

Supplementary Information for

Direct Growth of Flexible LiMn₂O₄/CNTs Lithium-Ion Cathodes

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Experimental section

1. Synthesis

A two-step hydrothermal process was used to synthesize the LiMn₂O₄/CNT nanocomposites. CNTs with length up to 100 micrometers and diameter at ~11 nm were produced from a chemical vapor deposition (CVD) based mass production method.¹ All the other chemicals were analytical grade and were directly used without any further purification. To make the LiMn₂O₄/CNT nanocomposites, the first step is to synthesize MnO₂/CNT nanocomposites. In a typical process, pristine CNTs were purified using a 18 % HCl solution and a 20 % HF solution alternatively to remove residual catalysts. Purified CNTs were washed using an enough amount of de-ionized water and then transferred into a H₂SO₄/H₂O₂ solution (volume ratio of H₂SO₄/H₂O₂=4:1) to oxidize the surface at 0 °C for 2 hr.² Then, 0.2 g of such weakly oxidized CNTs were transferred into a JJ-2 homogenate fluid shearing machine containing 300 mL of H₂O to shear at around 5000 r min⁻¹ for 2 hr. Hydrothermal synthesis of MnO₂/CNT nanocomposites was conducted according to the reported methods with some modifications.³⁻⁵ Specifically, 100 mL of 8 % KMnO₄ aqueous

solution was added into the above CNT suspension and stirred for 1 hr. The mixture was then transferred into a beaker and heated to 90 °C under stirring for 4 h for the redox reaction. After reaction, the mixture was filtered and washed by an enough amount of de-ionized water, and then dried under vacuum to obtain MnO₂/CNT nanocomposites. To make the LiMn₂O₄/CNT nanocomposites, 0.38 g of above MnO₂/CNT nanocomposites and 0.5 g of LiOH·H₂O were mixed with 80 mL of H₂O, and homogenized for another 1 h before transferring into a 100 mL teflon-lined autoclave. After a hydrothermal treatment at 180 °C for 4 days, the resulted precipitates were filtered and rinsed with water and acetone for several times and dried under vacuum at 90 °C for 12 h to obtain the flexible LiMn₂O₄/CNT nanocomposites.

To synthesize LiMn₂O₄ nanoparticles, we first synthesized birnessite-type MnO₂ by a co-precipitation method using KMnO₄ and MnSO₄ aqueous solution.⁶ The as-prepared birnessite-type MnO₂ was hydrothermal treated under the same condition as MnO₂/CNT composite.

2. Characterization

X-ray diffraction measurements were conducted on a Panalytical X'Pert Pro x-ray powder diffractometer using Cu-Kα radiation ($\lambda=1.54$ Å). Thermalgravimetric analysis (TGA) was conducted on a TGA Q50 instrument at a ramping rate of 10° min⁻¹ under an air flow. Nitrogen sorption isotherms were measured at 77 K with a Micromeritics ASAP 2020 analyzer. The specific surface areas were calculated by the Brunauer–Emmett–Teller (BET) method using a desorption branch in a relative pressure (P/P_0) range from 0.04 to 0.25. Scanning electron microscopy (SEM) experiments were conducted on a JEOL JSM-6700 instrument. Transmission electron microscopy (TEM) experiments were carried out on a FEI-T12 operated at 120.0 kV.

3. Electrochemical measurement

To test the electrochemical performance of the flexible lithium-ion cathodes, flexible $\text{LiMn}_2\text{O}_4/\text{CNT}$ nanocomposite films were cut into desired sizes. By comparison, to make composite LiMn_2O_4 electrode, 80% of as synthesized LiMn_2O_4 nanoparticles, 10% carbon black, and 10% poly(vinylidene fluoride) (PVDF) dispersed in N-methylpyrrolidinone (NMP) were mixed to form slurries. The homogenous slurries were coated on an Al substrate and dried at 80 °C for 30 min under vacuum. As formed electrodes were then pressed at a pressure of 2 MPa and further dried under vacuum at 100 °C for another 12 h. The mass loading was $\sim 2 \text{ mg cm}^{-2}$ on the current. The flexible $\text{LiMn}_2\text{O}_4/\text{CNT}$ and composite LiMn_2O_4 cathodes were then assembled into 2032-type coin cells, where glass fibers (Whatman) were used as the separators and lithium foils were used as both the counter and reference electrodes. The electrolyte solution was a 1 mol L^{-1} LiClO_4 in propylene carbonate (PC) solution. All the cells were assembled in a argon-filled glovebox. The cyclic voltammetry (CV) measurements were performed on a Bio-Logic VMP3 electrochemical workstation at a scan rate of 0.2 mV s^{-1} in a voltage range between 2.9 and 4.3 V (vs. Li/Li^+). Electrochemical impedance spectroscopy (EIS) tests of cells before and after cycling were carried out on a Solartron 1860/1287 Electrochemical Interface. The constant-current charge and discharge measurements were conducted by a LAND CT2000 at different current densities in a voltage range between 3.2 and 4.3 V (vs. Li/Li^+).

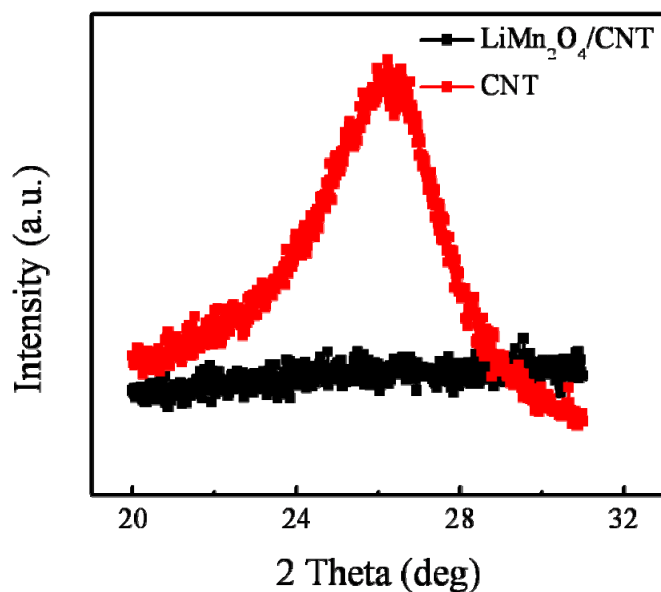


Fig. S1 Enlarged XRD patterns of LiMn₂O₄/CNT composite and CNTs at two theta from 20-30°.

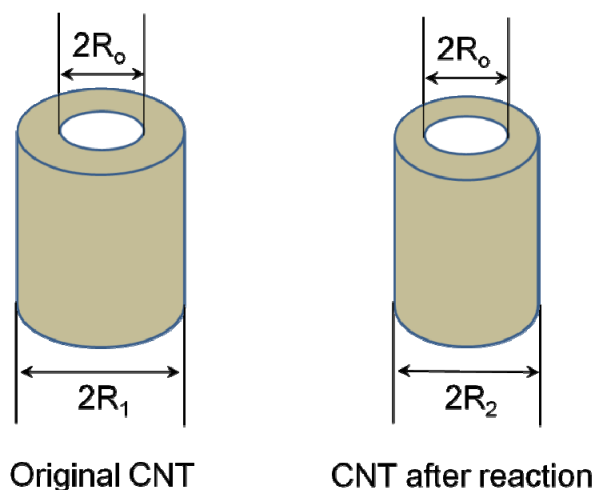
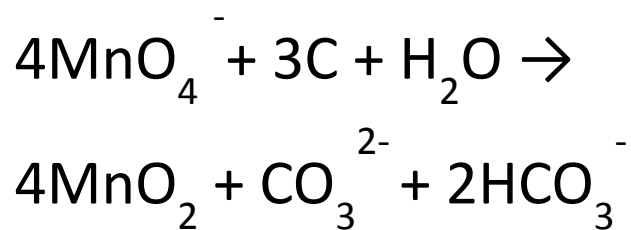


Fig. S2 Schemetic of CNT structure before (left) and after (right) hydrothermal reaction.

The stoichiometric reaction of CNT with KMnO₄ can be expressed as:



In such a reaction, 36 g of carbon consumed in the reaction can produce 476 g of MnO_2 . If we assume a percentage of x involved in our reaction, then we have:

$0.2 \text{ (CNT)} \cdot (1-x) + 476/36 \cdot (0.2 \cdot x) = 1.1 \text{ (CNT/MnO}_2\text{)}$, we get $x=0.45$. From TEM, we can use

$R_0=2.5 \text{ nm}$, $R_1=5.5 \text{ nm}$ and $R_2=4.25 \text{ nm}$. Assume a length of L for a CNT, the volume of carbon that was consumed in the reaction can be expressed by:

$\Delta V = 2\pi L(R_1^2 - R_0^2) - 2\pi L(R_2^2 - R_0^2) = 2\pi L(R_1^2 - R_2^2)$, therefore, the ratio of the consumed carbon to the original amount of carbon can be expressed by:

$2\pi L(R_1^2 - R_2^2) / 2\pi L(R_1^2 - R_0^2) = (R_1^2 - R_2^2) / (R_1^2 - R_0^2) = (5.5^2 - 4.25^2) / (5.5^2 - 2.5^2) = 0.5$. This value is close to that derived from the mass measurement.

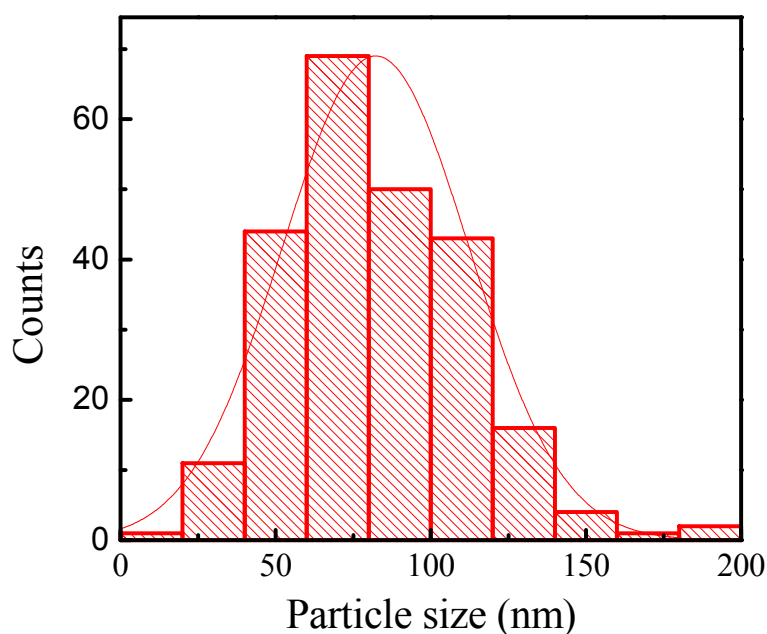


Fig. S3 The size distribution of LiMn_2O_4 nanoparticles in the nanocomposite cathodes.

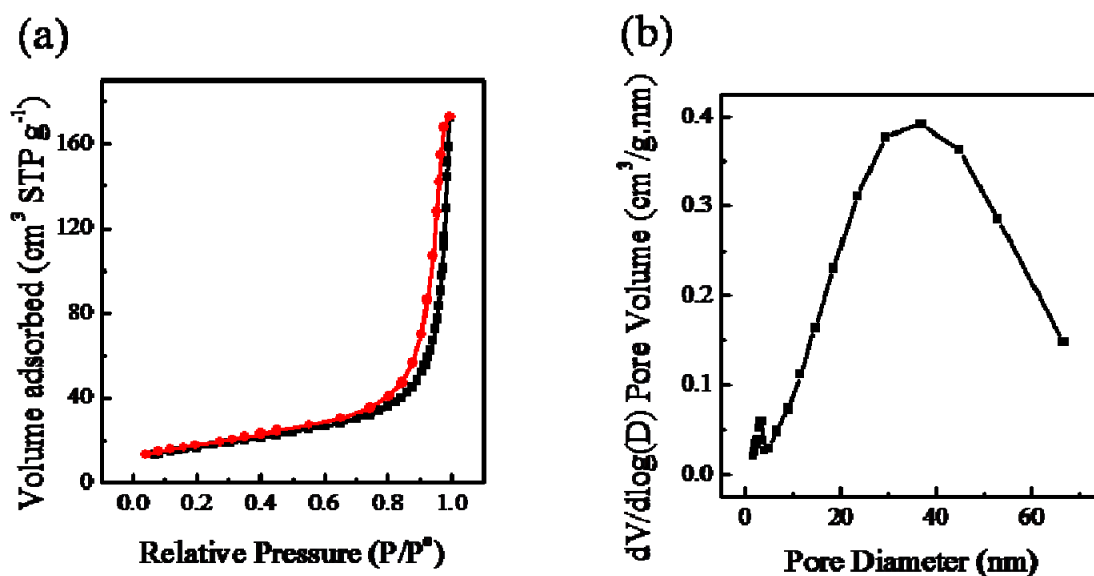


Fig. S4 (a) Nitrogen adsorption isotherms and (b) pore size distribution of LiMn₂O₄/CNT composites.

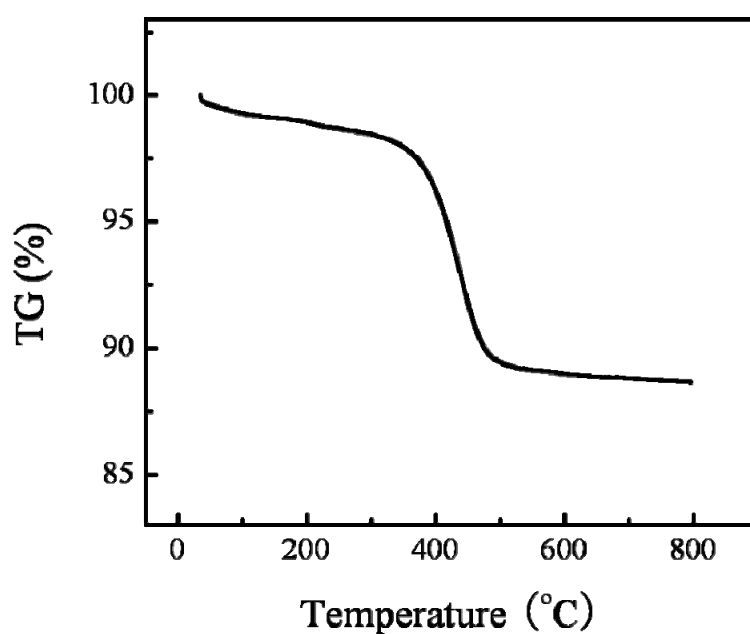


Fig. S5 Thermogravimetric analysis of the LiMn₂O₄/CNT nanocomposites. Less than 1% weight loss, which is ascribed to the removal of absorbed water, was observed below 200 °C. A substantial weight loss (~10%), due to the combustion of CNTs catalyzed by manganese oxide in air, was observed between 200 and 600 °C. Above 600 °C, no significant weight loss was observed;

the remaining 89 % of the weight is therefore attributed to the LiMn_2O_4 within the composite. By comparison, similar nanocomposites prepared from the reaction of KMnO_4 with mesoporous carbons⁷ or porous carbon aerogels⁸ show much lower oxide loading (<50 wt-%). This highlights the effectiveness of using CNTs to make high capacity electrodes.)

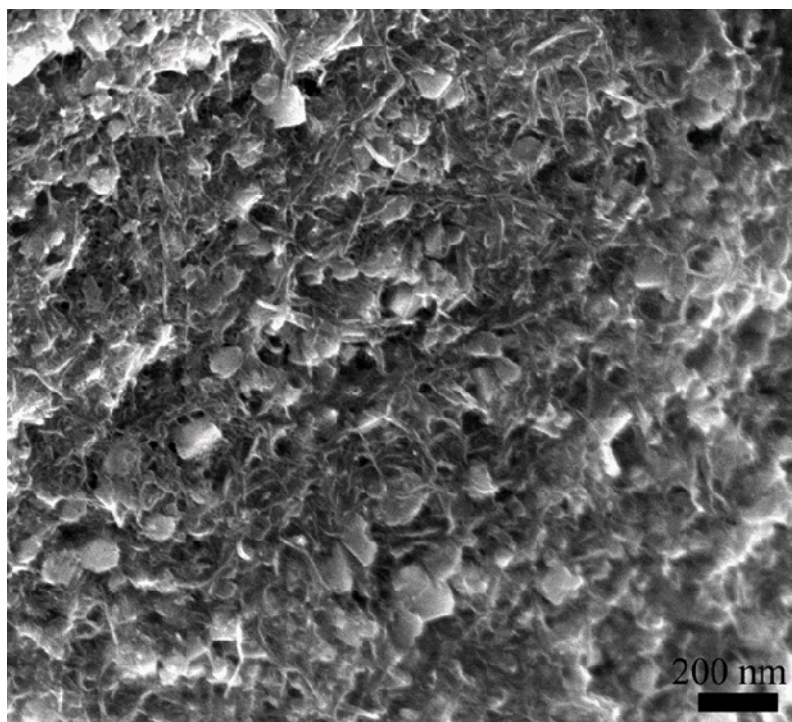


Fig. S6 SEM image of $\text{LiMn}_2\text{O}_4/\text{CNT}$ composite electrode after 85 cycles.

References

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