Electronic Supplementary Material (ESI) for Materials Chemistry Frontiers.

Experimental

Materials

3,3’,4,4’-biphenyl tetracarboxylic dianhydride (BPDA, >99.5%, Changzhou Sun Chem Chemical Co., Ltd.), p-phenylenediamine (PPD, >99%, Wuxi Changan Fine Chemical Factory), N,N-dimethylformamide (DMF) (Xilong Chemical Co., Ltd), potassium permanganate ($KMnO_4$, Sigma-Aldrich), lithium sulfide (Li_2S, 99.9%, Sigma-Aldrich) and sulfur (S, 99.5%, Aladdin Co. Ltd.) were used as received.

Preparation of MnO_2/N-rich CNF

BPDA and PPD (with a molar ratio of 1.05:1) were added to DMF in sequence to get a 13 wt% electrospinning solution. The blended solution was stirred at 0 °C for 12 hours. Electrospinning parameters were set as follows: applied voltage of 20-25 kV, tip-to-collector distance of 25 cm and flow rate of 0.8 ml h^{-1}. As-spun fibers were heated in a horizontal tubular furnace. Temperature of the furnace was first increased from room temperature to 250 °C at the rate of 5 °C min^{-1} and maintained for 0.5 hour in air flow. Then the temperature was increased to 370 °C at the rate of 1 °C min^{-1} and maintained for 0.5 hour. Then the temperature was increased to 400 °C at the rate of 1 °C min^{-1} and maintained for 0.5 hour for imidization. Then the temperature of the furnace was increased to 900 °C at the rate of 5 °C min^{-1} and maintained for 1 hour under N_2 atmosphere for carbonization.

The MnO_2/CNF composites were synthesized by a one-step facile redox method. In brief, 40 mg as-prepared CNF after a plasma treatment was soaked in 400 ml deionized (DI) water. Then 10 mg $KMnO_4$ was added and stirred until completely dissolved. After heating in a thermostatic oven at 80℃ for 24 h, the composites were washed with DI water and air-dried.

Characterizations

The morphology of MnO_2/CNF was observed by SU-8010 scanning electron microscope (SEM). Transmission electron microscopy (TEM) was performed on a JEM-2100F TEM/STEM operating at 200 keV. X-ray diffraction (XRD) analysis was performed using D/MAX-RM 2000 at a scanning rate of 5° min^{-1} in a range of diffraction angle 2θ from 10° to 80°. Raman spectra were performed by HORIBA LabRAM HR Evolution with an excitation laser beam with wavelength of 532 nm. X-ray photoelectron spectroscopy (XPS) measurement was investigated using a thermo ESCALAB 250 spectrometer. And XPS data was analyzed with Thermo Avantage software. The binding energy values were calibrated to the C 1s peak at 284.8 eV. The specific surface area and pore-size distribution of the composites were conducted by an automatic adsorption system (Bellsorp-mini) from adsorption isotherms of N_2 at 77 K with the Brunauer-Emmett-Teller method and density functional theory model. The content of MnO_2 in the interlayer was obtained by Thermogravimetric analysis (TGA, Mettler TGA Q5000) at the rate of 5 °C min^{-1} from 25 °C to 800 °C under air flow.

Cell assembly and electrochemical measurements

Sulfur, super P and PVDF were dispersed homogeneously in NMP to form a slurry (S: super P: PVDF=6:3:1 in weight). The slurry was then cast onto Al foil to get a thin slice in a diameter of 12 mm. The sulfur loading of cathode was about 1.65 mg cm^{-2}. All cells were assembled in a glove box with Ar atmosphere. CR2032-type coin cells were applied to perform the electrochemical experiments with lithium metal as the anode. Celgard 2400 membrane was utilized as the separator. The as-prepared MnO_2/CNF was cut into wafers in a diameter of 16 mm as the interlayer between separator and cathode. DOL and DME by 1:1 in volume with 1M LiTFSI (lithium bistrifluoromethanesulfonylimide) and 0.1 M $LiNO_3$ were used as the electrolyte.

Galvanostatical charge-discharge measurements of batteries were carried out in voltage range from 1.7 to 2.8 V (vs. Li/Li^+) by the Neware battery tester. A Chenhua electrochemical workstation CHI608E was employed to characterize the cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and voltammetric curves. CV tests were performed at a scan rate of 0.3 mV s^{-1} in a voltage range of 1.5-3.0 V. EIS measurements were carried out at open-circuit potential in the frequency range between 100 kHz and 10 mHz with a perturbation amplitude of 5 mV. Stainless steel sheets were directly applied on both sides of CNF or MnO_2/CNF membrane in cells to test voltammetric curves at a scan rate of 2 mV s^{-1}in a voltage range of 0-2.0 V.

Li_2S and S (in a 1:5 molar ratio) were added to a mixture of 1,2-dimethoxyethane (DME, 99.5%, Aladdin Co. Ltd., China) and 1,3-dioxolane (DOL, 99.8%, Aladdin Co. Ltd., China) (v/v, 1:1) with magnetic stirring in a glove box to synthesize a Li_2S_6 solution (0.3M) for testing the diffusion process of polysulfides.

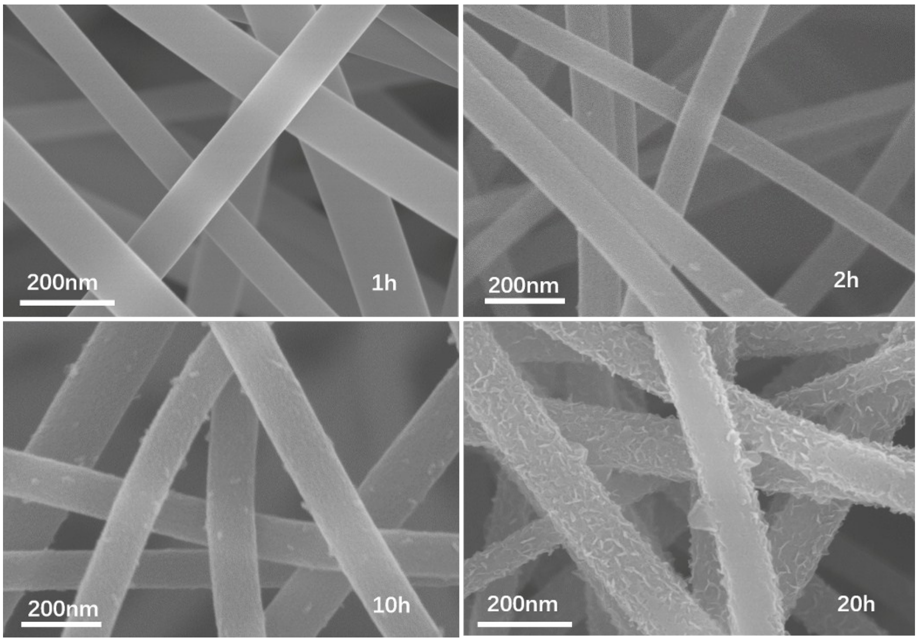

Fig. S1 The SEM images of the MnO_2/CNF after soaking in $KMnO_4$ for different reaction time

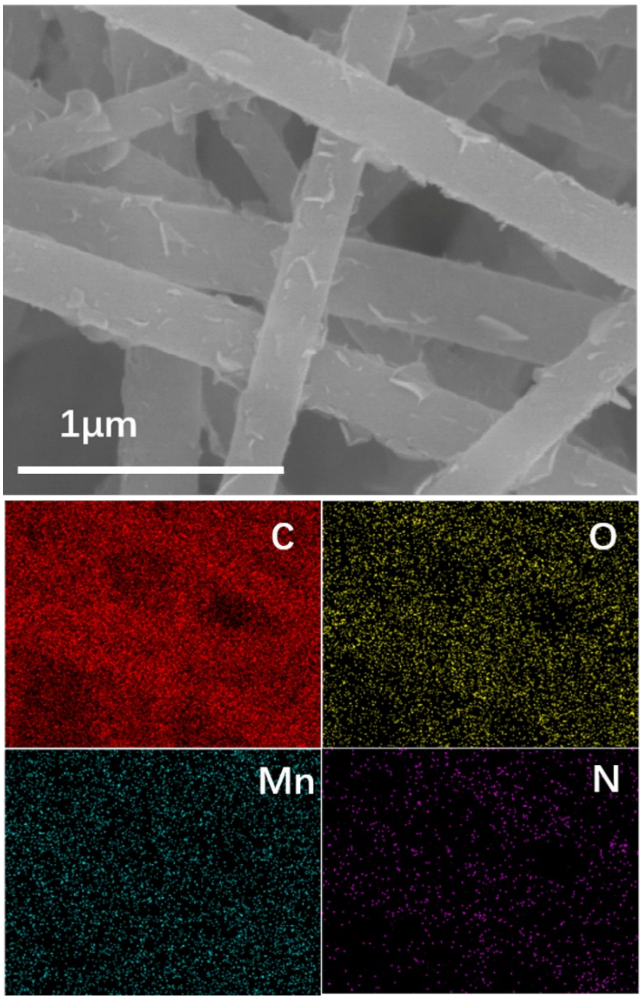

Fig. S2 Elements mapping of MnO_2/CNF

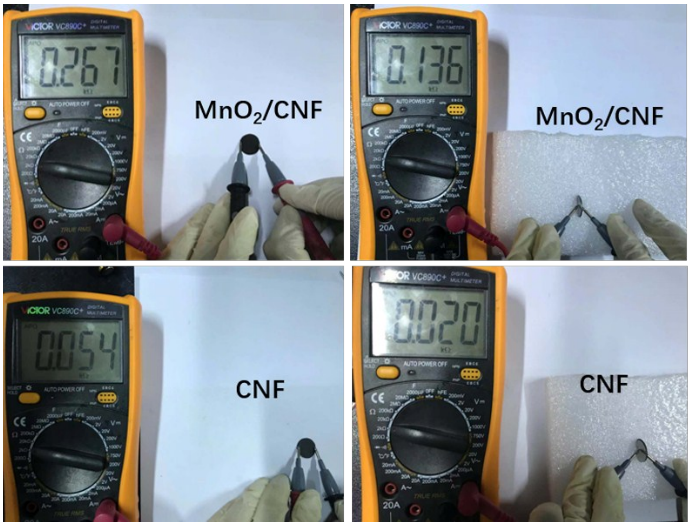

Fig. S3 Axial and radial resistance tests of CNF and MnO_2/CNF membrane

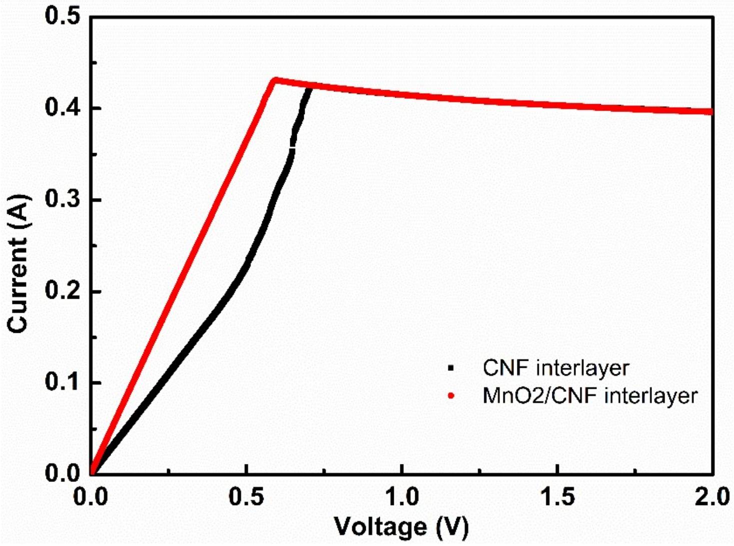

Fig. S4 Voltammetric curves of cells with CNF and MnO_2/CNF interlayer, without cathode and anode

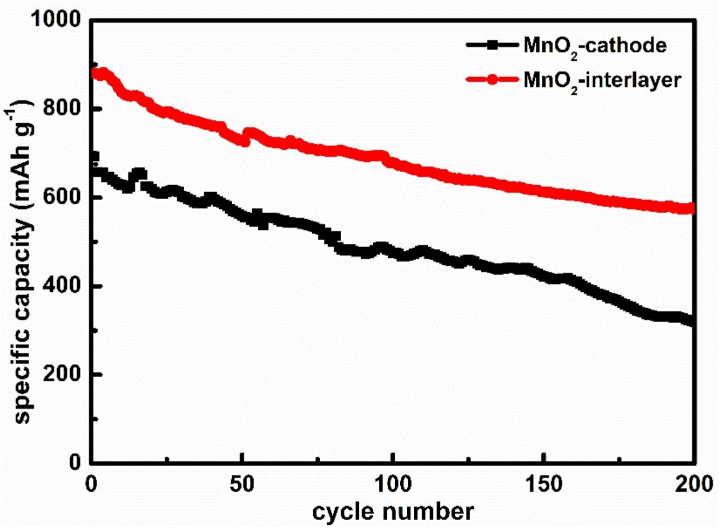

Fig. S5 Cycle performance of cells with MnO_2/CNF utilized as interlayer and cathode scaffold at 01C

Table S1. Potential gaps between corresponding reduction peaks and oxidation peaks in the CV curves in scan rate of 0.3 mV s^{-1} of different cells

	Without interlayer	CNF interlayer	MnO_2/CNF interlayer
The 1st platform	430 mV	380 mV	330 mV
The 2nd platform	600 mV	490 mV	480 mV

Table S2. The area ratio of Mn of different peaks of the MnO_2/CNF interlayer with and without Li_2S_6 solution

	Mn(Ⅱ)	Mn(Ⅲ)	Mn(Ⅳ)	Mn(Ⅱ)*	Mn(Ⅲ)*	Mn(Ⅳ)*
Before soaking	18.3%	32.5%	29.8%	11.7%	4.4%	3.3%
After soaking	29.6%	31.4%	21.6%	10.6%	3.3%	3.5%

* means different multiples