SUPPORTING INFORMATION

Network of Porous Carbon/ZnCo₂O₄ Nanotubes Derived from the Shell-Hybridized Worm-like Micelles for Lithium Storage

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Note S1:

PWs hold significant advantages when used as 1D template to construct the 1D hybrid nanotubes networks when compared with carbon nanotubes (CNTs) and electrospun nanofibers. Compared with CNTs, PWs can interact strongly with ZIFs, and the strong interaction can effectively control growth and distribution of the active materials. Compared with the electrospun nanofibers, PWs have the advantages including: 1) The hair-like shell can interact strongly with the precursor of TMO, while the core, which is entirely different from the shell, can be inert to the precursor. The strong interaction from the shell can control distribution and structure of the TMO efficiently, while the inert core facilitates formation of the tubular structure during the calcination process; 2) The diameters of electrospun nanofibers are usually above 100 nm, while the PWs in our work have a uniform core diameter of ~20 nm, which can endow the resultant tubular structure with a smaller diameter and thinner wall to obtain a higher specific surface area.

Note S2:

In the present study, the PWs that are highly pure, uniform and relatively long were used as the 1D template. These structural features are very helpful for formation of the HCNTs networks with the desirable structure. As described in the main text, the PWs were hybridized by ZIFs firstly to form the HPWs, and the HPWs have all the abovementioned structural features of the PWs. Besides, the HPWs are rigid and have random curvatures, and thus the stacking of the HPWs led to the HPWs networks with stacking pores. It is imaginable that due to the high length and curvatures, in the HPWs networks the HPWs were entangled with each other. After the calcination process, the HCNTs networks should inherit the structural features of the HPWs network like the stacking pores and the entanglements. The stacking pores contribute to the hierarchical pores of the HCNTs network, and the entanglements enhance the structural stability of the HCNTs network. During formation of the networks, the high purity in the morphology is also significant. In the systems with a relatively low morphological purity, there should be nanoparticles of other morphologies like spherical micelles or vesicles coexisting with the PWs. During formation of the networks, the nanoparticles may either be wrapped in the network or be excluded from the network. The wrapping should reduce the stacking voids and decrease the specific surface area, and the isolated particles should contribute less than the network to the performance. Either the wrapping or the exclusion should introduce defects into the structure of the networks and should have negative effects to the structural stability and the performance.



Figure S1. Photographic images of (a) crosslinked polymer worm-like micelles (PWs) suspension in anhydrous methanol after storage for 2 years, and (b) its Tyndall effect. The Tyndall effect can be clearly observed for the light opalescence suspension, indicating the PWs crosslinked by 1,4-dibromobutane have the excellent stability suspended in methanol.



Figure S2. FESEM images of (a) HPWs-0 and (b) HPWs-0.5, and TEM images of (c) HPWs-0 and (d) HPWs-0.5. The obtained HPWs network has a similar diameter of ~75 nm and a uniformly integrated Zn-Co-ZIFs shell.



Figure S3. XRD patterns of HPWs networks. The major diffraction peaks of each HPWs network match well with the simulated ZIF-8,¹ indicating the successful synthesis of the ZIF-8 structure.



Figure S4. TGA curve of HPWs-2 networks from 50 to 600 °C at the heating rate of 10 °C min⁻¹ in air. PWs in the HPWs-2 start to decompose at ~ 240 °C and the Zn-Co-ZIFs begin to degrade at ~ 350 °C. HPWs-2 contains ~ 15 wt% of PWs and has ~ 40 wt% of metal oxide after calcination.



Figure S5. FTIR spectra of HPWs, PWs and ZIF-8.

The interaction between PEG and ZIFs is essential for the formation of the uniform ZIF coating. This interaction can also be confirmed by Fourier Transform infrared (FTIR) spectroscopy. As shown in **Figure S5**, the broad peak at 1090 cm⁻¹ is the characteristic peak of the C-O stretching mode for PEG chains of PWs. The peak located at 1597 cm⁻¹ is attributed to C=C stretching vibration absorptions on pyridine ring for P4VP chains of PWs. After hybridization, in the spectrum of the obtained HPWs, the absorption bands due to the C=C stretching absorption of P4VP still locate at 1597 cm⁻¹, which means that there is no strong interaction occurring between the P4VP and ZIFs. However, the peak arising from C-O stretching of PEG shifts towards the lower frequency (1001 cm⁻¹) and overlap with one of the peaks of ZIF-8. Therefore, the peak at 1001 cm⁻¹ in the FTIR spectrum of HPWs becomes broader than that of ZIF-8, which indicates that there is a strong interaction occurring between PEG and ZIFs.



Figure S6. TEM images of (a) HCNTs-0 and (b) HCNTs-0.5, and FESEM images of (c) HCNTs-0 and (d) HCNTs-0.5. After calcination and annealing, HCNTs-0 and HCNTs-0.5 are also well maintained the network morphology of the HPWs precursors. After calcination, the HCNTs are uniform nanotube structure with an outer diameter of ~50 nm, a channel width of 30 nm and a wall thickness of ~10 nm. The tubular morphology and the structural size are similar to these of HCNTs-2.



Figure S7. HRTEM image of HCNTs-2 networks. It can be clearly observed that the metal oxide nanoparticles with the diameter below 5 nm are uniformly distributed in the carbon wall.



Figure S8. Representative XPS high resolution spectra of C, O, Zn and Co of HCNTs networks. (a, b, c) HCNTs-0; (d, e, f, g) HCNTs-0.5; (h, i, j, k) HCNTs-2. The chemical components and chemical bonding states of HCNTs networks are further studied by the high resolution spectra, confirming the presence of Zn(II) oxidation state in HCNTs-0, HCNTs-0.5 and HCNTs-2 and Co (III) oxidation state in HCNTs-0.5 and HCNTs-2. And the molar ratio of Zn and Co is calculated to be 1:0.45 for HCNTs-0.5 and 1:1.93 for HCNTs-2.

The high-resolution carbon spectra shown in **Figure S8a, S8d** and **S8h** exhibit the high-resolution carbon spectrums of HCNTs-0, HCNTs-0.5 and HCNTs-2, respectively. They all contain peak 1 at 284.5 eV attributed to the carbon single/double bonds (C–C/C=C), peak 2 at around 285.8 eV attributed to the oxygen-containing functional groups (C–OH/C–O–C) and peak 3 at near 289.3 eV attributed to small amount of carboxylic groups (COO).² There are three peaks at binding energies of 529.9, 531.5 and 532.2 eV can be found in the high-resolution O 1s spectrum (**Figure S8b, S8e** and **S8i**). The dominating peaks at 529.9 and 531.5 eV are respectively attributed to the typical metal–oxygen bonds and the oxygen in hydroxide ions.² And the additional weak peak at 532.2 eV is usually associated with

physically adsorbed water molecules. **Figure S8c, S8f** and **S8j** show the high-resolution Zn 2p spectrum. Two peaks centered at about 1021.8 and 1044.7 eV are attributed to the orbits of Zn 2p 1/2 and Zn 2p 3/2 of Zn(II) respectively.³ As shown in Figure **S8g** and **S8k**, in the high resolution Co 2p spectrum, there are two main peaks located at near 780.8 and 796.9 eV respectively assigned to Co 2p 3/2 and Co 2p 1/2. Two additional satellite peaks (marked as Sat.) at 789.6 and 806.2 eV are detected at about 9.0 eV above the main peaks of Co 2p 3/2 (780.8 eV) and 2p 1/2 (796.9 eV) respectively, which confirm the presence of the Co(III) oxidation state.^{2.4.5}



Figure S9. (a) N_2 adsorption-desorption isotherms; (b) the corresponding pore size distribution of HCNTs-0 networks and HCNTs-0.5 networks.

The specific surface area of the obtained HCNTs-0 and HCNTs-0.5 calculated by N₂ adsorption-desorption are as high as 805 and 807 m² g⁻¹, respectively. As shown in **Figure S9a**, the N₂ adsorption-desorption isotherm of HCNTs-0 and HCNTs-0.5 also display the type I isotherm at low relative pressure, showing the existence of micropores, and the type-H4 hysteresis loop at the medium relative pressure ($0.4 < P/P_0 < 0.8$), indicating the existence of mesopores.⁶ In **Figure S9b**, the pore size distribution calculated by the Barrett–Joyner–Halenda model reveals a predominant peak at ~ 30 nm corresponding to the tubular pores generated by the pyrolysis of PWs, and a satellite peak at below 5 nm deriving from ZIF skeleton and structure defect forming during calcination.



Figure S10. Cyclic voltammograms (CVs) at the scan rate of 0.1 mV s⁻¹ between 0.05 and 3.0 V (vs. Li/Li⁺) of (a) HCNTs-0 networks and (b) HCNTs-0.5 networks. The oxidation and deoxidization peaks are obvious in CVs cycles, corresponding to the flats of charge and discharge. And the well overlap between 3rd and 5th cycles indicates the good electrochemical reversibility of HCNTs networks electrode.

According to the reported studies,^{2, 7-11} the electrochemical reactions between the electrolyte and HCNTs-2 electrode during the lithiation-delithiation processes can be inferred as follows:

$$ZnCo_2O_4 + 8Li^{\dagger} + 8e^{-} \rightarrow Zn + 2Co + 4Li_2O$$
(1)

$$Zn + Li^{\dagger} + e^{-} \leftrightarrow 4LiZn$$
 (2)

$$Zn + Li_2O \leftrightarrow ZnO + 2Li^+ + 2e^-$$
(3)

$$Co + Li_2O \leftrightarrow CoO + 2Li^{+} + 2e^{-}$$
(4)

$$CoO + 1/3Li_2O \leftrightarrow 1/3Co_3O_4 + 2/3Li^+ + 2/3e^-$$
 (5)

The electrochemical reactions between the electrolyte and HCNTs-0.5 electrode during the lithiation-delithiation processes can be inferred as follows:

$$ZnCo_2O_4 + 8Li^+ + 8e^- \rightarrow Zn + 2Co + 4Li_2O$$
(1)

$$Zn + Li^{\dagger} + e^{-} \leftrightarrow 4LiZn$$
 (2)

$$ZnO + 2Li^{\dagger} + 2e^{-} \leftrightarrow Zn + Li_{2}O$$
(6)

$$Zn + Li_2O \leftrightarrow ZnO + 2Li^+ + 2e^-$$
(3)

$$Co + Li_2O \leftrightarrow CoO + 2Li^+ + 2e^-$$
(4)

$$CoO + 1/3Li_2O \leftrightarrow 1/3Co_3O_4 + 2/3Li^+ + 2/3e^-$$
 (5)

And the electrochemical reactions between the electrolyte and HCNTs-0 electrode during the lithiation-delithiation processes can be inferred as follows:

$$Zn + Li^{\dagger} + e^{-} \leftrightarrow 4LiZn$$
 (2)

$$ZnO + 2Li^{\dagger} + 2e^{-} \leftrightarrow Zn + Li_{2}O$$
(6)

 $Zn + Li_2O \leftrightarrow ZnO + 2Li^+ + 2e^-$



Figure S11. Charge-discharge voltage profiles at a current density of 0.1 A g^{-1} of (a) HCNTs-0 networks and (b) HCNTs-0.5 networks.

As shown in **Figure S11**, the voltage plateau in the initial discharge curve of HCNTs-0 and HCNTs-0.5 are clearly observed but become almost invisible in the subsequent discharge curves. The first discharge and charge capacities of HCNTs-0 are 2239 and 1023 mAh g⁻¹, respectively. As for HCNTs-0.5, the first discharge and charge capacities are 2460 and 1390 mAh g⁻¹. The irreversible capacity loss is mainly attributed to the formation of SEI layer.¹²⁻¹⁵ For the 5th-100th cycles, HCNTs-0 and HCNTs-0.5 also respectively have the capacity of 954 and 1003 mAh g⁻¹ with the voltage profiles overlap, indicating that the HCNTs networks exhibit good stability for reversible lithium storage.



Figure S12. Cycling performance and Coulombic efficiency of HCNTs networks at the current density of 0.5 A g⁻¹ during 600 cycles. HCNTs-0, HCNTs-0.5 and HCNTs-2 networks all hold excellent cycling stability with the specific capacities of 753, 807 and 918 mAh g⁻¹ after 600 cycles at 0.5 A g⁻¹, respectively. And the Coulombic efficiencies of all the HCNTs networks electrodes reach nearly 100% after 5 cycles, implying highly reversible electrochemical performance.



Figure S13. FESEM images of the HCNTs networks composite anode before (a, b, c) and after (d, e, f) cycling tests.



Figure S14. TEM images of the HCNTs networks composite anode before (a) and after (b) cycling tests.

FESEM and TEM characterization were applied to observe the morphology and structure of the HCNTs networks composite anode before and after cycling. The recycled HCNTs networks electrode was taken from a battery that was charged to the highest voltage (3 V, ie, nearly completely delithiation) after 600 cycles, and washed several times against ethanol to remove the organic electrolyte. It was then dried naturally for the subsequent FESEM (**Figure S13**) and TEM (**Figure S14**) characterizations.

As shown in **Figure S13**, the recycled HCNTs networks largely maintained the morphology before the cycles, indicating that the HCNTs networks designed and synthesized in the manuscript have good structural stability. Compared with the HCNTs before cycling (**Figure S13c**, an outer diameter of ~50 nm), the recycled HCNTs (**Figure S13f**) had a more smooth surface and larger outer diameters of ~ 62 nm because the SEI film formed during cycling and conformally coated on the surface of HCNTs. The TEM image

(Figure S14) showed that the HCNTs still retained a tubular structure after cycling, which also confirmed the structural stability of the HCNTs networks. Additionally, due to the formation of SEI film on the surface of HCNTs, the diameter of HCNTs after cycling increased from ~50 nm (Figure S14a) to ~63 nm (Figure S14b), which is consistent with the result of FESEM observations (Figure S13). Thus, such HCNTs networks exhibit excellent structural stability, which is favorable to improve the electrode performance, especially the circle life and charge-discharge stability.

Materials	Specific capacity	Capacity Retention	Specific surface area (m ² g ⁻¹)	Ref.
HCNTs-2	1124 mAh g ⁻¹ at 0.1 A g ⁻¹ 1006 mAh g ⁻¹ at 1 A g ⁻¹ 651 mAh g ⁻¹ at 5 A g ⁻¹	90% after 600 cycle at 1 A g ⁻¹	821	This work
ZnCo ₂ O ₄ HMBNFs	915 mAh g ⁻¹ at 0.2 A g ⁻¹ 680 mAh g ⁻¹ at 4 A g ⁻¹	53% after 700 cycle at 2 A g ⁻¹	16.7	[7]
Te@ZnCo2O4 nanofiber	969 mAh g ⁻¹ at 0.1 A g ⁻¹ 587 mAh g ⁻¹ at 1 A g ⁻¹	98% after 100 cycle at 0.1 A g ⁻¹	225	[9]
ZnCo2O4/CNF	650 mAh g ⁻¹ at 0.1 A g ⁻¹ 337 mAh g ⁻¹ at 1 A g ⁻¹	92% after 300 cycle at 0.45 A g ⁻¹	299.56	[8]
ZnCo ₂ O ₄ Nanocluster	884 mAh g ⁻¹ at 0.1 A g ⁻¹ 188 mAh g ⁻¹ at 3 A g ⁻¹	74.4% after 100 cycle at 0.1 A g ⁻¹	30	[16]
Zn _x Co _{3-x} O4 Hollow Polyhedra	1020 mAh g ⁻¹ at 0.9 A g ⁻¹ 692 mAh g ⁻¹ at 7.2 A g ⁻¹	97% after 50 cycle at 0.1 A g ⁻¹	65.58	[12]
RGO/ZnCo2O4 –ZnO– C/Ni	738 mAh g ⁻¹ at 0.5 A g ⁻¹ 5 588 mAh g ⁻¹ at 5 A g ⁻¹	150 cycle at 0.1 A g ⁻¹	NA	[17]
porous ZnCo ₂ O ₄ NRAs/nickel foam	1581 mAh g ⁻¹ at 0.2 A g ⁻¹ 528 mAh g ⁻¹ at 0.8 A g ⁻¹	71% after 80 cycle at 0.2 A g ⁻¹	59.4	[18]
ZnCo2O4 microspheres/NiSix nanowires on Ni foam	1408 mAh g ⁻¹ at 0.1 A g ⁻¹ 630 mAh g ⁻¹ at 2 A g ⁻¹	701 mAh g ⁻¹ after 340 cycle at 1 A g ⁻¹	49.8	[19]
ZCO/CNTs composites	924.3 mAh g ⁻¹ at 0.5 A g ⁻¹ 605.7 mAh g ⁻¹ at 2 A g ⁻¹	864 mAh g ⁻¹ after 150 cycle at 0.1 A g ⁻¹	NA	[20]
ZnCo₂O₄@Ag HSs	900 mAh g $^{-1}$ at 1 A g $^{-1}$	616 mAh g ⁻¹ after 900 cycle at 1 A g ⁻¹	23	[21]
Co ₃ O ₄ /ZnCo ₂ O ₄ coconut-like hollow spheres	1238 mAh g ⁻¹ at 0.1 A g ⁻¹ 644 mAh g ⁻¹ at 2 A g ⁻¹	78% after 300 cycle at 0.2 A g ⁻¹	NA	[22]

Table S1. Comparison of electrochemical performance of carbon/ZCO hybrid nanotubes(HCNTs) networks and recently reported ZCO-based anode materials.

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