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Electronic Supplementary Information

Novel preparation of nitrogen-doped graphene in various forms with aqueous ammonia under mild conditions

Gang Wang,[ab] Li-Tao Jia,*[a] Yan Zhu,[c] Bo Hou,[a] De-Bao Li[a] and Yu-Han Sun*[c]

[a] *State Key Laboratory of Coal Conversion, Institute of Coal Chemistry, Chinese Academy of Sciences, 030001 Taiyuan, Shanxi, P R China.*

Fax: + 81 351 404 1153; Tel: +81 351 412 1877;

E-mail: jialitao910@163.com

[b] *Graduate University of Chinese Academy of Sciences, 100049 Beijing, P R China.*

[c] *Low Carbon Conversion Center, Shanghai Advanced Research Institute, Chinese Academy of Sciences, 201203 Shanghai, P R China.*

E-mail: yhsun@sxicc.ac.cn

1. Experiments

1.1 Materials

Graphite powder was purchased from Aladdin Chemistry Co. Ltd (Shanghai, China). Aqueous ammonia (28 wt %) and 98 wt % H_2SO_4 were bought from Xilong Chem. Co. Ltd (Guangzhou, China). $NaNO_3$ and $KMnSO_4$ were from Kermel Chem. Reagent Co. Ltd (Tianjin, China). 30 wt% H_2O_2 was from Dongfang Chem. Co. (Tianjin, China). All the reagents were used as received without further purification.

1.2 Preparation of graphene oxide (GO)

GO was prepared by the Hummers' method[1] with further post treatments of ultrasonic processing and centrifugation. Typically, graphite powder (8000 meshes, 5g) and $NaNO_3$ (2.5g) were mixed with sulfuric acid (115mL, 98wt %) under magnetic stirring for 0.5h, then the mixture was put into an ice bath before $KMnSO_4$ (15g) was slowly added, and make sure the temperature remains below 20 °C. Subsequently, the reaction system was transferred to a water bath of 35 °C and maintained for 0.5h. After that, 230 mL of water was slowly added into the system. The diluted suspension was then stirred at 98 °C for 15 min, followed by another 700 mL of water added. And the reaction was terminated by the addition of H_2O_2 (50 mL, 30wt %). The mixture was filtered and washed with HCl (1 L, 1 mol/ L) and a large amount of distilled water in sequence. The resulting solid was dried and dissolved. The dispersion of graphite oxide was ultrasonicated under 40KHz for 30 min and centrifugated at 3000rpm for 30 min, obtaining stable collosol of GO.

1.3 Preparation of nitrogen-doped graphene (N-G)

Aqueous ammonia (8 mL, 28 wt %) was added into the above dispersion of GO (100 mL, 1.5 mg mL^{-1}) under magnetic stirring. Then the mixture was transferred into Teflon-lined autoclave and heated at 60-180 °C for 5 h without stirring before natural cooling. The products of N-graphene in the form of stable dispersion was sonicated for 30 min to remove the excessive or physisorbed ammonia before dried at 60 °C for 24 h and the products in the form of hydrogel were collected and dialyzed in water for 4 days to remove any impurities, then lyophilized for 24 h.

1.4 Preparation of reduced graphene oxide (rGO)

Reduced graphene oxide were prepared under the same hydrothermal condition above without the addition of ammonia.

1.5 Heat treatment of nitrogen-doped graphene

Heat treatment of the as-prepared nitrogen-doped graphene was carried out at various temperatures in Ar atmosphere. The samples were heated to the desired temperature in a heating rate of 10 °C min^{-1} and stayed for 1h before cooled in Ar. Then the samples were collected when temperature was below 50 °C.

2. Characterization

The UV-vis absorption spectra were collected on TU-1901 UV-vis spectrophotometer and the reaction mixture was diluted by a factor of 100 before measurement. The thickness of N-graphene sheet was measured by atomic force micoroscope in tapping mode using DI Nanoscope-IV Multimode AFM. The samples were diluted and drop dried in the air onto the surface of newly cleaved mica before measurement. The morphology of N-graphene was revealed by transmission electron microscope (TEM) and scanning electron microscope (SEM) using JEOL JEM-2010FEF and LEO 1530VP, respectively. The element mapping was also obtained using JEOL JEM-2010FEF. The XPS spectra were performed on ULVAC PHI-5800 spectrometer using monochromatic Al Kα radiation (1486.6 eV). The quantification was carried out on EASY ESCA data analysis software after calibration and Shirley background subtraction. Then the peaks were fitted using sum function model with 20% Lorentzian-80% Gaussian. Both the steady and dynamic rheological behaviors of N-G hydrogels were investigated on MCR 300 using a parallel-plate geometry of 25 mm at 25 °C and the gap distance was 1 mm. During the dynamic test, the oscillatory strain remains constant to be 0.2%. The Raman spectra of the samples were collected on HJY LabRAM HR800 using Ar^{+} laser (λ=514.5 nm) at room temperature. The Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFT) was carried out on EQUINOX 55 with a MCT detector. Thermal gravimetric analysis (TGA) connected with a sweep gas mass spectroscopy was accomplished on Evolution 16/18-OmniStar 20 under Ar gas flow (50 mL min^{-1}) at a heating rate of 10 °C min^{-1}.

3. Supplementary Figures

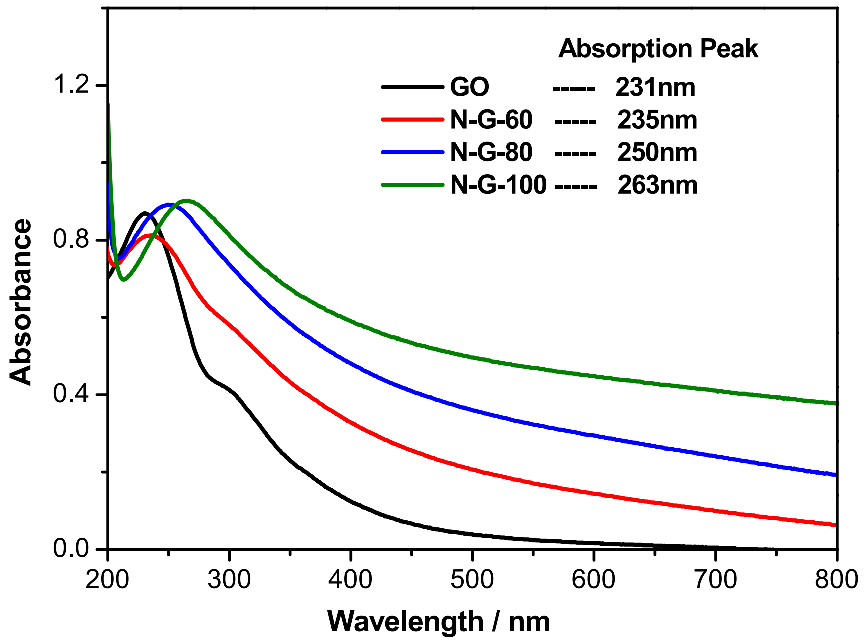

Fig. S1 UV-vis absorption spectra of GO, N-G-60, N-G-80 and N-G-100. The absorption peak of GO redshifts to higher wavelength as the reaction is performed, even at 60 °C. The absorption nearly in the whole spectra region was found enhanced compared with GO, indicating the restoration of the π-conjugated structure of graphene.

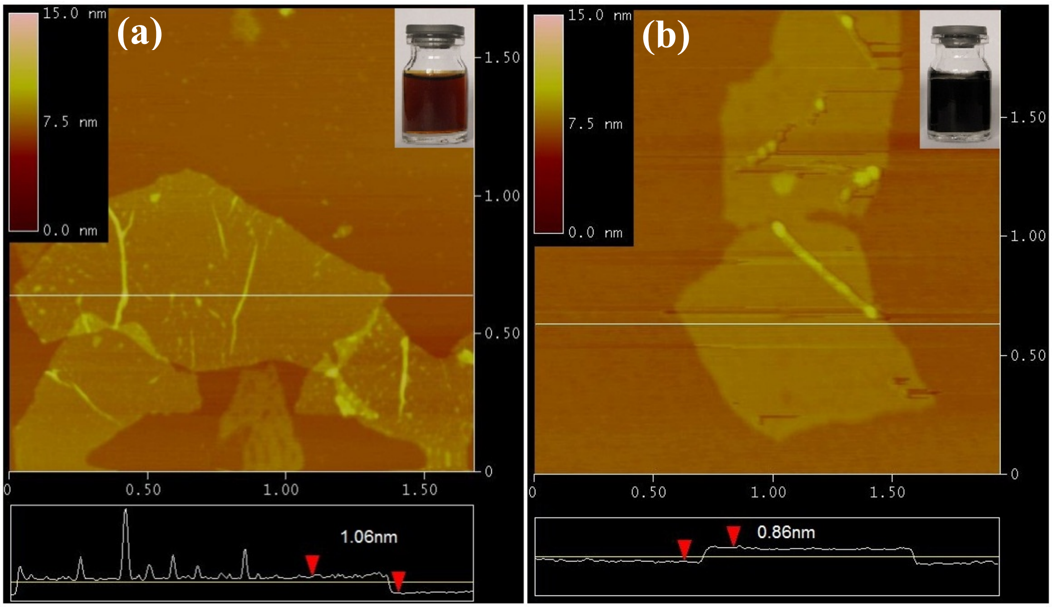

Fig. S2 AFM height images of (a) GO and (b) N-G-80 deposited on a newly cleaved mica.

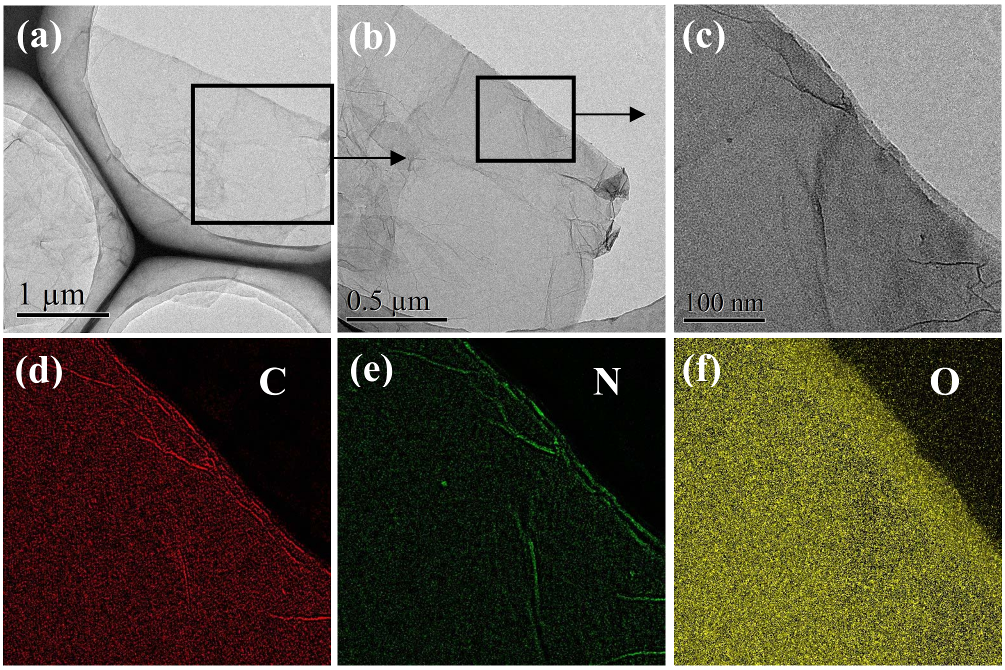

Fig. S3 (a, b and c) TEM images and (d, e and f) elemental mapping of C, N and O of N-G-100.

Table S1 Swelling power of the prepared hydrogels at various temperatures.

Samples	**N-G-120**	**N-G-140**	**N-G-160**	**N-G-180**
Swelling power	**204**	**183**	**181**	**168**

Swelling power is calculated from the equation $\mathbf{q_w=w_s/w_d}$, where q_w is the swelling power, w_s is the saturated weight and w_d is the dry weight of the gel.

Fig. S4 Photograph of hydrogels of rGO-180 (the left one) and N-G-180 (the right one).

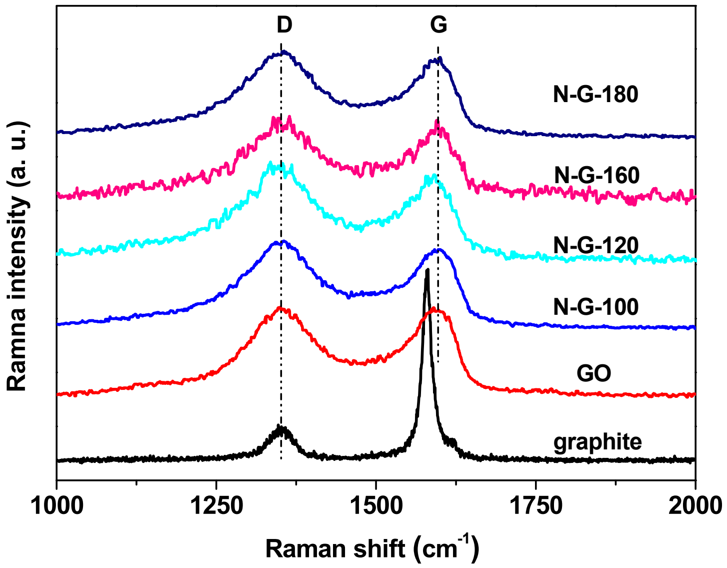

Fig. S5 Raman spectra of graphite, GO, N-G-(100, 120, 160, 180). The Raman spectra of N-G exhibited two strong features (D band located at ~1350 cm^{-1}and G band at ~1596 cm^{-1})and no 2D band. The D band and G band arise from doubly resonant disorder-induced mode and emission of zone-center optical phonons, respectively. The I_D/I_G (the intensity ration of D to G band) were used to estimate the defects density in graphene, and the I_D/I_G slightly increased from 1.00 to 1.08 with increasing the reaction temperature, indicating that a little more defect sites or nitrogen heteroatoms were incorporated into the graphene network. Compared to those of graphite, the broadening of D and G bands observed for N-G and GO should originate from the presence of heteratoms[2], such as O, N and H.

Table S2 The atomic ratios of N/C and O/C of GO and N-G samples calculated from XPS results.

Samples	**GO**	**N-G-60**	**N-G-80**	**N-G-100**	**N-G-120**	**N-G-140**	**N-G-160**	**N-G-180**
N/C (at/at)	0	0.091	0.108	0.125	0.071	0.072	0.072	0.077
O/C (at/at)	0.384	0.326	0.299	0.239	0.135	0.124	0.106	0.094
(N+O)/C	0.384	0.417	0.407	0.364	0.206	0.195	0.178	0.171

Samples		**N-G-F-60**	**N-G-F-80**	**N-G-F-100**				
N/C (at/at)		0.091	0.103	0.113				
O/C (at/at)		0.331	0.322	0.254				
(N+O)/C		0.422	0.425	0.367				

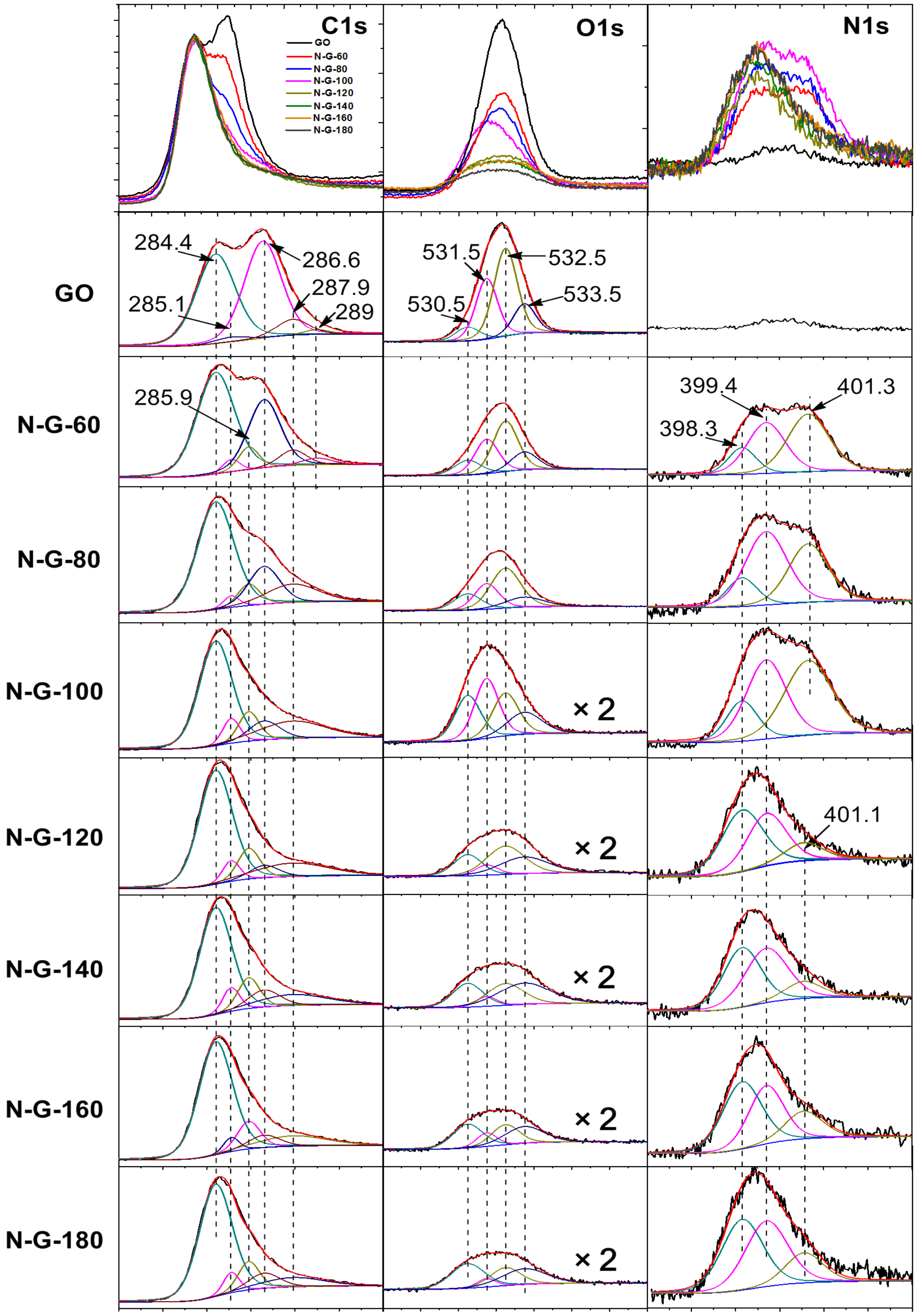

Fig. S6 High resolution XP C1s, O1s and N1s spectra of N-G prepared at various temperatures. The components located at 284.4, 285.1, 285.9, 286.6, 287.9 and 289 eV in C1s spectra can be assigned to C in graphite, C-OH, C-N, C-O-C, C=O and COOH groups. The components at 530.5, 531.5, 532.5 and 533.5 eV in O1s spectra can be ascribed to quinones, C=O, C-O and O-H groups.[3] For N1s spectra of N-G, the components at 398.3, 399.4, 401.1 and 401.3 can be attributed to pyridinic N, amino N, graphitic N and NH_4^+.

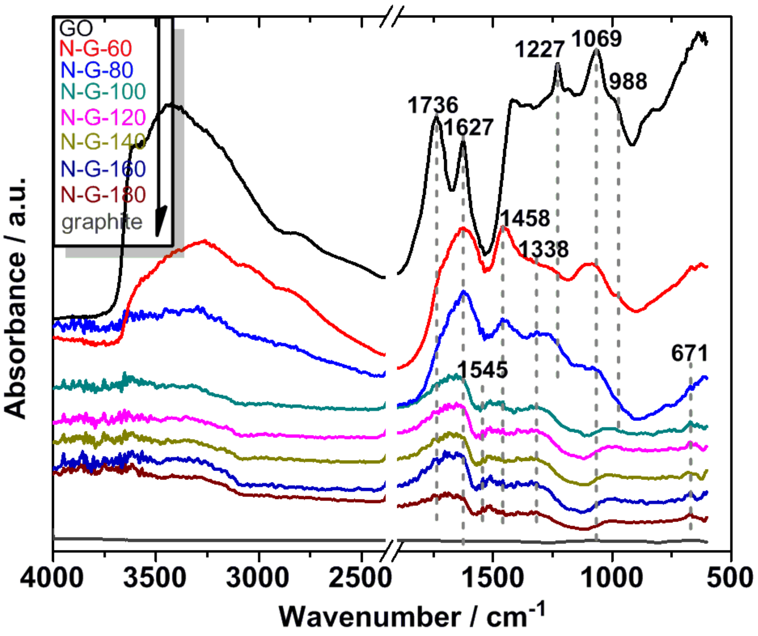

Fig. S7 Diffuse reflectance Infrared Fourier transform spectroscopy (DRIFTS) of GO, N-G samples prepared at 60-180 °C and graphite. Before measurement, the graphite powder (about 2 um) was dried at 90 °C for 4h to remove the adsorbed water.

4. References

1 W. S. Hummers and R. E. Offeman, *J. Am. Chem. Soc.*, 1958, **80**, 1339-1339.

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3 C.-M. Chen, J.-Q. Huang, Q. Zhang, W.-Z. Gong, Q.-H. Yang, M.-Z. Wang and Y.-G. Yang, *Carbon*, 2012, **50**, 659-667.