

Supplementary Material for

Synthesis of CoP@B, N, P co-doped porous carbon by supramolecular gel self-assembly method for lithium-sulfur batteries separator modification

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Detailed Experimental Section

Fabrication of CoP@BNPC composite material

Typically, 5 g sodium chloride (NaCl), 2 g glucose ($C_6H_{12}O_6$), 2 g melamine ($C_3N_3(NH_2)_3$) and 0.6 g cobalt nitrate hexahydrate ($Co(NO_3)_2 \cdot 6H_2O$) were dissolved in 40 mL deionized water. After complete dissolution, 2 ml newly prepared sodium borohydride solution (0.25 g mL^{-1}) was slowly added and stirred 2 h in water bath ($50 \text{ }^\circ\text{C}$) to form a light green uniform solution. Next, phytic acid ($C_6H_{18}O_{24}P_6$) was slowly added to form blue gel. Then the gel was transferred to Freeze dryer, the products after drying were ground to powder and $900 \text{ }^\circ\text{C}$ heat-treated at a heating rate of $5 \text{ }^\circ\text{C min}^{-1}$ under N_2 atmosphere and kept for 2 h. The obtained mixture was washed several times to remove NaCl, was denoted as CoP@BNPC after drying. For comparison, the sample without the addition of sodium borohydride ($NaBH_4$), was denoted as CoP@NPC; the sample without the addition of cobalt nitrate was prepared by the N and P co-doped carbon nanosheet, was denoted as NPC.

Preparation of the functional separators

The CoP@BNPC/PE modified separator was prepared using the traditional blade coating process. The PVDF (10 %), SP (10 %) and CoP@BNPC (80 %) were dispersed in NMP solvent and through fully grind to form uniform slurry, the slurry was coated on PE separator. The thickness of coating was controlled Within $10 \text{ }\mu\text{m}$ and then vacuum drying, was denoted as CoP@BNPC/PE. For comparison, the CoP@NPC and NPC modified separator (CoP@NPC/PE and NPC/PE) was also fabricated using the same process, respectively.

Preparation of polysulfides solution

Li_2S (0.046 g) and S (0.16 g) were added into 10 ml DOL/DME solution ($v/v=1:2$, DOL = 1,3-dioxolane, DME =1,2-dimethoxyethane) in an Argon-filled glove box. Then the solution was stirred for 48 h to form Li_2S_6 (0.1 M) solution at room temperature.

Material Characterization

X-ray diffraction (XRD) patterns of CoP@BNPC particle were performed on a D8 Advance (Bruker) diffractometer. Raman spectroscopy (Renishaw Invia spectrometer) was used to analyze the defects and graphitization degree of carbon materials. The morphology of the modified separator was characterized by high-resolution transmission electron microscopy (HRTEM, JEOL JEM-2100) and field emission scanning electron microscopy (FESEM, SU8010). X-ray photoelectron spectroscopy (XPS) was used to observe the chemical composition and element content. Using Micromeritics

TriStar II type 3020 type physical adsorption instrument to carry out N₂ adsorption-desorption test under 77k, measured the Brunauer–Emmett–Teller (BET) specific surface area and pore size distribution. The contact between the separator and the electrolyte was measured using an optical contact analyzer (Theta) to characterize the lyophilic of different separators. The CoP content in the composites were determined by inductively coupled plasma optical emission spectrometry (ICP-OES, Thermo Fisher, iCAP 7600 ICP-OES).

Battery Assembly and Electrochemical Measurements

To evaluate the practical effect of the prepared composites separators, it was assembled in the 2032 coin-type batteries to test its charge/discharge and cycling performance. For symmetric battery assembly, two same NPC, CoP@NPC, CoP@BNPC electrode are used as cathode and anode, adding 40 μL Li₂S₆ as electrolyte and active substance. The CV of symmetric batteries test using a CHI760E electrochemical workstation at a scanning rate of 10 mV s⁻¹ from -1.0 to 1.0 V.

The S cathode was prepared using our previous report¹. Typically, 80 g CNTs slurry dispersed in N-Methyl pyrrolidone (NMP) with a solid content of 5 wt.%, 12 g sublimed sulfur and 80 g ammonium sulfide solution (20 wt.%) were dispersed into water and stirred for 4 hours. After that, the reaction mixture was spray dried (YC-018, Shanghai Pilotech Instrument Equipment Co., Ltd.). An inlet air temperature of 130 °C and a nozzle pressure of 0.2 M Pa were applied with a flow rate of 15 mL min⁻¹. The collected products were used as cathode materials without any treatment. According to our previous report, the sulfur content in the positive electrode material prepared by this method is 75 wt %. 80 wt % cathode material, 10 wt % Super P (SP) and 10 wt % polyvinylidene fluoride (PVDF) were mixed into the uniform slurry and coated on the Al foil. The active material loading of sulfur were controlled at ~ 2.0 mg cm⁻² and ~ 5.0 mg cm⁻². The batteries were assembled in an Argon-filled glove box using the S cathode, modified separators or PE as separator, and Li foil as anode, respectively. The mixed solution of 1.0 M LiTFSI and 0.1 M LiNO₃ in DOL/DME (1:1 by volume; LiTFSI= lithium bis(trifluoromethanesulfonyl)imide) as electrolyte. Electrolytes without LiNO₃ additives were used to study the coulombic efficiency of batteries. The solvents used are super dry solvents with water content less than 10 ppm. Finally, the diameter of the positive electrode in the coin cell was 12 mm, and the amount of electrolyte used was 40 μL and 60 μL for conventional (2.0 mg cm⁻²) and thick (5.0 mg cm⁻²) electrodes, respectively. Charge/discharge tests are then performed to

evaluate the cycle stability on a LAND testing system at different rate (0.1, 0.2, 0.5, 1, 2 and 5 C) and the voltage range is from 1.8 V to 2.8 V.

Computational Details

Using the Vienna ab initio simulation package (VASP) ²⁻³ with the projected-augmented-wave (PAW) approach ⁴, the ab-initio molecular dynamics (AIMD) simulation were performed based on the spin-polarized density functional theory (DFT) at the level of generalized gradient approximation (GGA) with the Perdew–Burke–Ernzerhof (PBE) functional ⁵. The van der Waals (vdW) interaction was included using the DFT-D3 method ⁶⁻⁷. The plane-wave cutoff was set as 400 eV, and the threshold convergence for energy was set at 1×10^{-5} eV. To investigate the adsorption of LiPSs by the modified separator. A 4×4 three-layer CoP (101) ⁸ supercell was combined with N, P co-doped graphene (6 N atoms and 6 P atoms are randomly substituted, as shown in Figure S1a) to form a heterojunction, denoted as CoP@NPC. According to the XPS results, three B atoms randomly replace the carbon atoms near the N atoms on the CoP@NPC substrate (Fig. S1b), denoted as CoP@BNPC. For this module, a vacuum layer of more than 15 Å above the surface was chosen to avoid the periodic interaction. The first Brillouin zone was sampled in the Monkhorst–Pack grid ⁹ with a $2 \times 2 \times 1$ k-points mesh for the AIMD calculations. We chose 10 Li_2S_4 molecules uniformly placed on the substrate employing the Nose-Hoover thermostat and canonical (NVT) ensemble, the slab with molecules under 300 K a 30.0 ps and the time step was set to 2.0 fs AIMD based on density functional theory (DFT) was calculation. The mean square displacement (MSD) of Li and S atoms were calculated by vaspkit¹⁰ based on the AIMD results. The diffusion coefficient is defined as ¹¹

$$D = \lim_{t \rightarrow \infty} \left[\frac{1}{2dt} \langle [\vec{r}(t)]^2 \rangle \right],$$

where d equals to the dimension of the lattice and equals to 3 in this work. In brief, the slope of MSD divided by 6 equals the diffusion coefficient.

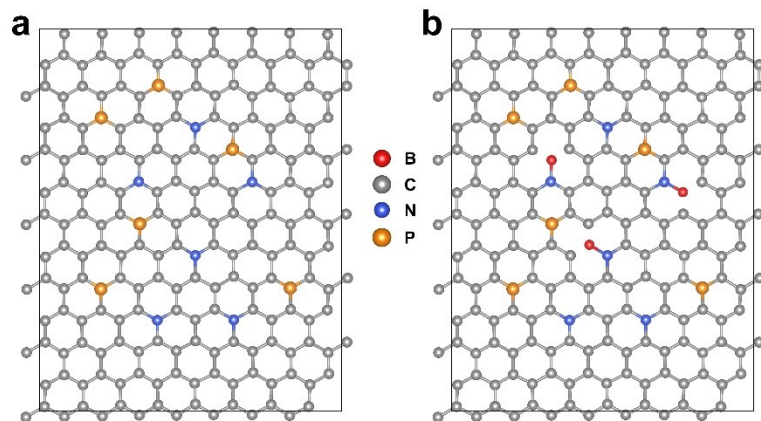


Figure S1. Initial structure of NPC (a) and BNPC (b).

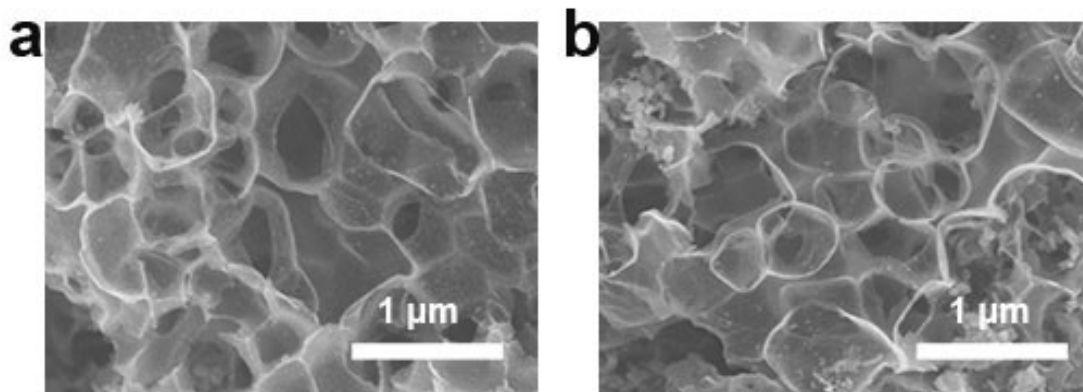


Figure S2. The SEM image of NPC and CoP@NPC material after removing the template

Table S1. ICP-OES results of CoP@NPC and CoP@BNPC.

Sample Name	m ^a / g	<i>C</i> _{Co} / mg L ⁻¹	CoP / wt%
CoP@NPC	0.1053	25.7	18.6
CoP@BNPC	0.1045	26.4	19.3

^a m – mass of sample consumed in the digestion process

For the ICP-OES measurements, the samples were dissolved in concentrated nitric acid (Guarantee reagent; Sinopharm Chemical Reagent Co., Ltd.) and diluted with a 2% HNO₃ solution to 500 mL.

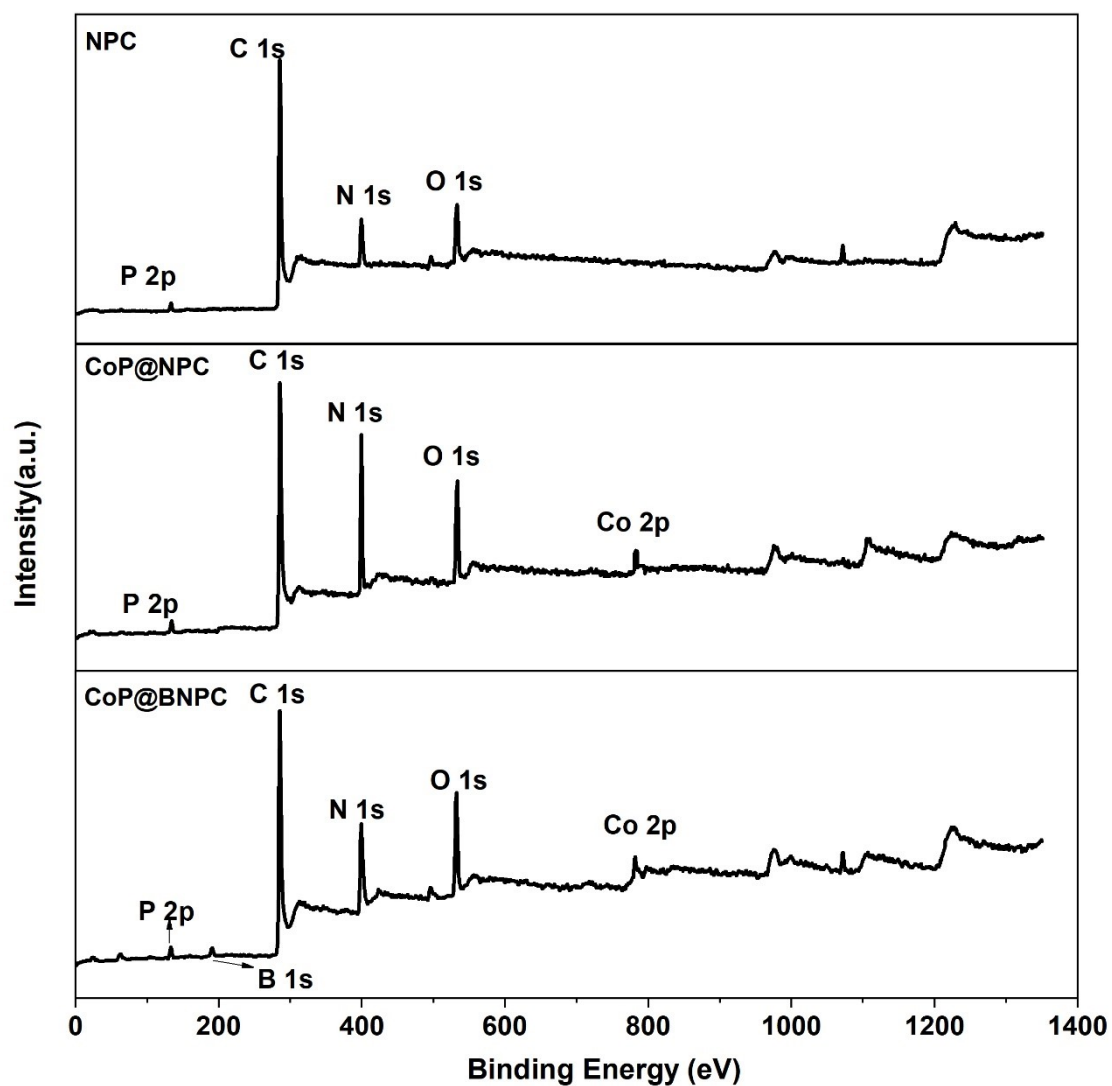


Figure S3. The XPS survey spectrum of NPC, CoP@NPC and CoP@BNPC.

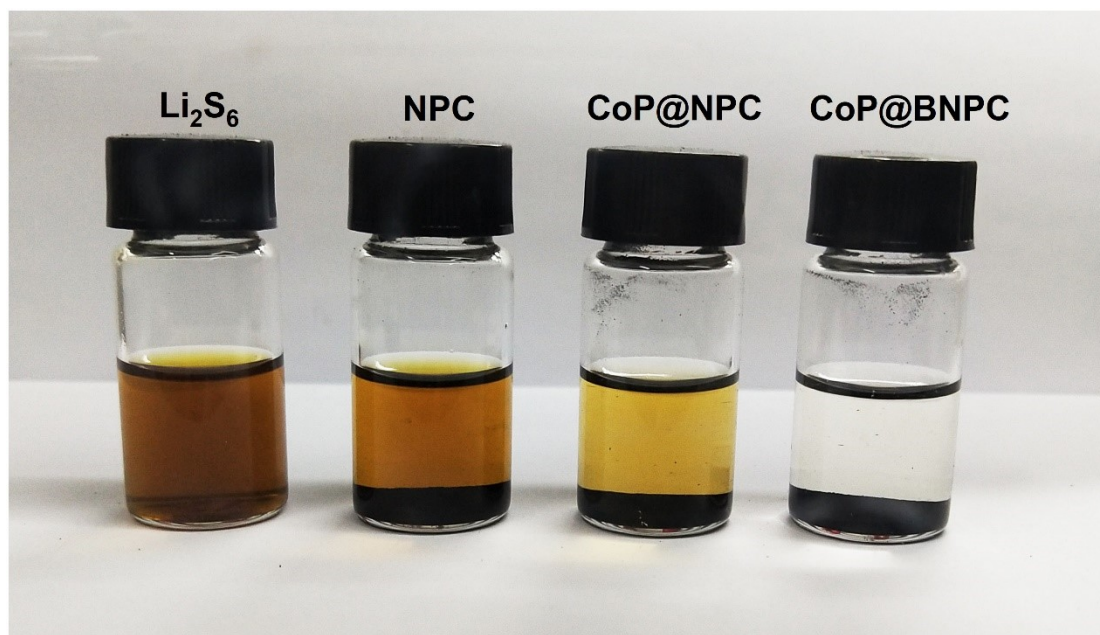


Figure S4. The adsorption experiment of the different materials.

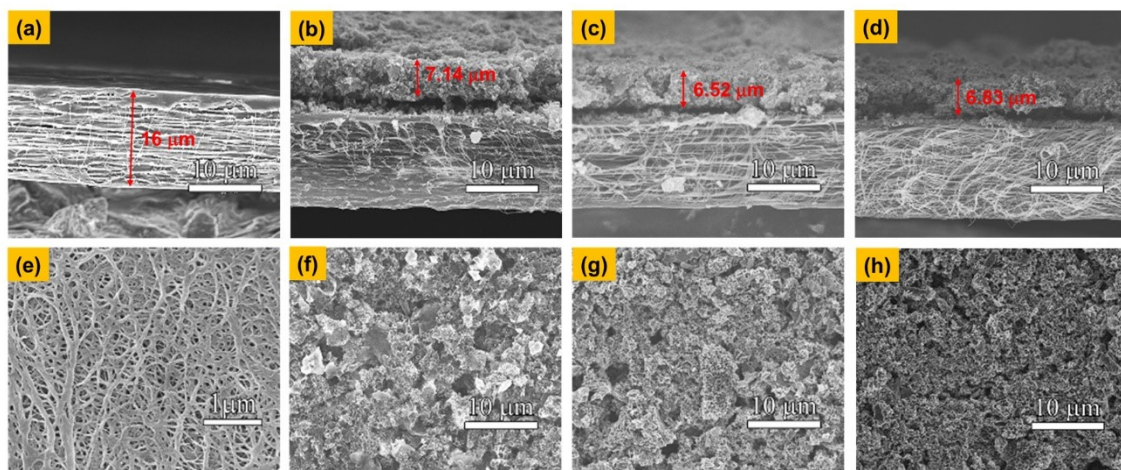


Figure S5. The cross-section and surface morphology of several different separators.

Table S2. Diffusion coefficient of Li and S atom on different substrate.

	Li atom		S atom	
	Slope	diffusion coefficient ($\text{cm}^2 \text{s}^{-1}$)	Slope	diffusion coefficient ($\text{cm}^2 \text{s}^{-1}$)
CoP@NPC	1.256	2.09×10^{-5}	1.268	2.11×10^{-5}
CoP@BNPC	0.412	6.87×10^{-6}	0.316	5.27×10^{-6}

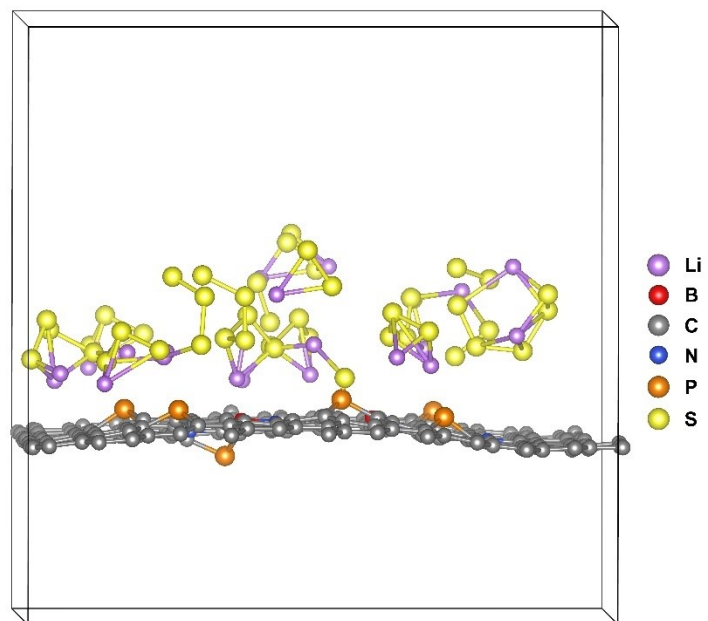


Figure S6. Geometric model of LiPS on BNPC after AIMD simulation.

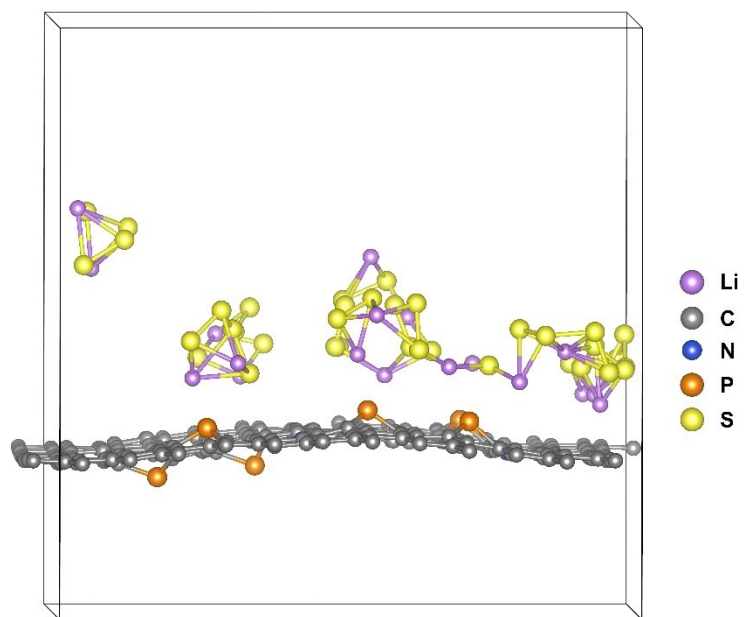


Figure S7. Geometric model of LiPS on NPC after AIMD simulation.

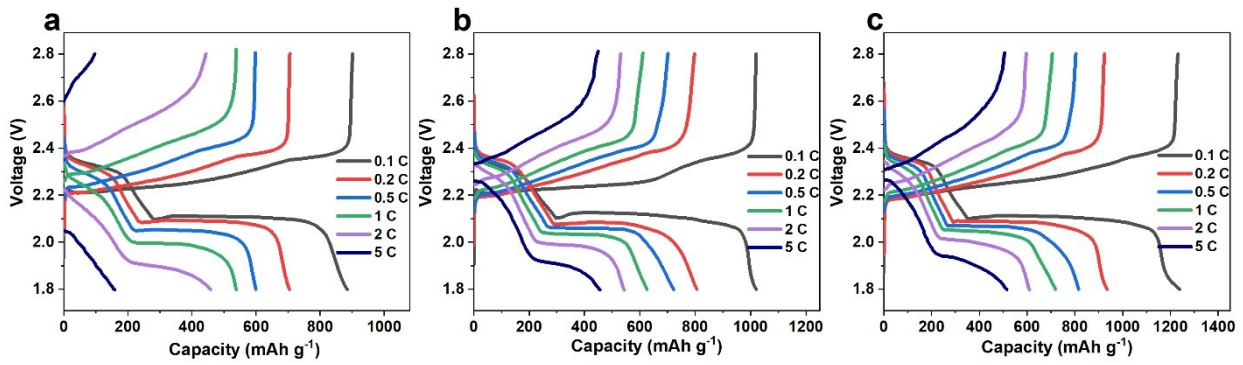


Figure S8. The charge and discharge curves of different rates with PE (a), NPC/PE (b), CoP@NPC/PE (c).

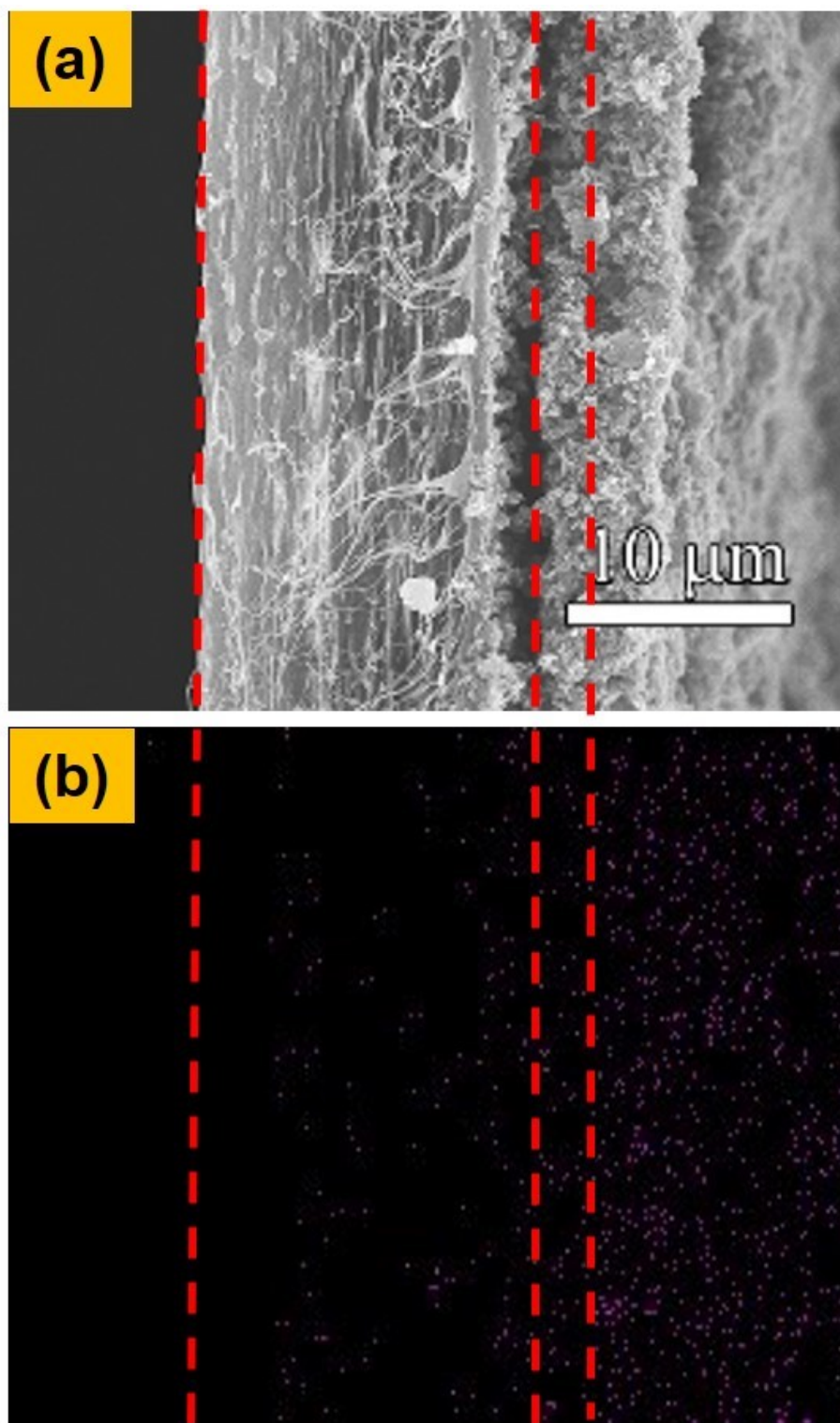


Figure S9. The cross-section of CoP@BNPC/PE separators (a) and element mapping of sulfur (b) after charge-discharge cycling.

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