Supporting Information

## Three-dimensional Microspheres Constructed by MoS<sub>2</sub> Nanosheets Supported on Multiwalled Carbon Nanotubes for Optimized Sodium Storage

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Figure S1. The SEM image of MWCNTs.



Figure S2. SEM images of MoS<sub>2</sub>-MSs/MWCNTs.



Figure S3. Thermal gravimetric curve of MoS<sub>2</sub>-MSs/MWCNTs composite.

Here,  $MoS_2$  was oxidized to  $MoO_3$  completely and MWCNTs were oxidized to  $CO_2$ . Therefore, the  $MoS_2$  content in the composite could be calculated to be about 69.1 wt%, according to the previously reported literatures.



Figure S4. CV curves of the initial five cycles for MoS<sub>2</sub>-MSs at 0.1 mV s<sup>-1</sup> within 0.01 and 3.0 V (V vs. Na/Na<sup>+</sup>).



Figure S5. Electrochemical performance of MWCNTs electrodes in the voltage window 0.01-3.0 V (V vs. Na/Na<sup>+</sup>): (a) Galvanostatic discharge/charge profiles of 2<sup>nd</sup>, 5<sup>th</sup>, 10<sup>th</sup>, 50<sup>th</sup> cycles at a current density of 0.1A g<sup>-1</sup>; (b) Cycling performance at 0.1A g<sup>-1</sup> over 100 cycles; (c) Rate capability at different current densities of 0.1, 0.2, 0.5, 1.0, 2.0 and 5.0 A g<sup>-1</sup>; (d) the charge-discharge curves at the various current densities.



**Figure S6.** Electrochemical performances of MoS<sub>2</sub>-MSs/MWCNTs || Na<sub>3</sub>V<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> full cell: (a) The Charge-discharge curves of Na||Na<sub>3</sub>V<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> and Na||MoS<sub>2</sub>-MSs/MWCNTs half batteries; (b) the first GCD curve at 0.1 A g<sup>-1</sup> in the voltage range of 0.5-3.3 V; (C) discharge/charge profiles of 5<sup>th</sup>, 10<sup>th</sup>, 20<sup>th</sup>, 50<sup>th</sup>, 100<sup>th</sup> cycles at 0.1A g<sup>-1</sup>; (d) cycling performance at 0.1 A g<sup>-1</sup> for 100 cycles.

The MoS<sub>2</sub>-MSs/MWCNTs $||Na_3V_2(PO_4)_3|$  full cell was assembled by using MoS<sub>2</sub>-MSs/MWCNTs and Na<sub>3</sub>V<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> as the anode and cathode, respectively. The current density and capacity of the full cell are based on the anode mass. **Figure S5b** shown the first charge and discharge specific capacities of full-cell were 737.03 and 216.68 mA h g<sup>-1</sup>, respectively, with a low Coulombic efficiency of 29.4 %. The obviously irreversible capacity is mainly attributed to the formation of the SEI layer [S1, S13]. After 100 cycles, the full cell delivers a discharge capacity of 70.96 mA h g<sup>-1</sup> (**Figure S5d**).



**Figure S7.** discharging-charging profiles of MoS<sub>2</sub>-MSs/MWCNTs (a) and MoS<sub>2</sub>-MSs (b) at various specific currents.



Figure S8. CV curves of MoS<sub>2</sub>-MSs at various scan rates from 0.1 to 1.0 mV s<sup>-1</sup>.



Figure S9. A single step of a GITT experiment.

The  $D_{\text{Na}^+}$  could be calculated using the formula:

$$D_{Na^+} = \frac{4}{\pi\tau} \left(\frac{m_B V_M}{M_B A}\right)^2 \left(\frac{\Delta E_s}{\Delta E_\tau}\right)^2$$

Where  $\tau$  represents the constant current pulse time;  $m_B$ ,  $M_B$ , and  $V_M$  are the mass, molar weight, and molar volume of the active materials, respectively. A is the total contact

area between the electrolyte and the electrode.  $\Delta E_s$  and  $\Delta E_{\tau}$  are the changes in steadystate voltage after subtracting the IR drop and the total transient change in cell voltage during a single titration (**Figure S8**).



**Figure S10.** SEM images of MoS<sub>2</sub>-MSs before cycling (a & b); after 100 cycles at 0.1 A  $g^{-1}$  (c); MoS<sub>2</sub>-MSs/MWCNTs before cycling (d & e); after 100 cycles at 0.1 A  $g^{-1}$  (f); after 1000 cycles at

2.0 A g<sup>-1</sup> (g-i).

**Table S1.** Comparison of the electrochemical performance of MoS<sub>2</sub>-MSs/MWCNTs composite with previously reported MoS<sub>2</sub>-based anode for SIBs.

Samples	Capacity	Retention	Rate property	Ref.
	(mA h g <sup>-1</sup> )		(mA h g <sup>-1</sup> )	
N-doped MoS <sub>2</sub> /C	599.7 mA h g <sup>-1</sup>	83.4 %	242 mA h g <sup>-1</sup>	<b>S2</b>
	at 0.1 A g <sup>-1</sup>	(50 cycles)	at 5 A g <sup>-1</sup>	
S/MoS <sub>2</sub> architectures	497.6 mA h g <sup>-1</sup>	83.0 %	243.3 mA h g <sup>-1</sup>	36
	at 0.1 A g <sup>-1</sup>	(100 cycles)	at 2 A g <sup>-1</sup>	
MoS <sub>2</sub> /NCF-MP	471.8 mA h g <sup>-1</sup>	101.7 %	217 mA h g <sup>-1</sup>	37
	at 0.1 A g <sup>-1</sup>	(100 cycles)	at 30 A g <sup>-1</sup>	
tulip-MoS <sub>2</sub> /NG	320 mA h g <sup>-1</sup>	99.4 %	216 mA h g <sup>-1</sup>	39
	at 0.1 A g <sup>-1</sup>	(100 cycles)	at 5 A g <sup>-1</sup>	
MoS <sub>2</sub> @CF	343 mA h g <sup>-1</sup>	104.9 %	6 171 mA h g <sup>-1</sup>	
	at 0.1 A g <sup>-1</sup>	(100 cycles)	at 5 A g <sup>-1</sup>	
MoS <sub>2</sub> /CNTs	495.9 mA h g <sup>-1</sup>	84.8 %	328.4 mA h g <sup>-1</sup>	41
	at 0.2 A g <sup>-1</sup>	(80 cycles)	at 0.5 A g <sup>-1</sup>	
graphene@MoS <sub>2</sub> @C	604 mA h g <sup>-1</sup>	86.1 %	304 mA h g <sup>-1</sup>	<b>S3</b>

	at 0.1 A g <sup>-1</sup>	(110 cycles)	at 5 A g <sup>-1</sup>	
MoS <sub>2</sub> /PDC	475 mA h g <sup>-1</sup>	85.6 %	301.5 mA h g <sup>-1</sup>	<b>S4</b>
-	at 0.2 A g <sup>-1</sup>	(340 cycles)	at 5 A g <sup>-1</sup>	
MoS <sub>2</sub> @C-CMC	352 mA h g <sup>-1</sup>	81.2 %	205 mA h g <sup>-1</sup>	<b>S5</b>
	at 0.08 A g <sup>-1</sup>	(100 cycles)	at 1 A g <sup>-1</sup>	
MoS <sub>2</sub> nanosheets	362 mA h g <sup>-1</sup>	91.2 %	225 mA h g <sup>-1</sup>	<b>S6</b>
/Carbon Fibers	at 0.1 A g <sup>-1</sup>	(100 cycles)	at 1 A g <sup>-1</sup>	
MoS <sub>2</sub> -reduced	345 mA h g <sup>-1</sup>	88.4 %	245 mA h g <sup>-1</sup> S	
graphene oxide (rGO)	at 0.1 A g <sup>-1</sup>	(50 cycles)	at 1 A g <sup>-1</sup>	
MoS <sub>2</sub> /C-MWCNT	617 mA h g <sup>-1</sup>	83.9 %	324 mA h g <sup>-1</sup> at	45
	at 0.2 A g <sup>-1</sup>	(300 cycles)	20 A g <sup>-1</sup>	
Nervous-like	571 mA h g <sup>-1</sup>	92.4 %	411 mA h g <sup>-1</sup>	46
MoS <sub>2</sub> /MWCNT	at 0.1 A g <sup>-1</sup>	(110 cycles)	at 2 A g <sup>-1</sup>	
Graphene-Wrapped	495.1 mA h g <sup>-1</sup>	82.5 %	345 mA h g <sup>-1</sup>	<b>S8</b>
MoS <sub>2</sub> (MoS <sub>2</sub> -G)	at 0.2 A g <sup>-1</sup>	(100 cycles)	at 1.6 A g <sup>-1</sup>	
MoS <sub>2</sub> -rGO/HCS	635 mA h g <sup>-1</sup>	86.9 %	364 mA h g <sup>-1</sup>	<b>S9</b>
	at 0.1 A g <sup>-1</sup>	(100 cycles)	at 5 A g <sup>-1</sup>	
MoS <sub>2</sub> @C nanotube	640 mA h g <sup>-1</sup>	80 %	370 mA h g <sup>-1</sup>	S10
composite	at 0.5 C	(200 cycles) at 5 C		
MoS <sub>2</sub> @C nanosheets	477 mA h g <sup>-1</sup>	86.3 %	284 mA h g <sup>-1</sup>	<b>S11</b>
@MoS <sub>2</sub> nanorods	at 0.1 A g <sup>-1</sup>	(100 cycles) at 4 A g-		
CNT@NCT@W-	530 mA h g <sup>-1</sup>		230 mA h g <sup>-1</sup>	
MoS <sub>2</sub> /C	at 0.1 A g <sup>-1</sup>		at 2 A g <sup>-1</sup>	
MoS <sub>2</sub> -C nanosheets	383.4 mA h g <sup>-1</sup>	101.3 %	275 mA h g <sup>-1</sup>	<b>S13</b>
	at 0.1 A g <sup>-1</sup>	(100 cycles)	at 8 A g <sup>-1</sup>	
N-MoS <sub>2</sub> /C	649 mA h g <sup>-1</sup>	78 %	387.9 mA h g <sup>-1</sup>	<b>S14</b>
	at 0.2 C	(200 cycles)	at 10 C	
1T-MoS <sub>2</sub> /CC arrays	768 mA h g <sup>-1</sup>	80 %	276 mA h g <sup>-1</sup>	53
	at 0.2 A g <sup>-1</sup>	(200 cycles)	at 2 A g <sup>-1</sup>	
MoS <sub>2</sub> -MSs/MWCNTs	550 mA h g <sup>-1</sup>	94.4 %	227 mA h g <sup>-1</sup>	This
composite	at 0.1 A g <sup>-1</sup>	(100 cycles)	at 10 A g <sup>-1</sup>	work

**Table S2.** The calculated values of SEI layer resistance ( $R_{SEI}$ ), charge-transfer resistance ( $R_{ct}$ ),  $\sigma$  and sodium-ion diffusion coefficient ( $D_{Na^+}$ ) for both samples.

Samples	$R_{SEI}(\Omega)$	$R_{ct}(\Omega)$	σ	$D_{Na^+}$ (cm <sup>2</sup> s <sup>-1</sup> )
MoS <sub>2</sub> -MSs	201.7	14.95	117.84	2.14×10 <sup>-11</sup>
MoS <sub>2</sub> -MSs/MWCNTs	19.05	78.72	16.67	0.89×10 <sup>-12</sup>

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