Supporting Information for

Facile production of graphene nanosheets comprising nitrogen-doping through in situ cathodic plasma formation during electrochemical exfoliation

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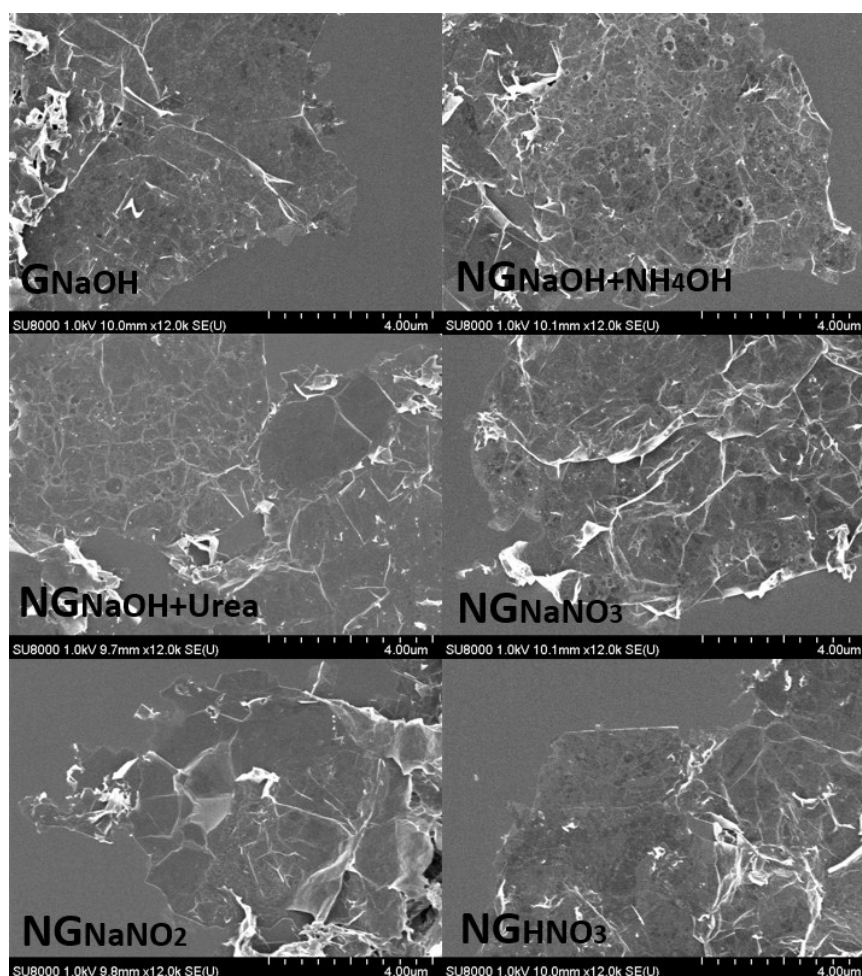Fax: +886-3-5724727
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Fig. S1. FE-SEM images of as-produced NGs. G_x and NG_x denote graphene and nitrogen-doped graphene, respectively, with x representing the electrolyte used in each process. These images reveal that the as-made graphene nanosheets had sharp edges and folded structures after exfoliation.
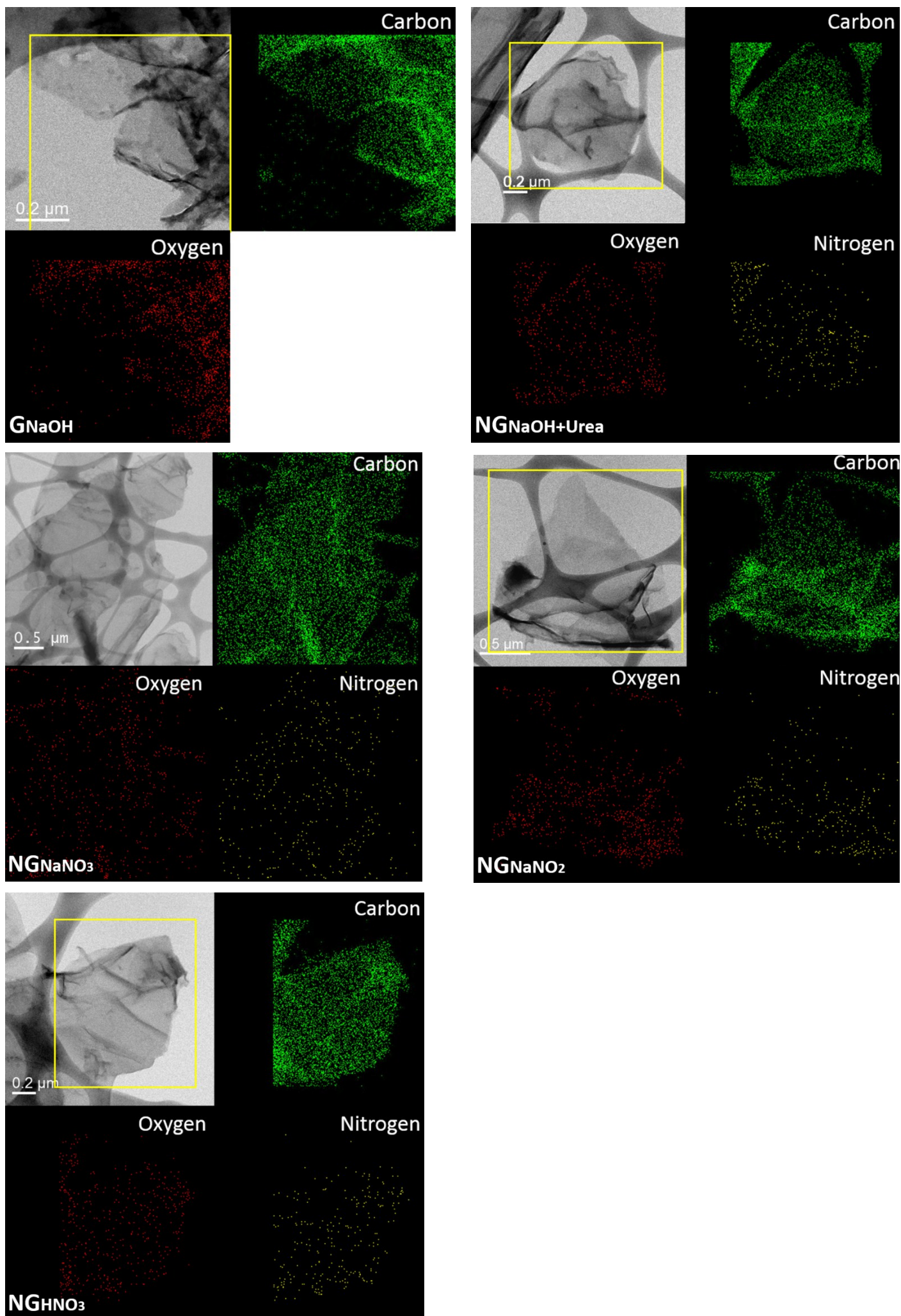
Fig. S2. Bright-field TEM images and EDS elemental mapping images of each NG produced through the

cathodic plasma process when using different electrolytes. The bright-field TEM images reveal that the samples remained few micrometers long and wide, with sharp edges. In addition to carbon atoms, oxygen and nitrogen atoms were both detected in the EDS elemental mapping images obtained through STEM measurements. The nitrogen atom distributions were quite normal and fitted the shapes of the chosen samples, suggesting that the cathodic plasma process did indeed dope nitrogen atoms into the graphene.
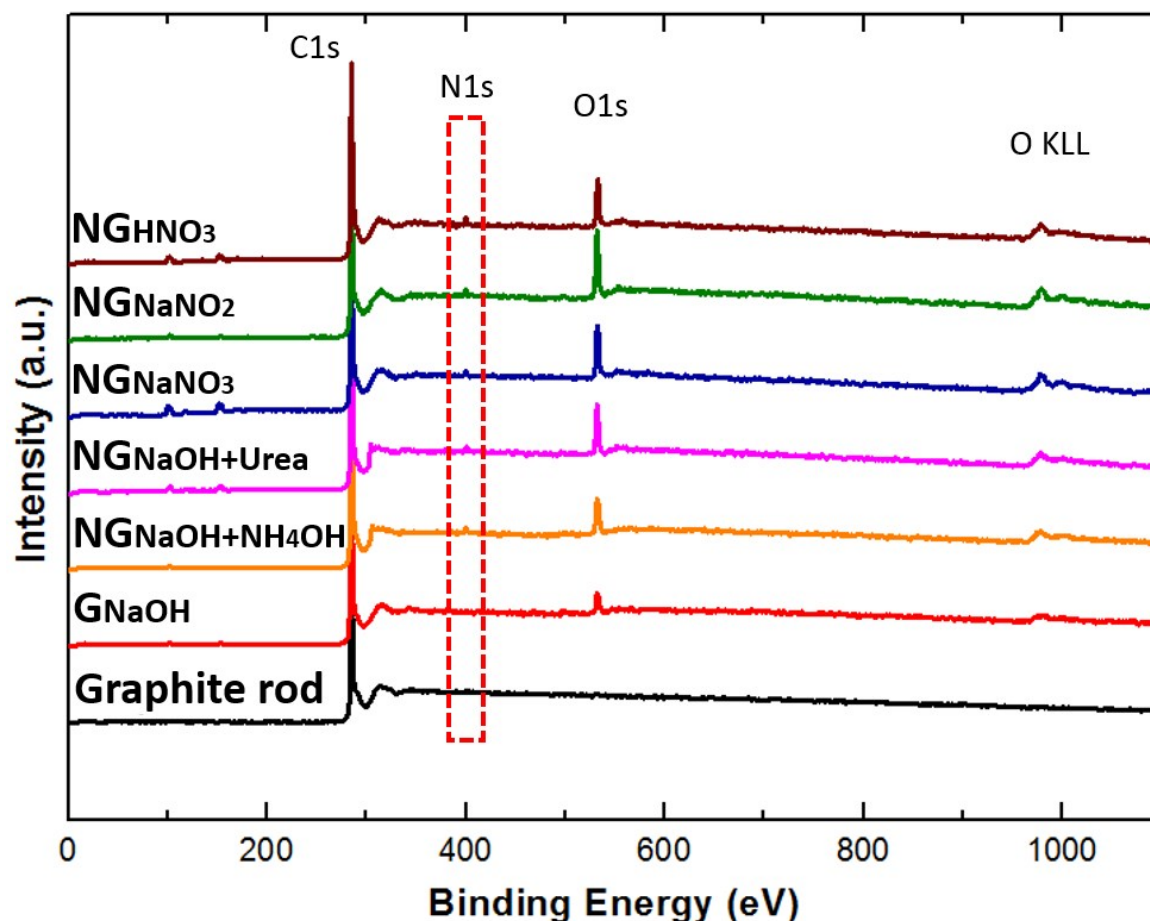

Fig. S3. XPS survey spectra of graphite rod and nitrogen-doped samples. In addition to successes using ammonia- and urea- containing aqueous electrolytes, nitrogen-binding signals in XPS measurements were also evident when using $NaNO_3$, $NaNO_2$, and HNO_3 as aqueous electrolytes, suggesting that nitrate and nitrite can also serve as dopants for NGs.

materials	XPS (at.%)			EA (wt%)			
	C	O	N	C	H	O	N
Graphite rod	99.98	0.02	–	99.97	0.01	0.02	–
G_{NaOH}	95.88	4.12	–	96.01	0.31	3.68	–
$NG_{NaOH+NH_4OH}$	91.07	8.22	0.71	90.05	1.23	8.10	0.62
$NG_{NaOH+Urea}$	88.39	11.01	0.60	91.86	1.01	6.59	0.54
NG_{NaNO_3}	88.84	10.47	0.69	89.98	1.13	8.39	0.50
NG_{NaNO_2}	88.13	11.20	0.67	89.81	1.13	8.58	0.48
NG_{HNO_3}	89.49	9.70	0.81	90.49	1.05	7.74	0.72

Table S1. Surface and bulk elemental compositions of graphite rod and NG samples prepared using various electrolytes.
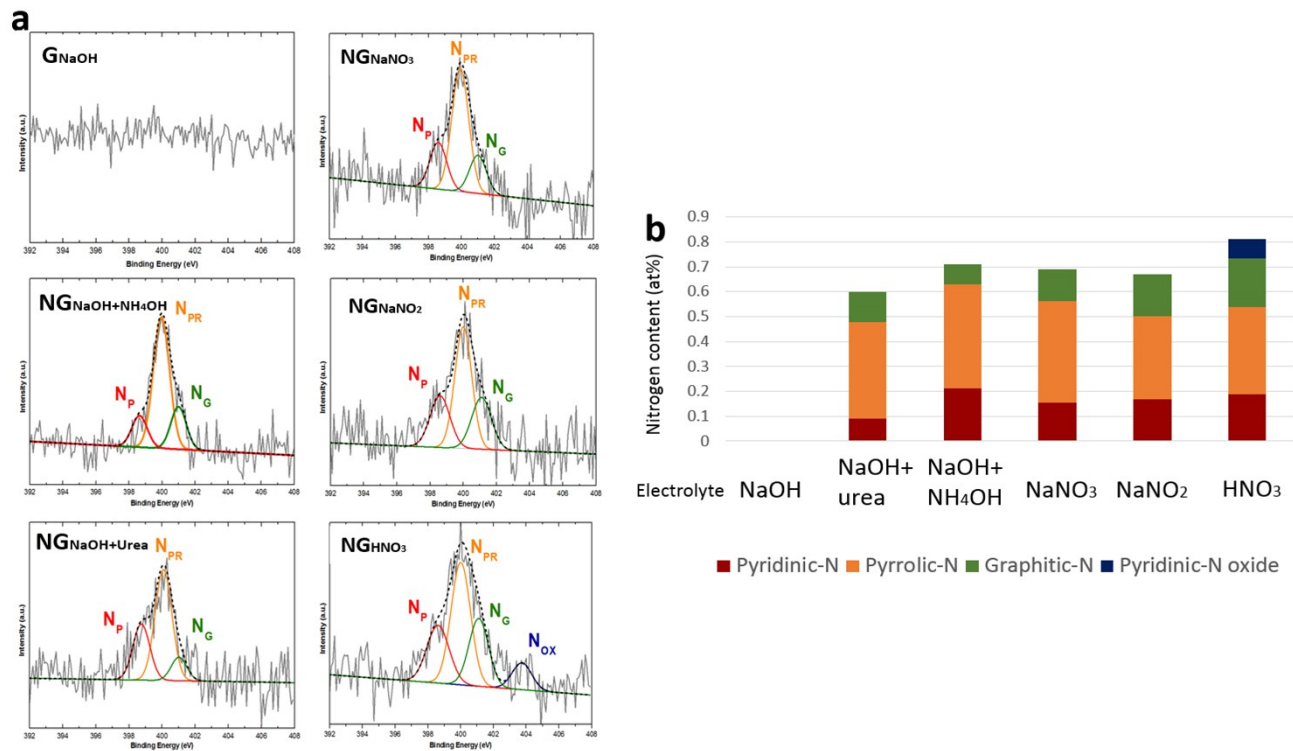
Fig. S4. (a) High-resolution N 1s XPS spectra with deconvoluted peak assignments and (b) contents of various nitrogen-bonding states for samples produced using various electrolytes. The N 1s spectra of the graphene samples doped using the various electrolytes were all deconvoluted by three Gaussian fittings. Interestingly, for NG_{HNO3} a signal for pyridinic-N oxide was detected at 403.8 eV, possibly because of the stronger oxidizing ability of HNO_3.
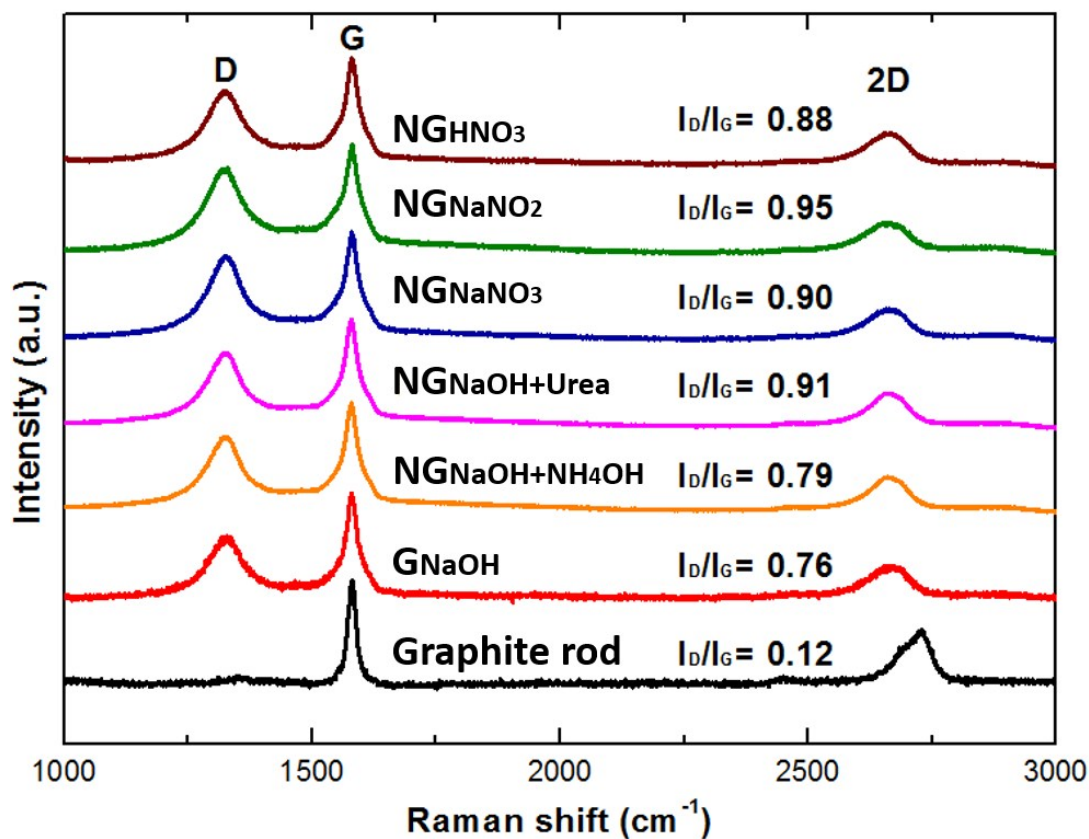

Fig. S5. Raman spectra revealing the D-, G-, and 2D-bands and I_D/I_G ratios of graphite rod and NG samples produced using various electrolytes. After the cathodic plasma process, the defect level in each sample increased dramatically upon decreasing the number of graphene layers.
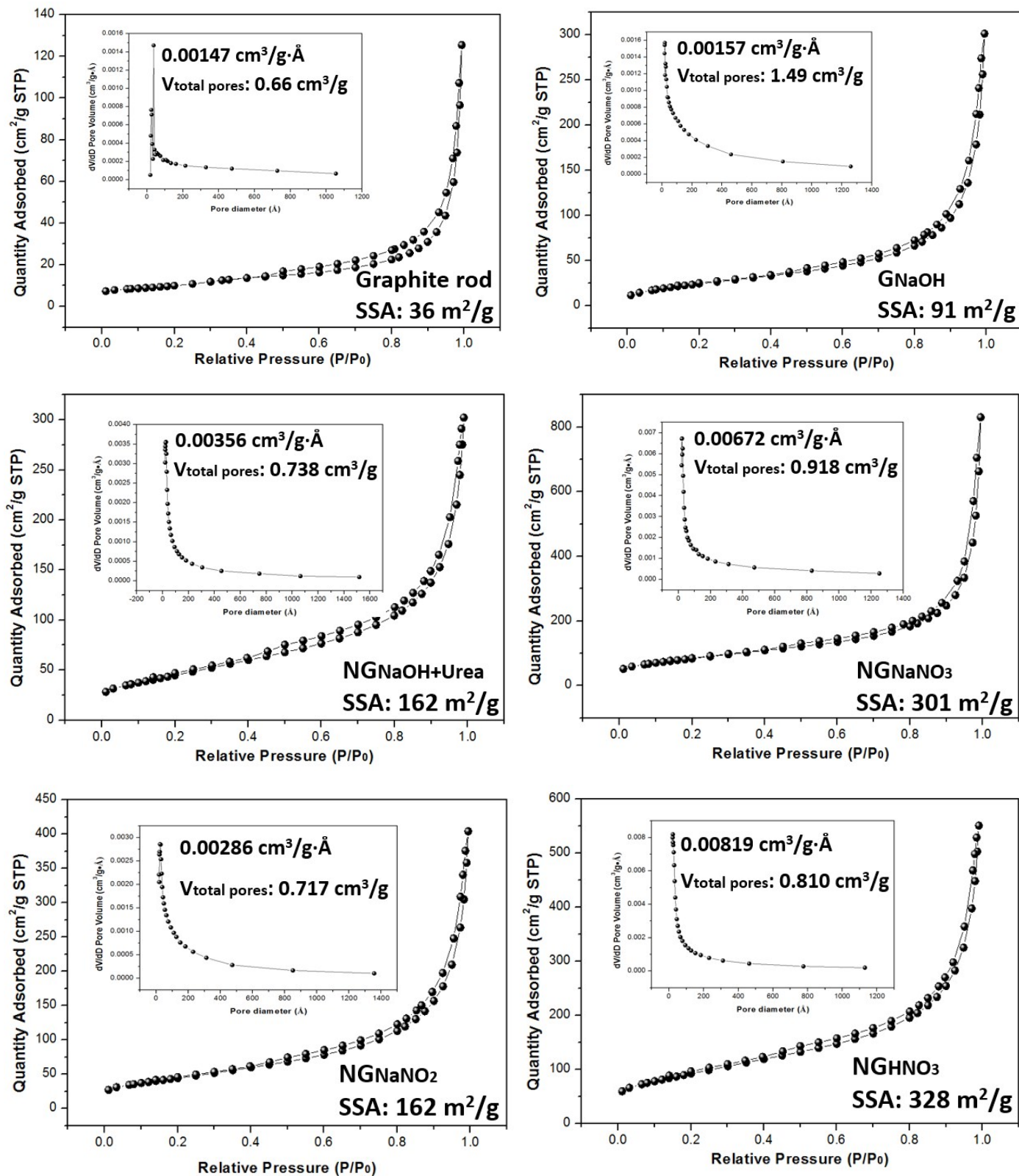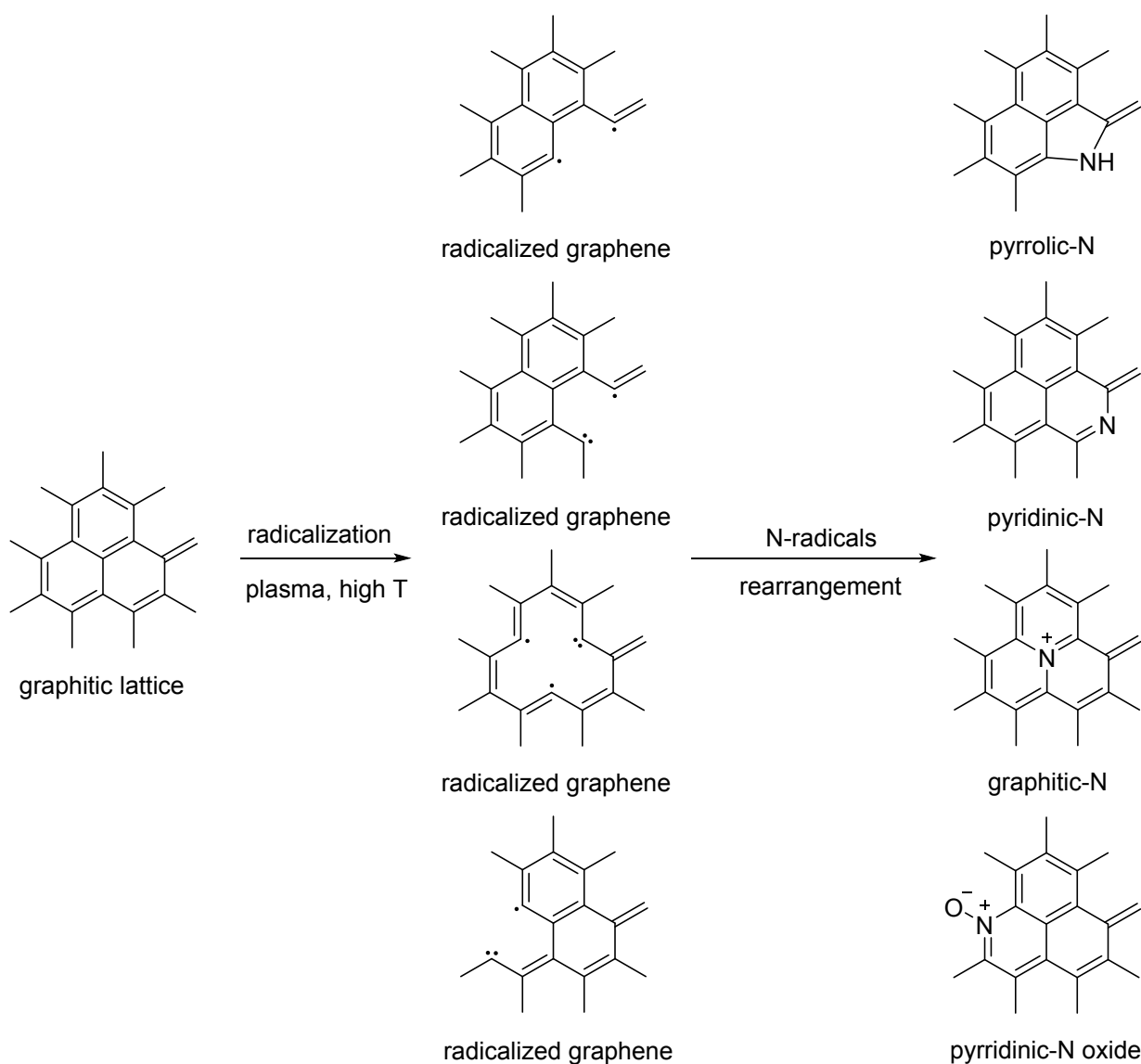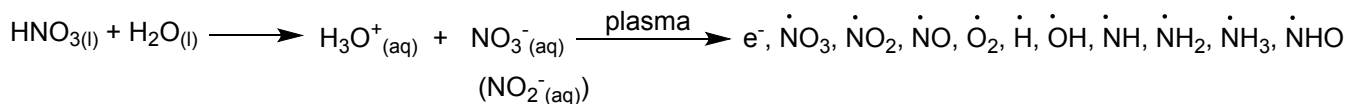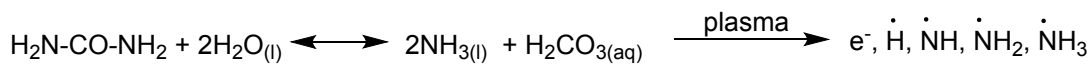
Fig. S6. Nitrogen adsorption/desorption curves for measurement of BET surface areas; insets: BJH pore size distributions of the graphite rod and the samples prepared through nitrogen-doping. The specific surface areas of the NGs could be tuned by varying the electrolyte.

$$H_2N\text{-}CO\text{-}NH_2 + 2H_2O_{(l)} \rightleftharpoons 2NH_{3(l)} + H_2CO_{3(aq)} \xrightarrow{\text{plasma}} e^-, \dot{H}, \dot{N}H, \dot{N}H_2, \dot{N}H_3$$

$$HNO_{3(l)} + H_2O_{(l)} \longrightarrow H_3O^+_{(aq)} + NO_3^-{}_{(aq)} \xrightarrow{\text{plasma}} e^-, \dot{N}O_3, \dot{N}O_2, \dot{N}O, \dot{O}_2, \dot{H}, \dot{O}H, \dot{N}H, \dot{N}H_2, \dot{N}H_3, \dot{N}HO$$
$$(NO_2^-{}_{(aq)})$$

graphitic lattice

radicalization
plasma, high T

radicalized graphene

radicalized graphene

radicalized graphene

radicalized graphene

N-radicals
rearrangement

pyrrolic-N

pyridinic-N

graphitic-N

pyrridinic-N oxide

Scheme S1. When urea dissolves into water, radicalized ammonia molecules can be generated which serve as the precursor of nitrogen containing radicals[1] such as $NH_3^\bullet$, $NH_2^\bullet$, $NH^\bullet$. After reacting with radicalized graphene and experiencing structural rearrangement[2] ,nitrogen-doped graphene with pyrrolic, pyridinic and graphitic bonding configuration of nitrogen atom was produced. On the other hand, when we use nitric acid or sodium nitrate/nitride as electrolyte, nitrogen-doped graphene can also be produced through cathodic plasma electrolysis. Here we propose a possible mechanism of nitrogen-doping process for the use of nitrate or nitrite anion as nitrogen-containing resources. When nitrate/nitrite anion experience cathodic plasma, relatively high temperature and electrical discharge can break N-O bonds[3] and produce radicals such as $NO_2^\bullet$, $NO^\bullet$ which possibly react with $H^\bullet$ or $OH^\bullet$ to form $NH_3^\bullet$, $NH_2^\bullet$, $NH^\bullet$ or $NHO^\bullet$ radicals that produce nitrogen-doped graphene in the same way. Due to the stronger oxidation ability of nitric acid, a small portion of pyrridinic-N oxide was detected via XPS measurement.

References

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