## Supporting Information

Asynchronous Reactions of "Self-matrix" Dual-crystal Effectively Accommodating Volume Expansion/Shrinkage of Electrode Materials with Enhanced Sodium Storage

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## Experimental

*Materials Synthesis:* The CNTs@FeOOH composites were synthesized via a hydrothermal method. Taking CNTs@FeOOH-II as an example, 0.4 g FeCl<sub>3</sub>.6H<sub>2</sub>O and 1.2 g urea were dissolved in 30 mL water by stirring for 10 min, and then 30 mg CNTs were added into the solution. After vigorous stirring for 30 min and ultrasonication for 20 min, the obtained homogenous solution was sealed into a 50 mL Teflon-lined autoclave. The autoclave was maintained at 95 °C for 2 h then naturally cooled down to room temperature. Finally, the as-prepared CNTs@FeOOH-II composites were collected by repeated centrifugation with deionized water and vacuum freeze drying. The CNTs@FeOOH-I and CNTs@FeOOH-III composites were further obtained by introducing appropriate amounts of CNTs.

Synthesis of bi-FeS<sub>2</sub> and pyrite FeS<sub>2</sub>: The precursor (CNTs@FeOOH) and appropriate amount of thiourea were separately placed on symmetric side of alumina vessel. The as-prepared bi-FeS<sub>2</sub> with various mass ratios were sulfurized by thiourea at 500 °C for 2 h under Ar atmosphere. The obtained bi-FeS<sub>2</sub>-II composite was further annealed at 400 °C for 2 h under Ar atmosphere to fabricate pyrite FeS<sub>2</sub>.

*Materials Characterization:* The powder XRD was measured by an X-ray diffractometer (D8 Advance of Bruker, Germany) with Cu/K<sub> $\alpha$ </sub> radiation ranging from 20° to 80°. XPS was performed on a VG ESCALAB MK II X-ray photoelectron spectrometer. The morphologies of the prepared samples were observed with field-emission scanning electron microscopy (SEM Hitach SU8010) and high-resolution transmission electron microscopy (HR-TEM, JEM-3000F). The content of CNTs was

determined on a TG-DTA7300 thermogravimetric analyzer (TGA) under air atmosphere at the heating rate of 10 °C min<sup>-1</sup> from room temperature to 800 °C.

*Electrochemical Test:* Electrochemical performance was investigated by CR2032 coin-type cells assembled in an argon filled glove box. The electrode slurry was fabricated using active materials, acetylene black and carboxymethyl cellulose (CMC) with a weight ratio of 7:2:1 in appropriate amount of water. Then the final slurry was cast onto Cu foil using a doctor blade, and dried in a vacuum oven at 80 °C overnight. The loading mass of dual-crystalline or pyrite FeS<sub>2</sub> composite is about 0.31~0.49 mg cm<sup>-2</sup>. The sodium foil was used as both reference and counter electrode. 1.0 M NaClO<sub>4</sub> and 5 % FEC were dissolved into ethylene carbonate (EC) and propylene carbonate (PC) (volume ratio of 1:1) as the electrolyte. Galvanostatic charge/discharge tests were conducted on a LAND CT2001A battery tester. Cyclic voltammetry was carried out using a Princeton Applied Research Versa STAT4 electrochemical workstation with a scan rate of 0.1 mV s<sup>-1</sup>. All electrochemical tests were conducted within the potential range of 0.01~3.0 V.



Fig. S1. SEM and TEM images of the CNTs.



**Fig. S2.** High- (the insets) and low-magnification SEM images of (a) CNTs@FeOOH-I, (b) CNTs@FeOOH-III, (c) bi-FeS<sub>2</sub>-I and (d) bi-FeS<sub>2</sub>-III.



Fig. S3. (a),(c) high- and (b),(d) low- magnification SEM images of FeOOH and  $FeS_2$  samples, respectively.



Fig. S4. (a) XRD pattern of the pure FeOOH. (b) Typical XPS survey spectrum and the high-resolution (c) C 1s, and (d) S 2p XPS spectra of bi-FeS<sub>2</sub>-II.

	Pyrite	Marcasite
bi-FeS <sub>2</sub> -I	40%	60%
bi-FeS <sub>2</sub> -II	47.6%	52.4%
bi-FeS <sub>2</sub> -III	51%	49%

**Table S1.** The calculated results for mass ratio of pyrite and marcasite phases in bi- $FeS_2$ -X (X= I, II and III) via K value calculation method.



**Fig. S5.** TGA curves of (a) pure FeOOH and CNTs@FeOOH-X (X=I, II and III) and (b) pure  $FeS_2$  and  $bi-FeS_2-X$  (X=I, II and III).

Equation S1. The content of active material was calculated by followed equation:

$$\mathbf{y} = \mathbf{W}_2 / \mathbf{W}_1$$

Where  $W_1$  is the mass residue rate of pure FeS<sub>2</sub> or FeOOH (both FeS<sub>2</sub> and FeOOH thermal treated final product is Fe<sub>2</sub>O<sub>3</sub>),  $W_2$  is the mass residue rates of CNTs@FeS<sub>2</sub> or CNTs@FeOOH composites, y is the content of active material in the composite.



**Fig. S6.** (a), (b) TEM images of bi-FeS<sub>2</sub>-II.



**Fig. S7.** (a) low- and (b) high- magnification SEM images of the pure pyrite phase. (c) XRD pattern of the pyrite  $FeS_2$  transformed from bi- $FeS_2$ -II.



**Fig. S8.** (a) CV curves and (b) charge/discharge profile of the pyrite FeS<sub>2</sub> transformed from bi-FeS2-II.



**Fig. S9.** Cycling performance and corresponding coulombic efficiency of CNTs at the current density of 0.1 A g<sup>-1</sup>.



**Fig. S10.** SEM images of the pyrite  $FeS_2$  and  $bi-FeS_2$ -II electrode surface (a), (c) before and (b), (d) after cycling, respectively.



Fig. S11. SEM images of bi-FeS<sub>2</sub>-I and bi-FeS<sub>2</sub>-III electrode surface (a), (c) before and (b), (d) after cycling, respectively. The insets are the corresponding high magnification SEM images.



**Fig. S12.** Optical images of separator in cycled (a) bi-FeS<sub>2</sub>-I and (b) bi-FeS<sub>2</sub>-II half cells.



Fig. S13. Nyquist plots of bi-FeS<sub>2</sub>-I, bi-FeS<sub>2</sub>-II and bi-FeS<sub>2</sub>-III before cycling.

Samples	Voltage window (V)	Current density (A g <sup>-1</sup> )	Specific Capacity (mA h g <sup>-1</sup> )	Ref.
FeS <sub>2</sub> microsphere	0.8-3	0.1 1	230 200	1
Co-doped FeS <sub>2</sub>	0.8-2.9	0.1 1	350 261	2
FeS <sub>2</sub> @C nanobox	0.8-2	0.1 1	560 502	3
FeS <sub>2</sub> -rGO	0.8-3	0.18	315.6	4
FeS <sub>2</sub> -rGO	0.8-2.8	0.09 1	370 280	5
FeS <sub>2</sub>	0.6-3	0.1	400	6
bi-FeS <sub>2</sub>	0.01-3	0.1 1	600+ 470	This work

**Table S2.** Electrochemical properties of various  $FeS_2$  under different voltage windows for SIBs.

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