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Sulfur Encapsulated in Porous Hollow CNTs@CNFs for High-Performance Lithium-Sulfur Batteries

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Experimental:

Materials

Polyacrylonitrile (PAN, Mw=150 000, Aldrich), polymethylmethacrylate (PMMA, Tokyo Chemical Industry Co., Ltd), nickel acetate ($Ni(Ac)_2 \cdot 4H_2O$, Advtechind), dimethylformamide (DMF, Aldrich).

Encapsulation of sulfur in porous hollow CNTs@CNFs

First, PAN/PMMA/$Ni(Ac)_2$ composite nanofibers were prepared by coaxial electrospining, where the inner and outer solution was PMMA solution (0.5 g) in DMF (10 mL) and a mixture of $Ni(Ac)_2 \cdot 4H_2O$ (1 g) and PAN (1 g) in DMF (20 mL), respectively. The tip-collector distance, flow rate for the coaxial solutions, and high voltage were fixed at 20 cm, 0.03 mm min^{-1}, and 21 kV, respectively (KATO Tech

Co., Ltd). PMMA could be distributed in the PAN matrix during the electrospinning process because of the use of the same DMF; thus PAN/Ni(Ac)$_2$/PMMA composite nanofibers were prepared. Second, the prepared nanofibers were pyrolyzed at 700 ºC in H$_2$(5 vol %)/N$_2$(95 vol %) for 6 h and then heated in vacuum for 6 h to produce CNTs@CNFs@Ni. A mixture of CNTs@CNFs@Ni and KOH (CNTs@CNFs@Ni:KOH=1/4, weight ratio) was heated at 750 °C for 1 h in a tube furnace under a nitrogen atmosphere. The resultant mixture was further treated with HNO$_3$ to remove the Ni particles to achieve porous hollow CNTs@CNFs. Third, the porous hollow CNTs@CNFs (60 mg) and sulfur (160 mg) were mixed together and treated in quartz tubes that were sealed under vacuum at 400 °C for 24 h to facilitate sulfur diffusion into the resulting carbon matrix. Finally, the composite materials were treated at 200 °C to vaporize the sulfur on the surface of the porous hollow CNTs@CNFs, denoted as CNTs@CNFs-S.

Characterization

The obtained materials were characterized by X-ray diffraction (XRD, Philips, X'Pert Pro MPD), transmission electron microscopy (TEM), high-resolution TEM (HRTEM, JEOL 2010F, Japan), energy-dispersive X-ray spectroscopy (EDS, Oxford), electron energy loss spectroscopy (EELS, Gatan, Enfina), and X-ray photoelectron spectroscopy (XPS, Kratos Axis 165, Manchester), respectively. The N$_2$ adsorption and desorption isotherms at 77 K were determined (Quantachrome, Autosorb-iQ) and the pore-size distribution was calculated by the Barrett-Joyner-Halenda (BJH) method. Thermogravimetric analysis (TGA, Perkin-Elmer) was performed in a flow of N$_2$ with a heating rate of 5 °C min^{-1}.

Electrochemical testing

The cathode electrode was fabricated by mixing the prepared materials (80 wt.%), carbon black (10 wt.%) and poly(vinyl difluoride) (10 wt.%, PVDF) binder. Carbon-black (CB)/sulfur composites were also prepared for comparison. Two-electrode coin cells with activate materials as cathode and lithium foil as anode were assembled for electrochemical testing. The electrolyte was a mixture of 1.5 M

$LiCF_3SO_3$ and 0.1 M $LiNO_3$ salts into a 1:1 vol/vol mixture of 1,2-dimethoxyethane and 1,3-dioxolane. Charge and discharge were conducted by using an Arbin automatic battery cycler at various current densities within a voltage range of 1.5-3 V. The cyclic voltammetry (CV) measurement was performed on a Solartron SI 1287 electrochemical workstation at a scan rate of 0.1 mV s^{-1}. The specific capacity was calculated based on the mass of sulfur.

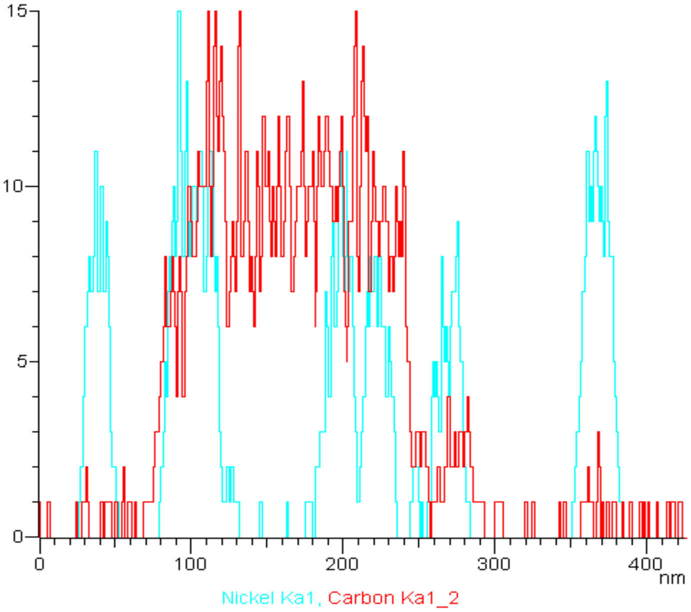

Figure S1. EDS line-scan profiles of the CNT@CNF@Ni.

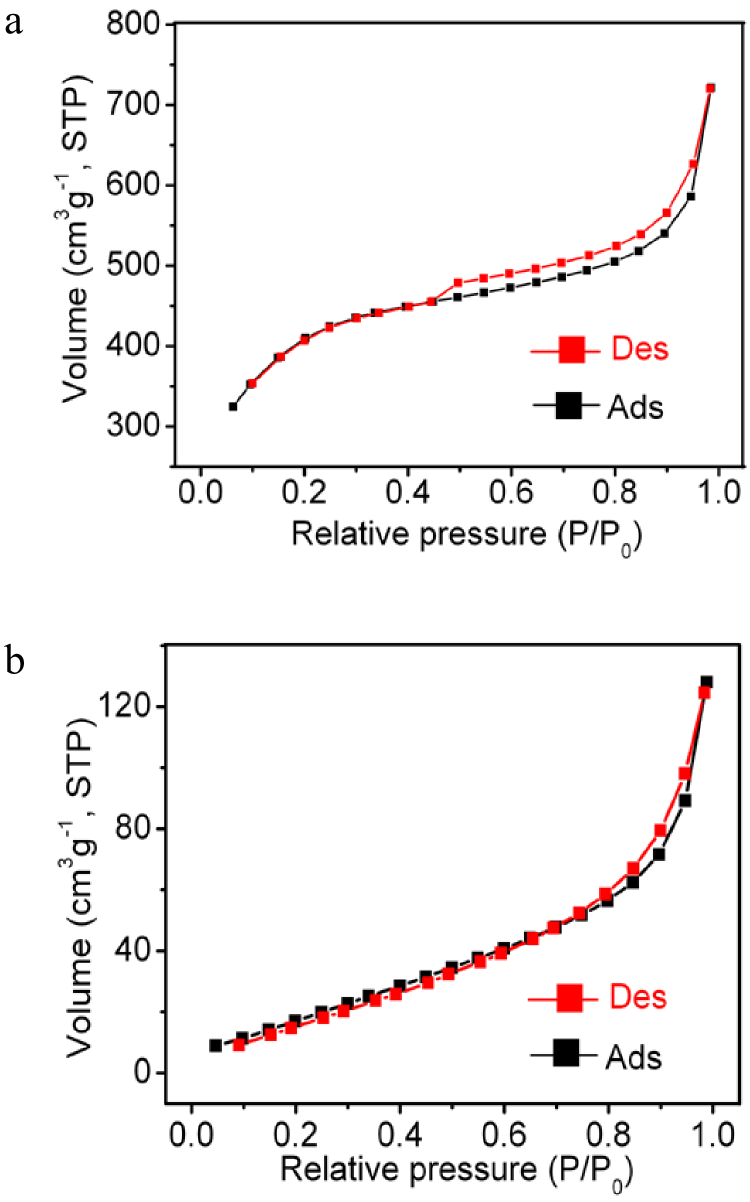

Figure S2. Nitrogen adsorption-desorption isotherms of the porous hollow CNTs@CNFs and CNTs@CNFs-S.

a

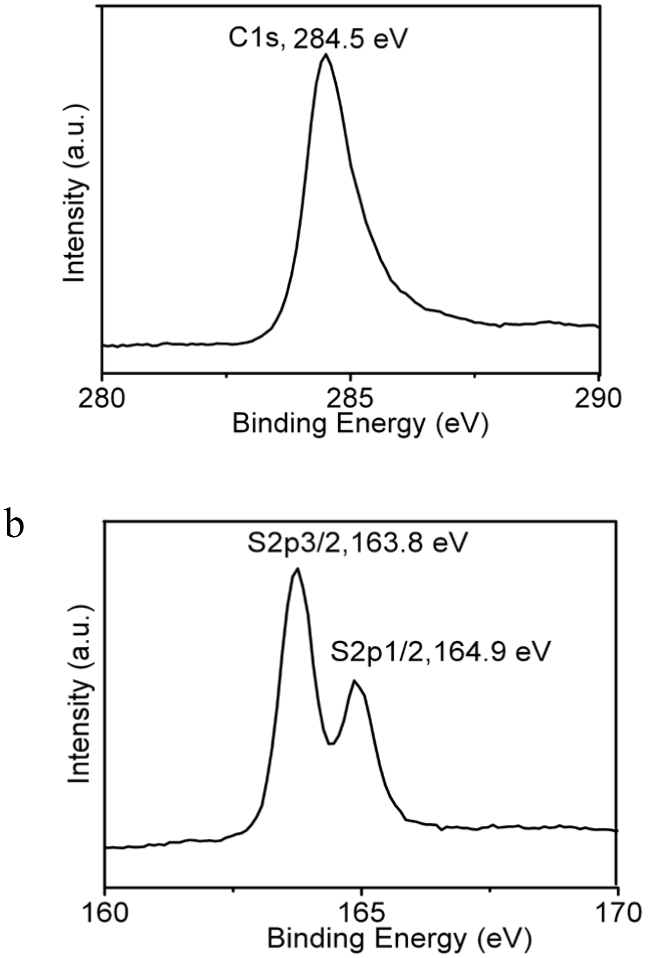

Figure S3. XPS spectra of porous hollow CNTs@CNFs-S. (a) C1s spectra and (b) S2p spectra.

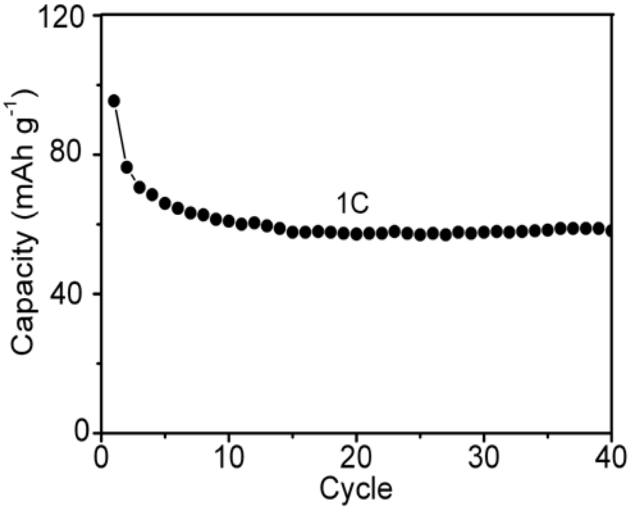

Figure S4. Cycling stability of CB-S electrode at 1 C