Supplementary Material (ESI) for Chemical Communications
This journal is (c) The Royal Society of Chemistry 2011

Supporting information

Ultrafine manganese dioxide nanowire network for high-performance supercapacitors

Hao Jiang [a, b, c], Ting Zhao [b], Jan Ma *[, a, b], Chaoyi Yan [b], Chunzhong Li [c]

[a] Temasek Laboratories, Nanyang Technological University, Singapore 637553, Singapore

[b] School of Materials Science and Engineering, Nanyang Technological University, Singapore 639798, Singapore

[c] Key Laboratory for Ultrafine Materials of Ministry of Education, School of Materials Science and Engineering, East China University of Science & Technology, Shanghai 200237, China

* Electronic mail: asjma@ntu.edu.sg (Prof. Jan Ma);

Part I: Synthesis, characterization and formation mechanism of the MnOOH nanowires

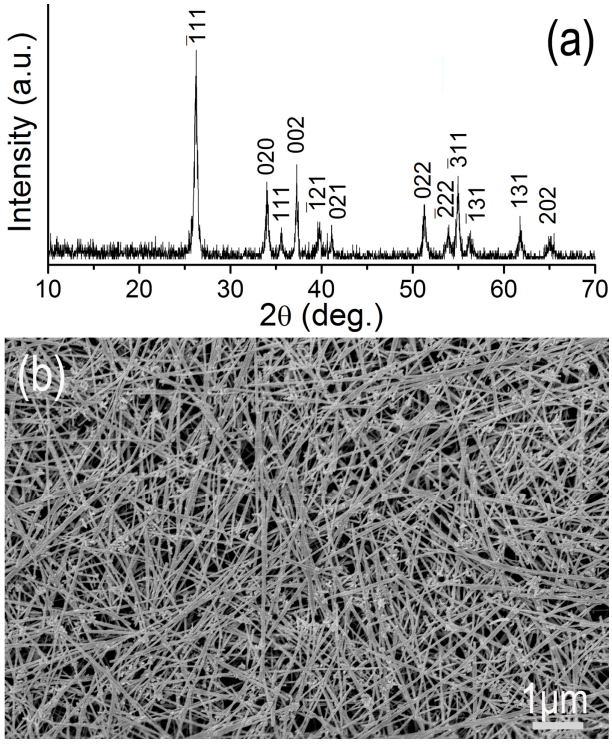

Figure S1 (a) XRD pattern and (b) SEM image of the as-synthesized MnOOH nanowires.

In a typical synthesis of the MnOOH nanowires, sodium dodecyl benzene sulfonate (SDBS, 0.3845 g) and Polyvinylpyrrolidone (PVP, Mw = 55,000, 0.2223 g) were dissolved in 35 mL of distilled water. When the solution was clarified, 1.2 mL of 0.5 M $Mn(NO_3)_2 \cdot 6H_2O$ and 2 mL of 0.2 M $KMnO_4$ was added to the above solution under continuous stirring, respecitively. The resulting cloudy solution was transferred into a 50 mL Teflon-lined stainless steel autoclave and heated at 180 °C for 4~6 h, and then naturally cooled down to room temperature. The precipitates, i.e. MnOOH nanowires, washed several times with distilled water and absolute ethanol, and dried at 60 °C for 6 h.

Figure S1(a) shows the XRD pattern of the as-synthesized MnOOH nanowires. All of the diffraction peaks can be indexed to the monoclinic MnOOH (JCPDS, 88-0649), and no other

characteristic peaks from impurities are detected in the spectrum. The corresponding SEM image is shown in Figure S1(b). It can be see that the sample is mainly composed of nanowires with average diameters of ~ 55 nm and lengths up to tens of microns. The formation process of the nanowires can be explained according by a polymer (PVP)-surfactant (SDBS)-assisted oxidation-crystallization mechanism. The use of PVP combining anionic surfactants to synthesize one-dimensional structures can be found in previous reports.[1-3] For example, Xie et al[1] fabricated one-dimensional SnO_2 nanostructures using PVP-SDBS system. For MnOOH nanowires, the formation process is similar to the growth of SnO_2 nanorods.[1] Briefly speaking, the interaction between PVP and SDBS micelle resulted in the adherence of SDBS micelles to PVP. Meanwhile, SDBS can act as stabilizers for the crystals, preventing their precipitation and aggregation. The SDBS stabilized particles adsorbed on the PVP chains. So, the complex of PVP and SDBS brings the particles together and with the reaction proceeding, the formed MnOOH nanowires are formed and well crystallized. The formation schematic image was illustrated in Figure S2.

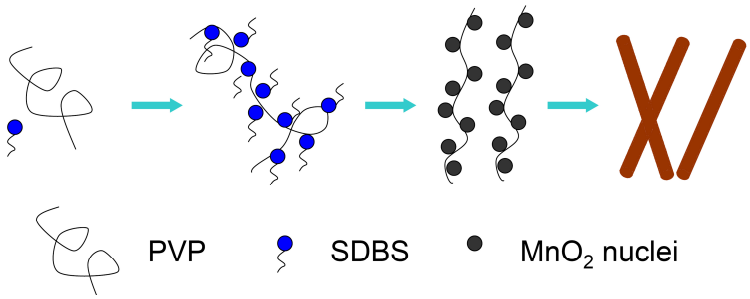

Figure S2 Schematic illustration of the formation process of MnOOH nanowires.

(1) Q. R. Zhao, Y. Xie, T. Dong and Z. G. Zhang, *J. Phys. Chem. C*, 2007, **111**, 11598.

(2) S. Stoll and J. Buffle, *J. Colloid Interface Sci.*, 1996, **180**, 548.

(3) E. Leontidis, T. Kyprianidou-Leodidou, W. Caseri and K. C. Kyriacou, *Langmuir*, 1999, **15**,

3381.

Part II: Characterization and electrochemical measurements

The as-prepared products were characterized with X-ray powder diffractometer (XRD; Siemens D5005, Cu Kα radiation) at a scan rate of 2 °C min^{-1}, scanning electron microscopy (FESEM; JEOL, JSM-7600F) and transmission electron microscopy (TEM; JEOL, JEM-2100F). The electrochemical measurements (Autolab PGSTAT30 potentiostat) were conducted using a three-electrode mode in a 1 M Na_2SO_4 solution. The working electrodes were prepared by mixing MnO_2 powder (80 wt.%) as active material with acetylene black (15 wt.%), and polytetrafluoroethylene (PTFE, 5 wt.%). A small amount of absolute ethanol was then added to those mixtures to make them more homogeneous. The mixtures were coated on the graphite paper and dried at 100 °C for several hours to removal the solvent. The reference electrode and counter electrode were Ag/AgCl electrode and platinum, respectively. Typical CV curves were measured between –0.1 and 0.9 V.

Part III: Supplementary Figures and Analysis

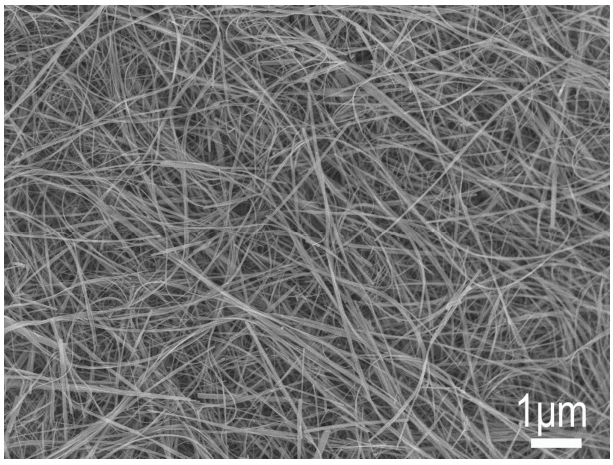

Figure S3 Low-magnification SEM images of the high aspect ratio MnO_2 nanowires.

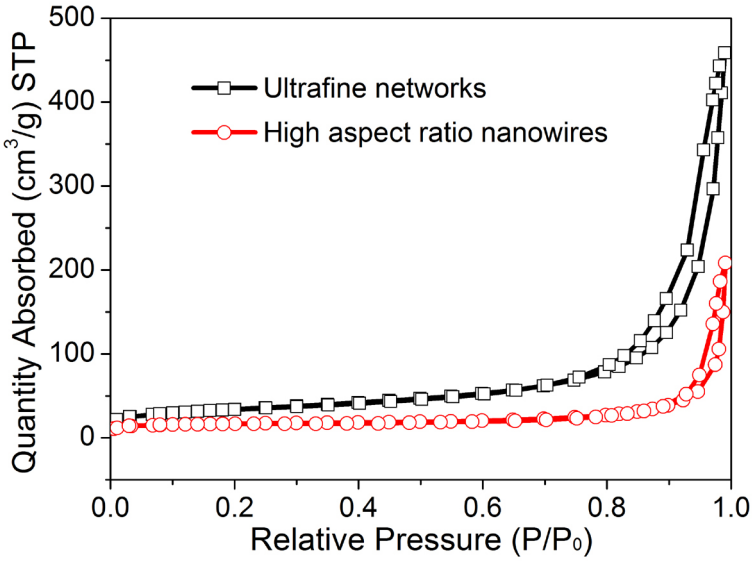

Figure S4 Nitrogen adsorption and desorption isotherms of the ultrafine MnO_2 networks and the high aspect ratio MnO_2 nanowires. The ultrafine MnO_2 networks show higher BET surface area of 121 m^2/g than that of the high aspect ratio nanowires (58 m^2/g).

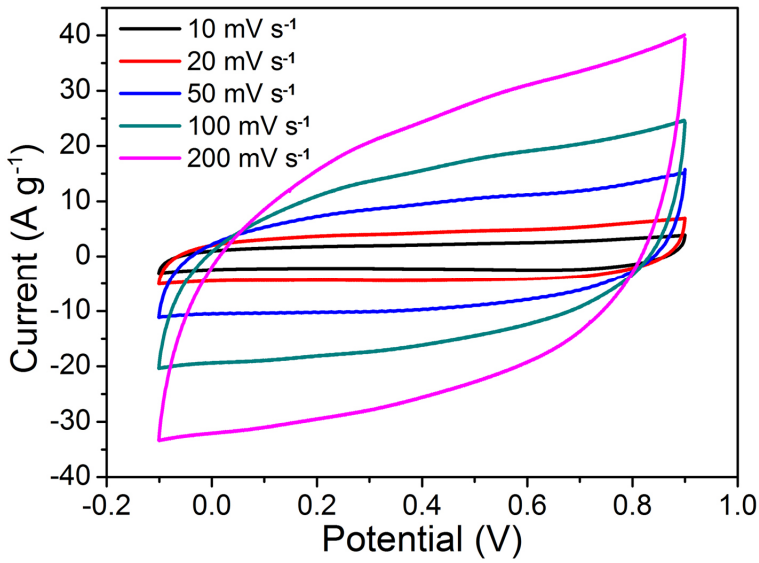

Figure S5 CV curves of the ultrafine nanowires networks at various scan rates from 10 to 200 mV s^{-1}.

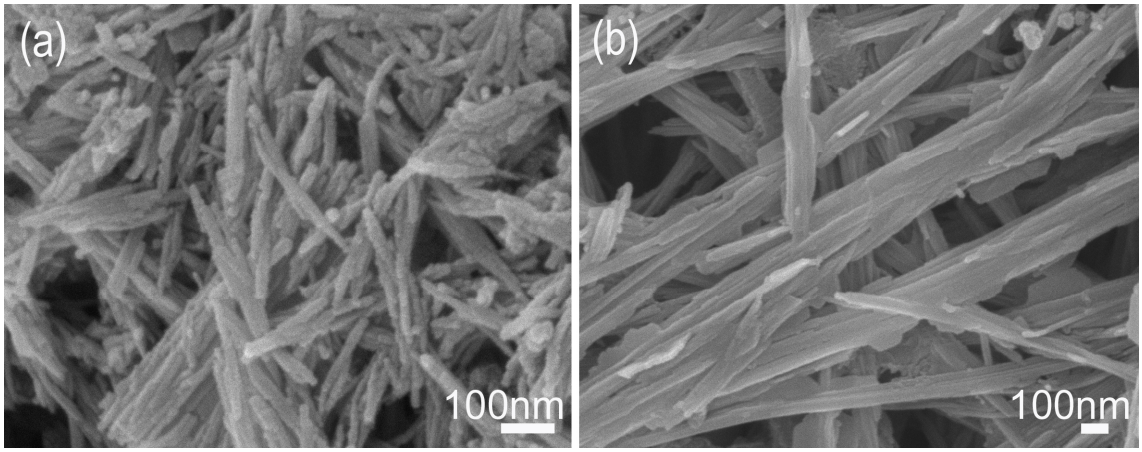

Figure S6 SEM images of the ultrafine MnO_2 nanowires (a) and the high aspect ratio MnO_2 nanowires (b) after 1000 cycles.

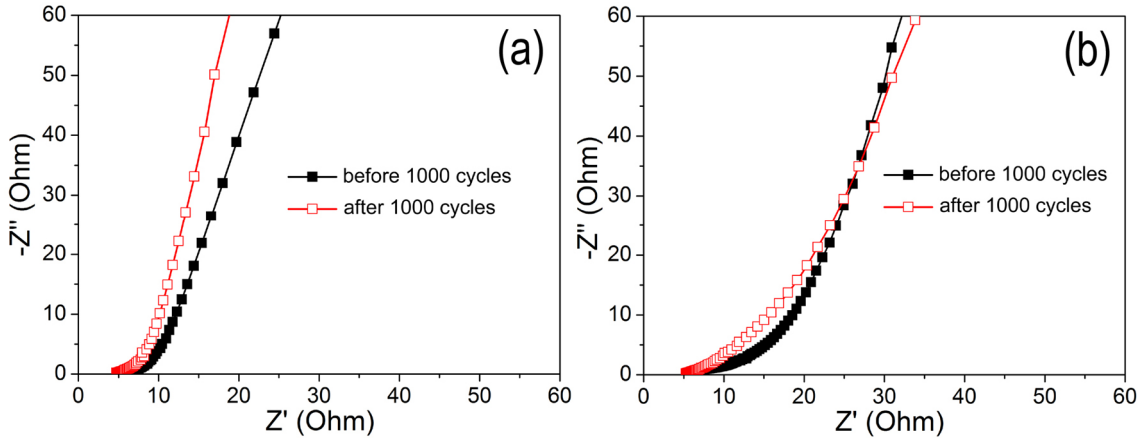

Figure S7 Nyquist plot of the untrafine MnO_2 nanowires (a) and high aspect ratio MnO_2 nanowires (b).

SEM examination after 1000 cycles and electrochemical impedance spectroscopy (EIS) analysis have been carried out. Figure S6 shows the SEM images of the two MnO_2 electrodes after 1,000 cycles. It can be observed that the ultrafine MnO_2 nanowires maintain the one-dimensional nanostructure with slight shortening after cycling. However, the high aspect ratio MnO_2 nanowires are aggregated together after cycling, which may have a detrimental effect on the capacitive properties. The Nyquist plots of the ultrafine MnO_2 nanowires and the high aspect ratio MnO_2 nanowires are also presented in Figure S7. It is known that an equivalent series resistance (ESR) is an important characteristics of supercapacitors measured at high frequency region where the curve intercepts on the real axis.[5] It can be seen that both of them show almost the same ESR, about 6.5 Ω, before cycling. After 1000 cycles, the ultrafine MnO_2 nanowires exhibited lower ESR (~ 5.0 Ω)

than the value of the high aspect ratio MnO_2 nanowires (~ 5.7 Ω) due to the activation of active material during the cycling process.[6] The higher ESR indicates the lower electrical conductivity of the sample. In addition, after 1000 cycles, the slope is close to 90° at low frequency region as shown in Figure S7(a), which indicates that the ultrafine MnO_2 nanowires have better capacitive behaviour than that of the high aspect ratio of MnO_2 nanowires. The EIS results further confirm the ultrafine MnO_2 nanowire is a better capacitive material in comparison with the high aspect of MnO_2 nanowires.

(5) (a) S. Devaraj and N. Munichandraiah, *J. Electrochem. Soc*., 2007, **154**, A901; (b) M. Toupin, D. Bélanger, I. R. Hill and D. Quinn, *J. Power Source*, 2005, **140**, 203.

(6) H. Q. wang, Z. S. Li, Y. G. Huang, Q. Y. Li and X. Y. Wang, J. Mater. Chem., 2010, 20, 3883.