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Supporting Information

## Multifunctional Nitrogen-doped Graphene Nanoribbon Aerogels for Superior Lithium Storage and Cell Culture

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**Figure S1.** FE-SEM (a, b) and TEM (c) images of pristine carbon nanotubes (CNTs) synthesized by a floating catalyst chemical vapor deposition method. d) Diameter distribution of CNTs based on Figure 2b. The diameters of CNTs range in 25-71 nm with average value of 43 nm. e) Nitrogen adsorption and desorption isotherm of CNTs. The BET surface area of CNTs is 49.6 m<sup>2</sup> g<sup>-1</sup>.



**Figure S2.** TEM images (a, b) of GONRs. The GONRs have flat structure and high aspect ratio without tube cavities, indicating that the CNTs have been fully unzipped. (c) GONRs can be well dispersed in water and form uniform colloidal dispersion confirmed by evident Tyndall effect when a beam of light passing through it. (d, e) AFM images of graphene nanoribbons of the original oxidation product which spin-casting onto the mica surface. (f) Thickness distribution of graphene oxide nanoribbons. The thicknesses of graphene oxide nanoribbons ranges in 6.3-32.6 nm based on the measurement of 30 nanoribbons (Fig. S2d,e). And the average thickness of graphene oxide nanoribbons is 18.5 nm namely consisted of 17-18 layers of graphene. (g) The typical line profiles showing the lines scans of different regions in Fig. 1a. (h) FE-SEM images and (j) TEM image of N-GNRA. The images show the

fishnet-like structure of GNR sheets with abundant nanoscale pores. And the diameters of GNRs range in 70-188 nm with average value of 121 nm based on imaged (Fig. S2i).



**Figure S3.** Time dependent formation of GNR hydrogel. The dispersion of GONRs (4 mg  $mL^{-1}$ ) with brown color firstly turned black then became sticky and finally transformed into hydrogel after hydrothermal at 95 °C for 2 h.



**Figure S4.** The influence of GONR concentration ( $C_{\text{GONR}}$ ) on the formation of GNR hydrogel. All of the hydrogels were obtained after hydrothermal reacting for 6 h at 95 °C. When the  $C_{\text{GONR}}$  was lower than 4 mg mL<sup>-1</sup>, only black powdery materials (2 mg mL<sup>-1</sup>) or incompact hydrogel (3 mg mL<sup>-1</sup>) was produced. The unsuccessful assembly could be ascribed to the difficult cross-linking of GNRs at low  $C_{\text{GONR}}$ . While perfect hydrogels could be formed when  $C_{\text{GONR}} \ge 4$  mg mL<sup>-1</sup>. In order to obtain aerogel with the low density, the  $C_{\text{GONR}} = 4$  mg mL<sup>-1</sup> was chosen.



Figure S5. XRD patterns of CNTs, GONRs, FGNRA and N-GNRA.



**Figure S6.** (a) Elemental analysis and (b) XPS of CNTs, GONRs, FGNRA and N-GNRA. (c) Table is the C/O and N/C atomic ratio of all samples based on the elemental analysis and XPS. The elemental contents (C, N, H, O) of N-GNRA are based on the elemental analysis of three different samples. Their N/C ratio are 7.6, 7.7, 7.6 atm% respectively and the average value is ~7.6 atm%. The C/O atomic ratio of GONRs is 1.20 as shown in elemental analysis, much

lower than the 21.16 of pristine CNTs, which means lots of oxygen containing functional groups were produced after the oxidation process. The C/O ratio increased to 3.02 after assembly due to the GONRs were slightly reduced by EDA. And the N/C ratio of FGNRA increased to 0.32 from zero of GONRs demonstrated the introduction of amino functional groups. The C/O ratio of final N-GNRA was 14.10, indicating most of functional groups were eliminated after the thermal treatment. While nitrogen atoms were doped into the carbon framework with a content of 7.6 atm%. The value change of C/O and N/C ratio of all samples based on XPS showed the same trends in accordance with elemental analysis.



**Figure S7.** (a) SEM image of N-GNRA. (b-d) C, O, N elemental mapping. The N-GNRAs mainly compose of C, O, N elements. The dots densities of all elements match with the selected part shown in SEM image, demonstrating their uniform distribution.



**Figure S8.** Fourier transform infrared spectroscopy (FTIR) of GONRs, FGNRA and N-GNRA. There are C-O (1136 cm<sup>-1</sup>, epoxy or alkoxy), C=O (1723 cm<sup>-1</sup>, carbonyl or carboxyl) functional groups attached to the surface or edges of GONRs.<sup>[1]</sup> Once the FGNRA formed, the peak intensity of C-O bonds dramatically dropped and the C=O bonds disappeared due to the reduction ability of EDA. While new group N-H was introduced through the ring-opening reaction of epoxy groups.<sup>[2,3]</sup> The functional groups were eliminated after the annealing treatment as shown in the curve of N-GNRA.



**Figure S9.** (a) Comparative thermal analysis (TGA); (b) Differential thermal analysis (DTA); (c) Raman spectra(excited by 633 nm laser) of CNTs, GONRs, FGNRA and N-GNRA.

The TGA and DTA curves show three different regions. The weight loss below 100 °C ascribes to the evaporation of chemically or physically absorbed water. The interval

distributes in 100-400 °C are due to the pyrolysis of functional groups.<sup>[4]</sup> The last region (400 -700 °C) corresponds to the oxidation of carbon framework.<sup>[5]</sup> The DTG plot derived from TG exhibits one single peak located at 595 °C for the pristine CNTs. While the GONRs exhibit two independent sharp peaks locate at 188 and 482 °C. The first peak corresponds to the pyrolysis of oxygen-containing functional groups. The second peak ascribes to GNRs which have large surface area and contain abundant edges, leading to less thermal stability than CNTs.<sup>[6]</sup> The amount of functional groups decreases after the EDA mediated assembly and three small peaks (locate at 153, 232, 322 °C) appear at the middle temperature zone, corresponding to the decomposition of C-OH, C-NH<sub>2</sub>, C-NH(R), respectively. The thermal stability of GNRs increases as the weight loss peak shifts to 543 °C due to the restored conjugation of graphene structure by EDA.<sup>[3]</sup> There is no peak in the DTA curve of N-GNRA, this means most of functional groups have been removed. However, the thermal stability of N-GNR becomes lower than that of the GNRs since the nitrogen doping process introduces many defects into the carbon framework as shown in the following Raman spectra.

Raman spectra were used to identify the structural differences between samples. There are D, G band locate around 1328, 1590 cm<sup>-1</sup> respectively (Figure S9c). The D band is a double-resonance Raman mode, which can be understood as a measurement of structural disorder coming from any defects. The G band originates from the in plane stretching vibrations of the C-C bonds in graphitic materials. The ratio of the D and G band ( $I_D/I_G$ ) can be used to estimate the defects density of carbon materials.<sup>[7]</sup> The  $I_D/I_G$  ratio of GONRs is 1.27, 2 times the value of pristine CNTs (0.65) because the oxidant creates defective sites on the graphene sheets and more exposure of edges. After partial reduction by EDA, the  $I_D/I_G$  value slightly rise to 1.38 owing to the increasing number of small domains of aromaticity which is responsible for the D peak.<sup>[1,8]</sup> The defects on GNRs are further added on account of the nitrogen doping thus the N-GNRA has the highest  $I_D/I_G$  ratio of 1.49.<sup>[9]</sup>



**Figure S10.** The amount of EDA vs the volume of GNR hydrogel. (a) Digital images of GNR hydrogel formed with different EDA amount (10-80 μl). The hydrogel cannot be formed without EDA adding. And there is evident volume shrinkage of samples with the increment of EDA amount especially after the treatment of freeze-drying as shown in images (b) (FGNRAs). (c) Blue curve represents the pH value of GONR dispersion after adding different amount of EDA (10-80 μl). Black and red curves show that a series of densities of FGNRA (5.7-54.7 mg cm<sup>-3</sup>) and N-GNRA (4.2-42.5 cm<sup>-3</sup>) can be obtained with different adding amount of EDA. As reported in the formation of graphene hydrogel using hydrothermal method, the pH value had great influence on their compressive strength and conductivity.<sup>[10]</sup> The most suitable pH value for the dispersion of GO is around 10 due to the ionization of carboxylic acid groups. EDA shows strong alkaline and can change the pH of GONRs dispersion. So suitable amount of EDA is needed in order to get proper pH of the mixture. As

shown in the blue curve, the addition of  $\geq 40 \ \mu L$  EDA into 5 mL of GONR dispersion with a concentration of 4 mg mL<sup>-1</sup> causes the increase of pH up to  $\geq 11.0$  and the shrinkage of the aerogel. Although, aerogel with the lowest density was obtained with 10  $\mu$ L EDA, large holes can be found in surface. Thus, the most suitable amount of EDA is 20 $\mu$ L as the aerogel has negligible volume shrinkage as well as a smooth surface.



**Figure S11.** (a) Digital images show partial compressibility of FGNRA. (b) The stress and strain curves of N-GNRA and FGNRA at a maximum strain of 60%. It clearly demonstrates that the irreversible deformation can be reduced from 21% for FGNRA to almost 0 for N-GNRA after annealing treatment.



**Figure S12.** (a, b) SEM images of nitrogen doped graphene aerogl (N-GA). The inset image in a) is the digital image of N-GA. Graphene oxide (GO, 4 mg mL<sup>-1</sup>) was used as precursor to synthesize N-GA through the EDA mediated hydrothermal process. Different with the hierarchical porous structure of N-GNRA, the N-GA is constructed by numerous of large graphene sheets with macropores.



**Figure S13.** (a) Cycling performance of N-GA tested at a current density of 0.1 A  $g^{-1}$  for the first three cycles then 0.5 A  $g^{-1}$  for the following cycles. b) Rate capability of N-GA tested at various current densities ranging from 0.2 to 3 A  $g^{-1}$ .



**Figure S14.** Electrochemical impendence spectra of N-GNRA and GNRs. The impendence of N-GNRA is only half value of GNRs. Nitrogen atom has additional lone pairs of electrons which contributes additional electrons and provides electron carriers for the conduction band.<sup>[11]</sup> Thereby, N-GNRA shows higher electrical conductivity than the GNRs without nitrogen doping.



**Figure S15.** Fluorescence micrographs of human medulloblastoma DAOY cells attached on the N-GNRA after culturing for 1 day.

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