glucose as a linker. Finally, TiO$_2$ nanobelt@Co$_9$S$_8$ composites were formed with the initial amorphous Co$_x$S$_y$ changing into crystalline Co$_9$S$_8$ after an annealing treatment of 650 °C for 10 h under Ar/H$_2$ atmosphere.

![Figure 1. Preparation process of TiO$_2$ nanobelt@Co$_9$S$_8$ composites.](image)

3.1. Characterization of Samples

Figure 2 shows the XRD pattern of obtained TiO$_2$ nanobelt@Co$_9$S$_8$ composites. Three diffraction peaks marked with blue rhombus can be assigned to (311), (222) and (440) planes of cubic-phase Co$_9$S$_8$ (JCPDS Card, No. 65-1765) [8]. The diffraction peaks located at 2θ=25.3°, 48.0°, 53.9°, 55.1° and 62.7° can be identified as anatase TiO$_2$ (JCPDS Card, No. 21-1272) [13]. The weak diffraction peak at 44.5° is attributed to TiO$_2$-B (JCPDS Card, No. 46-1237) [16]. Meanwhile, mixed phase TiO$_2$ nanobelt has been clearly demonstrated by the XRD patterns (Figure S1a and b). The Raman spectra of as-obtained TiO$_2$ nanobelt and annealed treated TiO$_2$ nanobelt also verify above results. As shown in Figure S1c and Figure S1d, two strong peaks located at 145 and 640 cm$^{-1}$ are attributed to both anatase and
TiO$_2$-B, and one weak peak at 517 cm$^{-1}$ is ascribed to anatase TiO$_2$. All the remaining peaks are originated from TiO$_2$-B [36]. EDS spectrum was measured to further verify the element composition and contents of the composites (Figure S2). The TiO$_2$ contents (wt %) in the composites is estimated as ~64%, in which C and Al is from the conductive substrates, and the signal of Pt arises from the conductive coating of Pt on the sample surface by sputtering [37]. The EDS elemental mapping of composites also provides an even element distribution of Ti, Co and S (Figure S3).

The morphology of TiO$_2$ nanobelt@Co$_9$S$_8$ composites was characterized by SEM and TEM techniques (Figure 3). The SEM image in Figure 3a clearly shows that some nanoparticles are evenly anchored on TiO$_2$ nanobelts, implying the formation of TiO$_2$ nanobelt@Co$_9$S$_8$ composites. Figure 3b exhibits its low magnified TEM images. It can be clearly observed that the TiO$_2$ nanobelt is uniformly coated with some small nanoparticles, which agrees well with the SEM data. The high magnified TEM image in Figure 3c shows the clear morphology of single TiO$_2$ nanobelt@Co$_9$S$_8$ composite. As can be seen, TiO$_2$ nanobelt presents an irregular porous nanostructure after acidizing and annealing. The related HRTEM image is demonstrated in Figure 3d, the d-spacings at 0.299 and 0.34 nm agree well with those from (311) planes of Co$_9$S$_8$ and (101) planes of TiO$_2$. The overlap of lattice fringes shows that small Co$_9$S$_8$ nanoparticles are grown on the surface of TiO$_2$ nanobelt likely induced by some chemical force effect. The SEM and TEM images of TiO$_2$ nanobelts and Co$_9$S$_8$ nanoparticles are also given as control samples (Figure S4). The nitrogen adsorption-desorption measurement was carried out to determine the surface area of TiO$_2$ nanobelt@Co$_9$S$_8$ composites. As shown in Figure S5a, a type-IV isotherm with a distinct hysteric loop for $P/P_0$ ranges from 0.5 to 1.0 could be observed, suggesting the mesoporous structure in the product. The surface area of TiO$_2$ nanobelt@Co$_9$S$_8$ composites is estimated as ~32.2 m$^2$.g$^{-1}$. The pore size ranges from 23 to 38 nm and the main peak is located at 38 nm (Figure S5b), which is in agreement with what observed in TEM images. As seen in the previous paper, the low surface area can suppress the unnecessary side reaction, such as inevitable electrolyte decomposition and formation of solid electrolyte interface (SEI) [38,39]. Thus, it could be supposed that the hierarchical mesoporous TiO$_2$ nanobelt@Co$_9$S$_8$ composites as anode materials should present good lithium storage performance.
which is far higher than that of single TiO$_2$ which is very similar to that of transition metal oxides-based anodes [41, 42]. Besides, it also arises from the redox peaks observed from CV results. The initial reversible capacity and coulombic efficiency of TiO$_2$ is mainly from the pseudocapacitive lithium storage of TiO$_2$ nanobelt and Co$_9$S$_8$ (Figure 4c), which is far higher than that of single TiO$_2$ nanobelt (Figure S6b). The capacity increase of TiO$_2$ nanobelt@Co$_9$S$_8$ composites could reach 714 mAh·g$^{-1}$ and 74%, respectively. The irreversible capacity for the first cycle could result from the electrolyte decomposition and formation of SEI layer [38, 39]. Inversely, a sharp anodic peak around 2.02 V can be assigned to the reversible oxidation of metallic Co, which overlaps with the charge process of Li$^+$ deintercalation from the anatase framework (Li$_x$TiO$_2$) [31]. Another two pairs of peaks located at 1.48/1.57 V and 1.54/1.65 V are ascribed to the surfaced-confined charge-transfer process (faradic pseudocapacitive lithium storage behavior) of TiO$_2$-B [31]. The CV curves of TiO$_2$ nanobelt further confirm the coexistence of anatase TiO$_2$ and TiO$_2$-B (Figure S6a). Figure 4b shows the galvanostatic discharge/charge voltage profiles of TiO$_2$ nanobelt@Co$_9$S$_8$ composites for the first, second and fifth cycles over 0.01–3.0 V at 0.1 A·g$^{-1}$. The first discharge curve shows multiple voltage plateaus mainly located at 1.6 and 1.2 V, which is in agreement with the redox peaks observed from CV results. The initial reversible capacity and coulombic efficiency of TiO$_2$ nanobelt@Co$_9$S$_8$ composites could reach 714 mAh·g$^{-1}$ and 74%, respectively. The irreversible capacity for the first cycle could result from the electrolyte decomposition and formation of SEI layer, which is very similar to that of transition metal oxides-based anodes [41, 42]. Besides, it also arises from the solvated lithium intercalation and subsequent reduction of the solvent [43]. The irreversible capacities are largely dependent on the external surface area of the electrode and also plausibly related to the irreversible conversion reaction of Co$_9$S$_8$ for the first cycle and volume change of the electrode during the conversion process [44]. The cycling performance of TiO$_2$ nanobelt@Co$_9$S$_8$ composites shows that a high reversible capacity of 889 mAh·g$^{-1}$ can be achieved after 100 cycles (Figure 4c), which is far higher than that of single TiO$_2$ nanobelt (Figure S6b). The capacity increase upon cycling is mainly from the pseudocapacitive lithium storage of TiO$_2$ nanobelt and Co$_9$S$_8$ nanoparticles [8]. Such good electrochemical performance could be attributed to the designed hierarchical composites. The Co$_9$S$_8$ nanoparticles attached to TiO$_2$ nanobelt can provide high capacity and improve conductivity for overall composites. Their small particle size and uniform dispersion of Co$_9$S$_8$ can effectively inhibit volume changes during cycling. Moreover, 1D TiO$_2$ nanobelt can enhance the electron transfer efficiency, and the TiO$_2$-B in the TiO$_2$ nanobelt will lead to a higher reversible capacity compared to pure anatase TiO$_2$ [45]. The interfaces between anatase and TiO$_2$-B nanodomains can also contribute to
additional lithium storage capacity [31]. More importantly, the anatase/TiO2-B nanobelt as backbone for Co9S8 can suppress the separation of Co9S8, its inherent cycling stability of TiO2 can also hinder the capacity loss of Co9S8 upon cycling. All the above factors facilitate the good electrochemical performances of TiO2 nanobelt@Co9S8 composites. The rate capability is another important kinetic factor to evaluate the electrochemical performance of TiO2 nanobelt@Co9S8 composites. As presented in Figure 4d, the average reversible capacity of TiO2 nanobelt@Co9S8 composites at a current density of 0.1, 0.2, 0.5, 1, 2 and 5 A·g⁻¹ is 707, 676, 605, 502, 473 and 260 mAh·g⁻¹, respectively, which is superior to those of the TiO2 nanobelt. The electrochemical performances of TiO2 nanobelt@Co9S8 composites at large current densities such as 1, 2 and 5 A·g⁻¹ are superior to those of Co9S8 nanoparticles. Surprisingly, when the current density returns back to 0.1 A·g⁻¹, the reversible capacity is still as high as 776 mAh·g⁻¹, which is higher than initial capacity value. This phenomenon is likely attributed to the enhanced capacitance contribution resulting from the so-called electrochemical milling effect. All the results mentioned show that the TiO2 nanobelt@Co9S8 composites could be considered as potential anode materials to be applied for LIBs.

![Figure 4](image)

**Figure 4.** Cyclic voltammograms (a), galvanostatic discharge/charge profiles (b), cycling performances (c) of the TiO2 nanobelt@Co9S8 composites and (d) rate performances of the TiO2 nanobelt@Co9S8 composites, TiO2 nanobelts and Co9S8 nanoparticles.

Figure 5a presents the cycling performances of TiO2 nanobelt@Co9S8 composites, TiO2 nanobelts and Co9S8 nanoparticles at 1 A·g⁻¹. Although the cycling stability of TiO2 nanobelt is the best among three kinds of materials, its reversible capacity is only 216 mAh·g⁻¹. The reversible capacity of TiO2 nanobelt@Co9S8 composites could retain at 369 mAh·g⁻¹ after 100 cycles. The electrochemical impedance spectra (EIS) were tested to further investigate the electrode process kinetics of three kinds of electrodes (Figure 3b). For all the electrodes before cycling, the depressed semicircle at high-to-medium frequencies is attributed to charge-transfer impedance (Rct), and a slope at low frequencies is associated with ion diffusion process inside the electrode (constant phase element, CPE) [46]. After cycling, the depressed semicircles are related to two overlapped interface impedances (SEI and Rct) [35]. The phase angle of slope for TiO2 is close to 45°, suggesting a diffusion-controlled feature of lithium
insertion/extraction. The phase angles of slope for both TiO₂ nanobelt@Co₉S₈ composites and Co₉S₈ are greater than 45°, indicating significant capacitive component in lithium insertion/extraction [8]. Compared to the fresh electrodes, the decrease of Rₙ for all the cycled electrodes suggests the electrochemically activation of anodes [47]. The relatively small Rₛ, SEI and Rₙct verify effective lithium and electron transfer of this composite during cycling.

Figure 5. Cycling performances (a), electrochemical impedance spectra (EIS) of TiO₂ nanobelts, Co₉S₈ nanoparticles and TiO₂ nanobelt@Co₉S₈ composites: before cycling (b), and after cycling (c).

3.3. Electrochemical Performance of TiO₂ Nanobelt@Co₉S₈ Composites for SIBs

The electrochemical performances of TiO₂ nanobelt@Co₉S₈ composites, TiO₂ nanobelt and Co₉S₈ nanoparticles for SIBs were also investigated (Figure 6). The CV curves are shown in Figure 6a, in the first cathodic scan, a strong peak located at ~0.46 V is likely to come from the formation of SEI film, and a small peak at 0.25 V is attributed to the intercalation process of Na⁺ into the TiO₂ lattice [28]. The wide peaks located at ~1.13 V and 0.86 V are commonly attributed to the formation of NaₓCo₉S₈ and further reduction process to Co and Na₂S, respectively. The cathodic peak for the second cycle shifts to ~0.89 V, owing to irreversible structural rearrangement of Co₉S₈. For the anodic process, an intense oxidation peak at ~1.76 V could be assigned to the oxidation reaction of Co metal to form Co₉S₈ or NaₓCo₉S₈ due to the irreversible reaction [48], which is in good accordance with previous reports [49]. The wide peak at ~0.52 V is associated with oxidation process of NaₓTiO₂ to TiO₂ and Na₁₋ₓTiO₂ [50]. The overlap of all the cathodic and anodic peaks in subsequent cycles demonstrates the good reversibility of TiO₂ nanobelt@Co₉S₈ composites. Moreover, two sloping voltage plateau located at about 0.9 and 0.5 V appear in the first discharge curves, while for the following cycles, only one obvious discharge voltage plateau can be found, which is located at around 0.9 V. For all of the charge process, just a wide voltage plateau is observed. The wide voltage plateau indicate the overlap of electrochemical reaction of TiO₂ and Co₉S₈ electrodes. All of the voltage plateaus in the discharge/charge curves of TiO₂ nanobelt@Co₉S₈ composites can agree with the corresponding CV curves (Figure 6b).
As new anode materials, they show high specific capacities and good cycling performances for both LIBs and SIBs. The initial discharge and charge capacity can reach 554 and 387 mAh·g$^{-1}$, respectively. Figure 6 shows the cycling performance of TiO$_2$ nanobelt@Co$_9$S$_8$ composites at 0.1 A·g$^{-1}$. The reversible discharge and charge capacity can reach 554 and 387 mAh·g$^{-1}$, respectively. After 100 cycles, the reversible capacity can still maintain at 258 mAh·g$^{-1}$, displaying good cycling stability of TiO$_2$ nanobelt@Co$_9$S$_8$ composites. The rate capability of TiO$_2$ nanobelt@Co$_9$S$_8$ composites are shown in Figure 6d. The reversible capacity is 388, 358, 322, 288 and 237 mAh·g$^{-1}$ at 0.1, 0.2, 0.5, 1 and 2 A·g$^{-1}$, respectively. When the current density goes back to 0.1 A·g$^{-1}$, the reversible capacity can return to 374 mAh·g$^{-1}$. The cycling performance and rate capacity of TiO$_2$ nanobelt@Co$_9$S$_8$ composites are better than those of single TiO$_2$ and Co$_9$S$_8$ for SIBs (Figure S7).

The EIS of three kinds of electrodes for SIBs were also measured (Figure S8), compared to fresh electrodes, all of the cycled electrodes exhibit smaller $R_{ct}$, and the $R_{ct}$ of TiO$_2$@Co$_9$S$_8$ is located between TiO$_2$ and Co$_9$S$_8$, which is possibly resulted from the good conductivity of Co$_9$S$_8$. The phase angles of slope for these electrodes are similar to those of LIBs. The TiO$_2$ nanobelt@Co$_9$S$_8$ composites with good electrochemical performances are of great potential to be used for both LIBs and SIBs.

4. Conclusions

In summary, we have successfully synthesized mixed phase TiO$_2$ nanobelt@Co$_9$S$_8$ composites. As new anode materials, they show high specific capacities and good cycling performances for both LIBs and SIBs. After 100 cycles, their reversible capacity for LIBs can retain at 889 and 369 mAh·g$^{-1}$ at 0.1 and 1 A·g$^{-1}$, respectively. Besides, an initial reversible capacity of 387 mAh·g$^{-1}$ can be obtained at 0.1 A·g$^{-1}$ for SIBs. Such good electrochemical performances of TiO$_2$ nanobelt@Co$_9$S$_8$ composites could be attributed to the hierarchical nanostructure and synergistic effect of Co$_9$S$_8$ nanoparticles and anatase/TiO$_2$-B nanobelts.

Supplementary Materials: The following are available online at http://www.mdpi.com/2226-4310/4/2/18/s1, Figure S1: XRD patterns and Raman spectra of (a) and (c) as-prepared TiO$_2$ nanobelts and (b) and (d) TiO$_2$ nanobelts obtained by a heat treatment of 650 °C under Ar/H$_2$ atmosphere, respectively, Figure S2: EDS spectrum of the as-prepared TiO$_2$ nanobelt@Co9S8 composites (the inset is the molar ratio of element Ti, Co and S, respectively), Figure S3: SEM image corresponding to EDS elemental mapping of Ti, Co and S of as-prepared TiO$_2$ nanobelt@Co9S8 composites, Figure S4: SEM images (a) and (c), TEM images (b) and (d) of TiO$_2$ nanobelts and Co9S8 nanoparticles, respectively, Figure S5: Nitrogen adsorption-desorption isotherm (a) and pore size distribution (b) of TiO$_2$ nanobelt@Co9S8 composites at 77.3 K, Figure S6: CV curves (a) of TiO$_2$...
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