

Supporting Information

Ultrafine Ni₁₂P₅ nanoparticle-embedded carbon with high catalytic activity sites as separator modifier towards high-performance lithium-sulfur batteries

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Experimental Section

Synthesis of PAA-NH₄ NSs: At first, PAA aqueous solution (0.2 g mL⁻¹, 1 mL), NH₃·H₂O (2 mol L⁻¹, 1.3 mL) were added to 100 mL of deionized water under ultrasonic sound for 30 min in a 500 mL conical flask. Afterwards, 400 mL of IPA was added dropwise to the flask by continuous uniform stirring. The solution gradually changed from colorless to milky white. The obtained PAA-NH₄ NSs were stirred at room temperature for further experiments.

Synthesis of MCNSs: The uNi₁₂P₅/C NSs was washed in HCl aqueous solution, the as-synthesized uNi₁₂P₅/C NSs were converted into acid-etched mesoporous carbon nanospheres (MCNSs).

Preparation of the CNTs/S cathode: The sulfur and CNTs were mixed at a mass ratio of 8:2 and ground in a mortar for 30 min. Then, the mixture was sealed in a vacuum glass tube and heated at 155 °C for 12 h to obtain CNTs/S powder. Then, the obtained CNTs/S, CNTs and PVDF were mixed in NMP at a mass ratio of 8:1:1. After stirring for 12 h, the slurry was uniformly coated on the carbon-coated aluminum foil and dried in vacuum at 80 °C overnight. The sulfur loading of the cathode is 1.0-1.5 mg cm⁻².

Characterization: Transmission electron microscopy (TEM) was performed using a JEOL-100CX transmission electron microscope at 80 kV (Hitachi, Japan). High-resolution transmission electron microscope (HR-TEM) characterizations were performed with a TECNAI G2 F20 transmission electron microscope at 200 kV accelerating voltage. Scanning electron microscopy (SEM) images were obtained by using an XL30 ESEM-FEG field emission scanning electron microscope (FEI Co.). The X-ray photoelectron spectrum (XPS) was performed with an ECSALAB 250 by using non-monochromated Al-K α radiation. N₂ adsorption-desorption measurements were performed using an intelligent gravimetric analyzer ASAP-2020M. Raman spectra

were recorded at room temperature with a JY HR-800 LabRam confocal Raman microscope in a backscattering configuration with an excitation wavelength of 488 nm. The X-ray diffraction (XRD) patterns were obtained on a D8 Focus diffractometer with Cu-K α radiation ($\lambda=0.15405$ nm). The thermogravimetric analysis (TGA) was carried out on a Shimadzu DTG-60H analyzer heated from room temperature to 600 °C at a ramp rate of 5 °C min⁻¹ under Ar.

Electrochemical Measurements: The CR2025 coin cell was assembled with CNTs/S cathode, lithium anode, and uNi₁₂P₅/C//PP modified separator for electrochemical measurements. The electrolyte/sulfur ratio was 20 μ L mg⁻¹. A solution of 1.0 mol L⁻¹ bis (trifluoro-methane) sulfonamide lithium (LiTFSI) dissolved in a mixed solvent of 1,2-dimethoxyethane (DME) and 1,3-dioxolane (DOL) with a 1:1 volume ratio containing LiNO₃ (0.1 mol L⁻¹) was used as the electrolyte. The electrochemical tests were carried out using Land CT2001 test station at different current densities with a potential window of 1.7-2.8 V vs Li/Li⁺. The CV curves were collected on a CHI760E electrochemical workstation at a scan rate of 0.1 mV s⁻¹ between 1.7 and 2.8 V.

Lithium Polysulfides Adsorption Test: The Li₂S₆ solution was prepared by dissolving stoichiometric amounts of Li₂S and sulfur with the molar ratio of 1:5 in 1,2-Dimethoxyethane (DME). The mixed solution was then magnetically stirred in an argon-filled glove box at 80 °C for 24 h. The uNi₁₂P₅/C NSs (20 mg), MCNSs (20 mg), or CNTs (20 mg) was dispersed to the 5 mL of Li₂S₆ solution (2 mM) for 12 h.

Assembly of Li₂S₆ Symmetric Cells and Kinetic Study: The electrode of symmetric cells was fabricated without the presence of elemental sulfur. Host materials (uNi₁₂P₅/C NSs or CNTs) and PVDF binder were mixed into the NMP with a weight ratio of 9:1 and then coated onto the electrodes. Li₂S₆ catholyte was prepared by adding Li₂S and S into Li-S electrolyte at a molar ratio of 1:5 (60 °C for 24 h). 30 μ L 0.5 M Li₂S₆ catholyte

was added into each coin cell. CV curves were measured at a scan rate of 50 mV s⁻¹ in a potential window of -1.0 to 1.0 V.

Measurement of the Lithium Sulfide Nucleation: Li₂S₈ catholyte was prepared by adding Li₂S and S into Li-S electrolyte with a molar ratio of 1:7 in tetraglyme with extra 1.0 mol L⁻¹ LiTFSI under continuous magnetic stirring for 24 h. 20 μL of the Li₂S₈ electrolyte was dropped onto the uNi₁₂P₅/C or CNTs cathode, while 20 μL blank electrolyte without Li₂S₈ was added to the anode side. The cell was first discharged at the current of 0.112 mA until the voltage reached 2.06 V, then held the voltage at 2.05V until the current decreased to 10⁻² mA.

Permeation Tests of LiPSs: The permeation tests were conducted with H-type sealed electrolytic cell. The Li₂S₆ solution was injected into the left side of the H-shaped glass tube, while the DME solution was injected into the other side without Li₂S₆. The solution was separated by the pristine separator, uNi₁₂P₅/C//PP modified separator, respectively. Digital pictures were recorded every 3 h to compare the infiltration of polysulfide.

Computational methods: All the calculations were performed within the framework of the density functional theory (DFT) as implemented in the Vienna Ab initio Software Package (VASP 5.4.4) code within the Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation and the projected augmented wave (PAW) method. The cutoff energy for the plane-wave basis set was set to 450 eV. The Brillouin zone of the surface unit cell was sampled by Monkhorst-Pack (MP) grids, with k-point mesh density of $2\pi \times 0.04 \text{ \AA}^{-1}$ for structures optimizations. The convergence criterion for the electronic self-consistent iteration and force was set to 10⁻⁵ eV and 0.01 eV/Å, respectively. The vacuum layer of 15 Å was introduced to avoid interactions between periodic images.

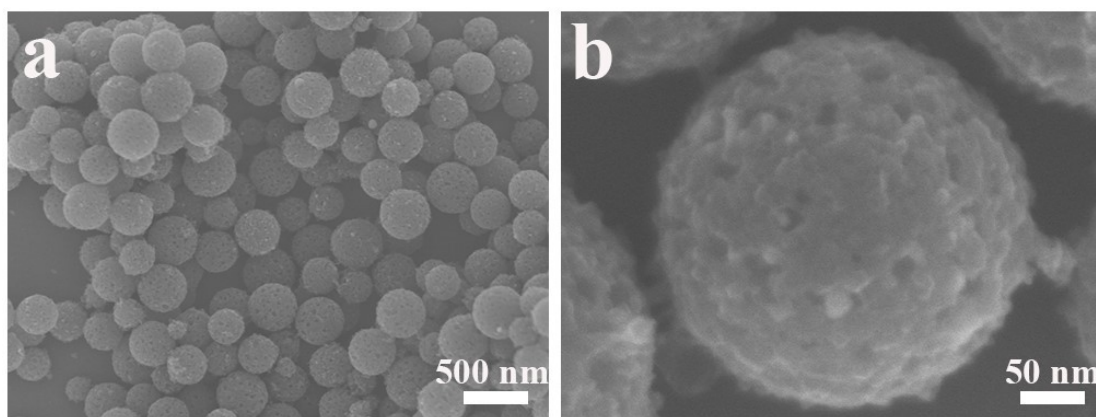


Fig S1. (a and b) SEM images of MCNSs.

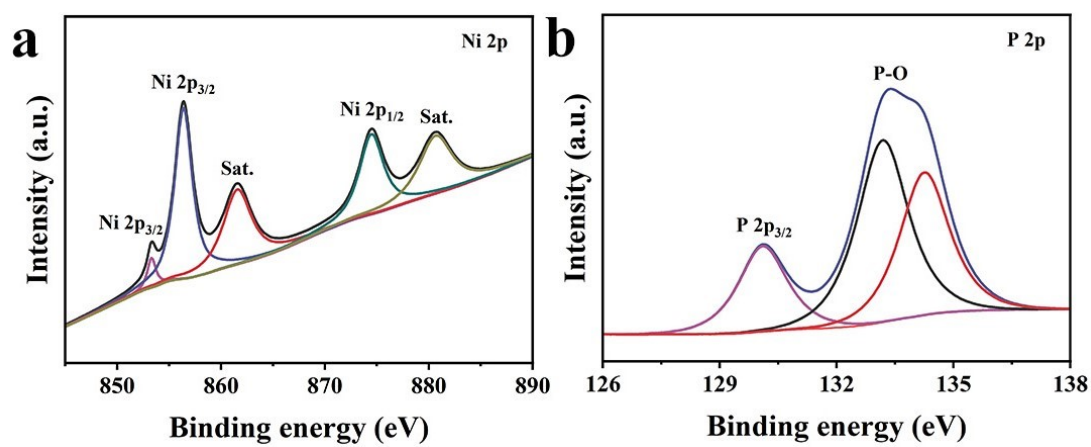


Fig S2. XPS survey spectrum of $\text{uNi}_{12}\text{P}_5/\text{C}$ NSs. (a) Ni 2p and (b) P 2p fitting spectra.

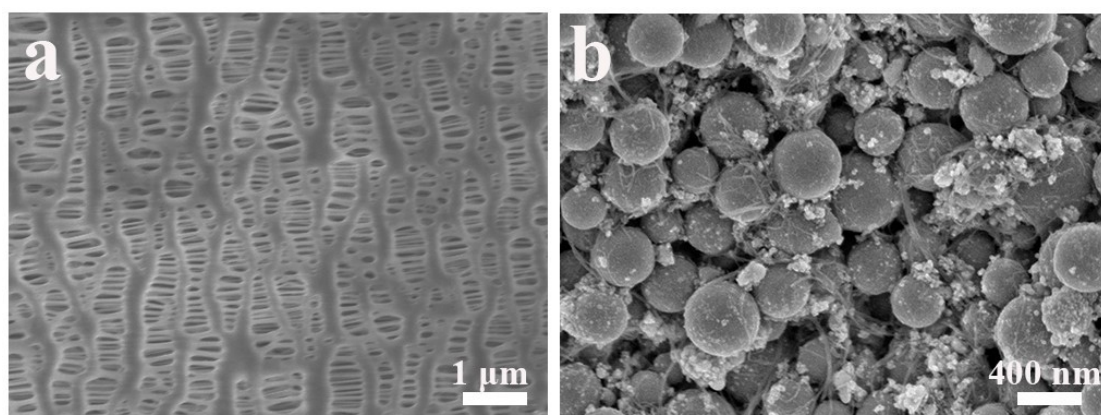


Fig. S3. SEM images of (a) PP separator, (b) modified layer images.

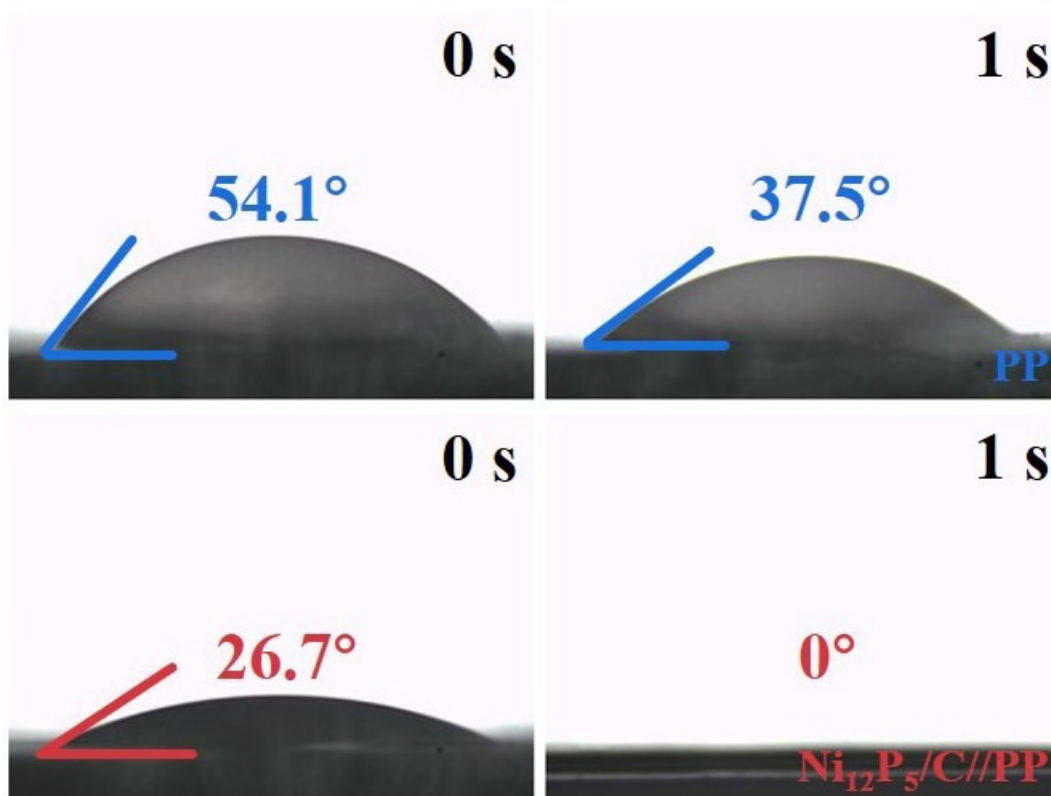


Fig. S4. The electrolyte contact angles of the pristine PP and uNi₁₂P₅/C//PP separator.

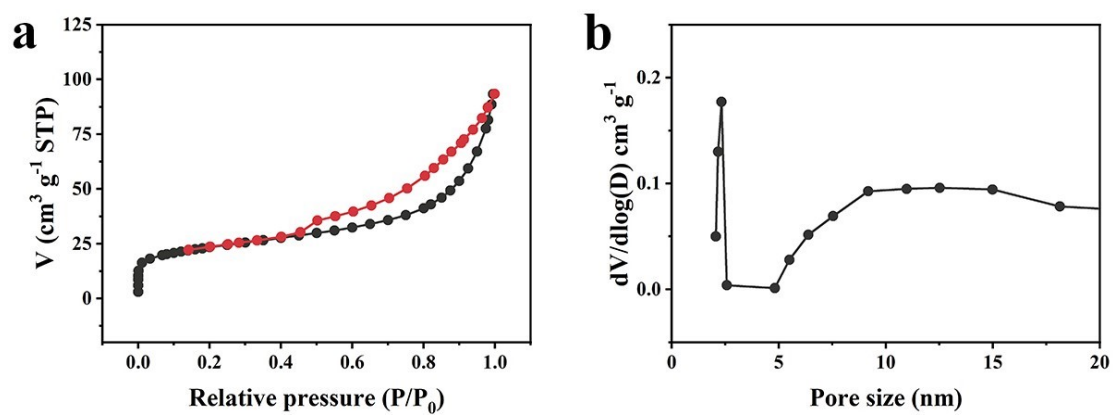


Fig. S5. (a) N₂ adsorption-desorption isotherm of uNi₁₂P₅/C NSs. (b) pore size distributions plot of uNi₁₂P₅/C NSs.

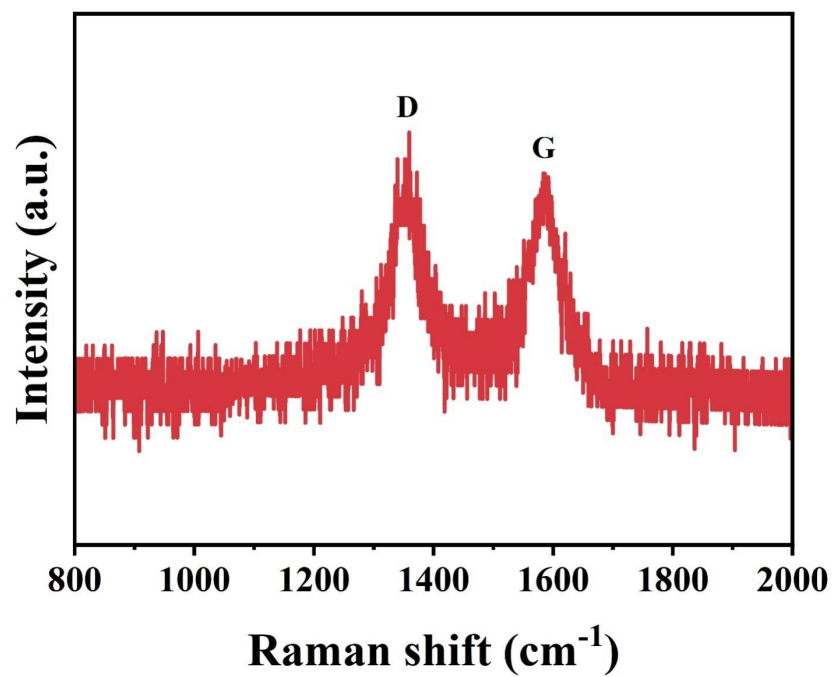


Fig. S6. Raman spectrum of uNi₁₂P₅/C.

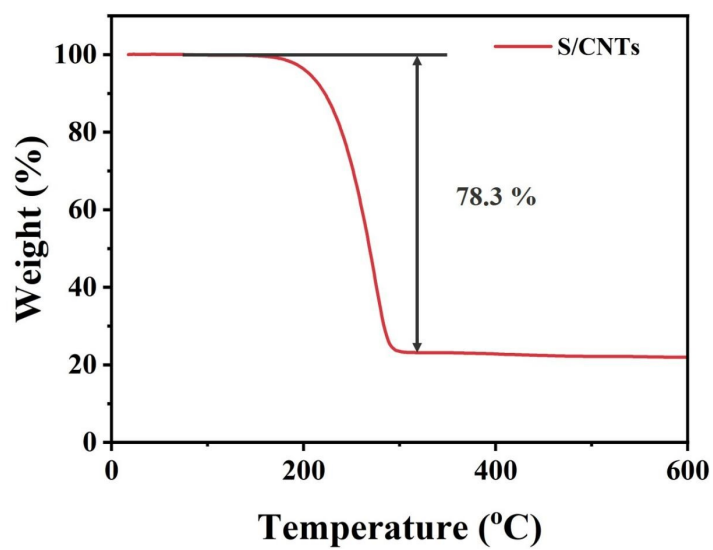


Fig. S7. TGA patterns of CNTs/S.

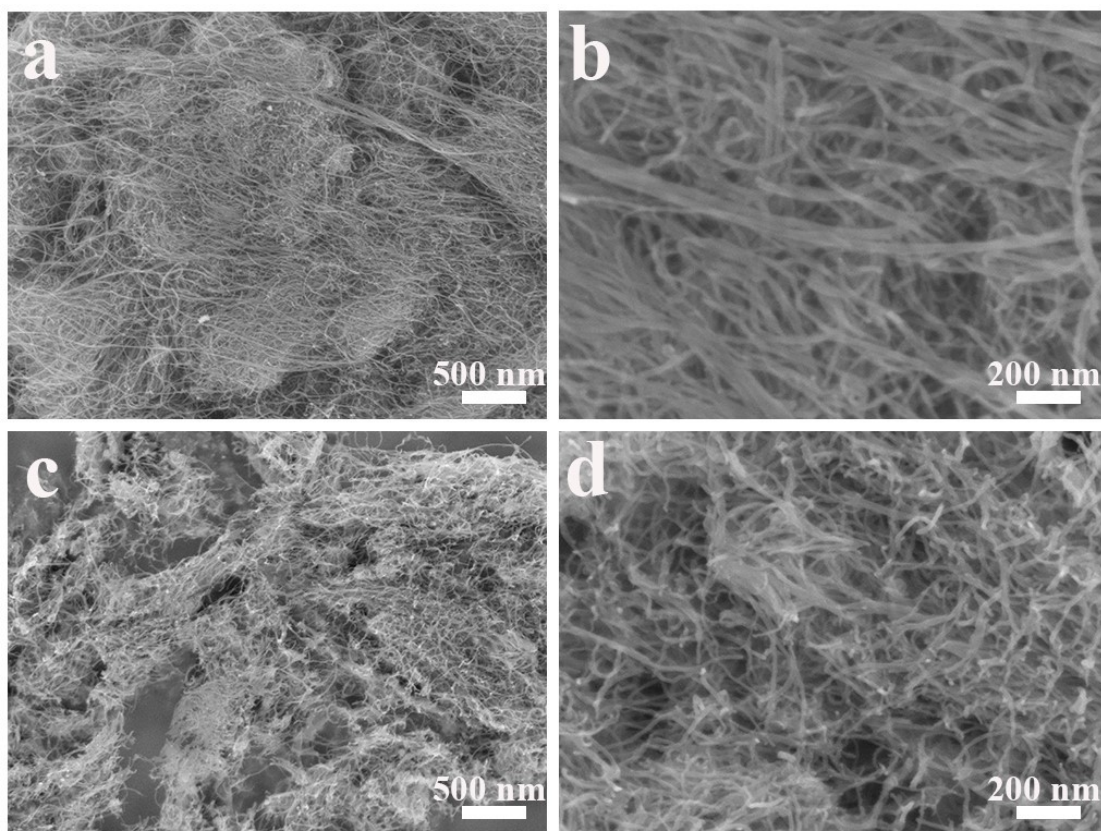


Fig. S8. SEM images of (a-b) CNTs and (c-d) CNTs/S.

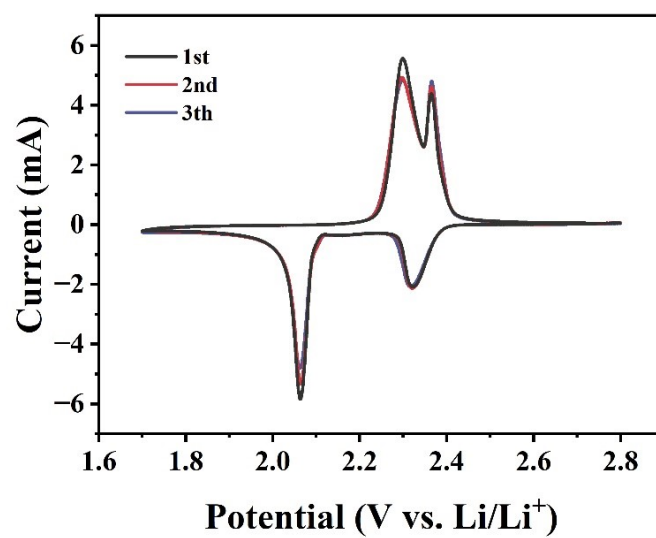


Fig. S9. CV curves of the first three cycles of $\text{uNi}_{12}\text{P}_5/\text{C}/\text{PP}$ cell.