

Supplementary Information for

Enhanced Performance of a MnO₂/Graphene-Sheet Cathode for Lithium ion batteries by Using Sodium Alginate as a Binder

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Supporting Experimental Section

All chemicals were of analytical grade. Graphene sheets (GS) were purchased from Xiamen Knano Graphene Technology Corporation Limited in P.R. China. MnO₂ nanoflakes growing on GS was synthesized by immersing GS into a KMnO₄ aqueous solution. 70 mg KMnO₄ was dispersed in 20 ml de-ionized water and heated to 80 °C. And 30 mg GS were added to the solution and the mixtures were maintained at 80 °C for 24 h. The pH of the solution was adjusted to 2.5 by adding HCl. The suspension was filtered and washed by de-ionized water, and then dried at 100 °C overnight. For comparison, pure MnO₂ nanoflake was directly prepared by immersing MnSO₄ into a KMnO₄ aqueous solution. The samples were characterized by X-ray diffraction test (XRD), scanning electron microscope (SEM), transmission electron microscope (TEM), X-ray photoelectron spectroscopy (XPS) and thermo-gravimetric analysis (TGA).

The electrochemical behaviors were measured *via* CR2025 coin-type test cells fabricated in a glove box filled with dry argon atmosphere. The working electrode consisted of 80 *wt.*% active material, 10 *wt.*% sodium alginate (SA) or 10 *wt.*% polyvinylidene difluoride (PVDF), and 10 *wt.*% ketjen black. The test cell consisted of working electrode (2.0 ± 0.2 mg/cm², using steel grid as current collector) and lithium sheet which was separated by a Celgard 2300 membrane and electrolyte of 1 M LiPF₆ in EC :DEC :DMC (1 :1 :1 in volume). Cyclic voltammetry tests were

operated on a CHI660D Electrochemical Workstation with various scan rates. The cells were tested by Land 2001A at room temperature.

Supporting Figures, Figure Captions and Related Depiction

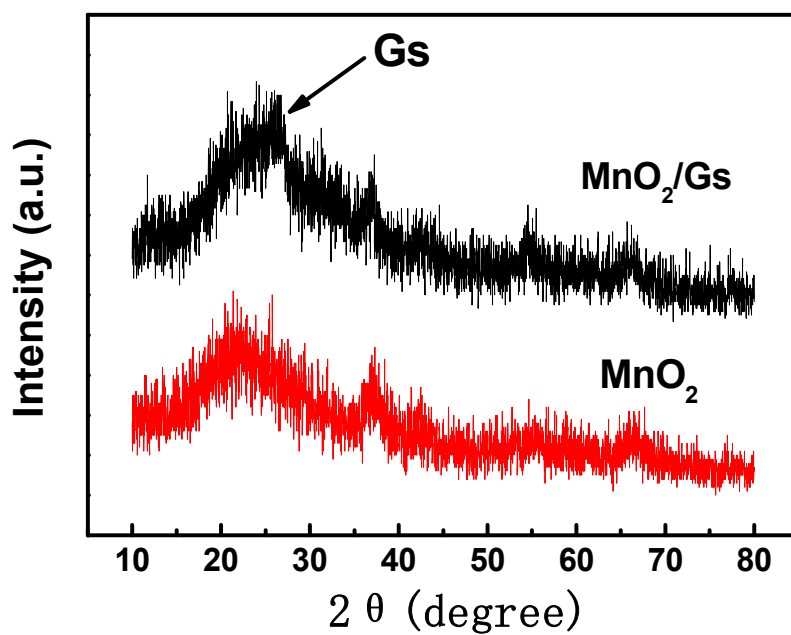


Figure S1. X-ray diffraction patterns of pure MnO₂ and MnO₂/GS hybrid.

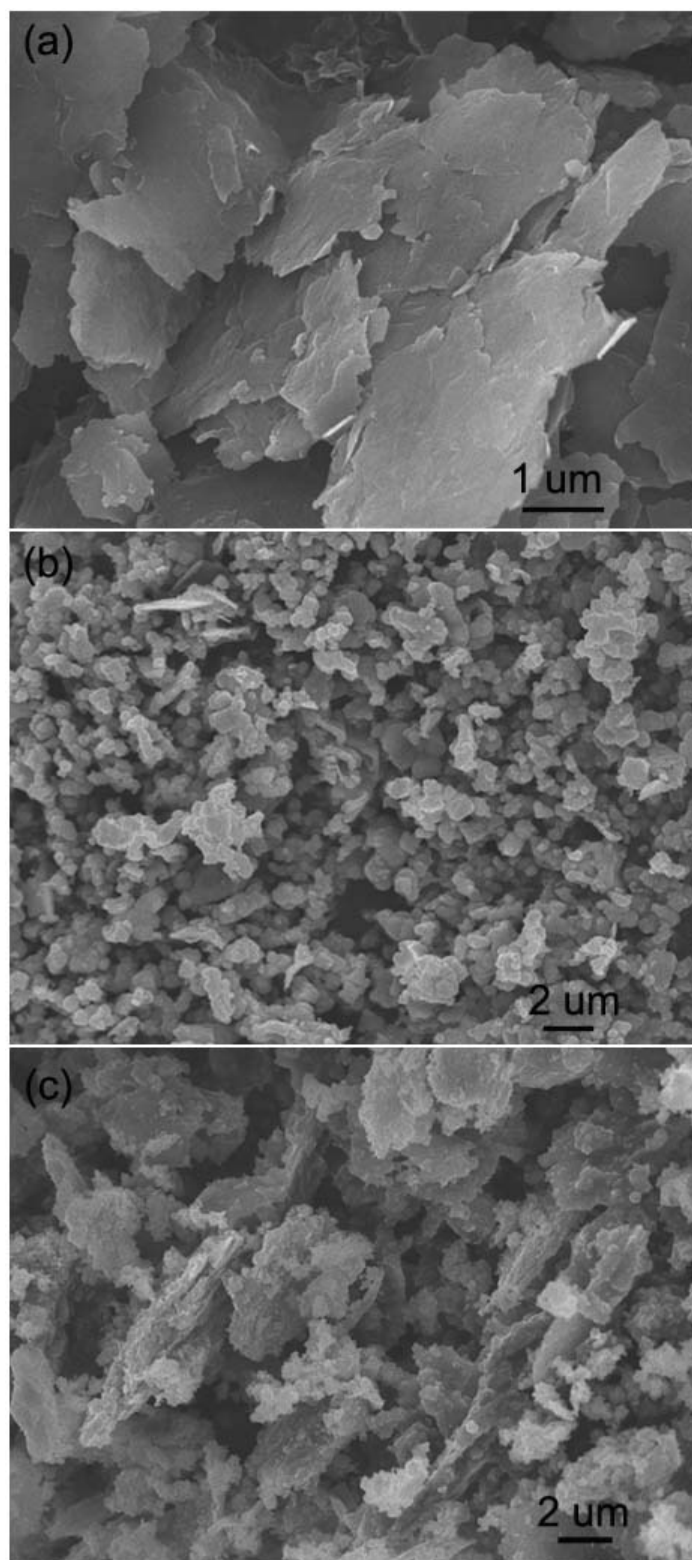


Figure S2. SEM images of (a) GS, (b) pure MnO₂ and (c) MnO₂/GS hybrid.

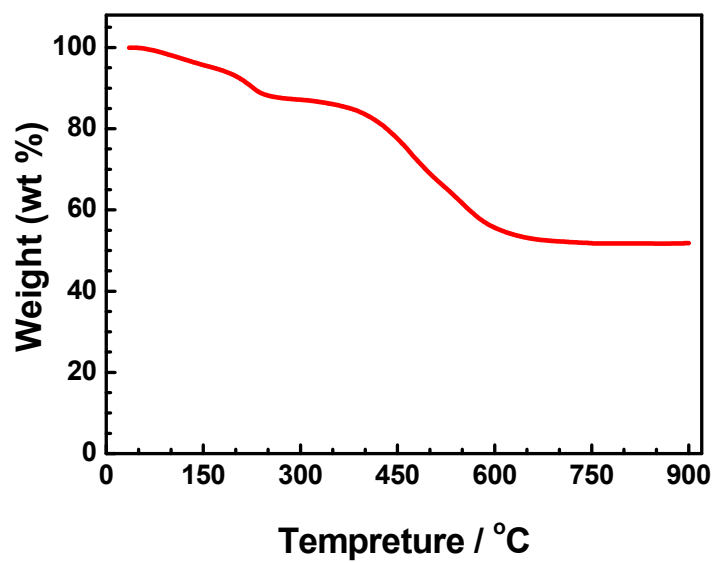


Figure S3. TGA curve of the MnO₂/GS hybrid.

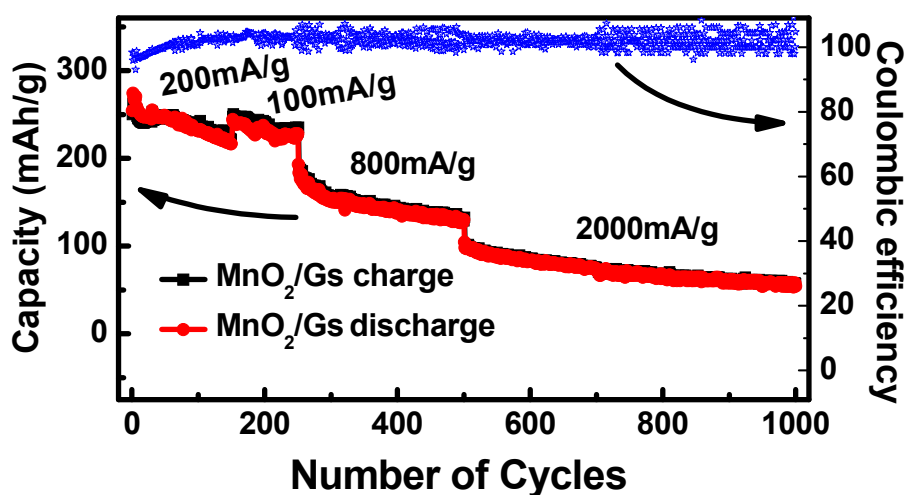


Figure S4. Long cycling performance and Coulombic efficiency of MnO₂/GS electrode with SA binder at different current densities.

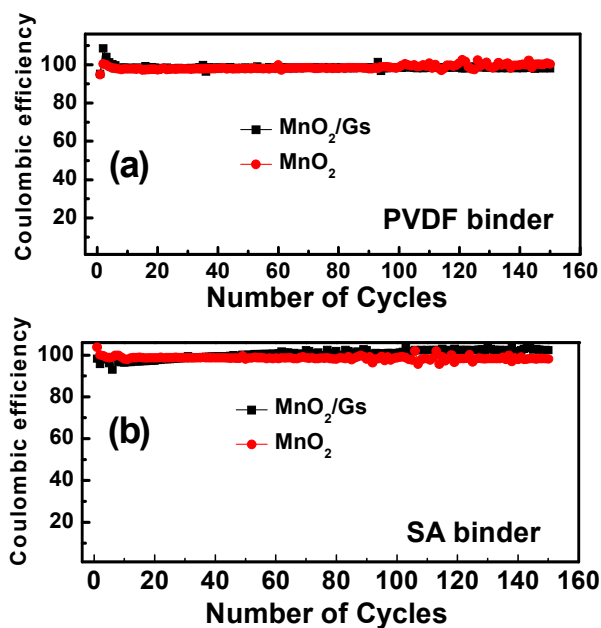


Figure S5. Coulombic efficiency of MnO₂ and MnO₂/GS electrodes with SA and PVDF binders.

The Coulombic efficiency of MnO₂ and MnO₂/GS electrodes with SA and PVDF binders were compared in figure S5. They all exhibited excellent Coulombic efficiency with ~100% retention after 150 cycles.

Table S1. Electrochemical performance of various MnO₂-related cathode materials reported in previous works.

Typical materials	Current density (mA/g)	First capacity (mA/g)	Cycle number	Remain capacity (mA/g)	Loss per cycle (mA/g)	Ref.
MnO₂	50	265	50	270	-	this work
	200	250	150	230	0.1	
	800	195	250	135	0.2	
	2000	110	500	55	0.1	
β-MnO ₂	300	190	50	120	1.4	1
	600	170	50	100	1.4	
	1500	155	50	120	0.7	
β-MnO ₂	15	285	50	200	1.7	2
	30	265	50	180	1.7	
	300	210	50	152	0.8	
β-MnO ₂	15	185	35	155	0.9	3
	30	112	35	85	0.8	
MnO ₂ *0.5H ₂ O	30	250	30	180	2.3	4
γ-MnO ₂	50	184	20	101	4.2	5

Refs.:

1. Ren, Y.; Armstrong, A. R.; Jiao, F.; Bruce, P. G. *Journal of the American Chemical Society* **2009**, *132*, 996.
2. Jiao, F.; Bruce, P. G. *Advanced Materials* **2007**, *19*, 657.
3. Bach, S.; Pereira-Ramos, J. P.; Willmann, P. *Electrochimica Acta* **2011**, *56*, 10016.
4. Liu, D.; Garcia, B. B.; Zhang, Q.; Guo, Q.; Zhang, Y.; Sepehri, S.; Cao, G. *Advanced Functional Materials* **2009**, *19*, 1015.
5. Zeng, J. H.; Wang, Y. F.; Yang, Y.; Zhang, J. *Journal of Materials Chemistry* **2010**, *20*, 10915.

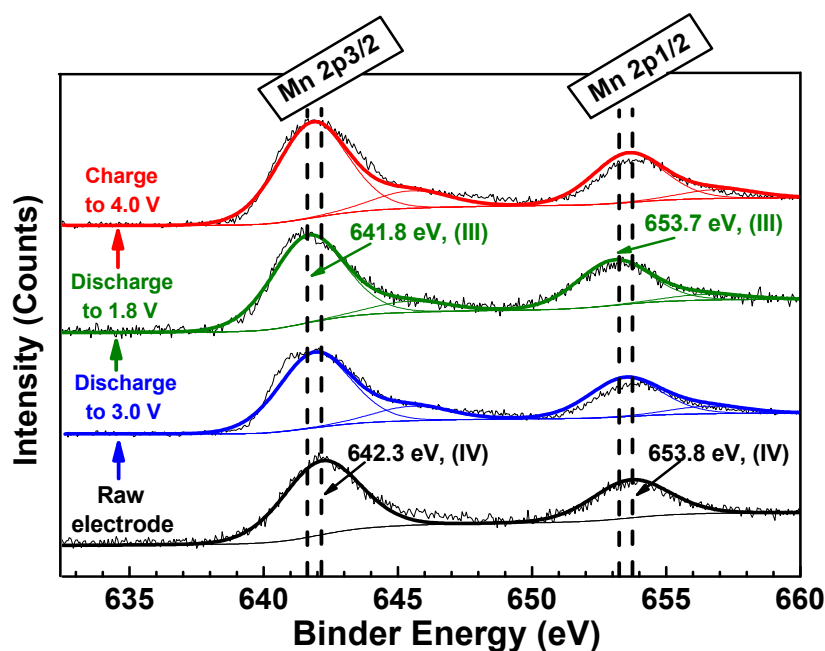


Figure S6. XPS spectra of Mn 2p for MnO₂/GS electrode with SA during one integrated cycle.

For clearly understanding the redox mechanism of MnO₂/GS electrode with SA binder, the XPS analyses for Mn valences were carried out and shown in Figure S6. From the XPS of raw electrode, the Mn 2p_{3/2} and Mn 2p_{1/2} peaks of the Mn(IV) chemical states appear around 642.3 and 653.8 eV. When battery is discharged to 3.0 V, the spectra shows that the Mn(III) and (IV) chemical states co-exist as the final products, corresponding to the co-existence of both LiMnO₂ [Mn(III)] and Li₂MnO₃ [Mn(IV)] phases.^{1,2} And there only exist Mn(III) chemical states (LiMnO₂) when battery is further discharged to 1.8 V. Note that the ratio of the peak intensity of Mn(III) almost disappeared and the Mn(IV) increased with the increasing voltage charged back to 4.0 V. Therefore, the reversible capacity of MnO₂ is theoretically derived from the reversible transformation between LiMnO₂ and MnO₂ phases during cycles. The high capacity of MnO₂/GS with SA depends on this available phase transformation.

Refs:

1. Lee, J.; Lee, J.-M.; Yoon, S.; Kim, S.-O.; Sohn, J.-S.; Rhee, K.-I.; Sohn, H.-J. *Journal of Power Sources* **2008**, *183*, 325.
2. Ogata, A.; Komaba, S.; Baddourhadjean, R.; Pereiramos, J.; Kumagai, N. *Electrochimica Acta* **2008**, *53*, 3084

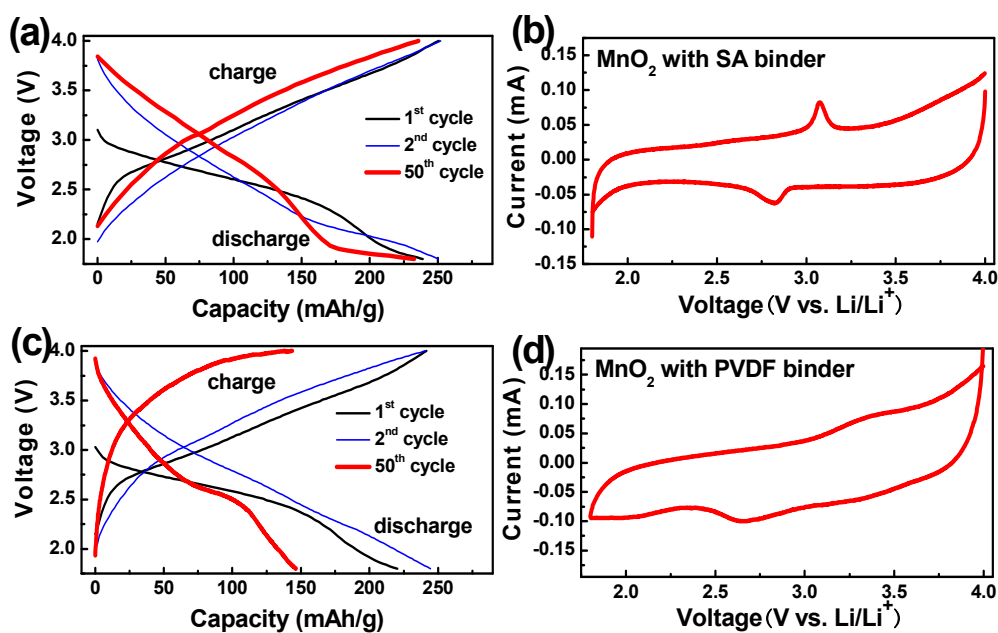


Figure S7. Discharge /charge (D /C) voltage profiles at 1st, 2nd and 50th cycles of MnO₂ electrodes with (a) SA and (b) with PVDF; (c) and (d) the corresponding cyclic voltammogram (CV) curves of each electrode after 100 cycles at a scan rate of 0.5 mV/s.

Note that the redox peaks of MnO₂ (see Figure S7d) almost disappear. This result is consistent with the pure MnO₂ related electrodes reported previously, which may be related to the expansion and aggregation during cycling (without both SA binder and GS buffer carrier) leading to increase impedance and further severe polarization.

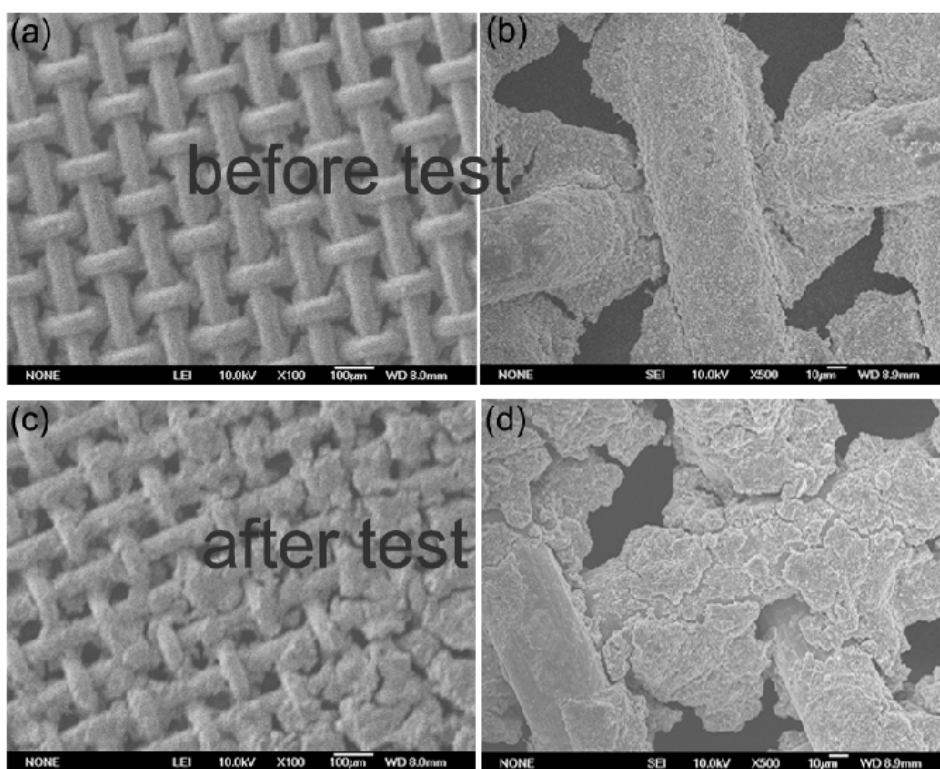


Figure S8. SEM images of MnO₂ electrode with PVDF before and after test.

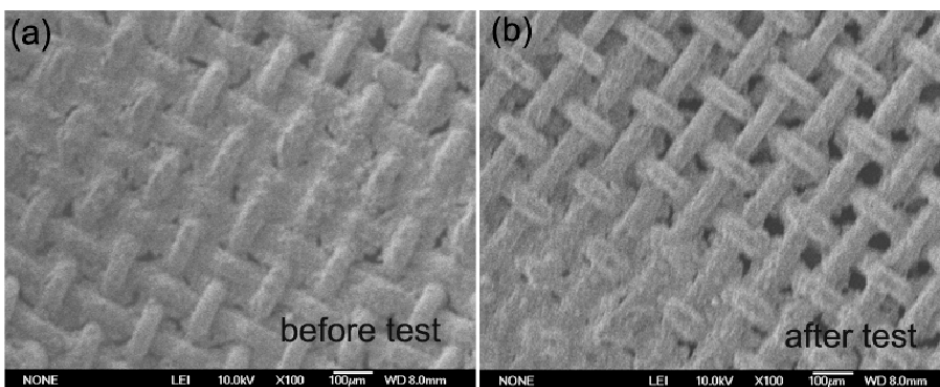


Figure S9. SEM images of MnO₂ with SA before and after test.