Supporting Information

Multiple covalent interactions and open-void co-involved Mn_3O_4/nitrogen-doped porous carbon fiber hybrids as flexible anodes for lithium-ion batteries

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1. Fabrication of $LiMn_2O_4$ cathode

Nanophase $LiMn_2O_4$ was prepared by a two-step method. Firstly, 100 ml of ethanol solutions containing manganese acetate ($Mn(Ac)_2{\cdot}4H_2O$, 20 mmol) and lithium acetate ($LiAc{\cdot}2H_2O$, 11 mmol) were evaporated under magnetic stirring at 90 °C to obtain a gray powder mixture. The resultant powders were further calcined at 750 °C in air for 6 h.

The $LiMn_2O_4$ cathodes were prepared by compressing a mixture of the $LiMn_2O_4$ powder, conductive material (Super P), and binder (polyvinylidene fluoride, PVDF) in weight ratios of 8:1:1 onto a round Al foil (1.1 cm^2). The density of the active material is about 2.7 mg cm^{-2}.

2. Supporting dates

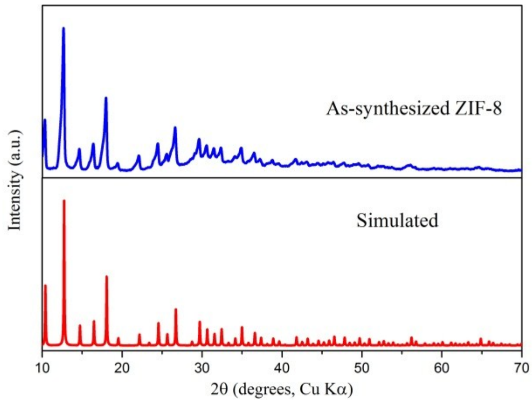

Fig. S1 XRD pattern of the as-prepared ZIF-8.

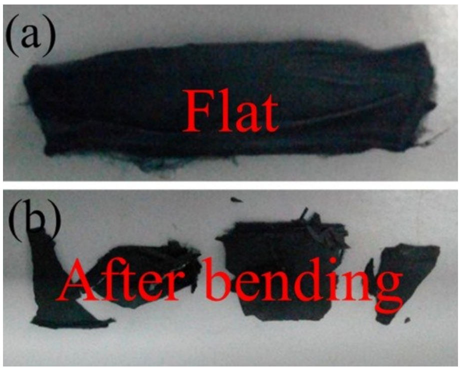

Fig. S2 Digital photographs of CFs mats before and after bending.

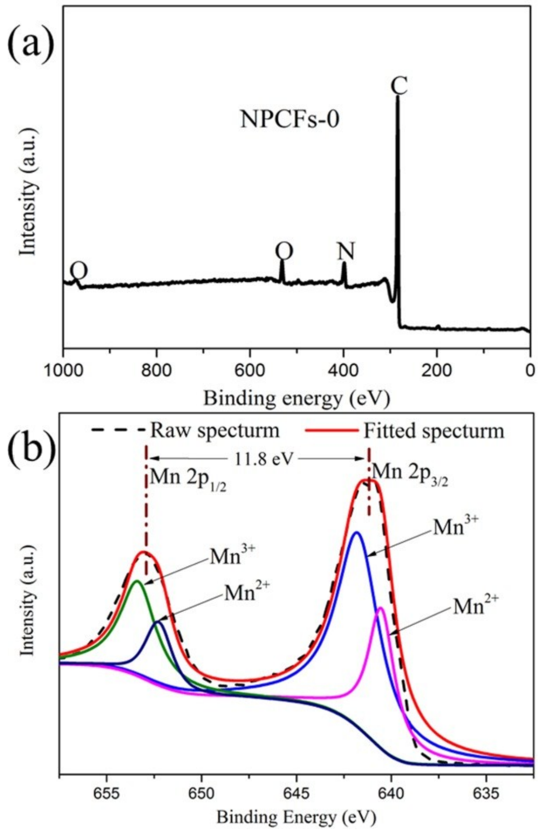

Fig. S3 (a) XPS survey spectra of NPCFs-0; (b) High-resolution XPS spectra of deconvoluted Mn 2p peak for the Mn_3O_4/NPCFs-1.4 product.

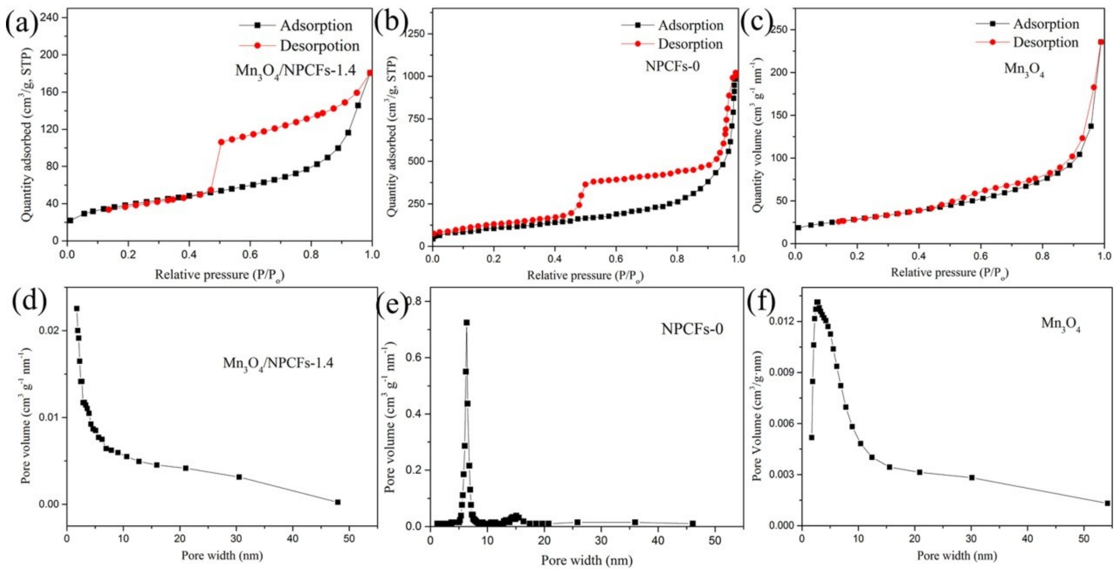

Fig. S4 Nitrogen adsorption–desorption isotherms of the as-synthesized products (a-c) and their corresponding pore size distribution curves (d-f) calculated from the adsorption branch by the BJH model.

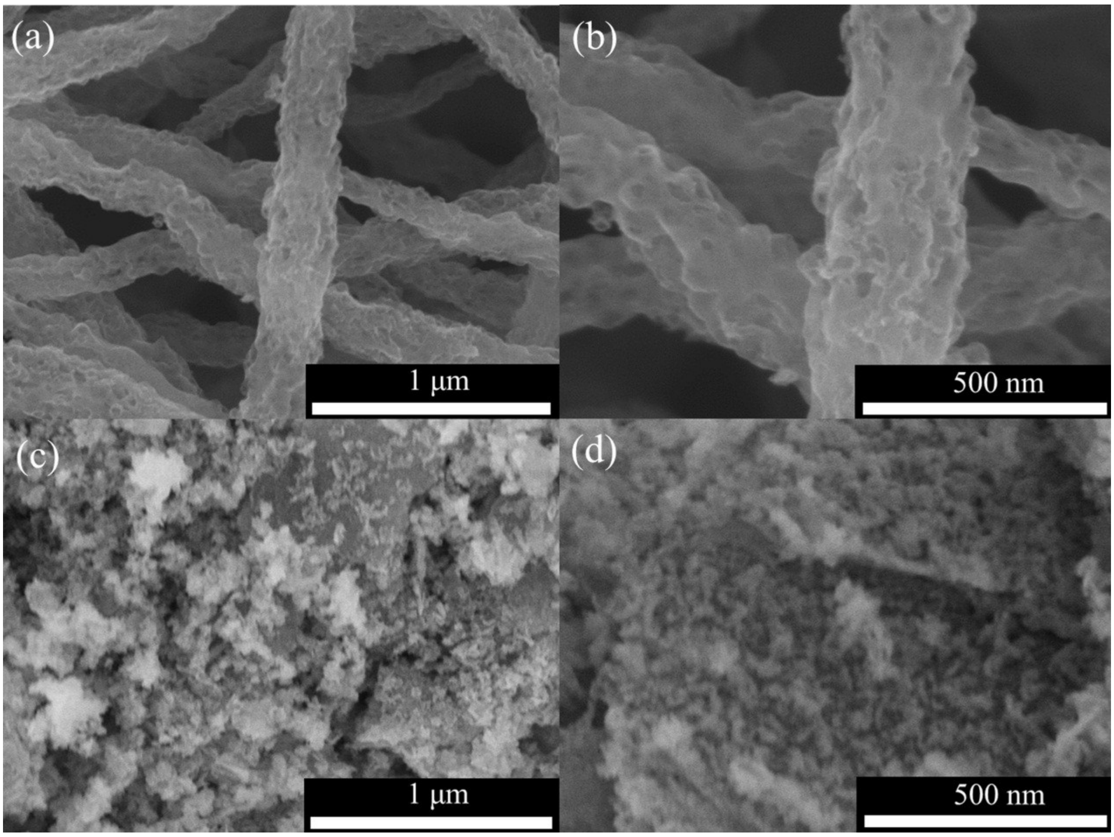

Fig. S5 SEM imagines of NPCFs-0 (a and b) and Mn_3O_4 compounds (c and d) at different magnifications.

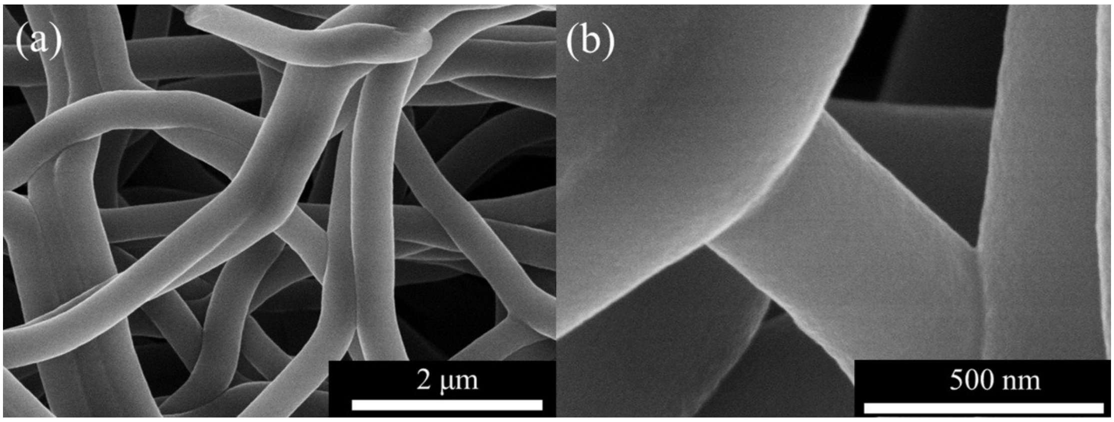

Fig. S6 FE-SEM imagines of CFs at different magnifications.

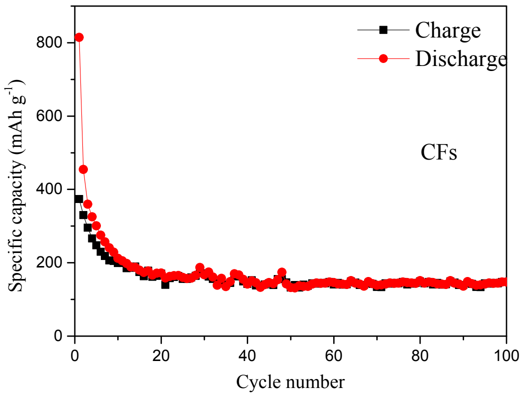

Fig. S7 Cycling test of CFs at a current density of 100 mA g^{-1}.

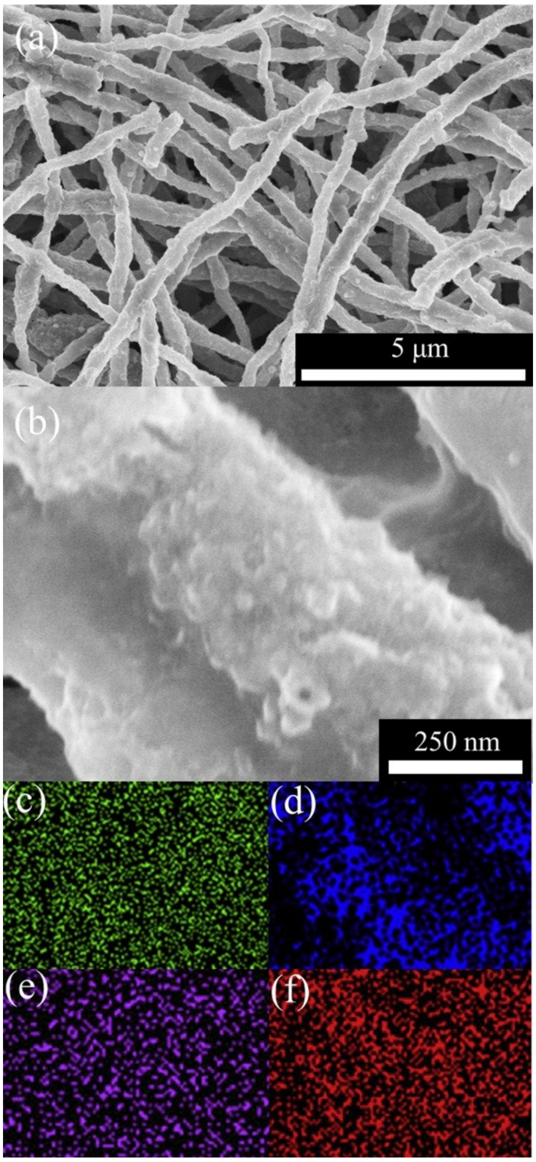

Fig. S8 (a and b) FE-SEM images of the Mn_3O_4/NPCFs-1.4 electrode after 100 cycles at different magnifications. (c-f) Elemental mapping images of C, N, O and Mn, respectively.

Table S1 The average discharge capacities during the rate test of Mn_3O_4, NPCFs-0 and Mn_3O_4/NPCFs hybrids. The discharge capacities for these three Mn_3O_4/NPCFs hybrids were calculated based on the weight of the whole composites.

Current density (A g^{-1})	0.05	0.1	0.2	0.3	0.5	0.8	1.0	1.5	2.0	2.5	0.05
Mn_3O_4/NPCFs-2 (mAh g^{-1})	641.3	525.5	390.1	258.9	150.9	51.6	2.9	2.4	2.3	1.9	535.8
Mn_3O_4 (mAh g^{-1})	561.0	187.0	40.6	9.6	4.6	3.6	1.5	1.4	1.2	1.1	74.18
Mn_3O_4/NPCFs-1.4 (mAh g^{-1})	1058.3	1006.0	892.1	775.6	666.0	586.5	552.9	482.9	408.8	320.7	1008.4
NPCFs-0 (mAh g^{-1})	592.7	487.6	398.3	335.9	246.2	211.2	185.9	170.7	160.6	152.533	484. 7
Mn_3O_4/NPCFs-1 (mAh g^{-1})	895.8	793.8	707.4	659. 4	585.9	516.9	470.5	418.5	336.2	247.1	878.9

To further understand the electrochemical results and lithiation activity of Mn_3O_4, the normalized capacity of Mn_3O_4 in Mn_3O_4/NPCFs hybrids was calculated according to the following equation:

$$C_{Mi} = \frac{C_{ti} - C_{Ci} \times (1 - W_M)}{W_M}$$

Where C_{Mi} (mAh g^{-1}) is the normalized capacity of Mn_3O_4 in Mn_3O_4/NPCFs hybrids at a current density of "i"; C_{ti} (mAh g^{-1}) is the average discharge capacity of the Mn_3O_4/NPCFs hybrids at a current density of "i", which is calculated based on the total weight of the whole composites; C_{Ci} (mAh g^{-1}) is the average discharge capacity of NPCFs-0 at a current density of "i"; W_M (wt%) is the mass loading of Mn_3O_4 in Mn_3O_4/NPCFs hybrids, which is analyzed by TGA.

Taking Mn_3O_4/NPCFs-1.4 as an example, the C_{ti} and C_{Ci} at 50 mA g^{-1} is calculated to be 1058 and 593 mAh g^{-1}, respectively. The W_M of Mn_3O_4/NPCFs-1.4 is 63.1 wt%. Therefore, the C_M at 50 mA g^{-1} is estimated to be 1330 mAh g^{-1}.

It should be mentioned that when the current density increased to 800 mA g^{-1} and higher, the discharge capacity of Mn_3O_4/NPCFs-2 is much smaller than that of NPCFs-0 (as shown in Table S1). Such an obvious capacity loss can be mainly attributed to the poor conductivity of Mn_3O_4 and the disappearance of open voids in Mn_3O_4/NPCFs-2 composites. The normalized capacities of Mn_3O_4 in Mn_3O_4/NPCFs-2 at 800 mA g^{-1} and higher current densities were denoted as 0 mAh g^{-1}.

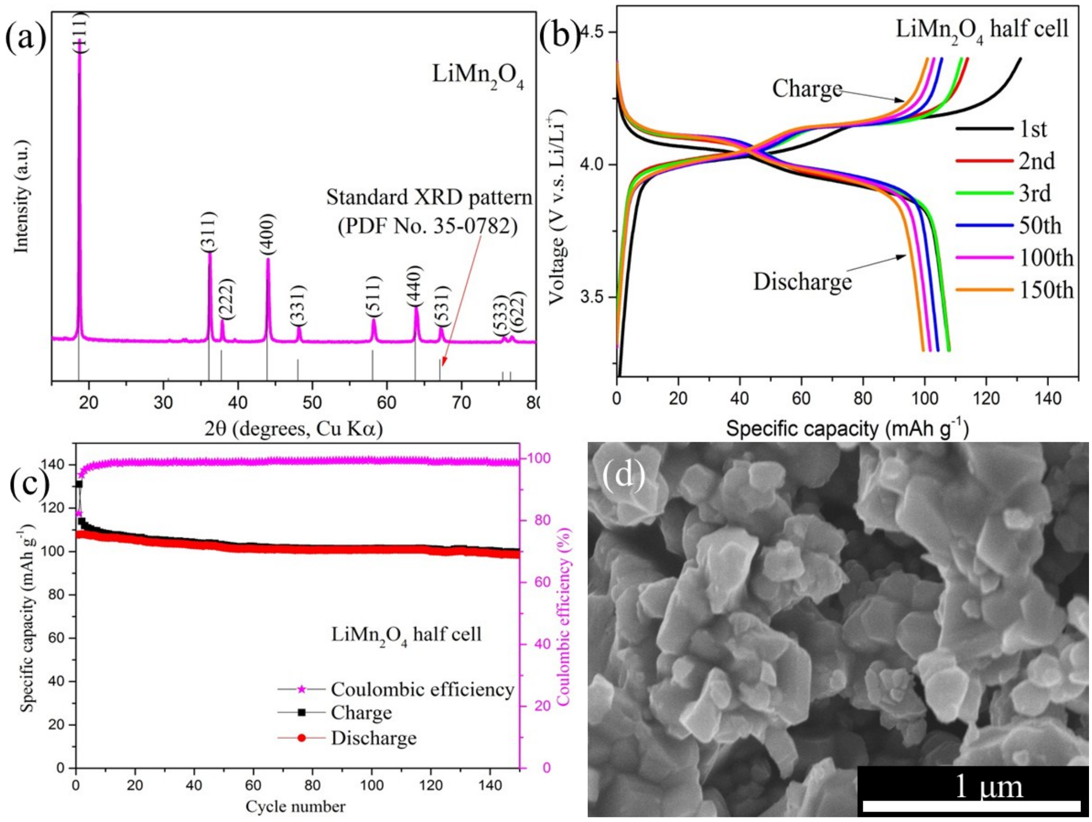

Fig. S9 (a) XRD pattern of the as-prepared $LiMn_2O_4$; (b) Charge/discharge profiles of $LiMn_2O_4$ cathode within a voltage range of 3.3-4.4 V; (c) Cycling performance of $LiMn_2O_4$ electrode at a current density of 100 mA g^{-1}; (d) FE-SEM imagine of $LiMn_2O_4$ nanoparticles.