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Supporting Information

α $MnMoO_4$/Graphene Hybrid Composite: High Energy Density Supercapacitor Electrode Material

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Materials used

Manganese chloride ($MnCl_2$), sodium molybdate dihydrate (Na_2MoO_4, $2H_2O$), sodium sulphate (Na_2SO_4), polyvinylidene difluoride, and N-Methylpyrrolidone were purchased from E. Merck Ltd. India. Nafion was purchased from Aldrich. Carbon black was obtained from Loba chemie, India. The GC electrode used was of 6 mm outer diameter and 3 mm inner diameter. All the chemicals were used as received without any further purification.

Characterizations

Morphological characterizations were carried out in terms of FESEM, SEM and TEM analyses by using Carl Zeiss-SUPRATM 40, Vega\\Tescan and TECNAI G2-20S-TWIN, respectively. For FESEM analysis the samples were sonicated in acetone and drop casted on an aluminum foil. For SEM analysis as prepared samples were used. A thin layer of gold was sputtered on the materials before FESEM and SEM analysis. The materials were well dispersed in acetone via sonication and then a drop was placed on a copper grid and dried before the TEM analysis. The electrochemical characterizations were carried out using Biologic sp-150 VMP-3 instrument with a three electrode system, where materials fabricated glassy carbon electrode was used as working electrode, Platinum electrode was used as counter electrode and a saturate calomel electrode was used as the reference electrode. The materials were well dispersed in 1.5% nafion solution in ethanol and then the slurry was attached to the GC surface carefully and vacuum dried

prior use. The AC electrical conductivity was measured using HIOKI 3532-50 LCR HI TESTER by applying an alternating electric field of 1volt amplitude. The DC electrical conductivity was measured using four point probe method with the disk type electrodes with thickness of 1.5 mm, 1.4 mm and 0.5 mm for the graphene, $MnMoO_4$ and Gr-$MnMoO_4$ (II), respectively prepared at 4×10^4 kg pressure. The crystallinity of the $MnMoO_4$ and all three Gr-$MnMoO_4$ composites was confirmed by the XRD analysis using Rigaku difractometer with a Cu Kα radiation (λ =1.54056 Å). A Renishaw Raman microscope equipped with a He−Ne laser excitation source at an excitation wavelength of 632.8 nm was used for the Raman characterization. FTIR analysis was carried out performed by IR spectrometer (NEXUS 870, Thermo Nicolet). Sample and KBr in a weight ratio of about 10:1 was mixed thoroughly and was pelletized for FTIR analysis. BET analysis was carried out using Quanta chrome autosorb instrument.

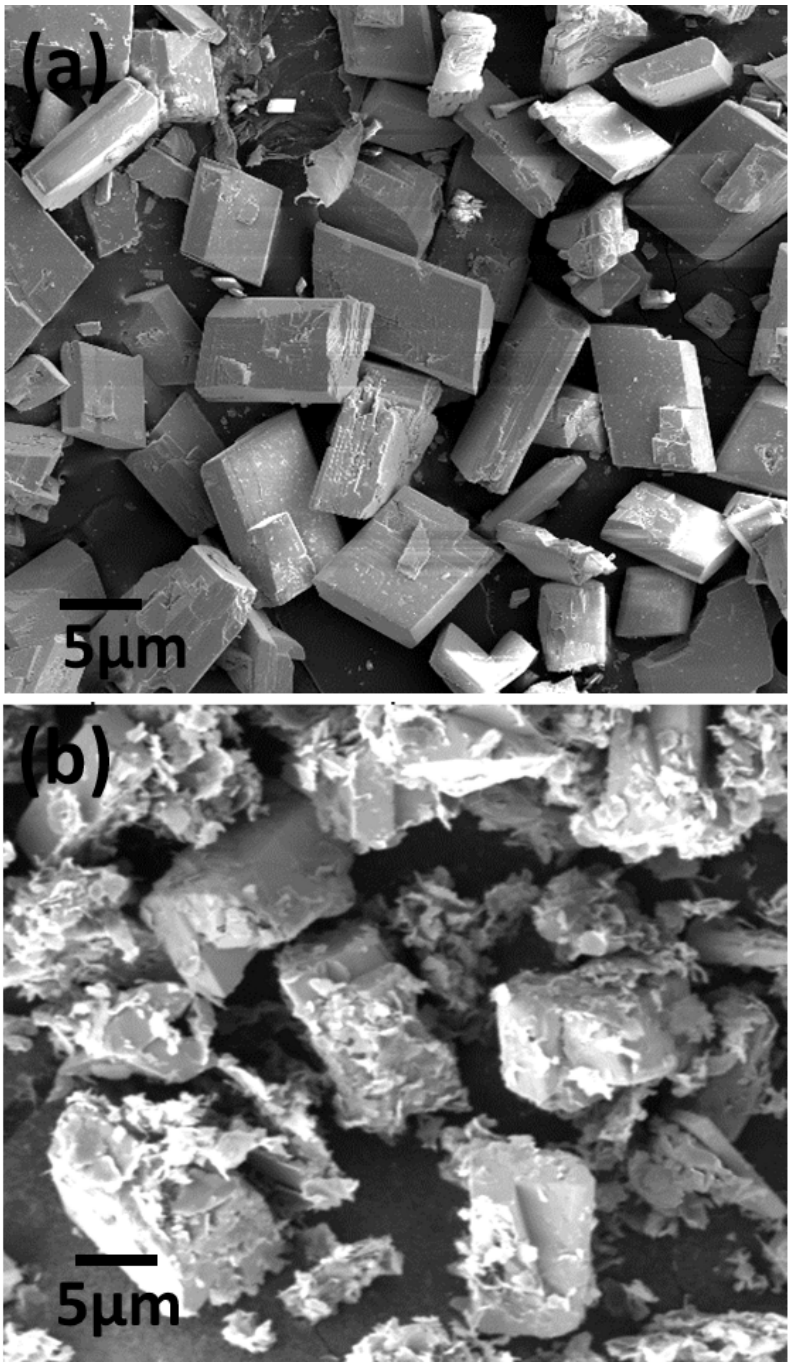

Fig. S1 SEM image of (a) $MnMoO_4$ and (b) Gr-$MnMoO_4$ (II).

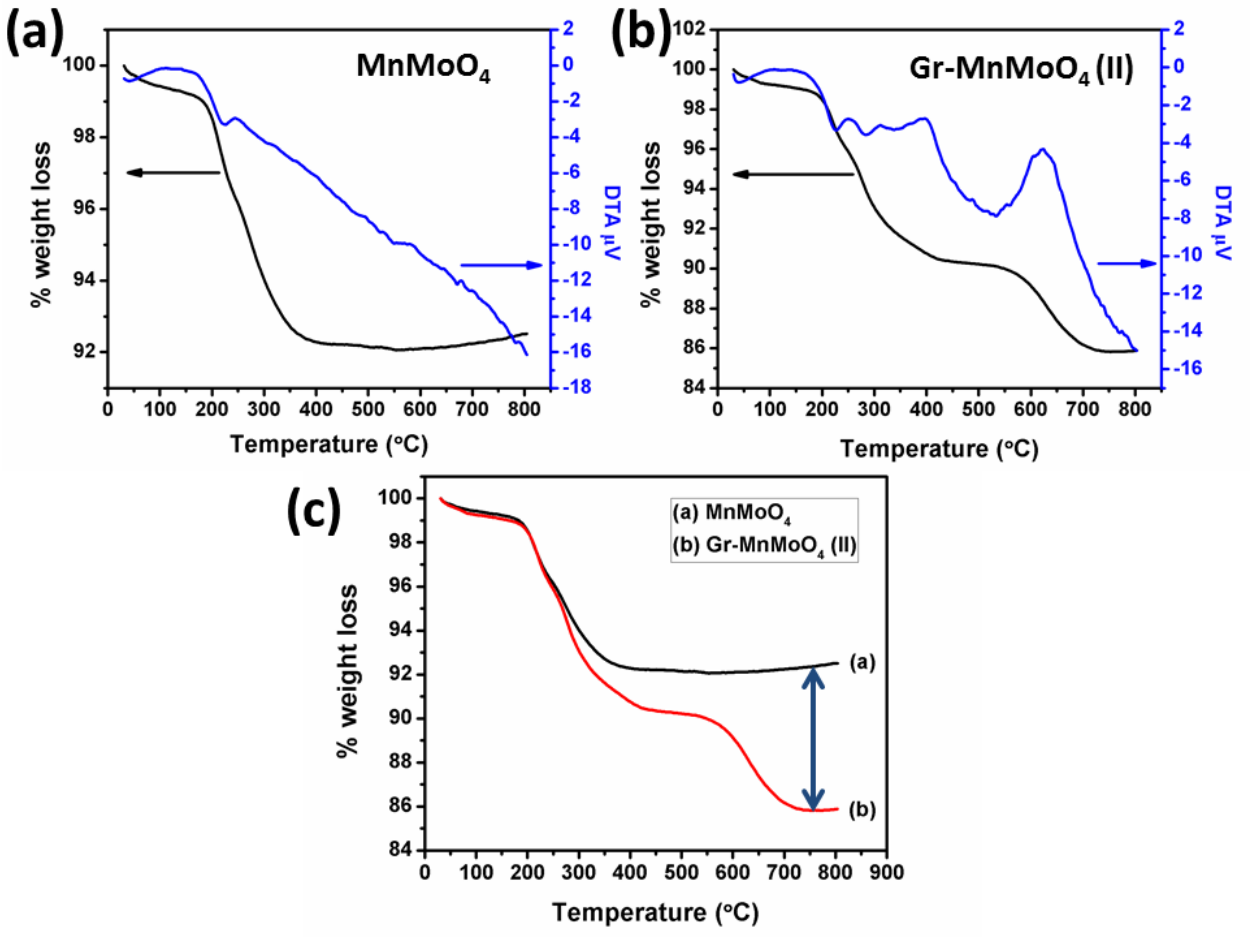

Fig. S2 TG DTA plots of (a) $MnMoO_4$, (b) Gr-$MnMoO_4$ (II) and (c) the comparative TGA plot of $MnMoO_4$ and Gr-$MnMoO_4$ (II) within the temperature range of 30°C-800°C.

The TGA plot exhibits that the thermal stability of the Gr-$MnMoO_4$ (II) is 6.66% lower than that of virgin $MnMoO_4$. So the % of graphene content in the Gr-$MnMoO_4$ (II) composite was determined to be 6.66% in the Gr-$MnMoO_4$ (II) composite.

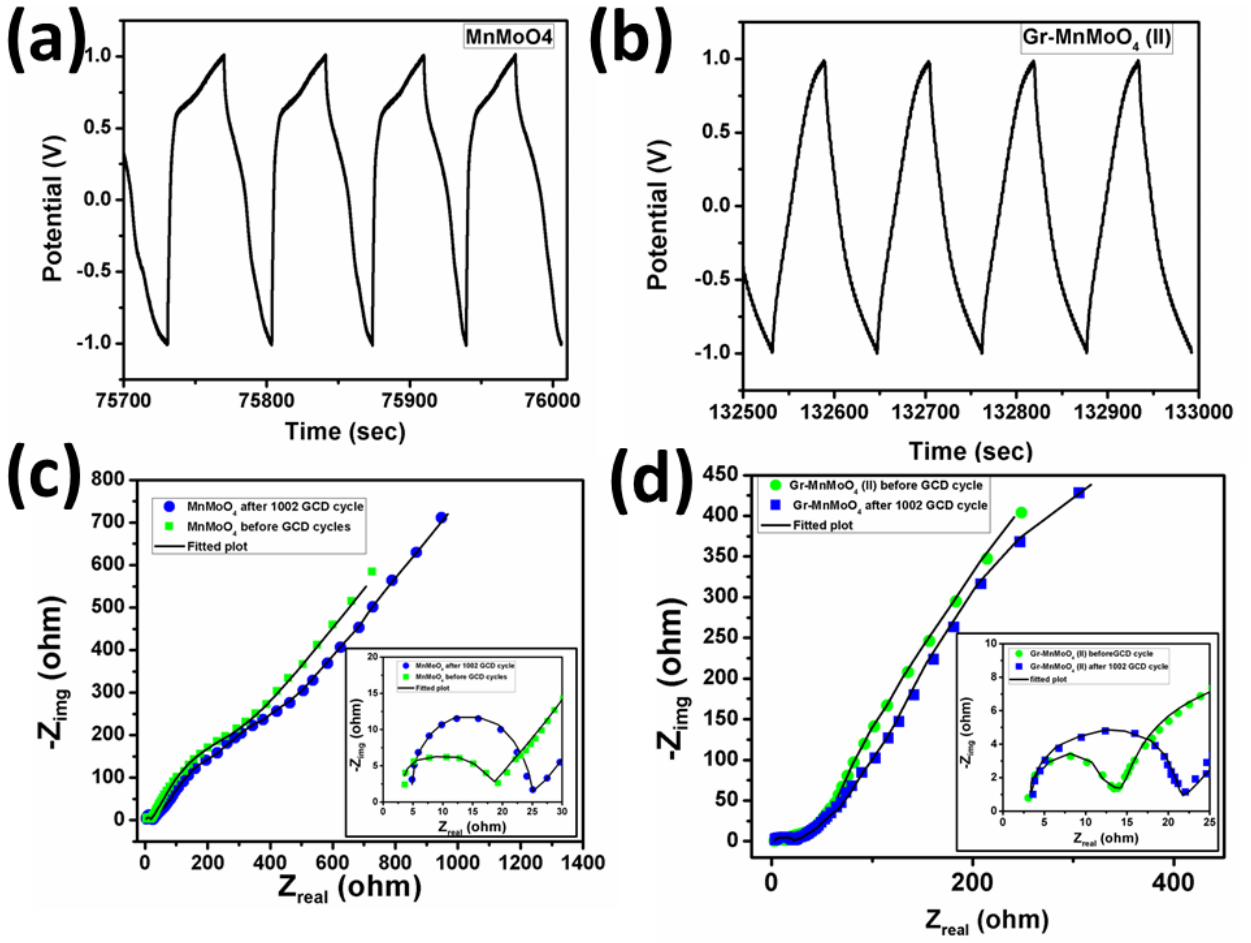

Fig. S3 indicates the last 4 GCD cycles (998th to 1002) of the $MnMoO_4$ (a) and Gr-$MnMoO_4$ (II) at a current density of 8 A/g, (b) and their respective EIS plot in terms of Nyquist plot before and after the 1002 GCD cycles in (c) and (d).

The linear nature of the GCD plot of Gr-$MnMoO_4$ (II) even after 1000 cycles indicates its excellent reversibility. An increased charge transfer resistance of 20.29 ohm and 18.33 ohm was achieved from the fitting plot. The specific capacitance calculated from the EIS plot after the GCD cycles was 173 F/g and 288 F/g for the $MnMoO_4$ and Gr-$MnMoO_4$ (II), respectively.

To validate the claim of the device fabrication of the Gr-$MnMoO_4$ (II) composite electrode and its superiority over $MnMoO_4$ electrode, the CV and the GCD tests were repeated at a high mass loading on (1.5×4 cm^2) Ni foam current collector. Material, carbon black, and polyvinylidene difluoride in a weight ratio of 80:10:10 were taken and a paste was made in 0.3 ml N-Methylpyrrolidone and the paste was coated over Ni foam and dried. The mass of the $MnMoO_4$ and Gr-$MnMoO_4$ (II) active material was calculated to be 15.2 mg and 15 mg, respectively. The CV plots of the $MnMoO_4$ and Gr-$MnMoO_4$ (II) at different scan rate of 5, 10, 30 and 50 mV/s is shown in Fig S4 (a) and (b), respectively. The slight difference in the peak positioning can be attributed to the variation of internal resistance. The almost mirror image current response of the CV plot of Gr-$MnMoO_4$ (II) during the positive and negative voltage sweep justify its excellent reversibility. The various specific capacitance obtained from the CV plot is shown in Table S1. The GCD plot of the $MnMoO_4$ and Gr-$MnMoO_4$ (II) at various current density of 2, 4,

6 and 8 A/g is shown in Fig. S4 (c) and (d), respectively. The various specific capacitances obtained for the $MnMoO_4$ and Gr-$MnMoO_4$ (II) at different current density is shown in Table S2. The specific capacitance value obtained with high mass loading using Ni foam current collector and with low mass loading using GC electrode are quite comparable. The maximum energy density of 131.66 and 206.66 Wh/kg was obtained at power delivery rate of 2000 W/kg. At the end of 1000 GCD cycle at 8A/g current density specific capacitance retention of 85.44 and 89.34% was achieved for $MnMoO_4$ and Gr-$MnMoO_4$ (II), respectively. All these results well justify the superiority of the Gr-$MnMoO_4$ (II) as electrode material for supercapacitor application.

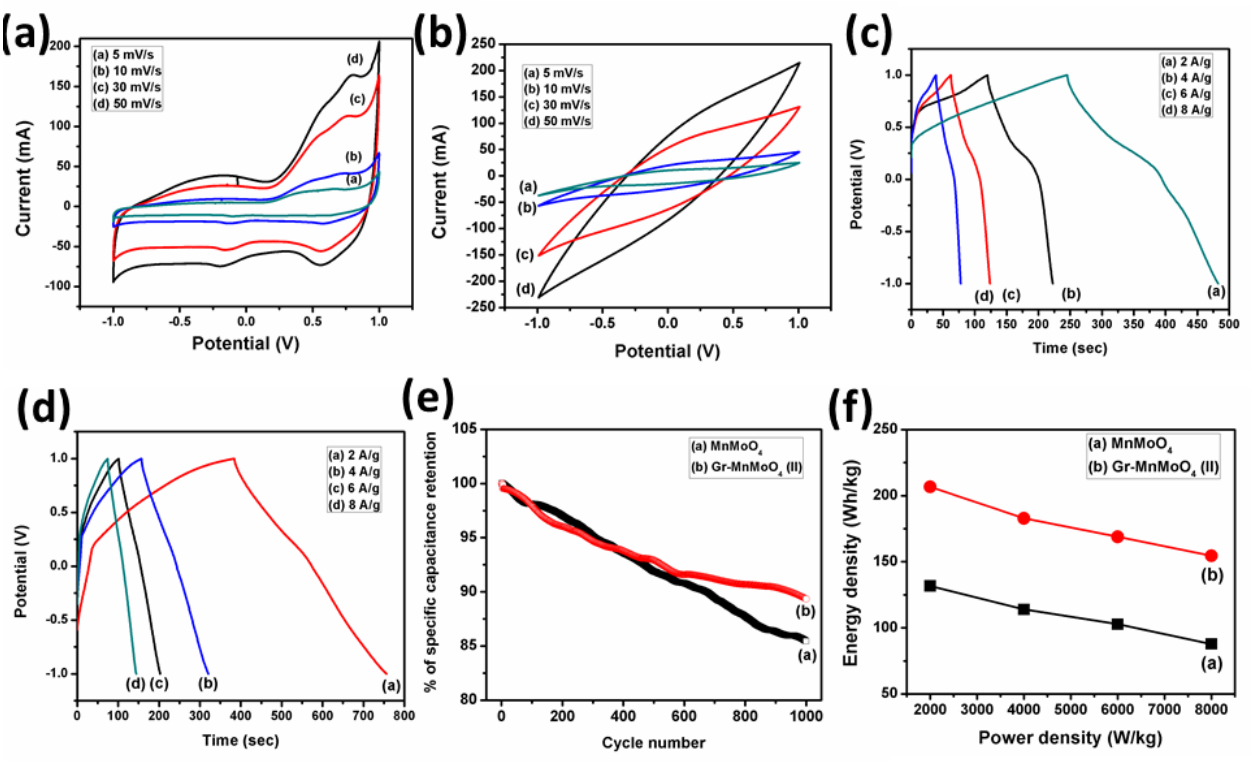

Fig. S4 CV plot of (a) $MnMoO_4$ and (b) Gr-$MnMoO_4$ (II) at various scan rate of 5, 10, 30 and 50 mV/s; GCD plot of (c) $MnMoO_4$ and (d) Gr-$MnMoO_4$ (II) at various current density of 2, 4, 6 and 8 A/g; (e) % of specific capacitance retention with cycle number and (f) variation of energy density with power density of $MnMoO_4$ and Gr-$MnMoO_4$ (II) electrode.

Table S1. Various specific capacitances obtained from $MnMoO_4$ and Gr-$MnMoO_4$ (II) composites at different scan rate.

Scan rate (mV/s)	5	10	30	50
SC of $MnMoO_4$ (F/g)	276	237	206	169
SC of Gr-$MnMoO_4$ (II) (F/g)	409	362	335	312

Table S2. Various specific capacitances obtained from $MnMoO_4$ and Gr-$MnMoO_4$ (II) composites at different current densities.

Current density (A/g)	2	4	6	8
SC of $MnMoO_4$ (F/g)	237	205	185	158
SC of Gr-$MnMoO_4$ (II) (F/g)	372	329	304	278