***Electronic Supplementary Information (ESI)***

# ‘Graphene-$MnO_2$’ Composite Supercapacitor Material accomplished tactically by using Liquid-Liquid and Solid-Liquid Interface Reaction Techniques.

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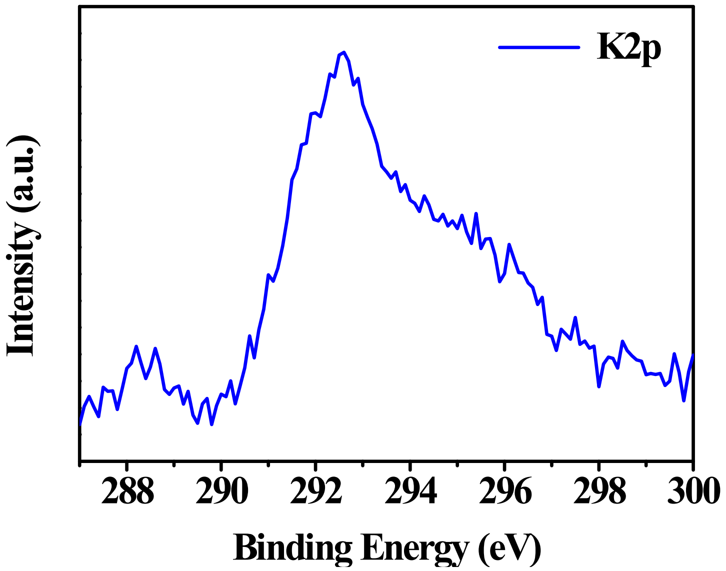


Fig. S1: XPS spectra for K2p of the composite GNS-$MnO_2$.

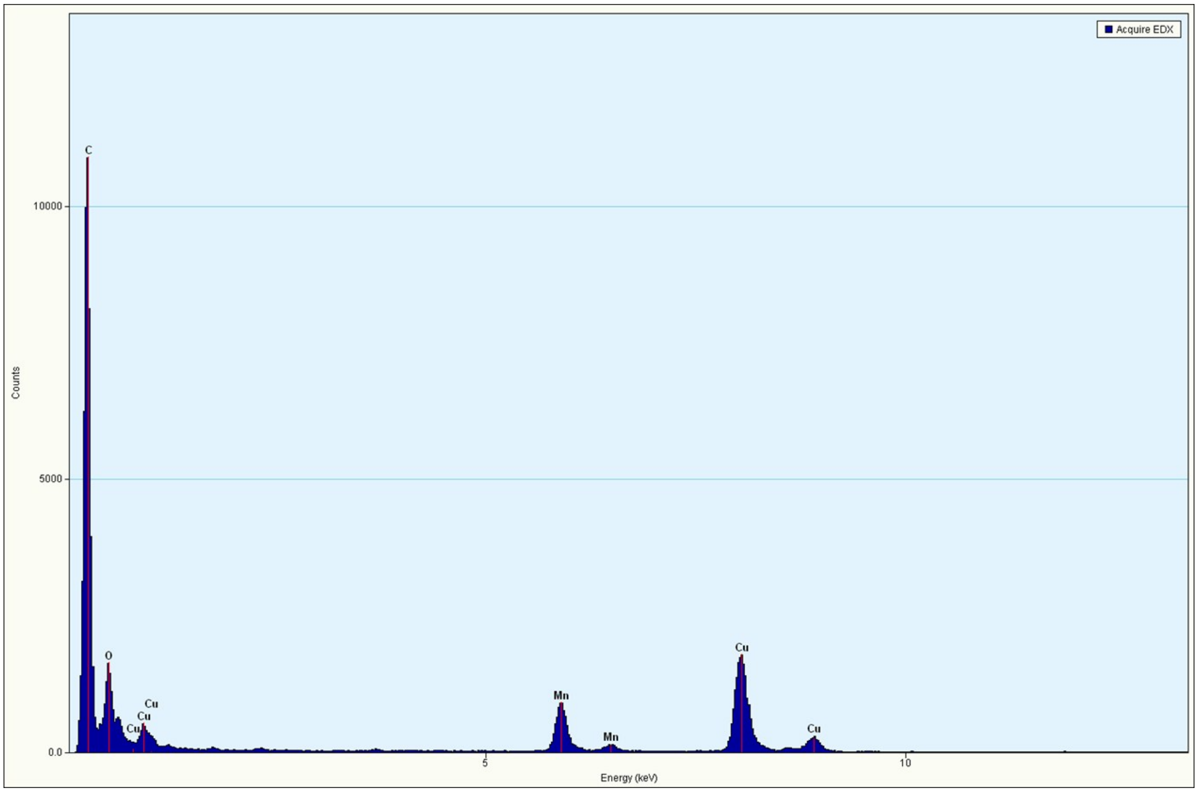


Fig. S2 : EDX taken on a GNS-MnO2 composite surface drop casted on Cu grid in TEM analysis.

| Peak | Integrated Intensity | Uncertainty |
|---|---|---|
| C-K | 36018.400 | 3750.180 |
| O-K | 4965.135 | 1720.000 |
| Mn-K | 6247.000 | 1717.020 |

Input FWHM = 134 eV @ 5.9 keV
Measured FWHM = 134.000 eV @ 5.9 keV
Calibration: 20.0000 eV/ch, 0.006719 eV at channel 0
Accelerating voltage: 200 kV
Alpha tilt: 18 degrees

***Quantification Results***
Correction method: None

| Element | Weight % | Atomic % | Uncert. % | Detector Correction | k-Factor |
|---|---|---|---|---|---|
| C(K) | 73.72 | 89.23 | 0.45 | 0.26 | 3.94 |
| O(K) | 6.7 | 6.09 | 0.09 | 0.49 | 1.974 |
| Mn(K) | 5.28 | 1.39 | 0.06 | 0.99 | 1.375 |

**Table S1:** Composition of GNS-$MnO_2$ by EDX quantitative analysis.

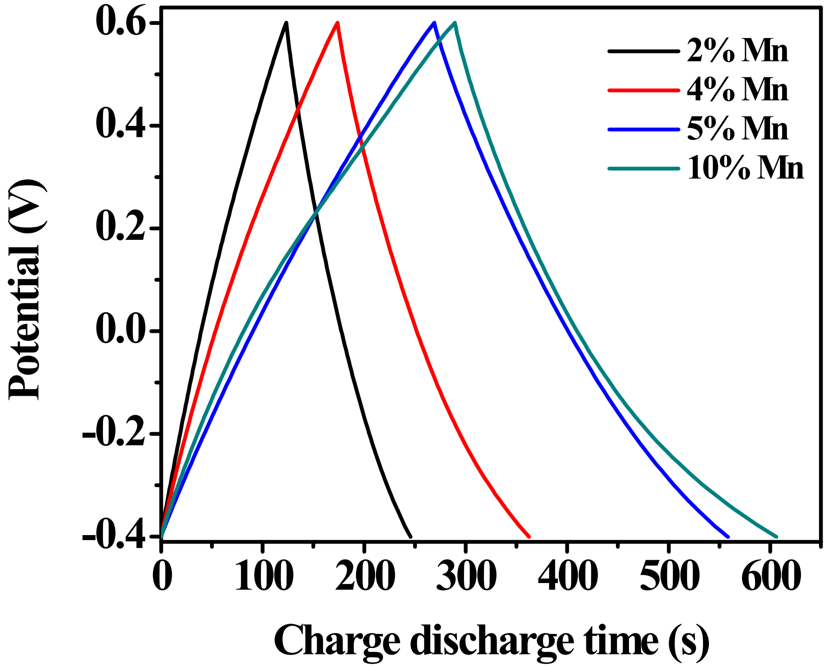


**Fig. S3:** Galvanostatic charge-discharge curves obtained for GNS-$MnO_2$ composite with varying Mn content by weight %.

The corresponding concentration of KMnO4 during experiment were $4\times10^{-4}$ M, $8\times10^{-4}$, $1\times10^{-3}$ and $0.5\times10^{-2}$ M for 2%, 4%, 5% and 10% Mn respectively with a SD = ±0.2%.

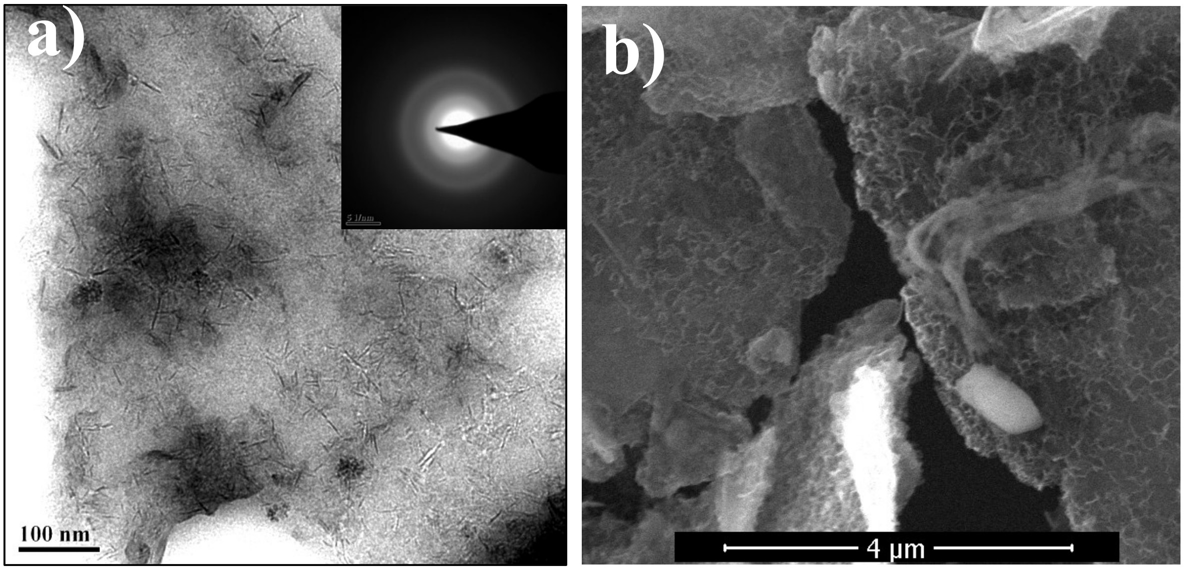


**Fig.S4** a) TEM image and b) FESEM image of GNS-$MnO_2$ electrode after the 5000 cycles of charge discharge.

| GNS | | $MnO_2$ | | GNS-$MnO_2$ | |
|---|---|---|---|---|---|
| Scan rate ($mVs^{-1}$) | Specific capacitance ($Fg^{-1}$) | Scan rate ($mVs^{-1}$) | Specific capacitance ($Fg^{-1}$) | Scan rate ($mVs^{-1}$) | Specific capacitance ($Fg^{-1}$) |
| 10 | 138 | 10 | 182 | 10 | 689 |
| 20 | 123 | 20 | 162 | 20 | 653 |
| 50 | 110 | 50 | 140 | 50 | 583 |
| 100 | 92 | 100 | 127 | 100 | 551 |
| 150 | 80 | 150 | 115 | 150 | 524 |
| 200 | 73 | 200 | 105 | 200 | 505 |
| Retention% | 52.83% | Retention% | 57.69% | Retention% | 73.29% |

**Table S2**: Scan rate Vs specific capacitance for GNS/FTO, $MnO_2$/FTO and GNS-$MnO_2$/FTO composite electrodes.

| GNS | | $MnO_2$ | | GNS-$MnO_2$ | |
|---|---|---|---|---|---|
| Current (I) μA | Specific capacitance ($Fg^{-1}$) | Current (I) μA | Specific capacitance ($Fg^{-1}$) | Current (I) μA | Specific capacitance ($Fg^{-1}$) |
| 20 | 116 | 20 | 187 | 20 | 683 |
| 40 | 94 | 40 | 166 | 40 | 625 |
| 60 | 86 | 60 | 144 | 60 | 593 |
| 80 | 83 | 80 | 136 | 80 | 565 |
| 100 | 70 | 100 | 119 | 100 | 542 |
| Retention% | 60.34% | Retention% | 63.63% | Retention% | 79.35% |

**Table S3:** Applied current Vs specific capacitance for GNS/FTO, $MnO_2$/FTO and GNS-$MnO_2$/FTO composite electrodes.

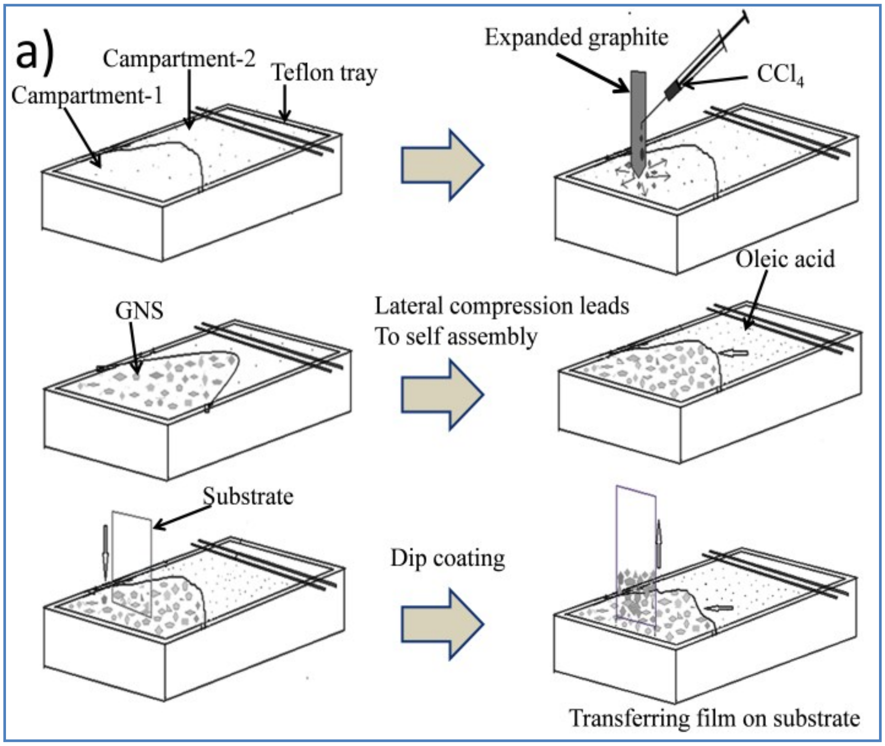
| GNS/FTO | | | $MnO_2$/FTO | | | GNS-$MnO_2$/FTO | | |
|---|---|---|---|---|---|---|---|---|
| Current (I) µA | E (Wh/kg) | P(W/kg) | Current (I) µA | E (Wh/kg) | P(W/kg) | Current (I) µA | E (Wh/kg) | P(W/kg) |
| 20 | 16.04 | 1443 | 20 | 25.97 | 1279 | 20 | 94.2 | 1318 |
| 40 | 13.6 | 2720 | 40 | 23.05 | 3070 | 40 | 86.2 | 2525 |
| 60 | 11.8 | 4282 | 60 | 20.00 | 4305 | 60 | 81.8 | 3778 |
| 80 | 11.4 | 4979 | 80 | 18.88 | 5355 | 80 | 78.0 | 4841 |
| 100 | 9.6 | 6471 | 100 | 16.52 | 6296 | 100 | 74.8 | 6235 |

**Table S4:** Applied current with respect to its energy densities and power densities for GNS/FTO and GNS-$MnO_2$/FTO composite electrodes.

## Preparation of graphene film on a suitable substrate via air-water interface reaction.

Our approach is to use intercalated graphite/expanded graphite as a precursor to graphene as it gets easily exfoliated during film formation procedure [1].

Natural graphite rod which is pointed at one end is used as a starting material. The tapered end was converted to expanded graphite by treating it with 98% concentrated sulphuric acid for 30 hrs at room temperature. In a typical experiment, expanded graphite was forced to exfoliate and in turn forms disperse layered graphene film on aqueous surface by a typical experimental arrangement as shown in Scheme S1. The procedure of formation and transferring the film to a substrate is described in the chronological steps as follows. The general method of the formation of graphene thin films at air-water interface is based on our earlier reported procedure for deposition of cadmium sulphide.[2] However; some modifications were introduced for the present purpose of formation of graphene film at air-water interface. In a typical procedure, deionised water (sub phase) was placed in a Teflon tray (15 cm x 15 cm x 2 cm) so that it formed a meniscus at the edges. The surface of the subphase is divided into two compartments by a Teflon thread barrier (Scheme S1). The tapered tip of the expanded graphite rod was arranged in such a way that it just touches the meniscus of the sub-phase in one of the compartment. A few drops of carbon tetrachloride were allowed to slide on expanded graphite rod which spread on entering the water surface. Along with it, GNS formed at the tip, touching water, also spread on the surface forming GNS/few layer graphene (FLGNS) on the subphase surface. After allowing all $CCl_4$ spread on the surface to evaporate naturally, the GNS/FLGNS film was then compressed laterally via a teflon thread barrier by spreading a drop of oleic acid on the surface of subphase in the other compartment of the tray. The spreading oleic acid (pressure 30 dynes $cm^{-1}$) acts as a piston. The as-formed compressed film on the subphase surface (water) was transferred on a glass/quartz or silicon wafer substrate by immersing the substrate vertically in the subphase where the compressed GNS/FLGNS film floats, at a constant rate of 0.5 cm/min. and lifting it vertically at the same rate so that the film covers the dipped area of the substrate (Langmuir Blodgett technique).



**Scheme S1** a) Schematic illustration of self-assembly of graphene films. (Figure is reproduced from the earlier report) [1].

The film was then washed with deionised water several times until it turned out to be of neutral pH. This film was then used for characterization. Calibration of the mass with respect to number of dips at a fixed dipping area was established by using quartz crystal microbalance (QCM-200).

**Scheme S2.**

Intended for application of thin films as a supercapacitor, it is a very crucial step to weigh exact amount of materials or to be able to determine the exact amount used in the process. We have used a quartz crystal microbalance which is able to determine the weight in the range of nanograms to microgram with a high precision.

The substrate used for the electrochemical characterization is FTO coated glass thus it is need to measure the mass of the deposited film over the FTO substrate. The process of mass measurement can be summarised as follow. The quartz crystal is first cleaned by using isopropyl alcohol (IPA), and then distilled water alternately followed by sonication in IPA for 10 minute, and finally washed by using distilled water. After drying crystal in vacuum oven for 30 min at

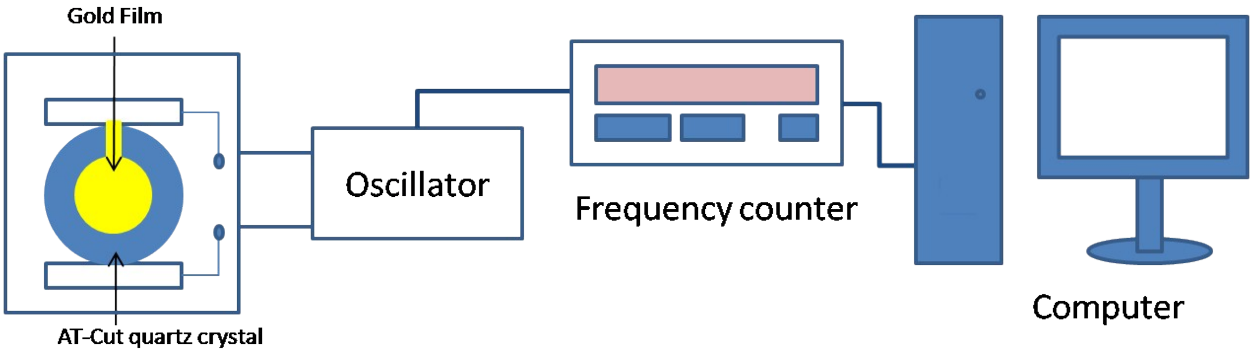
$90^0$C, it is placed in groove of machine (QCM-200) and blank run is taken. The previously deposited material for 10 dips (Over FTO substrate) is transferred over the gold coated quartz substrate by using drop cast method. 1:1 mixture of $CCl_4$: IPA was used as a solvent which ensures total wiping of material over the crystal. This process is a crucial and must be done neatly in a perfectly clean environment. The substrate is then heated at $90^0$C for 30 min. to evaporate the moisture and solvent from the material. After the drying, crystal is kept for measurement in the machine and the difference in frequency (Δ freq) of blank crystal and crystal with material is calculated.

The mass (m) is calculated by using Sauerbrey equation,[3, 4]

$$m = \frac{-\Delta freq. \times A \times \sqrt{(\mu q \times \rho q)}}{2 \times Fq^2}$$

Where,

Δ mass is the mass change, Δ freq is the resonant frequency change (Hz), $\mu_q$ is AT-cut quartz crystal constant, $\rho_q$ is the quartz crystal density, $F_q$ is the reference frequency, and $A$ is the surface area of the electrode ($cm^2$). The similar procedure is repeated for every composite material.



**Scheme S2:** Schematic representation of Quartz Crystal Microbalance (QCM)

The masses derived for from above measurements were 6.8, and 9.2 µg respectively for the GNS and GNS-$MnO_2$ composite electrodes.

## References:

[1] S. Patil, V. Patil, S. Sathaye and K. Patil, Facile room temperature methods for growing ultra thin films of graphene nanosheets, nanoparticulate tin oxide and preliminary assessment of graphene–tin oxide stacked layered composite structure for supercapacitor application, RSC Advances, 4 (2014) 4094-4104..

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[3] T. Lee, T. Yun, B. Park, B. Sharma, H. K. Song and B-S. Kim, *J.Mater. Chem*., 2012, 22, 21092-21099.

[4] S. Patil, A. Jadhav, S. Sathaye, K. Patil, To form layer by layer composite film in view of its application as supercapacitor electrode by exploiting the techniques of thin films formation just around the corner, *Electrochimica Acta*, 2018, 265, 556-568.