Supporting Information

Tulip-like MoS₂ with single sheet tapered structure anchored on N-

doped graphene substrates via C-O-Mo bonds for superior sodium

storage

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Figure S1. (a) SEM of MoS_2 nanosheets, (b) EDS spectrum of tulip- MoS_2/NG , which

discloses the presence of Mo, S, C, N and O elements in this architectures.



Figure S2. The corresponding pore size distribution.



Figure S3. High-resolution spectrum of S 2p.



Figure S4. TGA curves of the tulip-MoS₂/NG architecture, MoS₂ nanosheets and graphene.

Fig. S3 displays the TGA curves of tulip-MoS₂/NG architecture, MoS₂ nanosheets and graphene. Before the test, we put the samples in the vacuum oven and keep it for 12 hours at 80 °C to minimizing the effect of adsorbed water. 42% weight of the graphene loosed while heating from 50 °C to 200 °C, which attributed to the physically adsorbed water on the high surface area.¹ The exothermal peak at ~550 °C can be assigned the ignition of graphene.² The MoS₂ nanosheets display 13.6% weight loss from 200 to 600 °C, which is due to the oxidation of MoS₂ into MoO₃.^{2, 3} There were 26.4% weight loss while the formation of the tulip-MoS₂/NG from 200 to 600 °C. If the graphene were completely removed after combustion, the weight percentage of MoS₂ could be calculated by 0.864x = 0.736.⁴ Therefore, x = 0.852.



Figure S5. The discharge/charge curves of (a) pure MoS_2 nanosheets and (b) graphene at a current density of 100 mA g⁻¹.



Figure S6. The differential curves dQ/dV of the MoS₂ nanosheets.

The first cathode peak at 0.89 V is attributed to form Na_xMoS_2 . The peak of SEI film moves forward to 0.65 V, which is different from the tulip-MoS₂/NG architecture. The introduction of carbon materials in the system causes the formation of SEI film before the intercalation of Na-ion.⁵



Figure S7. The electrochemical performance of graphene. (a) Cycling performance at a charge current density of 100 mA g^{-1} and (b) capacity evolution at various current densities.

	Cumant	Initial		Final		
Materials	density (mAh g ⁻¹)	discharge capacity (mAh g ⁻¹)	Cycle number	capacity (mAh g ⁻¹)	Rate performance	Reference
MoS2@Metal organic derived N- doped carbon	200	1288	100	619	660, 580, 394 306 and 235 mAh g ⁻¹ at current densities of 0.1, 0.2, 0.5, 1 and 2 A g ⁻¹	21
TiO2@MoS2 @Carbon cloth	500	460	200	157	650, 550, 450 and 380 mA h g^{-1} at current densities of 0.1, 0.2, 0.4 and 0.8 A g^{-1}	22
MoS ₂ /Graphene	20	600	100	380	520, 500, 450, 400 and 350 mA h g^{-1} at current densities of 0.02, 0.04, 0.08, 0.16 and 0.32 A h g^{-1}	50
MoS ₂ @PEO	50	242	70	119	185, 162, 143, 127 and 112 mA h g^{-1} at current densities of 0.05,0.1, 0.25, 0.5 and 1 A g^{-1}	54
MoS ₂ /C nanofibers (Electrospinning)	100	470	600	284	401, 370, 317, 283, 247, 186, 148 and 89 mA h g ⁻¹ at current densities of 0.05, 0.1, 0.2, 0.5, 1, 2, 3 and 5 A g ⁻¹	55
MoS2-rGO	100	609	50	372	367, 293 264 and 209 mAh g^{-1} at current densities of 0.1, 0.25, 0.5 and 1 A g^{-1}	56
MoS2@Graphene paper	100	470	300	77	264, 200, 180, 150 and 80 mA h g ⁻¹ at current densities of 0.1, 0.2, 0.4, 1.6 and 3.2 A g ⁻¹	57
MoS2@C-CMC	80	450	100	286	382, 348, 321, 271, 230, and 205 mA h g ⁻¹ at current densities of 0.02, 0.04, 0.08, 0.32, 0.64, and 1 A g ⁻¹	58
E-MoS2/carbon fibers	1000	350	700	241	298, 281, 241, 222, 164, 138 and 104 mA h g ⁻¹ at current densities of 0.05, 0.1, 0.5, 1, 5, 10 and 20 A g ⁻	59
1T MoS2/graphene tube	50	630	200	313	350, 305, 287, 265, 257, 222, 208, 190, 175 mAh g ⁻¹ at current densities of 0.05, 0.1, 0.2, 0.3, 0.5, 0.8, 1, 1.5 and 2 A g ⁻¹	60
	100	673	100	320	366, 348, 331, 311, 293, 267 and	
Tulip-MoS ₂ /NG	1000	263	1000	179	$^{-}$ 216 mA h g ⁻¹ at current densities of	This work
	5000	241	1000	151	1	WULK

Table S1. A comparison of the electrochemical performance of tulip-MoS₂/NG architecture with MoS_2 anchored on other carbonaceous materials for Na⁺ batteries in

recent literature.



Figure S8. FT-IR spectra of tulip-MoS₂/NG architecture and MoS₂ nanosheets.

The surface organic groups of tulip-MoS₂/NG architecture and MoS₂ nanosheets were investigated by Fourier transform infrared (FT-IR) spectrometry. The stretching peak at 3050 to 3650 cm⁻¹ indicate that presence of the O-H on the surface of the MoS₂ particles.^{6,7} The peaks at 2340 and 2359 cm⁻¹ are due to the absorbed CO₂.⁸ The peak at 1689 cm⁻¹ is attributed to the C=O group of NMP.⁹ The peaks at 819 and 1262 cm⁻¹ belong to the C-N groups. The tulip-MoS₂/NG architecture has two peaks at 990 and 1080 cm⁻¹ corresponding to the Mo=O and C-O-C groups.^{10,11}(Figure S8)

In order to determine the environment in which the C-O-Mo bond exists. We have perfected the experiment to explore its possible mechanism.

Synthesis of the MoS₂/N doped graphene: Graphene oxide (0.04 g) Graphene oxide (0.04 g) was dispersed in ultrapure water (~50 mL). H₂CNSNH₂ (2.50 g) was added into the graphene oxide dispersion in a magnetic stirrer for 2 h. Then, MoO₃ (0.35 g) was added, and stirring was maintained to evenly distribute MoO₃ within the solution. After evaporation, the preform-1 was prepared. Then, the preform-1 was heated to 750 °C at a rate of 10 °C min⁻¹. Upon reaching 100 °C, the argon flow was shut off to keep a highly concentrated atmosphere of H₂S for the reaction with MoO₃ and the nitrogen atom into graphene. The reaction was then held for 2 h and naturally cooled to room temperature under argon atmosphere. Lastly, the product was washed with deionized water and ethanol individually, followed by freeze-drying. The MoS₂/N doped graphene was obtained.

Synthesis of the NMP-MoS₂: H₂CNSNH₂ (2.50 g) was added into deionized water by magnetic stirrer for 10 minutes. MoO₃ (0.35 g) was added into the above solution and kept stirring to make the MoO₃ distribute evenly in solution. Added NMP solution (~5 mL). After evaporation, the preform-2 was prepared. Then, heated the precursor to 750 $^{\circ}$ C using a rate of 10 $^{\circ}$ C min⁻¹ under an atmosphere of argon, followed by a 2h hold and cool to room temperature. The NMP-MoS₂ was obtained.



Figure S9. (a) XPS survey spectrum of the MoS_2/N doped graphene and the high-resolution spectra of (b) C 1s, (c) N 1s and (d) O 1s, (e) XPS survey spectrum of the N-MoS₂ and the high-resolution spectra of (f) C 1s, (g) N 1s and (h) O 1s.

The surface compositions and chemical states of the MoS₂/N doped graphene and the NMP-MoS₂ samples are investigated by X-ray photoelectron spectroscopy (XPS). The surface compositions of the MoS₂/N doped graphene are 24.9% Mo, 40.6% S, 22.9% C, 5.8% N and 3.9% O elements, respectively. The surface of the NMP-MoS₂ is composed of 16.2% Mo, 28.0% S, 10.6% C, 3.9% N and 38.3% O elements. (Figure S9a and e). The signal of the C 1s in the NMP-MoS₂ arises from the NMP molecular. There are no obvious difference in the C 1s spectra between MoS₂/N doped graphene and NMP-MoS₂, which can be attributed to the carbon atoms in different functional groups: C-C/C=C, C-N, C-O and O-C=O (Figure 2d, Figure S9b and f).¹² The N 1s spectrum of the NMP-MoS₂ displays pyridine nitrogen dominated (Figure S9g), indicating a distinct difference from tulip-MoS₂/NG (Figure 2e) and MoS₂/N doped

graphene (Figure S9c). Figure S9g shows the Mo $3p_{3/2}$ disappears in NMP-MoS₂, suggesting the bond of Mo-N exists on the surface between NG and MoS₂. Figure S9d and h shows the high-resolution O 1s spectrum of the samples. It is worth noting that there are distinct peaks at 532.2 eV of the NMP-MoS₂, which indicates that the NMP is the key to forming the C-O-Mo bond.^{13,14}

The conclusion can be drawn from the above analysis that the NMP molecular is the key to formation of the tapered MoS_2 assembled by single sheet anchored on N-doped graphene substrates. Ulteriorly, we think that the NMP molecule possibly acts as a bridge to connect the MoS_2 and NG.

Possible mechanism

The possible mechanism of the NMP molecule acting as a bridge to connect the MoS_2 and NG is proposed based on analysis of the relation of the products. As to NMP, because the N and O atoms have higher electronegativity than that of C atoms, the C=O double bond is possibly broken due to the O atom of NMP and the Mo atom of MoS_2 tend to form a coordination bond. (scheme S1).^{15,16}



Scheme S1. Possible mechanism of the critical role of NMP for bridging MoS2 and NG



Figure S10. (a) CV curves at different scan rates at 100 mA g^{-1} and (b) the corresponding log *i* vs. log *v* plots derived from peak currents of the MoS₂ nanosheets and (c, d) after 100 cycles.



Figure S11. (a) Impedance plots and equivalent circuit (inset) used for the EIS analysis and (b) the Z'- $\omega^{-1/2}$ curves in the low-frequency region of the tulip-MoS₂/NG and the MoS₂ nanosheets obtained after 5 cycles at 100 mA g⁻¹.

Table S2. The values of R_s and R_{ct} obtained by fitting data according to the equivalent circuit model presented.

	R _s (5th) (Ω)	$R_{\rm ct}$ (5th) (Ω)	<i>R</i> _s (100th) (Ω)	$R_{\rm ct}$ (100th) (Ω)
tulip-MoS ₂ /NG	48.31	57.93	78.44	95.92
MoS ₂ nanosheets	81.22	258.60	171.30	492.90

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