

## *Supplementary Information*

# **Hierarchically organized CNT@TiO<sub>2</sub>@Mn<sub>3</sub>O<sub>4</sub> nanostructures for enhanced lithium storage performance**

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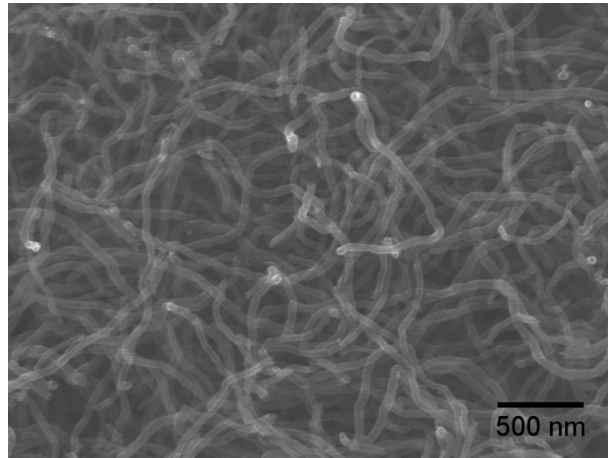
150090, China

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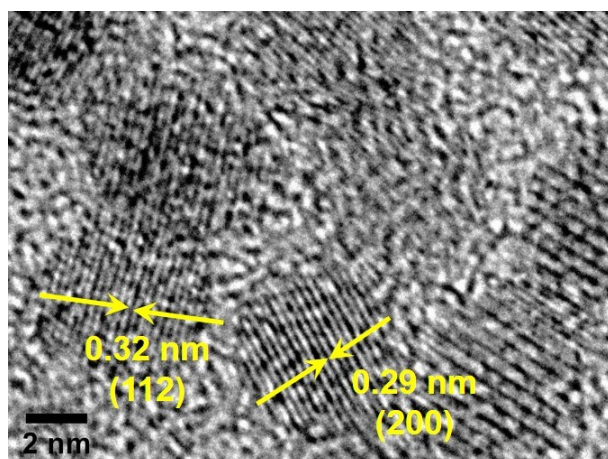
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\*Corresponding Authors.

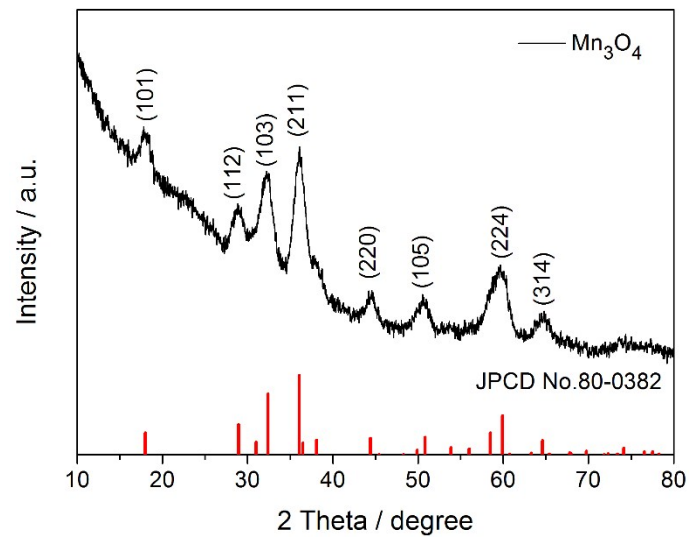
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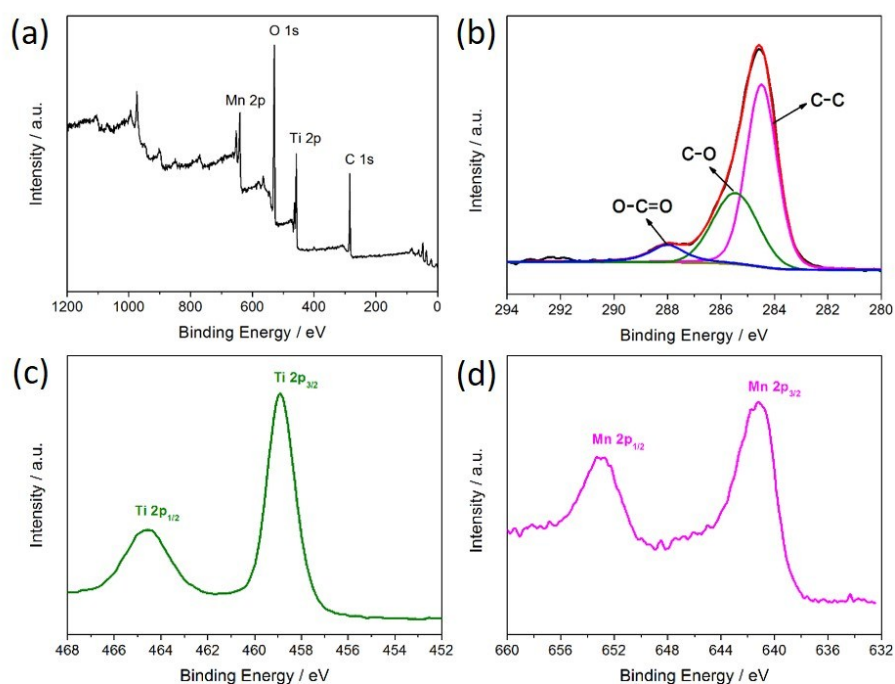
**Fig. S1** – SEM image of CNTs.



**Fig. S2** – HRTEM image of Mn<sub>3</sub>O<sub>4</sub> nanoparticles.



**Fig. S3** – XRD pattern of Mn<sub>3</sub>O<sub>4</sub> nanoparticles.

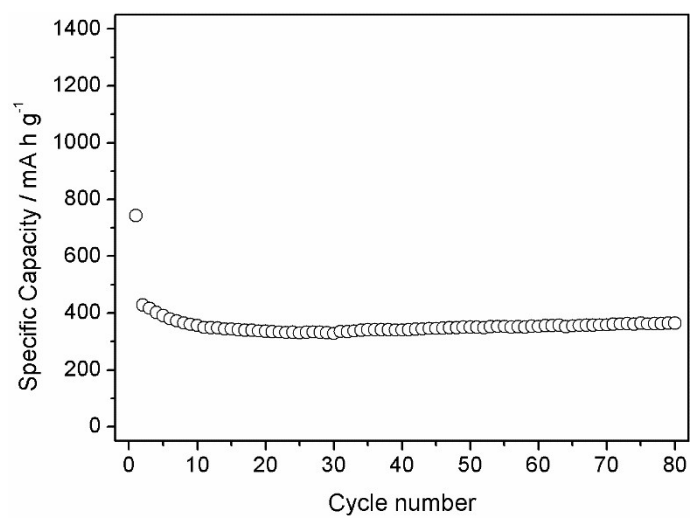


**Fig. S4** – (a) Wide-scan survey, (b) C 1s, (c) Ti 2p and (d) Mn 2p XPS spectra of CNT@TiO<sub>2</sub>@Mn<sub>3</sub>O<sub>4</sub> nanostructures. As to the C1s spectrum, the three peaks located at 284.5, 285.5, and 288.0 eV correspond to the carbon atoms in C-C, C-O, and C=O groups, respectively.<sup>1</sup> In the binding energy of 468-452 eV, the two peaks at 464.6, and 458.9 eV are assigned to Ti 2p<sub>1/2</sub> and 2p<sub>3/2</sub> orbitals.<sup>2</sup> The high-resolution Mn 2p spectrum shows two major peaks residing at 653.0 and 641.2 eV, which are attributed to Mn 2p<sub>1/2</sub> and 2p<sub>3/2</sub> orbitals, indicating that the Mn atoms are in the form of Mn<sub>3</sub>O<sub>4</sub>.<sup>3</sup>

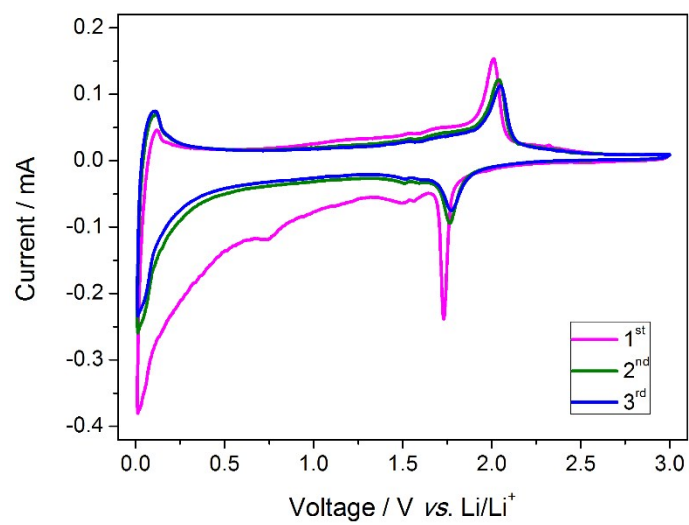
1 X. Hu, G. Zeng, J. Chen, C. Lu and Z. Wen, *J. Mater. Chem. A*, 2017, **5**, 4535-4542.

2 T. Xia, W. Zhang, J. B. Murowchick, G. Liu, X. Chen, *Adv. Energy Mater.* 2013, **3**, 1516-1523.

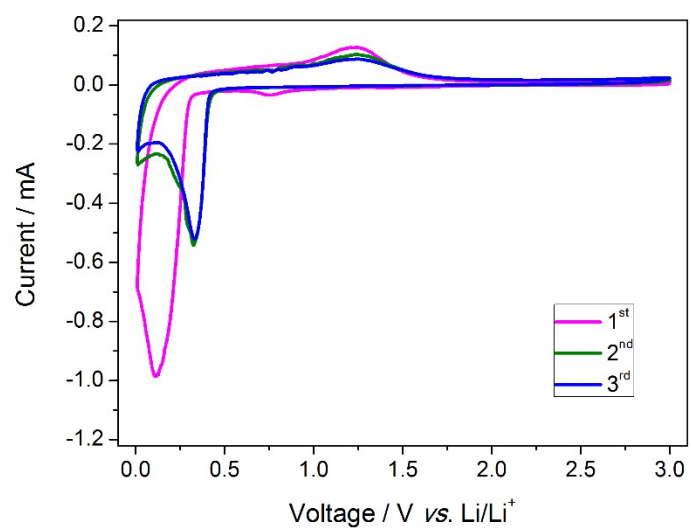
3 C. Wang, L. Yin, D. Xiang and Y. Qi, *ACS applied materials & interfaces*, 2012, **4**, 1636-1642.



**Fig. S5** – Cycle behavior of CNTs at a current density of 500 mA g<sup>-1</sup>.

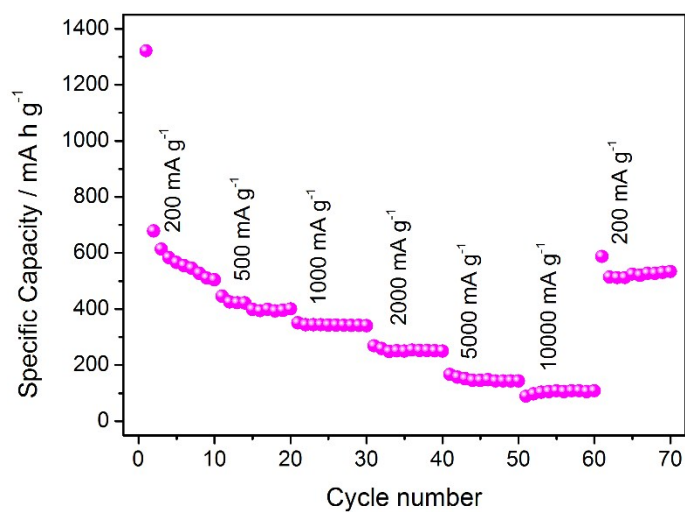


**Fig. S6** – Initial three CV curves of CNT@TiO<sub>2</sub> nanostructures.

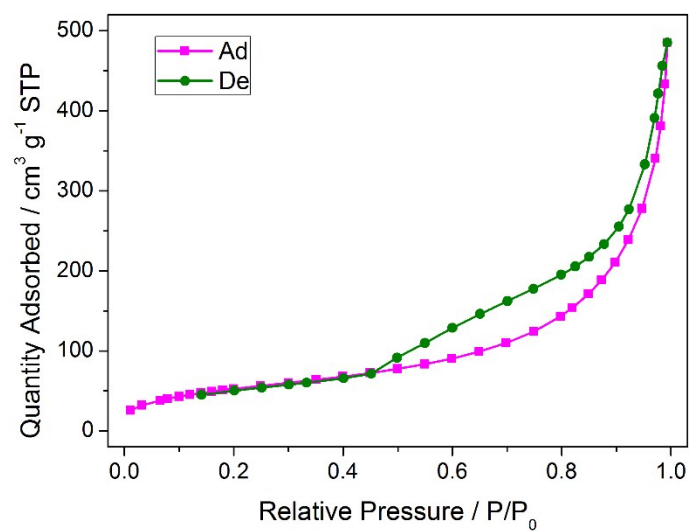


**Fig. S7** – Initial three CV curves of Mn<sub>3</sub>O<sub>4</sub> nanoparticles.

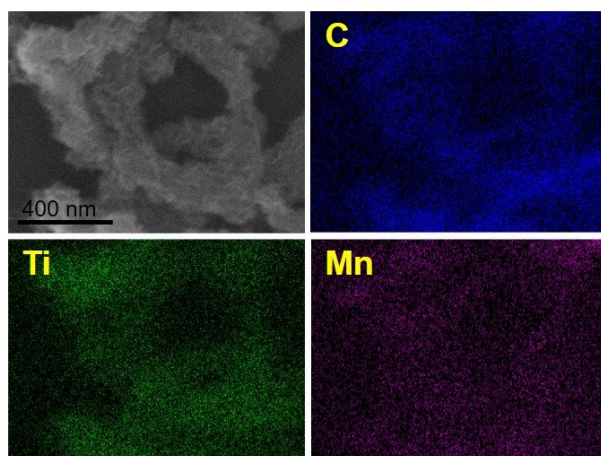




**Fig. S8** – Rate capabilities of CNT@TiO<sub>2</sub>@Mn<sub>3</sub>O<sub>4</sub> nanostructures. A fairly high reversible capacity is witnessed, being 679, 425, 344, 259 or 157 mA h g<sup>-1</sup> at 200, 500, 1000, 2000 or 5000 mA g<sup>-1</sup>. When the current density is increased to 10000 mA g<sup>-1</sup>, the reversible capacity is still as high as 97 mA h g<sup>-1</sup>. Note that even after deep cycling at 10000 mA g<sup>-1</sup>, the reversible capacity returns to 514 mA h g<sup>-1</sup> immediately when the current density is recovered to 200 mA g<sup>-1</sup>, further confirming good cyclability.



**Fig. S9** – Nitrogen adsorption–desorption isotherms of CNT@TiO<sub>2</sub>@Mn<sub>3</sub>O<sub>4</sub> heteroarchitectures, revealing a large BET surface area of 191.8 m<sup>2</sup> g<sup>-1</sup> which is favorable for lithium and electrolyte access.



**Fig. S10** – SEM image of the CNT@TiO<sub>2</sub>@Mn<sub>3</sub>O<sub>4</sub> nanostructures after cycling and the corresponding EDS maps of elemental C, Ti and Mn.

**Table S1.** The content of elemental C in  $\text{Mn}_3\text{O}_4$ ,  $\text{CNT@TiO}_2$  and  $\text{CNT@TiO}_2@\text{Mn}_3\text{O}_4$  nanostructures

|         | $\text{Mn}_3\text{O}_4$ | $\text{CNT@TiO}_2$ | $\text{CNT@TiO}_2@\text{Mn}_3\text{O}_4$ |
|---------|-------------------------|--------------------|--|
| C (wt%) | 12.01                   | 27.99              | 21.64                                    |