# Supporting Information

**A New Strategy to Effectively Alleviate Volume Expansion and Enhance Conductivity of Hierarchical MnO@C Nanocomposites for Lithium Ion Batteries**

Zhe Cui,[a,b] Qian Liu,[c] Chaoting Xu,[a] Rujia Zou[a,*], Jianhua Zhang,[a] Wenlong Zhang,[a] Guoqiang Guan,[a] Junqing Hu[a,*] and Yangang Sun[b,*]

[a] State Key Laboratory for Modification of Chemical Fibers and Polymer Materials, College of Materials Science and Engineering, Donghua University, Shanghai 201620, China

[b] College of Chemistry and Chemical Engineering, Shanghai University of Engineering Science, Shanghai 201620, China

[c]Department of Physics, Donghua University, Shanghai 201620, China

[*]Corresponding author, E-mail: rjzou@dhu.edu.cn

hu.junqing@dhu.edu.cn

syg021@sues.edu.cn

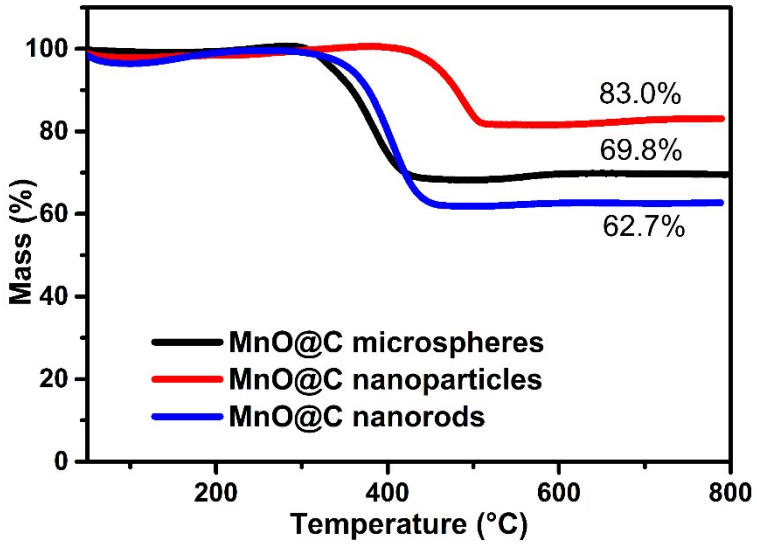


**Fig. S1** TG curves of MnO@C microspheres, MnO@C nanoparticles and MnO@C nanorods. In order to ascertain carbon content for MnO@C hierarchical microspheres, MnO@C nanorods and MnO@C nanoparticles, the TGA measurement has been conducted. As can be seen from Fig. 2, for MnO@C microspheres, the weight loss of ~0.86% below 200 °C should be ascribed to the adsorption of water,[1] and the weight gain of ~1.8% between 200~350 °C is due to the slightly oxidation of MnO to $Mn_2O_3$.[2] Subsequently, the huge weight loss of 32.44% is mainly attributed to the combustion of carbon to $CO_2$ and partial oxidation of MnO into $Mn_2O_3$.[2] Finally, it can be observed that after 500 °C, the weight gains of ~1.5 % and remains no change until 800 °C, indicating the entirely oxidation of MnO to $Mn_2O_3$.[3] According to previous reports,[4,5,6] MnO transforms to $Mn_2O_3$ after heating to 1050 °C in an oxygen atmosphere. Therefore, it is believable that the final weight of ~69.8% is entirely corresponding to $Mn_2O_3$ transformed from MnO, which suggests that the original MnO is calculated to ~62.7%， and the carbon content should be ~37.3%. The carbon content is approximately comparable to that of other MnO/C composition derived from Mn-MOF.[1,7,8] Similarly, the carbon content of MnO@C nanoparticles and MnO@C nanorods is calculated to ~26.4% and ~43.7%, respectively.

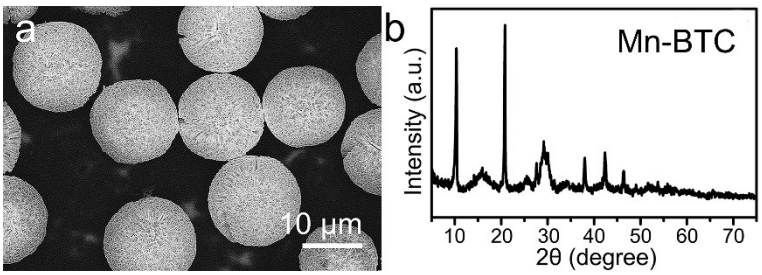


**Fig. S2** a) The low magnification SEM image. b) XRD pattern of Mn-BTC.

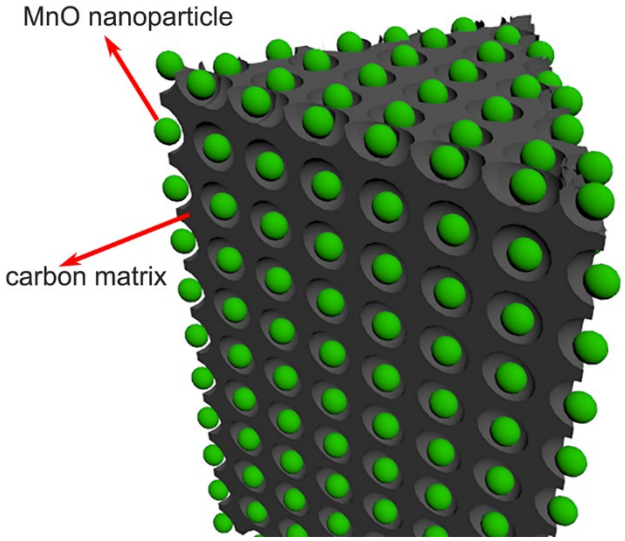


**Fig. S3** The schematic drawing for inner structure of single nanorod in MnO@C microsphere.

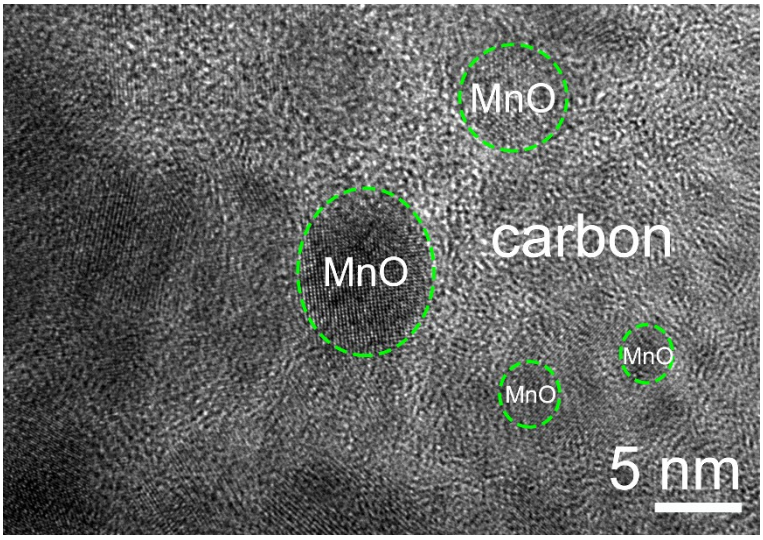


**Fig. S4** The HRTEM image of MnO@C microsphere taken from the middle area of single nanorod.

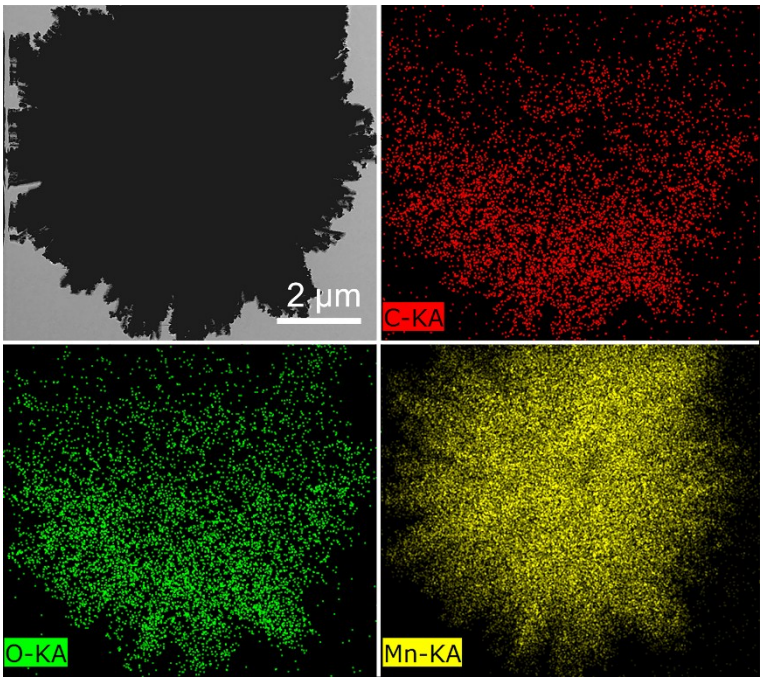


**Fig. S5** EDS mapping images of as-prepared MnO@C microsphere.

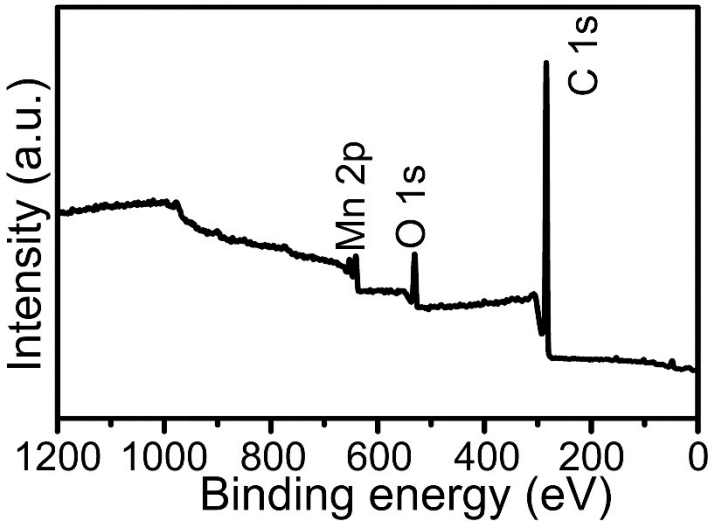


**Fig. S6** XPS survey spectrum of MnO@C microspheres.

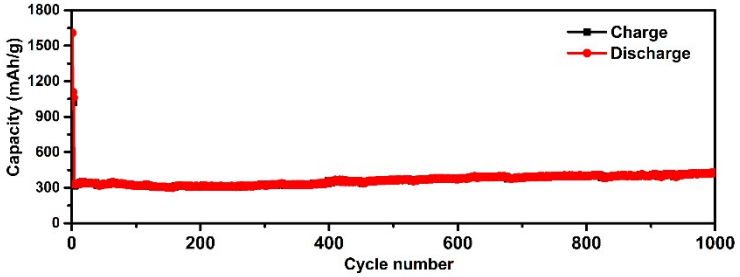


**Fig. S7** Cycling performance of MnO@C microsphere tested at 10 C for 1000 cycles.

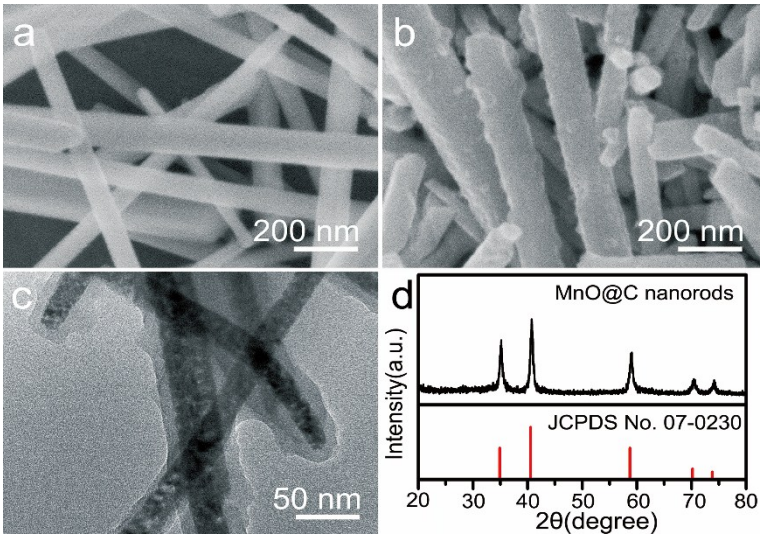


**Fig. S8** a) SEM images of $MnCO_3$ nanorods. b-d) SEM image (b), TEM image (c) and XRD patterns (d) of MnO@C nanorods. The $MnCO_3$ nanorods (Figure S5a) in a diameter of 70~140 nm were firstly synthesized through a hydrothermal route. The final product MnO@C nanorod has a diameter of 150~200 nm (Figure S5b) and an apparent carbon layer is in a thickness of 10~20 nm (Figure S5c). The XRD patterns (Figure S5d) can be also well-indexed to cubic MnO (JCPDS No. 07-0230).

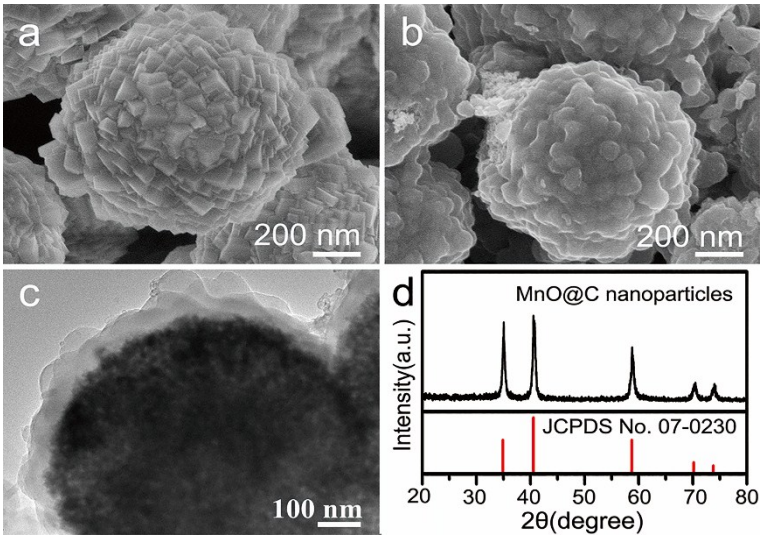


**Fig. S9** a) SEM images of $MnCO_3$ nanoparticles. b-d) SEM image (b), TEM image (c) and XRD patterns (d) of MnO@C nanoparticles. The $MnCO_3$ microsphere aggregated by nanoparticles was first prepared as show in Fig S6a. After coated by PDA and carbonized in an insert atmosphere, the MnO@C nanoparticles was obtained (Figure S6b). From the TEM image (Figure S6c), the carbon layer with a thickness of ~50 nm

could be obviously observed and the XRD pattern in Figure S6d further confirmed its structure information which could be indexed into the cubic MnO (JCPDS No. 07-0230).

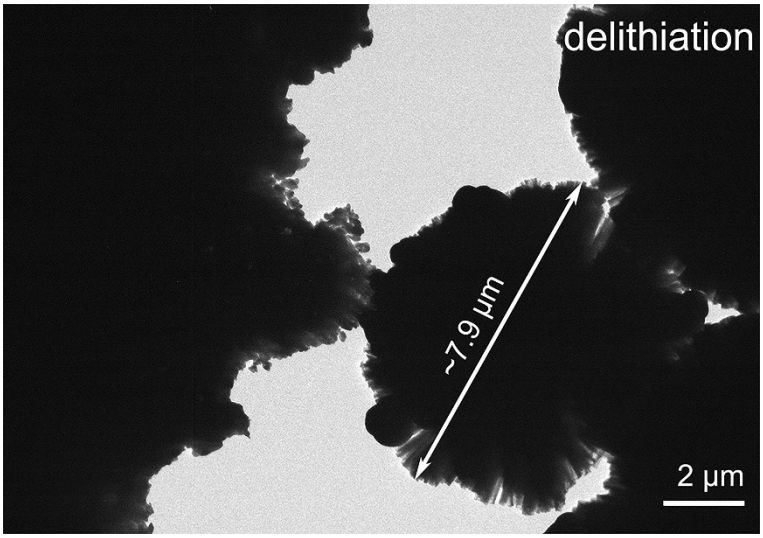


**Fig. S10** The TEM image of MnO@C hierarchical microsphere after lithiation.

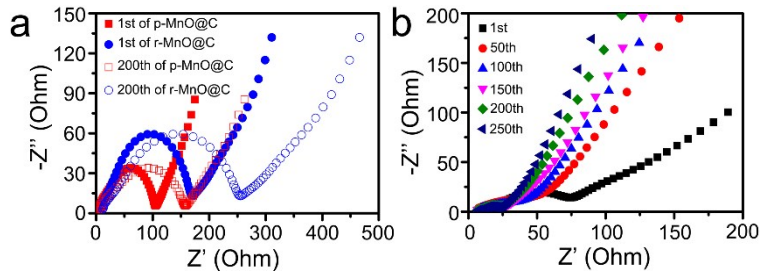


**Fig. S11** a) Nyquist plots of MnO@C nanorods and MnO@C nanoparticles. b) Nyquist plots of MnO@C microspheres in different cycles.

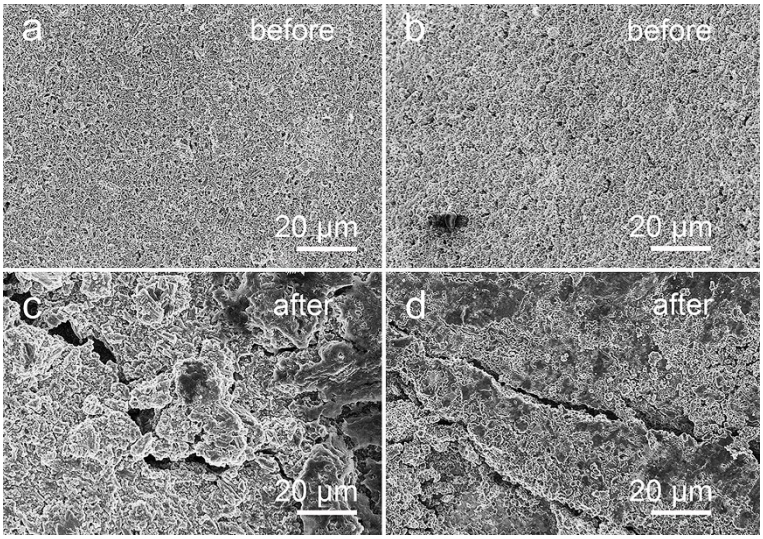


**Fig. S12** SEM images of the electrodes before cycles for MnO@C nanorods (a) and MnO@C nanoparticles (b), and after cycles for MnO@C nanorods (c) and MnO@C nanoparticles (d).

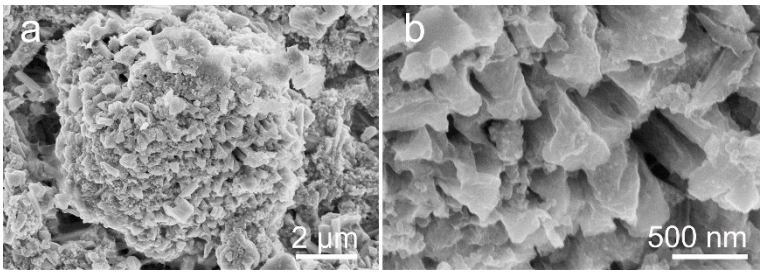


**Fig. S13** a) The low magnification and b) high magnification SEM images of MnO@C microspheres in the electrode after cycles.

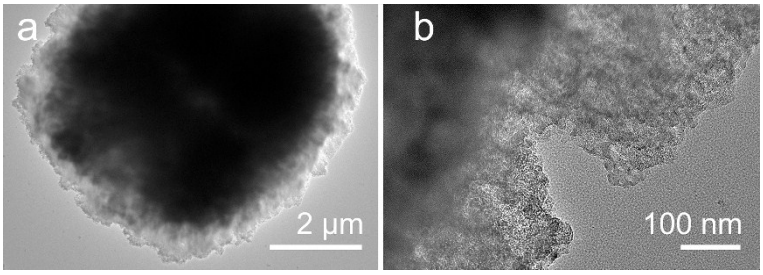


**Fig. S14** TEM images of MnO@C microsphere after 1000 cycles.

Reference:

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