## Supporting Information

# Ultrathin Double-Shell Nanotubes of Narrow Band Gap Titanium Oxide@Carbon as Efficient Polysulfide Inhibitors towards Advanced Lithium-Sulfur Batteries

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#### **1. Experimental section**

#### 1.1 Preparation of MnO<sub>2</sub> nanowires

MnO<sub>2</sub> nanowires (NWs) were prepared *via* a modified hydrothermal synthesis method.<sup>[51]</sup> In a typical experiment, 1 mmol of KMnO<sub>4</sub>, 1 mmol of NH<sub>4</sub>Cl and 1 mmol of polyvinyl pyrrolidone (PVP) were separately dispersed into 20 mL of deionized (DI) water, respectively, to form clear solutions under ultrasonication. Then, the mixed solution of NH<sub>4</sub>Cl/PVP was poured into the KMnO<sub>4</sub> solution. After stirring for 20 min at room temperature, the obtained homogeneous solution was poured into a Teflon-lined autoclave (100 mL in total volume) and placed in a stove and kept at 140 °C for one day. After cooling naturally to room temperature, the resultant materials were gathered by centrifugation, and then washed repeatedly with D.I. water. Finally, MnO<sub>4</sub> NWs were acquired after drying at 80°C overnight.

#### 1.2 Preparation of MnO<sub>2</sub>@TiO<sub>2</sub> nanowires

TiO<sub>2</sub> shell was deposited onto the surface of MnO<sub>2</sub> NWs *via* the kinetics-controlled sol-gel strategy.<sup>[SI]</sup> In a typical experiment, the as-synthesized MnO<sub>2</sub> NWs were firstly dispersed in absolute ethanol through sonication for at least 30 min, followed by addition of 0.25 mL of ammonia (NH<sub>2</sub>·H<sub>2</sub>O, 28-30 wt%) and were stirred at 45 °C for 1 h. Subsequently, tetrabutoxide titanate (TBOT, 0.4 mL) was diluted in 4 mL of ethanol and was gradually dropped into the mixture over a period of at least 10 min, the mixture was further agitated for one day under 45 °C. The intermediate materials MnO<sub>2</sub>@a-TiO<sub>2</sub> NWs were centrifuged and washed by the D.I. water repeatedly then dried. To synthesize MnO<sub>2</sub>@TiO<sub>2</sub> NWs with crystalline TiO<sub>2</sub> layers, the as-obtained nanocomposites were calcined at 500 °C for 2 h under the air atmosphere with a heating rate of 5 °C min<sup>+</sup>.

#### 1.3 Preparation of MnO<sub>2</sub>@TiO<sub>2</sub>@PDA nanowires

The as-synthesized MnO<sub>2</sub>@TiO<sub>2</sub> NWs were dispersed in 100 mL of Tris-buffer solution (10

mM, pH = 8.5). Soon afterwards, 50 mg of dopamine hydrochloride (PDA) was added and the mixture was agitated for 12 h at room temperature. The  $MnO_2@TiO_2@PDA$  NWs were obtained after being repeatedly centrifuged and washed with D. I. water followed by drying.

#### 1.4 Preparation of OVs-TiO<sub>2.x</sub>@NC nanotubes

To transfer anatase phase into rutile Ti<sup>+-</sup> phase and to create oxygen-vacancies, the asobtained MnO<sub>2</sub>@TiO<sub>2</sub>@PDA NWs were annealed under a reducing atmosphere containing a mixture gas of Ar: H<sub>2</sub> (90%:10%, volume ratio) at 700 °C for 3 h. Subsequently, the annealed products were dispersed in 80 mL of oxalic acid (H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>, 1 M) and stirred at 60 °C to completely remove the MnO<sub>2</sub> sacrificial template. Therefore, the final sulfur host material OVs-TiO<sub>2x</sub>@NC nanotubes were acquired. For comparison, TiO<sub>2</sub>@NC NWs were also synthesized through the same process except that they were annealed under pure argon atmosphere.

#### 1.5 Preparation of NC nanotubes

100 mg of MnO<sub>2</sub> NWs were homogeneously dispersed into 100 mL of Tris-buffer solution (10 mM, pH = 8.5). Then 50 mg of PDA was added and the mixture was agitated for 12 h at room temperature. MnO<sub>2</sub>@PDA NWs were obtained after being centrifuged, dried and annealed at 700 °C under Ar atmosphere for 3 h with a ramping rate of 3 °C min<sup>4</sup>. Then the NC host material was acquired by removing of MnO<sub>2</sub> template with the assistance of  $H_2C_2O_4$  solution.

#### 1.6 Preparation of OVs-TiO<sub>2x</sub>@NC/S nanotubes

 $OVs-TiO_{2x}@NC/S$  nanotubes were synthesized *via* a traditional melt diffusion method. Typically, the as-prepared  $OVs-TiO_{2x}@NC$  host and sublimed sulfur were uniformly mixed at a certain ratio in an agate mortar and then sealed in an ampoule bottle under vacuum. The mixture was further placed into a muffle furnace and heated at 155 °C for 10 h. Subsequently, the sample was heated to 200 °C for 30 min to assure that sulfur diffused entirely into the pores and the redundant sulfur on the outside surfaces was evaporated off the nanohybrids. After cooling down to room temperature, the OVs-TiO<sub>2x</sub>@NC/S nanotubes were obtained. The NC/S and TiO<sub>2</sub>@NC/S nanotubes were synthesized by similar method.

#### 1.7 Preparation of lithium polysulfide ( $Li_2S_6$ ) solution and visualized adsorption test

3 mM of lithium polysulfide (Li<sub>3</sub>S<sub>6</sub>) solution was prepared *via* dispersing a stoichiometric ratio of sulfur and lithium sulfide (Li<sub>3</sub>S) (mole ratio, 5:1) in a mixed solvent containing 1,2dimethoxyethane (DME) and 1,3-dioxolane (DOL) (volume ratio, 1:1). It was then intensely stirred for 24 h at 50 °C in argon-filled glovebox until all solids were completely dissolved. Subsequently, 5 mg of OVs-TiO<sub>3</sub>,@NC, TiO<sub>2</sub>@NC or NC absorbents were added into 5 mL of the Li<sub>2</sub>S<sub>6</sub> solution. Photos were taken after 12 h of absorption. Subsequently, supernatants of OVs-TiO<sub>3</sub>,@NC-Li<sub>3</sub>S<sub>6</sub>, TiO<sub>2</sub>@NC-Li<sub>3</sub>S<sub>6</sub> or NC-Li<sub>3</sub>S<sub>6</sub> samples were diluted with DME/DOL solvent in a proportion of 1: 100 and quantitative concentration were measured by ultravioletvisible (UV-vis) spectroscopy.

#### 1.8 Symmetric cell assembly and kinetic evaluation of polysulfide conversion

The electrode of symmetric cell was prepared without sulfur. Typically, the host material (OVs-TiO<sub>2\*</sub>@NC, TiO<sub>2</sub>@NC or NC) and poly(vinylidene fluoride) (PVDF) in a mass ratio of 9:1 were dispersed in the N-methyl pyrrolidone (NMP) under vigorous agitation to form the homogeneous slurry, which was then followed by coating onto the aluminum foil with a mass loading of ~ 0.2 mg cm<sup>2</sup>. Subsequently, the electrode was tailored into a diameter of 12 mm. Two pairs of equal electrodes served as the working and counter electrodes, respectively. A representative 2032-type coin cell was assembled and 15 µL of Li<sub>2</sub>S<sub>6</sub> (0.5 M) electrolyte containing 1 M lithium bis(trifluoromethylsulfonyl) imide (LiTFSI) in DME and DOL (1: 1 in

volume ratio) with 2 wt% of lithium nitrate (LiNO<sub>3</sub>) additive was added. CV measurement of the symmetric battery was conducted within the cut-off voltage between -1.0 and 1.0 V under different sweep rates.

#### 1.9 Measurements for Li<sub>2</sub>S nucleation

Li<sub>3</sub>S<sub>4</sub> solution (0.2 M) was prepared by combining Li<sub>3</sub>S and S (mole ratio of 1:7) into Li-S electrolyte under vigorous magnetic stirring. Identical electrodes used in the afore-mentioned kinetic study containing about 2 mg cm<sup>-2</sup> of OVs-TiO<sub>3.5</sub>@NC, TiO<sub>3</sub>@NC or NC served as the working cathode on the Al current collector and metal lithium was used as anode. 15  $\mu$ L of Li<sub>3</sub>S<sub>4</sub> (0.2 M) catholyte solution was dropped onto the cathode and then 15  $\mu$ L of control anolyte without Li<sub>3</sub>S<sub>4</sub> was dropped on the side of lithium anode. The cells were discharged to 2.06 V at a constant current of 0.10 mA, and potentiostatically maintained at 2.05 V until the current dropped below 10<sup>5</sup> A for Li<sub>3</sub>S to nucleate. According to the Faraday's law, the whole charge was collected to estimate the rate of nucleation and growth process of Li<sub>3</sub>S.<sup>[9]</sup>

#### 1.10 Li-S cell assembly and electrochemical performance measurements

Li-S electrode was prepared by mixing active materials (OVs-TiO<sub>2\*</sub>@NC/S), super C and polyvinylidene fluoride (PVDF) (8:1:1, mass ratio) in the N-methyl-2-pyrrolidone (NMP) solvent. Then the uniform slurry was coated onto aluminum foil and dried at 60°C under vacuum. The electrode was punched into 12 mm, and the sulfur mass loading of every electrode is typically 1.6 mg cm<sup>2</sup>. Thick electrodes with higher sulfur mass loading (3.3-13.8 mg cm<sup>2</sup>) were prepared by mixing OVs-TiO<sub>2\*</sub>@C/S, Super C and an-aqueous based binder (LA133) in a mixed solution containing D.I. water and n-propanol (volume ratio, 1:3). The CR2032 coin-type cell was assembled in an Argon glovebox, the oxygen and moisture contents are lower than 0.1 ppm. Lithium Metal and Celgard 2400 membrane were served as anode and separator, respectively. The electrolyte consisted of 1 M lithium

bis(trifluoromethylsulfonyl) imide (LiTFSI) in the mixture of DME and DOL (volume ratio, 1:1) solvents with 2 wt% of LiNO, additive. For each cell, the electrolyte / sulfur (E/S) usage ratio is precisely controlled at around 15  $\mu$ L<sub>utenequent</sub>/mg<sub>soluen</sub> for a typical electrode (1.6 mg cm<sup>2</sup>), 10  $\mu$ L/mg for the mass loading of 3.3, 5.6 and 7.8 mg cm<sup>2</sup>, while 5  $\mu$ L/mg for electrodes with higher sulfur loading (9.5 mg cm<sup>2</sup>). The galvanostatic discharge/charge measurement was conducted on a LAND CT2001A system within a voltage window of 1.7-2.8 V under different C-rates (1 C = 1672 mAh g<sup>2</sup>). The cyclic voltammetry (CV) measurements were tested on an Arbin electrochemical workstation (BT2000) under different scan rates. The electrochemical impedance spectroscopy (EIS) experiment was examined on the Gamry Instrument Warminster (PA, USA) within the frequency range of 0.01-10<sup>6</sup> Hz. All of the electrochemical experiments were carried at room temperature (25°C). The specific capacity of Li-S battery was calculated according to the active material sulfur.

#### 2. Materials characterizations

Field-emission scanning electron microscopy (SEM) images were recorded on a Nova NanoSEM 450, transmission electron microscopy (TEM) were conducted on a JEOL 2100F to observe the morphology and internal structure of the nanohybrids. The carbon and sulfur percentages of the hybrids were measured by a thermogravimetric analysis (TG, TA Instrument Q600 analyzer) under air and nitrogen atmosphere, respectively. The specific surface area ( $S_{mr}$ ) and pore size distribution of the samples were measured on a Quadrasorb SI analyzer at 77 K. The crystalline structures and phase transitions of the samples were revealed on the X-ray diffraction (XRD, Rigaku D/Max2550) *via* Cu K $\alpha$  radiation in the wide-angle range of 10-80°. The Raman spectroscopy was recorded on a Spex 1403 instrument with an excitation laser wavelength of 514.5 nm. The bonding characteristics and surface chemical states were examined by a X-ray photoelectron spectroscopy (XPS) on an Axis Ultra DLD

and manipulated at 15 kV 10 mA<sup>-1</sup>.

#### 3. Theoretical computations

For quantum density functional theory (DFT) studies, VASP package was used to deduce the binding energy ( $E_b$ ) between substrates and Li<sub>2</sub>S<sub>a</sub> (n=1, 2, 4, 6, 8), which are calculated by the following equation:

$$E_{\rm b} = E_{{\rm Li}_2{\rm S}_{\rm n} + {\rm TiO}_{2-x}} - E_{{\rm Li}_2{\rm S}_{\rm n}} - E_{{\rm TiO}_{2-x}} \quad (1)$$

 $E_{\rm b}, E_{\rm TiO_{2-x}}$  and  $E_{\rm Li_2S_n+TiO_{2-x}}$  are correlated to the energy of Li<sub>2</sub>S<sub>n</sub>, substrate and Li<sub>2</sub>S<sub>n</sub>-substrates, respectively.

As for TiO<sub>2</sub> (110) and TiO<sub>20</sub>(110), a 4×2 supercell containing 128 atoms and 126 atoms were employed as the substrates with the height of the vacuum layer being 15 Å, respectively, among which the lower two-layer atoms were fixed and the upper two-layer atoms were relaxed. The first confirmation of each molecule was acquired by the molecular mechanics (MM) mode (Forcite module). The DFT calculation was conducted on a Dmol3 module of Accelrys Material Studio. The exchange-correlation functional was derived from the Perdew-Burke-Ernzerhof (PBE) method with the Grimme's semiempirical DFT-D3 scheme of dispersion correction. The one-body wave function is enlarged from the DNP basis set. The core-electron interactions were calculated by the DFT semi-core pseudopotentials. During the DFT calculations, the cut-off energy for the planewave was 500 Ry. The convergence criterion was set to be  $1\times10^{\circ}$  eV and 0.01 eV/Å for energy and force, respectively.

### 4. Supporting Figures



Figure S1. SEM images (a,b) and TEM images (c,d) of MnO<sub>2</sub> NWs.



Figure S2. SEM images (a,b) and TEM images (c,d) of MnO<sub>2</sub>@TiO<sub>2</sub> NWs.



Figure S3. SEM (a,b) images and TEM images (c,d) of MnO<sub>2</sub>@PDA.



**Figure S4.** SEM images (a, b), TEM images (c, d and e) and HRTEM image (f) of TiO<sub>2</sub>@NC nanotubes.



Figure S5. SEM images (a,b) and TEM images (c,d) of NC nanotubes.



Figure S6. XRD patterns of (a) MnO<sub>2</sub>, (b) MnO<sub>2</sub>@TiO<sub>2</sub>, (c) NC, and (d) OVs-TiO<sub>2x</sub>@C/S samples.



**Figure S7.** XPS full-scan spectrum of (a) NC/S, (b) TiO<sub>2</sub>@NC/S, and (c) OVs-TiO<sub>2x</sub>@NC/S hybrids.



Figure S8. High-resolution XPS spectrum at the N 1s area of OVs-TiO<sub>2x</sub>@NC/S.



**Figure S9.** High-resolution XPS spectrum at the C 1s area of (b) OVs-TiO<sub>2x</sub>@NC/S and (c) OVs-TiO<sub>2</sub>@NC/S.



Figure S10. The Kubelka-Munk plots of TiO<sub>2</sub>@NC and OVs-TiO<sub>2x</sub>@NC.



**Figure S11.** Electronic conductivities of TiO<sub>2</sub>@NC, OVs-TiO<sub>2x</sub>@NC and NC samples measured by a four-probe conductivity meter.



Figure S12. (a)  $N_2$  adsorption-desorption isotherms and (b) pore size distributions of TiO<sub>2</sub>@NC and OVs-TiO<sub>2x</sub>@NC.

The pore size distribution of OVs-TiO<sub>2x</sub>@NC shows coexistence of meso-microporous feature. The mesopores can be regarded as reservoirs for enabling more sulfur loading, and the micropores can be deemed as physical confinement to prevent the dissolution of LiPSs. Moreover, the well-developed porous nanostructures can not only facilitate the sulfur conversion reactions but also shorten the pathway for lithium-ion transportation and diffusion.



Figure S13. TG curves of TiO<sub>2</sub>@NC and OVs-TiO<sub>2x</sub>@NC in air atmosphere.



**Figure S14.** Magnified CV curves of cathodic peaks (Peak I) within the voltage range of 1.8-2.1V.

OVs-TiO<sub>2x</sub>@NC/S electrode delivers a positive shift of the cathodic process towards higher potential when compared with NC/S and TiO<sub>2</sub>@NC/S control samples. Moreover, OVs-TiO<sub>2x</sub>@NC/S electrode exhibits shaper peak with higher intensity, larger CV integral area, smaller polarization and rapid reaction kinetics during the redox process.



**Figure S15.** CV curves of (a) NC/S, (b)  $TiO_2@NC/S$ , and (c) OVs- $TiO_{2x}@NC/S$  electrodes at 0.1 mV s<sup>4</sup> for the initial five scans.

CV curves of OVs-TiO<sub>2</sub>,@NC/S electrode overlap almost perfectly, without obvious peak shifts or current changes during the initial five cycles, indicating excellent cycle stability and high reversibility. In contrast, the CV curves of NC/S and TiO<sub>2</sub>@NC/S electrodes exhibit decreasing peak intensities with much more obvious capacity fading, which should be related to the loss of active materials through LiPSs dissolution.



Figure S16. The galvanostatic charge-discharge profiles of OVs-TiO<sub>2x</sub>@NC/S electrode with different E/S amounts at 0.2 C.

Theoretically speaking, the spare electrolyte will magnify the viscosity of the electrolyte because of the dissolution of LiPSs into the electrolyte, thus leads to low utilization rate of active materials.<sup>154</sup> Moreover, the low electrolyte usage triggers the sluggish transfer and diffuse of lithium ion, thus increases the resistance of the electrode. When E/S usage ratio is 5  $\mu$ L mg<sup>+</sup>, a low capacity of 1169 mAh g<sup>+</sup> is acquired and large potential polarization appears. When the E/S ratio was increased from 5 to 20  $\mu$ L mg<sup>+</sup>, Li-S batteries exhibit improved sulfur electrochemistry, particularly smaller voltage polarization and higher reversible capacities, due to the efficient wetting and infiltrating of electrolyte with the electrode and electrolyte interface.<sup>184</sup> When the E/S was increased to 15  $\mu$ L mg<sup>+</sup>, the capacity showed almost no change when compared with the case of 20  $\mu$ L mg<sup>+</sup>. In order to achieve excellent cycle performance and in light of the low electrolyte principle to acieve high-energy-density Li-S cells, the optimized E/S ratio was precisely fixed at 15  $\mu$ L mg<sup>+</sup> in this work under low sulfur mass loading.



**Figure S17.** (a) The first total discharge specific capacity combined with  $\Delta H_1$  (capacity in 2.1~2.4V) and  $\Delta H_2$  (capacity in 1.7 ~ 2.1V) of the NC/S, TiO<sub>2</sub>@NC/S and OVs-TiO<sub>23</sub>@NC/S electrodes at 0.2 C. (b) The ratio of  $\Delta H_2 / \Delta H_1$ .

As shown in Figure S16a, OVs-TiO<sub>2</sub>,@NC/S electrode delivers higher  $\Delta H_i$ (971 mAh g<sup>-</sup>) and longer platform  $\Delta H_i$  (401 mAh g<sup>-</sup>), which can be interpreted as that more S<sub>i</sub> transformation to LiPSs and more Li<sub>3</sub>S<sub>2</sub>/Li<sub>3</sub>S participation in the reaction, less dissolution of Li<sub>3</sub>S<sub>i</sub> in the electrolyte and enhanced adsorption ability towards LiPSs in the fast redox reaction, respectively.<sup>180</sup> Furthermore, the ratio between  $\Delta H_i$  and  $\Delta H_i$  ( $\Delta H_i/\Delta H_i$ ) can be ascribed to the electrocatalytic ability of LiPSs during conversion reaction: (1) sluggish kinetics reaction process in the solid  $\rightarrow$  liquid  $\rightarrow$  solid state and (2) shuttling behavior induced by the diffusion of long-chain LiPSs and result in the capacity decay during  $\Delta H_i$  process. Therefore, higher ratio  $\Delta H_2/\Delta H_i$  value indicates better catalytic activity toward LiPSs redox reaction.<sup>181</sup> As shown in Figure S16b, the  $\Delta H_2/\Delta H_i$  value of OVs-TiO<sub>2</sub>,@NC/S (2.42) is higher than that of TiO<sub>2</sub> @NC/S (2.15) and NC/S (2.07).



**Figure S18.** Galvanostatic charge-discharge profiles of (a) TiO<sub>2</sub>@NC/S and (b) NC/S electrodes for 300 cycles at 0.2 C.



**Figure S19.** (a) Cycle stability tests of pristine OVs-TiO<sub>2x</sub>@NC host electrode (without loading of sulfur) at 100 mA  $g^{-1}$  and (b) galvanostatic charge-discharge plots in the voltage range of 1.7-2.8 V.

To better calculate the utilization of sulfur in the OVs-TiO<sub>3x</sub>@NC/S electrode, pristine OVs-TiO<sub>2x</sub>@NC host material (without filling with sulfur) was used as a control sample and tested under the same voltage window of 1.7-2.8 V *vs*. Li/Li<sup>+</sup>. Obviously, the lithium storage capacity of OVs-TiO<sub>2x</sub>@NC is below 10 mAh g<sup>-1</sup>, thus the specific capacity of OVs-TiO<sub>2x</sub>@NC host contributing to Li-S battery is negligible. In view of the acquired first discharge capacity of the OVs-TiO<sub>2x</sub>@NC/S electrode (1372 mAh g<sup>-1</sup>), the sulfur utilization can be calculated to be as high as 82% (on the basis of sulfur theoretical capacity of 1675 mAh g<sup>-1</sup>).



**Figure S20.** (a) Schematic illustration of a Li-S cell model. (b) Digital photos of the NC/S,  $TiO_2@NC/S$ , and OVs- $TiO_{2*}@NC/S$  electrodes from disassembled coin cells after 100 cycles at 0.2 C after immersing in DOL solvent. (c) Digital photos of the NC/S,  $TiO_2@NC/S$  and OVs- $TiO_{2*}@NC/S$  separators from disassembled cells after 100 cycles at 0.2 C. (d) Low-magnification FE-SEM image of the OVs- $TiO_{2*}@NC/S$  electrode after 100 cycles at 0.2 C. (e) High-magnification FE-SEM image and its corresponding element mapping images of the carbon (f), sulfur (g), titanium (h) and oxygen (i) in the OVs- $TiO_{2*}@NC/S$  electrode after 100 cycles at 0.2 C.

After coin cells were disassembled, the NC/S, TiO<sub>2</sub>@NC/S and OVs-TiO<sub>2</sub>@NC/S electrodes were separately immersed into the DOL solvents for several times to remove the electrolyte on the surface of electrode slices for further SEM investigation. The visual

observation of the DOL solvent containing NC/S electrode (Figure S17b) and its corresponding separator (Figure S17c) delivers a much more "yellowish" color, whereas the TiO<sub>2</sub>@NC/S and OVs-TiO<sub>2\*</sub>@NC/S maintains transparent. This phenomenon validly testifies that OVs-TiO<sub>2\*</sub>@NC host possesses strong interaction towards LiPSs and restricts the dissolution of the electrolyte. The OVs-TiO<sub>2\*</sub>@NC/S electrode also well-maintains the 1D nanostructure appearance (Figure S17d), without any obvious structure twist or collapse, exhibiting excellent structural stability. Elemental mappings (Figure S17f-i) further testify uniform distributions of C, Ti, O and S elements in the OVs-TiO<sub>2\*</sub>@NC/S after cycling.



Figure S21. The SEM images of (a) NC/S, (b)  $TiO_2@C/S$  and (c) OVs- $TiO_{2a}@NC/S$  electrodes after 100 cycles at 0.2 C.

At the fully charged state, OVs-TiO<sub>2x</sub>@NC/S electrode almost maintains its original 1D nanostructure and a glossy morphology, without discernible detection of bulk Li<sub>2</sub>S/Li<sub>2</sub>S<sub>2</sub> particles agglomerations or deposits onto the surface of the electrode. For comparison, the NC/S and TiO<sub>2</sub>@NC/S electrodes suffer mechanical instability with fragmentation or collapse

in different degrees. Large quantity of Li<sub>2</sub>S<sub>2</sub>/Li<sub>2</sub>S was randomly deposited on the surface of the electrode, which testifies that sulfur had departed from the host material and serious dissolution occurred. As a result, OVs-TiO<sub>2x</sub> spices can be deemed as an excellent electrocatalyst and polysulfide immobilizer. It participates in the multi-step transformations of LiPSs, accelerates chemical redox reactions of LiPSs, decreases the occurrence of LiPSs dissolution and controls conversion of solid Li<sub>2</sub>S<sub>2</sub>/Li<sub>2</sub>S. The defect-rich polar chemical interactions will contribute, in some ways, to the improved sulfur cathode electrochemistry.



**Figure S22.** Cycle stability tests of NC/S, TiO<sub>2</sub>@NC/S, and OVs-TiO<sub>2\*</sub>@NC/S at the current density of 0.5 C.



**Figure S23.** CV curves of the (a)  $TiO_2@NC/S$  and (b) NC/S electrodes under various scan rates of 0.1-0.5 mV s<sup>4</sup> within the voltage window from 1.7 to 2.8 V.



**Figure S24.** CV peak plots of (a) first cathodic reduction process (peak A: Li<sub>2</sub>S<sub>2</sub>/Li<sub>2</sub>S  $\rightarrow$  Li<sub>2</sub>S<sub>8</sub>/S<sub>8</sub>), (b) second cathodic reduction process (peak B: 2.1-2.4 V, S<sub>8</sub> $\rightarrow$  Li<sub>2</sub>S<sub>4</sub>(4 $\leq$ x $\leq$ 8)) and (c) anodic oxidation process (peak C: 1.7-2.1 V, Li<sub>2</sub>S<sub>4</sub>(4 $\leq$ x $\leq$ 8)  $\rightarrow$  Li<sub>2</sub>S<sub>2</sub>/Li<sub>2</sub>S) versus the square root of the scan rates. (d) The  $I_p/v^{0.5}$  value at peak A, peak B and peak C are calculated by the corresponding fitted lines.

The kinetics data are calculated according to the peak current (*i*, mA) and scan rates (v, mV s<sup>4</sup>) based on the following power law:

$$i = av^b \tag{1}$$

Hereinto, *b* represents the adjustable parameter and is positively correlated with lithiumion diffusion, and is derived from the slope of the diagram of  $\lg i$  and  $\lg v$ . Traditionally, two characteristic value of *b* (*b* = 0.5 or 1.0) exists. In detail, *b* = 0.5 demonstrates the semiinfinite linear diffusion process in the electrode material, while *b* = 1.0 testifies the reaction is governed by the surface-controlled capacitive process.<sup>[SI]</sup> As shown in Figure S19a-c, the  $\lg i$  is in good linear relationship with  $\lg v$  at the sweep rates from 0.1 to 0.5 mV s<sup>1</sup>. The *b* values correlated with the peak A ( $b_a$ ), peak B ( $b_b$ ) and peak ( $b_c$ ) are also calculated and listed. Obviously, the value of  $b_b$  is larger than  $b_c$  all the time testifies that the solid-liquid state reaction ( $S_a \rightarrow Li_2S_a(4 \le x \le 8)$ ) is quicker than liquid-solid state reaction ( $Li_2S_a(4 \le x \le 8) \rightarrow$  $Li_3S_2/Li_3S$ ). This phenomenon manifests liquid-solid state reaction is the rate determining step of the sulfur cathodic process.<sup>198300</sup> In comparison with the *b* value of TiO<sub>2</sub>@NC/S and NC/S electrodes,  $b_a$ ,  $b_b$  and  $b_c$  of OVs-TiO<sub>2x</sub>@NC/S is obviously enhanced. Hence, these kinetics results demonstrate the incorporation of OVs-TiO<sub>2x</sub> can efficiently accelerate the catalytic kinetics reactions of polysulfides.

The lithium-ion diffusion procedure can be calculated by the following Randles-Sevcik equation: [S11.512]

$$I_{\rm p} = 2.69 \times 10^5 n^{1.5} A D_{\rm Li^+}^{0.5} C_{\rm Li^+} v^{0.5} \qquad (2)$$

Where  $I_p$  is the peak current, A;

*n*: The charge transfer number, while n = 2 is suitable for Li-S batteries;

A: The surface electrode area of active materials, cm<sup>2</sup>;

 $D_{\text{Li}^+}$ : The Li<sup>+</sup> diffusion rate, cm<sup>2</sup> s<sup>-1</sup>;

 $C_{\text{Li}^+}$ : The concentration of lithium-ion in the electrolyte, mol mL<sub>1</sub>;

v: The scan rate, V s<sup>-1</sup>.

When the peak current is in linear correlation with the square root of the sweep rate, the fitted line slope  $(I_p / v^{0.5})$  reflects the lithium-ion diffusion rate with all other parameters being constant, namely, n = 2, A = 1.13 cm<sup>2</sup> and  $C_{\text{Li}^+} = 10^{-3}$  mol mL<sup>-1</sup>.<sup>[S13]</sup>



**Figure S25.** The well-fitted Randles EIS equivalent circuit of NC/S, TiO<sub>2</sub>@NC/S and OVs-TiO<sub>2x</sub>@NC/S electrodes for Li-S batteries, while (a) is suitable for the fresh cell without the process of  $R_i$  and its relevant CPE1, (b) can be applied to the battery after cycling.<sup>[S14]</sup>

R.: The internal resistance of the electrolyte;

R<sub>i</sub>: The internal resistance of the solid electrolyte interface (SEI) film correlated with the insoluble  $Li_2S_2/Li_2S$ ;

R<sub>a</sub>: The charge-transfer resistance, related to the electrode reaction kinetics;

CPE1: Capacitance of the electrode bulk in high-frequency region;

CPE2: Capacitance of the charge transfer process at the interface between the sulfur and electrolyte;

W.: The semi-infinite Warburg diffusion impedance of the long-chain LiPSs.



**Figure S26.** Fitting of the complex impedance of cells with NC/S, TiO<sub>2</sub>@NC/S and OVs-TiO<sub>2</sub>.  $_{x}$ @NC/S versus  $\omega^{_{42}}$  in the low frequencies.

As shown in Figure 4i, the inclined straight line in the low-frequency region is associated with Warburg resistance (W<sub>o</sub>) pertaining to the diffusion resistance, and the lithium-ion diffusion of electrodes represent by Warburg factor ( $\sigma$ ). According to the calculation model of lithium-ion diffusion coefficient, the equations are shown as follows:<sup>[S15,S16]</sup>

$$|Z'| = R_e + R_{ct} + \sigma \omega^{-1/2}$$
(3)  
$$D(\text{Li}^+) = \frac{R^2 T^2}{2A^2 n^4 F^4 C^2 \sigma^2}$$
(4)

Whereas  $\sigma$  relates to Z' and the value can be acquired from the slope of fitted lines between Z' and  $\omega^{12}$ , and  $D(\text{Li}^+)$  is the diffusion coefficient of lithium-ion, *R* represents the gas constant (8.314), *T* expresses the absolute temperature (273.15K), *A* is the surface area of the electrode, n represents the electron number per mole in the oxidization process, *F* is the Faraday constant (96500) and *C* is the concentration of lithium-ion (10<sup>-1</sup> mol mL<sup>-1</sup>). The correlation between Z' and  $\omega^{12}$  in the low-frequency region of NC/S, TiO<sub>2</sub>@NC/S and OVs-TiO<sub>2</sub>.@NC/S electrodes are shown in Figure S25. After fitting, the OVs-TiO<sub>2</sub>.@NC/S electrode possesses a much lower  $\sigma$  value (1.49) than that of NC/S (22.82) and TiO<sub>2</sub>@NC/S (8.38) electrodes. The interfacial resistances of the Li-S batteries are decreasing when OVs-TiO<sub>2</sub>, is introduced, which implies a faster charge transfer rate and contributes to the improved interfacial kinetics reactions happened in the liquid phase.



Figure S27. The charge-discharge profiles of (a) NC/S and (b) TiO<sub>2</sub>@NC/S electrodes in the rate capability tests.



Figure S28. CV profiles of (a) TiO<sub>2</sub>@NC and (b) NC symmetric cells at a scan rate of 3 mV s<sup>4</sup>.

The large polarization suggests that TiO<sub>2</sub> would contribute little impact towards improving the electrochemical performance of Li-S batteries when compared with OVs-TiO<sub>2x</sub>. The redox reaction mechanism of the OVs-TiO<sub>2x</sub>@NC (Figure 6c) and TiO<sub>2</sub>@NC symmetric cells (Figure S24a) are illustrated as follows.<sup>[817]</sup>

Peak a:

Working electrode:  $S_{6^2} + 10e + 12Li^+ \rightarrow 6Li_2S$ 

Counter electrode:  $4S_{6^2} - 8e \rightarrow 3S_{8}$ 

Peak b:

Working electrode:  $6Li_2S - 10e \rightarrow S_{6^2} + 12Li^*$ 

Counter electrode:  $3S_{*} + 8e \rightarrow 4S_{6^{-1}}$ 

Peak c:

Working electrode:  $4S_6^2 - 8e \rightarrow 3S_8$ 

Counter electrode:  $S_6^2 + 10e + 12Li \rightarrow 6Li_2S$ 

Peak d:

Working electrode:  $3S_{8} + 8e \rightarrow 4S_{6}^{2}$ 

Counter electrode:  $6Li_2S - 10e \rightarrow S_6^2 + 12Li^*$ 



Figure S29. XPS spectra of Ti 2p for the TiO<sub>2</sub>@NC composite before and after adsorption test.



**Figure S30.** Schematic illustration of the formation process of Ti-S bond with coordination between the unsaturated Ti-metal centers (Lewis Acid) and terminal sulfur  $(S_{\tau})$  of  $S_{x}^{2}$  (polysulfides).

Disordered structural vacancies exist in Ti- and O- sub lattices of the OVs-TiO<sub>2x</sub>, therefore TiO<sub>2x</sub> is nonstoichiometric mixed with plenty of unsaturated Ti-metal centers.<sup>[518]</sup> As a consequence, both TiO<sub>2x</sub> with unsaturated Ti-centers and empty d orbitals can be deemed as Lewis acid.<sup>[519]</sup> Moreover, LiPSs exhibits a couple of different forms of sulfur atoms, including terminal (S<sub>7</sub>) and bridging (S<sub>8</sub>) sulfur. After LiPSs were dissolved in the electrolyte, it would produce lithium-ions and S<sub>x</sub><sup>2-</sup> chains.<sup>[519]</sup> Terminal (S<sub>7</sub>) sulfur atoms of the LiPSs chains (S<sub>x</sub><sup>2</sup>) possess lone electron pairs as the Lewis base. The coordination function between the unsaturated Ti-metal centers and sulfur atoms will give rise to the generation of coordinated covalent-type Ti-S bond towards Li-S batteries.<sup>[529]</sup>



**Figure S31.** (a) High-resolution O 1s spectrum of OVs-TiO<sub>2x</sub>@NC before and after adsorption of  $\text{Li}_2S_6$ . (b) High-resolution N 1s spectrum of OVs-TiO<sub>2x</sub>@NC before and after adsorption of  $\text{Li}_2S_6$ .

A small shift to lower binding energy of lattice oxygen (~530.5 eV) and Li-O bond (529.5 eV), demonstrates the existence of polar-polar interactions of TiO<sub>2x</sub> towards Li<sup>+</sup> and the formation of LiPSs (Ti-O-Li<sup>+</sup> style).<sup>[SI7]</sup> The shifting of N 1s peak in the OVs-TiO<sub>2x</sub>@NC-Li<sub>2</sub>S<sub>6</sub> to higher binding energy when compared with OVs-TiO<sub>2x</sub>@NC is mainly attributed to its new Ti-N-S interactions between nitrogen-doped carbon and lithium polysulfides.



**Figure S32.** Optimized configurations from top and side view of (a) C, (b)  $TiO_2$ , and (c)  $TiO_{2*}$ . C atom is gray, O atom is red, and Ti atom is greyish white. The green dotted circle highlighted the existence of oxygen-vacancies.



**Figure S33.** Optimized configurations of polysulfides ( $\text{Li}_2S_x$ , x = 1, 2, 4, 6, and 8) being adsorbed on (a) C, (b) TiO<sub>2</sub>, and (c) TiO<sub>2x</sub>.



**Figure S34.** The galvanostatic charge-discharge profiles of the OVs-TiO<sub>2x</sub>@NC/S electrode under various sulfur loading of 3.3, 5.6, and 7.8 mg cm<sup>2</sup> at the current density of 0.2 C.



**Figure S35.** The first charge-discharge curves of the OVs-TiO<sub>2x</sub>@NC/S electrode under sulfur loading of 9.5 mg cm<sup>2</sup> at 0.05 C with a low E/S=5 usage ratio.



**Figure S36.** (a) Cross-section SEM images of thick OVs-TiO<sub>2,x</sub>@NC/S electrode for high sulfur loading of 9.5 mg cm<sup>2</sup>. (b) Optical images of Li anode after cycling at 0.05C, (c, d) surface morphology of the Li anode after cycling at 0.05C (inset: the corresponding EDS spectrum of Li anode). The batteries were disassembled in Ar-filled glove box, and Li-anode was washed by DOL solvent for several times. After dried at the room temperature in Ar-filled glove box, Li anodes were transferred into a sealed container for SEM measurement.

**Table S1.** Comparisons of the lithium-ion diffusion rates  $(D_{Li^+}, cm^2s^1)$  of NC/S, TiO<sub>2</sub>@NC/S, and OVs-TiO<sub>2x</sub>@NC/S electrodes.

Sample	Peak A	Peak B	Peak C
NC/S	9.840×10 <sup>-8</sup>	1.214×10 <sup>-8</sup>	2.167×10 <sup>*</sup>
TiO <sub>2</sub> @NC/S	1.923×10 <sup>-7</sup>	1.762×10 <sup>-s</sup>	3.159×10 <sup>-s</sup>
OVs-TiO <sub>2x</sub> @NC/S	3.752×10 <sup>-7</sup>	3.622×10 <sup>-8</sup>	4.454×10-8

**Table S2.** Impedance parameters of the EIS spectra of NC/S, TiO<sub>2</sub>@NC/S, and OVs-TiO<sub>2x</sub>@N C/S electrodes before cycling.

Sample	$\mathbf{R}_{c}\left( \Omega ight)$	$\mathbf{R}_{_{\mathrm{ct}}}\left( \Omega ight)$
NC/S	8.65	56.42
TiO <sub>2</sub> @NC/S	5.77	32.15
OVs-TiO <sub>2x</sub> @NC/S	3.15	22.75

**Table S3.** Impedance parameters of the EIS spectra of NC/S, TiO<sub>2</sub>@NC/S, and OVs-TiO<sub>2</sub>.

Sample	$\mathbf{R}_{e}\left( \Omega ight)$	$\mathbf{R}_{s}(\mathbf{\Omega})$	$\mathbf{R}_{\text{ct}}\left( \Omega ight)$
NC/S	4.85	25.08	42.31
TiO <sub>2</sub> @NC/S	2.87	10.32	23.07
OVs-TiO <sub>2-x</sub> @NC/S	1.48	6.58	11.44

<b>Table S4.</b> Cycle performance comparison of our OVs-TiO <sub>2x</sub> @C/S electrode (	(sulfur	loading $\leq$
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Electrodes	Sulfur content (%)	Sulfur loading (mg cm²)	Current density (C)	Initial highest capacity (mAh g <sup>,</sup> )	Reversible capacity (mAh g <sup>1</sup> )	Decay rate (per cycle, %)	Cycle number	Reference
			0.2	1372	1194	0.043	300	
			0.5	1215	953	0.022	1000	
OVs-TiO <sub>2x</sub> @C/S	78.3	1.6	1	1086	792	0.014	2000	Our work
			2	1003	684	0.016	2000	
			5	834	531	0.012	3000	
TiO@G-S	65.2	1.0	2	831	455	0.226	200	[S21]
			0.1	1285	977	0.160	150	
TiO@C-HS/S	70.0	1.5	0.2	1190	750	0.074	500	[S22]
			0.5	1066	630	0.082	500	
S@TIN ND	70.0	15	0.2	1163	1036	0.218	50	[\$23]
5@ 1119-19F	70.0	1.5	1	1030	700	0.040	800	[323]
			0.2	1309	884	0.325	100	
C@TiN_S	71.0	11	1	-	741	-	150	[\$24]
Ce IIIV-5	71.0	1.1	2	-	570	-	300	[02+]
			3	-	453	-	300	
S@u-NCSe	70.1	1.0	3	706	484	0.016	2000	[S25]
			0.2	1305	954	0.180	150	
MoS <sub>2</sub> /S/rGO	70.0	1.0	0.5	1183	908	0.077	300	[S26]
			2	985	619	0.037	1000	

2mg cm<sup>2</sup>) with other recently reported Li-S batteries containing electrocatalysts.

			0.2	1187	896	0.123	200	
ZnS-CB/S	72.4	1.37	2	886	632	0.029	1000	[S27]
			5	661	388	0.041	1000	
S/YSC@Fe <sub>3</sub> O <sub>4</sub>	80.0	-	0.2	1366	1165	0.074	200	[S28]
			0.2	1368	1066	0.110	200	
CeO <sub>2</sub> /MMNC-S	63.6	1.4	1	1352	836	0.076	500	[S29]
			2	950	721	0.024	1000	
NILS @S@IG	72.0	1.05	0.5	1185	856	0.079	350	[\$30]
	72.0	1.05	20	348	195	0.022	2000	[330]
N CNTs/Co NEs	75 7		0.2	1262	1069	0.255	60	[\$31]
IN-CIN 15/CO-INI'S	13.1	-	1	1025	623	0.078	500	[551]
			0.1	1255	952	0.241	100	
HFeNG-S	86.5	2.0	0.5	1154	867	0.083	300	[S32]
			3	876	758	0.013	1000	
S@Co Fe P	71.0	1.0	0.2	1118	958	0.143	100	[\$33]
S@Co-Fe-P /1.0	1.0	1	863	678	0.043	500	[333]	
FeP/rGO/CNTs-S 75.0	75.0	1.0	0.1	1294	1038	0.198	100	[\$2/1
	15.0	1.0	1	841	673	0.040	400	[004]
PRC/Ni/S	76.1	2.0	0.2	1256	813	0.071	500	[S35]

	Sulfur		Current	Reversible	
Electrodes	content	Sulfur loading	density	capacity	Reference
	(%)	(ing cin <sup>-</sup> )	(C)	( <b>mAh</b> g <sup>.1</sup> )	
	70.2	1.6	5	848	0 1
UVS-110 <sub>2x</sub> @C/S	/8.3	1.6	8	675	Our work
TiO@G-S	65.2	1.0	2	831	[S21]
TiO@C-HS/S	70.0	1.5	2	655	[\$22]
S@TiN-NP	70.0	1.5	5	690	[\$23]
C@TiN-S	71.0	1.1	5	373	[S24]
S@u-NCSe	70.1	1.1	5	626	[S25]
Mas/s/rGO	70.0	1.0	7	657	[\$26]
M05 <sub>2</sub> /5/100	70.0	1.0	10	553	[320]
ZnS-CB/S	72.4	1.37	5	~600	[\$27]
S/YSC@Fe <sub>3</sub> O <sub>4</sub>	80.0	-	2	773	[\$28]
CeO <sub>2</sub> /MMNC-S	63.6	1.4	2	737	[S29]
NbS <sub>2</sub> @S@IG	72.0	1.05	3	910	[\$30]
N-CNTs/Co-NFs	75.7	-	3	684	[ <b>S</b> 31]
HEANC S	96 5	2.0	3	876	[\$20]
Hrenu-3	80.5	2.0	5	810	[332]
S@Co-Fe-P	71.0	1.0	2	741	[\$33]
FeP/rGO/CNTs-S	75.0	1.0	3	613	[\$34]
PRC/Ni/S	76.1	2.0	5	574	[\$35]

**Table S5.** Rate performance comparison of our OVs-TiO<sub>2x</sub>@C/S electrode (sulfur loading  $\leq$ 2 mg cm<sup>2</sup>) with other recently reported Li-S batteries containing electrocatalysts.

Electrodes	Sulfur loading (mg cm²)	Current density (C, mA cm²)	Areal capacity (mAh cm²)	Reference
	33	02111	3.81 (Initial)	
	5.5	0.2, 1.11	3.41 (200 cycles)	
	5.6	0 2 1 88	5.62 (Initial)	
OVATIO @C/S	5.0	0.2, 1.00	4.89 (200 cycles)	Our work
078-11022 @C/S	7 0	0.2.2.61	6.65 (Initial)	Our work
	7.0	0.2, 2.01	5.54 (200 cycles)	
	9.5	0.05, 0.80	9.78 (Initial)	
			8.01 (100 cycles)	
Tioracs	5.2	0.2.1.74	4.1(Initial)	[\$21]
110@0-5	5.2	0.2, 1.74	3.15 (300 cycles)	[321]
TiO@C-HS/S	4.0	0.2, 1.34	2.5 (50 cycles)	[\$22]
	3.1	0.2, 1.04	3.5 (Initial)	
S@TiN-NP	4.8	0.2, 1.61	4.5 (Initial)	[\$23]
	7.0	0.2, 2.35	7 (Initial)	
C@TiN-S	4.2	0.2, 1.41	3.44 (150 cycles)	[\$24]
		1 5 0 6	2.40 (Initial)	
S@u-NCSe	3.2	1, 5.36	1.78, (600 cycles)	[825]
MoS <sub>2</sub> /S/rGO	3.6	0.2, 1.21	2.57 (110 cycles)	[\$26]
ZnS-CB/S	7.1	0.2, 2.38	4.18 (200 cycles)	[\$27]

**Table S6.** Electrochemical performance comparison of our OVs-TiO<sub>2x</sub>@C/S electrode (sulfur loading  $\geq$  3 mg cm<sup>2</sup>) with recently reported Li-S batteries containing electrocatalysts.

S/YSC@Fe <sub>3</sub> O <sub>4</sub>	5.5	0.2, 1.84	6.07 (Initial)	[S28]	
CeO/MMNC S	3.4	05285	3.13 (Initial)	[\$20]	
	5.4	0.5, 2.85	2.08 (200 cycles)	[027]	
NHS @S@IG	3 25	1 5 44	1.76 (Initial)	[\$30]	
1003 @ 3 @ 10	5.25	1, 3.44	1.32 (200 cycles)	[330]	
	3 1	0.2, 1.04	2.9 (Initial)		
	5.1		2.39 (100 cycles)		
N CNTa/Ca NEa	5.2	0.2, 1.74	4.37 (Initial)	[021]	
N-CN15/CO-NFS	5.2		3.34 (100 cycles)	[331]	
	65	0.2, 2.18	4.25 (Initial)		
	0.5		2.96 (100 cycles)		
HEeNG S	3.0	0.1,0.50	3.8 (Initial)	[\$32]	
III CNO-5	5.0	0.1, 0.84	5.0 (Initial)	[552]	
	3.7	0.2, 1.24	3.8 (Initial)		
S@Co-Fe-P	5 5	0.2 1.85	4.6 (Initial)	[\$33]	
	5.5	0.2, 1.85	3.5 (100 cycles)		
FeP/rGO/CNTs-S	3.5	1, 5.86	1.75 (200 cycles)	[ <b>S</b> 34]	
PRC/Ni/S	4.0	0.2, 1.34	2.25 (Initial)	[\$35]	

#### **References for the Supporting Information**

- [S1] Z. Li, J. T. Zhang, X. W. Lou, Angew. Chem. Int. Ed. 2015, 54, 12886-12890.
- [S2] W. Li, J. P. Yang, Z. X. Wu, J. X. Wang, B. Li, S. S. Feng, Y. H. Deng, F. Zhang, D. Y.Zhao, J. Am. Chem. Soc. 2012, 134, 11864-11867.
- [S3] F. Y. Fan, W. C. Carter, Y. M. Chiang, Adv. Mater. 2015, 27, 5203-5209.
- [S4] Y. T. Liu, D. D. Han, L. Wang, G. R. Li, S. Liu, X. P. Gao, *Adv. Energy Mater*. 2019, 9, 1803477.
- [S5] L. L. Z , X. C , F. W, Z. Q. Niu, Y. J. Wang, Q. Zhang, J. Chen, ACS Nano 2018, 12, 9578-9586.
- [S6] R. Wang, J. L. Yang, X. Chen, Y. Zhao, W. G. Zhao, G. Y. Qian, S. N. Li, Y. G. Xiao, H. Chen, Y. S. Ye, G. M. Zhou, F. Pan, *Adv. Energy Mater.* 2020, **10**, 1903550.
- [S7] D. W. Su, M. Cortie, H. B. Fan, G. X. Wang, Adv. Mater. 2017, 29, 1700587.
- [S8] V. Augustyn, J. Come, M. A. Lowe, J. W. Kim, P. L. Taberna, S. H. Tolbert, H. D. Abruña, P. Simon, B. Dunn, *Nat. Mater.* 2013, **12**, 518-522.
- [S9] Y. Q. Tao, Y. J. Wei, Y. Liu, J. T. Wang, W. M. Qiao, L. C. Ling, D. H. Long, *Energy Environ. Sci.* 2016, 9, 3230-3239.
- [S10] N. X. Shi, B. J. Xi, Z. Y. Feng, J. C. Liu, D. H. Wei, J. Liu, J. K. Feng, S. L. Xiong, Adv. Mater. Interfaces 2019, 6, 1802088.
- [S11] J. L. Wang, F. J. Lin, H. Jia, J. Yang, C. W. Monroe, Y. Li, *Angew. Chem. Int. Ed.* 2014, 53, 10099-10104.
- [S12] S. R. Das, S. B. Majumder, R. S. Katiyar, J. Power Sources 2005, 139, 261-268.
- [S13] J. Q. Huang, T. Z. Zhuang, Q. Zhang, H. J. Peng, C. M. Chen, F. Wei, ACS Nano 2015,9, 3002-3011.
- [S14] J. Zhang, Y. Shi, Y. Ding, W. K. Zhang, G. H. Yu, Nano Lett. 2016, 16, 7276-7281.
- [S15] Y. Z. Wang, D. Adekoya, J. Q. Sun, T. Y. Tang, H. L. Qiu, Li. Xu, S. Q. Zhang, Y. L.

Hou, Adv. Funct. Mater. 2019, 25, 1807485.

- [S16] W. Liu, Bi, X. F. Bi, S. B. Yang, Adv. Mater. 2016, 28, 7672-7679.
- [S17] H. B. Lin, L. Q. Yang, X. Jiang, G. C. Li, T. R. Zhang, Q. F. Yao, G. Y. Zheng, J. Y. Lee, *Energy Environ. Sci.* 2017, **10**, 1476-1486.
- [S18] M. G. Kostenko, A. V. Lukoyanov, V. P. Zhukov, A. A. Rempel, J. Solid State Chem. 2013, 204, 146-152.
- [S19] Q. Pang, X. Liang, C. Y. Kwok, L. F. Nazar, *Nat. Energy* 2016, 1, 1-11.
- [S20] Z. H. Li, Q. He, X. Xu, Y. Zhao, X. W. Liu, C. Zhou, D. Ai, L. X. Xia, L. Q. Mai, Adv. Mater. 2018, 30, 1804089.
- [S21] Y. Chen, S. H. Choi, D. W. Su, X. C. Gao, G. X. Wang, Nano Energy 2018, 47, 331-339.
- [S22] Z. Li, J. T. Zhang, B. Y. Guan, D. Wang, L. M. Liu, X. W. Lou, *Nat. Commun.* 2016, 7, 1-11.
- [S23] Z. Y. Xing, G. R. Li, S. Sy, Z. W. Chen, Nano Energy 2018, 54, 1-9.
- [S24] Y. K. Wang, R. F. Zhang, Y. C. Pang, X. Chen, J. X. Lang, J. J. Xu, C. H. Xiao, H. L. Li,
- K. Xi, S. J. Ding, Energy Storage Mater. 2019, 16, 228-235.
- [S25] C. Q. Zhang, J. J. Biendicho, T. Zhang, R. F. Du, J. S. Li, X. H. Yang, J. Arbiol, Y. T. Zhou, J. R. Morante, A. Cabot, *Adv. Funct. Mater.* 2019, **29**, 1903842.
- [S26] Y. J. Wei, Z. K. Kong, Y. K. Pan, Y. Q. Cao, D. H. Long, J. T. Wang, W. M. Qiao, L. C. Ling, J. Mater. Chem. A 2018, 6, 5899-5909.
- [S27] J. Xu, W. X. Zhang, H. B. Fan, F. L. Cheng, D. W. Su, G. X. Wang, *Nano Energy* 2018, 51, 73-82.
- [S28] J. R. He, L. Luo, Y. F. Chen, A. Manthiram, Adv. Mater. 2017, 29, 1702707.
- [S29] L. B. Ma, R. P. Chen, G. Y. Zhu, Y. Hu, Y. R. Wang, T. Chen, J. Liu, Z. Jin, ACS Nano 2017, 11, 7274-7283.
- [S30] Z. B. Xiao, Z. Yang, L. J. Zhang, H. Pan, R. H. Wang, ACS Nano 2017, 11, 8488-8498.

- [S31] L. B. Ma, H. N. Lin, W. J. Zhang, P. Y. Zhao, G. Y. Zhu, Y. Hu, R. P. Chen, Z. X. Tie,
  J. Liu, Z. Jin, *Nano Lett.* 2018, 18, 7949-7954.
- [S32] Y. Z. Wang, D. Adekoya, J. Q. Sun, T. Y. Tang, H. L. Qiu, L. Xu, S. Q. Zhang, Y. L.Hou, *Adv. Funct. Mater.* 2018, **29**, 1807485.
- [S33] Y. Chen, W. X. Zhang, D. Zhou, H. J. Tian, D. W. Su, C. Y. Wang, D. Stockdale, F. Y. Kang, B. H. Li, G. X. Wang, ACS Nano 2019, 13, 4731-4741.
- [S34] S. Z. Huang, Y. V. Lim, X. M. Zhang, Y. Wang, Y. Zheng, D. Z. Kong, M. Ding, S. Y. A.
  Yang, H. Y. Yang, *Nano Energy* 2018, **51**, 340-348.
- [S35] Y. Zong, X. H. Xia, S. J. Deng, J. Y. Zhan, R. Y. Fang, Y. Xia, X. L. Wang, Q. Zhang, J.
- P. Tu, Adv. Energy Mater. 2017, 8, 1701110.