Supporting information for

High-performance asymmetric supercapacitors based on monodisperse MnO nanocrystals with high energy densities

Menggang Li^{1,2#}, Wenjuan Lei^{1,2#}, Yongsheng Yu^{1*}, Weiwei Yang^{2*}, Ji Li¹, Dafa Chen², Shichong Xu¹, Ming Feng¹ and Haibo Li¹

¹Key Laboratory of Functional Materials Physics and Chemistry of the Ministry of Education, Jilin Normal University, Changchun 130103, China

²MIIT Key Laboratory of Critical Materials Technology for New Energy Conversion and Storage, School of Chemistry and Chemical Engineering, Harbin Institute of Technology, Harbin, Heilongjiang 150001, China

These authors contributed equally.

Corresponding Authors *E-mail: yongshengyu80@sohu.com and yangww@hit.edu.cn

Experimental Section

Materials

Oleic acid (OAc, 85%), manganese chloride (MnCl₂·4H₂O, AR, 99.0%), 1octadecene (ODE, GC, >90%), Sodium oleate (NaOAc, CP), ethanol (AR, 95.0%), hexane (AR, 97%) were purchased from Aladdin. All chemicals were used without further purification. Besides, activated carbon (AC) was purchased from Kuraray (Shanghai) Co., Ltd.

Synthesis of manganese oleate.

The manganese oleate was prepared by reacting $MnCl_2 \cdot 4H_2O$ and NaOAc. 4 mmol $MnCl_2 \cdot 4H_2O$ and 8 mmol NaOAc were dissolved in a mixture solvent composed of 8 mL ethanol, 6 mL distilled water and 14 mL hexane. The resulting solution was heated to 70 °C and kept at that temperature for 4 hours. When the reaction was completed, the upper organic layer containing manganese oleate $(Mn(OAC)_2)$ was washed three times with distilled water in a separatory funnel. Then the mixture was dried in a vacuum oven at 60 °C for 12 hours.

Synthesis of monodisperse MnO nanocrystals (NCs).

Monodisperse MnO NCs were synthesized by the thermal decomposition of $Mn(OAC)_2$ in the presence of OAc and ODE. 4 mmol of the $Mn(OAC)_2$ and 2 mmol OAc were dissolved in 16 mL ODE under N₂ to purify at room temperature. The mixture was heated to 120 °C for 1 h to remove water. Then the mixture was heated to 320 °C with a heating rate of 3.3 °C/min and kept at this temperature for 1 h before it was cooled down to room temperature. The mixture was separated by centrifugation

and washed three times with hexane and ethanol. The precipitated MnO NCs were redispersed in hexane to form a stable colloidal solution. MnO NCs were dried in a vacuum oven at 60 °C for 12 hours.

Materials Characterization

X-ray diffraction (XRD) patterns were collected on a PAN analytical X'Pert Powder with Cu $K\alpha$ radiation ($\lambda = 1.5418$ Å). Transmission electron microscopy (TEM) images were acquired on a JEM-1400 operating at 100 kV (JEOL Ltd). Highresolution TEM (HRTEM) images were obtained on a Talos F200X with an accelerating voltage of 200 kV. The X-ray photoelectron spectroscopy (XPS) spectra was collected by XPS (Thermo Scientific, ESCALAB 250 XI). The specific surface area of MnO was measured according to the Brunauer-Emmett-Teller (BET) method.

Electrochemical Measurements

The working electrodes consist of active materials (monodisperse spherical MnO NCs), carbon black (Super-P), and polyvinylidene fluoride (PVDF) in a weight ratio of 75:15:10. The mixed slurry was pasted onto a pre-cleaned nickel foam with a geometrical area with 1 cm \times 1 cm followed by drying at 100 °C under vacuum. The loading mass of MnO on nickel foam was about 1.1 mg cm⁻². The electrochemical tests were evaluated in an aqueous 1.0 M Na₂SO₄ electrolyte by a three-electrode system, where a Pt foil serves as the counter electrode and a Ag/AgCl electrode as the reference electrode. All the tests were conducted in the CHI 660E electrochemical workstation. The cycling voltammetry (CV) curves were measured in a potential range of 0-0.8 V (*vs.* Ag/AgCl) at different scan rates, and galvanostatic charge-discharge (GCD) curves were measured at different current densities within a

potential range of 0-0.55 V. Electrochemical impedance spectroscopy (EIS) measurements were carried out by applying an AC voltage with 5 mV amplitude in a frequency range of 0.1-100 kHz at open circuit potential.

The specific capacitance can be calculated from the CV curves and GCD curves according to the Equation (1) and Equation (2):¹

$$C = \frac{\int i(V)dV}{m \cdot v \cdot \Delta V} \tag{1}$$

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

Where *C* (F g⁻¹) is the specific capacitance of the materials, *m* (g) is the mass of the electrode materials loading on the Ni foam, *v* (V s⁻¹) is the scan rate, ΔV (V) is the potential window in the CV curves or GCD curves, *i*(*V*) (A·V) is the voltammetric current, *I* (A) is the constant discharge current and Δt (s) is the discharge time.

Fabrication of the MnO//AC asymmetric supercapactitors

The ASCs were assembled using the MnO electrode as the positive electrode and the AC as the negative electrode. The preparation of the AC electrode is similar to the preparation of the MnO electrode. In order to achieve high electrochemical performance of ASCs, the charge balance of the positive and negative must be considered according to the charge balance theory ($q^+ = q^-$). The voltammetric charges (*Q*) are calculated based on the equation (3):²

$$Q = C \times \Delta V \times m \tag{3}$$

Where *C* is the specific capacitance (F g⁻¹) of each electrode measured in a three electrode systems, ΔV is the potential range (V) for the charge/discharge process, and *m* is the mass of the electrode active materials. To maintain a charge balance between

the cathode and anode, the mass ratio between the cathode (m_+) and anode (m_-) electrodes needs to follow the equation (4):

$$\frac{m_{+}}{m_{-}} = \frac{C_{-} \times \Delta V_{-}}{C_{+} \times \Delta V_{+}}$$
(4)

The electrochemical performance of the ASCs was evaluated by CV, GCD and EIS testing to assess the possibility of the MnO electrode for the practical application. The energy density (E, Wh kg⁻¹) and the power density (P, W kg⁻¹) were calculated with the equation (5) and equation (6):³

$$E = \frac{C \times \Delta V^2}{2 \times 3.6} \tag{5}$$

$$P = \frac{E \times 3600}{\Delta t} \tag{6}$$

Where *C* is the specific capacitance of the device, ΔV is the potential window applied during the charge-discharge measurements and Δt is the discharge time.



Supporting Figures

Fig. S1 The size distribution of MnO NCs.



Fig. S2 Nitrogen adsorption-desorption isotherms of MnO NCs.



Fig. S3 Specific capacitance of MnO electrode at different scanning rates.



Fig. S4 (a) CV curve of the pretreated Ni foam at a scan rate of 10 mV s⁻¹ and (b) GCD curve of the pretreated Ni foam at a current density of 1 mA cm⁻².



Fig. S5 The coulombic efficiency up to 5000 cycles at a current density of 4 A g⁻¹.



Fig. S6 Cycling stabilities of MnO electrode at a current density of 20 A g⁻¹ (inset shows the first and last 10 cycles of the GCD curves of the electrode)



Fig. S7 (a) The TEM image and (b) the size distribution of monodisperse MnO NCs after 5000

cycles



Fig. S8 Electrochemical performance of AC electrode. (a) CV curves at different scan rates, (b) the specific capacitance at different scan rates.



Fig. S9 CV curves of the MnO//AC ASC at different potential windows at a scan rate of 10 mV s⁻¹.



Fig. S10 EIS spectrum of assembled MnO//AC device. The insert is a zooming of high frequency region.

 Table S1 Impedance fitting parameters of MnO NCs electrode.

R_s		R _{ct}	
Fit (Ω)	Fitting error (%)	Fit (Ω)	Fitting error (%)
2.03	1.89	1.58	2.21

References

- 1 Z. Su, C. Yang, B. Xie, Z. Lin, Z. Zhang, J. Liu, B. Li, F. Kang and C. Wong. *Energy Environ. Sci.*, 2014, 7, 2652-2659.
- L. Wu, L. Hao, B. Pang, G. Wang and Y. Zhang. J. Mater. Chem. A, 2017, 5, 4629-4637.
- 3 C. Li, J. Balamurugan, T. D. Thanh, N. H. Kim and J. H. Lee. *J. Mater. Chem. A*, 2016, **5**, 397-408.