Electronic Supplementary Information for

Synthesis of MoS_2 nanosheet/graphene nanosheet hybrid materials for stable lithium storage

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Experimental Section

Preparation of graphite oxide: The graphite oxide was made from natural graphite flake (Alfa Aesar, 325 mesh) by using a modified Hummers method.[1]

Preparation of molybdenum disulfide nanosheets (MoS_2NS) aqueous suspension: The preparation follows an electrochemical lithiation approach reported previously.[2,3] In a typical synthesis, layered bulk material MoS_2 (Alfa Aesar, 325 mesh), Super-P carbon black, and poly(vinylidene fluoride) (PVDF) with mass ratio of 80:10:10 were mixed into homogeneous slurry with mortar and pestle to make working electrodes. The obtained slurry was pasted onto pure Cu foil (99.9 %, Goodfellow). The electrolyte was 1 M $LiPF_6$ in EC/DMC/DEC (1:1:1 v/v/v) (Novolyte Technologies). Glass fibers (GF/D) from Whatman were used as separators and pure lithium metal foil (Aldrich) was used as the counter electrode. The Swagelok-type cells were assembled in an argon-filled glove box. The electrochemical intercalation of MoS_2 in the working electrodes was performed using galvanostatic discharge at a current density of 40 μA on an Arbin BT2000 system. After the discharge process, the lithium intercalated electrodes was washed with acetone to remove the residual electrolyte, followed by dipping in deionized water, during which a large number of bubbles was observed and the separation between the balck film and Cu base was occurred. After sonicating the balck film in fresh deionized water for 10 min, the resulting balck suspension was centrifuged at 17000 rpm for 5 min to separate the bulk MoS_2 and the stable aqueous suspension of MoS_2 nanosheets, which was collected for further use and characterizations.

Preparation of MoS_2/reduced graphene oxide nanosheet/nanosheet hybrid (MoS_2NS/RGO): 2.3 mL of graphite oxide aqueous suspension (10.0 mg mL^{-1}) was dispersed in deionized water (90 mL), followed by mixing with the above MoS_2 nanosheets aqueous suspension (140 mL). The mixture was continuously sonicated to afford a homogeneous suspension. After being lyophilized, the obtained black powder

was loaded in a small glass beaker, which was further placed into a glass bottle containing 1 mL of hydrazine monohydrate (Alfa Aesar, 99%), without direct contact between the powder and the hydrazine monohydrate. After sealing, the glass bottle was maintained at 120 ^{o}C for 2 h to reduce the graphene oxide in situ. After cooling, the product was washed with ethanol six times to remove the adsorbed hydrazine monohydrate and byproduct, followed by drying at 70 ^{o}C under vacuum overnight to obtain the final hybrid, denoted as MoS_2NS/RGO.

Structural and Electrochemical Characterizations: SEM measurements were carried out on a Hitachi S-4800 field emission scanning electron microscope operated at 15 kV. TEM and HRTEM characterizations were performed on a Tecnai G2 F20 U-TWIN field emission transmission electron microscope operated at 200 kV. Thermogravimetric (TG) analysis was conducted on a TA-Q50 instrument. XRD measurements were recorded on a Rigaku D/max2500 diffractometer using Cu Kα radiation. AES spectra were characterized by a ULVAC-PHI PHI-700 scanning Auger microscope at 5 keV, Ar ions were used for step by step ion sputtering of surface layer. XANES measurements were determined on Beam-line 4B7B at Beijing Synchrotron Radiation Facility (BSRF). XPS spectra were obtained with an ESCALab220i-XL electron spectrometer from VG Scientific using 300W Al Kα radiation. Nitrogen adsorption and desorption isotherms at 77.3 K were carried out on a Nova 2000e surface area-pore size analyzer. Electrochemical experiments were performed using Swagelok-type cells. To make working electrodes, MoS_2NS/RGO, Super-P carbon black, and PVDF with mass ratio of 80:10:10 were mixed into homogeneous slurry with mortar and pestle. The obtained slurry was pasted onto pure Cu foil. The electrolyte was 1 M $LiPF_6$ in EC/DMC (1:1 v/v) (Novolyte Technologies). Glass fibers (GF/D) from Whatman were used as separators and pure lithium metal foil was used as the counter electrode. The Swagelok-type cells were assembled in an argon-filled glove box. Cyclic voltammetry was obtained with an Autolab PG302N at a scan rate of 0.1 mV s^{-1}. The charge and discharge measurements of the batteries were determined on an Arbin BT2000 system in the fixed voltage window between 5 mV and 3 V vs Li^{+}/Li at room temperature. Electrochemical impedance spectral measurements were carried out on a PARSTAT 2273 advanced electrochemical system over the frequency range from 100 kHz to 100 mHz.

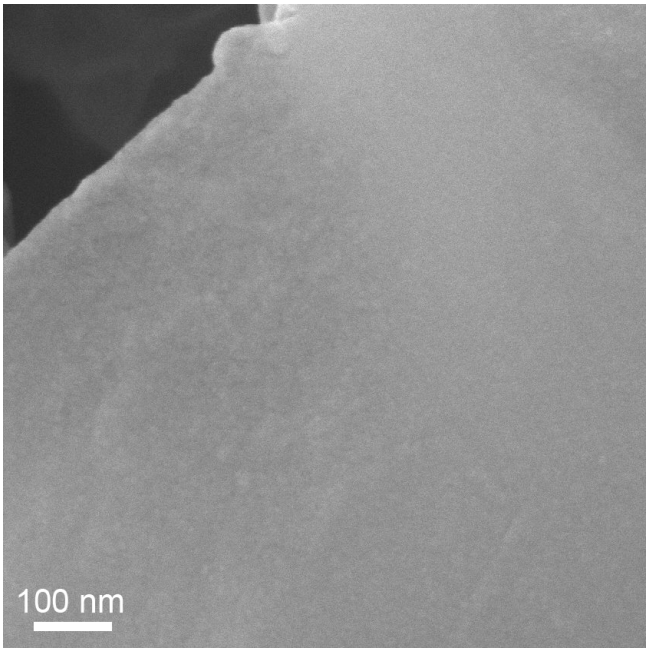

Figure S1. High-magnification SEM image of MoS_2NS/RGO.

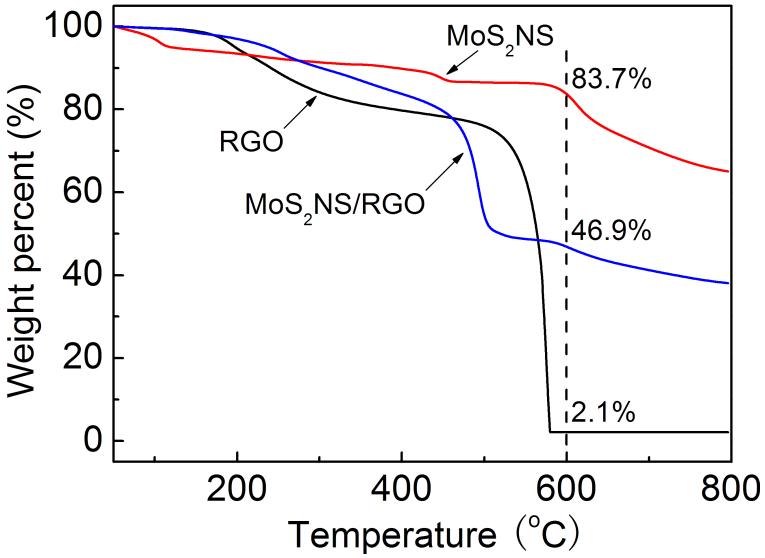

Figure S2. TG analysis curves of MoS_2 nanosheets (MoS_2NS), reduced graphene oxide (RGO), and MoS_2NS/RGO hybrid under air atmosphere at a heating rate of 10 ^{o}C min^{-1}. The content of MoS_2NS in the hybrid can be calculated based on the equation $W_{MoS_2NS} * X_{MoS_2NS} + W_{RGO} * (1-X_{MoS_2NS}) = W_{MoS_2NS/RGO}$, where W_{MoS_2NS}, W_{RGO}, and $W_{MoS_2NS/RGO}$ are residual weight percent of MoS_2NS, RGO, and MoS_2NS/RGO hybrid at 600 ^{o}C, and X_{MoS_2NS} is the content of MoS_2NS in MoS_2NS/RGO hybrid.

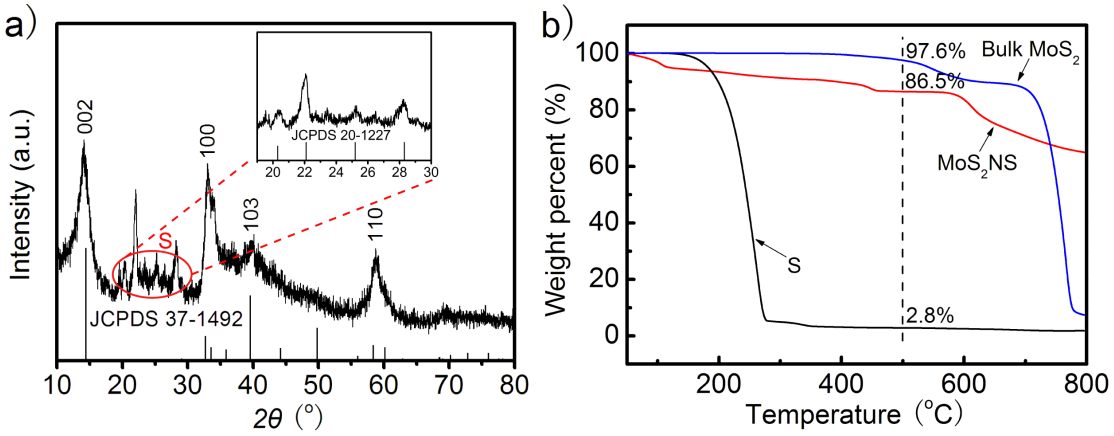

Figure S3. a) XRD pattern of MoS_2NS/RGO, inset shows high-resolution XRD pattern of sulphur. b) TG analysis curves of bulk MoS_2, MoS_2NS, and sulphur (S) under air atmosphere at a heating rate of 10 ^{o}C min^{-1}. We could calculate the contents of MoS_2 and sulfur in MoS_2 nanosheets based on the equation $W_{MoS_2} * X_{MoS_2} + W_{sulfur} * (1-X_{MoS_2}) = W_{MoS_2NS}$, where W_{MoS_2}, W_{sulfur}, and W_{MoS_2NS} are residual weight percent of MoS_2, sulfur, and MoS_2 nanosheets at 500 ^{o}C, and X_{MoS_2} is the content of MoS_2 in MoS_2 nanosheets. The contents of MoS_2 and sulfur in MoS_2 nanosheets are approximately 88.3 wt% and 11.7 wt%, respectively.

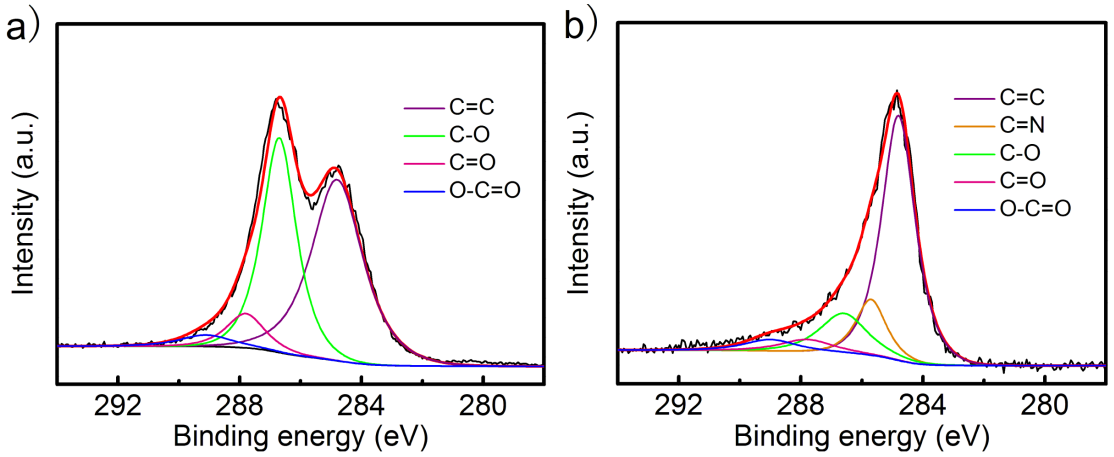

Figure S4. XPS C 1s spectra of a) GO and b) MoS_2NS/RGO. the main peaks centered at 284.8 eV corresponding to extensively delocalized sp^2-hybridized carbon atoms, and the independent peaks with binding energies of 285.7, 286.6, 287.8, and 289.0 eV can be attributed to carbon atoms in C=N, C-O, C=O, and O-C=O, respectively.

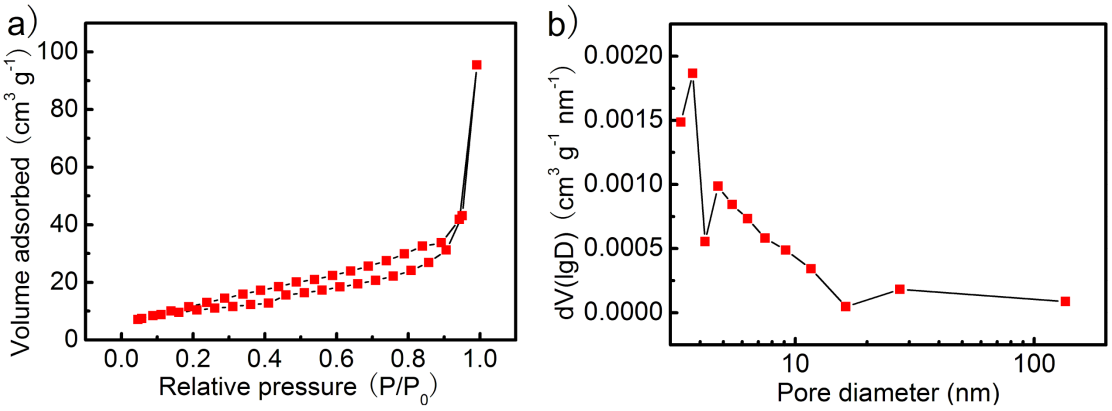

Figure S5. a) Nitrogen adsorption/desorption isotherms of MoS_2NS/RGO, (b) pore-size distribution plot calculated by the BJH formula with the desorption isotherm.

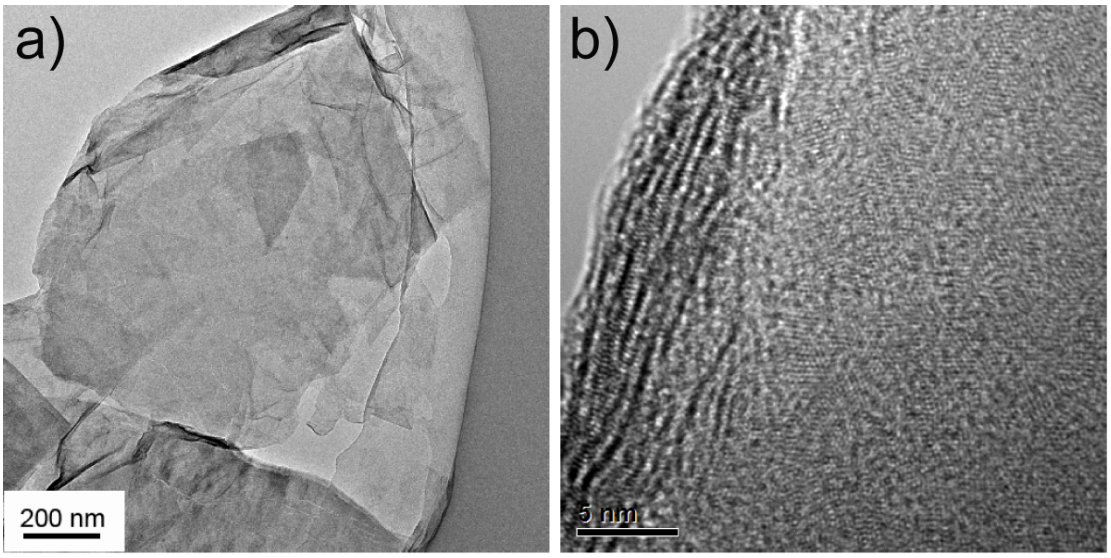

Figure S6. a)TEM image and b) HRTEM image of MoS_2 nanosheets.

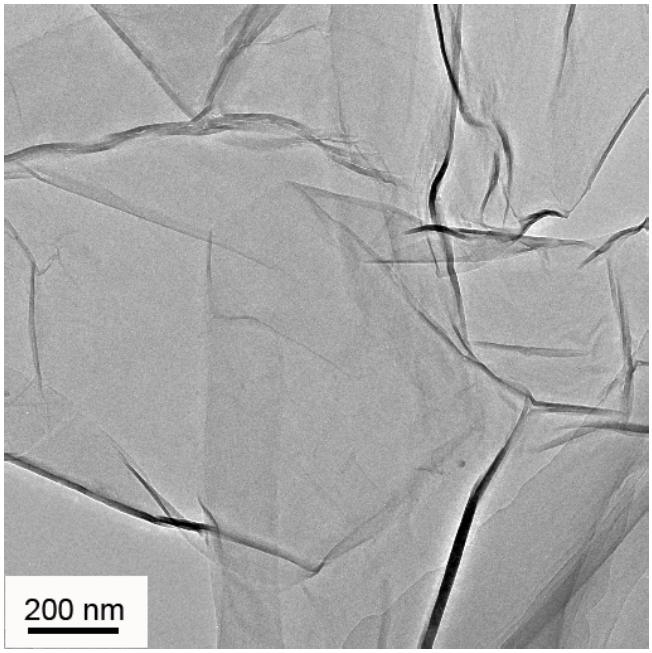

Figure S7. TEM image of reduced graphene oxide.

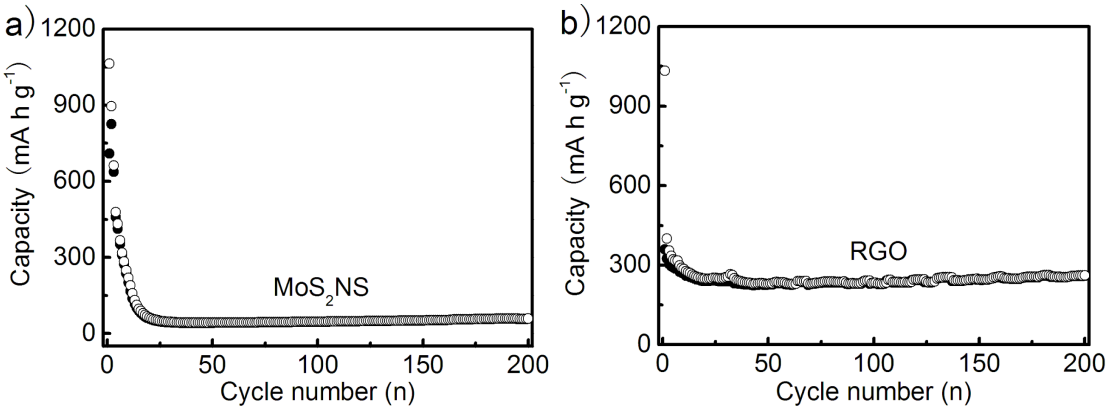

Figure S8. Cycling performance of MoS_2NS electrode and RGO electrode at a current density of 0.5 A g^{-1} in the voltage range of 0.005–3 V vs Li^+/Li.

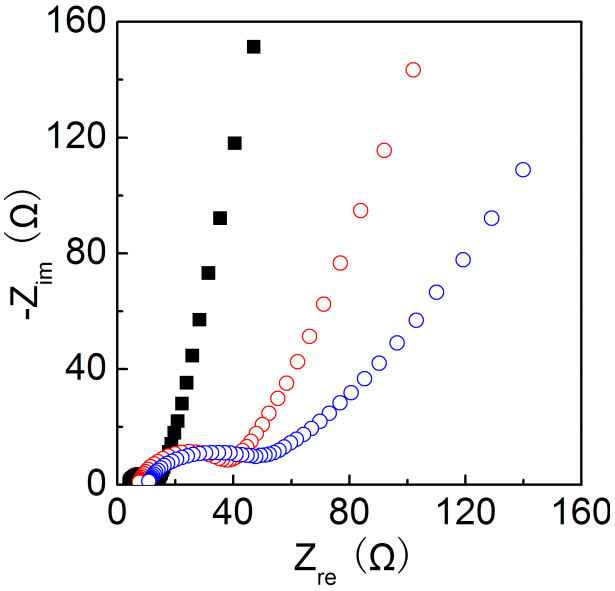

Figure S9. Nyquist plots of MoS_2NS/RGO electrodes before cycling (black squares), after 3 cycles (red cycles), and after 700 cycles (blue circles).

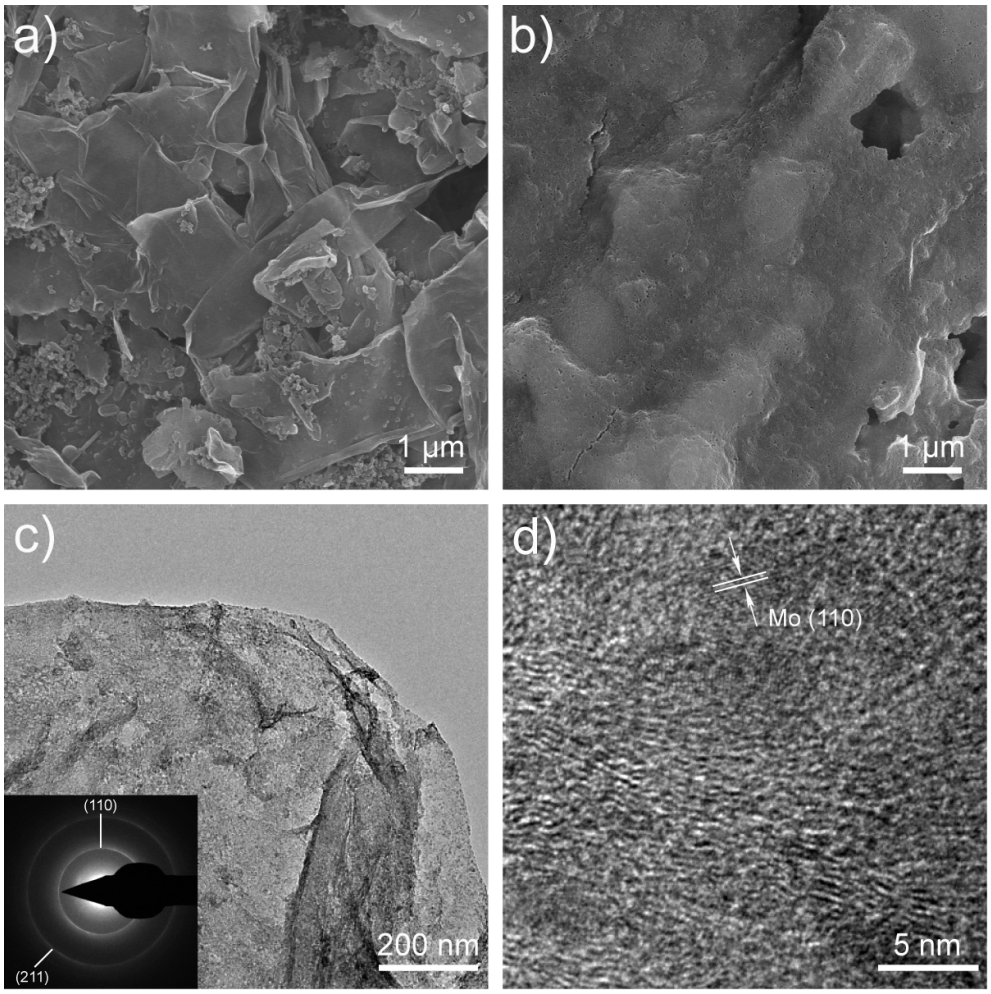

Figure S10. a), b) SEM images of as-prepared MoS_2NS/RGO electrode. b), c), d) SEM, TEM, and HRTEM images of MoS_2NS/RGO electrode after 700 cycles, the inset in c) shows the corresponding SAED pattern.

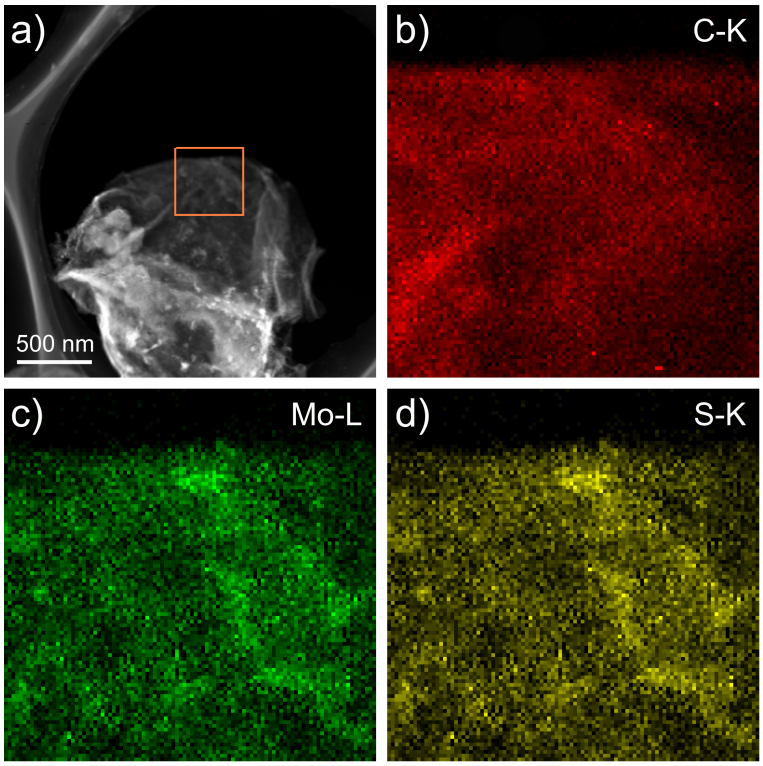

Figure S11. a) STEM image, b), c), and d) carbon, molybdenum, and sulfur element mapping images of MoS_2NS/RGO after 700 cycles, respectively.

References

1. W. S. Hummers and R. E. Offeman, *J. Am. Chem. Soc.*, 1958, **80**, 1339.
2. Y.-S. Hu, Y.-G. Guo, W. Sigle, S. Hore, P. Balaya and J. Maier, *Nat. Mater.*, 2006, **5**, 713.
3. Z. Zeng, Z. Yin, X. Huang, H. Li, Q. He, G. Lu, F. Boey and H. Zhang, *Angew. Chem. Int. Ed.*, 2011, **50**, 11093.