Electronic Supplementary Material (ESI) for Nanoscale Horizons.

Supporting Information

Exploring the structure evolution of MoS_2 upon Li/Na/K ion insertion and origin of unusual stability for potassium ion batteries

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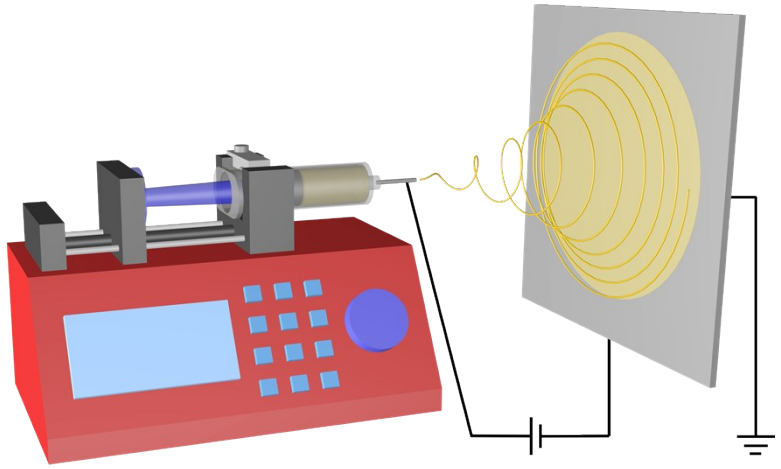

Figure S1. Schematic illustration of electrospinning setup.

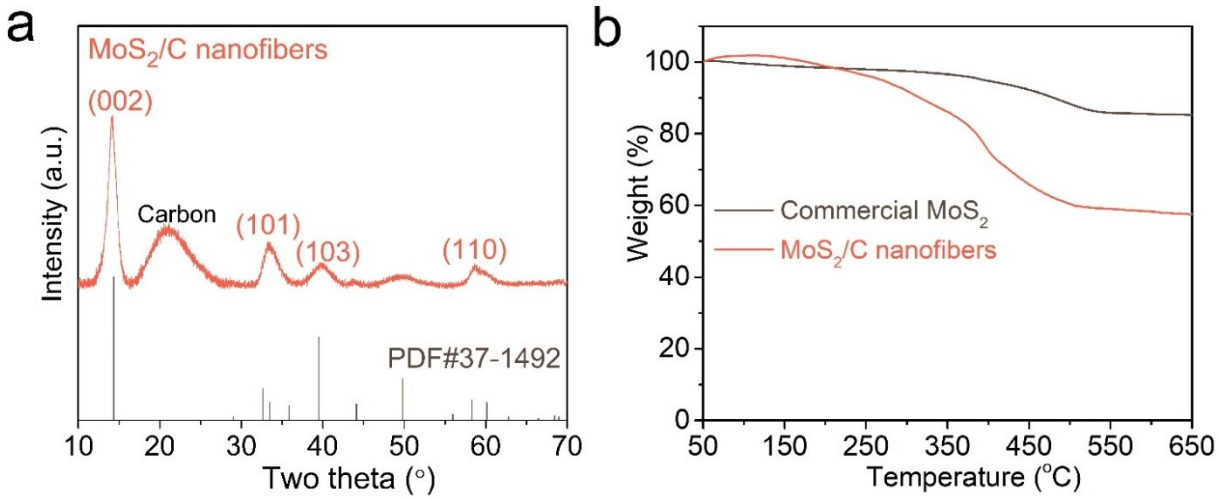

Figure S2. MoS_2/C nanofibers. (a) XRD pattern and (b) TG.

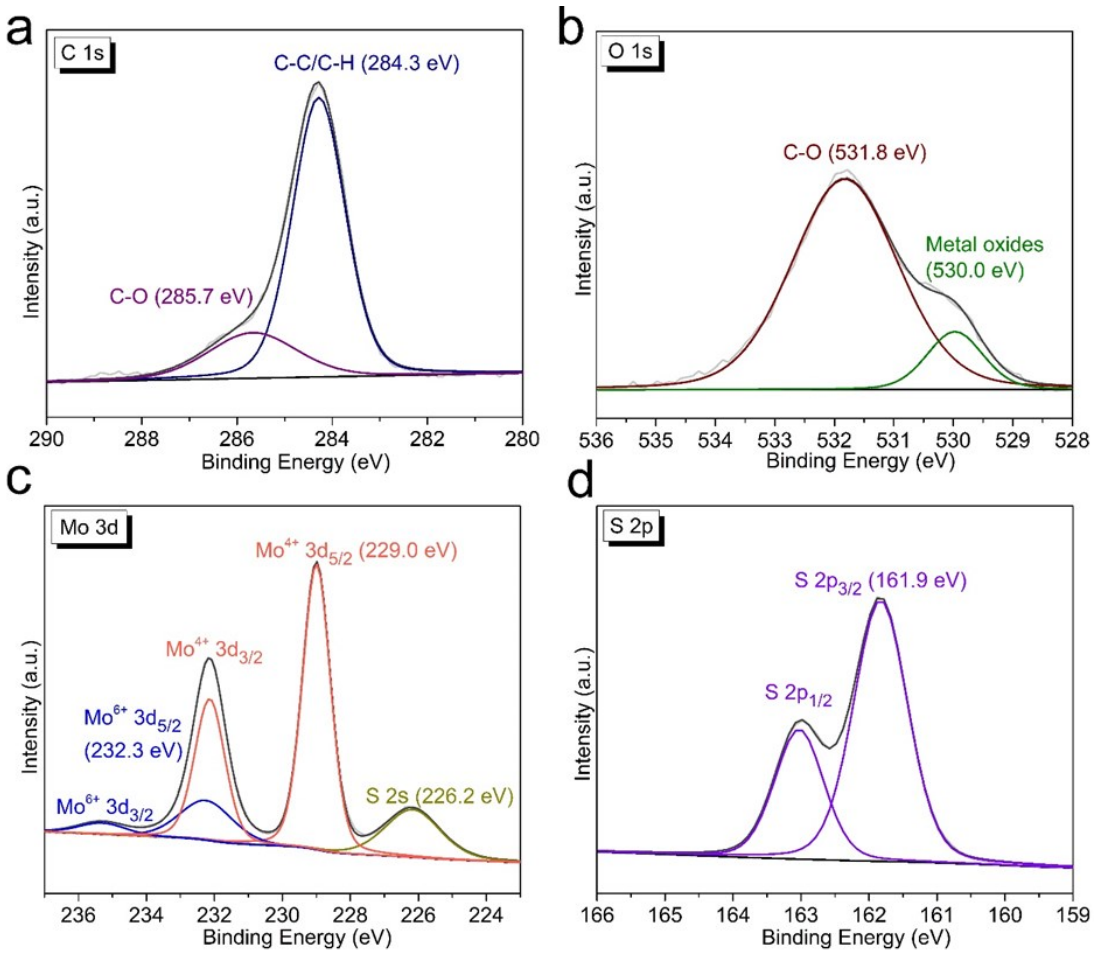

Figure S3 XPS spectra of MoS_2/C nanofibers. (a) C1s, (b) O1s, (c) Mo3d and (d) S2p.

Two obvious peaks located at 284.3 eV and 285.7 eV are observed in the C1s spectrum, which corresponded to C-C/C-H and C-O bonding, respectively.[1] The O1s spectrum shows two peaks at 531.8 eV and 530.0 eV, corresponding respectively to the C-O and metal oxides species. The Mo3d spectrum presents two pairs of peaks at 229.0 eV and 232.3 eV with spin-orbital splitting energy of 3.2 eV (Δ=3.2 eV), corresponding to Mo(Ⅳ) and Mo (Ⅵ) respectively.[2] Also, one peak at 226.2 eV is related to S2s. The S2p spectrum shows two doublet peaks at 161.9 eV and 163.1 eV (Δ=1.2 eV), which can be assigned to S 2p3/2 and S 2p1/2, respectively.[3, 4] Combing Mo3d and S2p spectra of MoS_2/C nanofiber, the presence of MoS_2 species is confirmed, and a small amount of Mo (Ⅵ) species in Mo 3d spectrum are originated from the oxide layer of the MoS_2/C nanofiber.

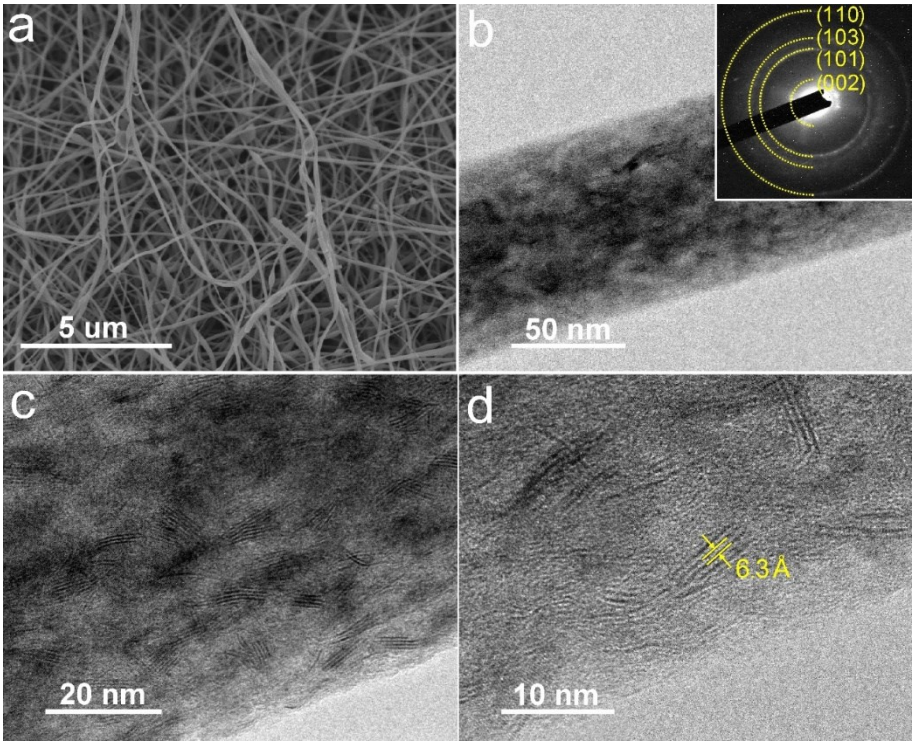

Figure S4. MoS_2/C nanofibers. (a) SEM image; (b, c) TEM images and (b inset) SAED pattern; (d) HRTEM image.

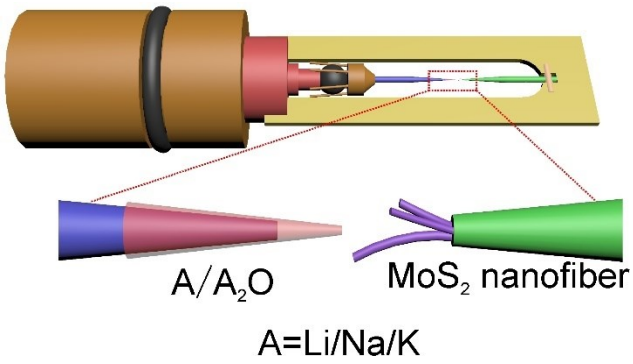

Figure S5. Schematic illustration of *in situ* TEM experiment setup.

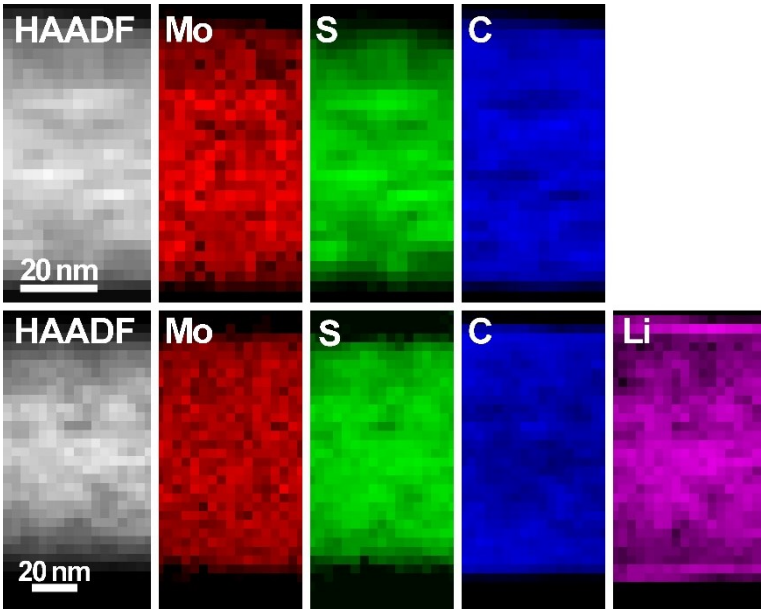

Figure S6 HAADF-STEM image and corresponding EELS elemental maps of MoS_2/C nanofibers before (up) and after (below) lithiation.

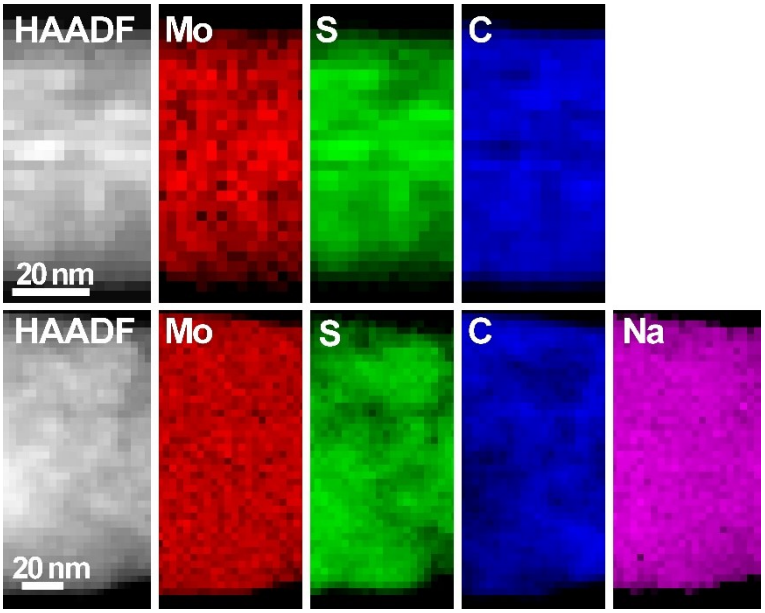

Figure S7 HAADF-STEM image and corresponding EELS elemental maps of MoS_2/C nanofibers before (up) and after (below) sodiation.

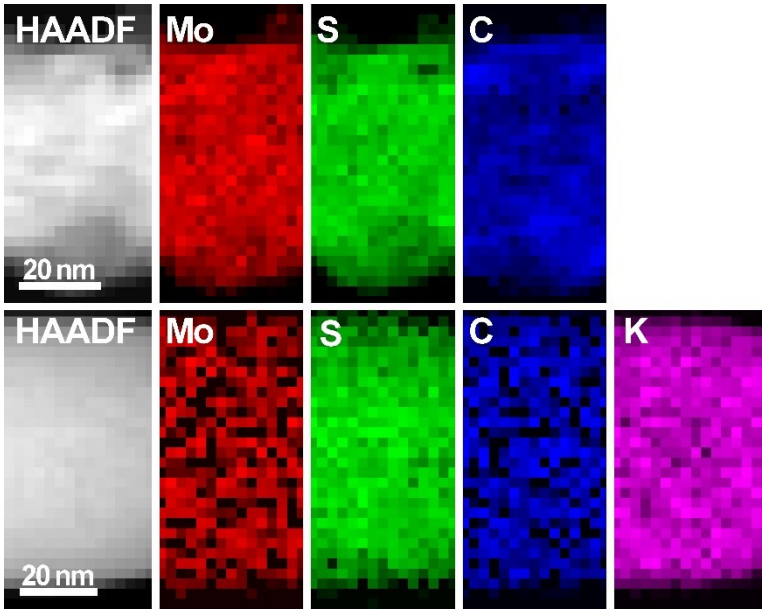

Figure S8 HAADF-STEM image and corresponding EELS elemental maps of MoS_2/C nanofibers before (up) and after (below) potassiation.

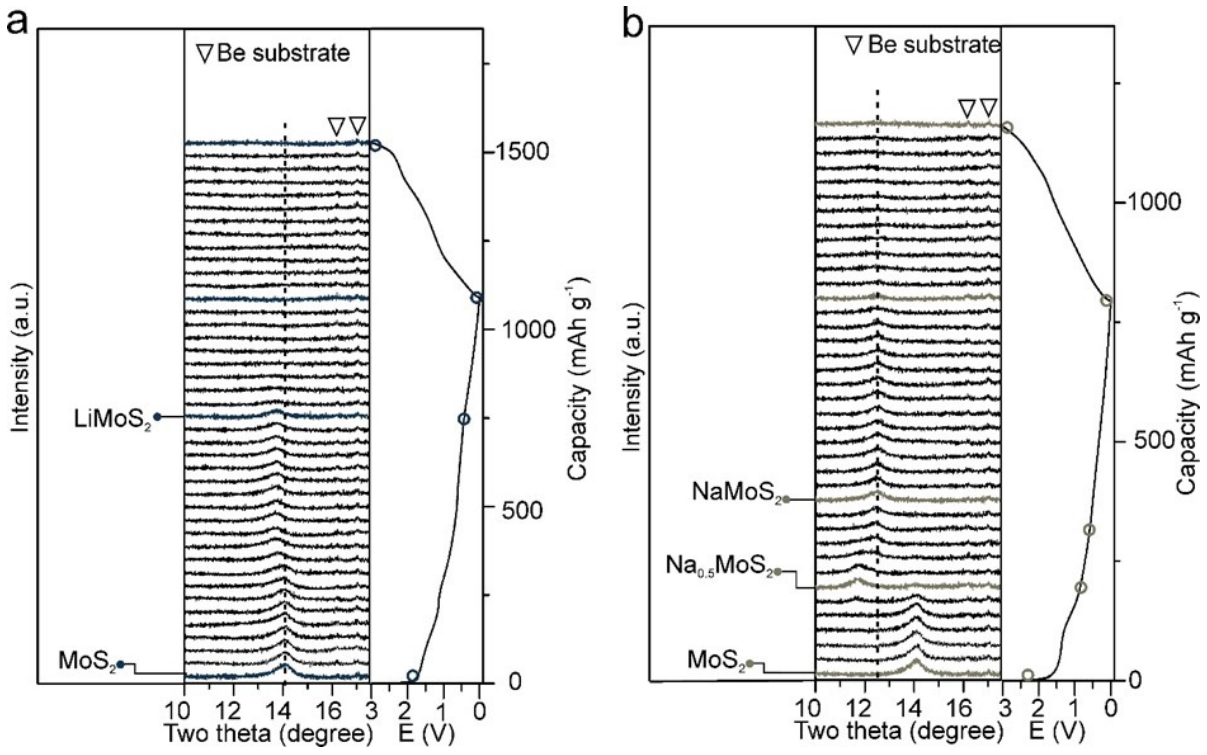

Figure S9 *In situ* XRD patterns of MoS_2/C nanofibers in the first cycle for (a) LIBs and (b) SIBs.

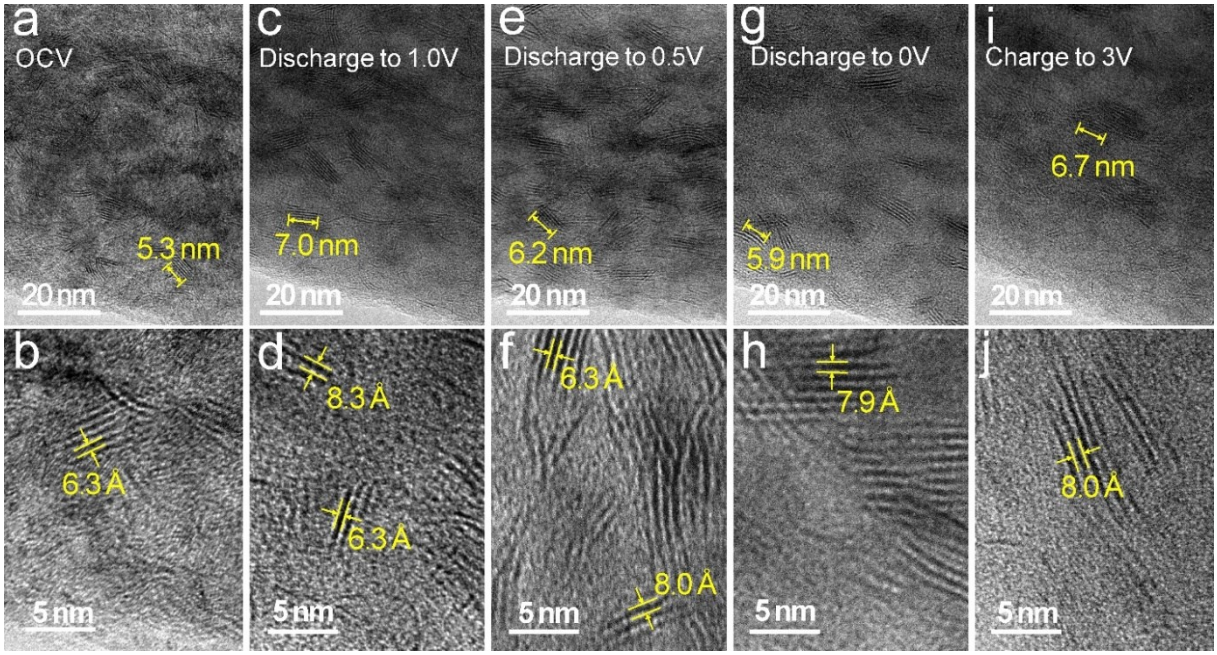

Figure S10. *Ex situ* TEM images of MoS_2/C nanofibers for PIBs on the first cycle. (a, b) OCV state; (c, d) discharge to 1.0 V; (e, f) discharge to 0.5 V; (g, h) discharge to 0 V and (i, j) charge to 3 V.

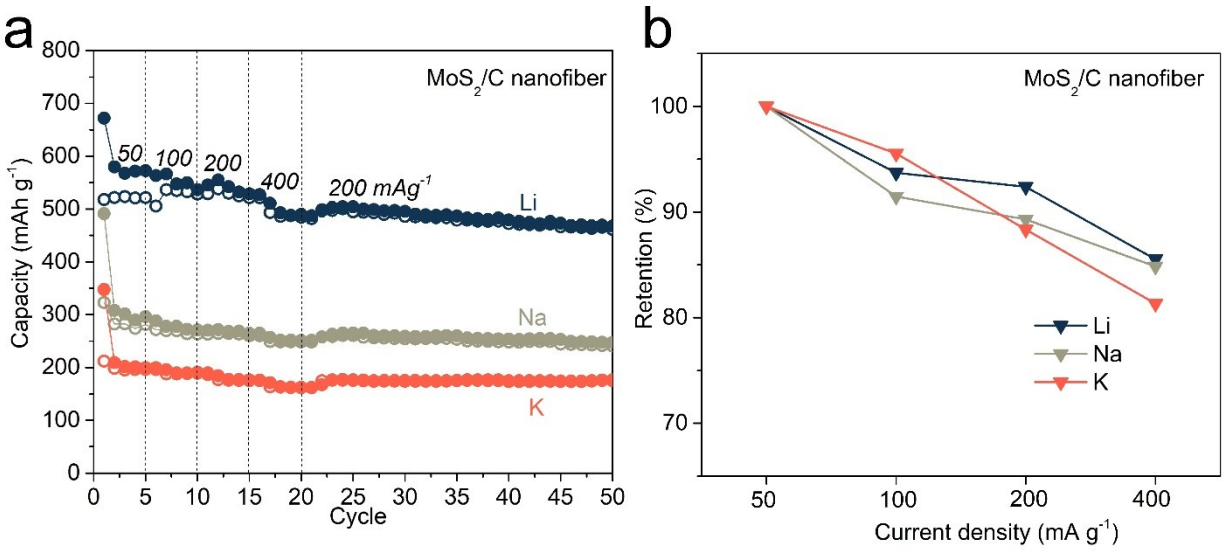

Figure S11 (a) Rate performance and (b) retention of MoS_2/C nanofibers in LIBs, SIBs and PIBs. (Retention is based on the discharged capacity in the fifth cycle).

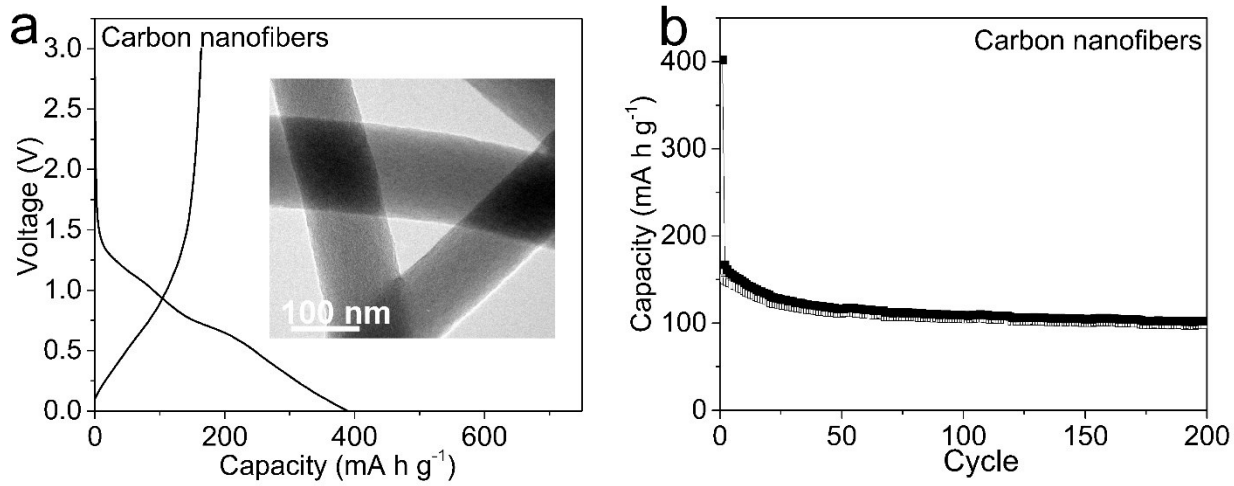

Figure S12. Carbon nanofibers. (a) Discharge and charge profiles at first cycle at 50 m A g^{-1} (inset: TEM image); (b) cyclic performance at 500 m A g^{-1}.

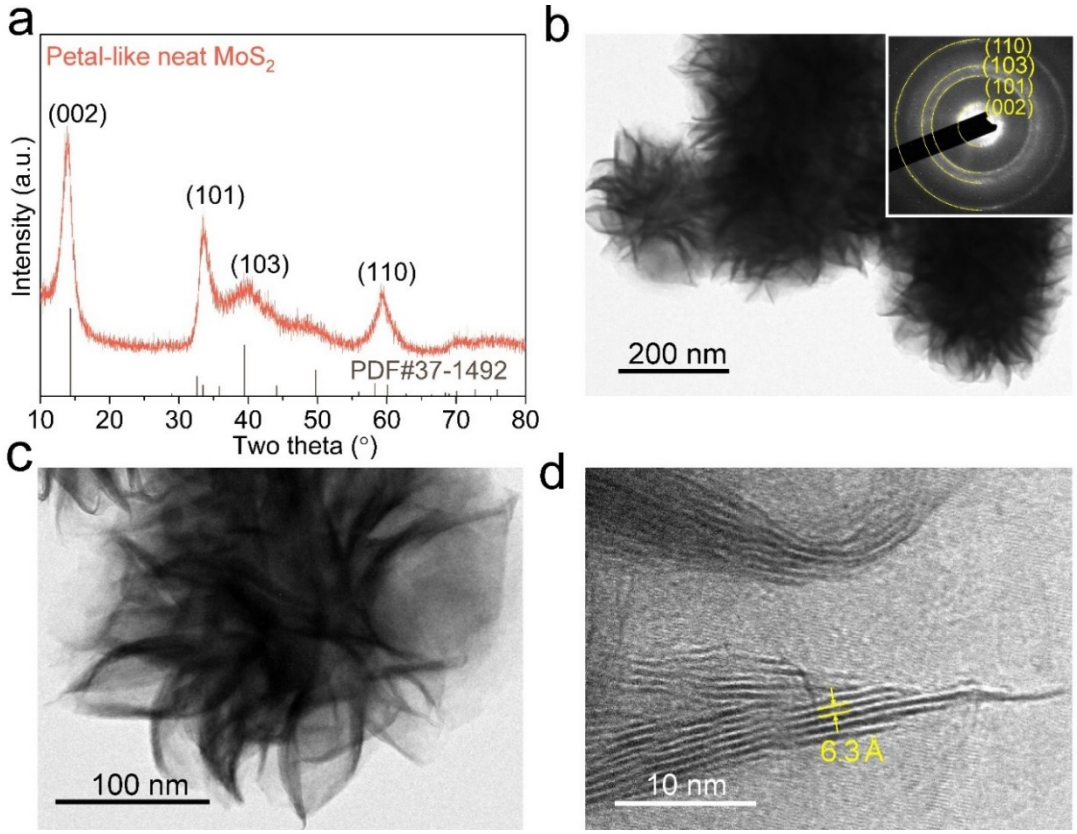

Figure S13. Petal-like neat MoS_2. (a) XRD pattern; (b, c) TEM images and (b inset) SAED pattern; (d) HRTEM image.

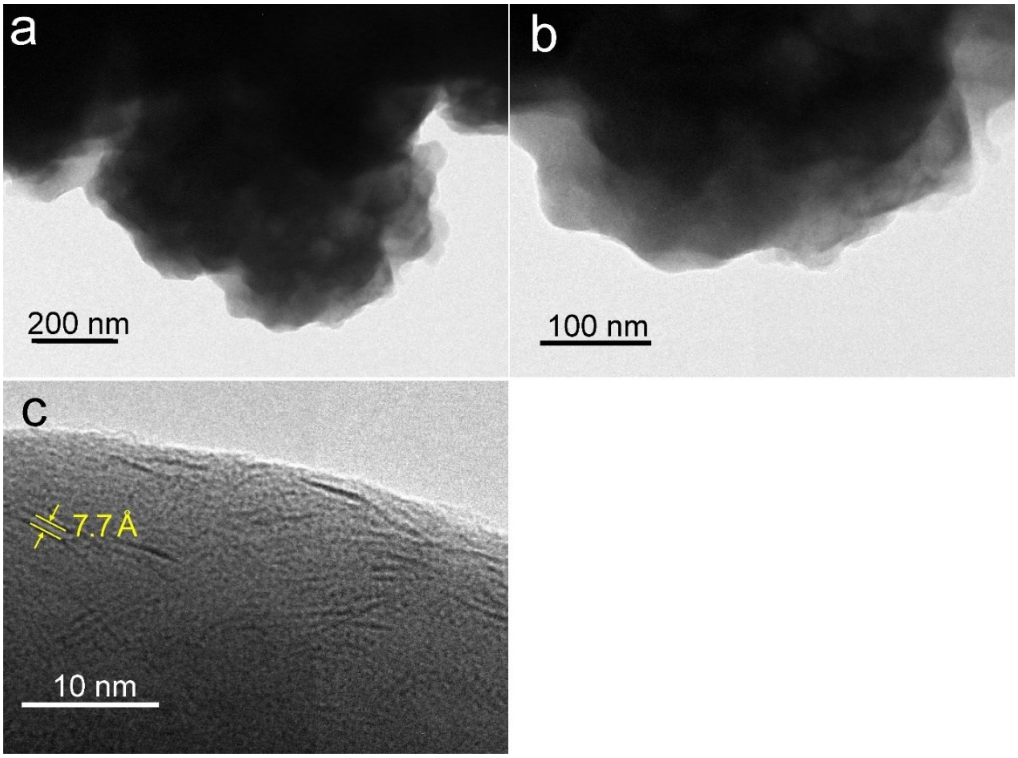

Figure S14 Petal-like neat MoS_2 cycled 200 times in PIBs. (a, b) TEM and (c) HRTEM images.

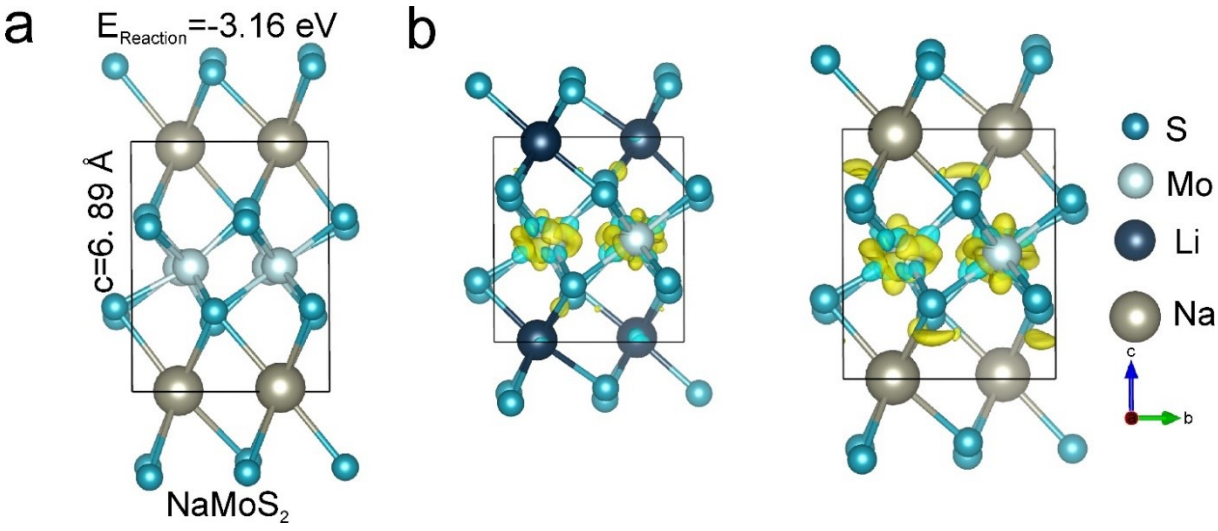

Figure S15. DFT simulations. (a) The calculated structures for $NaMoS_2$. (b) charge density difference distributions for $LiMoS_2$ and $NaMoS_2$.

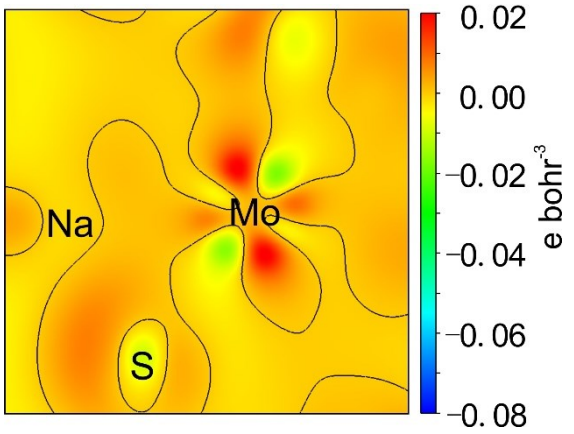

Figure S16. Two-dimensional charge density difference of $NaMoS_2$ across Na and Mo-S.

Table S1. Formation energy of conversion reaction calculated by DFT.

Reaction formula	Formation energy per equation, eV
$LiMoS_2 + 3Li \rightarrow 2Li_2S + Mo$	-4.46
$NaMoS_2 + 3Na \rightarrow 2Na_2S + Mo$	-3.16
$KMoS_2 + 3K \rightarrow 2K_2S + Mo$	-3.30

Table S2 Bader charges of $LiMoS_2$ calculated by DFT.

$LiMoS_2$						
#	X	Y	Z	CHARGE	Oxidation State	Element
1	-2.59625	4.351794	0.134735	2.131359	+0.87	Li
2	5.868415	1.429404	6.100381	2.131359	+0.87	Li
3	0.517746	4.465521	6.175856	2.132736	+0.87	Li
4	2.754427	1.315677	0.05926	2.132736	+0.87	Li
5	2.391099	3.387824	4.840575	6.962424	-0.96	S
6	0.881067	2.393374	1.394541	6.962349	-0.96	S
7	0.955075	0.435462	4.67217	6.9866	-0.99	S

8	2.317091	5.345736	1.562946	6.986556	-0.99	S
9	4.311079	0.493176	4.373794	7.053876	-1.05	S
10	-1.03891	5.288022	1.861322	7.053828	-1.05	S
11	-1.03702	3.367625	4.500062	7.007187	-1.01	S
12	4.309182	2.413573	1.735054	7.007164	-1.01	S
13	3.778862	4.345525	3.142108	12.8646	+1.14	Mo
14	-0.5067	1.435673	3.093008	12.86467	+1.14	Mo
15	0.865863	4.060564	3.116212	12.86171	+1.14	Mo
16	2.406303	1.720634	3.118904	12.86085	+1.14	Mo

Table S3 Bader charges of $NaMoS_2$ calculated by DFT.

$NaMoS_2$						
#	X	Y	Z	CHARGE	Oxidation State	Element
1	-2.68713	4.411477	0.115238	6.165944	+0.83	Na
2	6.011861	1.441757	6.780476	6.165944	+0.83	Na
3	0.557591	4.486844	6.851725	6.167469	+0.83	Na
4	2.76714	1.36639	0.043989	6.167469	+0.83	Na
5	2.406841	3.428325	5.153568	6.978188	-0.98	S
6	0.91789	2.424909	1.742146	6.978148	-0.98	S
7	0.981562	0.439282	4.975082	6.985821	-0.99	S
8	2.343169	5.413952	1.920632	6.985813	-0.99	S
9	4.381836	0.495296	4.688035	7.011752	-1.01	S
10	-1.05711	5.357938	2.207672	7.011705	-1.01	S
11	-1.04972	3.408524	4.80387	6.983182	-0.98	S

12	4.374454	2.44471	2.091837	6.983133	-0.98	S
13	3.824744	4.393717	3.476137	12.85711	+1.14	Mo
14	-0.50001	1.459517	3.419577	12.85718	+1.14	Mo
15	0.875727	4.111541	3.444425	12.85082	+1.15	Mo
16	2.449004	1.741693	3.451289	12.85032	+1.15	Mo

Table S4 Bader charges of $KMoS_2$ calculated by DFT.

$KMoS_2$						
#	X	Y	Z	CHARGE	Oxidation State	Element
1	4.270296	4.479503	0.136914	8.259457	+0.74	K
2	-0.89309	1.455631	7.408322	8.259471	+0.74	K
3	0.563109	4.541108	7.502254	8.258091	+0.74	K
4	2.814099	1.394026	0.042982	8.258051	+0.74	K
5	2.426208	3.475775	5.457142	6.965643	-0.97	S
6	0.951	2.459359	2.088094	6.965636	-0.97	S
7	1.001139	0.447763	5.276035	6.957248	-0.96	S
8	2.376069	5.487371	2.269201	6.957248	-0.96	S
9	4.462263	0.497803	4.986754	6.954054	-0.95	S
10	-1.08506	5.437331	2.558482	6.95402	-0.95	S
11	-1.06381	3.449415	5.101707	6.93455	-0.93	S
12	4.441016	2.485719	2.443521	6.934514	-0.93	S
13	3.878334	4.454059	3.806855	12.83436	+1.17	Mo
14	-0.50113	1.481075	3.738381	12.83442	+1.17	Mo
15	0.88392	4.170707	3.766507	12.83674	+1.16	Mo

16	2.493288	1.764427	3.778729	12.8365	+1.16	Mo

References

1. J. Ge, L. Fan, J. Wang, Q. Zhang, Z. Liu, E. Zhang, Q. Liu, X. Yu and B. Lu, *Adv. Energy Mater.*, 2018, **8**, 1801477.
2. Y. Fang, X. Y. Yu and X. W. Lou, *Angew. Chem. Int. Ed. Engl.*, 2019, **58**, 7744-7748.
3. B. Jia, Q. Yu, Y. Zhao, M. Qin, W. Wang, Z. Liu, C. Y. Lao, Y. Liu, H. Wu and Z. Zhang, *Adv. Funct. Mater.*, 2018, **28**, 1803409.
4. G. K. Veerasubramani, M.-S. Park, G. Nagaraju and D.-W. Kim, *J. Mater. Chem. A*, 2019, **7**, 24557-24568.