Supporting Information

Heterostructured Bi_2S_3-Bi_2O_3 Nanosheets with a Built-In Electric Field for Improved Sodium Storage

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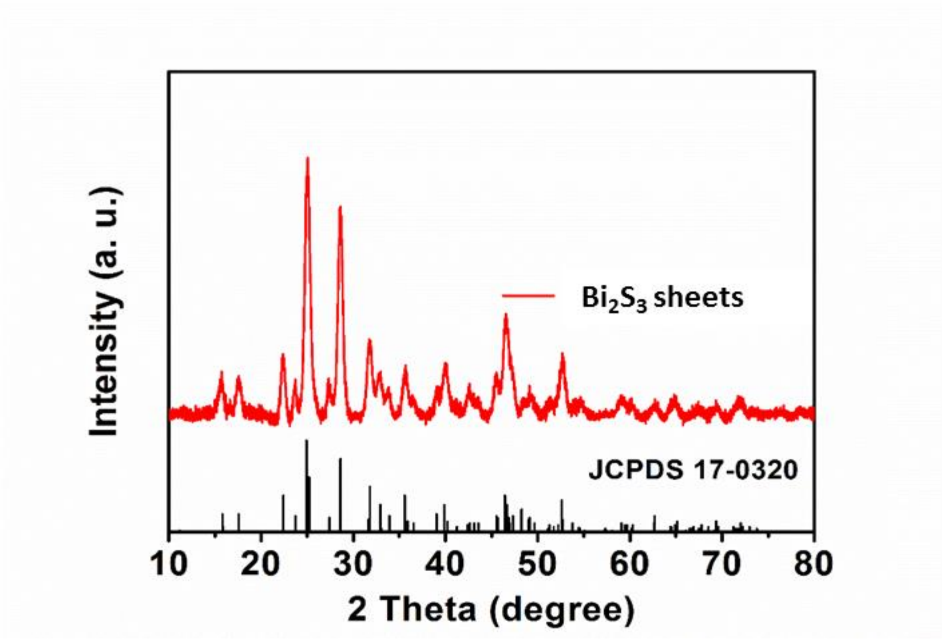

Figure S1 XRD pattern of Bi_2S_3 sheets.

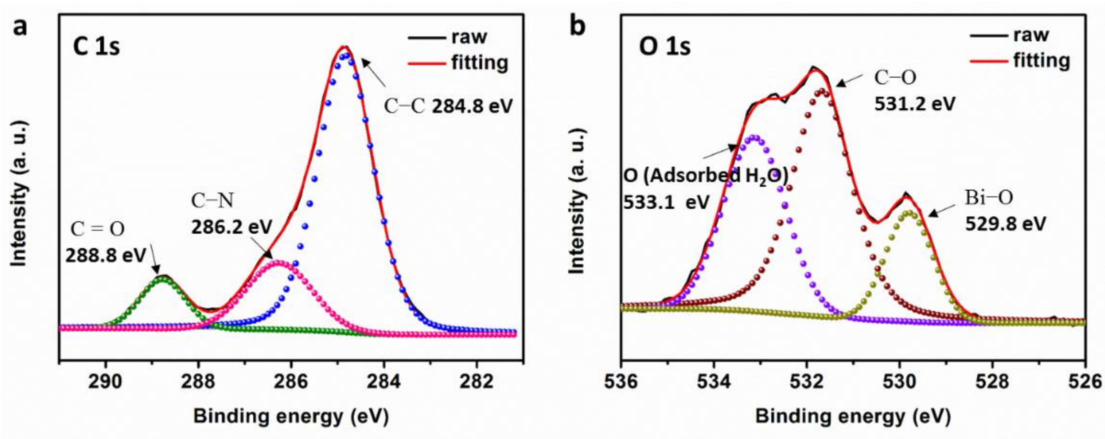

Figure S2 High resolution XPS spectra of (a) C 1s and (b) O 1s of BS-BO heterostructures. The C 1s spectrum can be fitted into three peaks at 284.8, 286.2 and 288.8 eV, which correspond to the binding energies of C−C, C−N and C=O, respectively. The O 1s XPS spectrum can be fitted by three peaks at binding energies of 533.1, 531.2 and 529.8 eV, which can be ascribed to adsorbed H_2O (OH_2O), C−O and Bi−O, respectively. [S-1] These results suggest the existence of other components such as CTAB and H_2O species adsorbed on the surface of BS-BO sample.

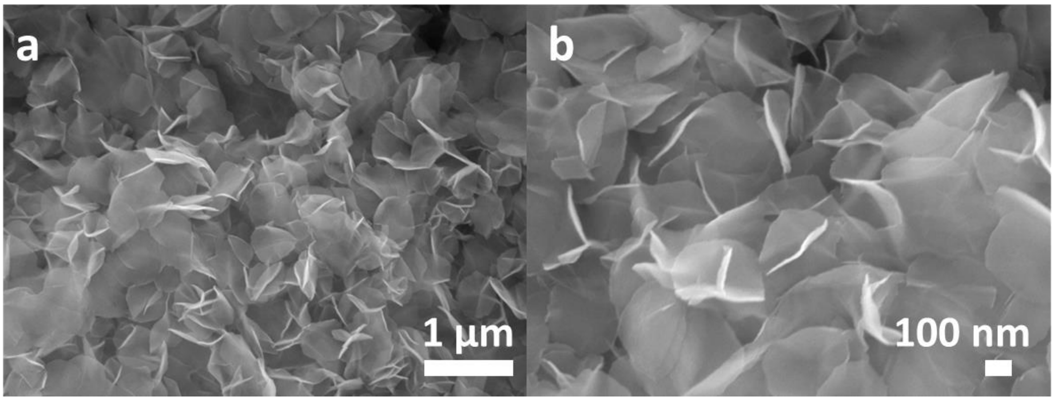

Figure S3 SEM images of Bi_2O_3 sheets at low (a) and high (b) magnifications.

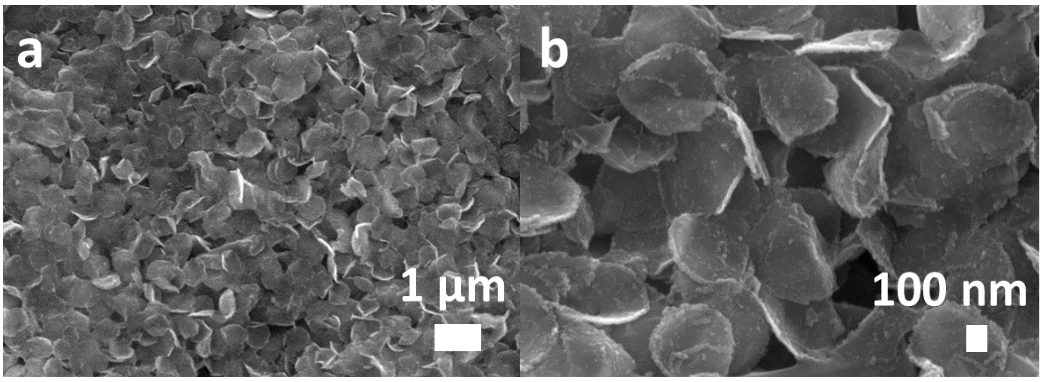

Figure S4 SEM images of Bi_2S_3 sheets at low (a) and high (b) magnifications.

Table S1. CHNS elemental analysis results of BS-BO heterostructured sheets. Measurements were conducted twice times to eliminate deviation. The average mass percentage of sulfur element in BS-BO is determined to be 14.83 *wt*%.

Sample	Mass (mg)	N(%)	C(%)	H(%)	S(%)	**S(%) Average**
BS-BO sheets	5.4150	0.25	4.48	0.382	14.933	**14.83 *wt*%**
	4.9170	0.26	4.61	0.417	14.725	

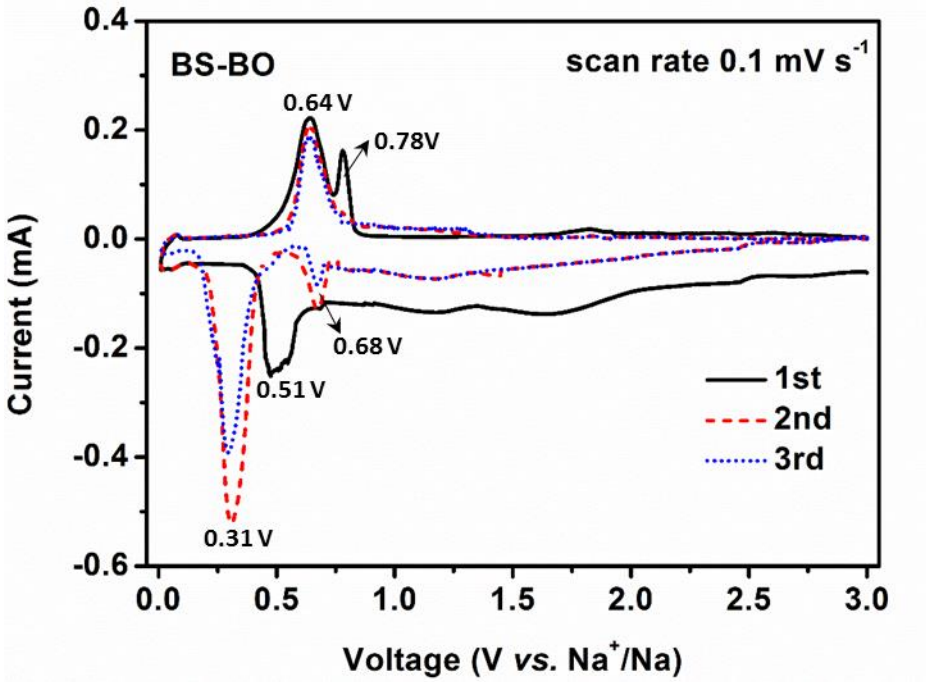

Figure S5 Cyclic voltammograms for the first three cycles of BS-BO electrode in SIBs at a scan rate of 0.1 mV s^{-1}.

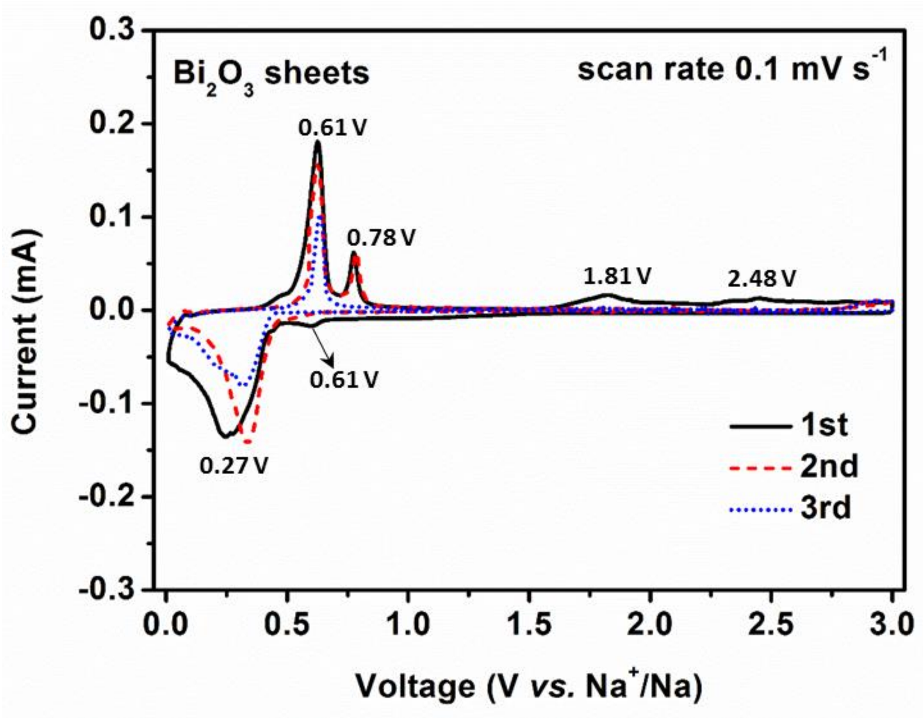

Figure S6 Cyclic voltammograms for the first three cycles of Bi_2O_3 electrode in SIBs at a scan rate of 0.1 mV s^{-1}. During the sodiation process, a weak peak located at 0.61 V and a broad intense peak at 0.27 V are observed. And these two peaks can be attributed to the reduction process of Bi_2O_3 to Bi, Bi and Na alloying process, respectively. During de-sodiation process, four anodic peaks at 0.61, 0.78, 1.81 and 2.48 V can be detected. The major anodic peaks are determined to locate at 0.61 V and 0.78 V. The CV results are in consistent with previous Bi_2O_3 based SIBs reports.[S-2]

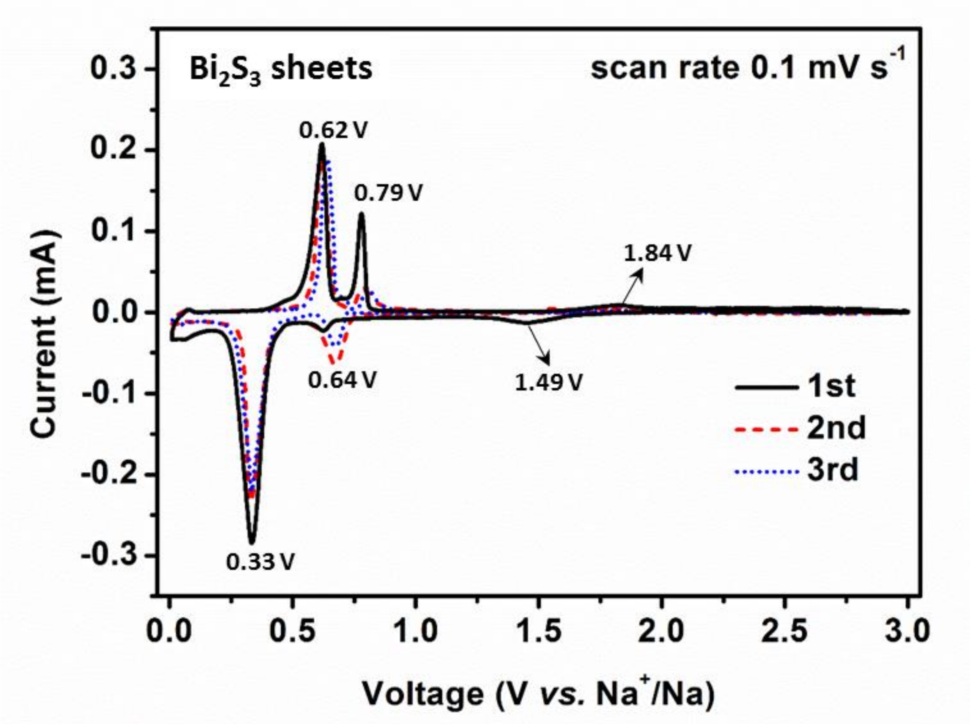

Figure S7 Cyclic voltammograms for the first three cycles of Bi_2S_3 electrode in SIBs at a scan rate of 0.1 mV s^{-1}. Upon sodiation, three weak peaks at 1.49 V, 0.64 V and 0.33 V can be detected. The peaks at 1.49 V and 0.64 V may be ascribed to Bi_2S_3 conversion process, and a sharp peak at 0.33 V are probably due to the alloying of Bi and Na. Upon de-sodiation, the Na_3Bi is de-alloyed into Bi and it is characterized by two sharp peaks at 0.62 V and 0.79 V. And the Bi might not fully recovers to Bi_2S_3 in our SIBs, [S-3, S-4] as evidenced by a weak peak at 1.84 V.

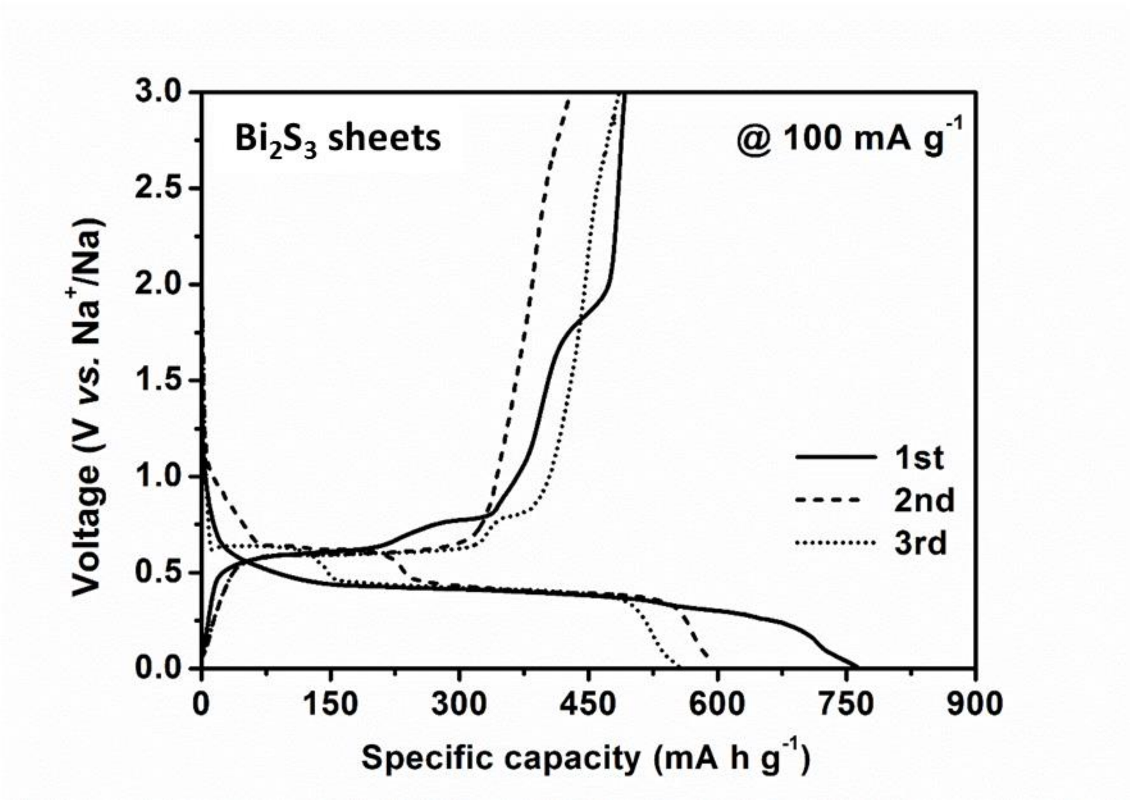

Figure S8 The typical charge/discharge profiles of Bi_2S_3 sheets at the current density of 100 mA g^{-1} for the initial three cycles.

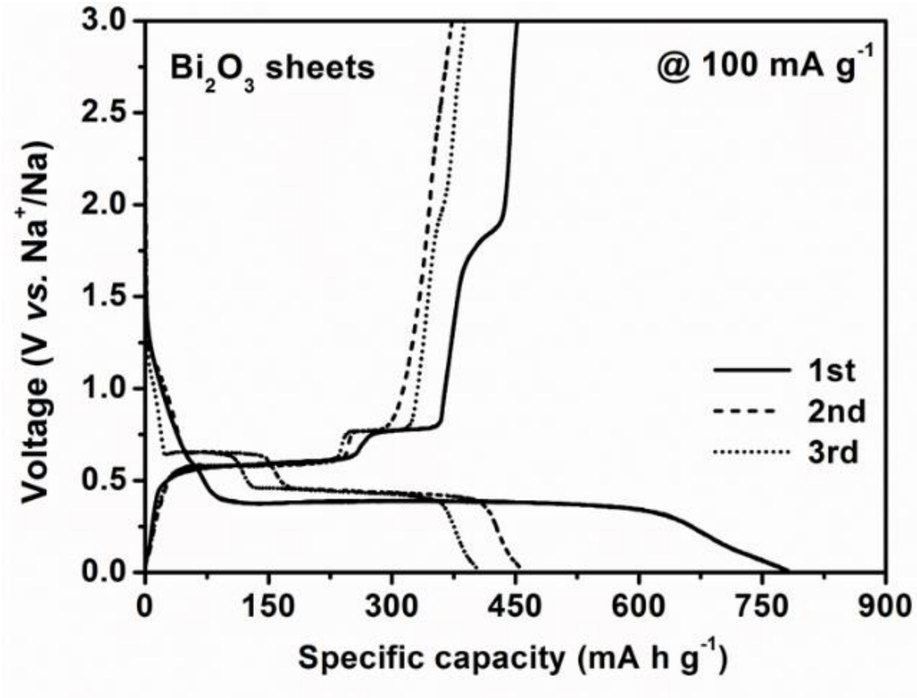

Figure S9 The typical charge/discharge profiles of Bi_2O_3 sheets at the current density of 100 mA g^{-1} for the initial three cycles.

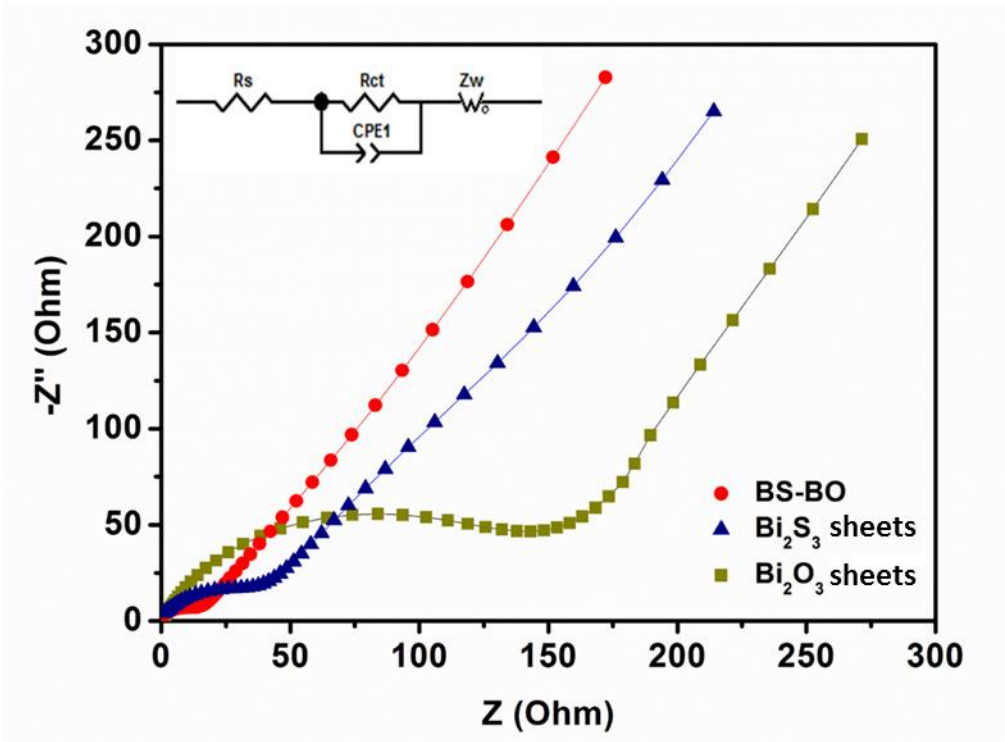

Figure S10 Nyquist plots of electrodes containing BS-BO, Bi_2S_3 sheets and Bi_2O_3 sheets. The equivalent circuit is inset.

References in Supporting Information:

[S-1] Kayaci, F.; Vempati, S.; Donmez, I.; Biyikliab, N.; Uyar, T. Role of zinc interstitials and oxygen vacancies of ZnO in photocatalysis: a bottom-up approach to control defect density. *Nanoscale* **2014**, *6* (17), 10224–10234.

[S-2] Kim, M. K.; Yu, S. H.; Jin, A.; Kim, J.; Ko, I. H.; Lee, K. S.; Mun, J.; Sung, Y. E. Bismuth oxide as a high capacity anode material for sodium-ion batteries. *Chem. Commun.* **2016**, *52* (79), 11775–11778.

[S-3] Yang, W. L.; Wang, H.; Liu, T. T.; Gao, L. J. A Bi_2S_3@ CNT nanocomposite as anode material for sodium ion batteries. *Mater. Lett.* **2016**, *167*, 102–105.

[S-4] Sun, W. P.; Rui, X. H.; Zhang, D.; Jiang, Y. Z.; Sun, Z. Q.; Liu, H. K.; Dou, S. X. Bismuth sulfide: A high-capacity anode for sodium-ion batteries. *J. Power Sources* **2016**, *309*, 135–140.