Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A. This journal is © The Royal Society of Chemistry 2019

Supporting Information

Rational Construction of MoS₂/Mo₂N/C Hierarchical Porous Tubular

Nanostructures for Enhanced Lithium Storage⁺

Song Yang,^{a,c} Yunqiang Zhang,^{a,c} Shulan Wang,^a Jian Shi,^b Xuan Liu,^{a*} and Li Li^{c*}

^aDepartment of Chemistry, School of Science, Northeastern University, Shenyang 110819, P. R. China.

^bDepartment of Materials Science and Engineering, Rensselaer Polytechnic Institute, Troy, New York, NY, 12180, USA.

^cSchool of Metallurgy, Northeastern University, Shenyang 110819, P. R. China.

Address all correspondence to the author. *Email: lilicmu@alumni.cmu.edu (L. Li); xuanliucmu@gmail.com (X. Liu)

This file includes:

Experimental section Figure S1 to S11 Table S1 to S6 Full Reference List

Experimental section

Materials

Ammonium molybdate $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, 99.98%), sodium molybdate dihydrate $(Na_2MoO_4\cdot 2H_2O, 99.8\%)$, and dopamine hydrochloride $(C_8H_{11}O_2N, 99.9\%)$ were obtained from Sigma Chemical Co. Thiourea (CH₄N₂S, 99.9%), aqua fortis (HNO₃, 65%), ammonium hydroxide $(NH_3\cdot H_2O, 28-30\%)$, ethanol (C₂H₆O), and glucose (GLc) were supplied by Sinopharm Chemical Reagent Co. All reagents are used as received without further purification.

Synthesis of MoO₃ nanorods

 MoO_3 nanorods were synthesized by a modified hydrothermal method according to the reported literature.^{S1} Typically, 0.525g of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ (99.98%) was dispersed into 15 mL of diluted HNO₃ solution containing 12.5 mL deionized (DI) water and 2.5 ml HNO₃ (65%) under ultrasonication for 5 min to form a clear solutions at room temperature. The obtained solution was then transferred into a 50ml Teflon-lined autoclave and maintained at 200 °C for 20 h. The white powders were collected by centrifugation following with thorough washing by DI water and ethanol for three times, and dried at 70 °C overnight to obtain the final product.

Synthesis of MoO₂/Mo₂N/C nanotubes

The hollow nanotubes were fabricated through a modified cooperative assembly-directed strategy at room temperature. 0.6g MoO₃ nanorods were homogeneously dispersed in 120 mL DI water by ultrasonication for 10 min. 0.3g dopamine hydrochloride was added into the solution until orange suspension observed under magnetic stirring. After that, 240 ml ethanol was added to the above solution and stirred for 5 min, following with the rapid addition of 1.8 mL NH₃· H₂O (28–30%). The mixture was under continuous magnetic stirring for 2 h at room temperature until the color change to bronzing. The precipitates were collected by centrifugation and rinsed by ethanol for several times. After drying under vacuum at room temperature, the sample was then annealed at 820 °C for 2h at a heating rate of 1 °C/min in Ar atmosphere to obtain the final product.

Synthesis of MoS₂/Mo₂N/C

In a typical synthesis, 20 mg MoO₂/Mo₂N/C nanotubes were uniformly disperse into 40 mL DI water with the addition of 0.05g glucose under stirring for 10 min. 0.16 g Na₂MoO₄·2H₂O with 0.32g thiourea was added and stirred for 1h. The as-obtained mixture was poured into a 100 mL Teflon-lined autoclave and heated at 200 °C for 24 h. The black precipitates were collected and washed with distilled water and ethanol for several times following with overnight dyring at 70 °C. The powders were then annealed at 700 °C for 2h with the heating rate of 1 °C/min under Ar atmosphere., The final powder was denoted as MoS₂/Mo₂N/C. In contrast, the control samples calcined at 600 and 800 °C for 2 h are designated as MoS₂/Mo₂N/C-600 and MoS₂/Mo₂N/C-800, respectively. MoS₂/C was synthesized with the same process but without the addition of MoO₂/Mo₂N/C nanotubes. Fixed amount of dopamine was added to make sure its carbon content is the same with MoS₂/Mo₂N/C. Similarly, MoS₂ was prepared without the addition of MoO₂/Mo₂N/C nanotubes and glucose.

Material Characterization

Thermogravimetric analysis (TGA) curves of the precursor were characterized by a TG instrument (NET ZSCH STA 409C) from room temperature to 900 °C at at the heating rate of 1 °C/min under Ar. X-ray diffraction (XRD) patterns of the as-prepared samples were collected on the X-ray diffractometer (PANalytical PW 3040/60) with Cu-K α radiation (λ =1.5406 Å). The electron binding energy of elements was analysed by X-ray photoelectron spectroscopy (XPS) using a ESCALAB 250Xi VG with Al-K α (1486.6 eV) as the X-ray source. Raman spectroscopy was elucidated though a Raman spectrometer with a 532 nm excitation wavelength (Renishaw 1000B). The four-probe testing instrument (RTS-8) was used to check the conductivity of as-prepared samples. The morphology and composition of the as-prepared samples were checked using a Hitachi S-4800 scanning electron microscope (SEM, accelerating voltage: 5.0 kV) equipped with energy-dispersive X-ray spectroscopy (EDS) analyzer while high magnification

images for structure and morphology of the as-prepared samples were recorded with JEOL JEM-2100 transmission electron microscope (TEM, acceleration voltage: 200 kV). N₂ adsorptiondesorption isotherms were taken using a Nova 2200e surface area/pore size analyzer to obtain the Brunauer-Emmett Teller (BET) specific surface area and porosity of the as-prepared sample. The pore size distribution of samples was analyzed by the nonlocal density functional theory (DFT) and the total pore volume was calculated from the adsorbed amount at pressure of $P/P_0 = 0.99$.

Electrochemical Measurements

CR 2025 type Li-ion half-cells were assembled for evaluating the electrochemical performances of the as-prepared samples as anode materials. The active material (80 wt%) and acetylene black (10 wt%) were then mixed uniformly with polyvinylidene fluoride (10 wt%) in N-methyl-2-pyrrolidone (NMP) to form the slurry. The slurry was then evenly coated on the surface of copper foil (current collector) as the working electrode. The electrode was then dried at 120 °C in vacuum for 10 h. The mass of active material was around 1.3 mg/cm² in each electrode. Finally, the half-cells were then assembled in Ar-filed glove box following with the electrodes further dried at 70 °C for 10 h under vacuum. Lithium foil and Celgard 2400 were used as the counter electrode and separator, respectively. 1 M LiPF₆ solution in ethylene carbonate (EC) and dimethyl carbonate (DMC) (1 : 1, by vol%) was used as the electrolyte. The CV and GCD curves were recorded in a potential window from 0.01 to 3.0 V (vs Li/Li⁺) using Land battery tester (LAND CT2001A) and Gamry instruments (CH660E), respectively. EIS measurements were tested in a frequency from 10⁻² to10⁵ Hz though CH660E.

Theoretical Calculations

DFT computations were performed by using the Vienna *ab* initio simulation package.^{S2} The ion-electron interaction is described with the projector augmented wave (PAW) method.^{S3} The electron exchange-correlation is represented by the functional of Perdew, Burke and Ernzerhof (PBE) of generalized gradient approximation (GGA).^{S4} A cutoff energy of 400 eV was used for the plane-wave basis set. To simulate the MoS₂ (002)/Mo₂N (111) heterostructures, MoS₂ (002) with two MoS₂ layers was constructed with lattice vector of a(4,3,0) and b(-3,1,0) to match with Mo_2N (111) of 6 atomic-layer-thickness by keeping the bottom three atomic-layers fixed. The averaged lattice parameters of the constructed MoS2 (002)/Mo2N (111) heterostructures are a=b=11.6399 Å. The van der Waals interactions between MoS₂ and Mo₂N were considered and described using the empirical correction in Grimme's scheme (DFT+D3).^{S5} A vacuum region of more than 15 Å was used to ensure the decoupling between the periodic images of the slab sheets. The Brillouin zone was sampled via Monkhorst-Pack method with $8 \times 8 \times 2$, $5 \times 5 \times 5$, and $3 \times 3 \times 1$ kpoint mesh for bulk MoS₂, bulk Mo₂N and MoS₂ (002)/Mo₂N (111) heterostructures, respectively. The convergence threshold for structural optimization was set to be 1.0×10^{-5} in energy and 0.01 eV/Å in force.



Fig. S1 (a) Photographs of the product dispersion in different stages; (b) precursor and $MoO_2/Mo_2N/C$ after first annealing; and (c) precursor and $MoS_2/Mo_2N/C$ after second annealing.



Fig. S2 XRD patterns of the samples at different stages of the synthetic processes.



Fig. S3 XRD patterns of (a) bulk MoS_2 , (b) as-prepared MoS_2 precursor, and (c) annealed MoS_2/C .



Fig. S4 Raman spectroscopy of MoS₂/Mo₂N/C.



Fig. S5 (a,b) SEM images of MoO₃ nanorods under different magnifications.



Fig. S6 (a,b) SEM images and (c-f) the elemental mapping images of $MoO_2/Mo_2N/C$ nanotubes.



Fig. S7 (a,b) SEM images of annealed MoS₂/C nanoflowers under different magnifications.



Fig. S8 CV curves for the first, second, and fifth cycles of (a) MoS_2/C , and (b) bulk MoS_2 electrodes.



Fig. S9 Electrochemical performances of MoS2/Mo2N/C-600 and MoS2/Mo2N/C-800 electrode: (a)Rateperformanceatvariousrates;and(b)Nyquistplots.



Fig. S10 (a) GCD curves at the current densitiy of 0.1 A/g for $MoS_2/Mo_2N/C$ electrode; (b) Comparison of the cycling performance at the current densitiy of 0.1 A/g of $MoS_2/Mo_2N/C$ electrode with other reported Mo-based anodes in LIBs; (c) The Nyquist plots of the $MoS_2/Mo_2N/C$ electrode after 4th and 200th GCD cycles.



Fig. S11 CV curves at different scan rates of (a) $MoS_2/Mo_2N/C$ electrode, (b) MoS_2/C electrode, and (c) bulk MoS_2 electrode; (d) The linear relationship between the peak current (I_p) and square root of the scan rate ($v^{1/2}$) for different electrodes.

Two primary charge storage mechanisms (surface controlled and diffusion controlled capapeity) existed. Surface controlled capacity involves the faradaic contribution from surface pseudocapacitor reaction and non-faradaic contribution from lithium ions adsorption/desorption. The diffusion controlled process is mainly related to lithium ions insertion/extraction within electrode materials. According to the following equation: $I=av^b$ (1)

where *I* is the measured current and *v*. the sweep rate, a and b the constants. b value can be determined by the slope of the $\log(I)$ versus $\log(v)$ plot.^{S14} The b value can be used to judge if the charge storage is surface controlled (b close to 1) or diffusion controlled (b approaches to 0.5) process.^{S15}

Element content (Atomic%)						
Samples	С	Ν	0	S	Мо	
MoS ₂ /Mo ₂ N/C	35.08	23.71	8.13	19.95	13.13	

Table S1. Chemical composition of the as-prepared materials recorded by XPS.

	MoS ₂ /Mo ₂ N/C	
Elements	Component (eV)/content (at.%)	Assignment
	284.6/35.09%	C=C
С	285.1/45.56%	C-C
	286.0/11.01%	C-O/C-N
	289.7/8.34%	C=O
	395.6/72.08%	Mo3p _{3/2}
Ν	397.9/19.22%	N1s (Mo3d _{5/2})
	401.0/ 8.7%	N-Q
	531.6/50.04%	C=O
0	532.3/39.24%	С-ОН
	533.4/10.72%	C-O-C
	162.6/70.63%	S2p _{3/2}
S	163.8/29.37%	S2p _{1/2}
	226.8/16.69%	S2s
Мо	229.7/46.49%	Mo3d _{5/2}
	232.9/36.82%	Mo3d _{3/2}

Table S2. XPS results of the $MoS_2/Mo_2N/C$ nanocomposites.

	- our proof
Samples	Conductivity (S/m)
MoS ₂	0.5
MoS ₂ /C	15
MoS ₂ /Mo ₂ N/C	168

Table S3. Conductivity values of the as-prepared samples.

Table S4. Surface area and pore volume values of $MoS_2/Mo_2N/C$.

Samples	$S_{ m BET}$	S _{micro} ^a	$S_{ m meso}{}^{ m b}$	V _{pore} ^c	$V_{\rm micro}^{\rm d}$	V _{meso} ^e
	(m^{2}/g)	(m ² /g)	(m^{2}/g)	(cm^{3}/g)	(cm^{3}/g)	(cm^{3}/g)
MoS ₂ /Mo ₂ N/C	95.8	0.26	92.4	0.35	0.002	0.33

^aS_{micro} is the surface area of the micropores. ^bS_{meso} is the surface area of the mesopores. ^cV_{total} is the total pore volume. ^dV_{micro} is the volume of the micropores and ^eV_{meso} is the volume of the mesopores.

Anode	Cycling capacity	Rate performance	Ref.
materials	007 11/		
	89^{\prime} mA h/g	0.45	
	(a) 200 cycles	945 mA h/g	
$MoS_2/Mo_2N/C$	(<i>a</i>) 0.1 A/g	(<i>a</i>) 0.1 A/g	Our work
	655 mA h/g	575 mA h/g	
	(a) 300 cycles	@ 5 A/g	
	@ 1 A/g		
		898 mA h/g	
MoO ₂ @Mo ₂ N hollow	815 mA h/g	@ 0.1 A/g	S6
nanostructures	@ 100 cycles	415 mA h/g	
	@ 0.1 A/g	@ 5 A/g	
MoS ₂ /polyaniline	748 mA h/g	1015 mA h/g	
nanowires	@ 50 cycles	@ 0.2 A/g	S7
	@ 0.1 A/g	320 mA h/g	
		@ 1 A/g	
Defect-rich MoS ₂	589 mA h/g	800 mA h/g	S11
ultrathin	@ 80 cycles	@ 0.1 A/g	
nanosheets	@ 0.1 A/g	412 mA h/g	
		@ 0.8 A/g	
	500 mA h/g	480 mA h/g	
Mesoporous Mo ₂ N	@ 20 cycles	@ 0.1 A/g	S12
nanobelts	@ 0.1 A/g	220 mA h/g	
		@ 4 A/g	
	855 mA h/g	875 mA h/g	S16
C ₃ N ₄ /NRGO/MoS ₂	@ 100 cycles	@ 0.1 A/g	
hybrid nanosheets	@ 0.1 A/g	280 mA h/g	
		@ 4 A/g	
	589 mA h/g	1184 mA h/g	S17
Few-Layer MoS ₂	@ 80 cycles	@ 0.1 A/g	
	@ 0.1 A/g	353 mA h/g	
		@ 2 A/g	
	1000 mA h/g	800 mA h/g	S18
MoS ₂ /PEO/graphene	@ 180 cycles	@ 0.1 A/g	
composite	@ 0.05 A/g	335 mA h/g	
_		@ 5 A/g	

Table S5. Comparison of the electrochemical performance of the as-prepared samples with otherreported Mo-based anode materials for lithium-ion battery.

Samples	$R_{ m e}\left(\Omega ight)$	$R_{ m ct}\left(\Omega ight)$
MoS ₂ /Mo ₂ N/C	5.79	25.11
MoS ₂ /Mo ₂ N/C-800	7.01	40.49
MoS ₂ /Mo ₂ N/C-600	8.13	53.08
MoS ₂ /C	9.88	96.56
MoS_2	16.99	144.09

Table S6. Equivalent series resistance (R_e) and charge transfer resistance (R_{ct}) of the as-prepared samples in a three electrode system.

References

- 1. Y. Zhang, S. Yang, S. Wang, H. K. Liu, L. Li, S. X. Dou and X. Liu, *Small*, 2018, 14, 1800480–1800489.
- 2. G. Kresse and J. Furthmuller, *Phys. Rev. B*, 1996, 54, 11169–11186.
- 3. P. E. Blochl, Phys. Rev. B, 1994, 50, 17953–17979.
- 4. J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1996, 77, 3865–3868.
- 5. S. Grimme, J. Antony, S. Ehrlich and H. Krieg, J. Chem. Phys., 2010, 132, 154104–154123.
- J. Liu, S. Tang, Y. Lu, G. Cai, S. Liang, W. Wang and X. Chen, *Energy Environ. Sci.*, 2013, 6, 2691–2697.
- L. Yang, S. Wang, J. Mao, J. Deng, Q. Gao, Y. Tang and O. G. Schmidt, *Adv. Mater.*, 2013, 25, 1180–1184.
- 8. G. Du, Z. Guo, S. Wang, R. Zeng, Z. Chen and H. Liu, *Chem. Commun.*, 2010, **46**, 1106–1108.
- 9. Z. Wan, J. Shao, J. Yun, H. Zheng, T. Gao, M. Shen, Q. Qu and H. Zheng, *Small*, 2014, **10**, 4975–4981.
- 10. S. Ding, D. Zhang, J. S. Chen and X. W. Lou, Nanoscale, 2012, 4, 95–98.
- 11. Z. Wu, B. Li, Y. Xue, J. Li, Y. Zhang and F. Gao, J. Mater. Chem. A, 2015, 3, 19445–19454.
- 12. H.-C. Park, K.-H. Lee, Y.-W. Lee, S.-J. Kim, D.-M. Kim, M.-C. Kim and K.-W. Park, J. Power Sources, 2014, 269, 534–541.
- 13. B. Zhang, G. Cui, K. Zhang, L. Zhang, P. Han and S. Dong, *Electrochimica Acta*, 2014, **150**, 15–22.
- 14. V. Augustyn, J. Come, M. A. Lowe, J. W. Kim, P.-L. Taberna, S. H. Tolbert, H. D. Abruña, P. Simon and B. Dunn, *Nat. Mater.*, 2013, **12**, 518–522.
- 15. B. Shen, R. Guo, J. Lang, L. Liu, L. Liu and X. Yan, J. Mater. Chem. A, 2016, 4, 8316-8327.
- 16. Y. Hou, J. Li, Z. Wen, S. Cui, C. Yuan and J. Chen, *Nano Energy*, 2014, 8, 157–164.
- 17. S. Zhang, B. V. R. Chowdari, Z. Wen, J. Jin and J. Yang, ACS Nano, 2015, 9, 12464–12472.
- 18. J. Xiao, X. Wang, X.-Q. Yang, S. Xun, G. Liu, P. K. Koech, J. Liu and J. P. Lemmon, *Adv. Funct. Mater.*, 2011, **21**, 2840–2846.