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Supporting Information

Exfoliated MoS_2 Nanosheets Confined in 3-D Hierarchical Carbon Nanotube@Graphene Architecture with Superior Sodium-Ion Storage

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Experimental Section

Polyelectrolyte Functionalization of MWCNTs and GO:

30 mg of carboxy-modified MWCNT was dispersed in DI water, ultrasonicated (250 W Branson Ultrasonifier, 20% amplitude) for 10 min in order to obtain a homogeneous dispersion of MWCNTs. The suspension was added drop by drop to a 3 mg.mL^{-1} polyallylamine hydrochloride (PAH, M_w ~17000 Sigma-Aldrich) solution and sonicated for 10 min. The mixture was then stirred for another 1 h to allow (+ve) charged PAH molecules adsorption onto (-ve) charged MWCNTs surface by simple electrostatic interaction. Now, these MWCNTs were washed by centrifugation- redispersion (×2) in order to remove the excess PAH molecules.

Graphene Oxide (GO) sheeets were synthesized from natural graphite flake (100 mesh, Aldrich) by an improved synthesis.[1]PAH-modification of GO sheets were done by the same process that for MWCNT-functionalization instead 30 mg of MWCNT was replaced by 60 mg of GO.

Synthesis of MoS-C and MoS-G:

The MoS-C nanocomposite was then produced by a hydrothermal method. In a typical process, 30 mg of PAH-modified MWCNTs first dispersed in 30 mL DI water, ultrasonicated for 15 min. A 30 mL aqueous solution containing Na_2MoO_4, $2H_2O$ (1.24 mmol) and thiourea (9.92 mmol) were then added drop wisely into CNT-dispersion. After ultrasonication and stirring for 15 min, the mixed suspension was transformed into 100 mL Teflon-lined stainless steel autoclave, which was then sealed and maintained at 230 ^{0}C for 24 h. After natural cooling of the autoclave, the black solid product was collected by centrifugation, washed several time with DI water (×2) and ethanol (×1), and dried in a vacuum oven at 60 ^{0}C for 12 h.

For MoS-G synthesis the whole process remain same as for MoS-C, except 20 mL precursor's solution (20 mL DI water + 1.24 mmol Na_2MoO4, $2H_2O$ + 9.92 mmol thiourea) and 60 mL (1 mg.mL^{-1}) of pre-sonicated PAH-modified GO suspension were mixed together before hydrothermal treatment.

Synthesis of MoS-GC:

A stable suspension of 15 mg PAH-modified MWCNT was mixed drop by drop in 1.0 mg.mL^{-1} (30 mL) GO aqueous dispersion under stirring and sonicated for 30 min to allow a better intercalation of individual MWCNT into the interlayer galleries of GO nanosheets; which then followed by two-step addition of 20 mL aqueous solution of Na_2MoO_4, 2 H_2O (1.24 mmol) and thiourea (9.92 mmol). Then the mixed precursor solution was heated to 230 ^{0}C in a sealed Teflon-lined autoclave and maintained at 230 ^{0}C for 24 h. The black precipitate was then collected, washed several times with DI water and ethanol. Finally, the product was collected after drying at 60 ^{0}C in a vacuum oven overnight.

Electrochemical Measurements:

Electrochemical measurements were performed with CR2032 coin-type cells in the voltage range 2.6 V-0.01 V. The working electrodes for coin cells were prepared by mixing accurately weighted as-prepared materials (MoS-GC / MoS-G / MoS-C, 75%), Super-P (C_{65}, 15%) as conductive additives, and carboxymethyle cellulose (CMC, 15%) sodium salt as a binder. The resultant slurry was painted on Cu-foil and dried at 60 ^{0}C in an air oven overnight. The typical active material loading of the negative electrodes were 1.2-1.5 mg.cm^{-2}. The cells were assembled in an Ar-filled glove box (Labstar, Mbraun, H_2O~0.5 ppm, O_2~0.5 ppm) by pressing together a nanohybride anode and Na-foil (Alfa Aesar) as reference/ counter electrode, separated by a borosilicate glass fibre (GF/D, Whatman) soaked in 1 M $NaClO_4$ in ethylene carbonate / propylene carbonate (1/1; v/v) with 5 wt % fluroethylene carbonate (FEC). The prepared cells were then aged for 6 h before any electrochemical testing to ensure good soaking of electrolyte into electrodes and separator. The galvanostatic charge- discharge tests were performed with Arbin Instrument, USA (BT 2000 model, USA) at various current rates with a potential range 2.6 V- 0.01 V (vs. Na/Na$^+$). Cyclic Voltammetry (CV) experiments were conducted by measuring *i-V* response with a potential limit of 2.6 V-0.01 V (vs. Na/ Na$^+$) at a scan rate 0.1 mV.s^{-1} using Biologic VMP-3 model, France. Electrochemical Impedance Spectroscopy (EIS) for each sample was taken at their corresponding OCV, within a frequency range of 1 MHz to 10 mHz and with a voltage amplitude ΔV= 5 mV. All electrochemical tests were measured at a constant temperature of 20 ^{0}C with control humidity.

Materials Characterization:

XRD patterns were collected on a RigakuSmartlab X-ray diffractometer equipped with Cu Kα radiation (operating voltage: 40 kV, current: 40 mA, λ=1.5418 Å). Raman spectra were detected by a WITec model Alpha 300 R with 488 nm laser excitation source. XPS spectra of MoS-GC was recorded with a SPECS spectrometerusing non-monochromatic Al Kα radiation (1486.6 eV) as an X-ray source run at 150 W (12 kV, 12.5 mA). CHN analysis was carried out with Thermo Finnigan Flash EA1112 series elemental analyser.Surface morphology of the samples was depicted by field emission scanning electron microscopy (FESEM, Carl Zeiss Ultra 55) and transmission electron microscopy (TEM, FEI TECNAI G^{2}S-Twin) operated at 300 kV. IR study was done byBruker Vertex 70 model.BET analysis was performed with Quantachrome Instruments Autosorb-1 model by degassing each sample at 100 ^{0}C for 3h. For *ex-situ* TEM analysis of cycled electrodes, the cells were first dismantled inside an Ar-filled glove box. The electrodes were then washed with dimethyl carbonate (DMC) to remove $NaClO_4$ salt and kept inside glove box for 12 h. After complete drying, the samples were scraped from electrodes and dispersed in IPA followed by ultrasonication.

in-situ TEM experimental setting: The open half-cell is constructed in an electrical probing TEM holder (Nanofactory Instrument AB). This holder has a dual-probe design, *i.e.* one Au rod is used as the sample holder with a small amount of MoS_2nanosheets attached on its tip; on the other side a STM tungsten (W) probe driven by Piezo-motor capable of 3-dimensional positioning with a step-size of 1 nm is used to mount Na metal counter electrode and a solid electrolyte of naturally grown sodium oxide and hydroxide (Na_2O+NaOH) on the Na metal. With an airtight cover, the TEM holder was transferred to TEM column with limited exposure to air (~5 s). When the Au rod was negatively biased to -3 V, sodiation for MoS_2nanosheetsoccurred. Both the TEM images and electron diffraction patterns were then recorded to monitor the structural evolution in the sodiation process.

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Materials	**Element %**		
	Carbon	**Hydrogen**	**Nitrogen**
MoS-C	**16.52**	**1.41**	**1.14**
MoS-G	**12.05**	**1.28**	**1.03**
MoS-GC	**13.23**	**1.32**	**1.05**

Fig. S1. Tabulated CHN analysis Data of MoS-C, MoS-G and MoS-GC composites.

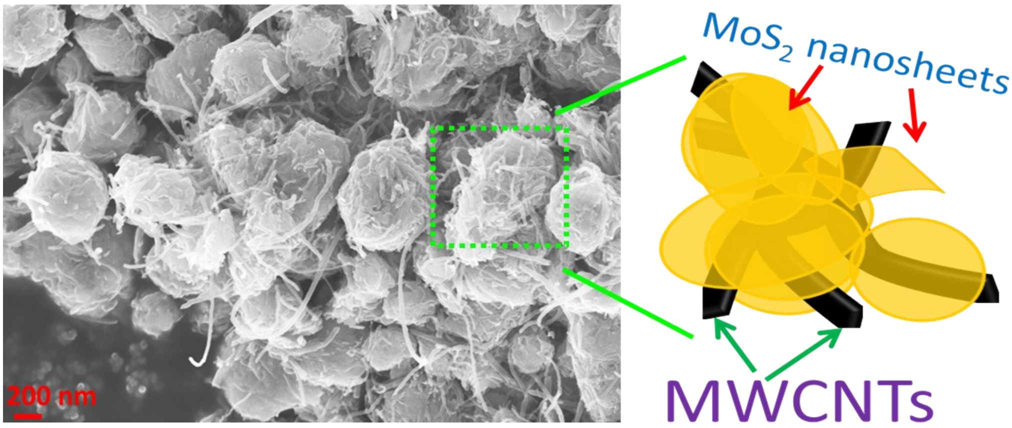


Fig. S2. FESEM image of MoS_2@MWCNT (MoS-C1) composite prepared without PAH modification of MWCNTs. With no surfactant modification, no verticle growth of MoS_2 onto MWCNT surface rather, agglomareted nanosheets lead to irregular submicron sized particles.

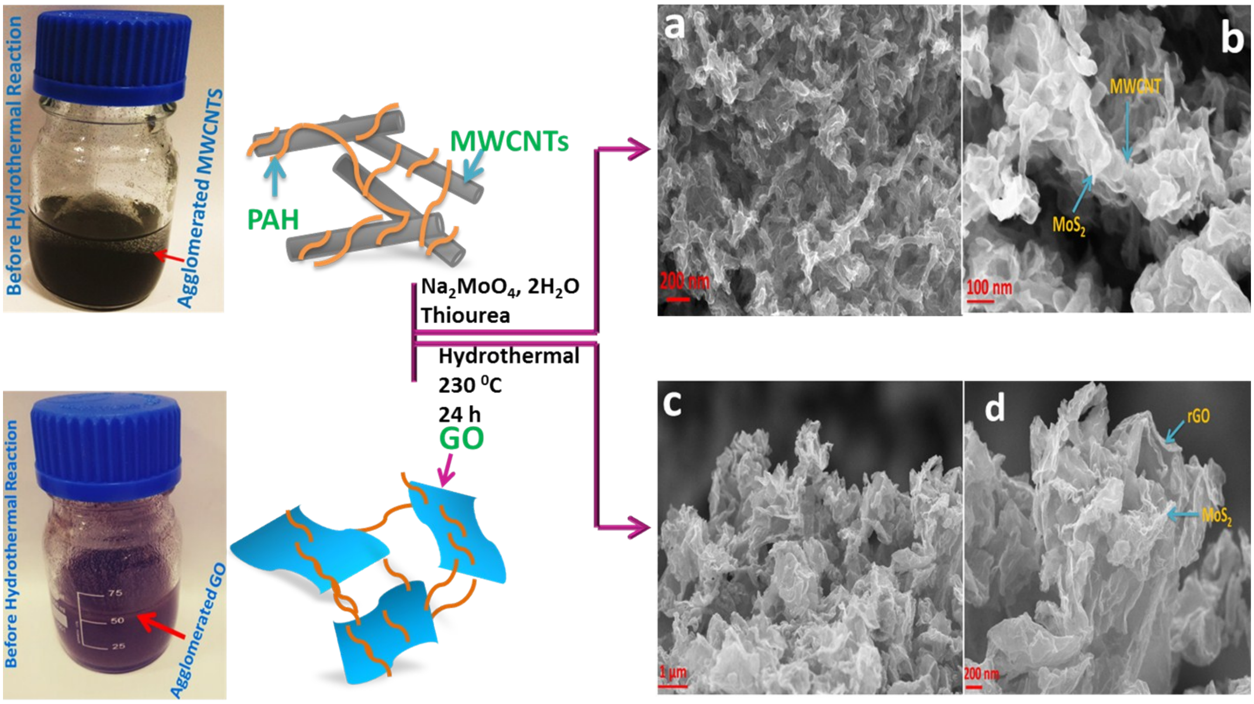


Fig. S3. FESEM images of MoS_2@MWCNT (S2a, S2b) and MoS_2@rGO (S2c, S2d) prepared by same hydrothermal method without removing excess PAH molecules from their suspension before precursors solutions are added.

In presence of excess PAH molecules in CNTs/GO suspension, due to their long-chain structure with enormous number of $–NH_3^+$ groups, they not only get adsorbed onto CNTs/GO surface, but can cross-linked number of adjascent CNTs/GO sheets leading towards bundle formation. Therefore, during hydrothermal treatment, irregular growth of MoS_2 results the agglomarated structure.

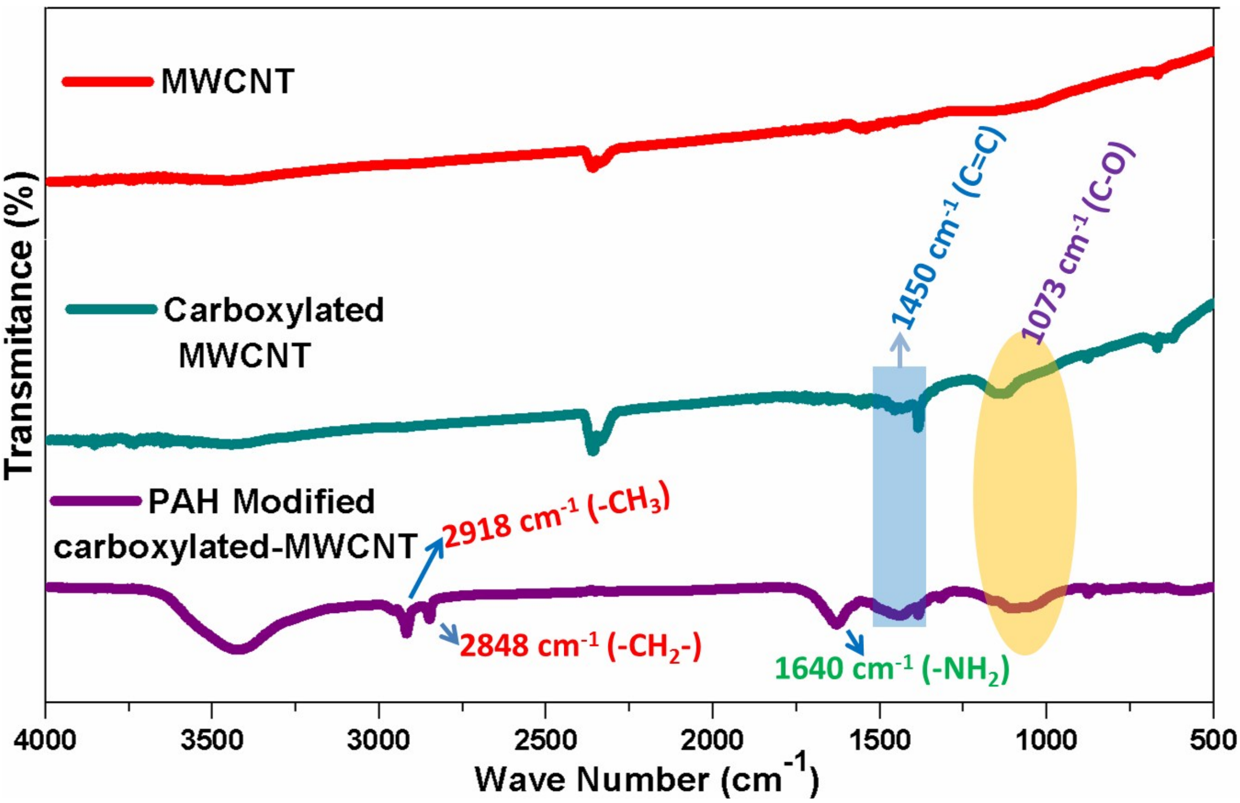


Fig. S4. FTIR spectra of MWCNT, carboxylated-MWCNT and PAH modified caboxylated-MWCNT.

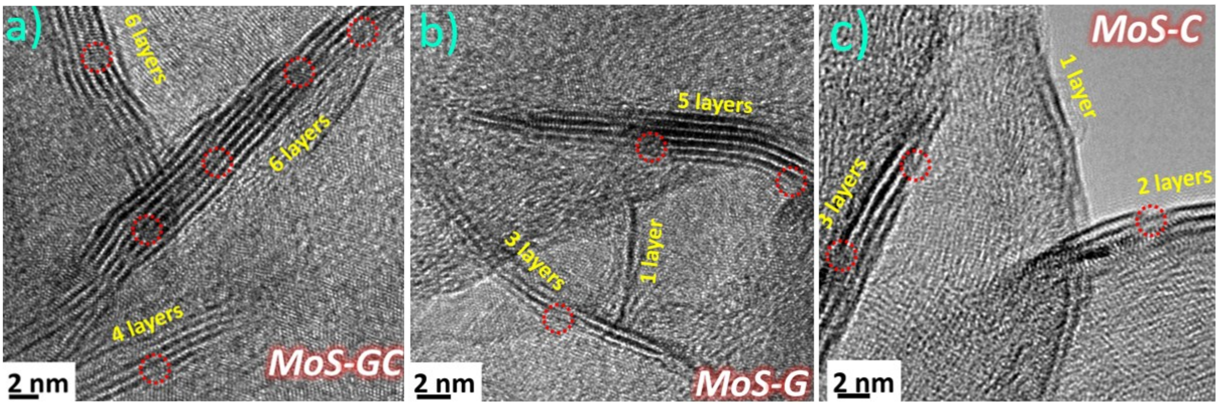
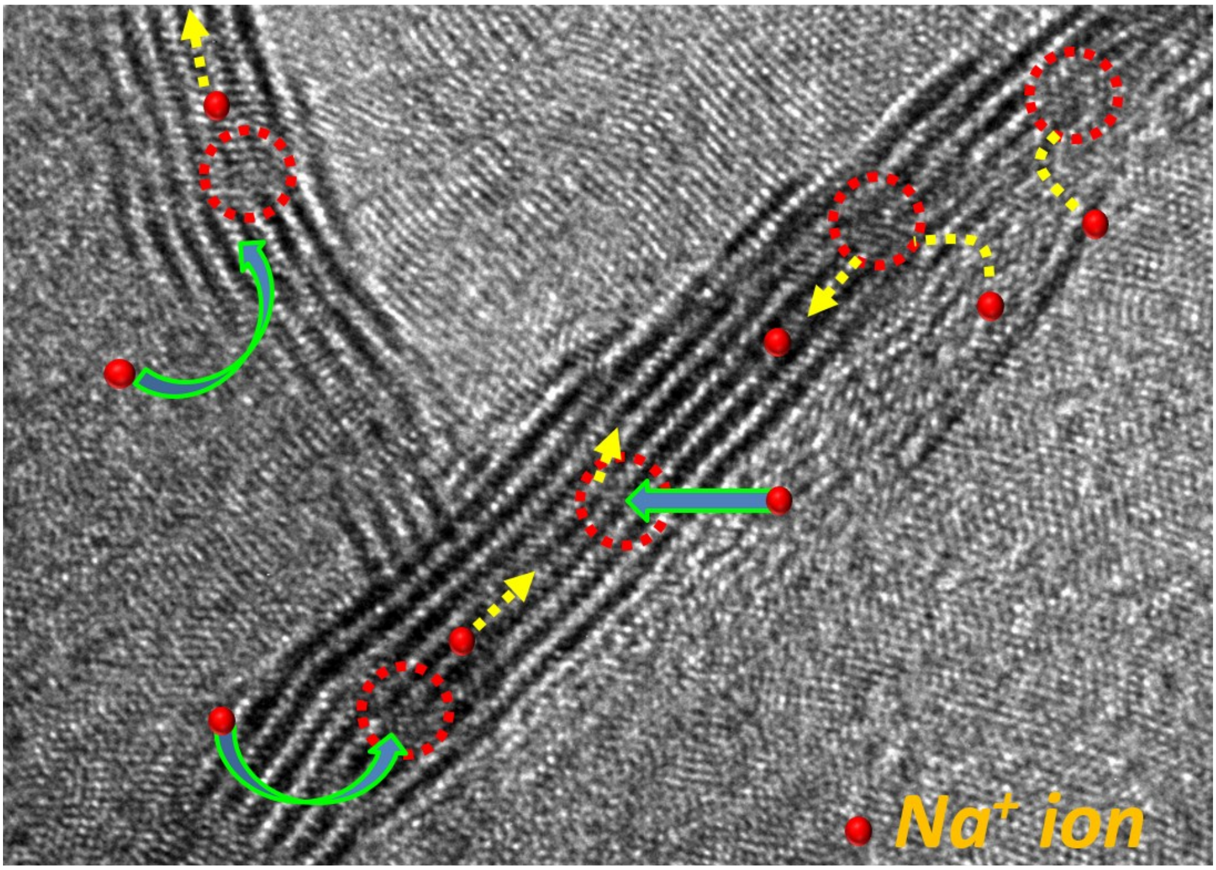


Fig. S5. HRTEM images of a) MoS-GC, b) MoS-G and c) MoS-C, showing their few-layered structure.



Advantages of having defects on MoS_2 crystal Lattice, which inceases the exposure of active edge sites and faciliates Na^+ ion diffusion thorougout MoS_2.

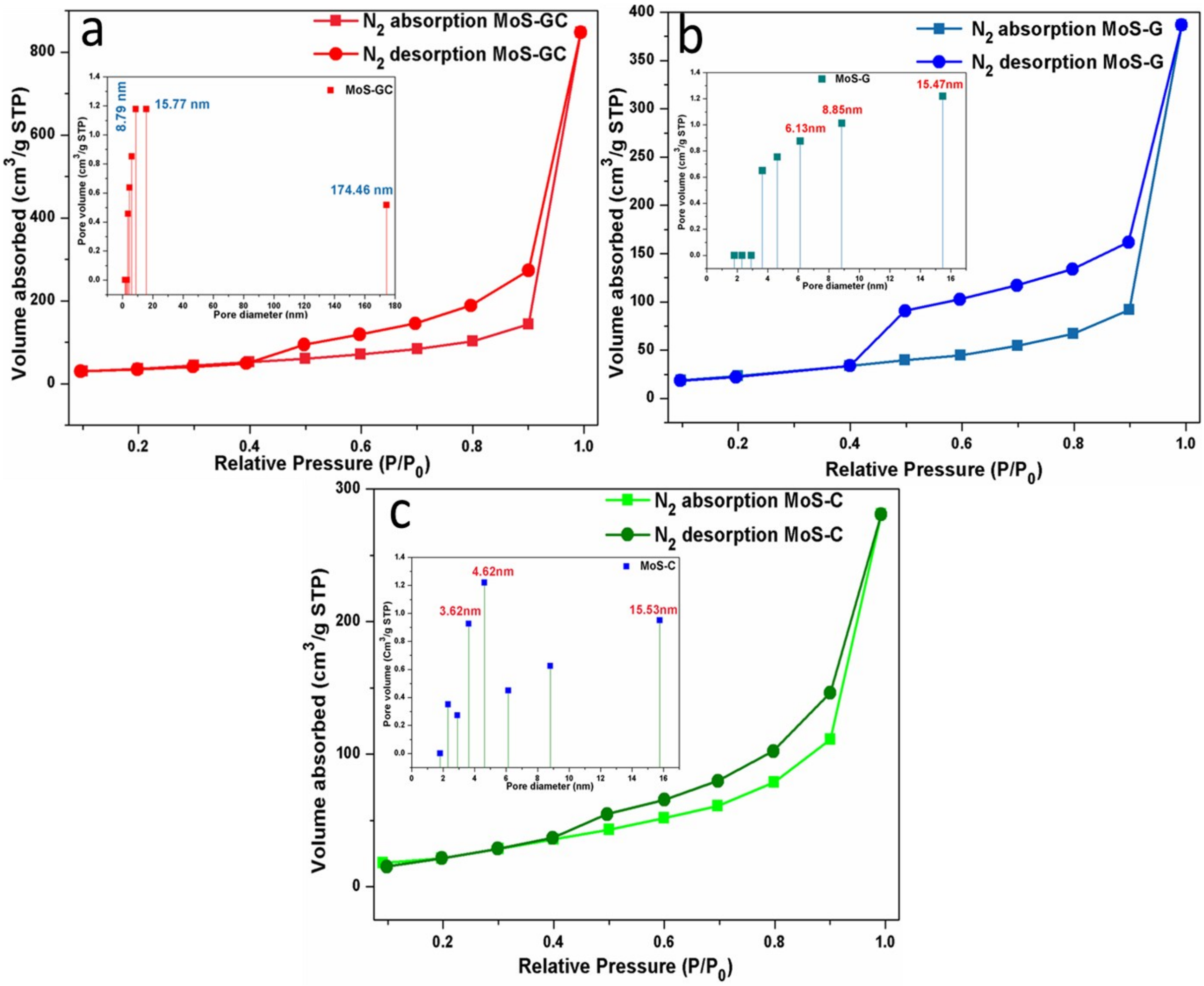


Fig. S6. N_2 adsorption-desorption isotherms and their corresponding pore size distribution patterns (in the inset) of the (a) MoS-GC, (b) MoS-G and (C) MoS-C.

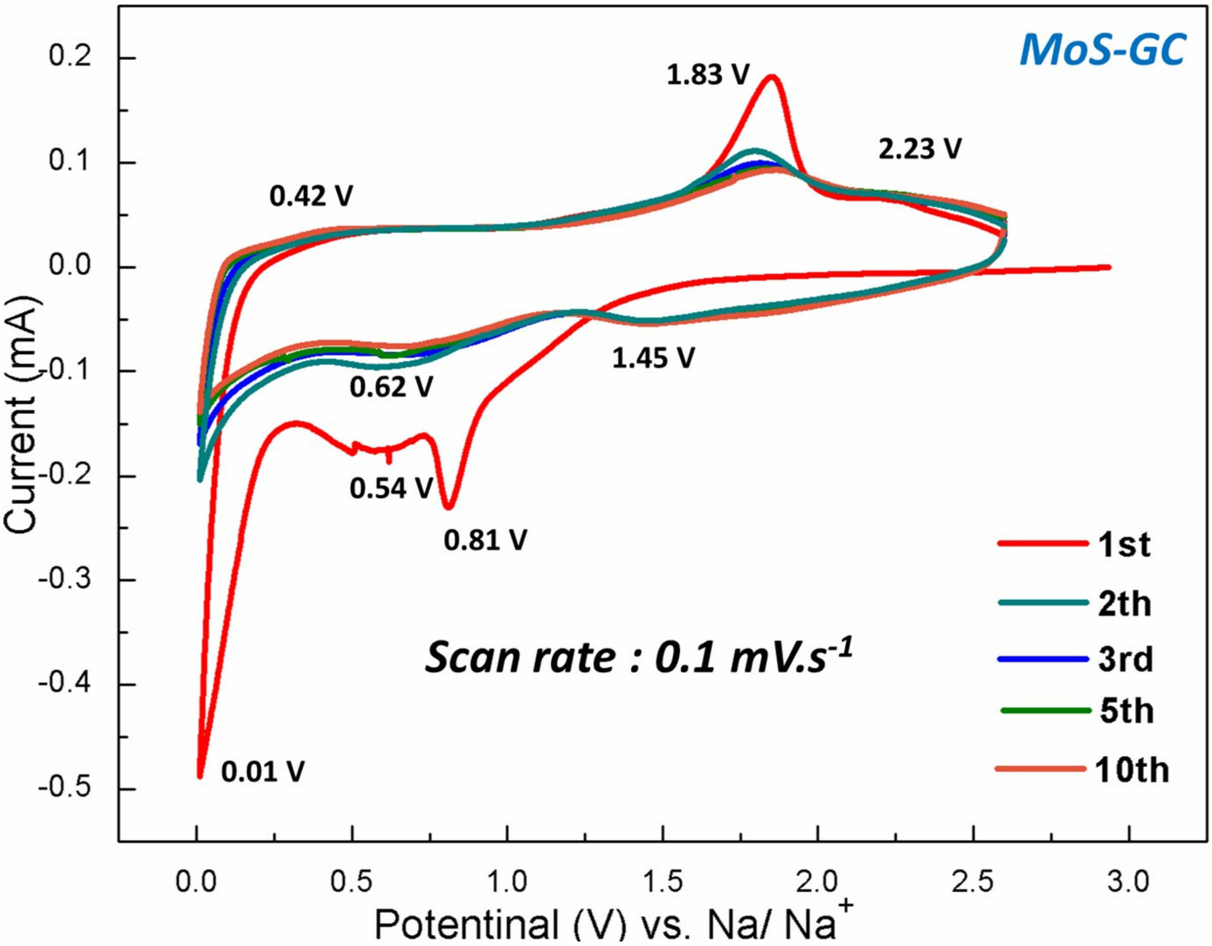


Fig. S7. Cyclic Voltammogram (CV) of MoS-GC electrode between 2.6-0.01 V with a scan rate 0.1 mV.s^{-1}.

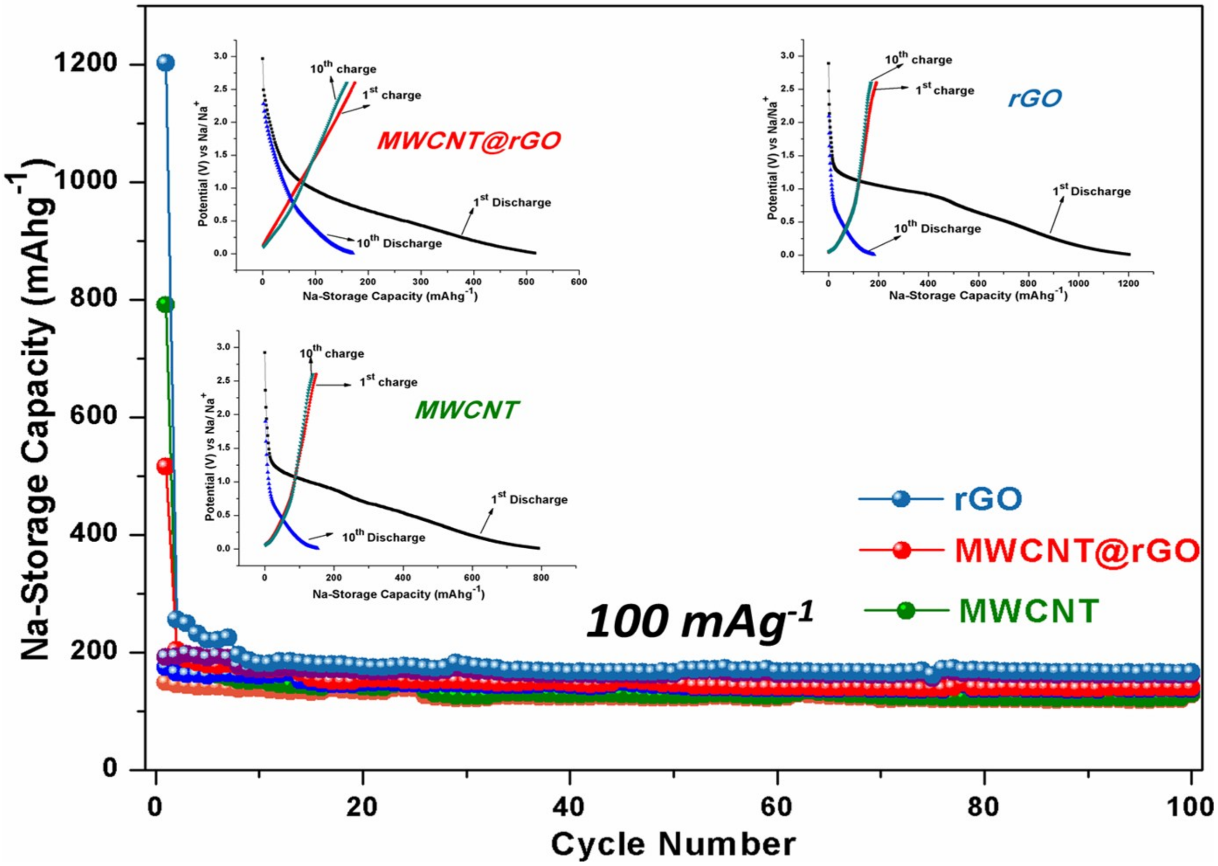


Fig. S8. Cycling performances of bare MWCNT@rGO, rGO and MWCNT electrodes at 100 mAg^{-1} within a voltage range 2.6 V-0.01 V (Inset: Galvanostatic discharge-charge profiles).

Bare rGO and MWCNT@rGO were prepared by the same hydrothermal route without adding MoS$_2$-precursors. Electrodes were fabricated by mixing 70% of MWCNT or rGO or MWCNT@rGO with 15% of SUPER-C and 15% CMC, and tested at 100 mAh^{-1} using 1 M NaClO$_4$ in EC:PC (1/1, v/v) + 5 wt% FEC, as an electrolyte. Despite of large irreversible capacity loss in first cycle rGO electrode delivers an average 179 mAhg^{-1} discharge capacity over 100 cycles. In contrast, the average discharge capacities for MWCNT and MWCNT@rGO electrode are 122 and 147 mAhg^{-1}, respectively.

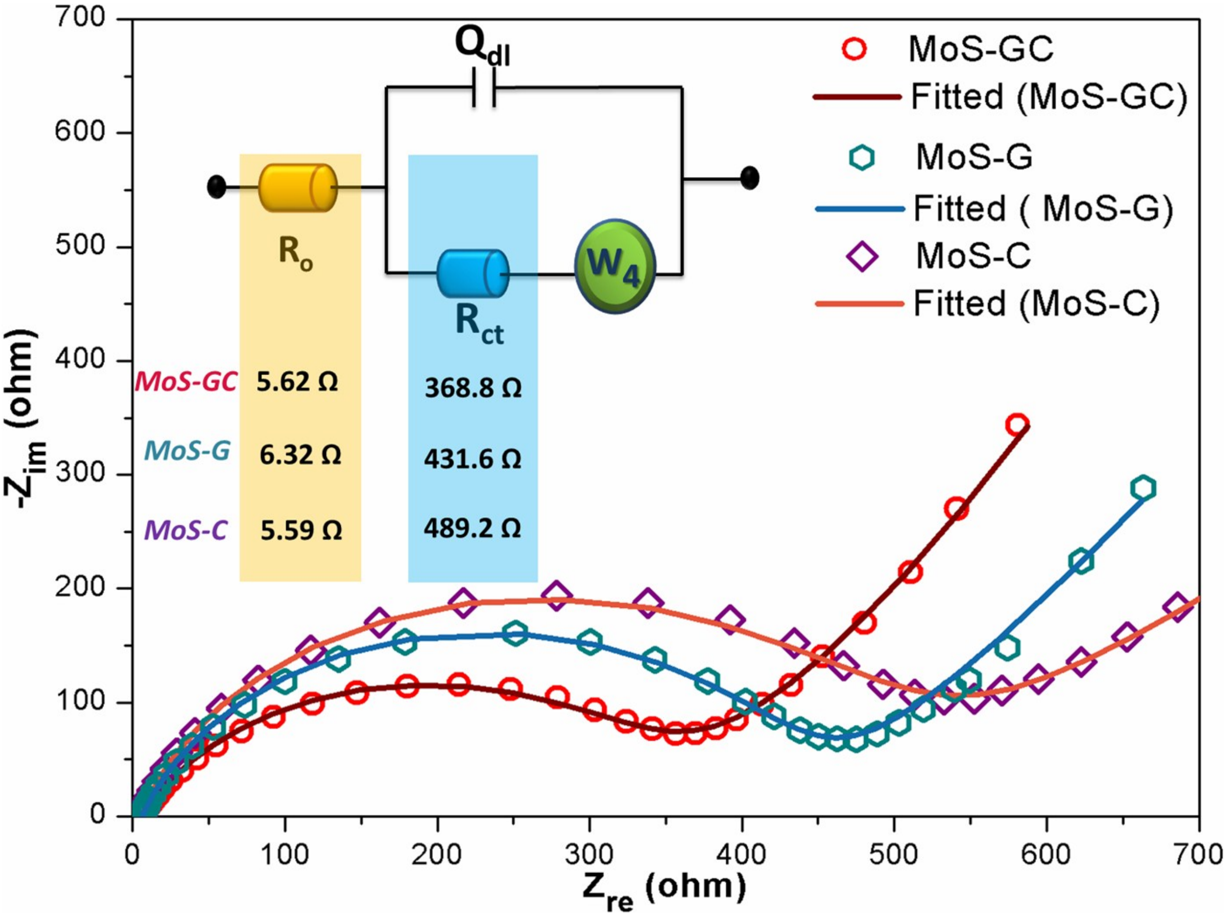


Fig. S9. The impedance spectra of (a) MoS-GC, (b) MoS-G and (c) MoS-C electrodes in the frequency range between 1 MHz to 10 mHz at 20 ^{0}C (dotted circle: experimental curve, continuous line: fitted curve, Inset: equivalent circuit, tabulated data of R_0 and R_{ct} value).

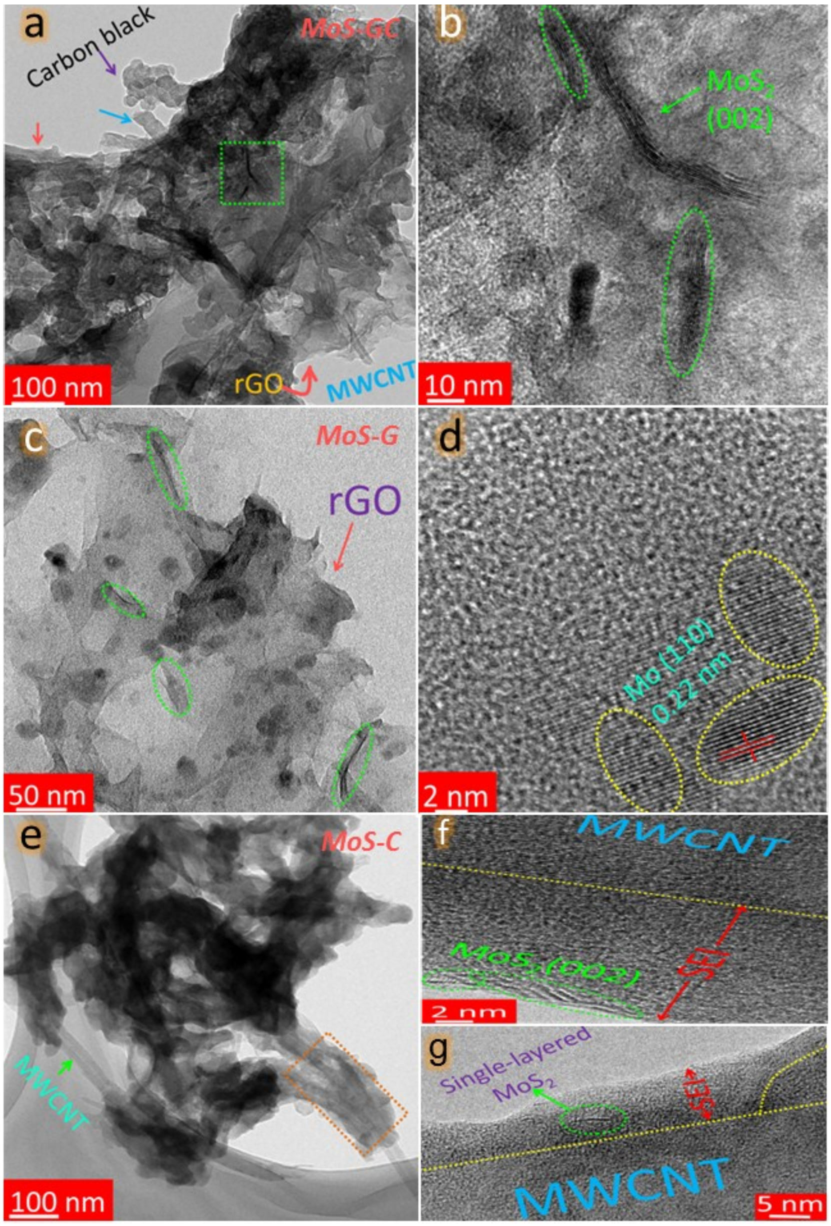
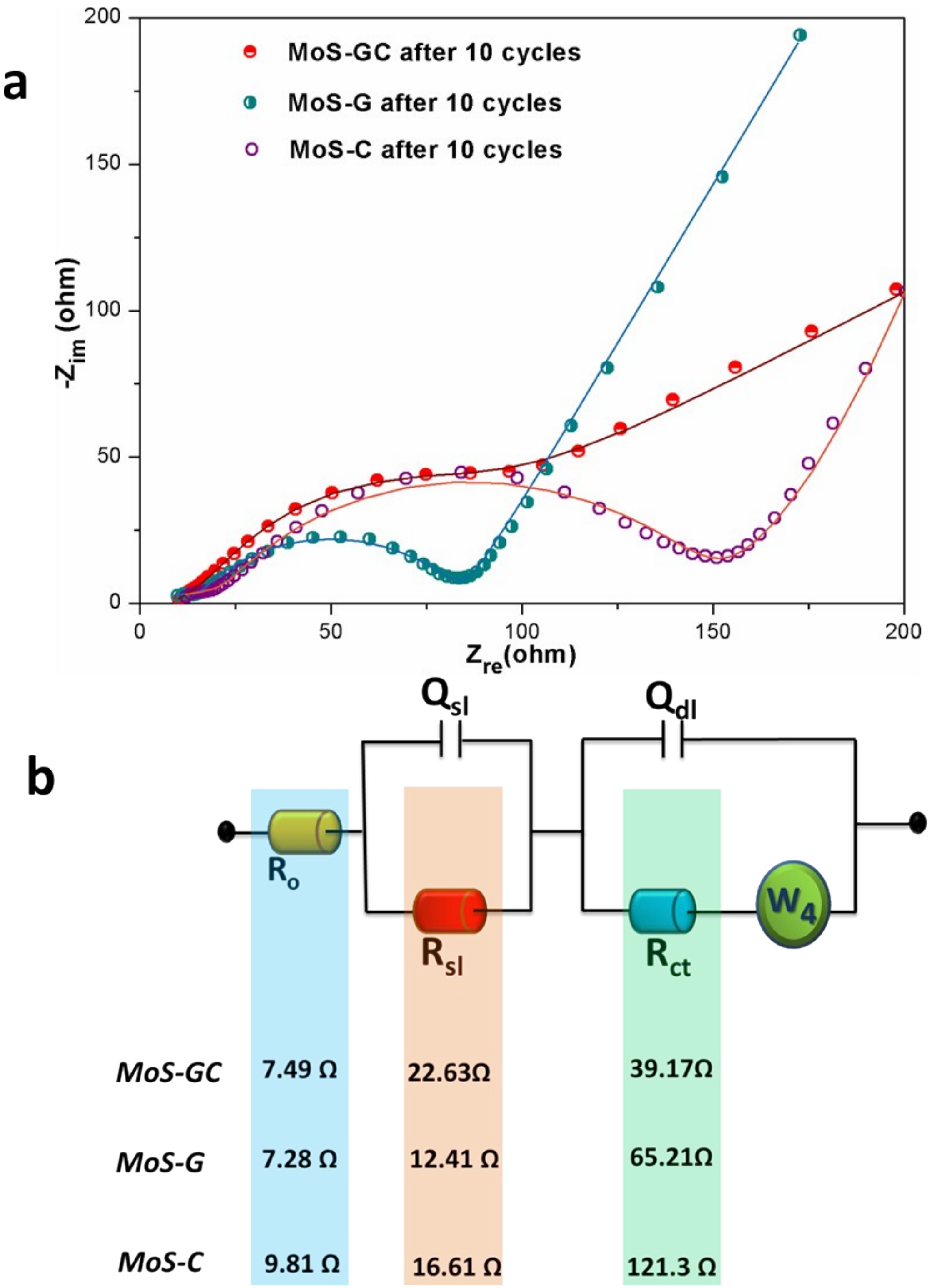


Fig. S10. TEM and HRTEM images for (a,b) MoS-GC, (c,d) MoS-G and (e-g) MoS-C electrodes after their 10th discharged-charged cycles.



	R_o	R_{sl}	R_{ct}
MoS-GC	7.49 Ω	22.63Ω	39.17Ω
MoS-G	7.28 Ω	12.41 Ω	65.21Ω
MoS-C	9.81 Ω	16.61 Ω	121.3 Ω

Fig. S11. (a) Nyquist plots of MoS-GC, MoS-G and MoS-C electrodes after 10th cycles of discharge-charge, (b) Corresponding equivalent circuit and tabulated data of ohmic resistance (R_0), SEI-resistance (R_{sl}) and charge-transfer resistance (R_{ct}) for cycled electrodes.

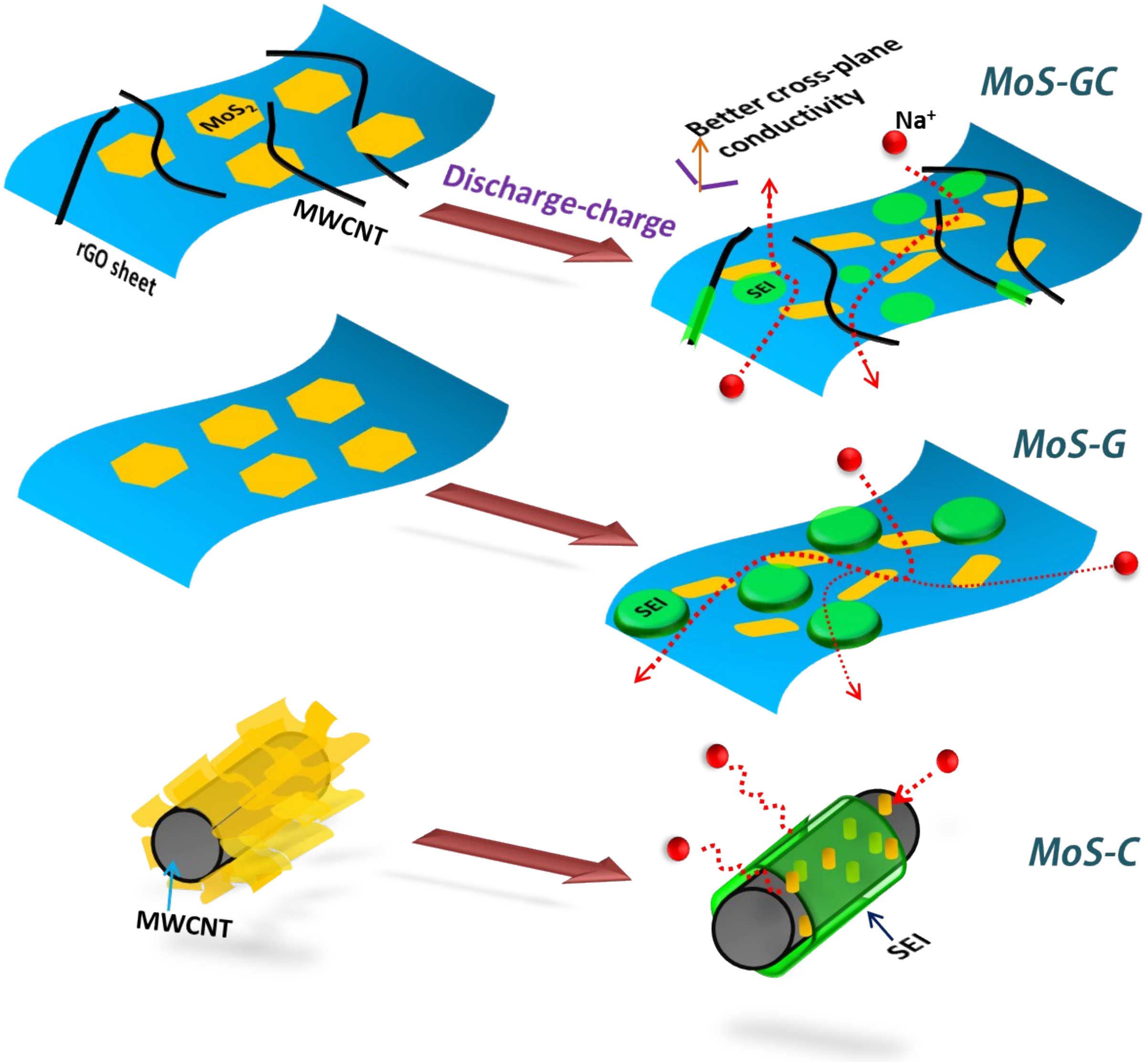


Fig. S12. Schematic illustration representing possible SEI formation and Na-ion diffusion through the active material in different composites during the course of discharge-charge.

Sr.No.	Electrodes	Voltage Range (V)	Specific Capacity (mAhg^{-1}) Current Density (mAg^{-1})				Capacity Retention(%)	Ref.
			10th Cycle	80th Cycle	250th Cycle	500th Cycle		
1	***MoS-GC***	0.01- 2.6V	640 (100) 546 (250) 520 (1 Ag^{-1}) 366 (2Ag^{-1})	685 (100) 570 (250) 472 (1Ag^{-1}) 331 (2Ag^{-1})	NA 556 (250) 435 (1Ag^{-1}) 294 (2Ag^{-1})	NA NA NA 251 (2Ag^{-1})	100 100 84 69	This Work
2	***MoS_2/Graphene***	0.01-3V	702 (20) ~305 (320)	~390 (20) ~227 (320)	NA ~186 (320)	NA	56 61	**R1**
3	***Vine-like MoS_2 nanofibers***	0.01-3V	835 (100mAg^{-1})	NA	NA	NA	86	**R2**
4	***MoS_2/nanofiber***	0.005-3V	~623 (1Ag^{-1})	~490 (1Ag^{-1})	NA	NA	79	**R3**
5	***MoS_2(Worm like)***	0.01-3 V	~480 (61.7 mAg^{-1})	~410.5 (61.7 mAg^{-1})	NA	NA	85.52	**R4**
6	***MoS_2/MWCNT***	0.001-2.5 V	537.3 (50 mAg^{-1}) 495.9 (200 mAg^{-1})	NA 410 (200 mAg-1)	NA NA	NA NA	91 84.8	**R5**

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