

Supporting Information

Fabrication of Pore-Rich Nitrogen-Doped Graphene Aerogel

Beibei Xie,^a Xiaodan Ren,^a Xiaobing Yan,^a Zhongyu Dai,^a Wanguo Hou,^a Na Du,^a Haiping Li^b
and Renjie Zhang^{abc*}

^a Key Laboratory of Colloid and Interface Chemistry of the Ministry of Education of the P. R. China, Shandong University, Jinan 250199, P. R. China

^b National Engineering Technology Research Center for Colloidal Materials, Shandong University, Jinan 250199, P. R. China

^c Key Laboratory of Special Functional Aggregated Materials of the Ministry of the P. R. China, Shandong University, Jinan 250199, P. R. China

*Corresponding author, Email: zhrj@sdu.edu.cn

Experimental Section

Materials

Graphite flakes (99.9995 %) with a lateral dimension of 2-15 μm were purchased from Alfa Aesar (USA). AA, DA and UA were purchased from Sigma-Aldrich. Potassium permanganate (KMnO_4), sulfuric acid (H_2SO_4 , 98 %), phosphate acid (H_3PO_4), hydrogen peroxide (H_2O_2 , 30 %), tris(hydroxymethyl)aminomethane (Tris), N,N-dimethylformamide (DMF), hydrochloric acid (HCl, 36-38 %) were purchased from Sinopharm Chemical Reagents Co., Ltd. They were all analytical grade reagents and directly used without further purification. Pure water with a resistivity of 18.2 $\text{M}\Omega\cdot\text{cm}$ at 25 $^\circ\text{C}$ was used in all experiments.

Preparation of GONSs with different size and oxidization degree as a precursor of GAs and NGAs

The preparation of the GONSs can be referred to our previous work based on an improved Hummers's method with some modifications.^{1,2} Briefly, a 9/1 (volume ratio) mixture of concentrated $\text{H}_2\text{SO}_4/\text{H}_3\text{PO}_4$ (180 mL/20 mL) was added the milled graphite flakes (1.0 g), followed by stirring for 12 h at 0 $^\circ\text{C}$ in an ice water bath. Sequentially, 3.0 g of KMnO_4 was added into the mixture at 15 $^\circ\text{C}$ and then stirred at 40 $^\circ\text{C}$ for 6 h. Another 3.0 g of KMnO_4 was added into the mixture followed by keeping stirring at 40 $^\circ\text{C}$ for 6 h and then at 85 $^\circ\text{C}$ for 30 min. The mixture was cooled to room temperature (rt) in a beaker (500 mL) and dropped into 85 mL H_2O_2 (30 %). The GONSs in the mixture were thoroughly washed with HCl (5.0 %) and water, then repeatedly centrifuged and washed with water until the pH value of the supernatant was neutral. The suspensions of GONSs (1.0 mg/mL) were subject to sonication (KQ-600KDB, 40 kHz, 300 W) for 0, 4, 8 h, respectively, to obtain different size and oxidation degree of GONSs, named as GONSs-0, GONSs-4, GONSs-8, respectively. The temperature of the sonication water bath was kept below 30 $^\circ\text{C}$.

Preparation of NGAs with different pore size and N content

The NGAs with different pore size and N content were prepared by using GONSs-0 (or GONSs-4, or GONSs-8) and DA as precursors. GONSs-0, GONSs-4, GONSs-8 were sedimented separately by a high speed centrifuge (Sigma 3-18K, Germany) (16554 g, 60 min; 26021 g, 60 min; and 27530 g, 90 min, respectively). Each sedimentation was dispersed in 20 mL of freshly prepared Tris-HCl buffer solution (pH=8.5). To each GONSs dispersion (20 mL, 1.0 mg/mL), the DA (20 mg) was added under stirring, followed by sonication (300 W, 40 min). Each mixture was then kept in a 50 mL Teflon-lined autoclaves at 180 $^\circ\text{C}$ for 12 h to obtain an N-containing graphene hydrogel. After naturally cooled down to rt, each hydrogel was carefully taken out, washed separately by water and ethanol, freeze-dried. Then, NGAs were obtained after annealing at 800 $^\circ\text{C}$ for 3 h under an Ar atmosphere, which consist of NGOSs. The obtained NGAs were called NGA-0, NGA-4, NGA-8, named after the different size and oxidation degree of GONSs-0, GONSs-4, GONSs-8, respectively.

Preparation of GAs

GAs were synthesized using GONSs as the only precursor without DA based on the hydrothermal method. The preparation process was similar to that of NGAs. Typically, 20 mL homogeneous GONSs-0 (or GONSs-4, or GONSs-8, 1.0 mg/mL) aqueous dispersion was kept in a 50 mL Teflon-lined autoclave at 180 $^\circ\text{C}$ for 12 h. After naturally cooled down to rt, the as-prepared GAs were taken out, washed sequentially with water and ethanol, freeze-dried and then annealed at 800 $^\circ\text{C}$ for 3 h under an Ar atmosphere. The GAs were called GA-0, GA-4, GA-8, also named after GONSs-0, GONSs-4, GONSs-8, respectively.

Characterization

Atomic force microscopy (AFM) height images and section analysis were obtained by AFM in tapping mode (Nanoscope IIIA, Digital Instruments Corp., USA). The AFM samples were prepared by dropping 5 μL of GONSs aqueous dispersion (50 $\mu\text{g}/\text{mL}$) on mica substrates followed by air drying. X-ray photoelectron spectroscopy (XPS) was taken on the Phi 5300 ESCA system (Perkin-Elmer, U.S.A) with the Mg ($K\alpha$) radiation (X-ray energy 1253.6 eV). The analysis spot area was $1.0 \times 3.5 \text{ mm}^2$. The XPS samples were prepared by dropping 100 μL GONSs aqueous dispersions (1.0 mg/mL) or GAs, NGAs DMF dispersions (1.0 mg/mL) onto silicon substrates followed by air drying. X-ray diffraction (XRD) patterns were collected through a D8 Advance diffractometer (Bruker, Germany) with the Cu $K\alpha$ target ($\lambda = 1.54184 \text{ \AA}$). Nitrogen (N_2) adsorption-desorption isotherms were recorded with an ASAP 2020 HD88 instrument (Micromeritics, USA) cooled by liquid N_2 . The pore size distribution of NGA-0, NGA-4 and NGA-8 was obtained by calculating the adsorption branch with a density functional theory (DFT) method. Scanning electron microscopy (SEM) measurement was carried out on a JSM-6700F (JEOL, Japan) instrument with an operating voltage of 3 kV. Transmission electron microscopy (TEM) images were obtained with the JEM-1011 TEM (JEOL, Japan) under an accelerating voltage of 100 kV. High-resolution TEM (HR-TEM) images were obtained on a JEM-2100 TEM with an acceleration voltage of 200 kV. Raman spectra were obtained using the LabRAM HR 800 system (Horiba JY, France) excited with the laser of 633 nm. Fourier transform infrared (FTIR) spectra were collected by using a Vertex-70 FTIR spectrometer (Bruker, Germany). The contact angle (CA) was measured on DSA10 contact angle goniometer (Krüss, Germany) at rt with a relative humidity (rh) of 30 %. The CA values were the average of at least three measurements of a 4 μL of pure water droplet on different locations of a flat surface of NGAs (length \times width \times height = $6 \times 6 \times 5 \text{ mm}^3$). The block NGAs (length \times width \times height = $10 \times 10 \times 5 \text{ mm}^3$) with flat surface were compressed into dense powders using a universal material testing instrument (Plos LR, China) at rt and 30 % rh to obtain the compressive strength of NGAs. Electrical conductivity of NGAs was measured by a standard four-probe method on a digital resistivity tester (RTS-8, China) at 100 mA. The distance between neighbouring tungsten carbide probes was about 5 mm. The results for each sample were the average of six measurements.

Electrochemical measurement

Cyclic voltammetry (CV) and differential pulse voltammogram (DPV) with various working electrodes were investigated on the CHI440C electrochemical work station with a three-electrode system. A glassy carbon electrode (GCE) or GAs-/NGAs- modified GCE, a saturated calomel electrode and a Pt electrode were used as working, reference and counter electrodes, respectively. Before coating, the GCE was polished using Al_2O_3 powder of 0.3 μm in diameter and rinsed separately with ethanol and water, sonicated for 15 min, and dried by high purity N_2 . 5.0 mg of GAs or NGAs were purposely broken and separately dispersed in 5.0 mL of DMF by sonication (300 W, 40 min). Then, 10 μL of the above suspensions were separately casted onto the GCE surfaces and dried under a near-infrared lamp (200 W).

Table S1. The size distribution of GONSs-0, GONSs-4 and GONSs-8. The I_D/I_G ratios for GONSs-0, GONSs-4 and GONSs-8; the ratios of $\text{Csp}^3/\text{Csp}^2$ (at./at.) and O/C (at./at.) are obtained by calculating the peak areas of GONSs-0, GONSs-4 and GONSs-8 in the C1s XPS spectra.

Sample	Size distribution (μm)	I_D/I_G	$\text{Csp}^3/\text{Csp}^2$ (at./at.)	O/C (at./at.)
GONSs-0	2.10-0.61	0.59	1.01	0.41
GONSs-4	1.60-0.30	0.81	1.17	0.49
GONSs-8	0.90-0.04	0.91	1.52	0.54

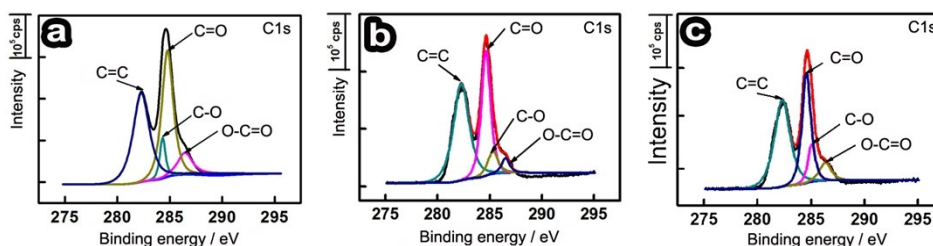


Figure S1. C1s XPS spectra of a) GONSs-0 and b) GONSs-4.

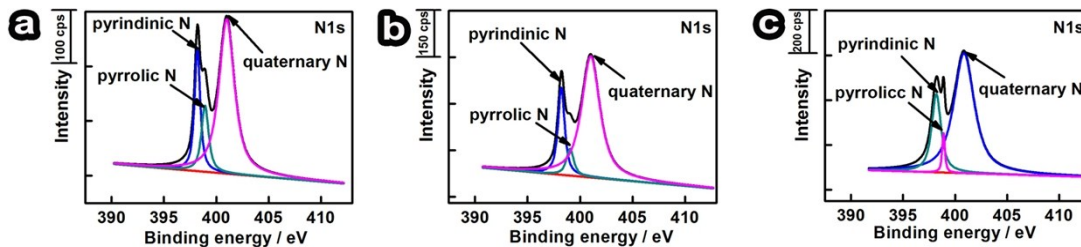


Figure S2. N1s XPS spectra of a) NGA-0, b) NGA-4, and c) NGA-8.

Table S2. C, O and N contents of NGAs obtained from XPS. The average pore size obtained from DFT method, pore volumes and BET specific surface area of NGAs.

Sample	C (atom %)	O (atom %)	N (atom %)	Average pore size (nm)	Pore volumes (cm ³ ·g ⁻¹)	BET specific surface area (m ² ·g ⁻¹)
NGA-0	84.25	12.55	3.20	9.1	0.428	660
NGA-4	74.73	16.82	8.45	6.2	0.419	960
NGA-8	81.64	9.39	8.97	3.8	0.408	1020

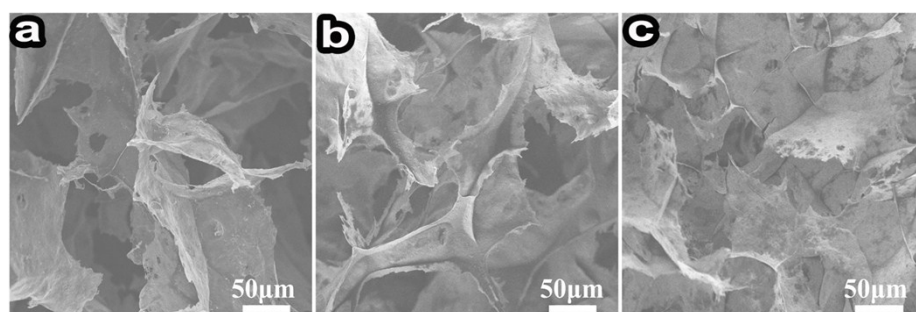


Figure S3. The SEM images of a) NGA-0, b) NGA-4 and c) NGA-8.

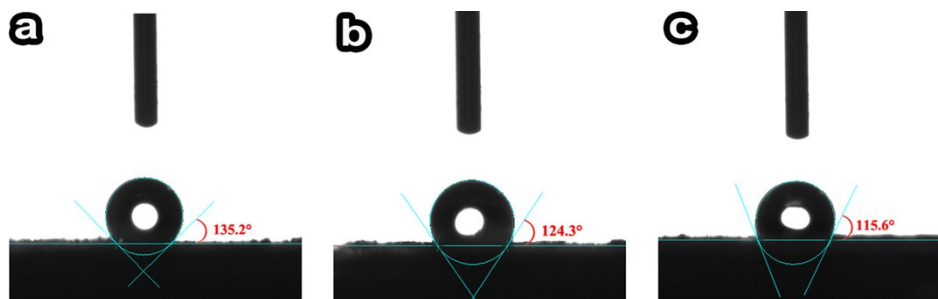


Figure S4. The optical images of a water droplet on the surface of a) NGA-0, b) NGA-4 and c) NGA-8.

Table S3. The electron transfer rate constant (K_s) for GCE/NGAs in AA, DA and UA calculated with the Laviron method. The electrical conductivity of NGAs was measured by a standard four-probe method.

Sample	K_s (s^{-1})			Electrical conductivity (S/cm)
	AA	DA	UA	
NGA-0	0.58	1.07	1.08	13.2
NGA-4	1.28	1.21	2.36	15.4
NGA-8	1.82	1.86	9.85	18.2

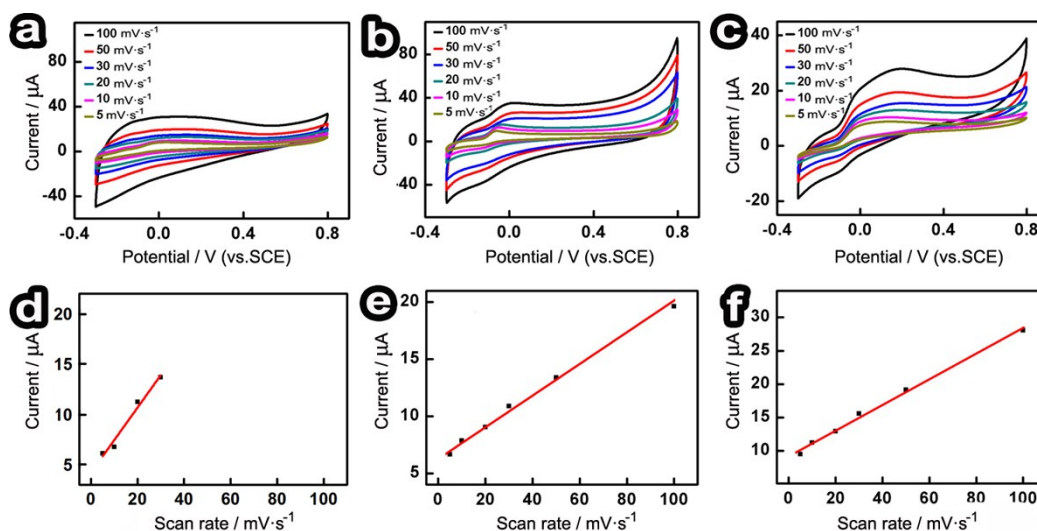


Figure S5. CV plots of 1.0 mM AA at different scan rates for a) GCE/NGA-0, b) GCE/NGA-4 and c) GCE/NGA-8 in 0.10 M PBS (pH=7.4). Plots of peak current against scan rate for d) GCE/NGA-0, e) GCE/NGA-4 and f) GCE/NGA-8.

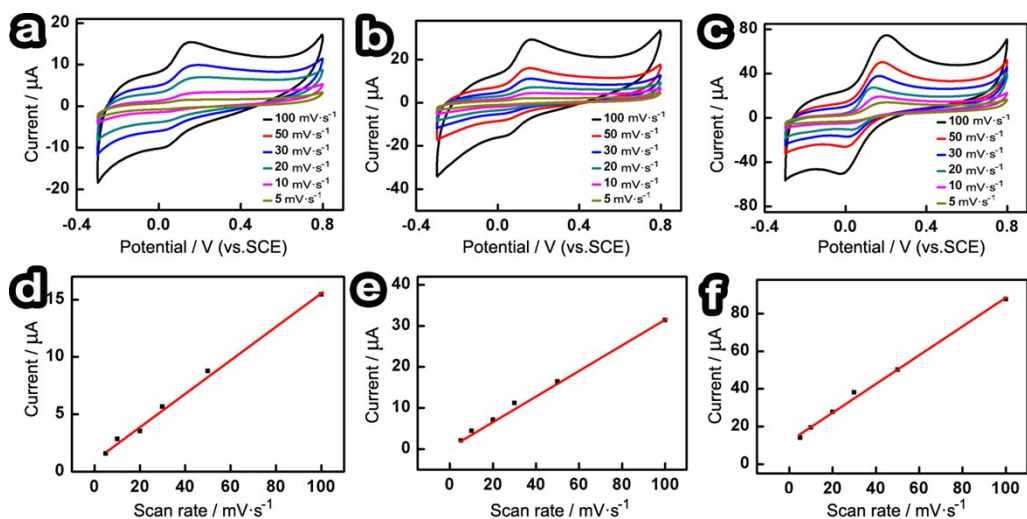


Figure S6. CV plots of 1.0 mM DA at different scan rate for a) GCE/NGA-0, b) GCE/NGA-4 and c) GCE/NGA-8 in 0.10 M PBS (pH=7.4). Plots of peak current against scan rate for d) GCE/NGA-0, e) GCE/NGA-4 and f) GCE/NGA-8.

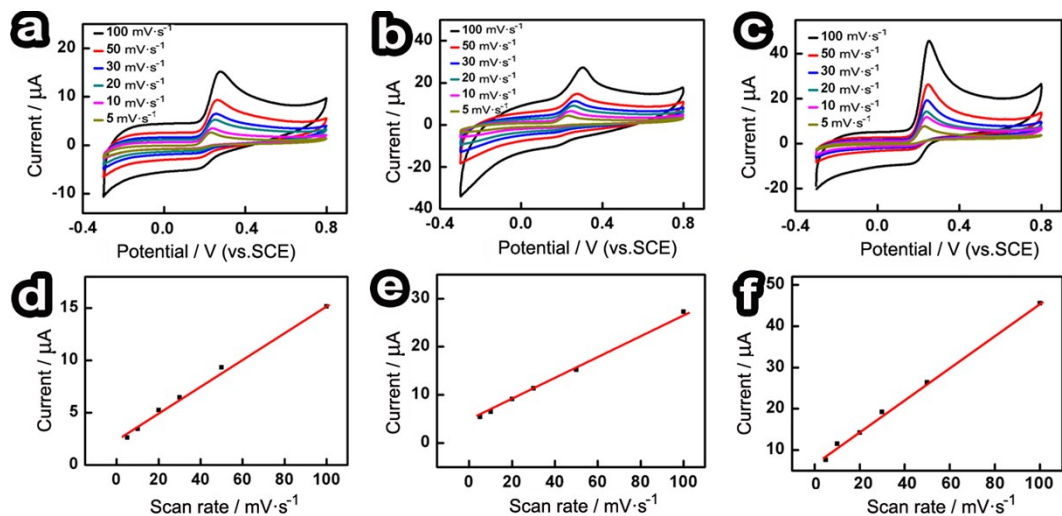


Figure S7. CV plots of 1.0 mM UA at different scan rates for a) GCE/NGA-0, b) GCE/NGA-4 and c) GCE/NGA-8 in 0.10 M PBS (pH=7.4). Plots of peak current against scan rate for d) GCE/NGA-0, e) GCE/NGA-4 and f) GCE/NGA-8.

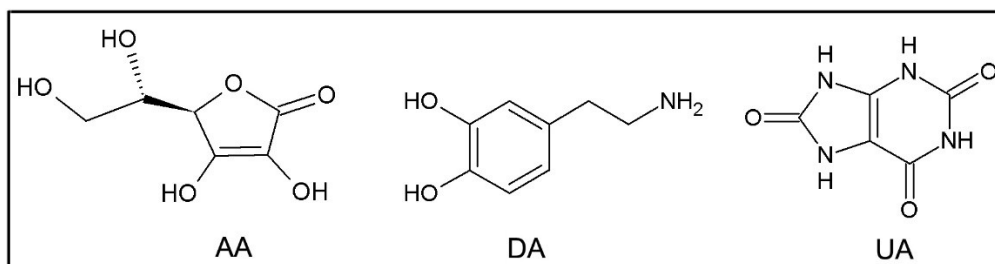


Figure S8. Chemical structures of AA, DA and UA.

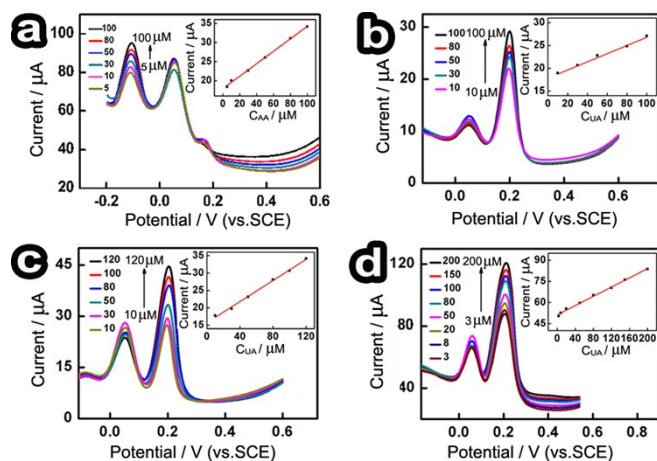


Figure S9. a) DPV plots for different concentrations of AA containing 10 μM DA and 20 μM UA for the electrode of GCE/NGA-8. DPV plots for different concentrations of UA containing 1.0 mM AA and 10 μM DA for the electrode of b) GCE/NGA-0, c) GCE/NGA-4, d) GCE/NGA-8.

Table S4. DPV data of AA, DA, and UA for GCE/NGA-0, GCE/NGA-4, and GCE/NGA-8.

Electrode	AA		DA		UA	
	$i_p / \mu\text{A}$	E_p / mV	$i_p / \mu\text{A}$	E_p / mV	$i_p / \mu\text{A}$	E_p / mV
GCE/NGA-0	1.82	-88	24.83	52	10.73	184
GCE/NGA-4	7.19	-92	44.75	44	20.16	180
GCE/NGA-8	15.09	-98	58.03	44	25.14	176

Table S5. The linear range (LR), detection limit (DL) and sensitivity of DA and UA for GCE/NGA-0, GCE/NGA-4, and GCE/NGA-8

	DA			UA		
	LR (μM)	Sensitivity	DL (μM)	LR (μM)	Sensitivity	DL (μM)
NGA-0	10-100	0.108	3.10	10-100	0.089	3.12
NGA-4	5-100	0.157	1.31	10-120	0.152	2.78
NGA-8	0.5-250	0.230	0.140	3-200	0.164	0.850

Table S6. Comparison of LR and DL of AA, DA and UA among GCE/NGA-8 and reported graphene materials modified electrodes.

Electrode	AA		DA		UA		Ref.
	LR (μM)	DL (μM)	LR (μM)	DL (μM)	LR (μM)	DL (μM)	
GO-templated Polyaniline Microsheets	150-1050	50	1-14	0.5	3-26	1	3
Chitosan-Graphene	50-1200	50	1.0-24	1	2.0-45	2	4
Nitrogen doped graphene aerogel	--	--	0.5-160	0.2	--	--	5
Gold Nanoparticle-Graphene Nanocomposites	--	--	0.2-20	0.1	--	--	6
NGA-8	5-100	1.32	0.5-250	0.15	3-200	0.85	this work

References

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