Supporting Information

One Pot synthesis of Ilmenite-Type $NiMnO_3$/“Nitrogen-Doped” Graphene nanocomposites as Next Generation Supercapacitors

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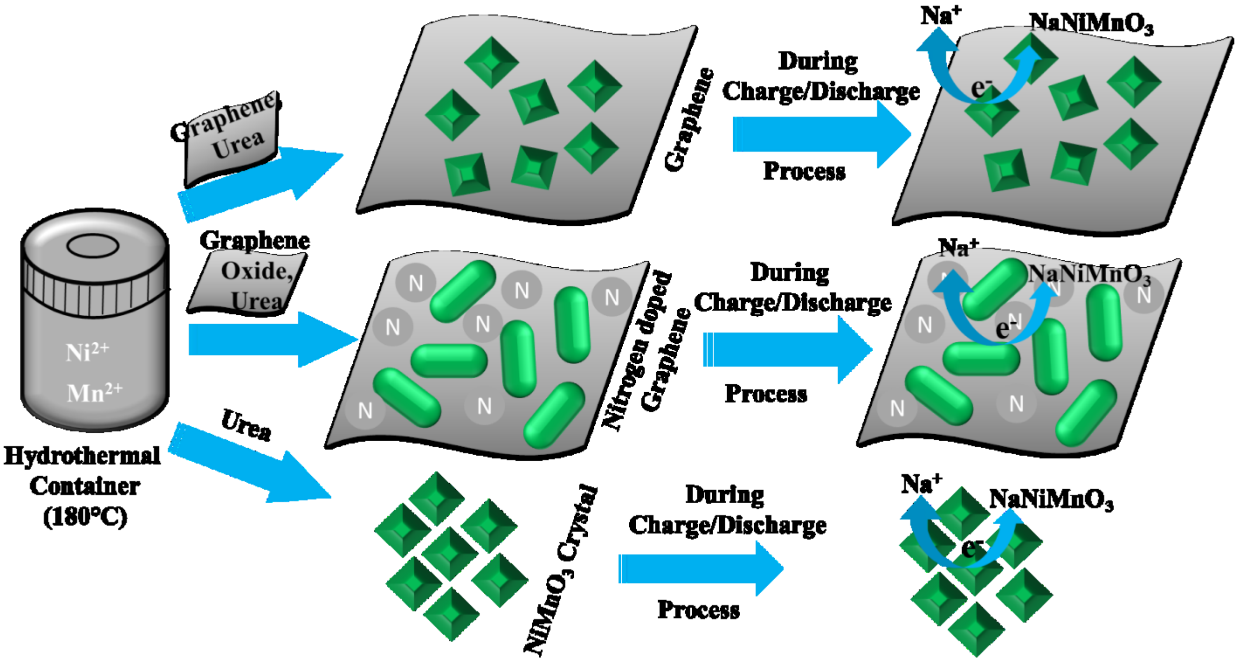


Scheme 1: First step represents the different crystal shape formed with the presence of graphene and graphene oxide and second step represents the proposed charge/discharge mechanism when Na_2SO_4 were used as electrolyte.

Electrochemical characterizations were carried out by a three electrode system. At first, the electrode was fabricated according to the following procedure. 1.0 mg of as prepared composites was dispersed in 1 ml of 1% nafion solution by sonication. After that, the solution was cast onto a glassy carbon electrode with diameter of 3 mm which was used as the working electrode. The electrode was fully dried before electrochemical characterization. Platinum wire and saturated calomel electrode were used as counter and reference electrode, respectively. Cyclic voltammetry and charge discharge test were carried out within the potential range of 0-0.8V. Electrochemical impedance spectroscopy (EIS) was also tested within the frequency range of 10^6 (initial) and 0.1 (final) Hz.

2. XRD Analysis

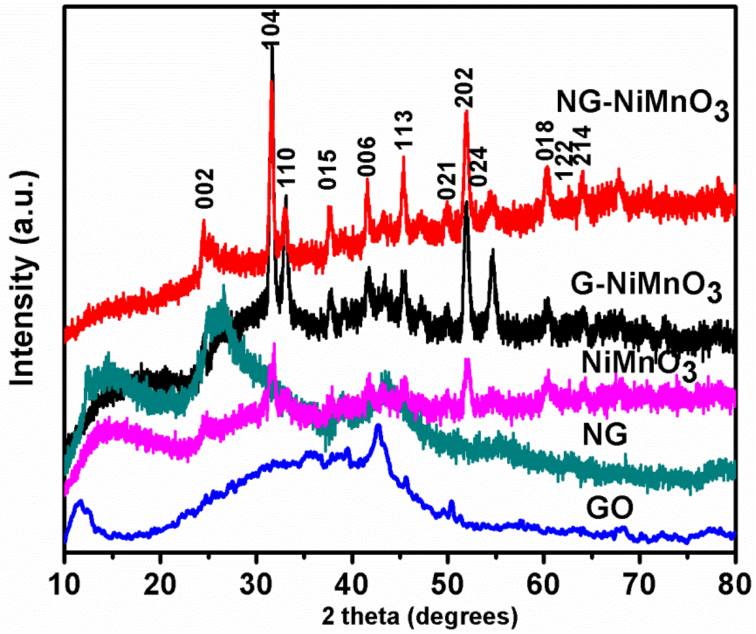


Fig. S1: XRD analysis of the as prepared composites

3. FTIR and Raman Analysis

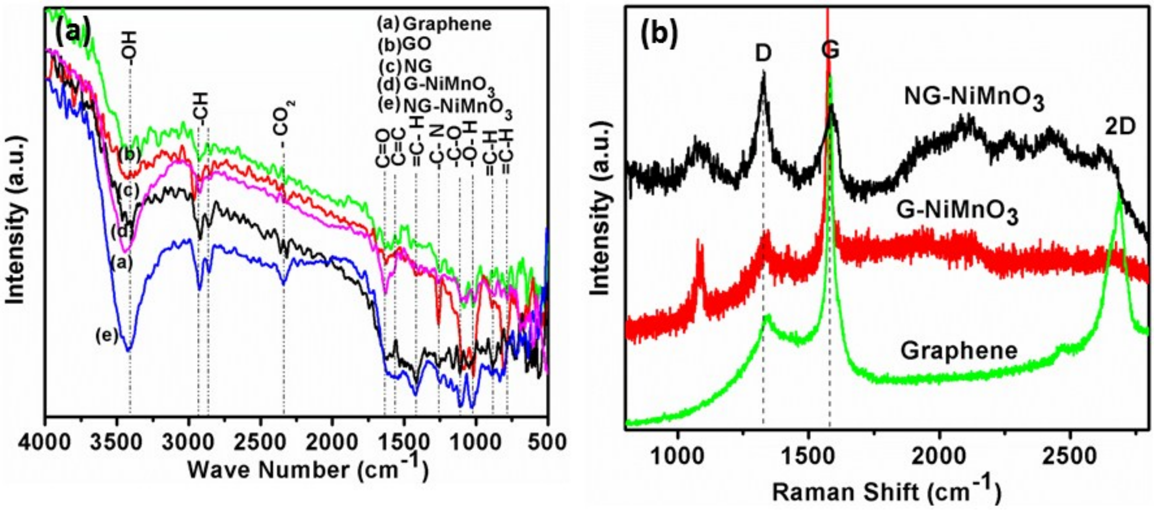


Fig. S2: (a) FTIR and (b) Raman spectroscopy of composites.

The FTIR spectra of all the samples show the presence of –OH (3421 cm^{-1}), C=O (1626 cm^{-1}) and phenol or alcohol or ether (1063 cm^{-1}). It shows the decreased intensity of the C=O bands (at 1626 cm^{-1}) and increased intensity of the C–H bands at 2924 cm^{-1} and 2854 cm^{-1} corresponding to stretch vibrations of the methylene group, indicates the reduction of graphene-COOH to hydroxymethylene group. The appearances of bands at 2918 cm^{-1} and 2852 cm^{-1} denote the stretching frequency of the CH_2 group, while the band at 1033 cm^{-1} indicates formation of the C–N bond. [1] Raman spectroscopy is one of the strong evidence to prove the nitrogen doping on graphene plane. As we can be seen the strong peaks appear at around 1326.5 cm^{-1}, 1589.3 cm^{-1}, 2690.27 cm^{-1} for the D, G, and 2D band, respectively. The G band related to the double degenerate E_{2g} phonons at the brillouin zone centre, whereas 2D and D band related to the zone boundary phonons. First one is the resulted to the first order Raman scattering process, but second pair generate from the second order double resonance process. The peak appeared at 1084.4 cm^{-1} may be due to the presence of $NiMnO_3$ which is absent in the sole graphene. For nitrogen doping i.e. the substitution of nitrogen with carbon lattice of graphene induced the enhancement of defective site inside the graphene site. So, the nitrogen doped graphene/$NiMnO_3$ composite shows the (I_D/I_G) value of 4.9. It proves the defective sites were present in the system. In the addition, the doping level can also be calculated from (I_{2D}/I_G) ratio. The (I_{2D}/I_G) ratio of NG/$NiMnO_3$ shows the value of 0.83 which means the doping level of nitrogen reached >2 x 10^{13} cm^{-2}.[2] So, huge number of nitrogen doping causes the improvement of graphene properties and expected to play a crucial role in the electrochemical performances.

4. XPS Analysis

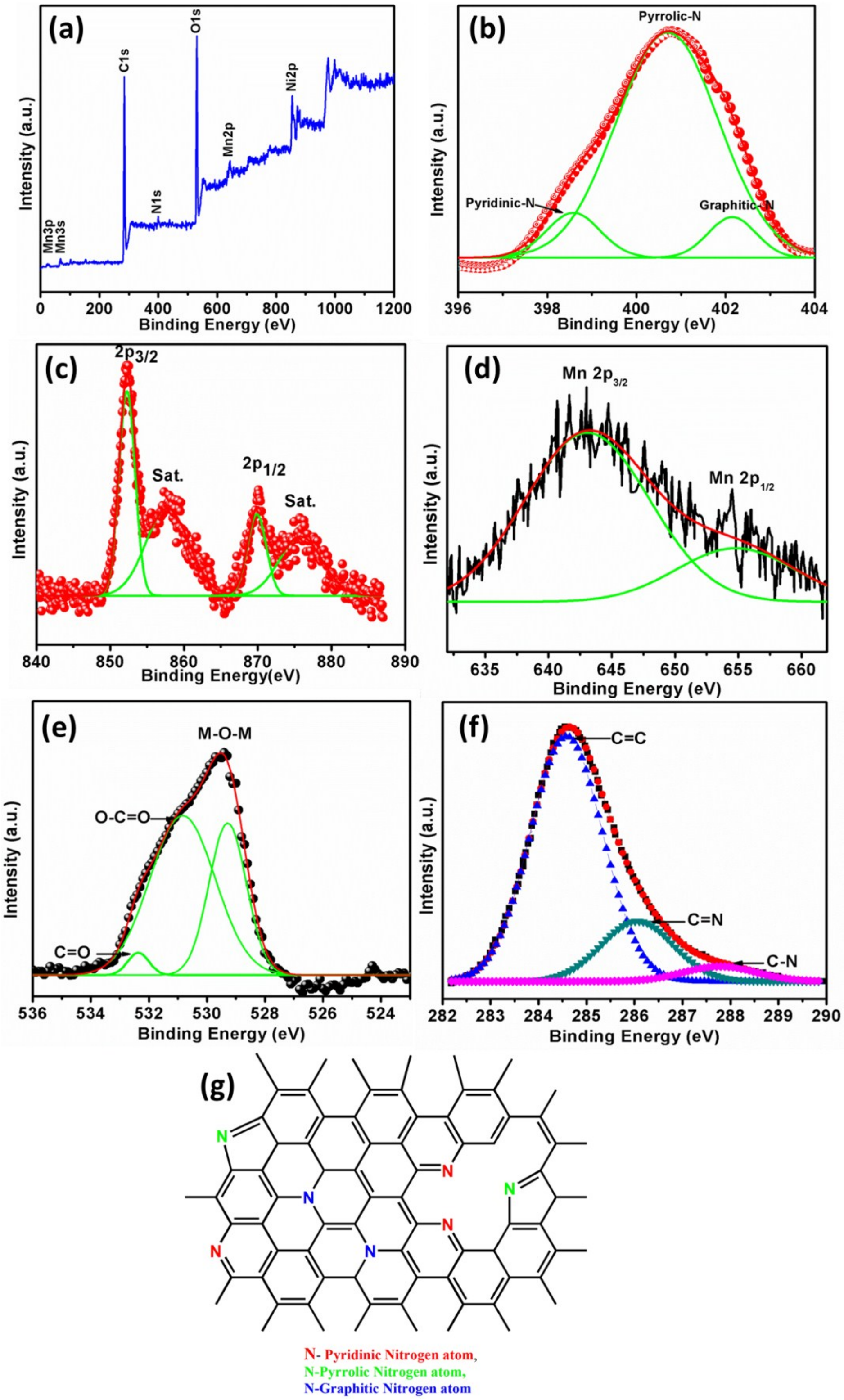


Fig. S3: XPS analysis of NG-NiMnO$_3$ composites (a) Survey (b) N1s (c) Ni2p (d) Mn2p (e) O1s (f) C1s (g) schematic structure of NG.

4.TGA Analysis

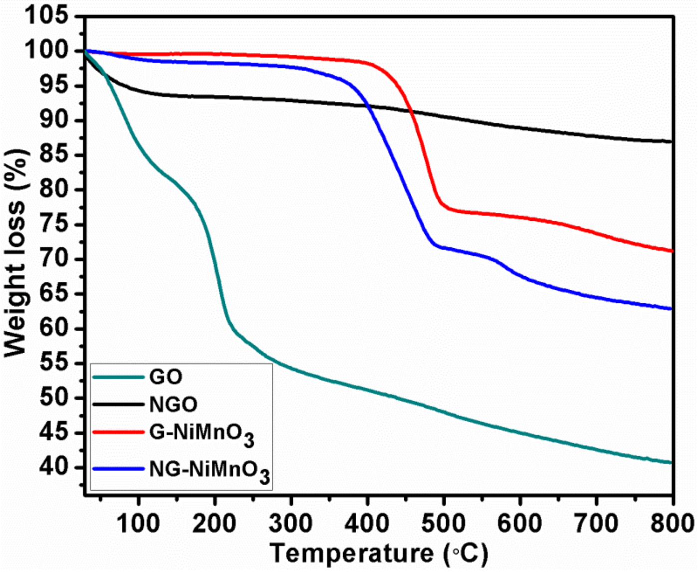


Fig. S4. TGA analysis of as prepared composites

Compared with other composites, the graphene oxide shows much lower thermal stability and onset temperature falls dramatically, may be due to the decomposition and vaporization of various oxygen containing functional groups. On the other hand, increased thermal stability of other composites indicates the removal of the thermally unstable functional groups such as -COOH, -OH, and epoxide groups of the GO sheets by reduction and incorporation of nitrogen in these labile sites. The presences of some functional group in the graphene surface lead to prevent the stacking and enhance the dispersibility of graphene. In addition, Metal ions first coordinate with these functional groups and anchored on to the graphene surface which may help to find out the position of reactive sites on the graphene surface. [3] From the TGA curves, three steps of weight loss are found. The first weight loss occurred upto 120°C, which is due to the removal of the physisorbed water. The large weight loss at about 400°C is attributed to the removal of reduced GO from the composites. The thermal stability of nitrogen doped graphene/$NiMnO_3$ is little bit less as compared with graphene/$NiMnO_3$, it may be due to the presence of nitrogen inside the carbon lattice minimizes the interaction with bi-metal. Finally, between 550°C and 750°C the graphitic carbon burns off accounting for the third burn stage.[4]

5. FESEM and HRTEM Study

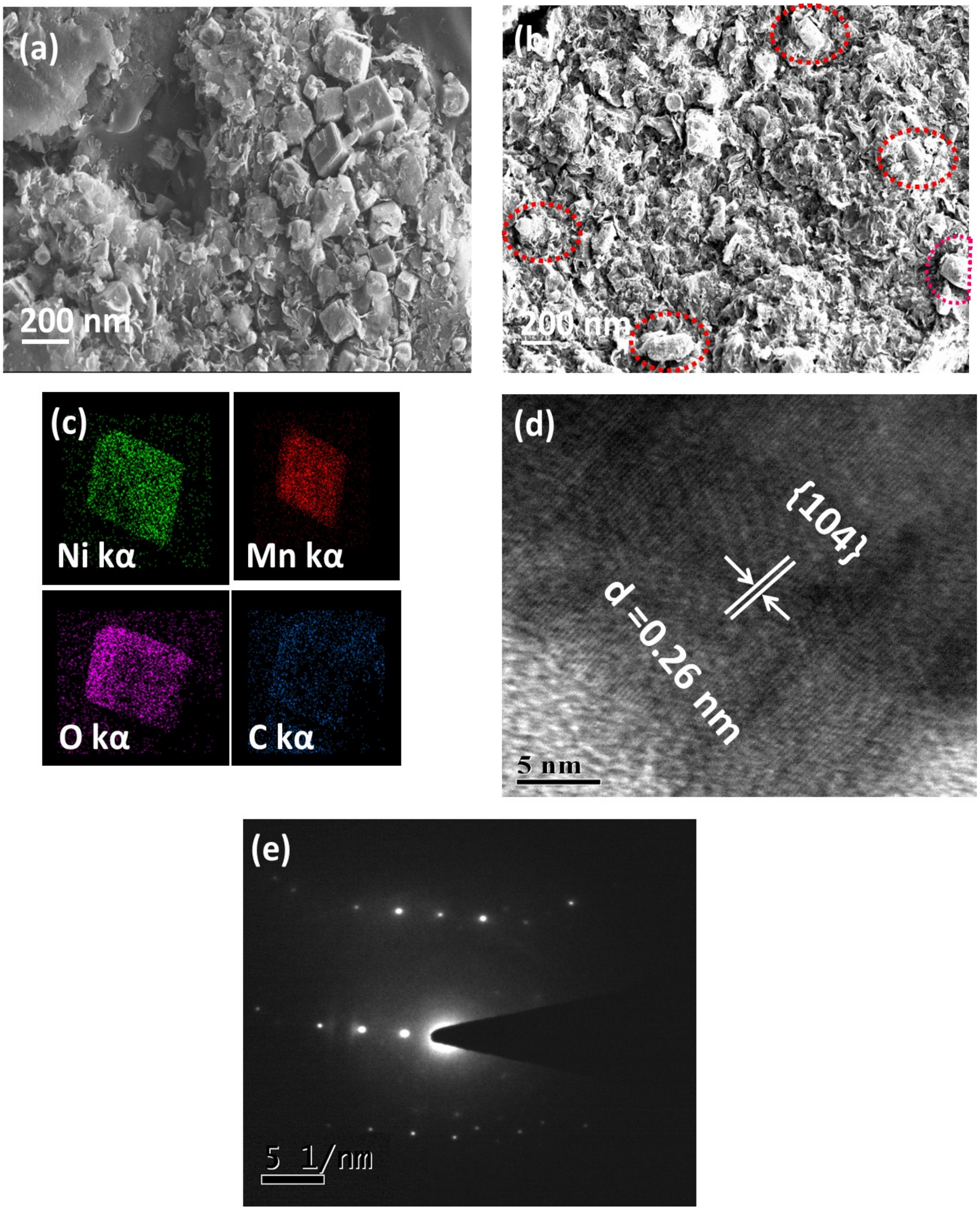


Fig. S5: SEM images of (a) G-$NiMnO_3$ and (b) NG-$NiMnO_3$; (c) EDS mapping , (d) lattice fringes (d=0.26 nm) and (e) SAED pattern of $NiMnO_3$ crystal.

6. Cyclic Voltammetry

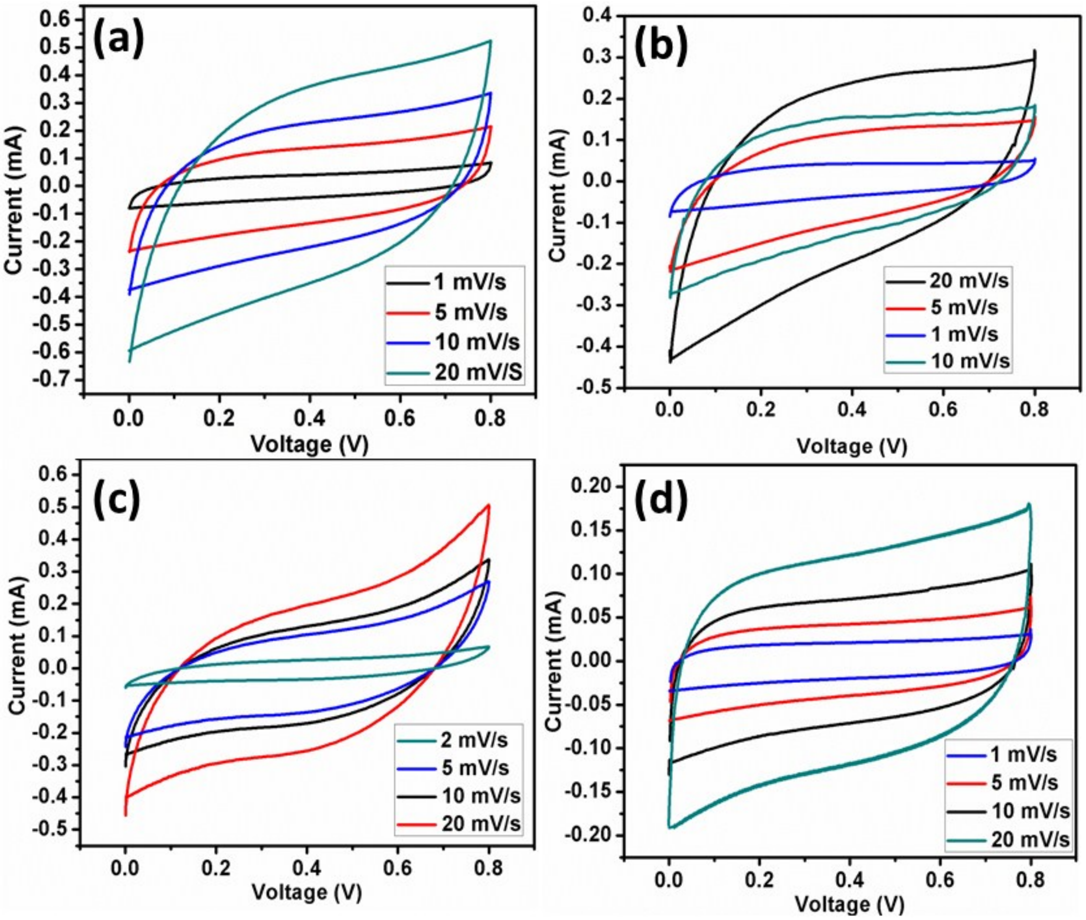


Fig. S6: Cyclic voltammetry of (a) NG-NiMnO$_3$, (b) G-NiMnO$_3$,(C) NG , and (d) NiMnO$_3$ at different scan rates.

7. Galvanostatic charge-discharge curve

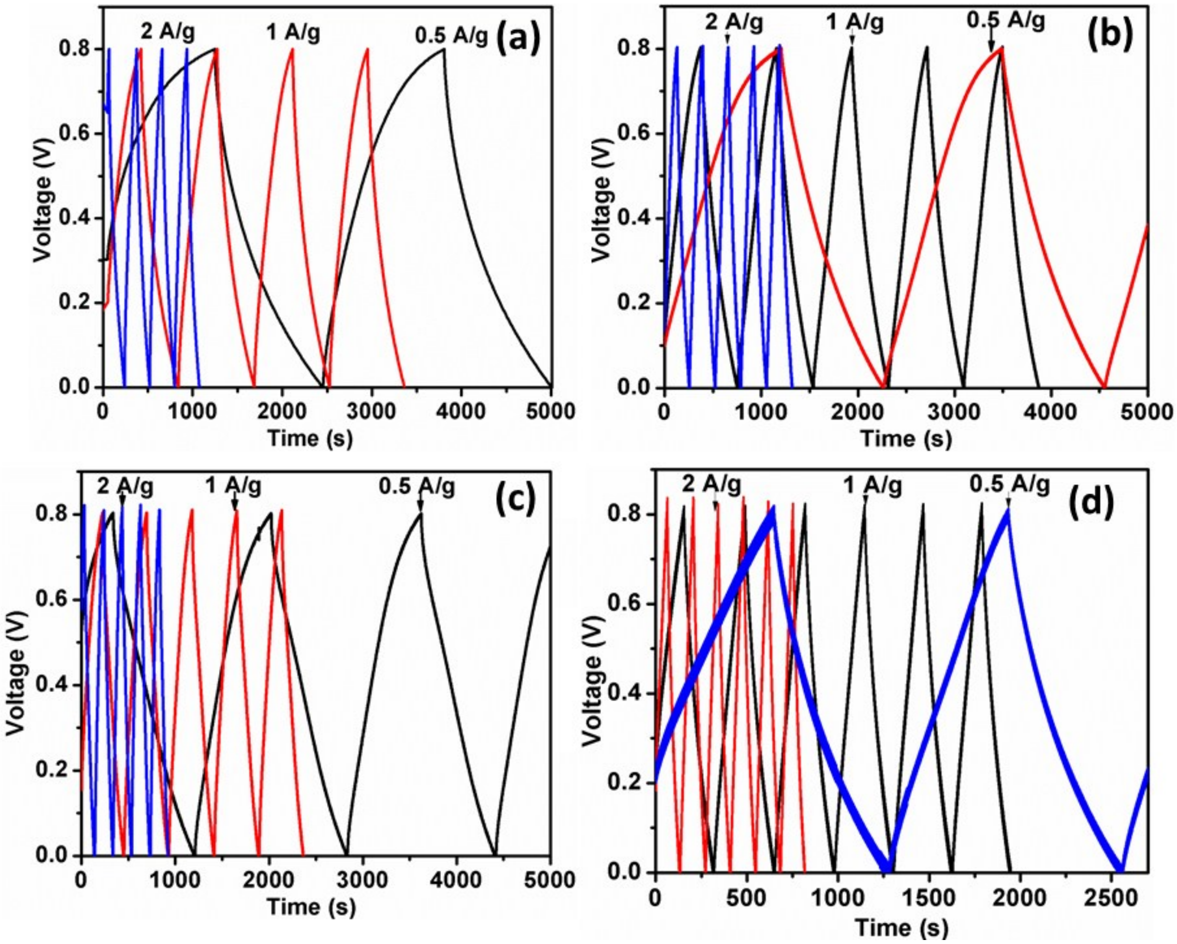


Fig. S7: Galvanostatic charge-discharge of (a) NG-NiMnO$_3$, (b) G-NiMnO$_3$, (c)NG , (d)NiMnO$_3$ at different current density.

8. Ragone plot and cycling stability of all composites

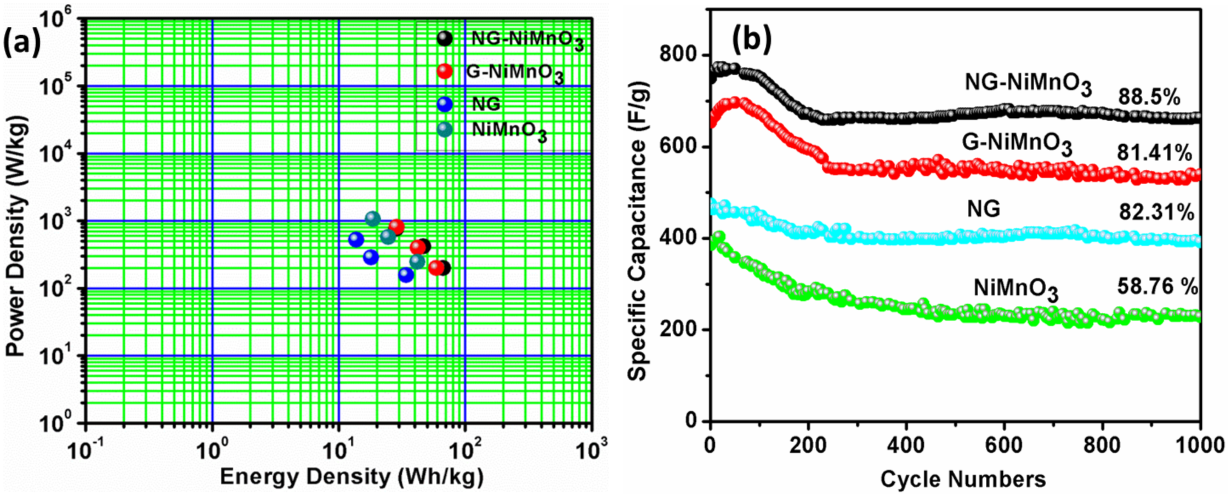


Fig.S8: (a) Ragone plot and (b) cyclic stability of all composites.

From the figure S8b, It is clearly shown the initially specific capacitance increases which is mainly due to electrode activation.

9. Tables

Table S1:Specific capacitance (F/g): Equation used for specific capacitance calculation

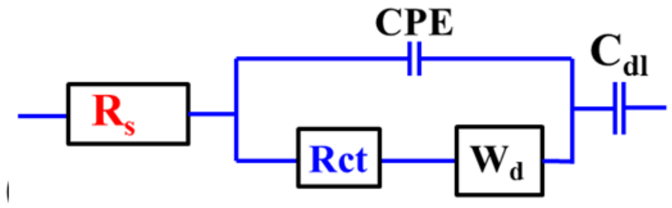
$$C_s = \frac{C}{m} = \frac{\int_{V_2}^{V_1} i(V)dV}{(V_1 - V_2)vm}$$

Where the term in the numerator, of above eq., represents the area of I-V curve and V_1, V_2 are the switching potential in cyclic voltammetry and m is the mass (0.10 mg) of all composites

Sample	**1 mV/s**	**5 mV/s**	**10 mV/s**	**20 mV/s**
NG-NiMnO$_3$	750.2	500.6	375.2	281.25
G-NiMnO$_3$	677.5	357.5	240.5	175
NiMnO$_3$	388.75	150	134.5	60.2
NG	475	375	238.75	179.3

Table S2: Value obtained from suitable circuit fitting

Circuit:



Sample	R_s (Ω)	R_{ct}(Ω)	CPE	a3	W_d(Ω)	C_{dl}
NG-NiMnO3	3.18	28.56	0.325×10^{-3}	0.95	5.3	5.54×10^{-3}
G-NiMnO3	34.48	190.3	0.246×10^{-3}	0.474	24.3	4.63×10^{-3}
NG	2.114	89.46	21.11×10^{-6}	0.68	17.68	3.8×10^{-3}
$NiMnO_3$	36	186	0.237×10^{-6}	0.737	9.81	0.171×10^{-3}

Table S3: Specific Capacitance (F/g) from GCD curve: Equation used for Specific capacitance calculation = Ixt/Vxm, Where $\frac{I}{m}$ is the used current density, t is time for discharging, V is the potential window

Sample	0.5 A/g	1 A/g	2 A/g
NG-$NiMnO_3$	749.2	523.5	320
G-$NiMnO_3$	666.2	476.5	322.5
$NiMnO_3$	386.19	203	155.17
NG	473	277.5	210.5

Table S4: Energy Density (Wh/kg)calculation= $E = \frac{1}{2} C_s V^2$

E is the energy density in Wh/kg, C_s is the specific capacitance obtained from CV measurements and V is the operating voltage range.

Sample	**0.5 A/g**	**1 A/g**	**2 A/g**
NG-$NiMnO_3$	66.59	46.53	28.44
G-$NiMnO_3$	59.21	42.35	28.66
$NiMnO_3$	34.28	18.04	13.79
NG	42.04	24.66	18.71

Table S5: Power density (W/kg) calculation= $P = E/t$,

where P is the power density in W/kg, E is the energy density in Wh/kg and t is the time in hours.

Sample	**0.5 A/g**	**1 A/g**	**2 A/g**
NG-$NiMnO_3$	200.27	415.18	765.88
G-$NiMnO_3$	199.02	399.10	809.85
$NiMnO_3$	155.42	286.09	522.56
NG	244.89	576.46	1069.14

References

1. K,-J. Huang, D.-J. Niu, J.-Y. Sun, C.-H. Han, Z.-W. Wu, Y. –L. Li, X.-Q. Xiong, *Colloids and Surfaces B: Biointerfaces*, 2011, **82**, 543.

2. A. Das , S. Pisana , B. Chakraborty , S. Piscanec , S. K. Saha , U. V. Waghmare , K. S. Novoselov , H. R. Krishnamurthy , A. K. Geim , A. C. Ferrari and A. K. Sood , *Nat. Nanotechnol.* 2008, **3**, 210.

3. J. Shen, M. Shi, B. Yan, H. Ma, N. Li and M.Ye, *Nano Res.* 2011, **4**, 795.

4. Victor Chabot,B.Kim, B.Sloper,C. Tzoganakis and A.Yu, *Scientific Reports* 2013,**3**,1.