

Electronic Supplementary Information (ESI) for Chemical Communications

Chem. Comm.

Supporting Information:

MoS₂/MWCNT hybrid as a superior anode in lithium-ion battery

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1. Experimental

1.1 Materials

Materials

Molybdenum disulfide ($<2\ \mu\text{m}$, particle size) was purchased from Sigma Aldrich, India. Multiwalled carbon nanotubes (MWCNT) were purchased from Shenzhen Nanotech Port Co., Ltd., China. The main range diameter, length and surface area of MWCNT are 10-20 nm, 5-15 μm and 40-300 m^2/g respectively. Also the purity of MWCNT, amorphous carbon and ash content present are $\geq 95\%$, $<3\%$ and $\leq 0.2\ \text{wt}\%$ respectively, as quoted by the supplier.

1.2 Preparation of MoS₂/MWCNT Hybrids

Initially, MoS₂ and MWCNTs were weighed in appropriate amounts in the ratios of MoS₂/MWCNT (3:1, 1:1, 1:3) respectively. Subsequently, each of the mixture was physically ground in a quartz mortar-pestle for 30 minutes, the time being monitored digitally. At the end of every 5th minute, the mortar was scrapped down to ensure proper grinding of MWCNTs with MoS₂. After 30 minutes of physical grinding, the mixture was collected by scrapping the edges of mortar and retained for further analysis.

2. Characterization

The samples, thus prepared, were characterized systematically by various techniques to investigate their properties. X-ray diffractograms (XRD) of all the samples were recorded on a Phillips, the Netherlands instrument with CuK $_{\alpha}$ radiation ($\lambda = 0.1541\ \text{nm}$) in 2θ ranges of 5-70° and 14-15° with scanning rates of 3° and 0.03° per min respectively. Particle size (D) of MoS₂ and its MWCNT hybrids were calculated

according to the Scherrer's equation, microstrain (ε) and dislocation density (ρ) were also calculated as follows^{1,2}:

$$D = \frac{k\lambda}{\beta_{2\theta} \cos \theta}, \text{ where } k \text{ is taken as } 0.94, \lambda \text{ the wavelength of X ray used and } \beta_{2\theta} \text{ is the}$$

full width at half maximum of (002) peak of MoS₂ and MoS₂/MWCNT hybrids,

$$\varepsilon = \frac{\beta_{2\theta} \cos \theta}{4}, \text{ where, } \beta_{2\theta} \text{ is the full width at half maximum of (002) peak of MoS}_2 \text{ and}$$

MoS₂/MWCNT hybrids and

$$\rho = \frac{15\varepsilon}{aD}, \text{ where the value of } a = 3.15 \times 10^{-8} \text{ \AA}^\circ.$$

The degree of graphitization (g) of as received MWCNTs was calculated to be 8.14%, using Maire and Mering equation^{3,4}:

$$g = \frac{0.3440 - d_{002}}{0.3440 - 0.3354} * 100\%;$$

Where, 0.3440 is the interlayer spacing of the fully non-graphitized carbon (nm), 0.3354 is the interlayer spacing of the ideal graphite crystallite and d_{002} is the interlayer spacing of MWCNTs calculated using Bragg equation from XRD pattern.

Field Emission scanning electron micrographs (FESEM) were recorded on a Zeiss scanning microscope on Carl Zeiss Supra 40 instrument at an accelerating voltage of 20kV, at various magnifications. Further morphological analyses of the samples were carried out by tunneling electron microscopy (TEM) on TECNAI G², SEI (Netherland) instrument operating at 200 kV. Raman analysis was carried out at room temperature on a Renishaw invia Raman microscope equipped with an argon-ion laser at an excitation wavelength of 514.5 nm.

Electrochemical properties of the prepared composites were evaluated in 2032 type coin cells vs Li/Li⁺ in an argon filled glove box (M'BRAUN, Germany). A typical electrode was prepared from a slurry of the composite powder (75 wt%), acetylene black (15 wt%) and PVDF binder (10 wt%) in n-methyl pyrrolidinone (NMP) solvent. The slurry was coated onto a 15 µm thick copper foil (current collector) and dried at 110°C in an oven for 12 h. After pressing the coated foil at 4.0 ton inch⁻², circular disks of 16.3 mm in diameter were cut and used as electrode. Typical weight of the active material (excluding acetylene black and PVDF) was 3-5 mg. 2032 type coin cells were assembled with these electrodes using Li metal as counter as well as reference electrode, LiPF₆ in EC: DMC (1:2 vol%) as electrolyte and Celgard 2300 as separator within an argon filled glove box (M'BRAUN, Germany) where the moisture and oxygen levels were both kept below 1.0 ppm. Gavanostatic charge-discharge measurements were carried out using an automatic battery tester (Model: BT2000, Arbin, USA) in the potential window of 0.01-3.0 V with constant current densities ranging from 100 mA g⁻¹ to 500 mA g⁻¹. Throughout the measurements, same current density was used for both charge and discharge. Cyclic voltammetry of the cells was carried out by a galvanostat-potentiostat (Model: PGSTAT 30, Autolab, the Netherlands) between 0.01 and 3.0 V at a scanning rate of 0.2 mVs⁻¹. In this paper, specific capacities were defined as the values per unit weight of active materials (both MoS₂ and CNT); discharge refers to the lithiation process of MoS₂ and charge refers to the corresponding de-lithiation process.

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Additional Supporting Data

Table S1. Particle size (D), microstrain (ϵ) and dislocation density (ρ) data for MoS₂ and its MWCNT hybrids.

Sample	D (nm)	ϵ	ρ (cm ⁻²)
MoS ₂	76.4	4.46x10 ⁻⁴	2.7x10 ¹⁰
MoS ₂ /MWCNT (1:3)	36.8	9.43x10 ⁻⁴	12.2x10 ¹⁰
MoS ₂ /MWCNT (1:1)	31.3	1.09x10 ⁻³	16.5x10 ¹⁰
MoS ₂ /MWCNT (3:1)	44.4	7.68x10 ⁻⁴	8.26x10 ¹⁰

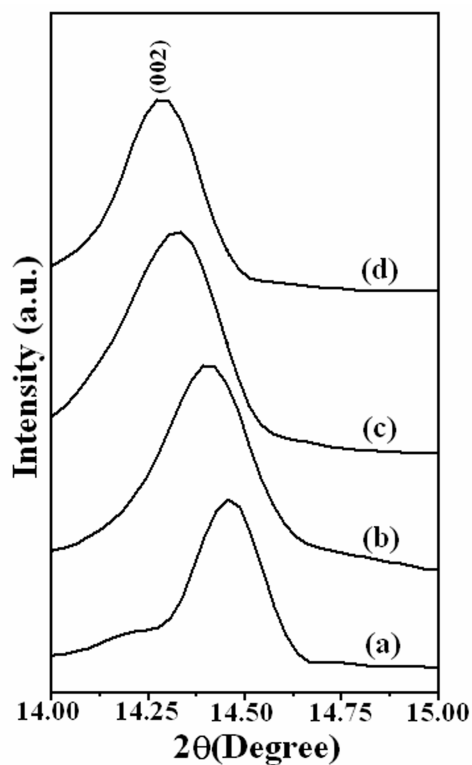


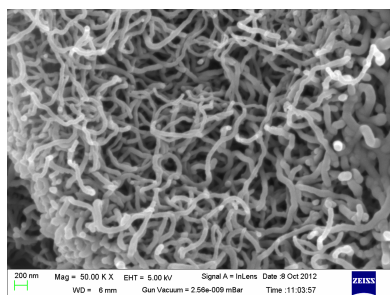
Fig. S1 Slow scan XRD patterns of (a) MoS₂, (b) MoS₂/MWCNT (3:1), (c) MoS₂/MWCNT (1:1) and (d) MoS₂/MWCNT (1:3). A gradual shifting of the peak maximum to lower 2θ is observed indicating an interaction between MoS₂ and MWCNT.⁵ Furthermore, it is also noted that the peaks are asymmetric in the hybrids, as they rise more steeply on the low angle side than on the high angle side.⁶ Such behaviour could be attributed to the presence of pronounced layer disorder in MoS₂/MWCNT hybrids with respect to pristine MoS₂.⁷ Imperfection of the crystallite as a result of lattice strain, dislocation and stacking faults are also known to contribute towards the broadening of X-ray diffraction peak of CNT/MoS₂ hybrids. Our calculation in Table S1

show that MoS₂/MWCNT (1:1) has lowest crystallite size, the highest microstrain and dislocation density.

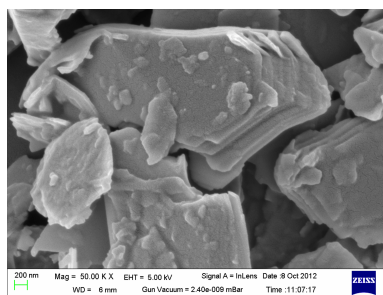
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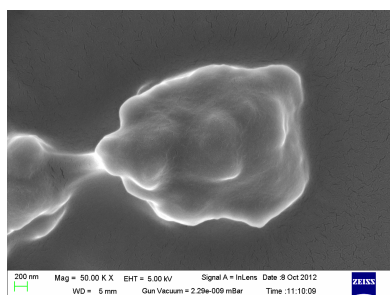
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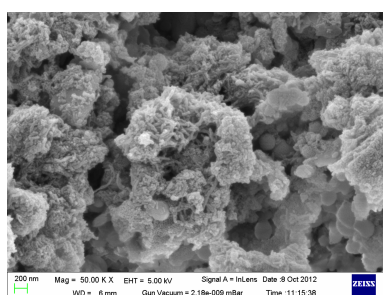
(a)



(b)



(c)



(d)

Fig. S2 FESEM images of (a) MWCNT, (b) MoS₂, (c) MoS₂/MWCNT (3:1) and (d) MoS₂/MWCNT (1:3).

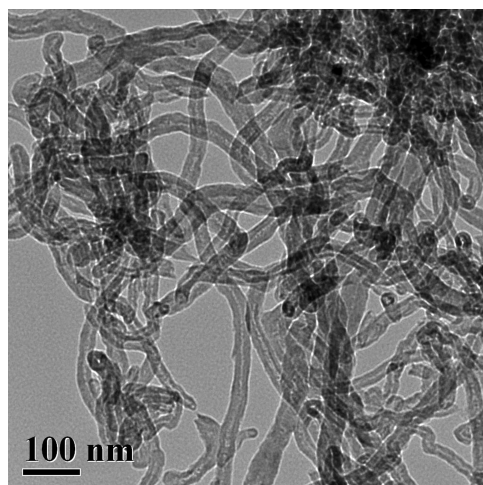


Fig. S3 HRTEM image of MWCNT.

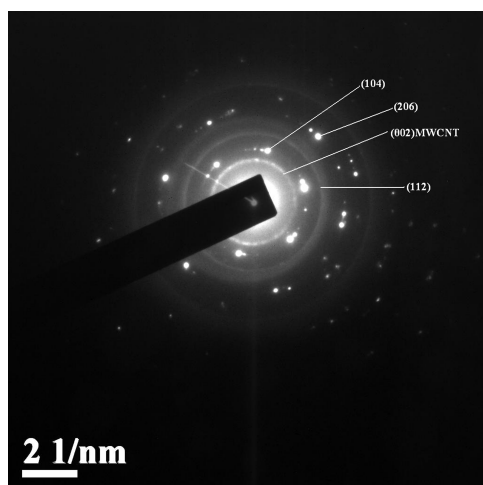


Fig. S4 SAED pattern of MoS₂/MWCNT (1:1) hybrid.

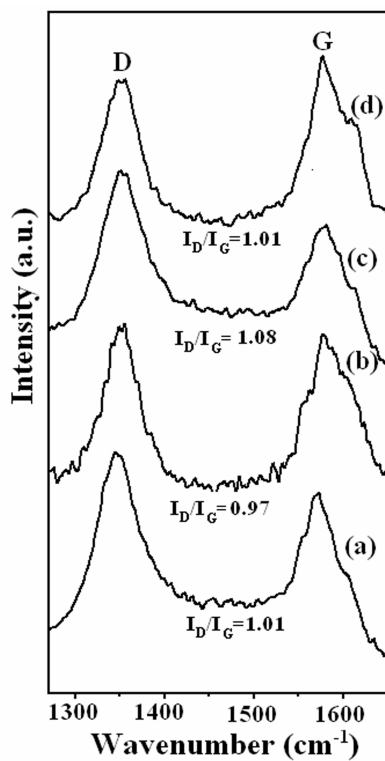


Fig. S5 Raman spectra of (a) MWCNT, (b) MoS₂/MWCNT (3:1), (c) MoS₂/MWCNT (1:1) and (d) MoS₂/MWCNT (1:3).

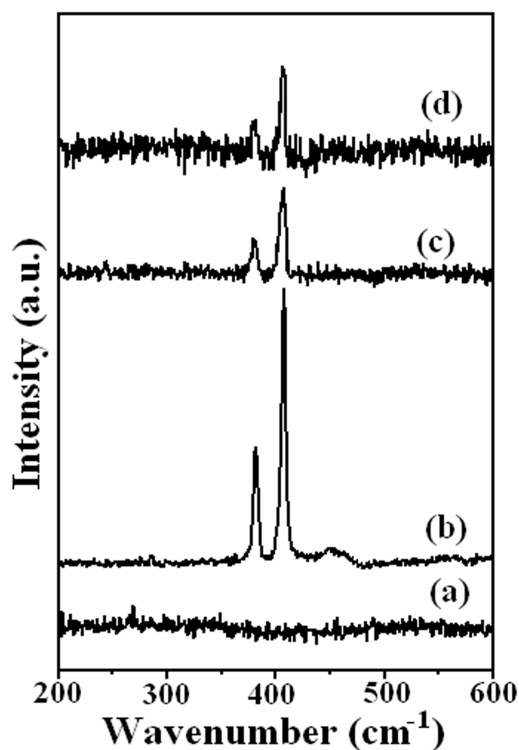


Fig. S6 Raman spectra of (a) MWCNT, (b) MoS₂/MWCNT (3:1), (c) MoS₂/MWCNT (1:1) and (d) MoS₂/MWCNT (1:3). Two sharp peaks appear at ~380 and 407 cm⁻¹ in case of MoS₂:MWCNT (3:1) hybrid and matched well with the literature. These are attributed to E_{2g}¹ and A_g¹ modes of hexagonal MoS₂ corresponding to in-layer displacements of Mo and S atoms and out of layer displacements of S atoms along the c-axis respectively.^{8,9} It is also observed that the intensity of these peak decreases .with increasing MoS₂:MWCNT ratio. This is in all probability due to the destruction in crystalline structure of MoS₂ on grinding with MWCNT.⁵

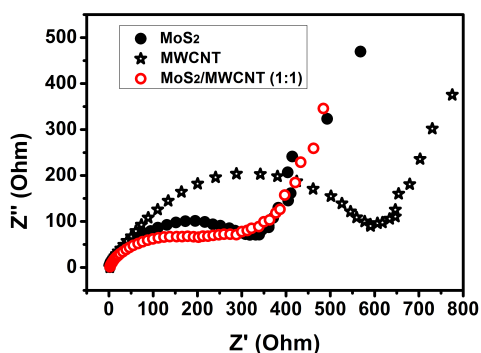
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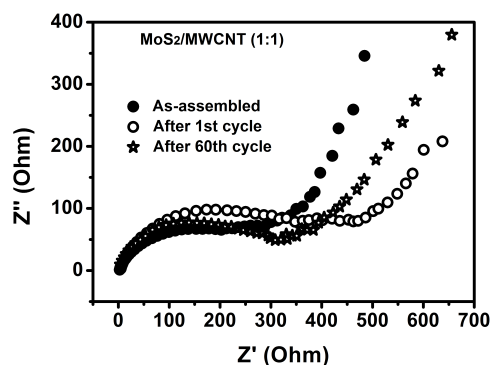
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7. Electrochemical impedance spectroscopy measurements

Electrochemical impedance spectroscopy measurements have been carried out in the frequency range of 10 mHz to 1 MHz using a galvanostat-potentiostat equipped with FRA (Model PGSTAT 30, Autolab, The Netherlands).



(a)



(b)

(a) Impedance spectra of MoS₂, MWCNT and MoS₂/MWCNT (1:1) hybrid in the as-assembled state and (b) Impedance spectra of MoS₂/MWCNT (1:1) hybrid at various stages: as-assembled, after the 1st cycle and after 60th cycle.

In general, the spectra show a depressed semicircle in the high and intermediate frequency region and sharp Warburg impedance at the low frequency region. Impedance data have been fitted using a Randles-like equivalent circuit model and the fitted values are given in the table below:

Sample	State	R_s (Ohm)	R_{ct} (Ohm)	W (Ohm)	CPE (μF)
MoS ₂	As-assembled	2.70	315	242	20
MWCNT	As-assembled	2.10	534	295	12
MoS ₂ /MWCNT (1:1)	As-assembled	2.66	234	215	19
MoS ₂ /MWCNT (1:1)	After 1 st discharge/charge	2.84	316	221	12
MoS ₂ /MWCNT (1:1)	After 60 th discharge/charge	4.06	320	251	20

It is observed that, in the as-assembled state, the electrolyte resistance (R_s) is similar for MoS₂, MWCNT and MoS₂/MWCNT (1:1) hybrid and the constant phase element (CPE) remains in the range of 12-20 μF . But, the charge-transfer resistance (R_{ct}) is the lowest for MoS₂/MWCNT (1:1) hybrid indicating a low kinetic polarization. Also, the results for and MoS₂/MWCNT (1:1) hybrid in various states shows only a slight rise in R_s and R_{ct} even after 60 discharge-charge cycles. Thus, the impedance data further supports the superior performance of and MoS₂/MWCNT (1:1) hybrid compared to either MoS₂ or MWCNT.