## **Supporting Information**

# **Confining MoSe<sub>2</sub> Nanosheets into N-Doped Hollow Porous Carbon Microspheres for Fast-Charged and Long-Life Potassium-Ion Storage**

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#### Synthesis of control samples

**Preparation of MoSe<sub>2</sub>@N-HCS-no-PDA**: The control sample MoSe<sub>2</sub> nanosheets confined into N-doped porous hollow carbon microspheres without PDA coating (MoSe<sub>2</sub>@N-HCS-no-PDA) was yielded by replacing Mo<sub>2</sub>N@C@C<sub>PDA</sub> with Mo<sub>2</sub>N@C through the same process.

**Preparation of MoSe<sub>2</sub>@HCS and N-HCS:** 6.0 g H<sub>24</sub>Mo<sub>7</sub>N<sub>6</sub>O<sub>24</sub>·4H<sub>2</sub>O was annealed at 300  $\Box$  for 10 h under Ar atmosphere with a heating rate of 3  $\Box$ ·min<sup>-1</sup> to obtain MO<sub>3</sub>. Then, MO<sub>3</sub> and C<sub>6</sub>H<sub>8</sub>O<sub>7</sub>·H<sub>2</sub>O were used to replace H<sub>24</sub>Mo<sub>7</sub>N<sub>6</sub>O<sub>24</sub>·4H<sub>2</sub>O and C<sub>6</sub>H<sub>17</sub>N<sub>3</sub>O<sub>7</sub>, respectively, and the subsequent preparation process was the same as MoSe<sub>2</sub>@N-HCS. Finally, MoSe<sub>2</sub> and carbon composite without N-doping was obtained (MoSe<sub>2</sub>@HCS). Compared with the preparation of MoSe<sub>2</sub>@N-HCS, carbon material (N-HCS) was synthesized without adding H<sub>24</sub>Mo<sub>7</sub>N<sub>6</sub>O<sub>24</sub>·4H<sub>2</sub>O and omitting the selenization step.



**Figure S1.** SEM images of microspheres (a-b) after spray drying and (c-d) after carbonizing without removing KCl. (e) XRD pattern and (f) SEM image of Mo<sub>2</sub>N@C.



**Figure S2.** (a) Survey XPS spectrum of MoSe<sub>2</sub>@N-HCS. (b) SEM image and (c) XRD pattern of N-HCS. (d) Se 3d and (e) C 1s spectrum of MoSe<sub>2</sub>@N-HCS.

Three peaks corresponding to C-C, C-O and C-N bonds could be found in the C1s spectrum, which indicated that there was a chemical bond between nitrogen and carbon.<sup>1, 2</sup>



**Figure S3.** EDS elemental analysis results of (a) MoSe<sub>2</sub>@N-HCS, (b) MoSe<sub>2</sub>@N-HCS-no-PDA and (c) N-HCS.



**Figure S4.** (a) Raman spectrum, (b) TG curve and (c) nitrogen adsorption-desorption isothermal curves of MoSe<sub>2</sub>@N-HCS.

The peaks located at 1346.6 and 1594.4 cm<sup>-1</sup> were indexed to the D-band and G-band of carbon material, with a high intensity ratio of 0.90 ( $I_D/I_G$ ), revealing the amorphous structure (**Figure S4a**). According to the TG curve (**Figure S4b**), the slight mass increased at 350  $\Box$  was due to the oxidation of MoSe<sub>2</sub> to MoO<sub>3</sub> and SeO<sub>2</sub>, and the subsequent decrease was attributed to the oxidation of C and the sublimation of SeO<sub>2</sub>. Finally, the content of MoSe<sub>2</sub> and N-HCS were calculated as 57.5 wt% and 42.5% for MoSe<sub>2</sub>@N-HCS, respectively.



Figure S5. (a) HAADF image and (b-d) element mapping images of Mo<sub>2</sub>N@C@C<sub>PDA</sub>.

The HAADF and corresponding element mappings images of  $Mo_2N@C@C_{PDA}$  displayed that C, Mo and N elements were uniformly distributed throughout the sphere, which was consistent with the XRD pattern of  $Mo_2N$  (**Figure S5**), further corroborating the presence of the intermediate of  $Mo_2N@C@C_{PDA}$ .



Figure S6. XRD patterns of (a) MoSe<sub>2</sub>@N-HCS-no-PDA, (b) MoSe<sub>2</sub>@HCS and (c) commercial MoSe<sub>2</sub>. SEM images of (d) MoSe<sub>2</sub>@N-HCS-no-PDA, (e) MoSe<sub>2</sub>@HCS and (f) commercial MoSe<sub>2</sub>.



**Figure S7.** (a) The voltage response during a single current pulse and (b) thickness of  $MoSe_2@N-HCS$  coated on copper foil for calculation of K<sup>+</sup> diffusion coefficient.

$$D = \frac{4}{\pi \tau} \left(\frac{m_B V_m}{M_B S}\right)^2 \left(\frac{\Delta E_S}{\Delta E_\tau}\right)^2 \quad \left(\tau \ll \frac{L^2}{D}\right) \text{ (Equation 1)}$$

For the convenience of calculation, the part of Equation 1, i.e.,  $\left(\frac{m_B V_m}{M_B S}\right)$ , could be equivalent to the thickness of anode materials (Figure S7b).<sup>3</sup>



**Figure S8.** Pseudocapacitive contribution (pink shadow area) to total capacity at a scan rate of (a)  $1.0 \text{ mV s}^{-1}$ , (b)  $0.5 \text{ mV s}^{-1}$ , (c)  $0.3 \text{ mV s}^{-1}$  and (d)  $0.1 \text{ mV s}^{-1}$ .



**Figure S9.** (a) Galvanostatic charge/discharge curves and (b) cycling performance at 100 mA  $g^{-1}$  of Prussian blue analogues  $K_{1.92}Fe[Fe(CN)_6]_{0.94} \cdot 0.5H_2O$ . (c) Galvanostatic charge/discharge curves of full cell at 200 mA  $g^{-1}$ .



**Figure S10.** HRTEM images of Mo<sub>2</sub>Se@N-HCS anode at (a) fully-discharged state (0.01 V) and (b) fully-charged state (3.0 V) in the first cycle.



**Figure S11.** (a-b) SEM images, (c)TEM image, (d) HRTEM image, (e) HAADF image and (f-j) element mapping images of MoSe<sub>2</sub>@N-HCS anode after 500 cycles at 1 A g<sup>-1</sup>.

In order to explore the reasons for the excellent rate and cycling performance, the structure and composition changes of  $MoSe_2@N-HCS$  after 500 cycles at 1 A g<sup>-1</sup> were

measured (Figure S11). SEM images and TEM image after cycling indicated that  $MoSe_2@N-HCS$  maintained a relatively complete structure (Figure S11a-c). The visible lattice fringes with the interlayer spacing of 0.67 nm and the element mappings of Mo, Se, C, N that were similar to the initial  $MoSe_2@N-HCS$  strongly confirmed that the  $MoSe_2@N-HCS$  had good cycle stability and reversibility (Figure S11d-i). It should be noted that the lattice fringes with the interlayer spacing of 0.28 nm corresponded to the incomplete reaction product  $Mo_xSe_y$  (y/x<2) (Figure S11d),<sup>4</sup> while the existence of K and F elements was attributed to the stable SEI film formed on the electrode surface (Figure S11j-k).

### **Electrochemical reactions:**

The electrochemical reactions could be expressed as follows:

Potassiation:

 $MoSe_2 + xK^+ + xe^- \rightarrow K_xMoSe_2 \quad (0.85 \text{ V}, 0.64\text{V}) \qquad (Equation S1)$  $K_xMoSe_2 + xK^+ + xe^- \rightarrow 2K_xSe + Mo \ (x = 1.7, 2) \quad (<0.43 \text{ V}) \quad (Equation S2)$ Depotassiation:

$$K_xSe + yMo \rightarrow Mo_ySe + xK^+ + xe^- \quad (y = 0.5, 0.79)$$
 (Equation S3)



**Figure S12.** The K migration paths, final state structures and transition state energy barriers  $(\Delta E_{Ts})$  of (a) MoSe<sub>2</sub> and (b) N-HCS.

Materials	Electrolyte	Binder	Cyclability	Rate performance		Ref.	
			[mAh g <sup>-1</sup> ]	Capacity	Current		
				[mAh g <sup>-1</sup> ]	[A g <sup>-1</sup> ]		
MoSe <sub>2</sub> /NP-	1 M KFSI in	PVDF	131 at 1 $A \cdot g^{-1}$ 288, 225, 0		0.1, 0.2,	5	
C- 2	EC:DEC		after 250	168, 124 and 0.5, 2 and			
			cycles	91 5			
$MoSe_2/N\square C$	1M KFSI in	CMC	258.02 at 100	300, 244,	0.1, 0.2, 4		
	EMC		mA g <sup>-1</sup> after	211, 195 and	0.5, 1 and		
			300 cycles	178	2		
MoSe₂⊂PNC-	1 M KFSI	PVDF	113 at 1 A g <sup>-1</sup>	<sup>1</sup> 260, 231, 0.1, 0.2,		6	
HNTs	in EMC		after 500	210, 202,	0.4, 0.6,		
			cycles	190, 176,	0.8, 1.0,		
				138, 104 and	2.0, 3.0		
				79.1	and 5.0		
MoSe <sub>2</sub> /C-700	0.8 M KPF <sub>6</sub>	CMC	316 at 100	320, 266,	0.1, 0.2,	7	
	in EC:DEC		mA g <sup>-1</sup> over	227, 197, 158	0.5, 1, 2		
			100 cycles	and 133	and 3		
N-MoSe <sub>2</sub> @C	0.8 M KPF <sub>6</sub>	PVDF	227 at 1 A g <sup>-1</sup>	g <sup>-1</sup> 368, 324, 0.2, 0.5,		8	
	in EC:DEC		after 5000	267, 224 and	2 and 5		
			cycles	169			
PMC	0.8 M KPF <sub>6</sub>	PVDF	226 at 1 A g <sup>-1</sup>	382, 342,	0.2, 0.4,	9	
	in EC:DEC		after 1000	304, 277, 254	0.6, 0.8,		
			cycles	and 224	1.0 and		
					2.0		
MoSe <sub>2</sub> @NCT	0.85 M	PVDF	74 at 1 A g <sup>-1</sup>	~240, 110	0.1, 1 and	2	
	KPF <sub>6</sub> in		after 400	and 65	2		
	EC:DEC		cycles				
MoSe <sub>2</sub> -on-NC	07 M KPF <sub>6</sub>	PVDF	247 at 1 A g <sup>-1</sup>	393, 328, 0.2, 0.5,		10	
	in EC:DEC		after 4800	291, 252, 215	1.0, 2.0,		
			cycles	and 171	3.0 and		
					5.0		
MoSe <sub>2</sub> /BC/CN	1 M KFSI	CMC-	415.5 at 0.1 A	367.6, 339.4,	0.1, 0.2,	11	
Ts	in EMC	Na	g <sup>-1</sup> after 250	301.0, 273.0	0.5, 1 and		

**Table S1.** The comparison of potassium storage performance of molybdenum selenide inrecently reported literatures.

			cycles	and 247.8	2	
HM-MoSe <sub>2</sub> /N-	1 M KFSI in	PVDF	7 172.5 at 0.5 A 219.4, 172.2		0.1, 0.5,	12
С	EC:DEC		g <sup>-1</sup> after 400	153.3, 121.5,	1.0, 2.0,	
			cycles	103.7 and	5.0 and 10	
				94.2		
MoSe <sub>2</sub> /N-C	0.8 M KPF <sub>6</sub>	PVDF	319 at 200	375, 363,	0.1, 0.2,	13
	in EC:DEC	in EC:DEC mA g <sup>-1</sup>		323, 292, 266	0.5, 1, 2	
			300 cycles	and 211	and 5	
MoSe <sub>2</sub> @10%r	1 M KPF <sub>6</sub>	PVDF	314 at 100	279.2, 220.4,	0.2, 0.5, 1	14
GO	in	mA g <sup>-1</sup> after		155.2 and	and 2	
	PC:EC:DE		50 cycles	77.8		
	С					
MoSe <sub>2</sub> @N-HC	1 M KFSI in	PVDF	158.3 at 2 A	290.5, 258.6,	0.2, 0.5 1,	This
S	EC:DEC		g <sup>-1</sup> after	231.3, 203.9,	2, 4, 8 and	work
			16700 cycles	168.3, 130.1	10	
				and 113.7		

Electrode	$R_{e}(\Omega)$	$\mathbf{R}_{\mathrm{SEI}}\left( \Omega ight)$	R <sub>ct</sub> (Ω)
MoSe <sub>2</sub> @N-HCS	3.501	20.17	624.1
MoSe2@N-HCS-no-PDA	4.457	10.51	1621
MoSe2@HCS	2.711	45.29	935.9
Commercial MoSe2	2.661	8.076	1662
N-HCS	2.535	3.203	1286

**Table S2.** The fitted impedance results of MoSe2@N-HCS, MoSe2@N-HCS-no-PDA,MoSe2@HCS, commercial MoSe2 and N-HCS.

Average D <sub>GITT</sub> (×10 <sup>-9</sup> cm <sup>2</sup> s <sup>-1</sup> )	MoSe2@N- HCS	MoSe <sub>2</sub> @N-HCS -no-PDA	MoSe <sub>2</sub> @ HCS	Commercial MoSe <sub>2</sub>	N-HCS
Discharged-state	3.781484	2.165466	2.68036	1.072173	2.488965
Charged-state	6.626458	4.880653	4.58726	1.672009	3.580949

**Table S3.** The average ion diffusion coefficients of MoSe2@N-HCS,MoSe2@N-HCS-no-PDA, MoSe2@HCS, commercial MoSe2 and N-HCS.

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