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# Generation of Three Dimensional Pore-Controlled Nitrogen-doped Graphene Hydrogels for High-Performance Supercapacitor by Employing Formamide as Modulator

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## 1. Experimental section

### 1.1. Synthesis of NGH-1, NGH -2, NGH -3, NGH -4.

In a typical synthesis, GO aqueous suspension and formamide were mixed under vigorous stirring. After 2h vigorous stirring, the mixed solution was transferred into a Teflon-lined stainless steel autoclave, a thermal treatment was performed for the Teflon-liner in an electric oven at 180°C for 12h. By altering the volume ratio of GO aqueous suspension and formamide ($V_{GO}$: $V_{formamide}$= 2:8, 4:6, 6:4, 8:2, respectively.), four NGHs were produced, referred as to NGH-1, NGH-2, NGH-3, NGH-4, respectively. Then the obtained NGHs were freeze-dried.

### 1.2 Characterization of catalysts

The morphology and structure of NGHs were observed under field emission scanning electron microscopy (FE-SEM, JSM-7800F (JEOL)). Low-resolution transmission electron microscopy (TEM) was carried out on a Zeiss LIBRA 200 FETEM instrument operating at 200 kV. The crystal structures of NGHs were confirmed using the automated X-ray diffraction equipment (XRD, Rigaku D/MaXIIIA, Japan). The surface area of NGHs is calculated from $N_2$ adsorption isotherms using Brunauer-Emmett-Teller BET (Shimadzu, Micromeritics ASAP 2010 Instrument). XPS was acquired using a Kratos XSAM800 spectrometer equipped with monochromatic Al X-ray source (Al KR, 1.4866 keV), and the binding energy was calibrated by using 284.6 eV as the C 1s peak energy.

### 1.3. Electrochemical activity tests

Electrochemical measurements: All electrochemical experiments were performed in a standard three-electrode cell at room temperature on a Parstat 2273 potentiostat/galvanostat workstation assembled with a model 636 rotational system (AMETEK) at room temperature. The cell is consisting of a glassy carbon working electrode (GC electrode, 5 mm in diameter, PINE: AFE3T050GC), an Ag/AgCl (saturated KCl) reference electrode, and a platinum foil counter electrode. All potentials in this study, however, are given relative to the reversible hydrogen electrode (RHE). The working electrodes were prepared by applying catalyst ink onto glassy carbon (GC) disk electrodes. In brief, the samples were dispersed in ethanol and ultrasonicated for 15 minutes to form a uniform catalyst ink. Well-dispersed sample ink was applied onto a pre-polished

GC disk. After drying at room temperature, a drop of 0.05 wt. % Nafion solution was applied onto the surface of the sample layer to form a thin protective film.

The samples were characterized by a cyclic voltammetry (CV) and galvanostatic charge−discharge cycling were performed at room temperature in 6 M aqueous KOH in the potential range 0 to 0.8 V (ORR). The scan rate for CV is 5, 10, 20, 50, 100, 200 mV/s, respectively.

Electrochemicalim- pedance spectroscopy (EIS) measurements were carried out using an electrochemical work station (CHI660b, Chen Hua Instruments Co. Ltd. , Shanghai).

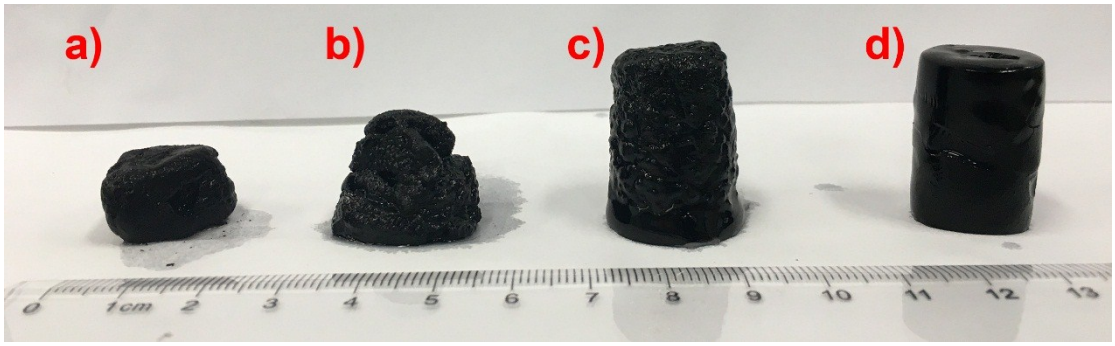


Fig. S1. Digital images of the NGHs; a). NGH-1, b). NGH-2, c). NGH-3, d). NGH-4,

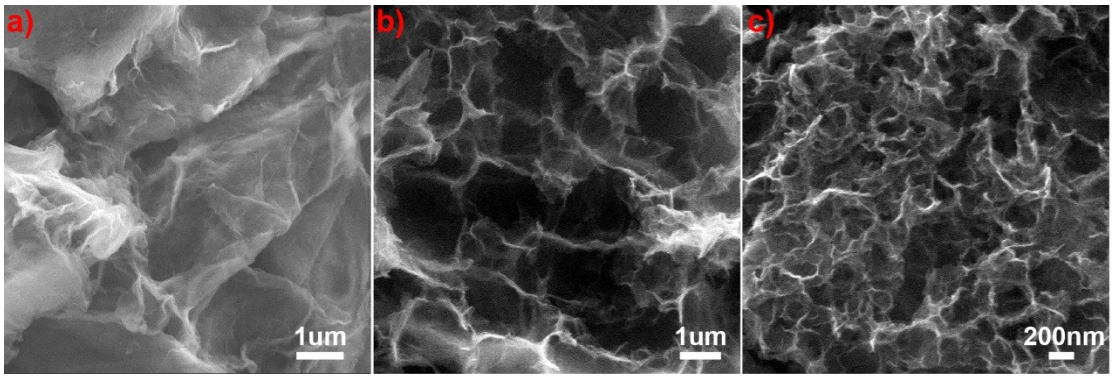


Fig. S2. SEM of graphene oxide (a) and NGH-3 (b, c)

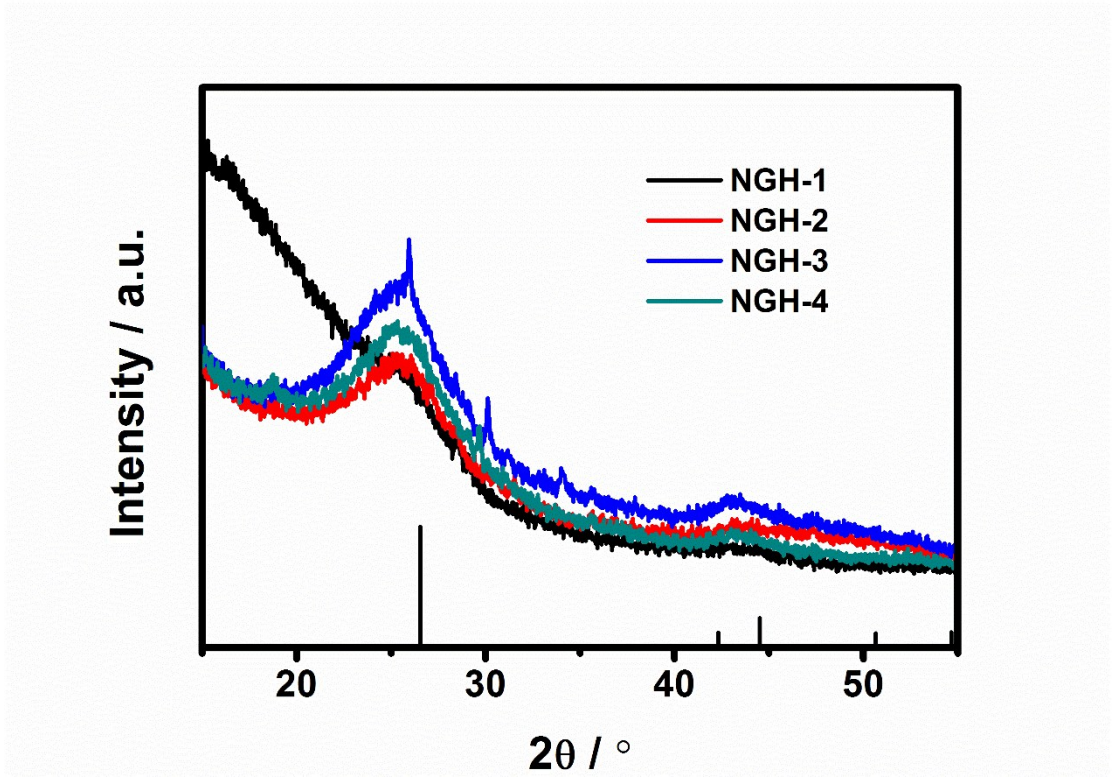


Fig. S3. XRD pattern of NGHs

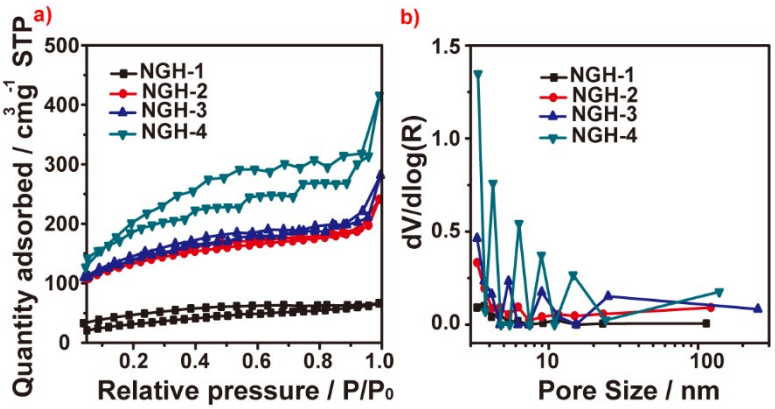


Fig. S4. (a) $N_2$ Adsorption (black line)- desorption (red line) isotherms of various NGHs; (b) Pore size distribution curves of various NGHs

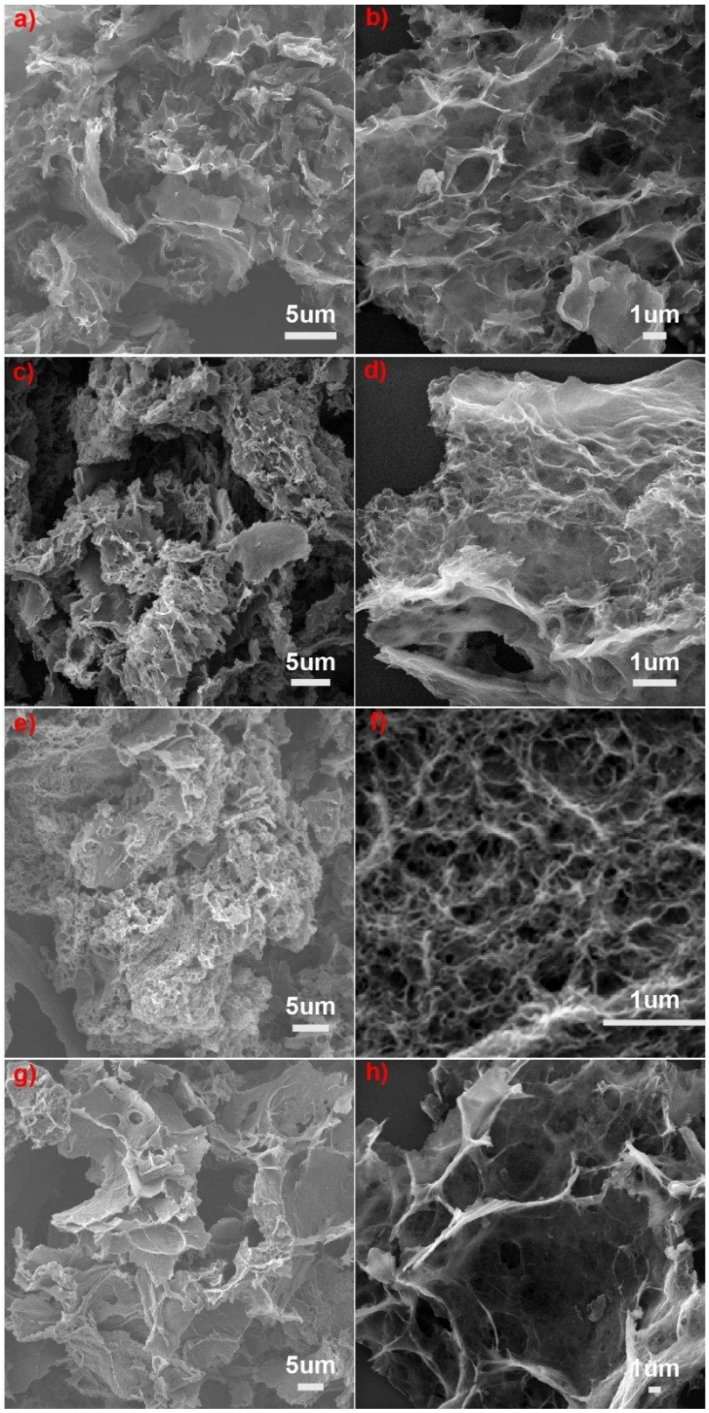


Fig. S5. SEM images of NGH-1(a, b); NGH-2(c, d); NGH-3(e, f); NGH-4(g, h);

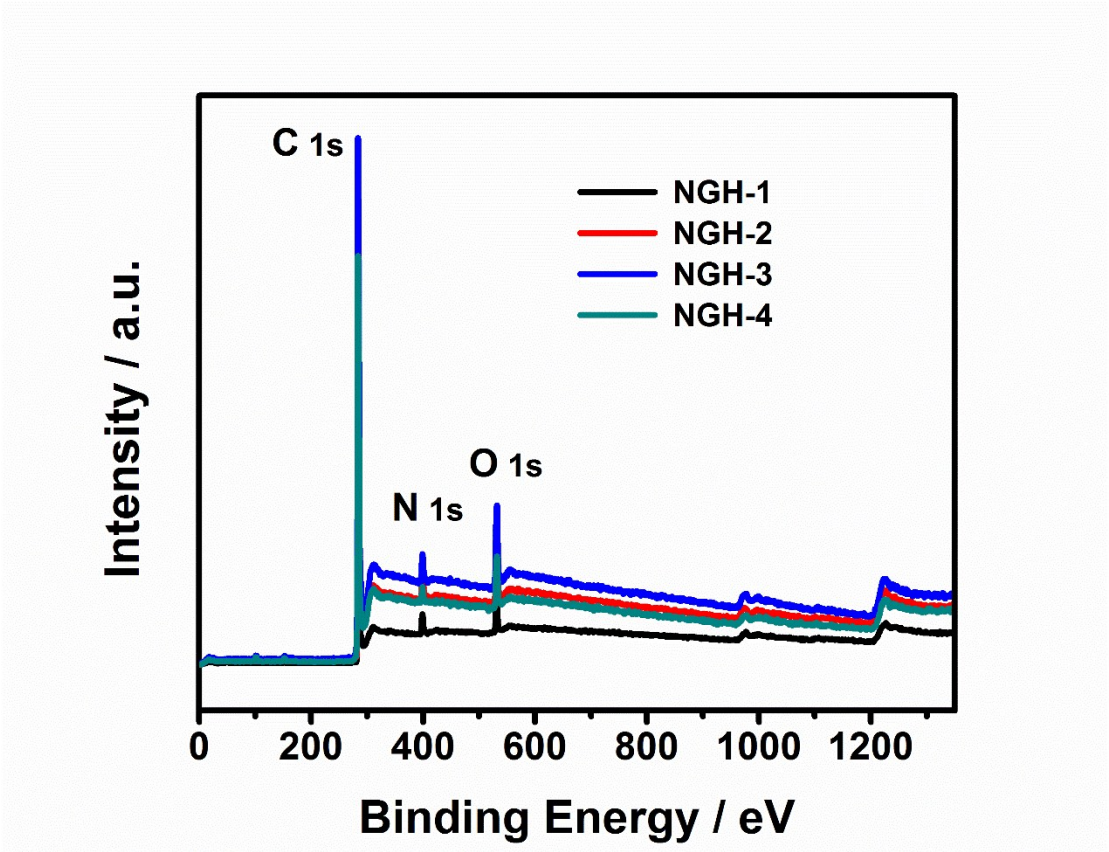


Fig. S6. XPS spectrum of NGHs.

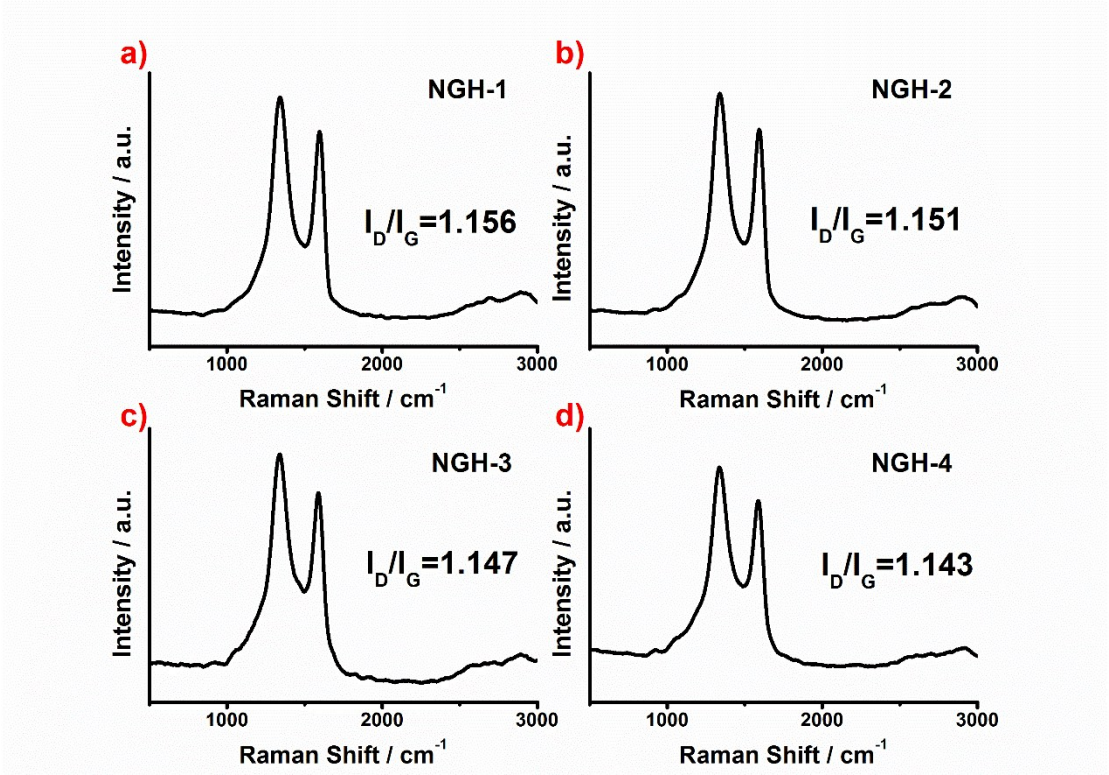


Fig. S7. Raman of NGH-1(a); NGH-2(b); NGH-1(c); NGH-1(d)

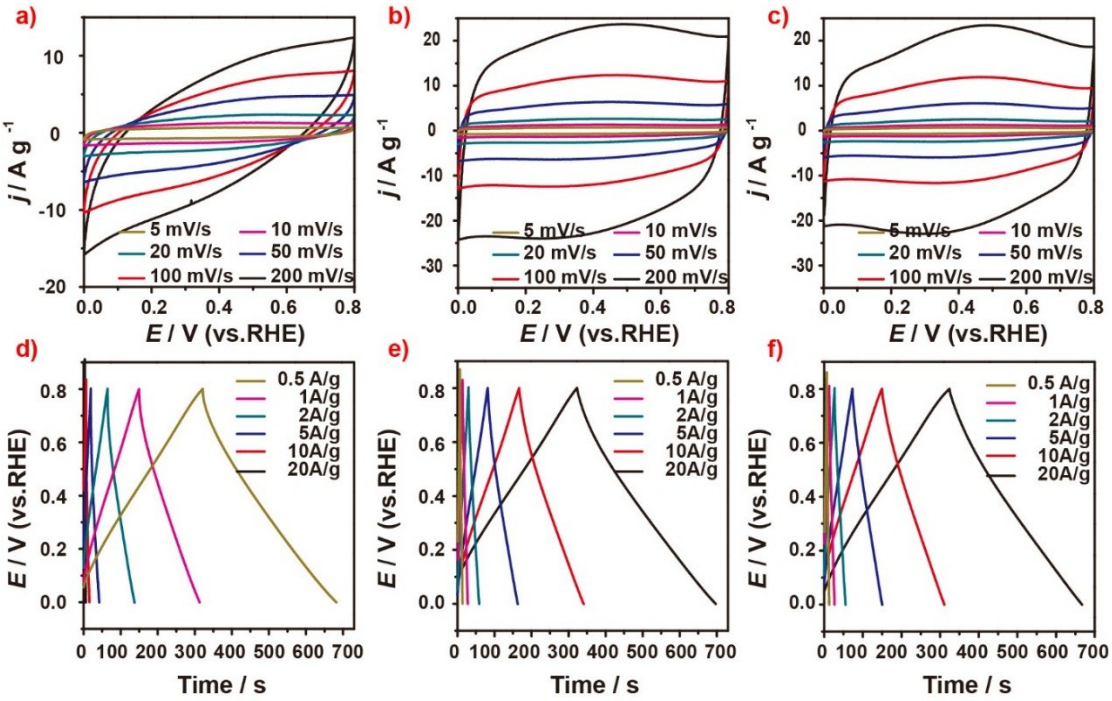


Fig. S8. (a, b, c) CV curves of NGHs for different scan rates. (d, e, f) Galvanostatic charge/discharge curves of NGHs under different constant currents. (a, d) NGH-1; (b, e) NGH-2; (c, f) NGH-4.

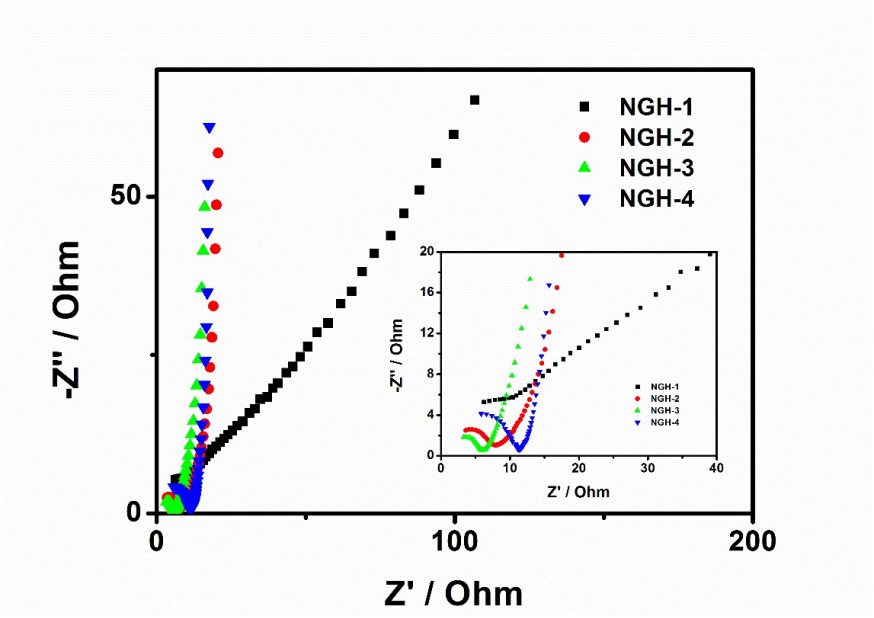


Fig. S9. Nyquist plots of the NGHs

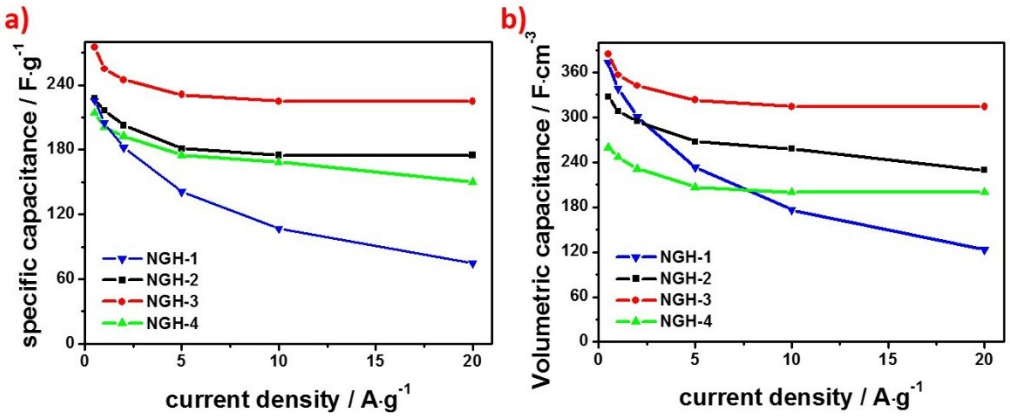


Fig. S10. The capacitance comparison of NGHs

Table. S1. The content of N.

| | NGH-1 | NGH-2 | NGH-3 | NGH-4 |
|---|---|---|---|---|
| N | 7.19 at.% | 4.93 at.% | 4.44 at.% | 2.71% |
| Pyridinic N | 32.72 at.% | 27.17 at.% | 26.28 at.% | 25.40 at.% |
| Nitrile N | 39.64 at.% | 48.27 at.% | 46.36 at.% | 52.54 at.% |
| Quaternary N | 27.62 at.% | 16.16 at.% | 14.55 at.% | 10.62 at.% |
| Pyridinic-N-oxide | 0 | 8.39 at.% | 12.81 at.% | 11.45 at.% |

Table. S2. Comparsion of NGH-3 with other graphene framework.

| sample | method | capacitance | rate | system | Ref. |
|---|---|---|---|---|---|
| **This work** | Hydrothermal Process | 275 F/g | 0.5A/g | 3 | / |
| **self-assembled graphene hydrogel** | Hydrothermal Process | 175F/g | 1A/g | 2 | ACS Nano, 2010, 4(7), 4324–4330. |
| **graphene aerogel** | Sol–gel | 128F/g | 0.05A/g | 2 | J. Mater. Chem., 2011, 21, 6494–6497 |
| **Graphene Hydrogels** | Hydrothermal Process | 220F/g | 1A/g | 2 | J. Phys. Chem. C 2011, 115, 17206–17212 |
| **B,N-doped-GA** | Hydrothermal Process | 239F/g | 1mV/s | 3 | Adv. Mater. 2012, 24, 5130–5135 |
| **N-doped-GA** | | 190F/g | | | |
| **B-doped-NG** | | 228F/g | | | |
| **Undoped-NG** | | 181F/g | | | |
| **Nitrogen-doped graphene sheets** | Hydrothermal Process | 161F/g | 0.5A/g | 3 | Electrochimica Acta, 2012, 85, 459-466. |
| **graphene aerogel - based mesoporous carbons** | Hydrothermal Process and calcination | 226F/g | 1mV/s | 3 | J. Am. Chem. Soc. 2012, 134, 19532−19535 |
| | | 168F/g | 2A/g | | |
| **graphene aerogel** | Hydrothermal Process | 176F/g | 1mV/s | | |
| **3D architectures of graphene** | Self-assembly | 151.6F/g | 0.5A/g | 3 | J. Mater. Chem., 2012, 22, 22459–22466 |
| **nitrogen-doped graphene hydrogels** | Hydrothermal Process | 190.1F/g | 10A/g | 2 | Nano Energy, 2013, 2, 249–256 |
| **nitrogen- and sulfur-codoped 3D mesoporous carbon** | calcination | 320F/g | 1A/g | 3 | ACS Appl. Mater. Interfaces, 2014, 6, 2657−2665 |
| | | 143F/g | 10A/g | | |
| **Nitrogen-Doped Graphene** | Microwave Irradiation | 200F/g | 0.5A/g | 3 | ACS Appl. Mater. Interfaces, 2014, 6, 6361–6368 |
| **RGO/CB** | vacuum filtration process | 95.7F/g | 0.5mV/s | 2 | Journal of Power Sources, 2014, 271, 269 |
| **Nitrogen-Doped Graphene Aerogels** | Hydrothermal Process | 176F/g | 10A/g | 2 | ACS Appl. Mater. Interfaces 2015, 7, 1431−1438 |
| | | 223F/g | 0.2A/g | | |
| **Crumpled** | Polymerization | 245.9F/g | 1A/g | 2 | Adv. Mater. 2012, |

| | | | | | |
|---|---|---|---|---|---|
| **Nitrogen-Doped Graphene** | and calcination | 302F/g | 5mV/s | 3 | 24, 5610–5616 |
| **HTrGO-B (ammonia solution treatment)** | Hydrothermal Process | 185F/g | 1A/g | 2 | Journal of Power Sources, 2013, 233, 313 |
| **Activated Graphene** | Microwave Irradiation and KOH activation | 165F/g | 1.4A/g | 2 | Science 332, 1537–1541 (2011). |
| **Activated Reduced Graphene Oxide Films** | KOH activation | 120F/g | 10A/g | 2 | Nano Lett. 2012, 12, 1806−1812 |
| **Activated Graphene based carbon** | Microwave Irradiation and KOH activation | 172F/g | 2A/g | 2 | ACS Nano, 2013, 7, 6899-6905 |
| **nitrogen-doped graphene hydrogels** | Hydrothermal Process | 246 F/g | 3A/g | 3 | J. Mater. Chem. A, 2014, 2, 8352–8361 |
| **3D hierarchical carbon** | sponge-templating with KOH activation | 188F/g | 1A/g | 3 | Adv. Mater. 2016, 28, 5222–5228 |
| **3D porous carbon fabrics** | Hydrothermal Process | 229 F/g | 1A/g | 3 | ACS Appl. Mater. Interfaces 2015, 7, 4257−4264 |
| **Reduced graphene oxide** | calcination | 182 F/g | 1A/g | 2 | Chem. Commun., 2015, 51, 5598-5601. |
| **3D Porous N-Doped Graphene** | Hydrothermal Process and calcination | 509 F/g | 1A/g | 3 | Adv. Mater. 2015, 27, 5171–5175 |
| **Reduced graphene oxide** | using redox additive electrolyte | 298F/g | 0.8A/g | 2 | Carbon ,2015, 90, 260 –273 |
| **Holey Graphene Oxide** | Hydrothermal Process and $H_2O_2$ activation | 283 F/g | 1 A/g | 3 | Nano Lett. 2015, 15, 4605−4610 |
| **Ultrathin porous carbon shell** | Calcination | 251 F/g | 1 A/g | 3 | Carbon, 2017, 111 419-427 |
| **graphene nanoribbons** | Calcination and KOH | 189 F/g | 0.1A/g | 2 | Nature Chemistry, 2016, 8, 718–724 |

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|---|---|---|---|---|---|
| | activation | | | | |
| **3D Graphene-like carbon** | Templating and calcination | 252 F g | 10mV/ s | 2 | Carbon, 2017, 111 128-132 |