Electronics Supplementary Information

Mesoporous-assembled MnO$_2$ with large specific surface area

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Experimental Details

Synthesis of Mesoporous-assembled MnO$_2$:

All the chemicals were of analytical grade, and directly used without further purification. The delaminated MnO$_2$ nanosheets were synthesized as reported in the literature.[1] The obtained delaminated MnO$_2$ nanosheets were centrifuged at a speed of 12000 rpm for 30 min and dried to obtain delaminated MnO$_2$ slurry with water content of about 50%. The NH$_4$HSO$_4$ powder was added into the slurry and grinding fully with a molar ratio of NH$_4$HSO$_4$/MnO$_2$=2.1, the mixture was calcined in muffle furnace at a heating rate of 2 °C/min to 175 °C for 5 h. The obtained material was washed with distilled water aided by ultrasonic, and dried at room temperature, the mesoporous-assembled MnO$_2$ was finally prepared. By changing the molar ratio of NH$_4$HSO$_4$/MnO$_2$, the mesoporous-assembled MnO$_2$ with different specific surface area were obtained by the similar process. The mesoporous-assembled MnO$_2$ were denoted as MnO$_2$ (x), where x represented the molar ratio of NH$_4$HSO$_4$/MnO$_2$.

Characterization

The structure of the samples was characterized by X-ray diffraction patterns (XRD, D/Max2550VB+/PC diffractometer with CuKα radiation). The morphology of the samples was observed by transmission electron microscopy (TEM, JEM-2010) at an acceleration voltage of 200 KV. X-ray photoelectron spectroscopy (XPS) spectra were collected on an AXIS ULTRA spectrometer (Kratos Analytical). All binding energies were calibrated using carbon C1s peak at 284.6 eV as a reference. Nitrogen adsorption/desorption isotherms were measured at 77 K on Quantachrome SI-3 analyzer. Samples were degassed at 120 °C for 12 h prior to the measurement. The specific surface areas of the samples were calculated using the Brunauer-Emmett-Teller (BET) method with the desorption data at the relative pressure (P/P_0) range 0.05-0.35. The total pore volumes were estimated at P/P_0=0.99. The pore size distribution (PSD) curves were calculated from the desorption branch using the nonlocal density functional theory (NLDFT) model.

Electrochemical measurements:

The electrochemical tests were performed with IVIUMSTAT electrochemical workstation (Ivium Technologies BV Co., Holland). The working electrode was prepared by mixing active material with acetylene black and polyvinylidene fluoride (0.02 g mL^{-1}, in N-methyl-ketopyrrolidine) at a weight ratio of 75:20:5. The slurry of the mixture was then pasted onto Ni foam current collector with a definite area of 2.0 cm^2 and pressed under a pressure of 100 kg cm^{-2}, an electrode with thickness about ~0.03 mm and density of ~1.0 g cm^{-3} is obtained, and the mass loading for each electrode is about 3.0 mg cm^{-2}. The electrochemical test of the electrode was performed in a conventional three-electrode system in 1 mol L^{-1} Na_2SO_4 electrolyte, in which platinum foil and saturated calomel electrode (SCE) were used as counter and reference electrodes, respectively. The capacitance (C) was calculated from the galvanostatic discharge process according to the following equation: C = I Δt /(m × ΔV), where I (A) is the discharge current, Δt (s) is the discharge time, m (g) is the mass of the active material, and ΔV (V) is the voltage change excluding the IR drop during the discharge process.
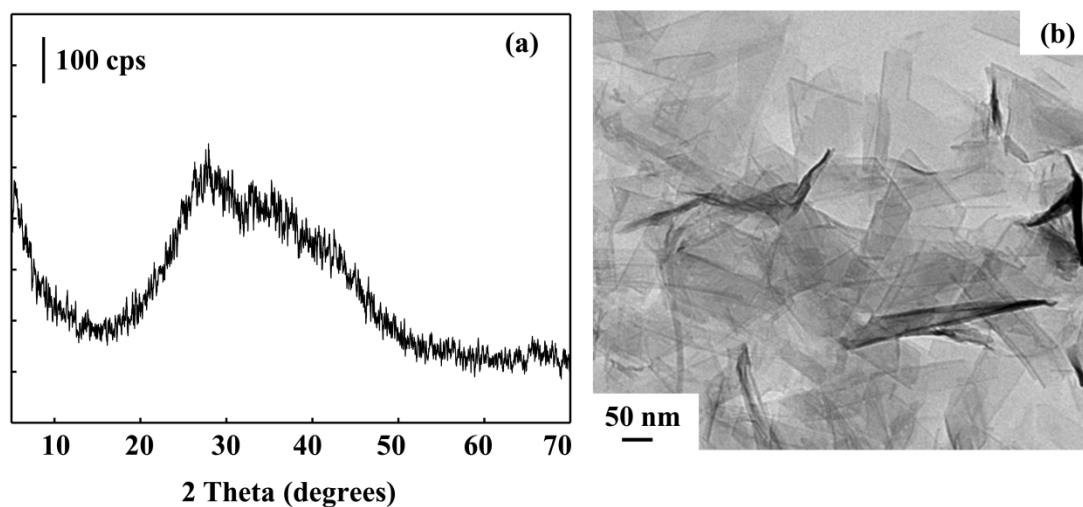
Supplementary Figures and Analysis

Fig. S1 XRD pattern (a) and TEM image (b) of the delaminated MnO_2 nanosheets.

The XRD pattern of manganese oxide slurry gives no clear peaks but only an amorphous halo (Fig. S1a†). It can give some information that the layered manganese oxide is delaminated into their individual primary plates.[2-4] Because the delaminated manganese oxide nanosheets are a metastable, it is only observed in the wet condition. As shown in Fig.1, the layered structure with basal spacing of 0.96 nm reappears by calcining at 175 °C, which indicate that the dissipation of interlayer water molecules cause the reassembling of disordered manganese oxide plates to form the stacked layer.
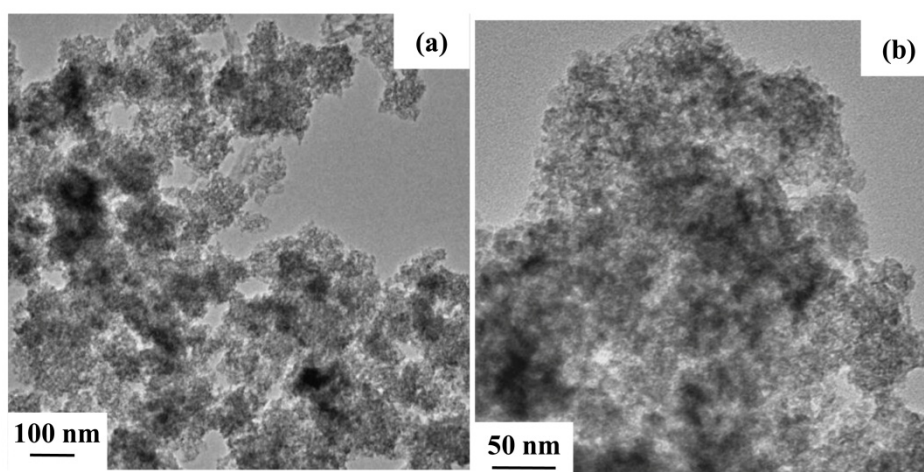

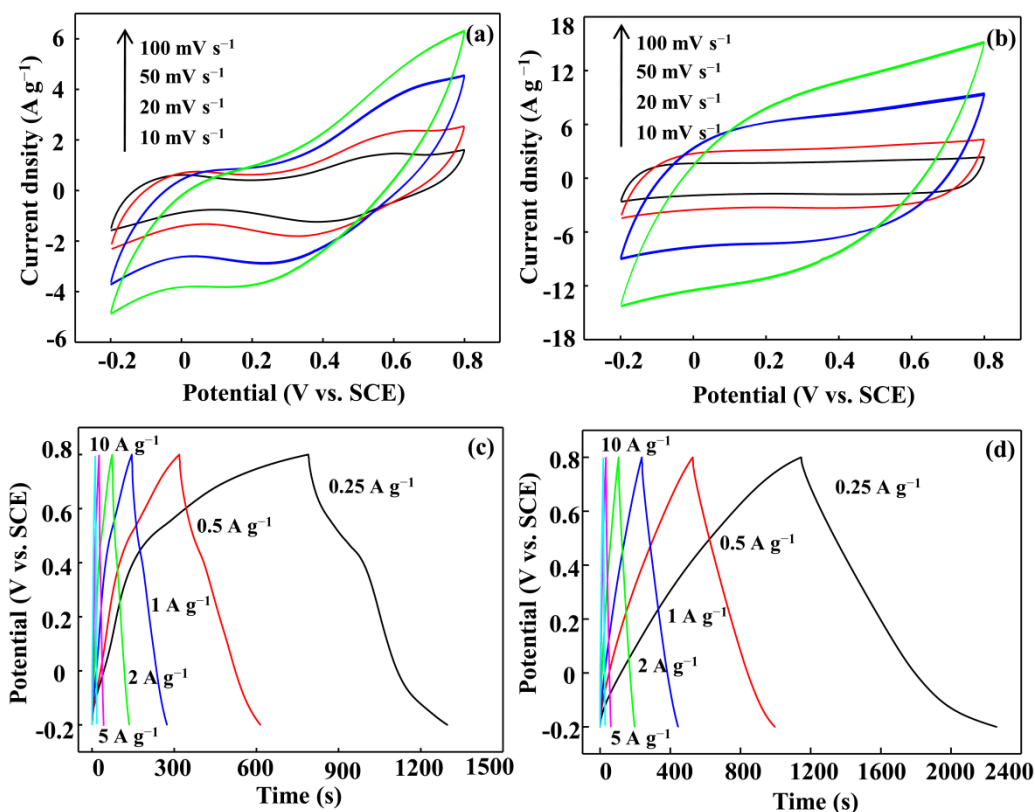**Fig. S2** TEM images of the as-synthesized MnO_2 by H_2SO_4 treatment.

Fig. S3 CV curves (a, b) and charge/discharge curves (c, d) of MnO_2 (0) and MnO_2 (2.1) at various scan rates and current densities in 1 M Na_2SO_4 solution.

The cyclic voltammetry (CV) curves of MnO_2 (0) electrode are distorted and have a pair of redox peaks, which is ascribed to a Faradic pseudocapacitance due to the intercalation/detercalation of protons or alkaline metal cations in MnO_2 (0) electrode. Also, their nonlinear charge/discharge profiles further confirm the pseudocapacitive behavior (Fig. S3†, left). In contrast, the CV curves of MnO_2 (2.1) electrode exhibit much larger enclosed areas and a quasi-rectangular shape with a mirror image feature, indicating the ideal electrical double-layer capacitance behavior and fast charging-discharging process characteristic.[5] At each current density, their charge/discharge curves are almost mirror symmetrical, suggesting that MnO_2 (2.1) electrode shows excellent electrochemical performance (Fig. S3†, right).
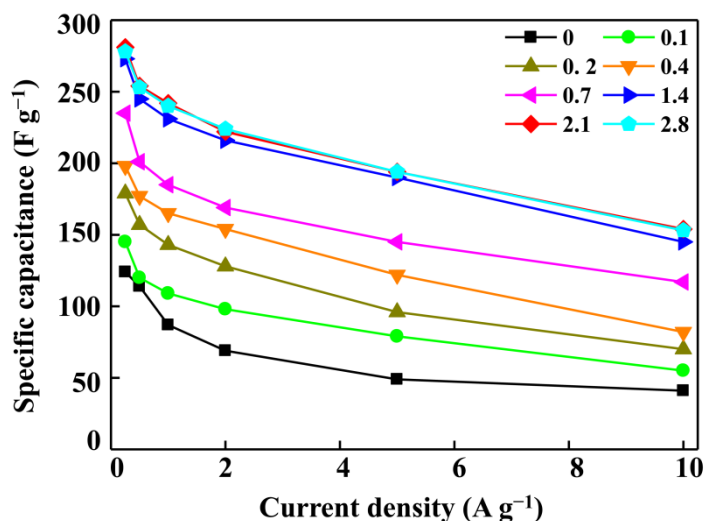
Fig. S4 The specific capacitance versus the current densities for MnO_2 electrode with different molar ratio of NH_4HSO_4/MnO_2 at different current densities.

The specific capacitances of the MnO_2 electrodes with different molar ratios of NH_4HSO_4/MnO_2 at different current densities are shown in Fig. S4. It can be seen that their specific capacitance decreases with the increase of the current density due to the kinetic limitation. For MnO_2 electrodes with high molar ratios of NH_4HSO_4/MnO_2, the capacitance retention from 0.25 to 10 A g^{-1} is relative better. The better rate performance are probably ascribed to their larger surface area and mesoporous structure, which facilitate the improvement of kinetics due to the increased reaction interface and the reduced diffusion path for ionic intercalation and deintercalation.[6]
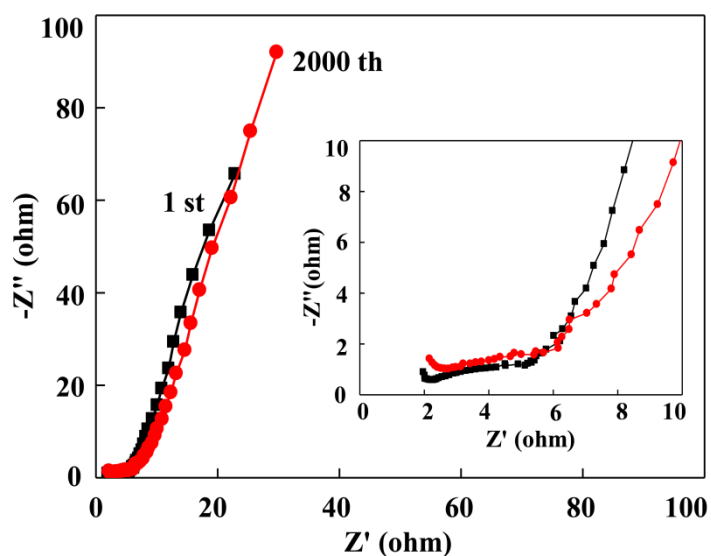

Fig. S5 Nyquist plots of MnO_2 (2.1) before and after 2000 cycles with inset showing the magnified plots in high frequency region.

Refenences

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