

Supporting Information

**Charge Storage Kinetics of Interconnected MnO<sub>2</sub> nano-needles/Reduced Graphene Oxide composite for High Energy Density Quasi-Solid-State Sodium Ion Asymmetric Supercapacitor**

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## Electrochemical formulas for calculation of various parameters -

1. Specific capacitance ( $C_{sp}$ , F/g) from the cyclic voltammograms (CV):

$$C_{sp} = \frac{\int idV}{2 * m * v * \Delta V} = \frac{\text{Area under the curve}}{2 * m * v * \Delta V} \quad (S1)$$

2. Specific capacitance ( $C_{sp}$ , F/g) from galvanostatic charge-discharge (GCD) plots:
  - (a) For three-electrode set up -

$$C_s = \frac{i * \Delta t}{m * \Delta V} \quad (S2)$$

- (b) For Asymmetric SC (ASC) device (two electrode system) [1] –

$$C_s = \frac{4 * i * \Delta t}{m * \Delta V} \quad (S3)$$

3. The energy density of ASC device ( $E$ , Wh/kg):

$$E = \frac{1}{2 * 4 * 3.6} C_s \Delta V^2 \quad (S4)$$

4. Power density of ASC) device ( $P$ , W/kg):

$$P = \frac{3600 * E}{\Delta t} \quad (S5)$$

Here  $i$  is current (in A),  $dV$  is the potential differential (in Volt),  $m$  is the active mass coated on electrode (in g) of active material,  $v$  is the scan rate (in V/s)  $\Delta V$  (V) is the potential window and  $\Delta t$  is the discharge time from GCD curves (in seconds).

5. Diffusion coefficient of ASC device ( $D$ , cm<sup>2</sup>s<sup>-1</sup>) [2,3]

$$D = 1/2[(R * T)/(AF^2n^2C\sigma)]^2 \quad (S6)$$

Here,  $R$ ,  $T$ ,  $A$  and  $F$  are the ideal gas constant, absolute temperature, active surface area of the electrode and faraday's constant, respectively.  $C$ ,  $n$  and  $\sigma$  represent the concentration of Na<sup>+</sup> ions, the number of electrons and Warburg coefficient, respectively. The  $\sigma$  is linearly related to real impedance  $Z'$  by the below equation

$$Z' = R_s + R_{ct} + \sigma \omega^{-0.5} \quad (S7)$$

Here,  $\omega$  is applied angular frequency (in Hz).

6. Mass ratio

$$\frac{q_+}{q_-} = \frac{m_+}{m_-} = \frac{C_{sp-} \oint \Delta V_-}{C_{sp+} \oint \Delta V_+}$$

(S8)

Here,  $q_+$ ,  $m_+$  and  $\Delta V_+$  represent the charge, mass and potential window of positive electrode, respectively whereas  $q_-$ ,  $m_-$  and  $\Delta V_-$  denotes the charge, mass and potential window of negative electrode, respectively.  $C_{sp-}$  and  $C_{sp+}$  describe the specific capacitance (in F g<sup>-1</sup>) of negative and positive electrode, respectively.

### Characterization Techniques

Powder X-ray diffraction (PXRD) was performed within the range  $2\theta = 5$  to  $90^\circ$  by using Panalytical X-Pert Pro diffractometer. The surface morphological study was evaluated by Field Emission Scanning Electron Microscope (FESEM) and High-Resolution Transmission Electron Microscope (HR-TEM) by utilizing Nova Nano FESEM-450 and Tecnai G2 20 S-TWIN technique, respectively. The ESCA + Omicron Nano Technology instrument was utilized for X-ray photoelectron spectroscopy (XPS) characterization of sample. Samples were also investigated by Raman spectroscopy by employing STR 500 Confocal Micro Raman Spectrometer with a wavelength of 532 nm to analyze the E<sub>2g</sub>, A<sub>1g</sub>, D and G bands of the synthesized samples. The multi-point surface area and pore size distribution of samples were obtained by nitrogen adsorption/desorption techniques (Nova Touch LX2 gas sorption analyzer, Quantachrome Instruments).

Electrochemical characterizations were performed on Metrohm AUTOLAB, PGSTAT30 electrochemical workstation and electrochemical impedance spectra (EIS) was recorded by using CHI Instrument (CHI760E).

### Synthesis of Graphene Oxide (GO) -

The modified Hummer's method was utilized to produce graphene oxide (GO) according to our previously reported research work [4]. In a flask with a flat bottom, 2 g of graphite powder was added to 50 ml of sulfuric acid while being constantly stirred at 300 rpm for 2 hours. The use of an ice bath helped to maintain the reaction temperature cooled. As an oxidizing agent, potassium permanganate (KMnO<sub>4</sub>) was then gradually added to the reaction mixture while being constantly stirred at 300 rpm for 8 hours. In order to prevent photochemical oxidation of the hydrogen peroxide, 30 ml of hydrogen peroxide in a flask covered with aluminum foil was then added to the mixture that had turned brown color. As a result, the mixture develops bubbles and becomes a yellowish-brown color. After washing the GO paste three times with 2 M HCl (to get rid of the metal ions), three times with ethanol, and many times with deionized water (until the pH of the supernatant reaches ~7), it was centrifuged at 7000 rpm for 45 minutes. The finished product was dried at 45 °C in a vacuum oven.

### Synthesis of reduced Graphene Oxide (rGO) -

100 ml of de-ionized (DI) water was used to sonicate 1 g of GO flakes for approximately 2 hours. 100 ml of deionized water were used to create a 4M KOH and 2M NaOH solution. Following this, the GO dispersion was incorporated into the mixture and stirred for an hour at 400 rpm. The

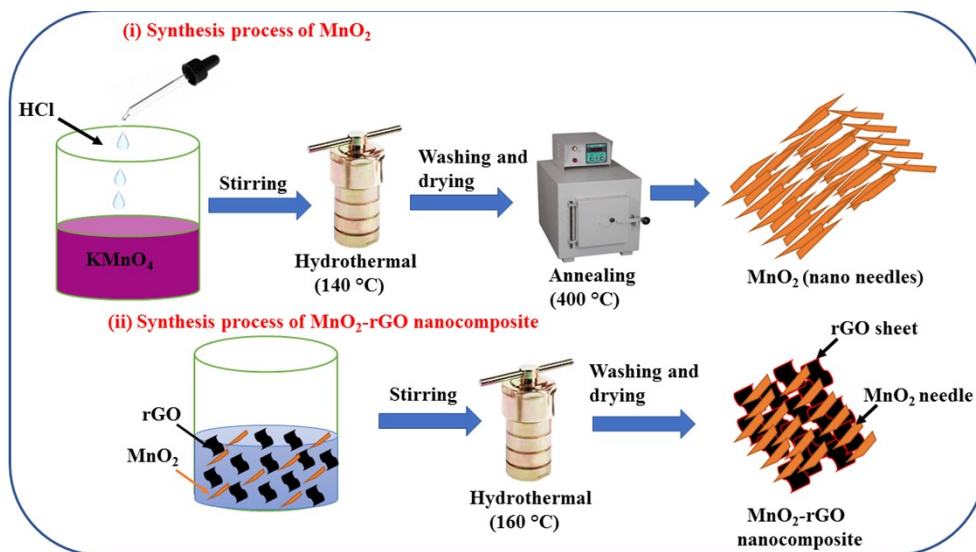
mixture was then transferred to a Teflon-lined stainless-steel autoclave and heated to 160 °C for 12 hours. The resulting, pitch-black rGO material was separated by centrifugation. The rGO was washed three times with ethanol and three times with DI water until the pH reached ~7. After that, the material was completely dried in a vacuum oven at 60 °C.

### **Fabrication of PVA-Na<sub>2</sub>SO<sub>4</sub> hydrogel membrane**

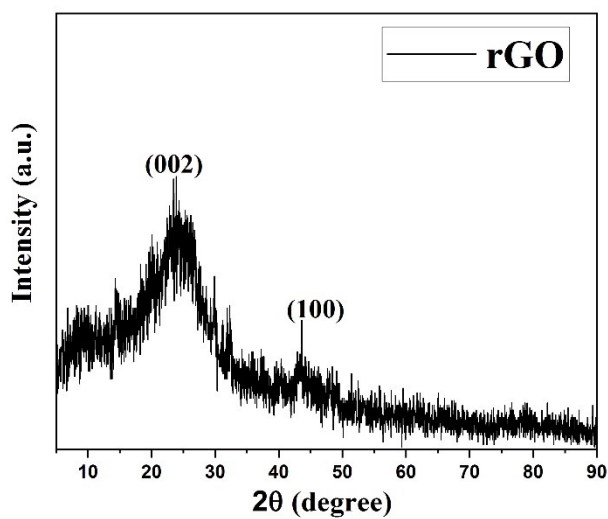
For the preparation of PVA-Na<sub>2</sub>SO<sub>4</sub> hydrogel membrane/film, PVA powder (10 wt %) was dissolved in de-ionized (DI) water under continuously stirring at 80 °C, until the PVA powder was completely dispersed. Then, the 10 ml solution of Na<sub>2</sub>SO<sub>4</sub> (1M) was added dropwise into the PVA solution by maintaining low temperature (close to 10 °C) using an ice bath. Then the solution was shifted into a borosilicate petri plate and the plate was maintained at room temperature for overnight to remove the trapped bubbles and solvent from the hydrogel membrane/film. The hydrogel membrane/film was extracted easily from the petri plate, and then membrane/film was completely soaked with 1M Na<sub>2</sub>SO<sub>4</sub> electrolyte for 12 hours to obtain PVA-Na<sub>2</sub>SO<sub>4</sub> hydrogel membrane/film. The fabricated hydrogel membrane/film was cut into (2 cm  $\times$  2 cm) pieces for utilization as the separator-less electrolyte in the quasi-solid-state asymmetric SC (ASC) devices.



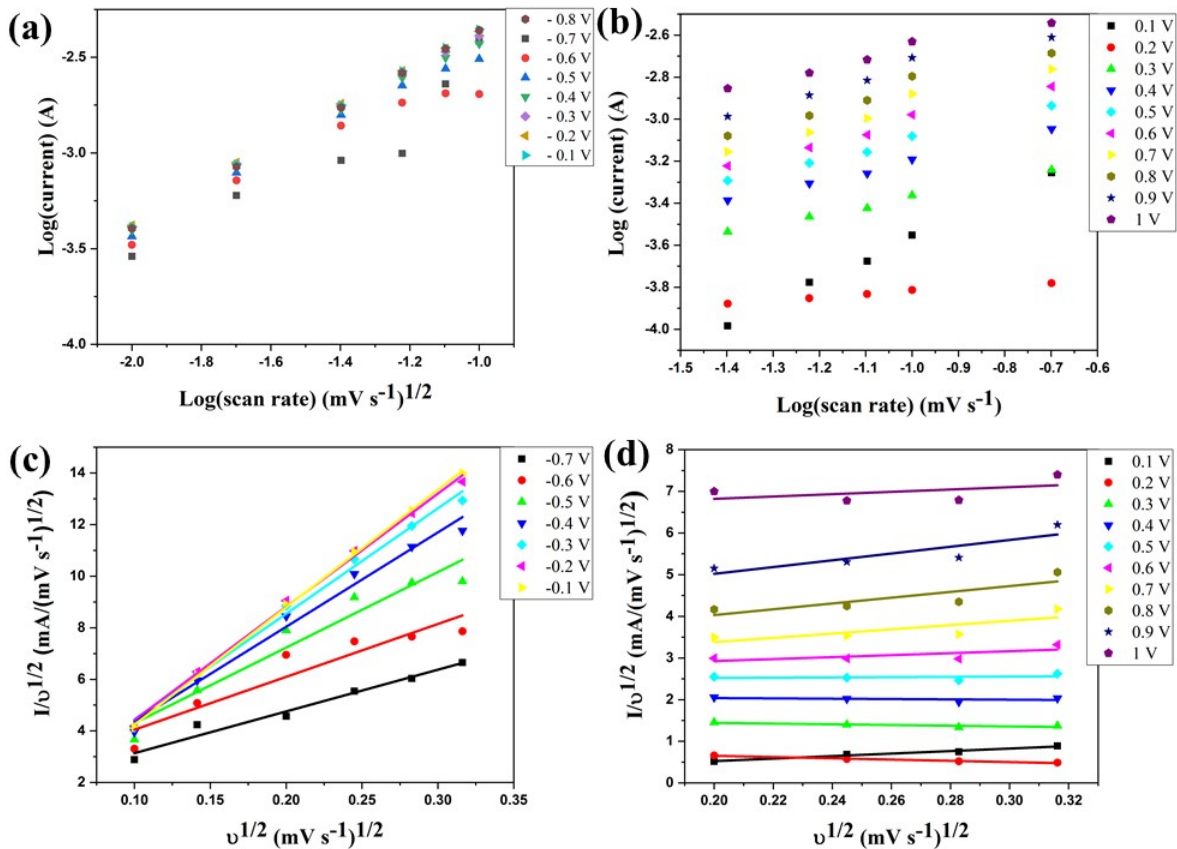
**Figure S1.** Prepared PVA-Na<sub>2</sub>SO<sub>4</sub> hydrogel membrane after soaked in 1M Na<sub>2</sub>SO<sub>4</sub>.



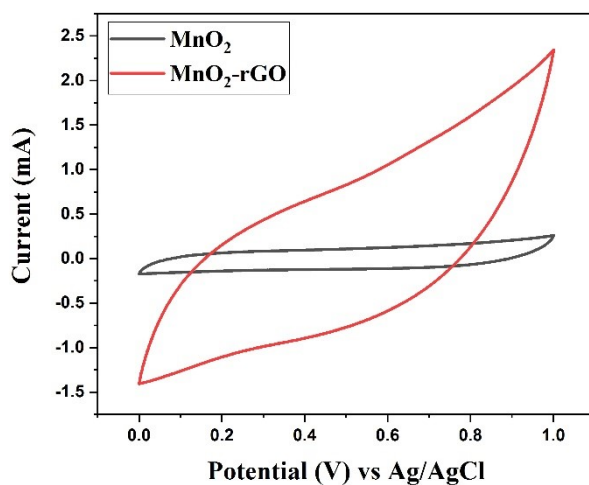
**Figure S2.** Graphical representation of synthesis strategy of  $\text{MnO}_2$  nano-needles and  $\text{MnO}_2$ -rGO nanocomposite.



**Figure S3.** XRD spectrum of rGO.



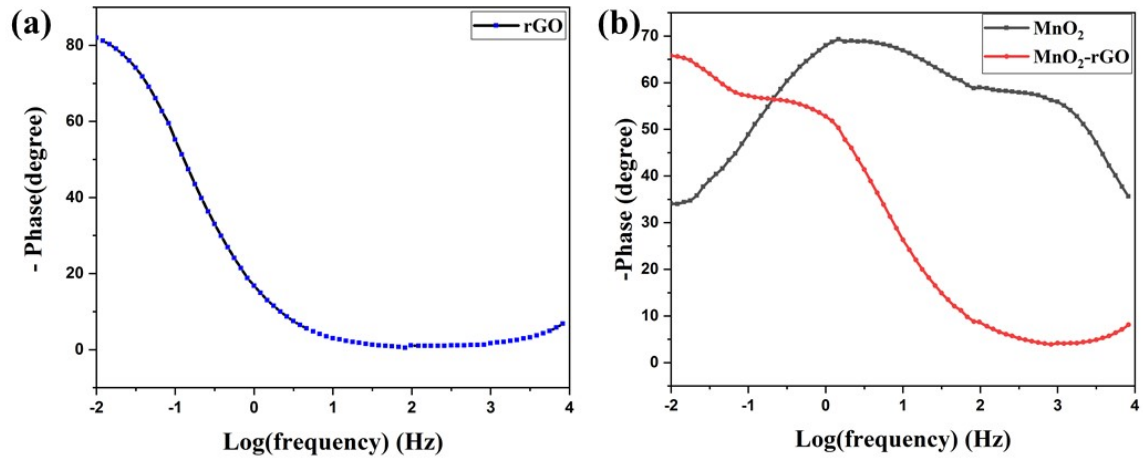
**Figure S4.** Linear fit plot between log(scan rate) and log(current) at different applied voltages of (a) rGO electrode, (b) MnO<sub>2</sub>-rGO electrode; Linear fit plot between  $v^{1/2}$  and  $I/v^{1/2}$  of (c) rGO electrode, (d) MnO<sub>2</sub>-rGO electrode.



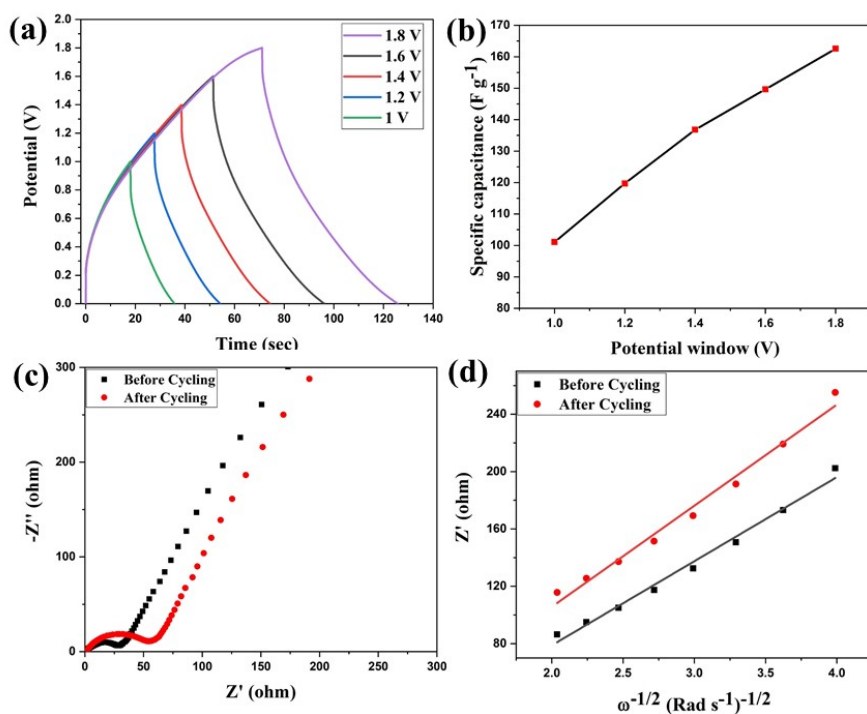
**Figure S5.** CV profile of MnO<sub>2</sub> and MnO<sub>2</sub>-rGO electrode (at 60 mV s<sup>-1</sup>).

**Table S1.** Fitted parameters of rGO, MnO<sub>2</sub> and MnO<sub>2</sub>-rGO electrodes

S. No.	Electrode	$R_s(\text{ohm})$	$R_{ct}(\text{ohm})$
1.	rGO	2.85	17.25
2.	MnO <sub>2</sub>	2.90	23.21
3.	MnO <sub>2</sub> -rGO	2.84	12.14



**Figure S6.** Bode phase plot of (a) rGO-electrode, (b) MnO<sub>2</sub> and MnO<sub>2</sub>-rGO-electrode.

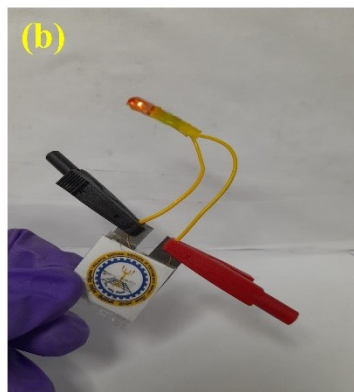
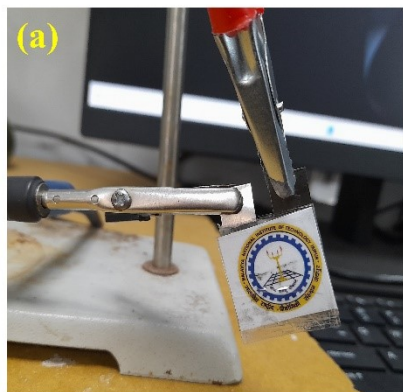


**Figure S7.** (a) GCDs of ASC device at several cell potential (b) variation of specific capacitance along with potential window (c) EIS Nyquist plot of fabricated ASC device (inset appropriate fitted circuit) (d) plot of ( $Z'$ ) vs.  $\omega^{-0.5}$  in low frequency region.

**Table S2.** electrochemical parameters of ASC (rGO || MnO<sub>2</sub>-rGO) device before and after the cycling.

S. No.	(rGO    MnO <sub>2</sub> -rGO)	R <sub>s</sub> (ohm)	R <sub>ct</sub> (ohm)	Slope ( $\sigma$ )	D (cm <sup>2</sup> s <sup>-1</sup> )
1.	Before cycle	1.8	22	58.66	2.15 * 10 <sup>-10</sup>
2.	After cycle	2.5	50	70.50	1.49 * 10 <sup>-10</sup>





**Figure S8.** Fabricated ASC device (a) while taking electrochemical results (b) lighting a bulb.

## Reference

- [1] P. Yang, W. Mai, Flexible solid-state electrochemical supercapacitors, *Nano Energy*. 8 (2014) 274–290. <https://doi.org/10.1016/j.nanoen.2014.05.022>.
- [2] N. Kanaujiya, N. Kumar, A.K. Srivastava, Y. Sharma, G.D. Varma, One-step synthesized mesoporous MnO<sub>2</sub>@MoS<sub>2</sub> nanocomposite for high performance energy storage devices, *J. Electroanal. Chem.* 824 (2018) 226–237. <https://doi.org/10.1016/j.jelechem.2018.07.046>.
- [3] Y. Bai, L. Zhao, C. Wu, H. Li, Y. Li, F. Wu, Enhanced Sodium Ion Storage Behavior of P2-Type Na<sub>2/3</sub>Fe<sub>1/2</sub>Mn<sub>1/2</sub>O<sub>2</sub> Synthesized via a Chelating Agent Assisted Route, *ACS Appl. Mater. Interfaces*. 8 (2016) 2857–2865. <https://doi.org/10.1021/acsami.5b11848>.
- [4] M. Saquib, R. Yadav, R. Vyas, A. Sharma, M.K. Banerjee, K. Sachdev, *Materials Today : Proceedings* Synthesis and evaluation of reduced graphene oxide for supercapacitor application, *Mater. Today Proc.* (2020). <https://doi.org/10.1016/j.matpr.2020.05.403>.