Supporting Information

Experimental and theoretical evidence of ion engineering in nanocrystalline molybdenum disulfide memristor for non-filamentary switching actions and ultra-low-voltage synaptic features

D. Das[†*], J. Asirvatham[†], MA. Luong[#], A. Claverie[#], P. Johari[†*] and A. Kanjilal[†*]

[†]Department of Physics, School of Natural Sciences, Shiv Nadar University, NH-91, Dadri, Gautam Buddha Nagar, Uttar Pradesh 201314, India

[#] CEMES-CNRS, 29 Rue Jeanne Marvig, 31055 Toulouse, France

[*]Corresponding authors: dd209@snu.edu.in, priya.johari@snu.edu.in, aloke.kanjilal@snu.edu.in

Keywords: Nanoengineering, 2D materials, Non-filamentary memristors, Neuromorphic electronics, DFT, Artificial neural network

Table of Contents

1. Thickness and roughness measurements

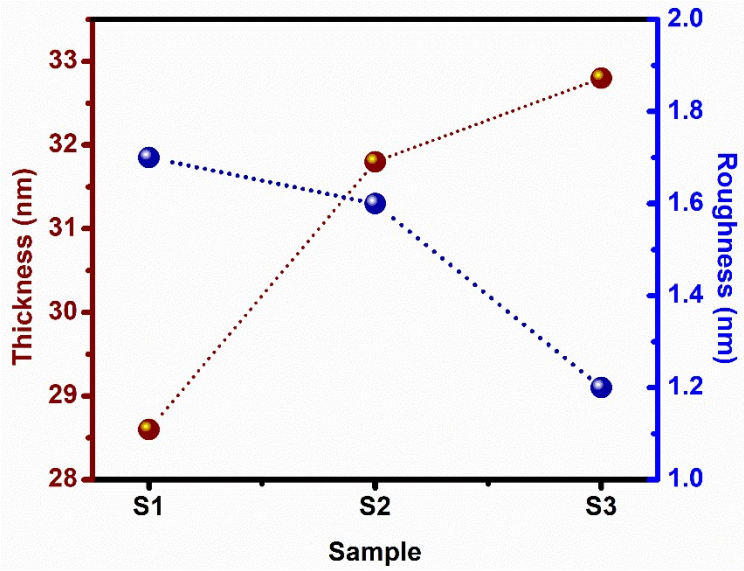


Figure S1. The thickness (roughness) of samples S_1, S_2, and S_3 was 28.6 (1.7), 31.8 (1.6), and 32.8 (1.2), respectively, measured using Bruker DektakXT surface profilometer.

2. Asymmetry analysis

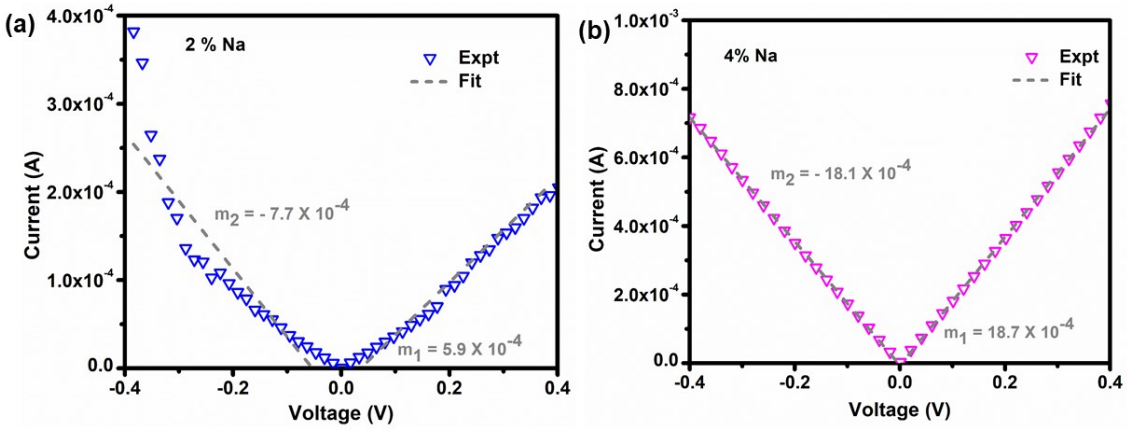


Figure S2: Current-voltage curves of (a) 2 wt. % Na and (b) 4 wt. % of Na fitted with a linear equation. It reveals the asymmetric nature of 2 wt. % Na.

3. Endurance of sample S_1

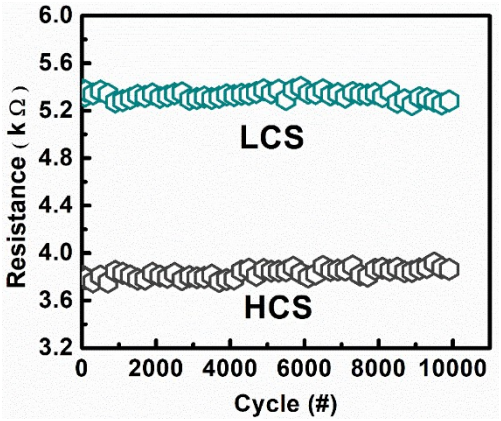


Figure S3. Endurance characteristics of sample S_1 for up to 10^3 cycle

4. Endurance of sample S_3

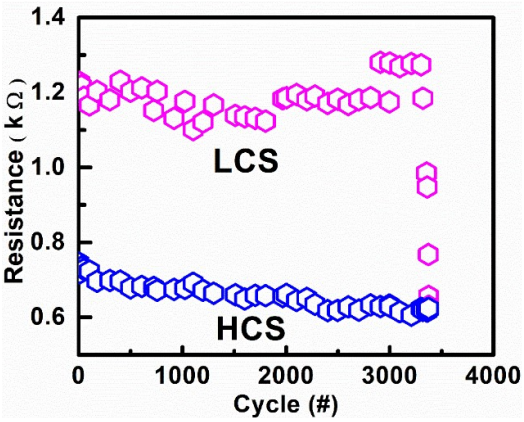


Figure S4. Endurance characteristics of sample S_3, after 3400 cycles the LCS merged to HCS.

5. Bending test

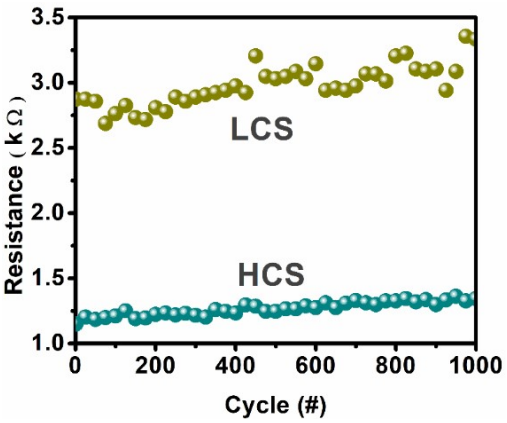


Figure S5. Device response with bending cycle

6. Alteration of layer thickness, current, and conductance variations with the applied voltage

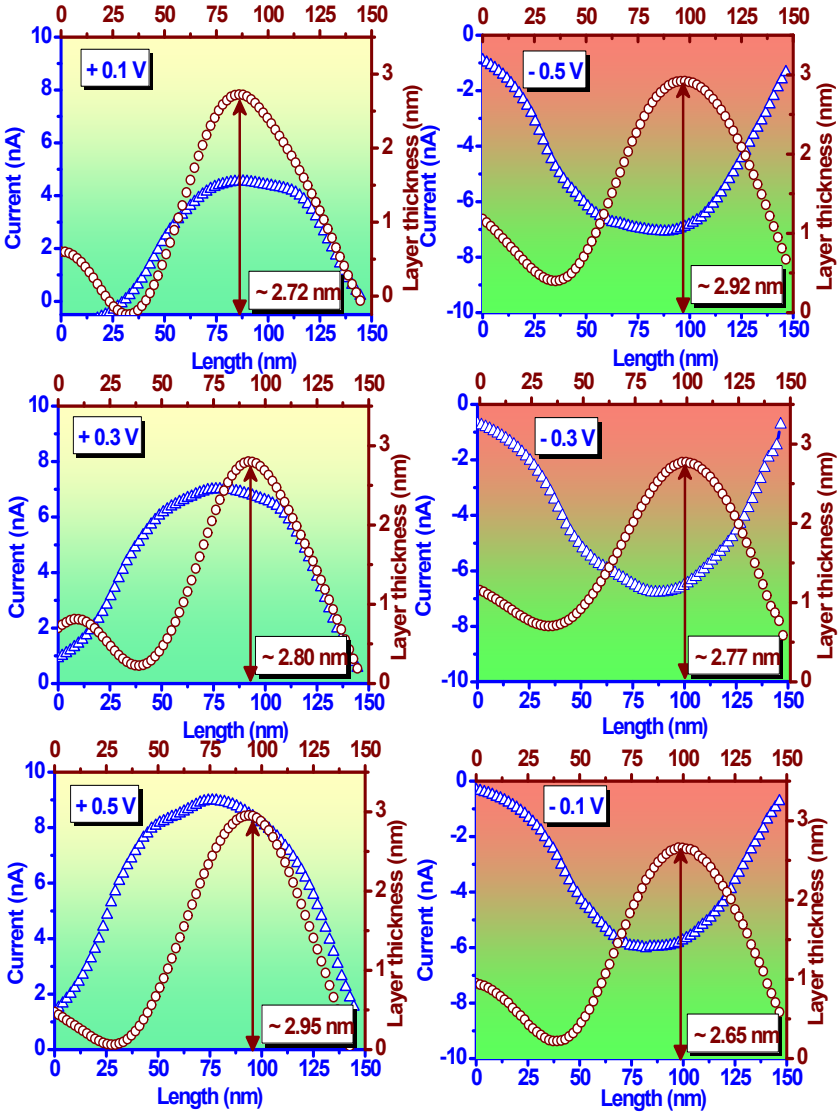


Figure S6. Change of layer thickness and current with applied bias.

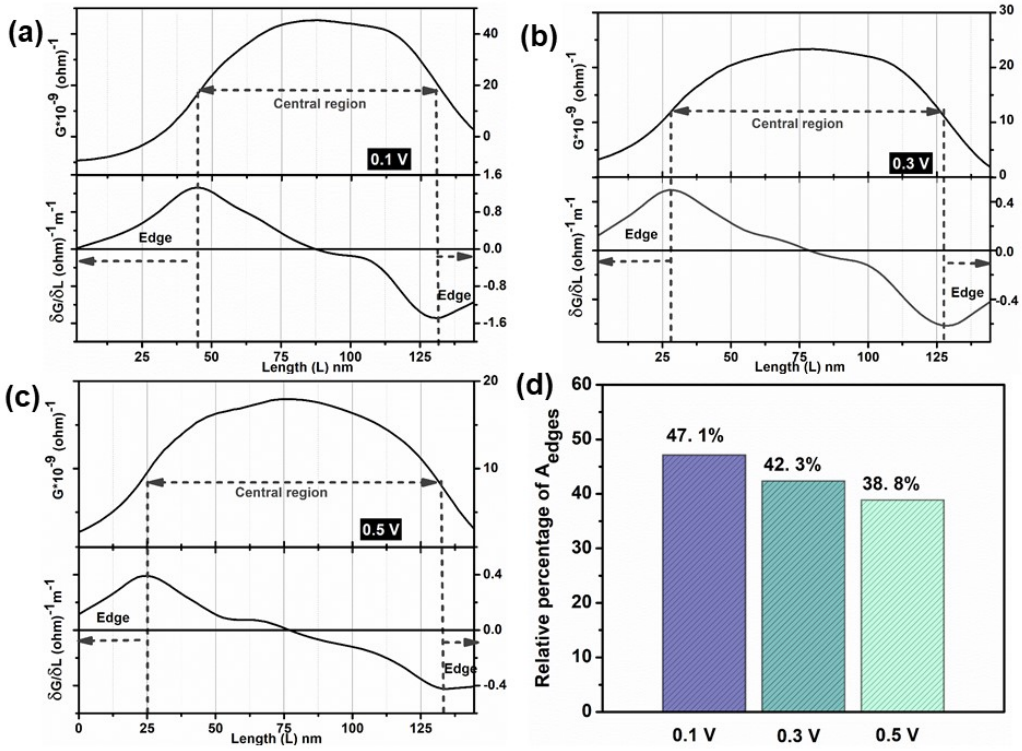


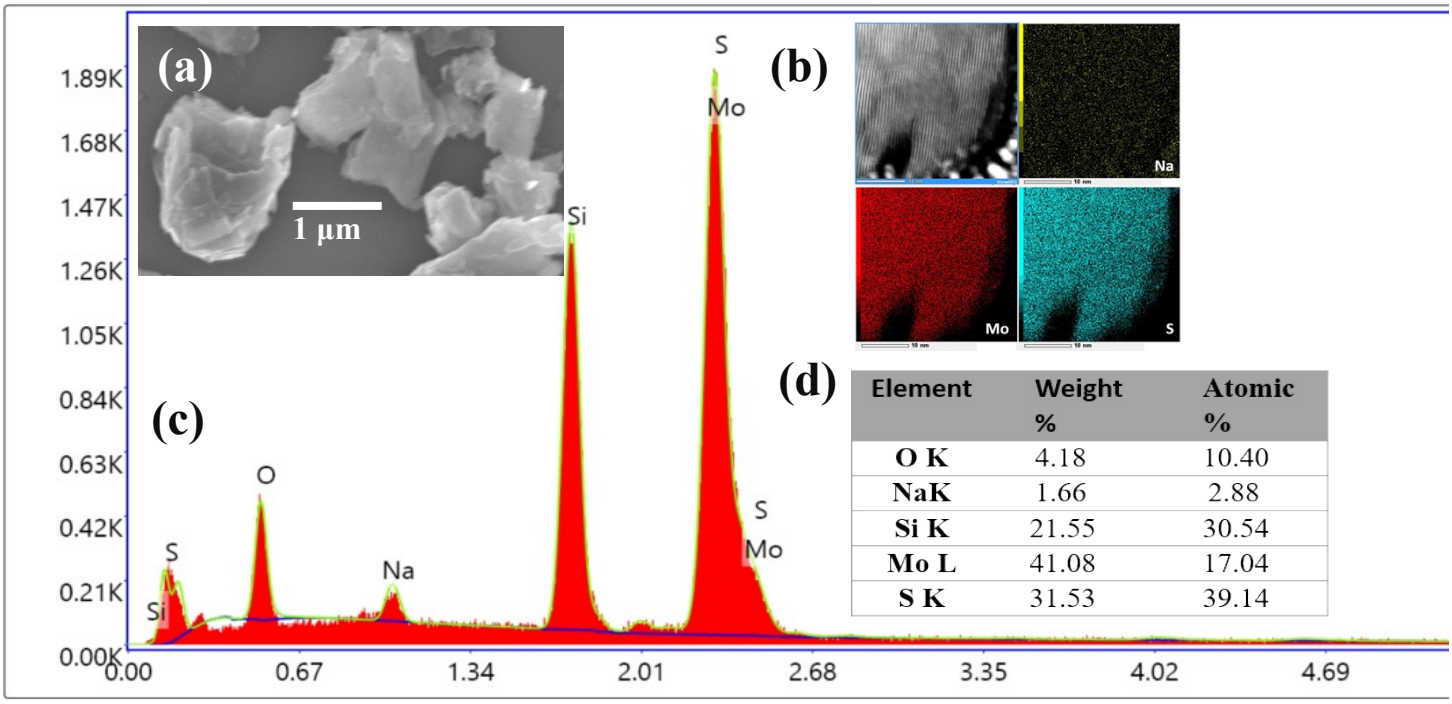
Figure S7: Conductance variations (top) and its first-order space derivative (bottom panel) at the edges and the central region of the nanocrystal for three different applied voltages (a) 0.1V, (b) 0.3V and (c) 0.5 V; (d) Presents the relative area percentage of A_{edges} with A_{centre} for 0.1V, 0.3V, and 0.5V

We derive the conductance (G) distribution along the nanocrystal's surface from the current scan. It is shown at the top panels of Figure S7 a-c. Subsequently, we calculate its first-order space derivative (i.e., δG/δL, at the bottom panels of Figure S7 a-c), which relates to the carrier density [Reports on Progress in Physics 83.3 (2020): 036501]. Then, we calculate the area under the curve for two different regions, which are marked as edge and central regions in Figure S6 a-c.

$$A = A_{edges} + A_{centre} = \int_{edges} \left(\frac{\delta G}{\delta L}\right) dL + \int_{centre} \left(\frac{\delta G}{\delta L}\right) dL$$

Finally, we determine the relative percentage change of A_{edges} with A_{centre} for the three different potentials of 0.1V, 0.3V, and 0.5V (as shown in Figure S7d). It shows that the initial A_{edges} percentage was 47.1% for 0.1V and then drops to 38.8% for 0.5V. Therefore, it is reasonable to claim that the edges of nanocrystals become less conducting as the electric potential increases. Furthermore, a relative decrease in A_{edges} implies an increase in A_{centre}, and an increase in A_{centre} suggests an increase in carrier density (present case Na-ion) at the central region. As a result, we may reasonably argue that as potential increases, more Na-ions move from the edges to the central region.

7. Scanning electron microscopy results



Element	Weight %	Atomic %
O K	4.18	10.40
NaK	1.66	2.88
Si K	21.55	30.54
Mo L	41.08	17.04
S K	31.53	39.14

Figure S8 (a) High-resolution SEM image of Na:MoS_2 flakes (b) Elemental analysis of the fabricated Na:MoS_2 flakes using energy-dispersive X-ray spectroscopy (EDX) technique. The distribution maps of Na, Mo, and S are presented in yellow, red, and cyan colors, respectively (c) Spectral distribution, and (d) atomic concentration.

8. Band structure and PDOS

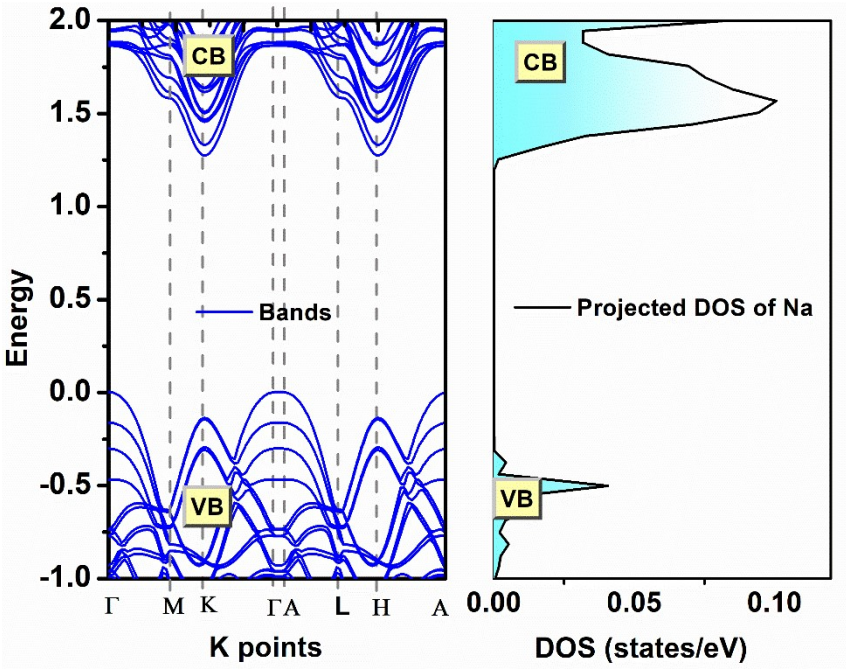


Figure S9: Band structure calculations along with the Na-projected density of states to show the influence of Na at the bottom of the conduction band.

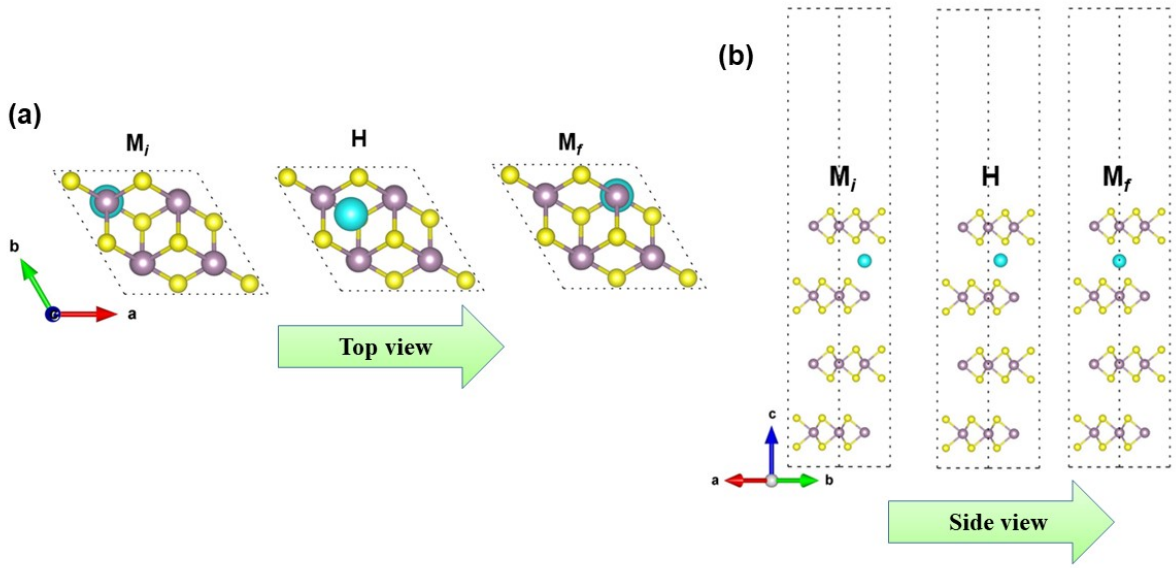
9. vdW correction (DFT-D3 method)

Table S1: Total energy of pristine and Na:MoS_2 using PBE and vdW (D3) method

	Without vdW correction (PBE)	vdW correction	
		Without	With dipole

		dipole correction	correction
Pristine (E_{MoS_2})	-348.772	-366.936	-366.935
Na: MoS_2 (E_{Na+MoS_2})	-350.773	-368.938	-368.938
Difference in energy ($E_{Na+MoS_2} - E_M$)	-2.001	-2.002	2.003

*We checked the impact of vdW correction in our simulations using the DFT-D3 method with Becke-Johnson damping [*Journal of computational chemistry 32.7 (2011): 1456-1465*] to show the invariance of our results against different DFT functional. The details of the simulations are listed below. An overall shift in ground state energy at the lower energy side was noticed for the vdW correction (as compared with the standard PBE functional) in both the pristine MoS_2 and Na: MoS_2 systems. However, their relative change in energy is remaining unaltered; it proposes that our general arguments remain intact for other functionals.*



10. Na-diffusion path

Figure S10. The Na diffusion path (a) top view (b) side view.