Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information

Amorphous MoS_x thin film Coated Carbon Fiber Paper as 3D electrodes for long cycle life Symmetric Supercapacitors

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Experimental methods:

Synthesis of amorphous MoS_x on carbon fiber paper (CFP/a-MoS_x): Molybdic acid, (MAA, H_2MoO_4) and thioacetamide (TAA, CH_3CSNH_2) were purchased from Sigma-Aldrich Corporation. An exactly 0.225 gram of TAA and 0.121 g of MAA were accurately weighed and then dissolved into 80 ml of deionized (DI) water, with constant stirring for 15 min in order to achieve complete dissolution. The carbon fiber paper (CFP, Toray, TGP-H-120) substrate is basically hydrophobic in nature due to its sp^2 hybridization of carbon atoms present in the graphitic structure. In a typical hydrothermal synthesis, wettability is of CFP is an important criterion in order to achieve the uniform deposition (with good adhesion) of MoS_x onto the substrate. To induce the hydrophilicity in CFP, a small piece of CFP is placed inside the plasma chamber followed by activation using oxygen plasma with a power of 18 W for 15 min. After plasma cleaning, the CFP is immediately transferred into a Teflon-lined autoclave followed by the transfer of TAA and MAA mixed precursor solution into the same autoclave and then sealed tightly. The autoclave was then placed inside an electric oven and maintained the reaction temperature at 200 °C for 24 h. Once the hydrothermal reaction was completed, the autoclave was retained inside the electric oven until it cooled down naturally to room temperature. The resulting amorphous MoS_x coated CFP was taken out and washed with DI water for several times to remove the loose MoS_x deposits adsorbed on the substrate. After rinsing, a-MoS_x deposited CFP (CFP/a-MoS_x) was dried in an electric oven at 40 °C for 12 hrs.

Material Characterization: Surface morphology of the bare CFP and amorphous MoS_x coated CFP (CFP/a-MoS_x) was examined using scanning electron microscopy (NanoSEM, S-3400N). High-resolution transmission electron microscopy (HR-TEM, FEI, Talos F200X) was used to examine the cross-sectional image, microstructure, thickness, elemental composition and amorphous nature of MoS_x. A thin slice of TEM sample was prepared using focused ion beam equipped scanning electron microscopy (FIB-SEM, FEI, Quanta 3D) with Ga^+ ion source at 30kV. First of all, the region of interest for lamella preparation is identified using SEM. Then the epoxy coating (~30 nm) followed by the protective layer of platinum coating (~140 nm) was deposited on the target milling area of 7x1.5 µm using gas injection system (GIS). A beam current of 20 nA was applied for coarse milling, followed by the lifting out of lamella using the microprobe. Further, the as detached lamella was transferred from the microprobe to TEM copper grid by the assistance of Pt deposition using GIS. Once the lamella was transferred to TEM grid, exactly 4 nA beam current was applied for medium milling, followed by 1 nA beam current was used for fine milling until the desired thickness was reached for electron transparency. The lamella attached TEM grid was used for TEM analysis. The lower magnification TEM image of as-fabricated lamella using FIB milling is shown in Fig. S5. The chemical composition and oxidation state of elements were analyzed using X-ray photoelectron spectroscopy (XPS, Thermo Fisher, UK). The amorphous nature of MoS_x was examined using X-ray diffraction (XRD, Bruker-D8 ADVANCE) using Cu Kα emission ($\lambda = 1.5406$ Å) with a step-size of 0.02° and the and Raman spectroscopy (WITech, alpha300R) using 532 nm laser excitation, after calibrating the Raman shift with a silicon reference at 521 cm^{-1}.

Capacitance Calculation: From the CV curves, the cell capacitance of the symmetric supercapacitor (C_{cell}) was calculated according to the following equation. [1]

$$C_{cell} = (\int I(V)dv\ ) / (v\Delta V) \quad [F] \qquad ----- \quad (S1)$$

where C_{cell} is the measured device capacitance (F), $\int I(V)dv$ is the integral area of the CV loop, v is the scan rate (Vs^{-1}), and ΔV is the potential window (V).

From the CD curves, the cell capacitance of the symmetric supercapacitor (C_{cell}) was computed as follows: [2]

$$C_{cell} = (I\Delta t) / (\Delta V) \qquad [F] \qquad ----- \quad (S2)$$

where I is the discharge current (A), Δt is the discharge time (s), and ΔV is the potential window (V).

The areal specific capacitance of a cell (C_m) and the areal specific capacitance of the electrode (C_s) were calculated as follows: [1, 2]

$$C_{m=}\ C_{cell}/A \qquad [F\ cm^{-2}] \qquad ----- \quad (S3)$$

$$C_{E\ =}\ 2\ x\ C_{cell} \qquad [F] \qquad ----- \quad (S4)$$

$$C_{s=} C_E/A \qquad [\mathrm{F\ cm^{-2}}] \qquad ----- \quad (S5)$$

where C_{cell} *is* the cell capacitance of the symmetric supercapacitor (F) which could be obtained either from CV or CD curves using equations (S1) or (S2), C_E is the single electrode capacitance (F), A is the geometric area of an electrode (cm^2), C_m is the area normalized cell capacitance (F cm^{-2}), and C_s is the geometric area normalized electrode capacitance (F cm^{-2})

Energy density (E) and power density (P) of the symmetric device were calculated as follows:

$$E = \frac{0.5\ C_m V^2}{}$$

$$P = \frac{E\ x\ 3600}{\Delta t} \qquad [\mathrm{W\ cm^{-2}}] \qquad (S7)$$

Where C_m is the areal specific capacitance of a cell, *V* is the potential window (V) and Δt is the discharge time (s).

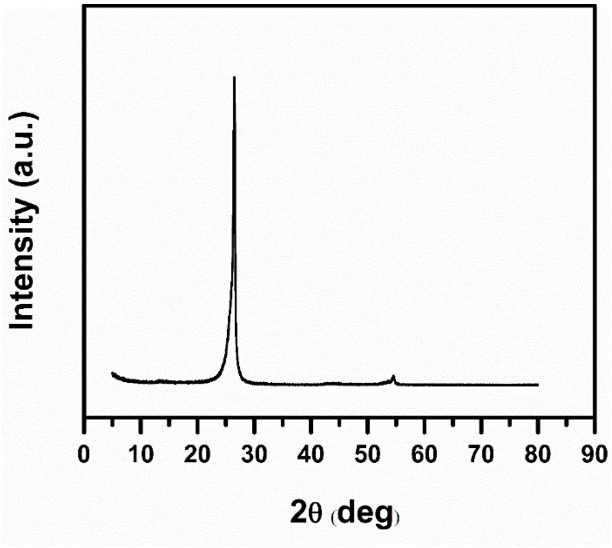

Fig. S1 X-ray diffraction pattern of CFP/a-MoS$_x$.

The XRD pattern of CFP/a-MoS$_x$ is shown in Fig. S1. Diffraction peaks appear at 2θ = 26.5° and 54.5° correspond to the (002) and (004) planes of carbon fiber paper paper (JCPDS no.41-1487).

Except carbon fiber peaks, there is no characteristic peaks of molybdenum sulfide is observed, which infers that the as deposited MoS_x is amorphous in nature.

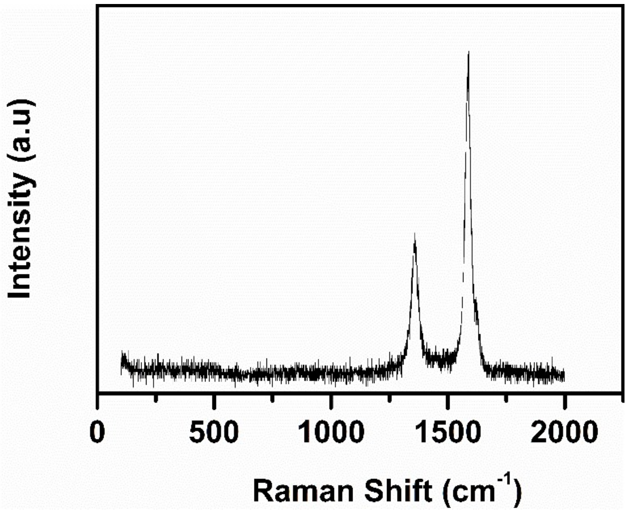

Fig. S2 Raman spectrum of CFP/a-MoS_x.

Fig. S2 shows the Raman spectrum of CFP/a-MoS_x. The typical peaks observed at 1358 cm^{-1} and 1587 cm^{-1} correspond to the D and G band of carbon fiber paper. Except D and G band of carbon material, there is no characteristic peaks (E^1_{2g} and A_{1g} modes) of molybdenum sulfide is observed.

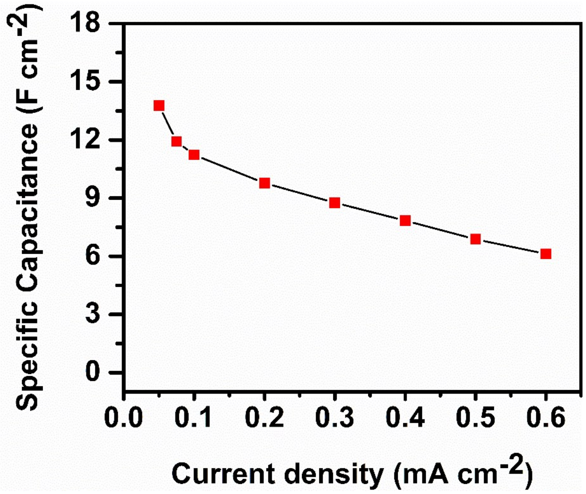

Fig. S3 Relationship of areal specific capacitance of electrode Vs current densities

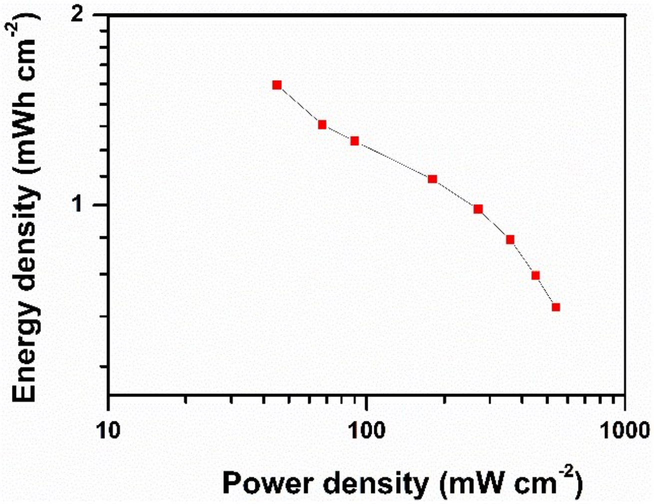

Fig. S4 Ragone plot of symmetric device showing the areal energy and power densities

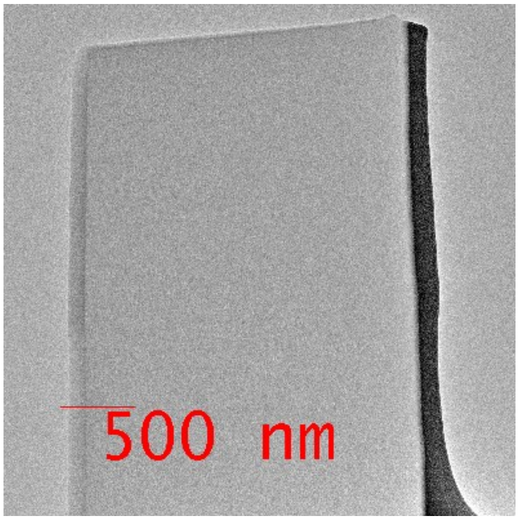

Fig. S5 shows the lower magnification TEM image of as-prepared lamella using FIB milling.

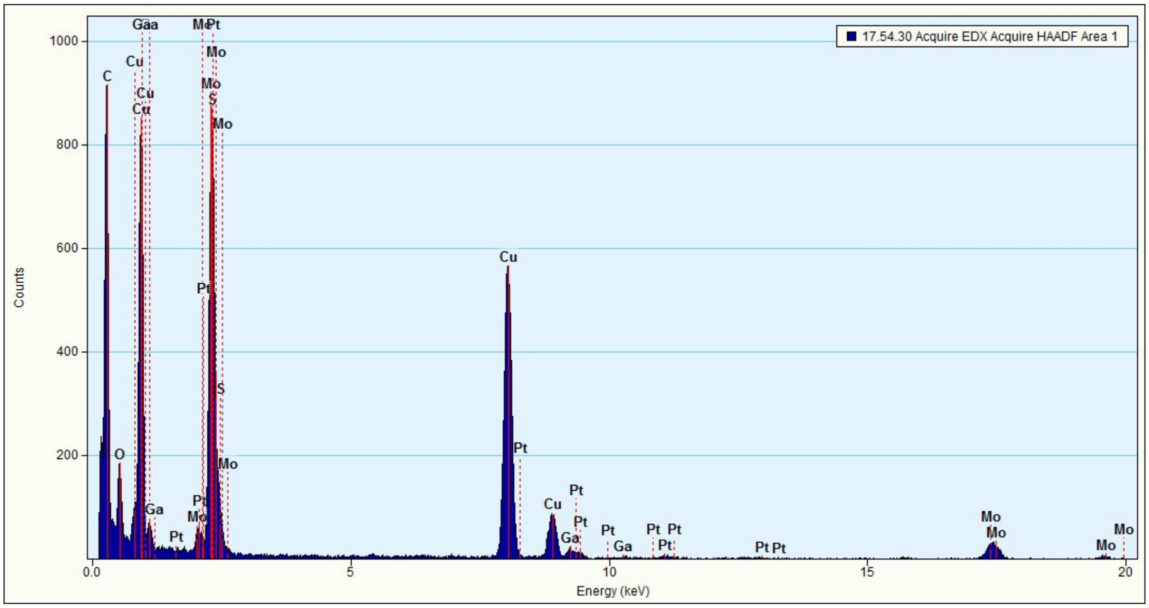

Fig. S6 EDS spectrum of MoS_x measured at the small portion of STEM image in Fig. 1f (see main manuscript)

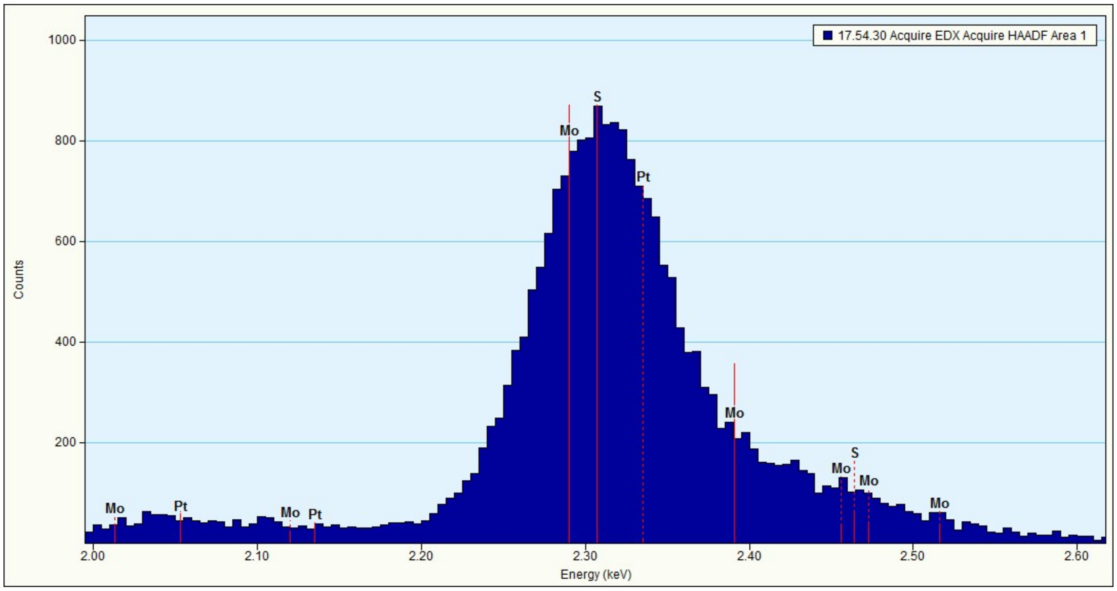

Fig. S7 The magnified EDS spectrum of MoS_x (from 2.0 to 2.6 keV region) extracted from Fig. S6.

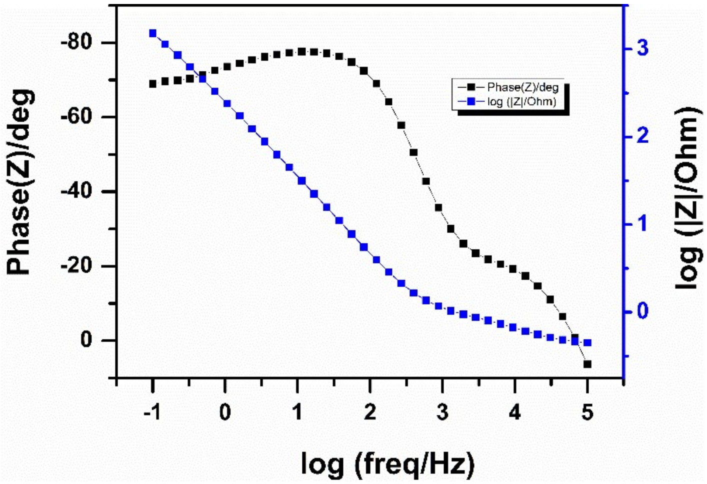

Fig. S8 Electrochemical impedance spectrum showing the frequency responsive Bode plot of the symmetric supercapacitor

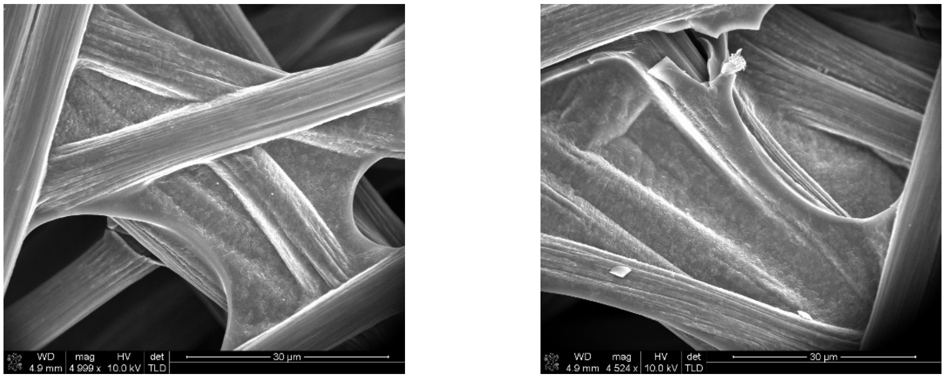

Fig. S9 SEM images of CFP/a-MoS$_x$ electrodes after long-term charge-discharge cycling (Post-mortem analysis)

Table S1. XPS data of CFP/a-MoS$_x$: Deconvoluted S2p orbital.

Sulfur 2p orbital		Peak position (eV)
S^{2-}	$2p_{3/2}$	161.9
	$2p_{1/2}$	163.2
S_2^{2-}	$2p_{3/2}$	163.9
	$2p_{1/2}$	164.9

Table S2. Electrochemical performance comparison of CFP/a-MoS$_x$ material with other molybdenum sulfide materials.

Sl. No	Electrode material	Experimental condition	Specific capacitance (mF cm^{-2})	**Specific capacitance of CFP/a-MoS$_x$** (mF cm^{-2})	Ref.
1	MoS$_2$ nanowall films	CV@1 mV s^{-1} (3-electrode configuration)	$C_s = 70$	**$C_s = 83.9$ - CV@1 mV s^{-1} (2-electrode configuration)**	[3]
2	Exfoliated MoS$_2$	CV@5 mV s^{-1}	$C_m = 1.83$	**$C_m = 20.4$**	[4]
3	Exfoliated MoS$_2$–graphene composite	CV@5 mV s^{-1}	$C_m = 4.29$	**$C_m = 20.4$**	[4]
4	Exfoliated MoS$_2$	CV@10 mV s^{-1}	$C_m = 2$	**$C_m = 16.8$**	[5]
5	Bulk MoS$_2$	CV@10 mV s^{-1}	$C_m = 0.5$	**$C_m = 16.8$**	[5]
6	Exfoliated MoS$_2$	CD@0.25 mA cm^{-2}	Cs = 1.65	**$C_s = 8.76$ - CD@0.3mA cm^{-2}**	[4]

CV - cyclic voltammetry; CD – charge-discharge measurement;

C_s – specific capacitance of single electrode; C_m – specific capacitance of symmetric device

References

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