## **Supporting information for**

## Rooting Bismuth Oxide Nanosheets into Porous Carbon Nanoboxes as a Sulfur Immobilizer for Lithium-Sulfur

## **Batteries**

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**Table S1.** Comparison of electrochemical performances of Bi<sub>2</sub>O<sub>3</sub>@Co/N-PC@S electrode with previously reported bismuth salt or MOF derived carbon material electrodes.

Products	Synthetic method	Electrode formulation <sup>a</sup>	Cycling stability (A/B/n) <sup>b</sup>	Ref.
RGO/ZIF-67	infiltration	Binder-free	704/1/10	[S1]
MOF derived nitrogen doped porous carbon	infiltration	80:10:10	608/1/300	[S2]
Co <sub>9</sub> S <sub>8</sub> /C-S	Dispersed and volatilization	80:10:10	680/1/300	[S3]
MOF-derived cobalt–graphitic carbon nanocages	infiltration	80:10:10	718/1/500	[S4]
CNTs/Co <sub>3</sub> S <sub>4</sub> –NBs	Dispersed and volatilization	80:10:10	752/1/500	[S5]
ZIF-67 @LDH	infiltration	70:20:10	653/0.5/100	[S6]
CoAl-LDH@ZIF-67	infiltration	75:15:10	599/2/650	[S7]
MOF-derived porous N-Co <sub>3</sub> O <sub>4</sub> @N-C	Dispersed and volatilization		568/0.2/500	[S8]
Bi <sub>2</sub> S <sub>3</sub>	Ball milling and infiltration	70:15:15	673/2/10	[\$9]
Cu <sub>3</sub> BiS <sub>3</sub> /S	infiltration	80:10:10	487/0.2/100	[S10]
S@MOF-525(Cu)	infiltration	70:20:10	700/0.5/200	[S11]
S@MIL-100(V)/rGO	infiltration	70:20:10	500/0.5/200	[S12]
TiO <sub>2</sub> @NC-S	Dispersed and volatilization	70:30	712/1/500	[ <b>S</b> 13]
ZIF-8-S	infiltration	60:30:10	710/1/50	[S14]
Ni-MOF/S	infiltration	80:10:10	689/0.1/200	[S15]
Bi <sub>2</sub> O <sub>3</sub> @Co/N-PC@S	infiltration	80:10:10	732/1.5/500	This work

<sup>*a*</sup>Weight ratio of the active material, carbon and binder. PVDF was used as binder if not mentioned. Other values used were specified.

 ${}^{b}A/B/n$  means the capacity of A (mAh g<sup>-1</sup>) remained after *n* cycles at the certain current density of B (C).



Figure S1. SEM images of Bi<sub>2</sub>O<sub>3</sub>@Co/N-PC@S.



**Figure S2.** High angle annular dark field scanning transmission electron microscopy (HAADF-STEM) image of Bi<sub>2</sub>O<sub>3</sub>@Co/N-PC@S.



**Figure S3.** (a, b) TEM images, (c) HAADF image, (d–f) HRTEM images of Bi<sub>2</sub>O<sub>3</sub>@Co/N-PC@S composite and corresponding (g) SAED pattern.



Figure S4. EDX spectrum of cobalt and bismuth.



Figure S5. TGA curve of Bi<sub>2</sub>O<sub>3</sub>@Co/N-PC

Figure S5 showed the TGA curves of  $Bi_2O_3@Co/N-PC$ , which were carried out in air from 50 to 750 °C. It could be seen that the weights of the as-prepared composites decrease rapid near the 250 °C, and then maintain stable after 300 °C. This is due to the complex reactions including the formation of CoO and volatilization of carbon. The total reaction can be simply written as:

$$C(s) + O_2(g) \rightarrow CO_2(g)$$
(1)

$$2Co(S) + O_2(g) \rightarrow 2CoO$$
 (2)

According to the variation of TGA curve, 51% of the original weight was kept for the final products, i.e., the total amount of the formed CoO and Bi<sub>2</sub>O<sub>3</sub>. On the basis of the equation (2) and given the fact that the atomic ratio of Co/Bi was about 4:1 (Figure S4), the mass content of Bi<sub>2</sub>O<sub>3</sub>, and Co in the Bi<sub>2</sub>O<sub>3</sub>@Co/N-PC were thus calculated as about 22 wt.%, and 22.9 wt.%, respectively. Based on this result, it could be seen that the mass content of carbon was about 55.1 wt.% (100 wt.% - 22 wt.% - 22.9 wt.%) in the Bi<sub>2</sub>O<sub>3</sub>@Co/N-PC host.



**Figure S6.** Cycling performance and Coulombic efficiency of Bi<sub>2</sub>O<sub>3</sub>@Co/N-PC@S electrodes at a current density of 0.2 C rates for 200 cycles.



**Figure S7.** Cycling performance and Coulombic efficiency of Co/N-PC@S electrodes at a current density of 0.2 C rates for 200 cycles.



**Figure S8.** Coulombic efficiency of  $Bi_2O_3@Co/N-PC@S$  and Co/N-PC@S electrodes at 1.5 C rates.



**Figure S9.** Coulombic efficiency of Bi<sub>2</sub>O<sub>3</sub>@Co/N-PC@S and Co/N-PC@S electrodes at different C rates.



Figure S10. Discharge/charge curves of Co/N-PC@S electrodes at different C rates.



Figure S11. Coulombic efficiency of Bi<sub>2</sub>O<sub>3</sub>@Co/N-PC@S electrodes at 10 C rates.



**Figure S12.** CV curves of  $Li_2S_6$  symmetric cells using  $Bi_2O_3@Co/N-PC$  and Co/N-PC electrodes under the voltage window of -1 to 1 V at a scan rate of 2 mV s<sup>-1</sup>.

To further analyze the influence of different system on the redox process of lithium polysulfides, we assembled symmetrical cells using  $Bi_2O_3@Co/N-PC$  and Co/N-PC as electrodes with electrolytes containing 0.2 M of  $Li_2S_6$ . CV was conducted on these symmetrical cells to analyze the redox behavior of  $Li_2S_6$ . As shown in Figure 12, the redox currents of  $Li_2S_6$  in  $Bi_2O_3@Co/N-PC$  hybrid system are much larger than that of the Co/N-PC, indicating the best catalytic activity of  $Bi_2O_3@Co/N-PC$  for the redox of lithium polysulfides.



**Figure S13.** Co/N-PC@S electrode galvanostatic discharge–charge voltage profiles at 0.25 C from the 2nd cycle to the 250th cycle.



Figure S14. CV curves of (a)  $Bi_2O_3@Co/N-PC@S$  and (b) Co/N-PC@S before and after 500 cycles under 2 mV s<sup>-1</sup>.

Figure S14 shows both of two electrodes occurred hysteresis, anodic and cathodic peaks migrated positive and negative after long cycles. It meant the kinetics of electrode reaction became dully. Meanwhile the intensity of anodic peak for two electrodes both evolved weaker after 500 cycles. it proved that transmission reaction would not sufficient with increasing of cycles, this is main reason that capacity of high voltage plateau became fewer and fewer.



**Figure S15.** (a) High discharge plateau voltage and (b) low discharge plateau voltage of Bi<sub>2</sub>O<sub>3</sub>@Co/N-PC@S and Co/N-PC@S electrodes at different C rates.

Figure S15 shows the high and low discharge plateau voltages of Bi<sub>2</sub>O<sub>3</sub>@Co/N-PC@S and Co/N-PC@S electrodes at different C-rates. Low discharge plateau voltage of Co/N-PC@S changed from 2.09 V at 0.25 C to 1.99 V at 2 C, decreased about 4.8%. The Bi<sub>2</sub>O<sub>3</sub>@Co/N-PC@S system displays much better performance, from 2.12 V at 0.25 C to 2.06 V at 2 C, decreased 2.8%, indicating the low polarization and fast redox reaction by synergistic efficiency between bismuth oxides and carbon matrix.



**Figure S16.** (a) adsorption ability tests of the bare representative lithium polysulfide  $Li_2S_6$ , (b) adsorption ability tests of bismuth oxide with the representative lithium polysulfide  $Li_2S_6$ , (c) adsorption ability tests of Co/N-PC with the representative lithium polysulfide  $Li_2S_6$ .



**Figure S17.** (a, b) TEM images of Co/N-PC@S and the corresponding (c) charge density maps reconstructed from the region as red dot rectangle marked in (a); (d) the charge density variation of the boundary of Co/N-PC@S extracted from the region as the white arrow marked in (c).

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