Electronic Supplementary Information

Synthesis of Peanut-like Hierarchical Manganese Carbonate Microcrystals via Magnetically Driven Self-assembly for High

Performance Asymmetric Supercapacitor

Yongfu Tang ^{a*}, Shunji Chen ^a, Teng Chen ^{a, b}, Wenfeng Guo ^a, Yanshuai Li ^a, Shichun Mu ^{c*},

Shengxue Yu^a, Yufeng Zhao^a, Fusheng Wen^d, Faming Gao^a

^[a] Hebei Key Laboratory of Applied Chemistry, College of Environmental and Chemical

Engineering, Yanshan University, Qinhuangdao, Hebei, 066004, China

^[b] Key Laboratory of Mesoscopic Chemistry of MOE, School of Chemistry and Chemical

Engineering, Nanjing University, Nanjing 210093, China

^[c] State Key Laboratory of Advanced Technology for Materials Synthesis and Processing, Wuhan

University of Technology, Wuhan, 430070, China

^[d] State Key Laboratory of Metastable Materials Science and Technology, Yanshan University,

Qinhuangdao, 066004, China

Experimental and Methods

1. Preparation of the peanut-like MnCO₃ microcrystals

The MnCO₃ microcrystals with the peanut-like morphology were synthesized via a facile hydrothermal process at 120 °C with ascorbic acid as the carbonate source and the sulfourea as the structure-direction agent. The preparation in detail of the peanutlike MnCO₃ microcrystals was described as follows. Firstly, 0.2 g MnCl₂·4H₂O and 0.2

^{*}Corresponding author. Tel.: +86 13780351724

E-mail address: tangyongfu@ysu.edu.cn (Y. Tang); msc@whut.edu.cn (S. Mu)

g ascorbic acid were dissolved by 20 mL of deionized water, respectively. The obtained MnCl₂ solution and ascorbic acid solution were mixed in a beaker to form a uniform solution. Subsequently, the sulfourea (0.077mg) dissolved in 20 mL of alkine solution (pH~8) was added dropwise to the aforementioned mixed solutions under the vigorous stirring. Then, the obtained brown mixed solution was transferred into 100 ml Teflonlined stainless-steel autoclave, which was heated in an oven at 120 °C for 24 h. After autoclave being cooled to room temperature naturally, the obtained brown MnCO₃ precipitate was washed several times using the deionized water and the ethanol alternately. The final products were collected by vacuum drying at 60 °C for 24 h. A series of similar samples were obtained via different hydrothermal time (2 h, 4 h, 8 h and 12 h) to investigate the influence of the hydrothermal reaction time on the phase structure and morphology of the MnCO₃ nanocrystals/microcrystals. To explore the formation mechanism of the peanut-like MnCO₃ microcrystals, another two Mn-based samples were prepared using two similar hydrothermal processes for 24 h. The first sample was obtained in the absence of ascorbic acid (denoted as MS sample), while the second sample was obtained in the absence of sulfourea (denoted as MA sample).

2. Physiochemical characterization

X-ray diffraction (XRD) patterns were obtained from a Bruker AXS D8 diffractometer with Cu K α radiation as the excitation source in an angle range of 20°~70°. Transmission electron microscope (TEM, HT7700, 100 kV) was used to investigate the morphologies of the MnCO₃ microcrystals. Scanning electron microscope (SEM, KYKY-2800B, 15 kV) equipped with an energy dispersive

spectrometer(EDS) was used to further characterize the microstructures and elemental compositions of the sample, which was pre-coated with Au. To avoid the effect of conducting resin on the C element mapping of MnCO₃ microcrystals, silicon chip was used as the substrate for EDS measurement. X-ray photo-electron spectra (XPS) was performed on a PHI QUANTERA II X-ray photoelectron spectrometer with Al K_{α} radiation at 0.6 eV. The magnetic properties of the samples were analysized by a vibrating sample magnetometer (VSM).

3. Fabrication of the working electrodes and electrochemical measurement

The working electrodes were prepared as follows. The peanut-like MnCO₃ powder was mixed with acetylene black and polyvinylidene difluoride (PTFE, 1% wt) at a mass ratio of 80:15:5. The obtained slurry was coated on the nickel foam $(1\times1cm^2)$. The work electrodes were obtained by pressing the active materials coated nickel foam at 10 MPa for 30 s. The cycle voltammetry (CV) and electrochemical impedance spectroscopy (EIS) measurements of the working electrode were performed on a CHI 660A workstation (CH Instrument Corp. USA). All of the tests were carried out under a three-electrode system in 2 M KOH electrolyte. The galvanostatic chargingdischarging (GC) of the working electrode was carried out through a Land CT 2001A battery tester (Land Instrument Corp., Wuhan, China) in 2.0 M KOH electrolyte. The reference electrode and counter electrode in these electrochemical measurements are Hg/HgO and Pt film $(1\times1cm^2)$, respectively. To investigate the practical application of the MnCO₃ microcrystals, an asymmetric supercapacitor (designated as PM//HMC supercapacitor) were assembled with the peanut-like MnCO₃ electrode as the positive electrode and a home-made carbon electrode as the negative electrode with the weight loading of 5.3/2.8 mg cm⁻², respectively. Due to the higher stability of the carbon materials which was used as the negative electrode, slight excess of positive mass loading (~ 10 %) was designed based on the capacity balance as equation of $C^+ \cdot m^+ = C^- \cdot m^-$, where C⁺ and C⁻ are represent of capacities (mAh g⁻¹) of the positive and negative electrodes, respectively. The m⁺ and m⁻ are the mass loading (g) of positive and negative electrodes, respectively. The CV and GC measurements of the PM//HMC supercapacitor were carried out on the CHI 660A workstation and the Land CT 2001A battery tester, respectively.

Supplementary Equations

$$MnCO_3 + OH^- \xrightarrow{Charge} Mn(OH)CO_3$$
 (S1)

$$C_s = \int I \cdot \mathrm{d}t \,/\, m \cdot \Delta V \tag{S2}$$

where C_s (F g⁻¹), I (A), dt (s), ΔV (V) and m (g) represent the specific capacitance, discharge current, differential discharge time, potential range of discharge and the mass of active material.

$$C_{\text{T/EDLC}} = S_{\text{mic}} \times C^{\text{mic}} + S_{\text{ext}} \times C^{\text{ext}}$$
(S3)

where the $C_{\rm T}$, $S_{\rm mic}$, $S_{\rm ext}$ are represent for the theoretic electric double layer capacitance of the MnCO₃ microcrystals, the specific surface area from the micropores and from the external surface of the peanut-like MnCO₃ microcrystals, respectively. The $C^{\rm mic}$ and $C^{\rm ext}$ are the surface specific capacitances related to the respective surface areas [1, 2]. In the Shi's study [1], the $C^{\rm mic}$ and $C^{\rm ext}$ values of activated carbon fibers are the 7.5 ± 1 μ F cm⁻² and 14.5 ± 5 μ F cm⁻², respectively. The *C*^{mic} and *C*^{ext} values of the activated carbon microbeads are 19.5 ± 7 μ F cm⁻² and 74 ± 20 μ F cm⁻², respectively. For the Barbieri's study [2], these two values are 7.6 μ F cm⁻² and ~ 7.6 μ F cm⁻² based on a series of carbon materials including Vulcan XC 72, MM192, Black Pearl 2000, W30, W37, W54.5, K1500, K2200 and K2600. Therefore, we can cite the highest value (74 μ F cm⁻², based on that all the surface area is from external surface) to evaluate the limited *C*_{T/EDLC} for the peanut-like MnCO₃ microcrystals. Therefore, the *C*_{T/EDLC}(MnCO₃) is lower than 80.72 m² g⁻¹ × 74 μ F cm⁻² = 59.7 F g⁻¹, which is markedly lower than the measured value (293. 7 F g⁻¹). This result indicates that most of the capacitance of the peanut-like MnCO₃ microcrystals electrode is derived from the pseudocapacitance.

Supplementary Tables

Table S1 Comparison for the electrochemical properties of the as-obtained peanut-

Activited materials	Electrolyte	Specific capacitance (F g ⁻¹)	Cycle number	Capacitance retention (%)	Refs
Peanut-like MnCO ₃	2 М КОН	293.7 (0.25 A g ⁻¹) 275.7 (0.5 A g ⁻¹)	6000	71.5	this work
MnCO ₃ nancrystals	6M KOH	159 (5 mV s ⁻¹)			[3]
Mesoporous MnO ₂	6 M KOH	220 (5 mV s ⁻¹)			[4]
MnO ₂ nanorods	1 M NaOH	186 (0.5 A g ⁻¹)	2000	94	[5]
MnO ₂ /MWCNT	1 M KOH	250.5 (2 mV s ⁻¹)			[6]
Mn ₃ O ₄ @Graphene	6 M KOH	256 (5 mV s ⁻¹)			[7]
Mn ₃ O ₄ -Graphene	5 M KOH	140 (10 mV s ⁻¹)	1000	96	[8]
MnOOH nanorods@rGO	6 M KOH	268 (0.5 A g ⁻¹)			[9]
Mn ₃ O ₄ NP@GO	6 M KOH	202 (0.5 A g ⁻¹)	1400	> 100	[10]

like MnCO₃ electrode with the reported Mn-based active materials.

Tak	ble S2 Comparison of the performances between the as assembled PM//HMC	

Positive materials//Negative materials	Energy density (Wh kg ⁻¹)	Power density (W kg ⁻¹)	Cycle number	Capacitance retention (%)	Refs
PM//HMC	14.7	90.2	5000	80	this work
MnO ₂ //activated carbon(AC)	10.4	14.7	1200	> 90	[11]
MnO2@GO//CNT	12.5	110	5000	95	[12]
MnO ₂ //PEDOT	13.5	120.1			[13]
3D GO/MnO ₂ //3D GO/MnO ₂	6.8	62	5000	82	[14]
MnO ₂ //carbon nanotubes	10.4	2000	1000	90	[15]
MnO ₂ //Fe ₃ O ₄	8.1	405			[16]
MnO ₂ //Bi ₂ O ₃ nanoflowers	11.3	352.6	4000	85	[17]
Ag-Mn ₃ O ₄ //AC-5	8.1	222.6	1000	86	[18]
RuO ₂ /TiO ₂ nanotube//AC	5.7	1207	1000	90	[19]
Co(OH) ₂ //AC	13.6	153			[20]
Ni-Co oxide//AC	12	95.2	2000	85	[21]

supercapacitor with the reported supercapacitors

Supplementary Figures



Fig. S1 XPS spectrum of C 1s and O 1s of the peanut-like MnCO₃ microcrystals.



Fig. S2 TEM images of MS (a) and MA (b) samples.



Fig. S3 (a) XRD patterns of as synthesized products at 2 h, 4 h, 8 h, 12 h, 24 h and 36 h, (b) Room temperature M-H loops of the MnCO₃ products synthesized by hydrothermal process at 4 h, 8 h, 12 h and 24 h, respectively. The inset gives an enlarged image at a smaller magnetic field intensity.

Discussion on magnetic-driving self-assembly: The magnetic properties of the MnCO₃ products obtained at different hydrothermal reaction times were analyzed by magnetic hysteresis loops with the measured magnetic field intensity from 20 kOe to - 20 kOe (**Fig. S3b**). The shape of the M-H loops demonstrates the ferromagnetic behavior of all the MnCO₃ products obtained at 4 h, 8 h, 12 h and 24 h. The peanut-like rhombohedral MnCO₃ microcrystals obtained at 24 h exhibits the largest magnetic field intensity, which should be attributed to the order arrangement of the MnCO₃ nanowires (shown in TEM images of **Fig. 3**) in the peanut-like MnCO₃ microcrystals. Moreover, the highest crystallinity of the peanut-like MnCO₃ microcrystals (sharpest peaks in the XRD patterns of **Fig. S3a**) is another reason for its highest magnetic field intensity.



Fig. S4. SEM images of the MnCO₃ products obtained at different hydrothermal reaction times of

4 h (a), 12 h (b), 24 h (c) and 36 h (d), respectively.



Fig. S5 (a) CV curves in the 2.0 M KOH electrolyte at scan rate of 1 mV s⁻¹, (b) GC curves at the current density of 0.5 A g^{-1} , (c) specific capacitances at different current densities and (d) electrochemical impedance spectra (The inset shows the smaller range image) of the MnCO₃ electrodes with different morphologies, which were obtained at different reaction times.

Symbols of the samples in Fig. S5:

F-NW (2 h): Floccules-like MnCO₃ nanowires obtained at 2 h;

T-NW (4 h): Thickened MnCO₃ nanowires obtained at 4 h;

C-NW (8 h): Cross-link MnCO₃ nanowires obtained at 8h;

NW/P-MC (12 h): MnCO₃ nanowires mixed with peanut-like microcrystals obtained at 12 h;

P-MC (24 h): Peanut-like MnCO₃ microcrystals obtained at 12 h;

Sample	R _s	R _{ct}	W	CPE
F-NW (2 h)	0.95	0.63	3.02	0.99
T-NW (4 h)	0.65	0.16	0.67	1.23
C-NW (8 h)	0.71	0.33	1.01	1.10
NW/P-MC (12 h)	0.76	0.58	2.12	0.99
P-MC (24 h)	0.57	0.51	1.51	0.97

 Table S3. The corresponding experimental parameters are obtained based on fitting equivalent

 circuit in Fig. S5d.

Discussion: The CV curves at 1 mV s⁻¹ (**Fig. S5a**) and the charge/discharge curves at 0.5 A g⁻¹ (**Fig. S5b**) of all the MnCO₃ electrodes obtained at different hydrothermal times with different morphologies of F-NW (2 h), T-NW (4 h), C-NW (8 h), NW/P-MC (12 h) and P-MC (24 h) are also measured under the same conditions. Obviously, the CV curve of peanut-like MnCO₃ electrode (obtained at 24 h, purple dashed line in **Fig. S5a**) shows the biggest CV curve area, suggesting its highest specific capacitance, which is in good agreement with the charge/discharge results (**Fig. S5b**).

Among the MnCO₃ electrodes (**Fig. S5c**) obtained at different reaction times, the peanut-like MnCO₃ electrode exhibits the highest specific capacitance, which should be ascribed to the unique peanut-like microstructure. The continuous nanowires, the blocks of the micron-level peanut-like structure, endow the peanut-like MnCO₃ electrode high electronic conduction, which is confirmed by the the lowest ohmic resistance of peanut-like MnCO₃ electrode detected by the EIS spectrum (**Fig. S5d**).



Fig. S6 SEM image (a) and the corresponding enlarged image (b) of peanut-like MnCO₃ electrode after continuous cycling for 6000 cycles. (c) EDX spectrogram of honeycomb-like structure in **Fig. S9b**. XRD pattern (d) and EIS spectrogram (e) of peanut-like MnCO₃ at different state of charges (SOC).

Discussion: Morphology changes before and after 6000 cycles are observed in **Fig. S6c** and **S6d**. Differing from the structures consisted of various nanowires, the honeycomb-like structures formed after continuous cycling for 6000 cycles profits from the existence of OH⁻, as braced by the EDX spectrogram in **Fig. S6c**. Furthermore, this honeycomb-like structure is not easy to collapse during the charge/discharge process, which contributes the superior cycle stability of the MnCO₃ microcrystals electrode. As exhibited in the XRD pattern (**Fig. S6d**), the diffraction peak at about 37° (dotted vertical line) gradually shifts to lower angle, when the MnCO₃ electrode is charged from 0 % to 100 %, simultaneously, the significant added peaks at about 27° and 33° (dotted square frame) also can be detected, both of which indicates that the intercalation of OH⁻ induces the lattice expansion and the phase transition of the peanut-like MnCO₃. **Fig. S6e** and its inset show the EIS spectra of peanut-like MnCO₃ electrode at different state of charges. The smallest semicircle diameter found at the SOC of 100 % reveals that the electrode possesses the highest reaction activity at this moment, confirming the insertion of OH⁻ ions.

References

[1] H. Shi, Activated carbons and double layer capacitance, *Electrochim. Acta*, 1996, 41, 1633-1639.

[2] O. Barbieri, M. Hahn, A. Herzog, R. Kötz, Capacitance limits of high surface area activated carbons for double layer capacitors, *Carbon*, 2005, 43, 1303-1310.

[3] S. Devaraj, H. Y. Liu and P. Balaya. MnCO₃: a novel electrode material for supercapacitors, *J Mater. Chem. A*, 2014, **2**, 4276-4281.

[4] Q. Zhou, X. Li, Y. G. Li, B. Z. Tian, D. Y. Zhao and Z. Y. Jiang. Synthesis and Electrochemical Properties of Semicrystalline Gyroidal Mesoporous MnO₂, *Chinese J. Chem.*, 2006, 24, 835-839.

[5] R. S. Kalubarme, H. S. Jadhav and C. J. Park. Electrochemical characteristics of two-dimensional nano-structured MnO₂ for symmetric supercapacitor, *Electrochim*.

Acta, 2013, 87, 457-465.

[6] X. Xie, L. Gao, Characterization of a manganese dioxide/carbon nanotube composite fabricated using an in situ coating method, Carbon, 2007, 45, 2365-2373.

[7] B. Wang, J. Park, C. Wang, H. Ahn, G. Wang, Mn₃O₄ nanoparticles embedded into graphene nanosheets: Preparation, characterization, and electrochemical properties for supercapacitors, Electrochim. Acta, 2010, 55, 6812-6817.

[8] Y. Liu, D. He, H. Wu and J. Duan. Graphene and Nanostructured Mn₃O₄
 Composites for Supercapacitors, Integrated Ferroelectrics, 2013, 144(1), 118-126.

[9] Y. Cao, Y. Xiao, Y. Gong, C. Wang, F. Li, One-pot synthesis of MnOOH nanorods on graphenefor asymmetric supercapacitors, Electrochim. Acta, 2014, 127, 200-207.

[10] Y. Xiao, Y. Cao, Y. Gong, A. Zhang, J. Zhao, S. Fang, F. Li, Electrolyte and composition effects on the performances of asymmetric supercapacitors constructed with Mn₃O₄ nanoparticles-graphene nanocomposites, J. Power Sources, 2014, 246, 926-933.

[11] Y. T. Wang, A. H. Lu, H. L. Zhang, W. C. Li, Synthesis of Nanostructured Mesoporous Manganese Oxides with Three-Dimensional Frameworks and Their Application in Supercapacitors, J. Phys. Chem. C, 2011, 115, 5413-5421.

[12] G. Yu, L. Hu, M. Vosgueritchian, H. Wang, X. Xie, J. R. McDonough, X. Cui, Y.
Cui, Z. Bao, Solution-Processed Graphene/MnO₂ Nanostructured Textiles for HighPerformance Electrochemical Capacitors, Nano Lett., 2011, 11, 2905-2911.

[13] V. Khomenko, E. Raymundo-Pinero, E. Frackowiak, F. Beguin, Nanostructured transition metal oxides for aqueous hybrid electrochemical supercapacitors, Applied

Physics A, 2006, 82, 567-573.

[14] Y. He, W. Chen, X. Li, Z. Zhang, J. Fu, C. Zhao, E. Xie, Freestanding Three-Dimensional Graphene/MnO₂ Composite Networks As Ultralight and Flexible Supercapacitor Electrodes, ACS nano, 2012, 7, 174-182.

[15] H. Jiang, C. Z. Li, T. Sun, J. Ma. A green and high energy density asymmetric supercapacitor based on ultrathin MnO₂ nanostructures and functional mesoporous carbon nanotube Electrodes, Nanoscale, 2012, 4, 807-812.

[16] T. Cottineau, M. Toupin, T. Delahaye, T. Brousse, D. Belanger, Nanostructured transition metal oxides for aqueous hybrid electrochemical supercapacitors, Appl. Phys. A, 2006, 82, 599-606.

[17] H. Xu, X. Hu, H. Yang, Y. Sun, C. Hu, Y. Huang, Flexible Asymmetric Micro-Supercapacitors Based on Bi₂O₃ and MnO₂ Nanoflowers: Larger Areal Mass Promises Higher Energy Density, Adv. Energy Mater., 2014, 1401882 (1-7).

[18] S. Nagamuthu, S. Vijayakumar, G. Muralidharan, Ag Incorporated Mn₃O₄/AC Nanocomposites Based Supercapacitor Devices with High Energy Density and Power Density, Dalton Transactions, 2014, 43(46), 17528-17538.

[19] Y. G. Wang, Z. D. Wang, Y. Y. Xia. An asymmetric supercapacitor using RuO₂/TiO₂ nanotube composite and activated carbon electrodes, Electrochim. Acta, 2005, 50, 5641-5646.

[20] Y. Tang, Y. Liu, S. Yu, S. Mu, S. Xiao, Y. Zhao and F. Gao. Morphology controlled synthesis of monodisperse cobalt hydroxide for supercapacitor with high performance and long cycle life, J. Power Sources, 2014, 256, 160-169.

[21] C. Tang, Z. Tang, H. Gong, Hierarchically Porous Ni-Co Oxide for High Reversibility Asymmetric Full-Cell Supercapacitors, J. Electrochem. Soc., 2012, 159(5), A651-A656.