Synergistic Interface and Structural Engineering for High Initial Coulombic Efficiency and Stable Sodium Storage in Metal Sulfides

Chunrong Ma[1,2], Zhengguang Fu[3,4], Yanchen Fan[5], Hui Li[1,2], Zifeng Ma[6], Wei Jiang[1,2], Guangshuai Han[7*], Haoxi Ben[1,2*], and Hui (Claire) Xiong[8*]

Prof. Chunrong Ma, Hui Li, Wei Jiang, Haoxi Ben

College of Textiles & Clothing, Qingdao University, Qingdao 266071, China; Key Laboratory of Bio-Fibers and Eco-Textiles, Qingdao University, Qingdao 266071, China

Zhengguang Fu

School of Polymer Science and Engineering, Qingdao University of Science and Technology, Qingdao 266110, China; Qingdao Institute of Bioenergy and Bioprocess Technology, Chinese Academy of Sciences, Qingdao 266101, China

Yanchen Fan

PetroChina Shenzhen New Energy Research Institute, Shenzhen, 518000, China

Zifeng Ma

School of Chemistry and Chemical Engineering, Shanghai Jiao Tong University, Shanghai 200240, China

Guangshuai Han

Institute for Advanced Study, Tongji University, Shanghai 200092, China

Claire (Hui) Xiong

Micron School of Materials Science and Engineering, Boise State University, Boise, ID 83725, United States, *E-mail: clairexiong@boisestate.edu (corresponding author)

Experimental sections

Materials Characterization

Synthesis of ZIF-67: In a typical procedure, a 50 mL aqueous solution containing cetrimonium bromide (CTAB, 15 mg) and $Co(NO_3)_2 \cdot 6H_2O$ (1.2 g) was rapidly injected into 300 mL aqueous containing 2-methylimidazole (1.5 g). The mixed solution was then stirred at room temperature for 20 min. The resulting ZIF-67 nanocubes were collected through several cycles of centrifugation and washing with deionized water and ethanol.

Synthesis of ZIF-67@TiO$_2$: The prepared ZIF-67 (0.1 g) were dispersed in ethanol and then dropped into a small amount of water. After stirring for 30 min, 80 µL of tetrabutyl titanate (TBOT) in ethanol was injected into the mixture. After injection, the temperature was increased to 80 °C under refluxing conditions for 100 min. The precipitate was isolated using centrifugation, washed with ethanol, then dried at 70 °C overnight.

Synthesis of CoS/TiO$_2$-SC: In a typical synthesis, ZIF-67@TiO$_2$ (100 mg) were dispersed in water at room temperature. After 10 min of magnetic stirring, Na-CMC (15 mg) were added to the above solution in sequence. The homogenized solution was then mixed with a predetermined volume of GO suspension (2 mg mL^{-1}) with the precise control of weight ratio of ZIF-67@TiO$_2$ to GO as 5:1. The resulting suspension was ultrasonicated for 30 min and then placed in a glass vial, which was later immersed in liquid nitrogen for 10 min. The unidirectional frozen cryogels were then freeze-dried for 24 h, and taken out from the glass vial as ZIF-67@TiO$_2$-impregnated GO monoliths. Finally, sublimed sulfur powders were placed in the upper vent, and ZIF-67@TiO$_2$-impregnated GO monoliths were placed in the lower vent of the quartz tube furnace with a weight ratio of 7:1. Then, they were heat-treated in a tube furnace, starting from ambient temperature to 550 °C at 3 °C min^{-1} in an Argon atmosphere and maintained for 120 min.

Materials Characterization: The crystal structure of the sample was investigated by XRD (Bruker with a Cu Kα X-ray source (λ =1.5418 Å). The morphology of the sample was collected by SEM and TEM. The surface chemical state of the

sample was determined by XPS and Raman spectra. A modified 2032 cell with a 1.0 mm hole was used for in situ XRD tests. The cell was discharged and charged between 0.01 and 3 V at 0.2 C.

Electrochemical Measurements: The 2032-type coin cells were assembled using Na metal as a reference electrode and electrolyte of 1M $NaPF_6$ in the mixture of DEGDME. The working electrode was prepared by mixed as-prepared sampled, 10% super P and 10% CMC. The mass loading of active materials is 1.1-1.2 mg cm^{-2}. Galvanostatic charge-discharge measurements were conducted by a Land battery cycler. CV tests were performed at a scan rate from 0.1 to 2 mV s^{-1} using a CHI605D electrochemical workstation. EIS was recorded on AUTOLAB.

DFT Calculation: Density Functional Theory (DFT) calculations were carried out with the gradient corrected exchange–correlation functional of Perdew, Burke, and Ernzerhof (PBE) under the projector augmented wave (PAW) method as implemented in the VASP code. The energy cut-off was set at 450 eV. As for periodic interface model construction, to minimize the lattice mismatch between

CoS and TiO_2. All atoms were fully relaxed until the force on them was less than 0.01 eV Å^{-1}. Both spin-polarized and van der Waals (vdW) calculated by the DFT-D method of Grimme were taken into consideration. The band offset of the junction was obtained by alignment of the Fermi level, which was calibrated by the core level of sulfur.
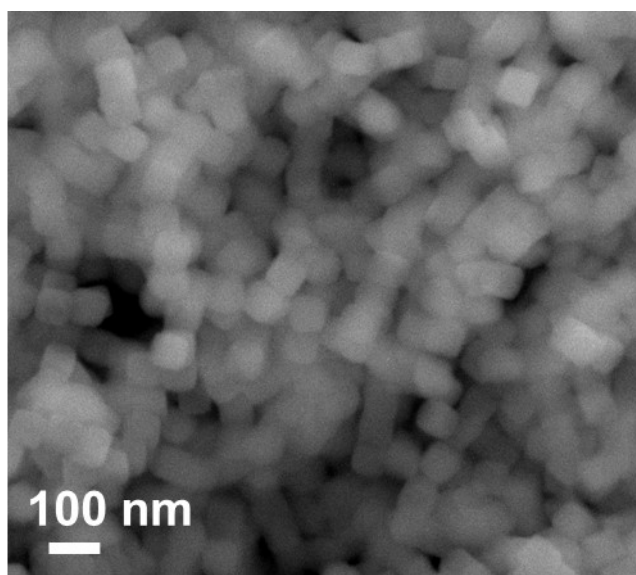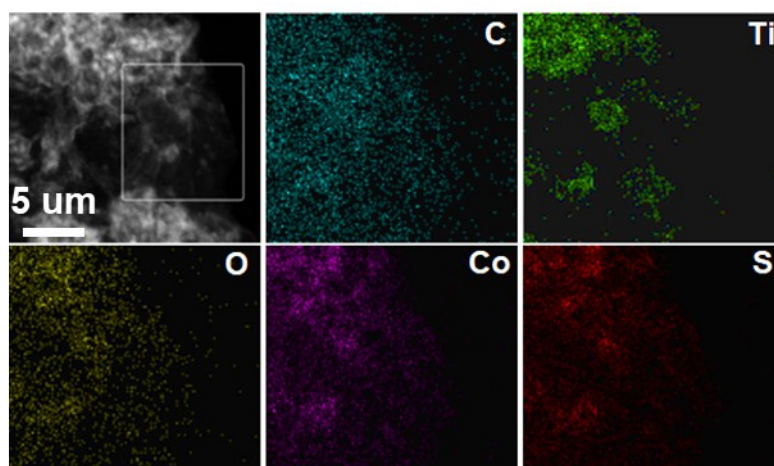
Figure S1. SEM image of ZIF-67.

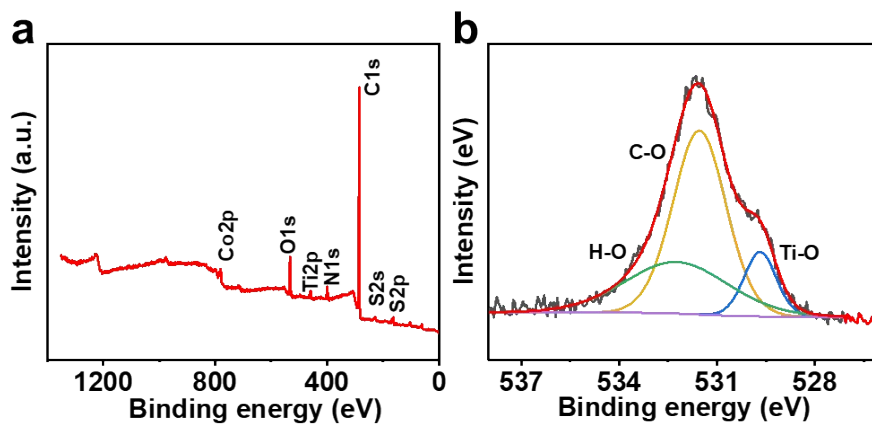Figure S2. the EDX mapping images of CoS/TiO$_2$-SC composite.

Figure S3. a) XPS spectrum of CoS/TiO₂-SC, and b) High-resolution spectra of O1s
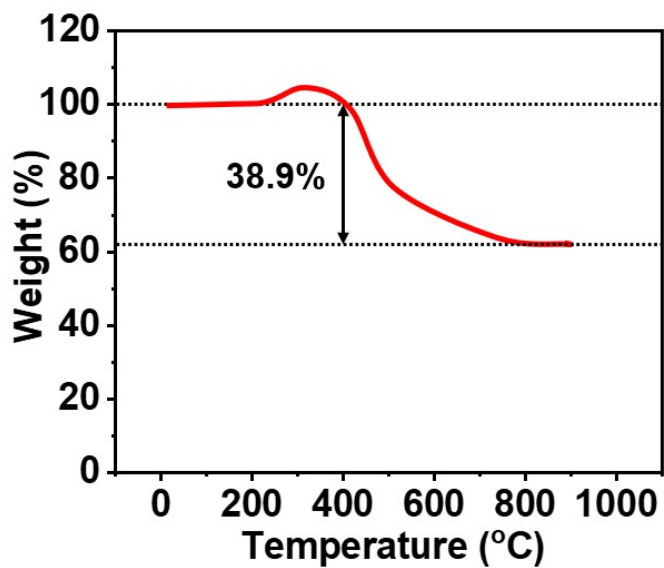

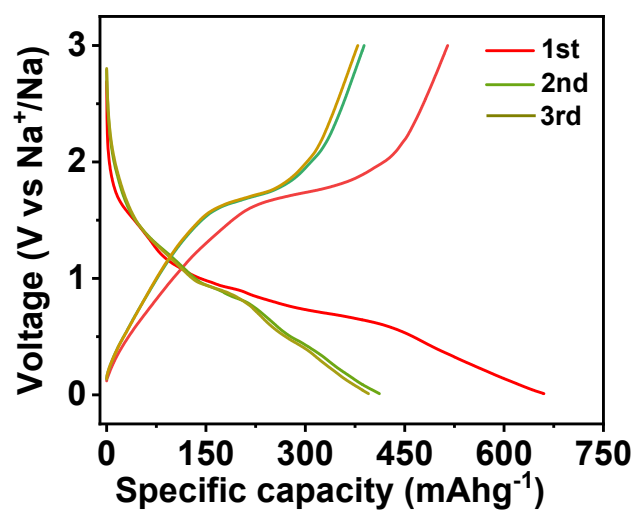Figure S4 TGA curve of CoS/TiO₂-C composite.

Figure S5. The charge/discharge profiles of CoS-SC electrode.
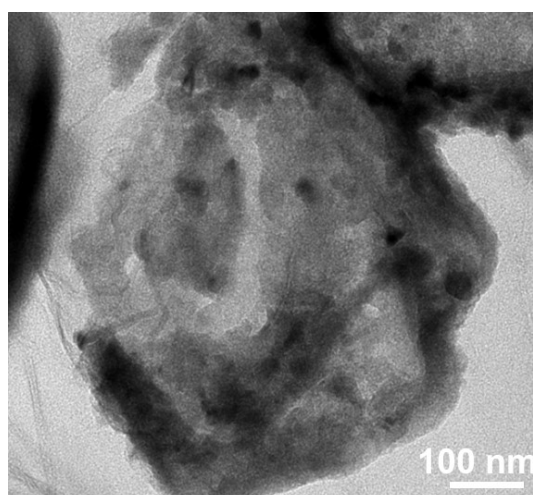

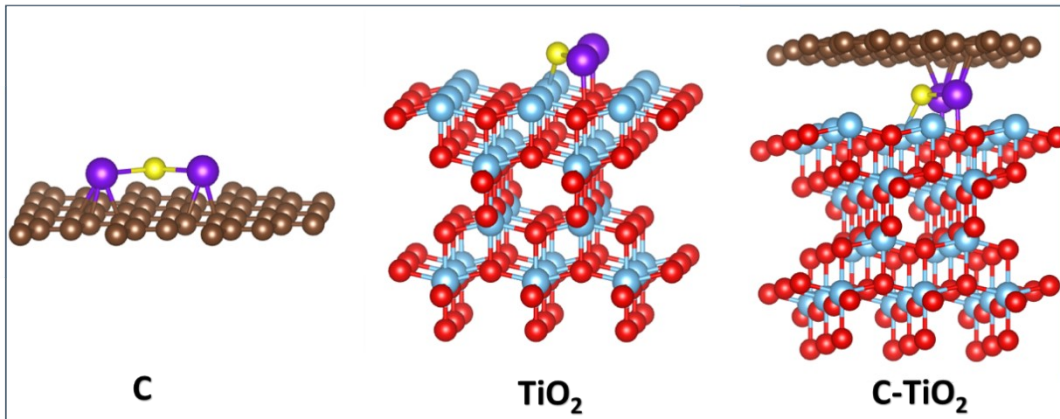Figure S6. The TEM image of CoS-SC composite after 100 cycles.

Figure S7. the Na$_2$S adsorption at C, TiO$_2$, and C/TiO$_2$ interface.
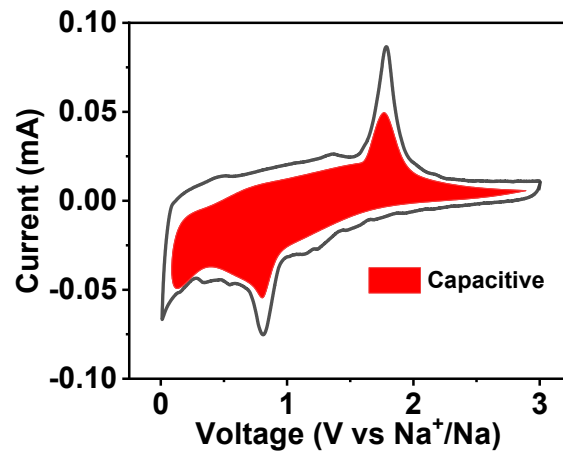

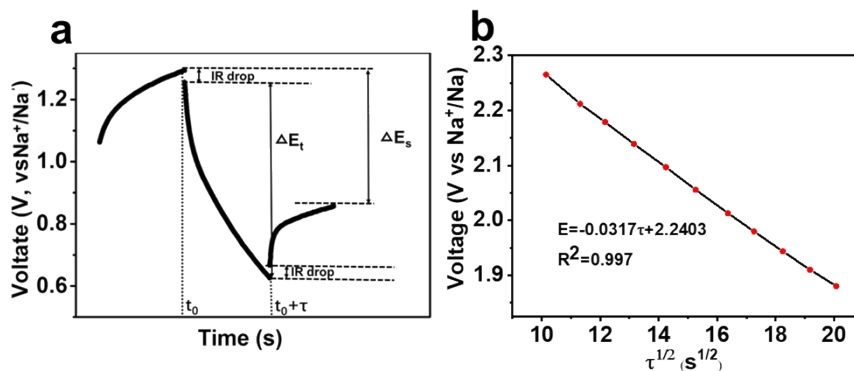Figure S8. The capacitive contribution to the total current density at 0.2 mVs^{-1}.

Figure S9. a) Schematic of GITT technique and b) Linear behavior of the E vs $\tau^{1/2}$ relationship.

The diffusion coefficient can be expressed as the following equation:

$$D_{Na+} = \frac{4}{\pi}\left(\frac{m_B V_M}{M_B A}\right)^2 \left(\frac{\Delta E_s}{\tau(dE_\tau)/d(\sqrt{\tau})}\right)^2 \quad (\tau \ll L^2/D_{Na+}) \qquad (1)$$

In this equation, τ(s) is the constant current flux time, m_B (g) is the active mass of the electrode, V_M (cm^3 mol^{-1}) is the molar volume of the electrode, M_B (g mol^{-1}) is the molecular weight, A (cm^2) is the surface area of the electrode, L (cm) is the thickness of the electrode, E_S (V) is the total change in cell voltage during a single step and $E\tau$ (V) is the voltage change in the steady state during a single step.

If E versus $\sqrt{\tau}$ shows a linear behavior during the current pulse, the equation can be transformed into:

$$D_{Na+} = \frac{4}{\pi}\left(\frac{m_B V_M}{M_B A}\right)^2 \left(\frac{\Delta E_s}{\Delta E_t}\right)^2 \quad (\tau \ll L^2/D_{Na+}) \qquad (2)$$
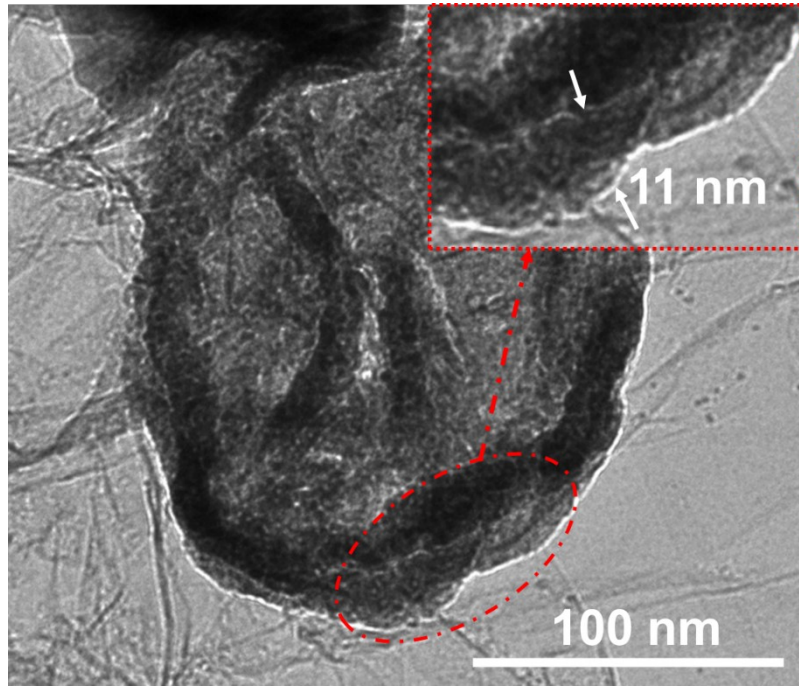

Figure S10. The TEM image of CoS/TiO$_2$-SC electrode in EC/DEC-based electrolyte.