Electronic Supplementary Information

Synthesis of Multi-shelled MnO₂ Hollow Microspheres via an Anion-adsorption Process of Hydrothermal Intensification

Experimental section

Chemicals

 $KMnO_4$ (potassium permanganate), HCl (hydrochloric acid, 37%wt), NaOH, KNO₃, citric acid and $Mn(Ac)_2 \cdot 4H_2O$ were analytical grade which supplied by Beijing Chemical Co. Ltd. and were all used without further purification. Carbon black, polyvinylidene fluoride (PVDF), N-methyl pyrroliddinone (NMP) and Ni foam current collector (diameter: 1.5 cm) were supplied by Xilong Chemical Co. Ltd. and were used as received. All the electrochemical experiments were carried out on a CHI660D workstation (CH instruments, Inc) at room temperature.

Synthesis of multi-shelled MnO₂ hollow microspheres

The synthesis of quadruple-shelled MnO_2 hollow microspheres was described below as a typical example. Carbonaceous microspheres prepared by the emulsion polymerization reaction of sucrose under the hydrothermal conditions as described elsewhere were used as templates.^[1] Then 0.3 g CMSs were added into 20 mL deionized water in a Teflon-liner of a stainless steel autoclave. After magnetic stirring for 2 min and followed with ultrasonic treatment for 20 min, the pH value was manipulated with concentrated HCl solution to around 2.5. Then 0.05-0.111 g KMnO₄ was added to the solution and dissolved through magnetic stirring. After that, Teflon-liner was sealed into the stainless steel autoclave. Then the autoclave was kept in an electric oven at 100 °C for 45 min and then cooled down to room temperature. The product was centrifuged and washed with deionized water for three times, and dried at 70 °C for more than 12 h. Finally, the final product was synthesized after an annealing process: heated from room temperature to 450 °C in air, and stayed at 450 °C for 2 h, then was cooled down to room temperature naturally. By adjusting the adding amount of KMnO₄ and the heating rate, single-, double- and triple-shelled MnO₂ hollow microspheres were produced. Detailed experimental parameters are listed in Table S1 in the ES1.

Synthesis of thick single-shelled MnO₂ hollow microspheres by ion-absorption method at ambient condition

The as-prepared CMSs were used as hard template and were also added into 20 mL of deionized water. After two minutes' magnetic stirring and 20 min ultrasonic treatment, the pH value was manipulated with concentrated HCl solution to almost 2.5. Then KMnO₄ was added and the solution was stirred for 45 min. Afterwards, the sample was centrifuged and washed with deionized water for several times, and dried at 70 °C for more than 12 h. Then single-shelled MnO₂ hollow microspheres were synthesized after the same annealing process as above(heated in a muffle furnace from room temperature to 450 °C in air, and held at 450 °C for 2 h, then cooled down to room temperature naturally).

Synthesis of MnO₂ nanoparticles

The MnO₂ nanoparticles have been synthesized by sol-gel method. 24.2 g Mn(Ac)₂ · 4H₂O, 0.6 g KNO₃ and 10.5 g citric acid were all dissolved into 100 ml deionized water. Then the pH value was manipulated with ammonia to around 5. After magnetic stirring for several minutes, this solution was replaced in a culture dish. The sample was firstly dried at 60 °C to get a sol-gel solution and then was further dried at 100 °C to form xerogel. Finally, this xerogel was calcined at 400°C for 24 h to get MnO₂ nanoparticles.

Characterizations

Powder X-ray diffraction (XRD) patterns were carried out on a Smartlab 9000 instrument (Rigaku, Japan) [Cu K α radiation], operating at 40 kV and 200 mA. Scanning electron microscopy (SEM) images were obtained using a JSM-6700F microscope operating at 5.0 kV. Transmission electron microscopy (TEM) images, High resolution transmission electron microscopy (HRTEM) images and selected area electron diffraction (SAED) images were all done achieved via JEM-2100F instrument using an accelerating voltage of 200 kV. FTIR spectrum was obtained using the Fourier transform infrared spectroscopy (FTIR) (Vector-22). We used an ESCALAD 220i-XL electron spectrometer from VG Scientific with 300 W Al K α radiation to get the XPS (X-ray photon spectroscopy) data and the binding energies were corrected by the reference of C 1s (284.8 eV).The Raman spectrum was carried out on a JY HR800 laser Raman spectrometer with a 532 nm excitation. The TGA-DTA (thermo-gravimetric analysis - differential thermal analysis) data were obtained by a DTA-60(Shimadzu, Japan) under air atmosphere with a heating rate of 5 °C min⁻¹. The specific surface area was determined by nitrogen adsorption/desorption (Quantochromes Autosorb-1MP sorption analyzer) with prior degassing under vacuum at 200 °C over night.

Electrochemical measurements

The multi-shelled MnO₂ hollow microspheres based electrodes were prepared as follows: active materials (MS-MnO₂-HMSs), carbon black and polyvinylidene fluoride (PVDF) binder were mixed with a similar mass ratio as other works of 7:2:1, with NMP used as the solvent to form a slurry. Then the slurry was spread onto the Ni foam current collectors which worked as a working electrode, and then was placed into a vacuum oven at 120 °C (loading amount of active materials: ~2.5 mg/cm²). All the electrochemical experiments were carried out on a CHI660D workstation (CH instruments, Inc) at room temperature with Hg/HgO electrode as reference electrode and platinum foil worked as counter electrode in a conventional three-electrode system in 1M NaOH electrolyte solution . Cyclic voltammetry (CV) was carried on over a voltage range of 0-0.8 V at various scan rates (5, 10, 20, 50, 100 and 200 mV/s) and galvanostatic charge-discharge was carried on over the potential window in the range of 0.1-0.56 V at various current densities (0.5, 1, 2, 5 and 10 A/g). The average specific capacitance (*C_{sp}*) which was determined from the CV curves was calculated as the following Equation (1):

$$C_{sp} = \frac{1}{m\Delta V} \int i dt \tag{1}$$

 ΔV , *m* and *i* are the voltage range of one scanning segment(V), mass of the electrode material(mg) and the current(mA), respectively.

The specific capacitance (C_{sp} , F/g) which was determined from the galvanostatic charge/discharge curves calculated as the following Equation (2):

$$C_{sp} = \frac{C}{m} = \frac{I\Delta t}{m\Delta V} \tag{2}$$

m (g) is the mass of the active materials, ΔV (V)represents the voltage change after a full charge or discharge, *I* (A) is the charge/discharge current and Δt (s) is the discharging time^[2].



Fig. S1 SEM image (a) and FTIR pattern (b) of the as-used CMS templates. (inset is the HRSEM image of the CMS templates)



Fig. S2 TEM image (a) and XRD patterns (b) of the sample via the method of solution adsorption at ambient condition with K_2MnO_4 as Mn-precursor.



Fig. S3 TEM image of thick single-shelled MnO₂ hollow microspheres via simple solution-adsorption method at ambient condition.



Fig. S4 XPS survey spectra of the as-prepared intermediate after hydrothermal adsorption.



Fig. S5 (a) EDX curve of the as-prepared intermediate after hydrothermal adsorption, (b-e) HAADF-STEM element mapping images the as-prepared intermediate: (c) C, (d) Mn, (e) O



Fig. S6 XPS survey spectra of the quadruple- shelled MnO_2 hollow microspheres (a) and the magnification of the Mn 2p region (b).



Fig. S7 The Raman spectrum of quadruple-shelled MnO₂ hollow microspheres.

Raman characterization has also been conducted to investigate the existence of carbon after annealing step. It has been reported that the peaks at 1550 cm⁻¹ and at 1350 cm⁻¹ represent the vibration of sp² graphitic carbon and the vibration mode of sp³ carbon atoms chemically bonded to oxygen-containing groups and carbon at the edge of the graphitic sheets whilst, respectively ^[3]. In Fig. S7, we can hardly figure out the existence of G- and D- band peak. What's more, the Raman sharp peak at 647 cm⁻¹ is due to the symmetric stretching vibration (MnO) perpendicular to direction of the MnO₆ octahedral which characterizes the (2×2) tunnel species of α -MnO₂ materials. Another weak peak at 366 cm⁻¹ is ascribed to the bending modes of Mn-O. ^[4]

In addition, the TGA-DTA curves with no further mass lose in Fig. S12 and the heating conditions we chose (450 $^{\circ}$ C 2 h) both can prove that there isn't any carbon existing after annealing process.



Fig. S8 SEM images of single-, double- and triple-shelled MnO₂ hollow microspheres.



Fig. S9 The statistic histograms of multi-shelled MnO_2 hollow microspheres.



Fig. S10 a) TEM and b) SEM images of the as-prepared MnO₂ nanoparticles.



Fig. S11 TEM image of triple-shelled MnO_2 hollow microspheres obtained with 0.2 g KMnO₄ addition.



Fig. S12 TGA-DTA curves of the intermediate after hydrothermal adsorption under air atmosphere at a heating rate of 5 °C min⁻¹.



Fig. S13 XRD patterns of the as-prepared MnO_2 nanoparticles.



Fig. S14 CV curves of the as-prepared(a) single-, (b) double-, and (c) triple-shelled MnO_2 hollow microspheres and (d) MnO_2 nanoparticles at different scan rates of 5, 10, 20, 50, 100, 200 mV/s.



Fig. S15 Galvanostatic charge/discharge curves of the as-prepared (a) single-, (b) double-, and (c) triple-shelled MnO_2 hollow microspheres and (d) MnO_2 nanoparticles under different current densities.



Fig. S16 SEM images of the (a, b) triple-shelled MnO_2 hollow microspheres and (c, d) quadruple-shelled MnO_2 hollow microspheres before and after 4000th cycle, respectively. (The nanoparticles in the images are the added carbon black)



Fig. S17 Nitrogen adsorption and desorption isotherms(a) and pore-size distribution curves(b) of the as-prepared single-, double-, triple- and quadruple-shelled MnO₂ hollow microspheres and MnO₂ nanoparticles.

Table S1 Summary of synthesis conditions of the as-prepared various multi-shelled MnO₂ hollow microspheres

Structures	KMnO ₄ mass (g)	CMS mass(g)	Water (ml)	Hydrothermally enhanced adsorption	Calcination temperature(°C)	Heating rate (°C/min)
Single-shelled	0.05	0.3	20	100°C 45min	450	5
Double-shelled	0.08	0.3	20	100°C 45min	450	5
Triple-shelled	0.111	0.3	20	100°C 45min	450	5
Quadruple-shelled	0.111	0.3	20	100°C 45min	450	1

Table S2 Specific surface area and pore volume of as-prepared various multi-shelled MnO₂ hollow microspheres and MnO₂ nanoparticles according to the BET measurements.

Structures	Specific surface area (m ² /g)	Pore volume (cm³/g)
Single-shelled	29.95	0.0966
Double-shelled	31.36	0.0967
Triple-shelled	49.09	0.1508
Quadruple-shelled	99.36	0.3397
Nanoparticles	15.64	0.0634

Reference

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