Mesoporous Nanowire Array Architecture of Manganese Dioxide for Electrochemical Capacitor Applications

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Experimental procedures

All chemical reagents were AnalaR grade and used as received without further purification. Nonionic surfactant polyoxyethylene (10) cetyl ether (Brij 56, $C_{16}EO_{10}$) was purchased from Aldrich. The manganese acetate ($MnAc_2{\cdot}4H_2O$), potassium acetate (KAc), sodium sulfate (Na_2SO_4) and ethanol (99.9 %) were obtained from Shanghai Chemical Reagent Co. All aqueous solutions were prepared using high purity water (18 MΩ cm resistances).

AAO/Ti/Si substrates were prepared according to our previous reports[1]. The electrolyte was a binary system of 60 wt% surfactant Brij 56 and 40 wt% aqueous solution containing $MnAc_2$ (0.5 mol L^{-1}) and KAc (0.51 mol L^{-1}). The electrodeposition was conducted at 40 °C by means of a Chenhua CHI760b model Electrochemical Workstation (Shanghai), with a three-electrode cell consisting a saturated calomel electrode (SCE) as reference electrode, a 1.0 cm × 1.0 cm platinum plate as counter electrode and AAO/Ti/Si substrates (1 cm^2 in area) as the working electrode. The electrodeposition experiments were all carried out at a constant potential of 1.0 V vs. SCE to give a totally passed charge of 0.22 C for the same required amount of MnO_2. After deposition, the nanowire arrays were first immersed in ethanol for 6 h which was regularly replaced every 2 h to remove the surfactant and other soluble materials. Thereafter, in order to remove the AAO film, all the prepared MnO_2 nanowire array electrodes were immersed in (0.1 mol L^{-1}) NaOH for 15 min and then washed with water several times.

XRD data were collected using a Rigaku D/MAX 2400 diffractometer (Japan) with Cu Kα radiation (k = 1.54056 Å) operating at 40.0 kV, 60.0 mA. The surface

morphology of the MnO_2 nanowire array was examined by FESEM (JEOL JSM-S4800). TEM images were performed on a JEOL JEM-1230 (Japan) equipped with a GATAN BioScan Camera 792 (U.S.A.).

Cyclic voltammetric and chronopotentiometric measurements were all performed in 0.5 mol L^{-1} Na_2SO_4 aqueous solution using CHI760B Electrochemical Workstation.

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References

1 C. L. Xu, S. J. Bao, L. B. Kong, H. Li, and H. L. Li, *J. Solid State Chem.* 2006, **179**, 1351.

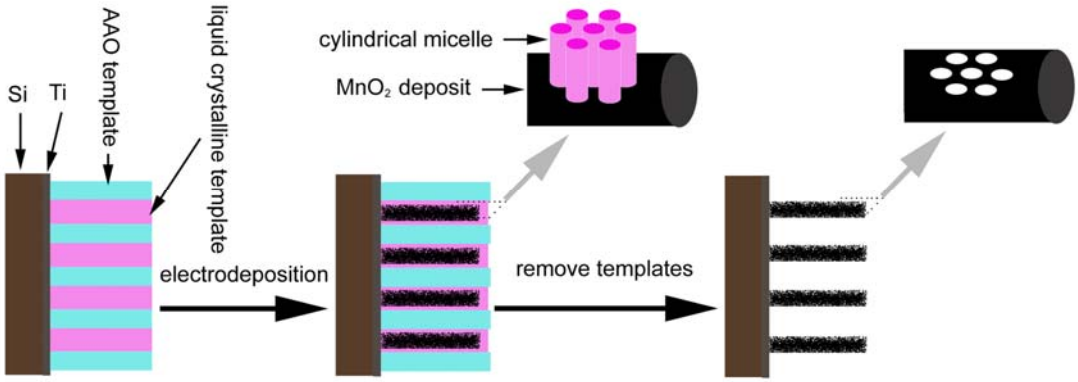

Fig. S1. Procedure of the electrodeposition of mesoporous MnO_2 nanowire arrays from conjunct template of AAO and liquid crystal on the surface of AAO/Ti/Si substrates.

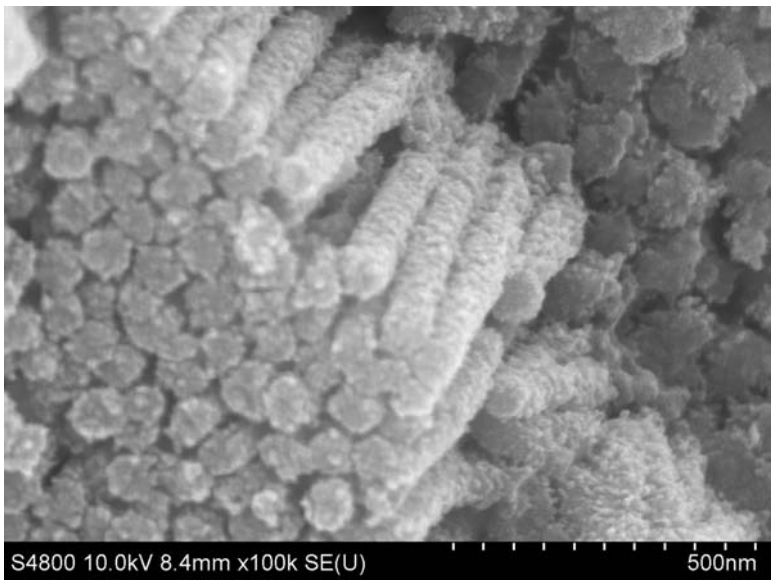

Fig. S2. High magnification FESEM image of the mesoporous MnO_2 nanowire arrays.

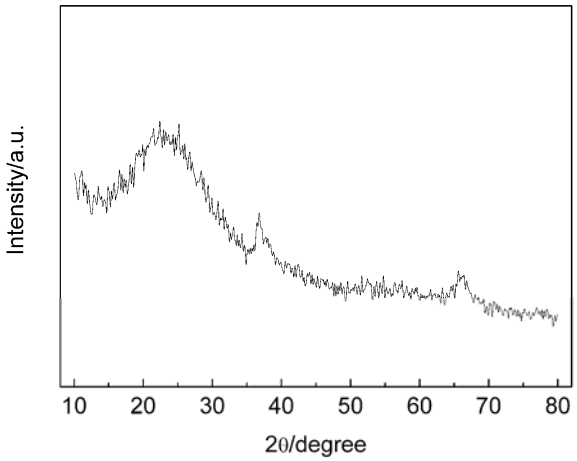

Fig. S3. XRD pattern of as-synthesized mesopoeous MnO_2 nanowire arrays

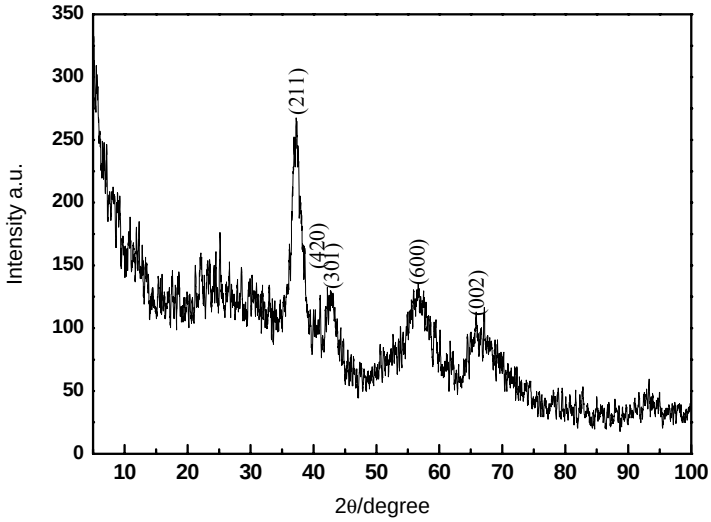

Fig. S4. XRD pattern of the mesopoeous MnO_2 nanowire array heat-treated at 450℃