Supporting Information

Hydrothermal synthesis of nitrogen-doped graphene hydrogels using amino acids with different acidities as doping agents

Tao wang[a], Luxiang Wang[a], Dongling Wu[a], Wei Xia[b], Hongyang Zhao [a] and Dianzeng Jia*[a]

FT-IR spectroscopy characterization

In order to confirm the unreacted reagent has been removed after purification process, the chemical structure of NGasp, NGgly, and NGarg were investigated by FT-IR spectroscopy. For comparison, three kinds of amino acid (DL-aspartic acid, L-glycine and L-arginine), GO-aspartic acid, GO-glycine, GO-arginine and RGO were also investigated. The preparation process of GO-aspartic acid, GO-glycine and GO-arginine were as follows: 0.15 g DL-aspartic acid, L-glycine, and L-arginine were dissolved in 30 mL GO solution (2 mg mL^{-1}), respectively. The mixture was magnetically stirred for 12 h at room temperature and then centrifuged at 17000 rpm for 30 minutes. Finally, the collected sample was dried in oven at 100 °C for 12 h. The as prepared sample were labeled as GO-aspartic acid, GO-glycine and GO- arginine, respectively. During the preparation process of GO-arginine, we found that the color of the mixture of GO and arginine changed to black after stirred about half an hour, which imply that GO was partially reduced by arginine. Actually, using arginine as reducer to reduce GO has also been reported. [s1]

Fig. S1 shows the FT-IR spectrum of DL-aspartic acid, L-glycine, L-arginine, GO, GO-aspartic acid, GO- glycine, GO- arginine, RGO, NGasp, NGgly, and NGarg, respectively. The peak at 2601-3140 cm^{-1} in DL-aspartic acid, L-glycine, L-arginine belong to the vibration absorption band of -NH_3^+. The typical peaks of GO appear at 1738 cm^{-1} (C=O carboxyl stretching vibration), 1640 cm^{-1} (C=C in aromatic ring), 1405 cm^{-1} (C-OH stretching) and 1050-1226 cm^{-1} (C-O-C in epoxide). The wide peak appearing at 3000-3590 cm^{-1} could be assigned to the hydroxyl groups. Compared with that of pure amino acid, the FT-IR spectrum of GO-aspartic acid, GO-glycine and GO-arginine show generally similar to GO, suggesting that after mixing with GO, amino acids was not adsorbed heavily by GO. It should be noted that the peak at 1738 of cm^{-1} of GO-arginine disappeared, which was due to the partially reduction of GO by arginine acid.[s1] Furthermore, for the spectrum of RGO, NGasp, NGgly and NGarg, the peak at 3425 cm^{-1} was assigned to the hydroxyl groups. The peaks of these spectrums at 1050-1738 cm^{-1} were very weak, which indicated that GO was reduced after hydrothermal reaction. However, a new peak at 1533 cm^{-1} (N-H stretching vibration) appeared in NGasp, NGgly and NGarg, indicates the formation of -C-NH-C- bands due to the reaction between the epoxide group and the amine group. The weak peak of NGasp in 1533 cm^{-1} can be attributed to its low N content (1%). The above mentioned results indicated that the unreacted reagents were indeed removed after the purification process.

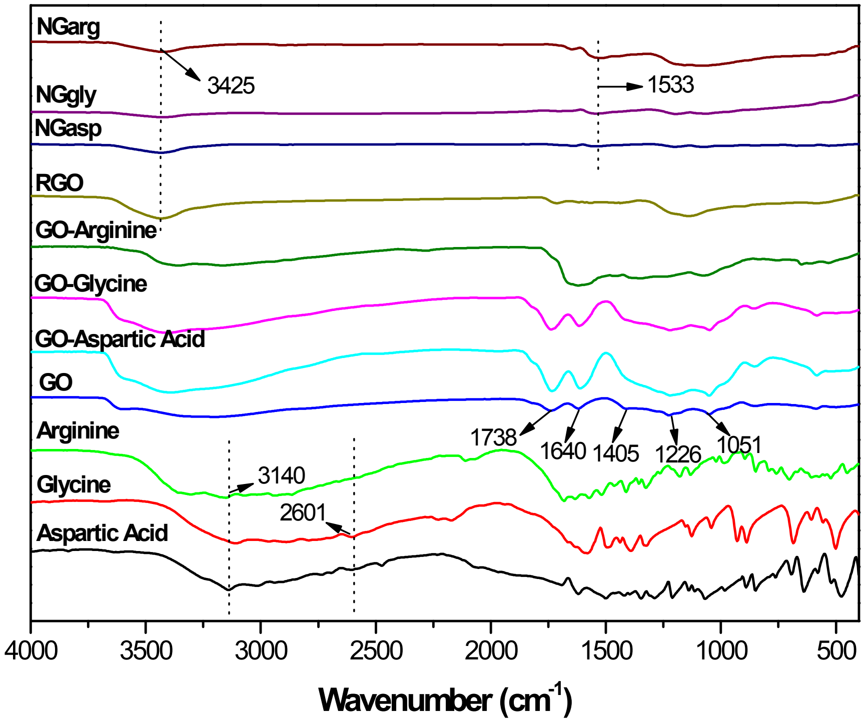

Fig. S1 FT-IR spectra of DL-aspartic acid, L-glycine, L-arginine, GO, GO-aspartic acid, GO- glycine, GO- arginine, RGO, NGasp, NGgly, and NGarg.

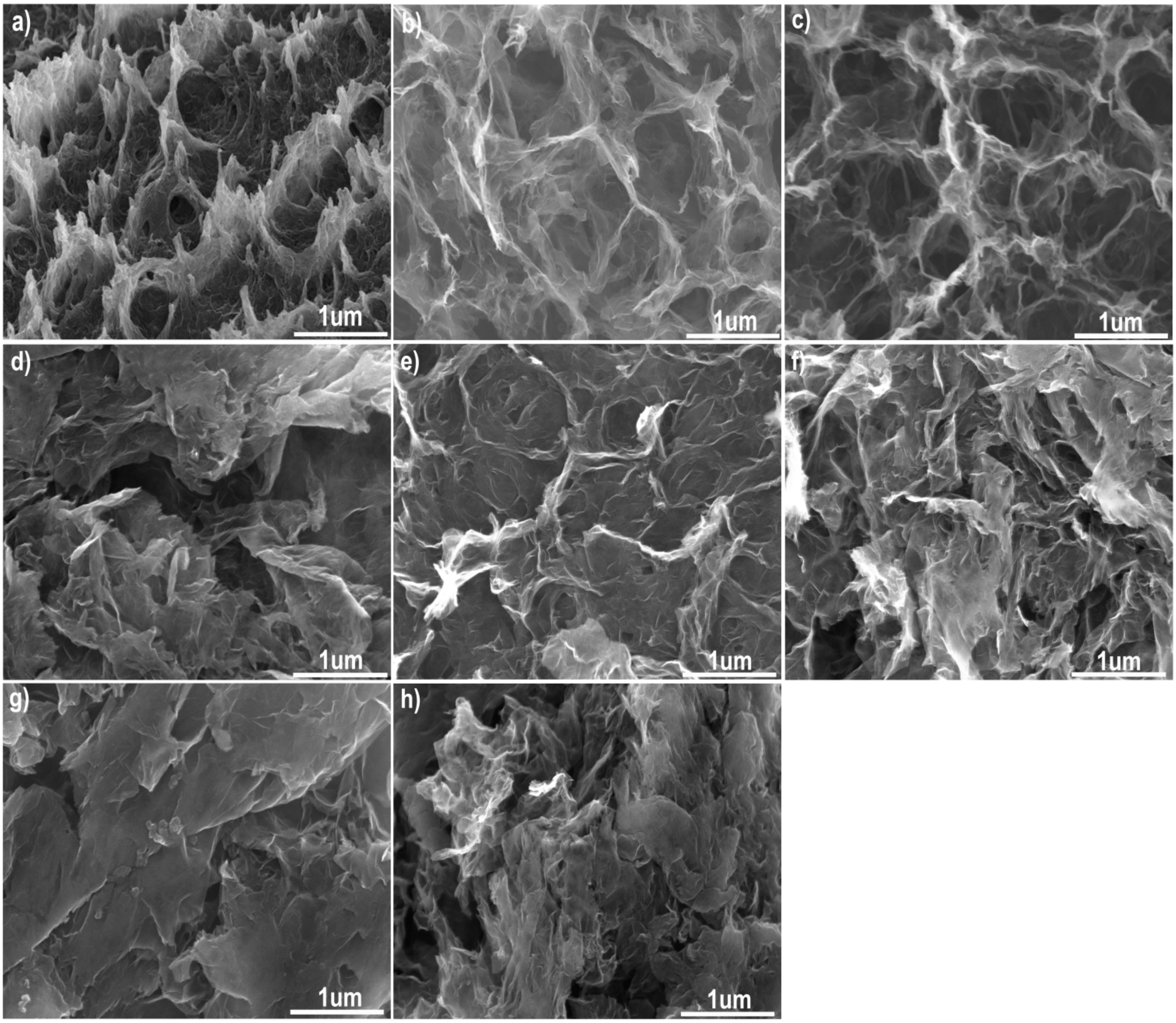

Fig. S2 SEM images of the samples prepared by adding different amino acids with different acidities. (a) NGasp1 (DL-aspartic acid, acidic), (b) NGasp10 (DL-aspartic acid, acidic), (c) L-Glutamic Acid (acidic), (d) L-Leucine (neutral), (e) L-Alanine (neutral), (f) L-Threonine (neutral), (g) L-Lysine (basic) and (h) L-Histidine (basic), respectively.

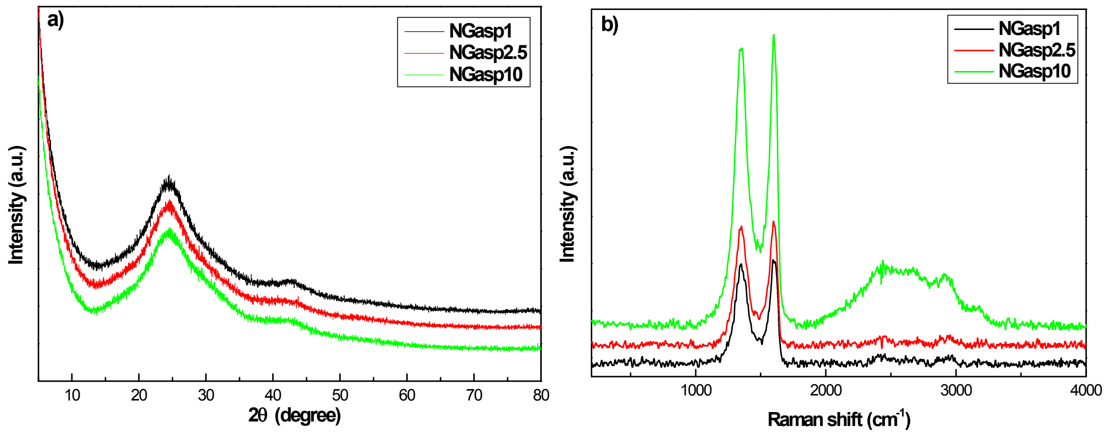

Fig. S3 (a) XRD patterns and b) Raman spectra of NGasp1, NGHasp2.5 and NGasp10, respectively.

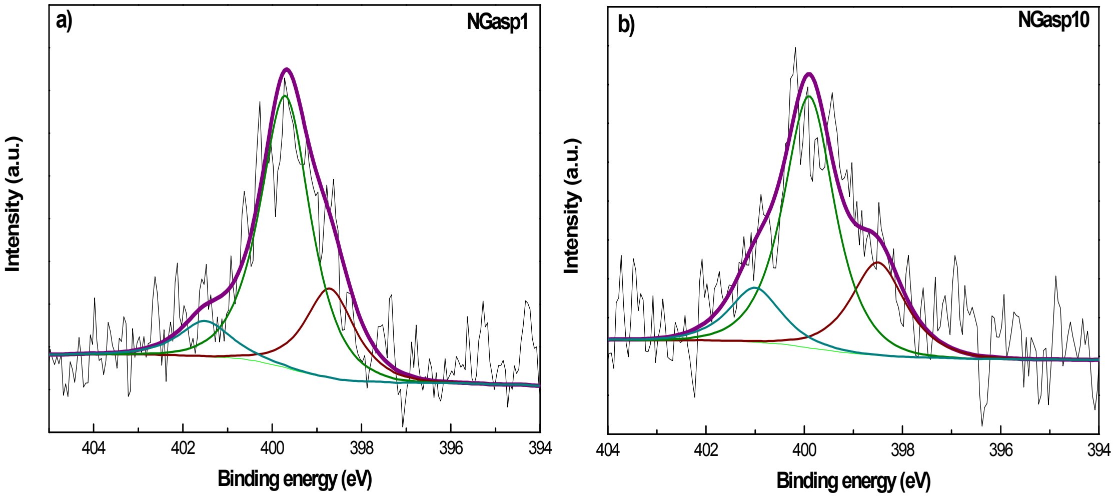

Fig. S4 (a) and (b) N 1s region spectra of NGasp1 and NGasp10 samples.

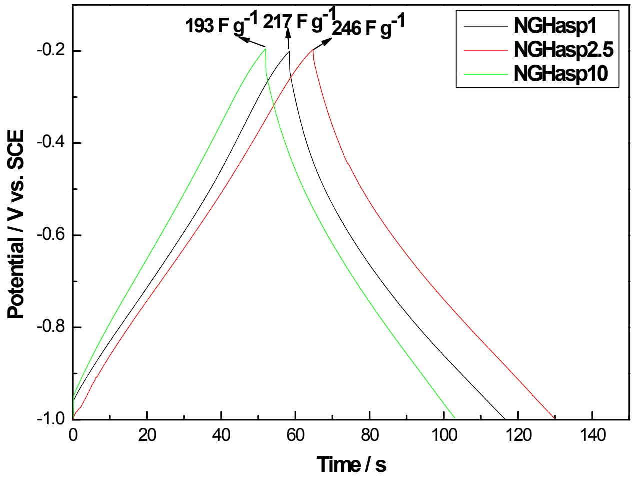

Fig. S5 Galvanostatic charge/discharge curves for NGasp1, NGasp2.5 and NGasp10, respectively tested at current density of 3A $g^{-1.}$

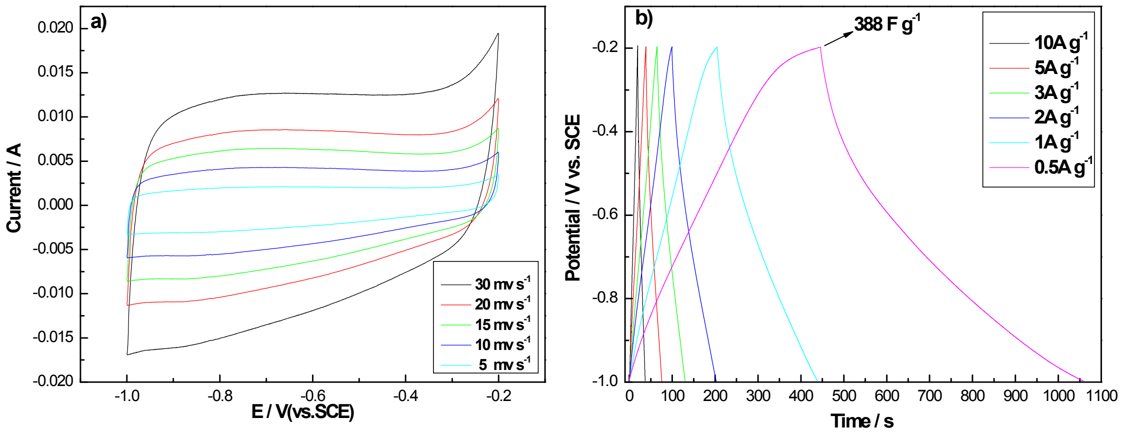

Fig. S6 (a) CV for NGasp measured at different scan rate. (b) Galvanostatic charge/discharge curves for NGasp tested at current densities of 0.5-10 A g^{-1}.

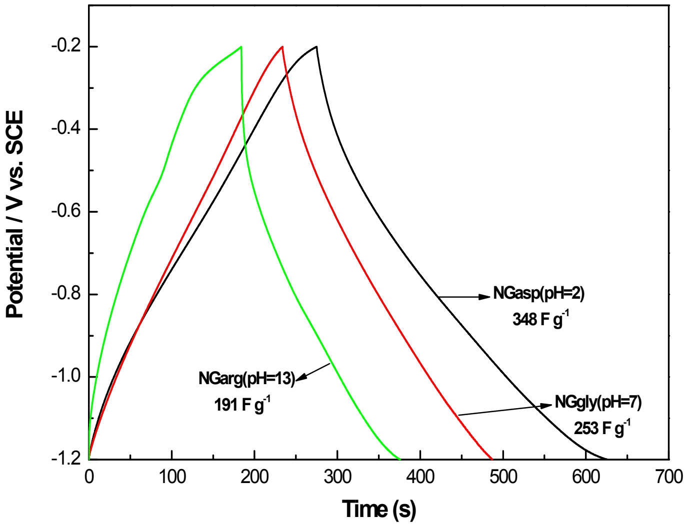

Fig. S7 Galvanostatic charge/discharge curves for NGasp (pH=2), NGgly (pH=7) and NGarg (pH=13), respectively tested at current densities of 1 A g^{-1}.

Table S1 Summary of the d-spacing for NGasp1 and NGasp10.

Samples	$2\theta(^0)$	d(nm)
NGHasp1	24.42	0.364
NGHasp10	24.64	0.361

Table S2 Elemental content and chemical composition in NGasp1 and NGasp10 samples tested by XPS.

Samples	**C_{XPS}(at.%)**	**O_{XPS}(at.%)**	**N_{XPS}(at.%)**	**Pyridinic N%(at.%)**	**Pyrrolic N%(at.%)**	**Quaternary N%(at.%)**
NGHasp1	84.9	14.2	0.9	0.25	0.57	0.08
NGHasp10	83.7	15.1	1.2	0.4	0.64	0.16

[S1] M.J. Fernández-Merino, S. Villar-Rodil, J.I. Paredes, P. Solís-Fernández, L. Guardia, R. García, A. Martínez-Alonso and J.M.D. Tascón ,*Carbon*, 2013, **63**, 30-44.