Supporting Information

A Novel RGO/N-RGO Supercapacitor Architecture for Wide Voltage Window, High Energy Density and Long-Life via Voltage Holding Tests

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The reduced graphene oxide (RGO) and nitrogen-doped RGO (N-RGO) were synthesized and reported in the literature [1, 2]. The reduced graphene oxide (RGO) was synthesized in the following steps; (i) we mixed 500 mg of GO powder in the 500 ml of deionized (DI) water under stirring to make homogenous solution, and after that (ii) the hydrazine hydrate (1.75 mol) was mixed with above papered GO solution at 100 °C for 16 h under vigorous stirring to finally acquire the RGO precipitate. Finally, this black precipitate was filtered, washed several times with DI water & ethanol, and dried in vacuum to obtain RGO.

The nitrogen-doped reduced graphene oxide (RGO) was prepared with the following steps; (i) the prepared 30 mg of GO was mixed in the 60 ml de-ionized (DI) water under stirring, (ii) further the 900 mg of urea was slowly added in the GO solution as nitrogen (N) dopant under stirring for 30 min and (iii) after that this prepared solution was filled in the autoclave of 100 ml capacity and kept it under the convection oven at 160 °C for 12 h. Finally, the obtained precipitate was centrifuged, washed with DI water and ethanol for several times, and dried at 80 °C in vacuum to obtain nitrogen-doped reduced graphene oxide (N-doped RGO).

The morphologies, microstructure, and elemental composition of reduced graphene oxide (RGO) and nitrogen heteroatom doped RGO (N-RGO) were examined and discussed. The transmission electron microscopy (TEM, JEOL JEM 2100F) was used to study the morphology, structure, and color mapping of RGO and N-RGO samples. Raman spectra were investigated by using a spectrophotometer (Horiba JOBIN YVON, Lab RAM HR) with an operating wavelength of 532 nm. The elemental composition of RGO and N-RGO samples were studied by x-ray photoelectron spectroscopy (XPS), Kα, Thermo Scientific, UK.

In this experimental section, we discussed the preparation of reduced graphene oxide (RGO) and nitrogen heteroatom doped RGO (N-RGO) electrodes, and after that, the fabrication
of the supercapacitor device. To prepare the working electrodes, we used RGO as active material and polyvinylidene fluoride (PVDF) as a binder (a mass ratio of 9:1) in n-methyl pyrrolidone (NMP) as a solvent to prepare the paste. This paste was coated onto the porous Ni foam with an active working area of 1 cm² and dried in the convection oven under vacuum at 65 °C for 5h. Similarly, we prepared the working electrodes of 3 at% nitrogen-doped RGO (N-RGO). Finally, the two-electrode (two-cell) assembly of symmetric supercapacitor (SSC) device was fabricated by using the RGO and N-RGO (RGO/N-RGO). The total mass of 2.32 mg was used in the fabrication of the RGO/N-RGO SSC. The supercapacitor device was fabricated in three steps by using RGO and N-RGO electrodes, a separator (Whatman filter paper, grade 2), and the electrolyte gel (PVA/Na₂SO₄). In step I, the electrolyte gel was prepared by mixing 1 g polyvinyl alcohol (PVA) (Mₜw = 31,000 – 50,000) and 1 g Na₂SO₄ in 14 mL DI water at 90 °C for 3h under vigorous stirring until the electrolyte solution becomes transparent. The PVA (polyvinyl alcohol), the biodegradable synthetic polymer, is widely used in gel polymer electrolytes (here, we used PVA/Na₂SO₄) for supercapacitors, due to low cost, non-toxicity, and hydrophilic nature. The vital role of PVA in gel polymer electrolytes are their ability to solvate large amounts of alkali-metal salts due to the presence of polar groups (-OH), reduction of electrolyte leakage risk, high chain flexibility, high mechanical strength, excellent chemical stability, and durability.³⁴⁵ In step II, the RGO & N-RGO working electrodes and separator were soaked into the above-prepared PVA/Na₂SO₄ electrode gel solution for 10 min. In step III, the RGO & N-RGO electrodes and separator were sandwiched to form a solid-state supercapacitor device and dried at room temperature for 30 min. The electrochemical properties of RGO/N-RGO SSC were investigated by using an electrochemical workstation Compact.h of IVIUM Technologies.

The charge storage kinetics of RGO/N-RGO SSC were investigated by using the following Eq. S1 [6].
\[ i_p = s v^m \]  
(S1)

where \( i_p \) is the peak current, \( s \) is a constant, and \( v \) is the scan rates. The \( m \) provides essential information about charge storage kinetics, e.g., \( m = 1 \) (capacitive storage) whereas \( m = 0.5 \) (diffusion-limited process) of RGO/N-RGO SSC.

The specific capacitance of the RGO/N-RGO SSC was evaluated by using the area under the discharge curves at various current density. The specific capacitance \([C_s \text{ (F g}^{-1})]\) was calculated by using the following Eq. S2 [7].

\[
C_s = \frac{2I \times \int V \, dt}{m \times V} 
\]  
(S2)

where \( I \) is the discharge current, \( \int V \, dt \) is an area under discharge curve, \( m \) is the total mass deposited on both electrodes, and \( V \) is the potential window.

The energy density \((\rho_E, \text{ Wh kg}^{-1})\) and power density \((\rho_p, \text{ W kg}^{-1})\) of RGO/N-RGO SSC was calculated by using the following Eq. S3 and Eq. S4, respectively [7].

\[
\rho_E = \frac{I \times \int V \, dt}{m \times 3.6} 
\]  
(S3)

\[
\rho_p = \frac{\rho_E \times 3600}{t} 
\]  
(S4)

where \( I \) is the discharge current, \( \int V \, dt \) is an area under discharge curve, \( m \) is the total mass deposited on both electrodes, and \( t \) is the total discharge time.
XPS (X-ray photoelectron spectroscopy) was utilized to study the elements and chemical composition of RGO and N-RGO. Fig. S2(a) shows the XPS survey spectra of RGO and N-RGO. The carbon (C) & oxygen (O) peaks and C, nitrogen (N) & O peaks in the XPS survey spectra strongly support the successful synthesis of the RGO and N-RGO, respectively. Fig. S2(b) shows the enlarged portion of the XPS survey spectra to highlight the presence of the nitrogen (N) element in the N-RGO as compared with RGO.
Fig. S2: (a) XPS survey spectra of RGO & N-RGO and (b) enlarged portion of RGO and N-RGO to investigate the presence of nitrogen (N).
Fig. S3: XPS narrow scan spectrum of carbon C1s peak and oxygen O1s peak of RGO.
Fig. S4: CV plots of (a) RGO and (b) N-RGO electrodes.
Fig. S5: GCD plots of (a) RGO and (b) N-RGO electrodes.
The specific capacitance of the RGO and N-RGO electrodes were evaluated by using the discharge time of GCD plots [Fig. S5(a, b)] at various current density. The specific capacitance \(C_s \text{ (F g}^{-1}\)] was calculated by using the equation \(C_s = I \Delta t / m \Delta V\) [8], where \(I\) is the discharge current, \(\Delta t\) is discharge time, \(m\) is the mass deposited on the electrodes, and \(V\) is the potential window. Here, we used \(~ 1.38\) mg for RGO electrodes and \(1.41\) mg for the N-RGO electrode.

![Graph showing specific capacitance vs. current density](image)

**Fig. S6:** Specific capacitance of RGO and N-RGO electrodes at different current densities.

According to the following Eq. S5, the self-discharge by Ohmic leakage resistance (potential driving model) indicates the dissipation in cell voltage under open-cell conditions of RGO/N-RGO SSC [9];

\[
V = V_o e^{-t/RC} \tag{S5}
\]

where \(V\) is the supercapacitor voltage during self-discharge, \(V_o\) is the initial potential (2.2 V in
present work), $t$ is the discharge time, $RC$ is the time constant of the self-discharge process.

Furthermore, for the diffusion-controlled model, the self-discharge curves of RGO/N-RGO SSC displayed a linear relationship between supercapacitor potential window $V$ and self-discharge time $t^{1/2}$ according to the following Eq. S6 [9];

$$V = V_o - mt^{1/2}$$  \hspace{1cm} (S6)

where $m$ is the diffusion parameter of the RGO/N-RGO SSC, which shows the diffusion rate of the electrolyte ions near the electrode surfaces.

![Fig. S7: Equivalent circuit.](image)

Furthermore, to examine the Warburg coefficient ($\sigma$), the real ($Z'$) and imaginary ($Z''$) part of impedance spectroscopy (Randles plots) were fitted to angular frequency ($\omega^{1/2}$) [Fig. S8] by using the Eq. S7 [10].

$$Z_W = \sigma \omega^{-1/2} - j\sigma \omega^{-1/2} = \omega^{-1/2} \sigma (1 - j)$$  \hspace{1cm} (S7)

where $j$ is the imaginary number, $\omega$ is the angular frequency, and $\sigma$ is the Warburg coefficient.
Fig. S8: (a) Real impedance ($Z'$) and (b) imaginary impedance ($Z''$) vs. frequency ($\omega^{-1/2}$) plots (Randles plots) of RGO/N-RGO SSC before/after 10,000 GCD cycles & 8h voltage holding tests.
Fig. S9: Bode plots of RGO/N-RGO SSC before/after 10,000 GCD cycles & 8h voltage holding tests.

By using Fig. S7, the estimated values of equivalent series resistance ($R_s$) are 6.8 $\Omega$, 14.4 $\Omega$ & 13.5 $\Omega$; charge-transfer resistance ($R_{ct}$) are 2.2 $\Omega$, 4.2 $\Omega$ & 7.1 $\Omega$ and Warburg impedance ($W_z$) are 9.3 $\Omega$, 21.6 $\Omega$ & 36.8 $\Omega$ before, after 10000 GCD cycles & 8h voltage holding tests (VHTs), respectively. These low resistance values from the EIS plot suggest high ionic conductivity and fast ion movements, which results in high rate capability. Fig. S8 shows the real and imaginary part of impedance vs. $\omega^{-1/2}$ (Randles plot) curves, fitted by using Eq. S7 to determine the Warburg coefficient ($\sigma$) of the RGO/N-RGO SSC before, after GCD cycles & VHTs. The $\sigma$ is inversely proportional to the diffusion coefficient, which illustrates the rate of charge
transfer. From Fig. S8, the evaluated value of $\sigma$ is 81.33, 50.24, and 55.07 $\Omega$ s$^{-1/2}$ before, after 10000 GCD cycles & 8h VHTs, respectively. These results justify the self-discharge mechanisms with the role of diffusion related electrochemical process. Fig. S9 represents the Bode plots of RGO/N-RGO SSC. The phase shift angles ($\Phi$) of RGO/N-RGO SSC are -72.1º, -52.5º, and -60.5º at the low frequency of 0.10 Hz before, after 10000 GCD cycles & 8h VHTs, respectively, exhibiting good capacitive nature.

After stability tests, we investigated the morphology and composition of RGO and N-RGO electrodes used in the RGO/N-RGO SSC. We de-assembled RGO/N-RGO SSC, and after that, RGO and N-RGO electrodes were cleaned by NMP and for DI-water and dried under vacuum in a hot air oven. Finally, the morphology and composition of RGO and N-RGO electrodes of RGO/N-RGO SSC were studied by using FESEM and EDX (S-4800 HITACHI, Ltd., Japan), respectively.

Fig. S10: (a, b) FESEM images, (c) FESEM image selected for EDX and (d) EDX spectrum of RGO.
Fig. S11: (a, b) FESEM images, (c) FESEM image selected for EDX and (d) EDX spectrum of N-RGO.
Table S1: Comparative study of reduced graphene oxide (RGO) and nitrogen heteroatom doped reduced graphene oxide (N-RGO) as electrode materials for supercapacitor device (two-electrode systems) applications.

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Electrode Material(s)</th>
<th>Capacitance</th>
<th>Energy density</th>
<th>Stability</th>
<th>Self-discharge</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>GCD</td>
<td>VHTs</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>RGO/N-RGO</td>
<td>158.2 mA h g(^{-1})</td>
<td>106.3 W h kg(^{-1})</td>
<td>95.5 % (10,000 cycles)</td>
<td>0.54 V (after 8 h)</td>
<td>Present work</td>
</tr>
<tr>
<td>2</td>
<td>RGO</td>
<td>110.3 mA h g(^{-1})</td>
<td>22.1 W h kg(^{-1})</td>
<td>89.4 % (10,000 cycles)</td>
<td>0.7 V (after 2 h)</td>
<td>[1]</td>
</tr>
<tr>
<td>3</td>
<td>N-RGO</td>
<td>141.1 mA h g(^{-1})</td>
<td>28.2 W h kg(^{-1})</td>
<td>95.4 % (10,000 cycles)</td>
<td>0.7 V (after 8 h)</td>
<td>[2]</td>
</tr>
<tr>
<td>4</td>
<td>RGO</td>
<td>109.3 F g(^{-1})</td>
<td>--</td>
<td>100 % (1000 cycles)</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>5</td>
<td>N-RGO</td>
<td>138.3 F g(^{-1})</td>
<td>--</td>
<td>94 % (1000 cycles)</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>6</td>
<td>GNCN</td>
<td>294 F g(^{-1})</td>
<td>26 W h L(^{-1})</td>
<td>93 % (5000 cycles)</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>7</td>
<td>G/GONs</td>
<td>47.4 F g(^{-1})</td>
<td>6.6 W h kg(^{-1})</td>
<td>93 % (5000 cycles)</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>8</td>
<td>GH</td>
<td>191 F g(^{-1})</td>
<td>9.8 W h kg(^{-1})</td>
<td>95 % (10,000 cycles)</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>9</td>
<td>JGF</td>
<td>58 F cm(^{-3})</td>
<td>2.78 mW h cm(^{-3})</td>
<td>95.5 % (10,000 cycles)</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>10</td>
<td>N-GNS</td>
<td>144 F g(^{-1})</td>
<td>80.5 W h kg(^{-1})</td>
<td>94.3 % (2000 cycles)</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>11</td>
<td>N-RGO</td>
<td>96.4 F g(^{-1})</td>
<td>20.9 W h kg(^{-1})</td>
<td>83 % (1500 cycles)</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>12</td>
<td>GF</td>
<td>135 F g(^{-1})</td>
<td>15.4 W h kg(^{-1})</td>
<td>--</td>
<td>--</td>
<td>[18]</td>
</tr>
</tbody>
</table>

Table S1 abbreviations: GCD – galvanostatic charge/discharge; VHTs – voltage holding tests;
References


