Supporting Information


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Experimental Section

Materials preparation

Preparation of HPCC: In a typical experiment, 25 g Ni(NO\textsubscript{3})\textsubscript{2}·6H\textsubscript{2}O solution (20 wt \%) was added into 50 g NaOH solution (10 wt \%), and then suffered a continuously stirring for 4 h for the uniformly formation of Ni(OH)\textsubscript{2} dispersion. Then, 25 g ethanol solution of phenolic resin (20 wt \%) was droply added in above dispersion under intense stirring. The formed uniform mixture was evaporated at 60 °C to remove solvent, and then was carbonized under a mixture atmosphere (5\% H\textsubscript{2} -95\% Ar) via a 2 h heat treatment under 200 °C and a following 4 h pyrolysis under different temperatures of 500, 600, 700 and 800 °C. Finally, the obtained products were washed with 3 M HCl solution and deionized water and then dried at 80 °C. The final products prepared at different pyrolysis temperature are denoted HPCC-500, HPCC-600, HPCC-700 and HPCC-800. For comparison, the hierarchical porous carbon with few CNTs (denoted HPC) was prepared with a pyrolysis temperature of 600 °C in the pure Ar atmosphere.

Preparation of HPCC-S hybrid: 65 wt \% sulfur and 35 wt \% HPCC were uniformly mixed through grinding and then this mixture was heated at 155 °C for 12 h in a sealed vessel filled with N\textsubscript{2} protection. Then, the temperature was increased to 250 °C and kept for 0.5 h to vaporize the superfluous sulfur on the outer surface of the HPCC. After cooling down to the room temperature, the HPCC-S hybrids were obtained.

Materials characterization

All as-prepared materials were characterized by wide angle X-ray diffraction (XRD,
Rigaku), scanning electron microscopy (SEM, HITACHI-4800) equipped with an
energy-dispersive X-ray spectroscopy (EDS), transmission electron microscopy (TEM,
FEI TECNAIG2 F30) and thermogravimetric analysis (TG-DSC, Netzsch, STA449).
Raman spectra was recorded with a HORIBA HR800 using 532 nm incident radiation.
The surface area and pore volume of the samples were determined by nitrogen gas
adsorption at 77 K with an automated adsorption apparatus (Micrometrics, ASAP
2020). The surface area was determined from the Brunauer-Emmett-Teller (BET)
equation and pore size distribution (PSD) of HPCC was calculated based on
adsorption-desorption using the density functional theory (DFT).

Electrochemical measurements
The electrode was prepared by mixing the HPCC-S, carbon black, and polyvinylidene
difluoride (PVDF) with a weight ratio of 8:1:1 in N - methyl pyrrolidone (NMP)
solvent to form a slurry. Then the slurry was coated onto a carbon-coated aluminum
foil using a doctor blade and dried at 60 °C under vacuum for 10 h. The mass loading
of sulfur in the obtained cathode is ~1.0 mg cm$^{-2}$. The coin cell (CR2032) with a
metallic lithium anode was assembled in an Ar-filled glove box (Mbraun) to evaluate
the electrochemical performance of the as-obtained sample. The microporous
polypropylene sheet (Celgard 2500) was used as the separator. The electrolyte was
1M bis (trifluoromethane) sulfonamide lithium salt (LiTFSI) dissolved in a mixture of
1,2-dioxolane(DOL) and dimethoxymethane(DME) (1:1 by volume) with adding 1 wt %
LiNO$_3$. The electrolyte added in each coin cell was about 40 μL. Cyclic voltammetry
(CV) experiment and electrochemical impedance spectroscopy (EIS) were carried out
using electrochemical workstation (PRASTAT P4000). The galvanostatic charge/discharge performance test and the rate capability at different C-rates were performed using a Land 2001A cell test system (Wuhan, China) at 298K. The EIS spectra were obtained in the frequency range of 100 kHz to 10 MHz with an AC voltage amplitude of 5 mV at the open-circuit potential.

7 Supplementary Figures

Fig. S1 XRD patterns of the uncarbonized phenolic resin/ Ni(OH)$_2$ precursor, HPCC before and after washing. Na$_2$CO$_3$ was formed by the CO$_2$ from the decomposition of phenolic resin with Na$^+$ ions. Besides, Ni(OH)$_2$ was decomposed into NiO and then reduced into Ni by the formed carbon and H$_2$ under high temperature.
Fig. S2 SEM image of HPCC particles with the size of about 1-3 μm.

Fig. S3 HRTEM images of HPCC obtained at different temperature. With the increasing temperature, the thickness of CNTs wall decreases and the graphitic degree of CNT wall increases.
Fig. S4 TG curve of HPCC-600 in air atmosphere with a heating rate of 5 °C min⁻¹.

Fig. S5 TG curves of HPCC-600-S hybrid and pure sulfur under N₂ atmosphere with a heating rate of 5 °C min⁻¹.
Fig. S6 Cycling performance of HPCC-S cathodes at current density of 0.5 C.

Fig. S7 Rate performance of HPCC-S under different current densities.
Fig. S8 CV profiles of HPC-S with a scan rate of 0.1 mV s^{-1}

Fig. S9 Charge-discharge profiles of HPC-S at different rates

Table S1 EDS analysis of HPCC-600

<table>
<thead>
<tr>
<th>Element</th>
<th>C</th>
<th>O</th>
<th>Ni</th>
<th>Na</th>
</tr>
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<tbody>
<tr>
<td>Weight Ratio (%)</td>
<td>87.6</td>
<td>11.6</td>
<td>0.6</td>
<td>0.2</td>
</tr>
</tbody>
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