Heterostructured Bi$_2$S$_3$–Bi$_2$O$_3$ Nanosheets with a Built-In Electric Field for Improved Sodium Storage

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ABSTRACT: Constructing novel heterostructures has great potential in tuning the physical/chemical properties of functional materials for electronics, catalysis, as well as energy conversion and storage. In this work, heterostructured Bi$_2$S$_3$–Bi$_2$O$_3$ nanosheets (BS–BO) have been prepared through an easy water-bath approach. The formation of such unique BS–BO heterostructures was achieved through a controllable thioacetamide-directed surfactant-assisted reaction process. Bi$_2$O$_3$ sheets and Bi$_2$S$_3$ sheets can be also prepared through simply modifying the synthetic recipe. When employed as the sodium-ion battery anode material, the resultant BS–BO displays a reversible capacity of $\sim$630 mAh g$^{-1}$ at 100 mA g$^{-1}$. In addition, the BS–BO demonstrates improved rate capability and enhanced cycle stability compared to its Bi$_2$O$_3$ sheets and Bi$_2$S$_3$ sheets counterparts. The improved electrochemical performance can be ascribed to the built-in electric field in the BS–BO heterostructure, which effectively facilitates the charge transport. This work would shed light on the construction of novel heterostructures for high-performance sodium-ion batteries and other energy-related devices.

KEYWORDS: Bi$_2$S$_3$–Bi$_2$O$_3$ nanosheets, heterostructure, built-in electric field, sodium-ion batteries, anode

INTRODUCTION

The demand for low-cost, high-efficiency energy storage technologies is greatly increasing to utilize renewable energy resources and reduce environmental pollution. Rechargeable lithium-ion batteries (LIBs) are undoubtedly one of the most successful candidates among various energy storage devices.\(^1\)\(^–\)\(^3\) Recently, sodium-ion batteries (SIBs) are emerging as a promising alternative to commercial LIBs because of the abundant, inexpensive sodium resources and their similar redox chemistry to LIBs.\(^7\) Nevertheless, because the ionic radius of Na$^+$ ions is much larger (102 pm) than that of Li$^+$ ions (76 pm), most investigated electrode materials suffer from huge volume expansion during sodiation/de-sodiation processes, resulting in low specific capacity and limited cycle life.\(^5\)\(^–\)\(^8\) Hence, the pursuit of SiB electrode materials with high specific capacity and stable cycling performance remains a major challenge.

Metal chalcogenides, such as FeS$_2$,\(^6\) FeSe$_2$,\(^10\) Sb$_2$S$_3$,\(^11\) and Sb$_2$Se$_3$,\(^12\) have attracted considerable attention in sodium storage because of their high specific capacity and intriguing layered structure. Bi$_2$S$_3$ is a well-known layered $p$-type semiconductor with a band gap of approximately 1.3 eV, and it displays enormous potential in thermoelectrics,\(^13\)\(^–\)\(^14\) photodetectors,\(^19\)\(^–\)\(^21\) as well as electrochemical energy conversion and storage.\(^22\)\(^–\)\(^24\) For sodium storage, Bi$_2$S$_3$ is capable to display gravimetric and volumetric capacities of 625 mA h g$^{-1}$ and 4250 mA h cm$^{-3}$, respectively.\(^25\)\(^–\)\(^26\) Bi$_2$O$_3$ is also a typical layered semiconductor with a band gap of 2.8 eV (n-type semiconductor).\(^27\) For sodium storage, the Bi$_2$O$_3$ possesses a high theoretical capacity of 690 mA h g$^{-1}$\(^1,28,29\) Despite their high theoretical capacities, the sodium storage performances of Bi$_2$O$_3$ and Bi$_2$S$_3$ are usually unsatisfactory. For instance, the Bi$_2$O$_3$/C composite displayed a short life span of only 20 cycles.\(^29\) The Bi$_2$O$_3$@rGO nanocomposite exhibited a capacity retention of 70.2% after 200 cycles.\(^30\) The binder-free and flexible Bi$_2$O$_3$/C delivered a specific capacity of 430 mA h g$^{-1}$ after 200 cycles.\(^31\) The Bi$_2$S$_3$@CNT nanocomposite delivered a capacity of only 84.8 mA h g$^{-1}$ after 60 cycles at 60 mA g$^{-1}$\(^32\). Further enhancement of the sodium storage performance of Bi-based anodes still remains a great challenge.

Constructing heterostructures composed of at least two components with different band gaps has great potential in...
tuning the physical/chemical properties of functional materials.32–36 Because of the unique interface effect, many advantages have been realized in heterostructures in various energy storage devices. Of particular note is the fact that Guo et al. proposed a conceptual model of SnS/SnO2 heterostructures with built-in electric fields and thus boosted charge transfer capability.37 Using an ultrathin Bi2MoO6 nanosheet as an example, the same group interpreted the electric-field effect based on density functional theory (DFT) calculations.38 Recently, Yu et al. confirmed that unbalanced charge distribution would occur within crystals and induce built-in electric fields, leading to boosted lithium-ion transfer dynamics.39 Herein, inspired by the built-in electric field effect and enhanced charge transfer in heterostructured materials, we designed Bi2S3−Bi2O3 (BS−BO) heterostructures and explored them in SIB application. Detailed characterizations demonstrated that the formation of such unique BS−BO heterostructures was achieved through a controllable thioacetamide (TAA)-directed surfactant-assisted reaction process. Bi2O3 sheets and Bi2S3 sheets can also be prepared by simply modifying the synthetic recipe. The BS−BO, as an anode for SIBs, delivers a reversible capacity of 630 mA h g−1 at 100 mA g−1. Besides, the BS−BO also demonstrates better cycling stability and rate capability compared with the Bi2O3 sheet and Bi2S3 sheet counterparts. The improved sodium storage performance makes the BS−BO heterostructures a promising anode for SIBs, and the facile synthetic approach also provides new insights into the construction of novel heterostructures.

■ EXPERIMENTAL SECTION

Synthetic Procedures. For the synthesis of BS−BO heterostructures, 0.243 g of Bi(NO3)3·5H2O and 0.125 mL of HNO3 (14 M) were first added into 5 mL of deionized water, leading to the formation of a milky suspension. Then, a sulfurization agent solution was prepared by dissolving 0.125 g of hexadecyl trimethyl ammonium bromide (CTAB) and 0.075 g of TAA in 60 mL of deionized water through ultrasonication. The abovementioned milky suspension was added into the sulfurization solution dropwise with constant stirring. The mixture was incubated at 30 °C for 3 h. The final product was collected by centrifugation and thoroughly washed with deionized water and ethanol three times. The synthesis of Bi2S3 sheets is similar to that of BS−BO heterostructures except that a higher amount of TAA (0.375 g) was used. If no TAA was used in the synthesis, Bi2O3 sheets were obtained through the incubation of milky suspension at 30 °C for 3 h.

Characterization. Field-emission scanning electron microscopy (FESEM) images were collected with a JEOL-7100F microscope. X-ray diffraction (XRD) patterns were obtained with a D8 ADVANCE X-ray diffractometer using Cu Kα radiation (λ = 1.5418 Å). Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images were recorded by using a JEM-2100F STEM/EDS microscope. The Fourier transform infrared (FTIR) instrument used was a Nicolet 60-SXB spectrometer. X-ray photoelectron spectroscopy (XPS) measurements were conducted using a VG MultiLab 2000 instrument. CHNS element analysis was conducted on a Vario EL cube Elementar.

Electrochemical Measurements. The sodium storage behaviors were characterized by an assembly of CR2016 coin cells. The working electrodes were prepared by mixing the as-prepared products, carboxyl methyl cellulose, and acetylene black at a weight ratio of 80:10:10. The slurry was casted onto an aluminum (Al) foil and completely dried in a vacuum oven at 70 °C overnight. The average mass loading was about 1.3 mg cm−2. A sodium metal foil was utilized as the counter electrode and the reference electrode; a glass fiber membrane was used as the separator. The electrolyte was a solution of 1 M trifluomethanesulfonate (NaCF3SO3) in diethylenglycol dimethylether. Galvanostatic discharge—charge tests were conducted on a multichannel battery testing system (LAND CT2001A) at a potential range of 0.01–3.0 V versus Na+/Na. Cyclic voltammetry (CV) was tested with an Autolab CH1760e electrochemical workstation. Electrochemical impedance spectroscopy (EIS) measurements were performed on an Autolab PGSTAT 302N electrochemical workstation over the frequency range of 100 kHz–0.01 Hz. All abovementioned measurements were performed on at room temperature.

Results and Discussion

Microstructure and Morphology Characterization. The schematic illustration for the construction of various nanostructures is briefly depicted in Figure 1. First, Bi2O3 sheets are synthesized through a facile water-bath process at room temperature. For the synthesis of BS−BO heterostructures, TAA is utilized as the sulfurization agent and the Bi2O3 sheet is used as the precursor. The BS−BO heterostructured sheets can be achieved by using an appropriate amount of sulfurization agent and suitable sulfurization time. When an excess amount of sulfurization agents is employed, the Bi2O3 sheets transform into Bi2S3 sheets completely.

Figures 2a and S1 depict the XRD patterns of Bi2O3, BS−BO heterostructure, and Bi2S3. As shown in Figure 2a, all the diffraction peaks of the Bi2O3 precursor can be indexed to the cubic phase Bi2O3 (JCPDS 052-1007). The peaks exhibit broad full width at half maximum and weak intensity, implying the low-crystalline feature of Bi2O3. This result agrees well with previous literature that highly crystallized cubic phase Bi2O3 is difficult to be achieved at room temperature without further annealing.38 After moderate sulfurization, the diffraction peaks for Bi2O3 still remain; meanwhile, new peaks belonging to the orthorhombic phase Bi2S3 (JCPDS 17-0320) appear. The XRD pattern of Bi2S3 is presented in Figure S1, confirming the successful synthesis of pure orthorhombic phase bismuth sulfide (JCPDS 17-0320). No obvious peaks from Bi2O3 can be observed, suggesting that the Bi2O3 is completely converted into Bi2S3 with an enough amount of the sulfurization agent.

The FTIR spectra of the Bi2O3 precursor and the BS−BO heterostructure are presented in Figure 2b. The bands detected at 533, 711, and 957 cm−1 can be observed in both Bi2O3 and BS−BO. For BS−BO, the emerging new band at 619 cm−1 is attributed to C−OH and C−N stretching vibrations, respectively. These bands indicate the existence of CTAB species and H2O absorbed on the surface of the final products.

![Figure 1. Schematic illustration of the synthesis process of Bi2O3 sheets, BS−BO heterostructured sheets, and Bi2S3 sheets.](Image)
The XPS survey spectra of Bi$_2$O$_3$ and BS–BO heterostructure are provided in Figure 2c. Signals from Bi, O, and C elements can be observed in the XPS spectrum of Bi$_2$O$_3$. After sulfurization, the S 2s peak at 225.1 eV can be detected in BS–BO, confirming the successful incorporation of S. Figure 2d shows the high-resolution XPS spectra of Bi$_2$O$_3$ and BS–BO heterostructure. For Bi$_2$O$_3$, the two strong peaks located at 164.1 and 158.3 eV can be ascribed to Bi 4f$^{7/2}$ and Bi 4f$^{5/2}$, respectively. For BS–BO, the peaks with a binding energy of 162.8 and 157.6 eV are correlated with Bi 4f$^{7/2}$ and Bi 4f$^{5/2}$ in Bi$_2$S$_3$, respectively. Moreover, the Bi 4f$^{7/2}$ and Bi 4f$^{5/2}$ peaks for Bi$_2$O$_3$ shift toward higher energies by approximately 0.5 eV, which is because of the coupling effect resulted from the strong chemical bonding between Bi$_2$O$_3$ and Bi$_2$S$_3$. The peak centered at 160.4 eV in BS–BO is ascribed to S 2p transition, which further confirms the formation of BS–BO heterostructure.

Figure 2. (a) XRD patterns of Bi$_2$O$_3$ sheets and BS–BO heterostructures. (b) FTIR spectra of Bi$_2$O$_3$ sheets and BS–BO heterostructures. (c) XPS survey spectra of Bi$_2$O$_3$ sheets and BS–BO heterostructures. (d) High-resolution Bi 4f XPS spectra of Bi$_2$O$_3$ sheets and BS–BO heterostructures.

Figure 3. Morphology characterizations of BS–BO heterostructures. SEM images (a,b), TEM images (c,d), HRTEM image (e), STEM images (f,g), and corresponding elemental mapping images (from the red rectangle area in (f) of Bi (h), S (i), O (j) of BS–BO heterostructured sheets.
which the Bi2S3 shows darker mass-thickness contrast (high-recognized by the contrast in the TEM image (Figure 3d), in Figure 3c). The heterostructure feature can be clearly observed on the surface of BS
3b). When further examined under TEM, the wrinkles can be clearly seen (Figure S3). The Bi2O3 sheets are wrinkled rather than flat (Figure S3a). The thickness of the Bi2O3 sheets is less than 20 nm (Figure S3b). TAA was utilized as the sulfurization agent to convert Bi2O3 into Bi2S3.44 The amount of the sulfurization agent plays a vital role in the synthesis. If an excess amount of TAA, Bi2O3 nanosheets are determined to be 14.83%. The abovementioned results indicate that sheet-like BS–BO heterostructures have been successfully constructed.

Sodium Storage Performance. The sodium storage behaviors of BS–BO, Bi2S3, and Bi2O3 sheets were examined in CR2016 coin cells. CV was first employed to investigate electrochemical performance of BS–BO (Figure S5). During the first cathodic scan, a broad reduction peak located at 0.51 V can be observed. This peak splits into two peaks at around 0.31 and 0.68 V in the subsequent scans, suggesting the evolution might be associated with irreversible activation. The first oxidation process of BS–BO is featured by two peaks at around 0.64 and 0.78 V, which are different from the typical oxidation peaks of Bi2O3 (Figure S6) and Bi2S3 anodes (Figure S7). Because of the homogeneous distribution at nanoscale and strong chemical interactions between Bi2S3 and Bi2O3, the electrochemical redox process of BS–BO cannot be directly recognized as the simple overlap of its two counterparts. As CV cycles proceed, the profiles of BS–BO change slightly with less pronounced current responses.

The first three galvanostatic charge–discharge profiles of BS–BO, Bi2O3, and Bi2S3 at a current density of 100 mA g−1 are shown in Figures 4a, S8, and S9, respectively. The first discharge and charge capacities for BS–BO are 821 and 571 mA h g−1, corresponding to a relatively low initial Coulombic efficiency of 69.5%. The irreversible capacity loss might be caused by the generation of solid electrolyte interphase films. In detail, the initial discharge plateau of BS–BO at around 1.55 V representing the activation process is almost lost in the

Figure 4. Electrochemical performances of BS–BO, Bi2S3, and Bi2O3 electrodes for sodium storage. (a) Typical charge–discharge profiles of BS–BO at a current density of 100 mA g−1 for the initial three cycles. (b) Cycling performance of BS–BO at 100 mA g−1 for 20 cycles. (c) Cycling performance of BS–BO, Bi2S3, and Bi2O3 sheets at a current density of 200 mA g−1. (d) Rate performances of BS–BO, Bi2S3, and Bi2O3 sheets at different current densities.
The main charge plateau is located at 0.61 V, which is ascribed to the dealloying process from Na$_3$Bi to metallic Bi and the oxidation of Bi to Bi$^{3+}$.25 The cycling performance and the corresponding Coulombic efficiency of BS–BO at a current density of 100 mA g$^{-1}$ are shown in Figure 4b. A large capacity loss occurs in the first cycle. The second discharge capacity can reach 630 mA h g$^{-1}$, which is slightly higher than the theoretic capacity of Bi$_2$S$_3$ (625 mA h g$^{-1}$) and approaches the theoretical capacity of Bi$_2$O$_3$ (690 mA h g$^{-1}$). After 20 cycles, the BS–BO is capable of delivering a discharge capacity of 477 mA h g$^{-1}$, corresponding to a capacity retention of 76% (against the second discharge capacity). Additionally, the Coulombic efficiency increases significantly during the initial six cycles and stabilizes at around 98% in the subsequent processes.

For comparison, the cycling performances of BS–BO, Bi$_2$S$_3$, and Bi$_2$O$_3$ at a current density of 200 mA g$^{-1}$ are provided in Figure 4c. The capacity of Bi$_2$O$_3$ decays fast from the start of cycling. After 50 cycles, the capacity of Bi$_2$O$_3$ is merely around 109 mA h g$^{-1}$. A similar severe capacity decay is also observed in Bi$_2$S$_3$. With respect to BS–BO, the capacity decay is mild. The capacity retentions for BS–BO, Bi$_2$S$_3$, and Bi$_2$O$_3$ sheets (against second discharge capacity) are 43, 11, and 2%, respectively. The great enhancement in capacity retention confirms the advantages of the novel BS–BO heterostructure.

To further demonstrate the good sodium storage performance of BS–BO, the rate performances of the three samples were measured with the applied current densities increasing from 50 to 2000 mA g$^{-1}$ and then reducing back to 100 mA g$^{-1}$ (Figure 4d). As can be seen clearly, the BS–BO exhibits a remarkably improved rate performance at a variety of current densities. The reversible discharge capacities are approximately 620, 574, 518, 460, 404, and 314 mA h g$^{-1}$ at 50, 100, 200, 500, 1000, and 2000 mA g$^{-1}$, respectively. Besides, when the current density reduces to 100 mA g$^{-1}$, an average capacity of 468 mA h g$^{-1}$ can be restored for the BS–BO. In contrast, both Bi$_2$S$_3$ and Bi$_2$O$_3$ sheets suffer from severe capacity loss at a high rate and exhibit poor capacity recovery ability. These results demonstrate that the constructed BS–BO heterostructure is beneficial to the rate capability when compared with the Bi$_2$S$_3$ or Bi$_2$O$_3$ counterparts.

EIS measurements were performed to investigate the kinetic characteristic and charge transfer resistance of various electrodes. All typical Nyquist plots provided in Figure S10 exhibit a slope line in the low frequency region and a semicircle in the high–medium frequency region. It can be clearly observed that the semicircle diameter for BS–BO is much smaller than those for Bi$_2$S$_3$ and Bi$_2$O$_3$ sheets. After simulation, the charge transfer resistance ($R_{ct}$) values for the BS–BO, Bi$_2$S$_3$, and Bi$_2$O$_3$ sheets are calculated to be 17.8, 42.6, and 209.2 Ω, respectively. The EIS results confirm the enhanced charge transport in BS–BO heterostructures.

The improved sodium storage performance originates from the novel design of BS–BO heterostructures with three distinctive merits. First, a built-in electric field within the heterostructure can accelerate the charge transfer. A possible mechanism of the evolution of built-in electric fields in BS–BO is illustrated in Figure 5. The Bi$_2$O$_3$ is a n-type semiconductor featured with a relative wide band gap of 2.8 eV, while Bi$_2$S$_3$ is a typical p-type semiconductor with a narrow band gap (1.3 eV).26 In the BS–BO heterostructure, BS–BO p–n heterojunctions formed at the interface can induce a built-in electric field with a direction from Bi$_2$O$_3$ ($E_0 \approx 2.8$ eV) to Bi$_2$S$_3$ ($E_0 \approx 1.3$ eV).45 It can be anticipated that during the discharge process, this electric field can facilitate the immigration of Na$^+$ ions. On the other hand, Bi$_2$O$_3$ is converted into Na$_2$O after full sodiation. Meanwhile, Bi$_2$S$_3$ is sodiated into Na$_3$Bi and Na$_2$S.37 As evidenced in the literature, more Na$^+$ ions might be released at the sulfide area (Bi$_2$S$_3$-domained area) after full de-sodiation on account of its higher reversibility relative to some oxides (Bi$_2$O$_3$-domained area).37,46 Consequently, when subject to the charge process, an electric field could be formed with a direction from Bi$_2$O$_3$ to Bi$_2$S$_3$ owing to the potential difference, which will promote the transfer of Na$^+$ ions. Therefore, within the BS–BO heterostructure, the induced built-in electric field would provide a driving force for Na$^+$ ions and remarkably improve the charge transfer kinetics, resulting in good rate capability. Secondly, the strong chemical interaction between Bi$_2$O$_3$ and Bi$_2$S$_3$ would be helpful to the elastic effects of the nanostructures upon sodiation/de-sodiation.47 Last but not the least, the thin nanosheets design can effectively decrease the diffusion pathway of Na$^+$ ions, which further promotes the electrochemical kinetics. In a word, the synergetic effect of enhanced charge transfer kinetic, strong chemical interaction, and nanoscale size design makes BS–BO nanosheets a promising material for the high-performance sodium-ion battery anode.

**CONCLUSIONS**

In summary, BS–BO heterostructured nanosheets have been constructed via an easy water-bath approach. The present method has been demonstrated to be a TAA-directed surfactant-assisted process. When applied in sodium storage, the BS–BO heterostructure displays a promising performance: it delivers a reversible discharge capacity of 630 mA h g$^{-1}$ at 100 mA g$^{-1}$ with relative good stability. Moreover, the BS–BO heterostructure exhibits improved rate capability compared to
Bi$_2$S$_3$ and Bi$_2$O$_3$ counterparts, which can be originated from the synergetic effect of enhanced charge transfer in the heterostructures, strong chemical interaction, and nanoscale size design. This work suggests that the construction of novel heterostructures can be a promising approach toward high-performance sodium-ion battery and related energy storage applications.

**REFERENCES**


(30) Nithya, C. Bi$_2$O$_3$@ reduced graphene oxide nanocomposite: An anode material for sodium-ion storage. ChemPlusChem 2015, 80, 1000–1006.


