Self-Assembly of Mesoporous Nanotubes Assembled from Interwoven Ultrathin Birnessite-type MnO₂ Nanosheets for Asymmetric Supercapacitors

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Porous nanotubes comprised of MnO₂ nanosheets were fabricated with a one-pot hydrothermal method using polycarbonate membrane as the template. The diameter and thickness of nanotubes can be controlled by choice of the membrane pore size and the chemistry. The porous MnO₂ nanotubes were used as a supercapacitor electrode. The specific capacitance in a three-electrode system was 365 F g⁻¹ at a current density of 0.25 A g⁻¹ with capacitance retention of 90.4% after 3000 cycles. An asymmetric supercapacitor with porous MnO₂ nanotubes as the positive electrode and activated graphene as the negative electrode yielded an energy density of 22.5 Wh kg⁻¹ and a maximum power density of 146.2 kW kg⁻¹; these values exceeded those reported for other MnO₂ nanostructures. The supercapacitor performance was correlated with the hierarchical structure of the porous MnO₂ nanotubes.

With increasing demand for sustainable and renewable power sources in modern electronic industries, supercapacitors have attracted tremendous attention because of their high power density, excellent pulse charge-discharge characteristics, long cycling life and safe operation.¹⁻³ Up to now, various materials, including carbonaceous materials,⁴⁻⁵ conducting polymers,⁶ transition metal oxides/hydroxides,⁷⁻⁸ and hybrid composites,⁹⁻¹⁰ have been widely investigated as electrodes for supercapacitors. Compared to carbonaceous materials and conducting polymers, transition-metal oxides/hydroxides exhibit larger electrochemical capacitances and energy densities as they can provide a variety of oxidation states for efficient redox charge transfer which could satisfy the needs of high-performance supercapacitors. Hence, there has been extensive interest in developing the attractive transition metal oxide (such as MnO₂¹¹, Co₃O₄¹², NiO¹³, VOₓ¹⁴, and CuO¹⁵) for supercapacitors.

In particular, manganese dioxide (MnO₂) has been extensively investigated as a supercapacitor electrode material due to its low cost, high natural abundance, high theoretical capacity (~1370 F g⁻¹), and non-toxicity.¹¹⁻¹⁶,¹⁸ The electrochemical performance of MnO₂ has been found to be strongly influenced by a variety of factors including preparation conditions, particle size, morphology, and degree of crystallinity, and others. While nanosheets, hollow spheres, nanoflowers, nanowires/nanorods, thin films, and nanotubes have all been reported, the synthesis of MnO₂ with controllable particle size, morphology, and high crystallinity remained as a challenge. Among these structures, MnO₂ nanotubes can provide high surface area and a large surface-to-volume ratio to allow effective contact with the electrolyte ions, affording short ion diffusion paths and fast kinetics. The nanotube morphology can also accommodate large volume changes during the charge-discharge cycle and thereby improve the life of the electrode.³³⁻³⁴ Although significant research has been devoted to the synthesis of MnO₂ nanotubes, there was no effective method for the production of porous MnO₂ nanotubes with precise morphological control. Dong et al.³⁵ reported the synthesis of porous MnO₂/TiO₂ coaxial arrays via a two-step procedure based on an electrodeposition process, while elegant, the process is also complicated and tedious. Zhu et al. prepared the porous MnO₂ nanotubes using a hydrothermal method coupled with post-treatment. But the thickness of the MnO₂ wall and the diameter of the nanotube are difficult to control.³⁶ This motivated us to search for a simple way to prepare porous MnO₂ nanotube with controllable morphology.
In this work, we introduce a novel and effective one-step hydrothermal approach for the synthesis of porous MnO₂ nanotubes. The as-prepared MnO₂ nanotubes were porous and consisted of MnO₂ nanosheets with thickness of about 6 nm. The interconnected MnO₂ nanosheets in a mesoporous tubular structure can facilitate ion insertion/extraction and electron transport in the electrodes. An asymmetric supercapacitor with these porous MnO₂ nanotubes as the positive electrode and activated graphene as the negative electrode in 1 M Na₂SO₄ electrolyte had an energy density of 22.5 Wh kg⁻¹ with a maximum power density of 146.2 kW kg⁻¹.

Results

The morphology of MnO₂ nanotubes can be tailored by varying the pore size of the polycarbonate (PC) membrane, the concentration of Mn precursors, the processing temperature and the time. PC membranes with pore size of 200 nm, and a processing temperature of 140 °C were investigated in this study (Figs. S1 and S2 showed the SEM images of the PC membrane). The structure and phase purity of the as-prepared MnO₂ samples were examined by X-ray powder diffraction (XRD, Figure 1a). The diffraction peaks at about 12.5°, 25.2° and 37° from the as-prepared 200-nm diameter MnO₂ nanotubes matched the standard XRD pattern of birnessite-type manganese oxide crystal (JCPDS 80-1098, \( a = 5.149 \, \text{Å}, \, b = 2.843 \, \text{Å}, \, c = 7.716 \, \text{Å} \)). No other peaks that would be associated with another phase or impurity were observed. Fourier transform infrared spectroscopy (FT-IR) was used to characterize the functionality of MnO₂ nanotubes and the results were shown in Figure 1b. The main absorption bands were found at 3433, 1635, 1116, 517, and 487 cm⁻¹, respectively. The broad band around 3433 cm⁻¹ represented the O-H stretching of the interlayer water molecules, while the weak band at 1635 cm⁻¹ was probably due to the bending vibrations of the O-H groups from the adsorbed water molecules. The absorption peak at 1116 cm⁻¹ was attributed to the –OH bending vibrations combined with Mn atoms. The peaks at 517 and 487 cm⁻¹ were the main characteristic absorption bands of birnessite, corresponding to Mn-O stretching modes of the octahedral layers in the birnessite structure which was consistent with the previous XRD result.

An illustration of the formation of MnO₂ nanotubes was shown in Figure 2a. The MnO₂ nuclei were firstly formed in a short time and adsorbed on the surface of the polycarbonate. As the hydrothermal reaction further proceeded, Ostwald ripening process took place, in which the smaller particles were consumed while the bigger ones grew into nanosheets with a lamellar structure. Subsequently, the nanosheets were self-assembled into porous MnO₂ nanotubes.
due to the “oriented attachment” and “self-assembly” processes\(^\text{46}\), which involved a spontaneous self-organization\(^\text{43,44}\) of the adjacent nanosheets.

Scanning electron microscope (SEM) images (Figure 2b–2d; see also Fig. S3) revealed that the average diameter of the MnO\(_2\) nanotubes was about 200 nm, which is coincided with the average pore diameter of the original polycarbonate (PC) membrane. However, the length of the MnO\(_2\) nanotubules ranged from 4 to 8 \(\mu\)m, which was shorter than the thickness of the PC membrane (Fig. S2). The length of the MnO\(_2\) nanotubes was not uniform due to the fracture during the removal of the PC template. All the nanotubes were made of MnO\(_2\) nanosheets. Each nanotube had flaky appearance, and the assembly of ultrathin nanosheets into interconnected porous structure provided large and open active area. The porous and hollow nanotubes were further elucidated by Transmission electron microscopy (TEM, Figure 3). High-resolution TEM (HRTEM, Figure 3b and c) images of the nanosheets clearly showed that the birnessite-type MnO\(_2\) nanostructures were crystallized with the interplanar distance of 0.253 and 0.212 nm, corresponding to the (200) and (−112) plane of the birnessite-type MnO\(_2\), respectively\(^\text{41,42,45}\). The interplanar spacing of MnO\(_2\) nanosheet is 0.7 nm, corresponds to the typical interplanar spacing of the (001) plane of birnessite-type MnO\(_2\) that prefers forming two-dimensional flaky structures. The corresponding selected area electron diffraction (SAED) pattern of MnO\(_2\) that prefers forming two-dimensional flaky structures.

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The contact resistances of the MnO\(_2\) electrodes (before and after discharge current, \(\Delta t\) is the discharge time, \(\Delta V\) (V) is the potential window, and \(m\) (g) is the mass of the active material in the electrode. The specific capacitance of the MnO\(_2\) nanotubes was \(365 \text{ F g}^{-1}\) at the current density of \(0.25 \text{ A g}^{-1}\); this value exceeded many MnO\(_2\) electrodes in previous reports (Table S1)\(^\text{41,46–54}\). The corresponding volumetric capacitance of the total electrode including the current collector (Ni foam) was estimated to be about \(107.4 \pm 3 \text{ F cm}^{-3}\) according to the thickness (\(68 \pm 2 \mu\)m) of the compressed MnO\(_2\)/Ni foam electrode. Furthermore, we have measured the electrochemical properties of two reference samples (commercial MnO\(_2\) and MnO\(_2\) nanosheets obtained without PC template) for comparison (Fig. S5). According to the discharge time from the charge/discharge curves (Fig. S5), the as-prepared MnO\(_2\) nanotubes show a much higher specific capacitance than the commercial MnO\(_2\) (\(14.3 \text{ F g}^{-1}\)) and MnO\(_2\) nanosheets (\(194.5 \text{ F g}^{-1}\)). The results show that the MnO\(_2\) nanotubes are a promising candidate for the electrode materials for supercapacitors. The enhanced capacitive performance can be attributed to 1) the hierarchical-mesoporous nanotubular structure facilitated the ion insertion/extraction; and 2) the interconnected porous ultrathin MnO\(_2\) nanosheets cannot only shorten the ion diffusion paths, but also ensure a high utilization of the active materials (since the redox reaction was surface reaction only and the bulk metal oxide did not contribute). The specific capacitance of MnO\(_2\) nanotubes electrode at various current densities was shown in Figure 4c. When the current density was increased from 0.25 to 10 A g\(^{-1}\), the specific capacitance can still be as high as \(202.7 \text{ F g}^{-1}\) (decreased about 45%), indicating the good rate capability of the MnO\(_2\) nanotubes.

The Nyquist plots of MnO\(_2\) nanotubes electrode before and after 3000 cycles were obtained using AC electrochemical impedance spectroscopy (EIS) in the frequency range from 100 kHz to 0.01 Hz at open circuit potential by applying an AC voltage with 5 mV amplitude. The Nyquist plots in Figure 4d were composed of one semicircle in the high-frequency region and a linear part in the low-frequency region, which illustrated typical capacitor behavior. The contact resistances of the MnO\(_2\) electrodes (before and after 3000 cycles) were 1.6 and 2.0 \(\Omega\), respectively, indicating good conductivity of the electrolyte and assembly of the cell. The equivalent circuit for the Nyquist plots was shown as an inset in Figure 4c (see Supplementary Table S2 for simulation result). After 3000 cycles, only a slight increase of the charge transfer resistance (Rct) from 3.9 to 7.4 \(\Omega\) was observed.

Figure 4e showed the long-term cycling performance of the MnO\(_2\) electrode by galvanostatic charge-discharge process at the current density of \(5 \text{ A g}^{-1}\) for consecutive 3000 cycles. The specific capacitance

![Figure 3](https://www.nature.com/scientificreports/)

**Figure 3** | (a) Low-magnification TEM image of an individual porous MnO\(_2\) nanotube. (b) Detailed images of the terminal nanosheets of the MnO\(_2\) nanotube. (c) HRTEM image of the MnO\(_2\) nanosheets (the red boxed region in (b)). Bottom-right inset is the corresponding SAED pattern.
of the MnO₂ nanotube-based electrode maintained about 90.4% of its initial value after 3000 cycles, demonstrating the good stability of the MnO₂ nanotubes as a supercapacitor’s electrode. In addition, the charge-discharge curves of the last 10 cycles were shown as the inset in Figure 4e. The similar symmetric triangular charge-discharge curves (as comparing to the initial curve) indicated no significant structural change of the MnO₂ nanotubes electrode during the charge/discharge processes. Meanwhile, the SEM images of the MnO₂ nanotubes
An asymmetric supercapacitor was fabricated using the MnO2 nanotubes as the positive electrode and the activated graphene (AG) as the negative electrode with 1.0 M Na2SO4 aqueous electrolyte (Figure 5a). The SEM images and the electrochemical properties of the AG were shown in Figure S8 and S9 (see Supplementary Information). In the design cell, the mass ratio of the positive electrode (0.7 mg) to the negative electrode (1.3 mg) was fixed at 0.5 on the basis of the specific capacitance values and the potential windows of the two materials. The asymmetric device exhibited capacitive behavior with nearly rectangular-shaped CV curves without obvious redox peaks with the operating voltage up to 2.0 V (Figure 5b). Figure 5c showed the voltage window from 0 to 1.8 V at the scan rates of 5, 10, 20, 50 and 100 mV s\(^{-1}\). The CV profile of the asymmetric cell remained relatively rectangular at a high scan rate of 100 mV s\(^{-1}\), which demonstrated good charge/discharge properties and rate capability of the asymmetric supercapacitor.

**Discussion**

The galvanostatic charge-discharge curves at various current densities were shown in Figure 5d. It can be seen that the potentials of the charge-discharge lines are nearly proportional to the charge or discharge time, indicating a rapid I–V response, small equivalent series resistance (ESR) and ideal capacitive characteristics. The EIS results (see Supplementary Fig. S10) of the asymmetric supercapacitor before and after 10000 cycles test confirmed the relative small change (see Supplementary Fig. S11) of the asymmetric supercapacitor resistance (ESR) and ideal capacitive characteristics. The EIS results demonstrated good charge/discharge properties and rate capability of the asymmetric supercapacitor.

Electrochemical measurements. A three-electrode system was used to measure the response of the MnO2 nanotubes as the working electrode using 1 M Na2SO4 aqueous solution as the electrolyte, with a platinum plate as the counter electrode and saturated calomel electrode (SCE) as the reference electrode, respectively. The working electrode was prepared by mixing 70 wt% active material (MnO2 nanotubes), 20 wt% acetylene black and 10 wt% polyvinylidene fluoride (PVDF) in N-methyl-2-pyrrolidone (NMP) and the slurry was spread onto a foam nickel current collector (1 \(\times\) 1 cm\(^2\)). The electrode was heated at 120 °C for 12 h to evaporate the solvent and then uniaxially pressed under 10 MPa. The electrode contained 2 mg of active materials (MnO2 nanotubes alone).

The asymmetric supercapacitor was measured with a two-electrode system, including two slices of electrode material with the same size, a Whatman filter paper soaked in 1 M Na2SO4 solution before being connected to the working electrode as the positive electrode using 1 M Na2SO4 aqueous electrolyte, delivering an energy density of 22.5 Wh kg\(^{-1}\) and a maximum power density of 146.2 kW kg\(^{-1}\). The results indicated that the mesoporous MnO2 nanotube is a promising candidate in electrochemically stable supercapacitors for practical applications. Such unique nanosheets-built MnO2 nanotubes might also be used in broad fields including dye wastewater treatment and gas sensors. Furthermore, the proposed synthetic methodology would open new opportunities of other transition metal oxides for high-performance supercapacitors.

**Methods**

**Materials.** All the chemical reagents were purchased from Alfa Aesar, which are of analytical purity and used without any further purification. The polycarbonate (PC) membrane filters (Whatman 110606; pore diameter: 200 nm) were used for the fabrication of mesoporous MnO2 nanotubes.

**Preparation of nanotubes comprised of MnO2 nanosheets.** Prior to being used, the PC substrate was treated by hydrochloric acid (1 M) to remove the impurities on the surface of PC. The MnO2 nanotubes were prepared in KNO3 solution using the PC as the template. In a typical synthetic procedure, the treated PC membrane was immersed in KNO3 solution (0.02 M; 30 mL) under ultrasonication for 20 minutes. The mixture (including the PC membrane) was transferred into a Teflon-lined stainless steel autoclave which was subsequently maintained at 140 °C for 24 h. The MnO2/PC membrane composite was then taken out from the solution and dissolved away PC in dichloromethane to obtain pure MnO2 sample. Finally, the MnO2 sample was washed with distilled water and ethanol, and dried at 60 °C to obtain the porous MnO2 nanotubes.

**Electrochemical characterization.** A three-electrode system was used to measure the performance of the MnO2 nanotubes as the working electrode using 1 M Na2SO4 aqueous solution as the electrolyte, with a platinum plate as the counter electrode and saturated calomel electrode (SCE) as the reference electrode, respectively. The working electrode was prepared by mixing 70 wt% active material (MnO2 nanotubes), 20 wt% acetylene black and 10 wt% polyvinylidene fluoride (PVDF) in N-methyl-2-pyrrolidone (NMP) and the slurry was spread onto a foam nickel current collector (1 \(\times\) 1 cm\(^2\)). The electrode was heated at 120 °C for 12 h to evaporate the solvent and then uniaxially pressed under 10 MPa. The electrode contained 2 mg of active materials (MnO2 nanotubes alone).

The asymmetric supercapacitor was measured with a two-electrode system, including two slices of electrode material with the same size, a Whatman filter paper as separator, and two pieces of nickel foil as the current collectors. In the two-electrode system, MnO2 nanotubes were the positive electrode, and activated graphene (AG) mixed with 20 wt% acetylene black and 10 wt% polyvinylidene fluoride (PVDF) in N-methyl-2-pyrrolidone (NMP) to form a paste and then pressed into uniform sheet was the negative electrode. The two electrodes were assembled together with Whatman filter paper soaked in 1 M Na2SO4 solution before being connected to the potentiostat. The electrochemical performance in both three-electrode and two-electrode configurations were carried out on the CHI 660E electrochemical station.
The cyclic voltammetry (CV) and galvanostatic charge-discharge techniques were employed to investigate the electrochemical performance of the electrodes. All the operating current densities were calculated based on the mass of active materials (mass of MnO₂ nanotubes for three-electrode system and the total weight of MnO₂ nanotubes with AG for two-electrode system). The electrochemical impedance spectroscopy (EIS) was conducted in the frequency range between 100 kHz and 0.01 Hz with a perturbation amplitude of 5 mV versus the open-circuit potential.

**Figure 5**  
(a) Schematic illustration of the asymmetric supercapacitor configuration. (b) CV curves of MnO₂ nanosheets-built nanotubes//AG asymmetric supercapacitor measured at different potential window at a scan rate of 50 mV s⁻¹. (c) CV curves of the asymmetric supercapacitor measured at different scan rates between 0 and 1.8 V. (d) Galvanostatic charge-discharge curves at different current densities. (e) The energy density vs. power density of the MnO₂ nanotubes//AG asymmetric supercapacitor in a Ragone plot for fuel cells, conventional batteries, conventional capacitors, and ultracapacitors. (f) Digital image of a red-light-emitting diode (LED) lighted by the MnO₂ nanotubes//AG device.
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**Author contributions**

Y.X.Z., L.L.Z. and Q.L. conceived and designed the experiments. M.H. and F.L. prepared self-assembled nanostructures and the supercapacitor electrodes, and conducted the electrochemical measurements. Z.Y.W. helped with TEM and electrochemical measurements and initial studies. R.S.R. helped with modification of manuscripts and kind discussion on details. Y.X.Z., Z.Y.W. and Q.L. wrote the manuscript. All the authors commented on the manuscript.

**Additional information**

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