Electronic Supplementary Information

A Multicore Close-Packed Ultrathin-MnO$_2$@N-doped Carbon-Gear Yolk-Shell Micro-Nanostructures as Highly Efficient Sulfur Hosts for Li-S Batteries

Weixi Yan$^a$, Shipei Chen$^a$, Ming Wen$^a$, Qingsheng Wu$^a$, Shuhong Yu$^b$

$^a$School of Chemical Science and Engineering, Shanghai Key Laboratory of Chemical Assessment and Sustainability, Tongji University, Shanghai 200092, P. R. China.
E-mail: m_wen@tongji.edu.cn

$^b$Department of Chemistry, University of Science and Technology of China, Hefei National Laboratory for Physical Sciences at the Microscale, Jinzhai Road 96, Hefei 230022, P. R. China.
E-mail: shyu@ustc.edu.cn

† These authors contributed equally to this work.

Keywords:
Clustered MnO$_2$-S@NC-gear composite, Yolk-shell nanostructure, Cathode material, Li-S battery
Experimental section

Chemicals:
All chemicals used in this work were of analytical grade and were directly used without further purification.

Preparation of the Ultrathin-MnO$_2$:
Typically, purification, the ultrathin-MnO$_2$ was synthesized by a “Baeyer test for unsaturation” reaction. KMnO$_4$ (1 g) was dissolved in deionized water (500 mL). Then oleic acid (10 mL) was added with mechanical stirring for 2 hours. The black products were collected by washed by water and ethanol, respectively.

Preparation of the clustered MnO$_2$@CG and MnO$_2$@NCS Composite:
As contrast samples, the monodispersed MnO$_2$@NCG composites were synthesized under the same process as illustrated in preparation of the multicores close-packed MnO$_2$@NCG composite (Experiment section) in body content without the first addition of TEOS; the preparation of MnO$_2$@CG has similar synthesis condition except for the addition of ethane diamine (2 mL); the multicores close-packed MnO$_2$@NCS could be gained under the above process without the second addition of TEOS.

Preparation of the NCG and CG
Preliminary products SiO$_2$ were obtained via a Stöber synthesis method. TEOS (0.5ml), resorcinol (40 mg), formaldehyde (37 wt%, 0.056 mL) and ethane diamine (2 mL) were added into the mixed solution composed of ammonia (28wt%, 1 mL) and SiO$_2$ (100 mg), deionized water (30 mL). After vigorously stirring for 2 hours, the product N-doped carbon-internal-gear (NCG) was then centrifugally washed and dried at 60°C. If the TEOS was not been added, the N-doped carbon smooth shelled hollow spheres (NCS). And the CG would be acquired when removed the ethane diamine during the process described above.
Supporting Tables and Figures

**Table S1.** BET specific surface, pore volume and BHJ average pore diameter of MnO$_2$.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Specific surface area $\text{m}^2\text{ g}^{-1}$</th>
<th>Pore Volume $\text{cm}^3\text{ g}^{-1}$</th>
<th>Pore Diameter $\text{nm}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>MnO$_2$</td>
<td>208.93</td>
<td>0.92</td>
<td>10.35</td>
</tr>
</tbody>
</table>

**Table S2.** The simulation results of the equivalent circuit and EIS spectra in Figure 3D.

<table>
<thead>
<tr>
<th>Samples/Impedance</th>
<th>$\text{Re} / \Omega$</th>
<th>Std. error</th>
</tr>
</thead>
<tbody>
<tr>
<td>MnO$_2$-S@GNC</td>
<td>18.9</td>
<td>1.3</td>
</tr>
<tr>
<td>MnO$_2$-S@GC</td>
<td>74.02</td>
<td>3.2</td>
</tr>
<tr>
<td>MnO$_2$-S</td>
<td>111.5</td>
<td>2.9</td>
</tr>
<tr>
<td>S</td>
<td>208.9</td>
<td>2.3</td>
</tr>
</tbody>
</table>
Scheme S1. Design strategy of the clustered MnO$_2$-S@NCG.

Fig. S1. Schematic illustration of the synthesis process of NCG.
Fig. S2 (A) SEM image (a), low (b) and high (c) magnification TEM images of SiO$_2$@SiO$_2$-N-RF; (B) SEM image (a), low (b) and high (c) magnification TEM images of NCG after carbonization and etching SiO$_2$; (C) SEM image (a), low (b) and high (c) magnification TEM images of CG.
Fig. S3. Schematic illustration of the synthesis process for NCS.

Fig. S4. (A) SEM image and (B-D) TEM images of NCS at different magnification.

Note: Based on the synthesis mechanism of the gear liked carbon hollow spheres, using SiO$_2$ nanospheres as hard templates through the similar process of the synthesis of MnO$_2$@NCG (Exp. section), the hollow N-doped internal C-gear (NCG) spheres could be obtained. In Fig. S2A, the SEM and TEM images show that the average diametre of the SiO$_2$@SiO$_2$-N-RF spheres is about 100 nm. After etching SiO$_2$, the morphology and structure of NCG keep stably, besides, there are gear liked carbon spikes on the inner surface of the NCG (Fig. S2B). In addition, the size of hollow is determined mainly by the size of the original hard template. So the NCG shell can be successfully obtained in this work. As a contrast the N-doped carbon smooth-shelled-hollow-spheres (NCS) has been synthesised via SiO$_2$ as hard template then added N-RF alone, the Schematic illustration of the synthesis process and the morphology were shown in Fig. S3 and Fig. S4.
Fig. S5. (A) SEM and (B) TEM images of the clustered MnO$_2$@SiO$_2$ at different magnification; (C) The clustered ultrathin-MnO$_2$: (A) SEM, (B) TEM images at different magnification.

Note: There have been studies on the preparation of microemulsion spheres by using emulsion stabilizer to aggregate monodisperse nano-spheres, and the size of the final aggregation product can be controlled by controlling the diameter of emulsion spheres. The disadvantage of this method is that the preparation process is complicated, which requires extremely high stirring speed and temperature treatment. Herein, a one-step method was developed to successfully prepare multicores close-packed composite. The experimental process may be as follows: with the help of surfactant CTAB, the nanometer ultrathin-MnO$_2$ self-assembly into micronspheres, while TEOS hydrolyzed on the MnO$_2$ to generate SiO$_2$ then wrap it. In Figure S5A-B, the MnO$_2$@SiO$_2$ composite with good dispersion and a particle size of 3–5 μm consists of nanospheres (~100 nm). From TEM images (Fig. S5Ba), it can be further observed that clustered MnO$_2$@SiO$_2$ microspheres are closely packed and grown by small MnO$_2$@SiO$_2$
nanospheres, and the formation mode is shown in the two-dimensional illustration in the inste of Fig. S5Aa. The higher magnification TEM image (Fig. S5Bb) further shows that the ultrathin-MnO$_2$ is wrapped by SiO$_2$ externally, with a thickness of about 20 nm. In order to further study the internal structure composition, SiO$_2$ was etched and the morphology of products was shown in Fig. C. Firstly, after etching, the morphology of the micron sphere is maintained and uniformly dispersed, as shown in the two-dimensional illustration in the inset of Fig. S5 Ca. Furthermore, as can be seen from the TEM images, there are spaces inside the micron sphere, indicating that the material is uniform aggregation of ultrathin-MnO$_2$. Besides, a single ultrathin-MnO$_2$ can also be clearly seen in the high magnification TEM image (Fig. S5 Cc).
**Fig. S6.** SEM images the clustered MnO$_2$@SiO$_2$@SiO$_2$/N-RF(A); MnO$_2$@NCG (B) after carbonization and ejecting SiO$_2$; the clustered MnO$_2$-S@NCG (C) without residual sulfur on the surface.

**Fig. S7.** (A, B) STEM images of MnO$_2$-S@NCG in bright and dark field; (C) Photographs of the valid S solution infiltration process of sulfur-CS$_2$ solution (a) and MnO$_2$-S@NCG-CS$_2$ solution (b).
Fig. S8. The ultrathin-MnO$_2$: (A) SEM, (B) TEM images; (C) XRD pattern.

**Note:** The X-ray diffraction (XRD) pattern was investigated in the range of the diffraction angle ($2\theta$) of 10–70° shown in Fig. S8C. The diffraction peaks at $2\theta$=12.3, 24.3, 36.6, 65.7° correspond to the crystal plane (001), (002), (100), and (110) of the monoclinic birnessite MnO$_2$ crystal structure (JCPDS 80-1098), respectively, indicating that the ultrathin-MnO$_2$ owns layered structure. Moreover, from $2\theta$=12.3°, the crystal plane spacing is calculated to be 0.72nm, consistent with HRTEM results.
Fig. S9. (A) N\textsubscript{2} adsorption-desorption isotherms for MnO\textsubscript{2}; (B) The corresponding pore size distributions.

Fig. S10. XPS spectra of MnO\textsubscript{2}-S@NCG: (A) full survey spectrum, (B-E) high-resolution spectra for Mn 2p, S 2p, N 1s, C 1s, respectively.
Fig. S11. SEM and TEM images of MnO$_2$-S@NCS at different magnification.

Fig. S12. Discharge-charge voltage profiles of MnO$_2$-S@NCS at various rates.

Rs: series resistance; Rct: charge-transfer resistance; Ws: adsorption impedance; Wo: the semi-infinite Warburg diffusion impedance.

Fig. S13. The corresponding equivalent circuit of Nyquist plots for MnO$_2$-S@NCG.
**Fig. S14.** (a) SEM and (b,c) TEM images of S@CG (A) and MnO$_2$-S@CG (B).

**Note:** As contrast, the S@CG was prepared through employing hollow-CG as S host material to be with sulfur infiltration. The corresponding morphology characterization is shown in Fig. S14. As can be seen from the SEM, the composite is a monodisperse nanosphere, and the overall morphology maintains excellent dispersion. The diameter of a single microsphere is ~80 nm. The TEM images of the S@CG demonstrate the sulfur successfully permeate into the hollow sphere with the remaining space, it favors the S volume expansion in the application of lithium-sulfur batteries, and the remaining internal space can further enhance the mass loading of the S. Thus, the valid S solution infiltration strategy is convenient, which can not only effectively adjust the mass loading of S but also does not leave S block outside.
Fig. S15. (A) SEM, (B) TEM, (C) HRTEM images and (D) corresponding SAED pattern of MnO$_2$-S.

Note: MnO$_2$-S has been prepared through a new valid S solution infiltration strategy infiltrate the S onto ultrathin-MnO$_2$ carrier. The corresponding morphology was shown in Fig. S15. The SEM and low magnification TEM images demonstrate that MnO$_2$-S remains spherical with good dispersion and no residual sulfur block, which again testify the advantages of valid S.
solution infiltration strategy. Compared with the MnO$_2$ (Fig. S8B), the MnO$_2$-S clearly shows that S successfully adsorbed on the ultathin-MnO$_2$. In the selected area electron diffraction (SAED) pattern, the Debye-Scherrer rings corresponding to the diffractions of the (110) planes of MnO$_2$ and (212), (222), (026) planes of S, which predicates the existence of MnO$_2$ and S. According to EDS datas (Fig. S16A), the mass of S in the complex accounted for 47%. The XRD diffraction peak (Fig. S16B) is also consistent with the standard card JCPDS 08-0248 of S. Fig. S16C and S16D also show the XPS spectra of Mn 2P and S 2P, thus proving the successful load of S on ultrathin-MnO$_2$. 
Fig. S17. Gravimetric Cycling performance of the clustered MnO$_2$-S@NCG.

(E/S ratio: 25 µL mg$^{-1}$,  S loading: ~2.3 mg cm$^{-2}$).

Fig. S18. Cyclic voltammograms profiles of the clustered MnO$_2$-S@NCG composite at scan rate of 1 mV s$^{-1}$.
Fig. S19. XRD pattern of pristine ultrathin-MnO$_2$ (a) and treated with Li$_2$S$_4$ (b).

**Note**: To further obtain more information about the interaction mechanism between ultrathin-MnO$_2$ and LiPSs. The contrastive XRD pattern of pristine ultrathin-MnO$_2$ and treated with Li$_2$S$_4$ after 15 min in DME/DOL solution (100 mL, 1:1, vol%) has been studied in Fig.S19. All the characteristic peaks of ultrathin-MnO$_2$ were missing, while a new broad reflection peak appeared at and the peak at $2\theta = 36.4^\circ$ is assigned to (211) plane of Mn$_3$O$_4$ hausmannite phase (JCPDS 24-0734), indicating the partially transform of ultrathin-MnO$_2$ into new Mn$_3$O$_4$ phase. The reason could be explained as follows: the redox reaction between ultrathin-MnO$_2$ and LiPS lead to the Mn$^{4+}$ reducted to Mn$^{3+}$ and Mn$^{2+}$.

**References**