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Electronic Supplementary Information

One-Step Electrochemical Synthesis of Tunable Nitrogen-Doped Graphene

*Fengliu Lou, Marthe Emelie Melandsø Buan, Navaneethan Muthuswamy, John Charles Walmsley, Magnus Rønning and De Chen**

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S1 AFM and TEM images of C-Graphene

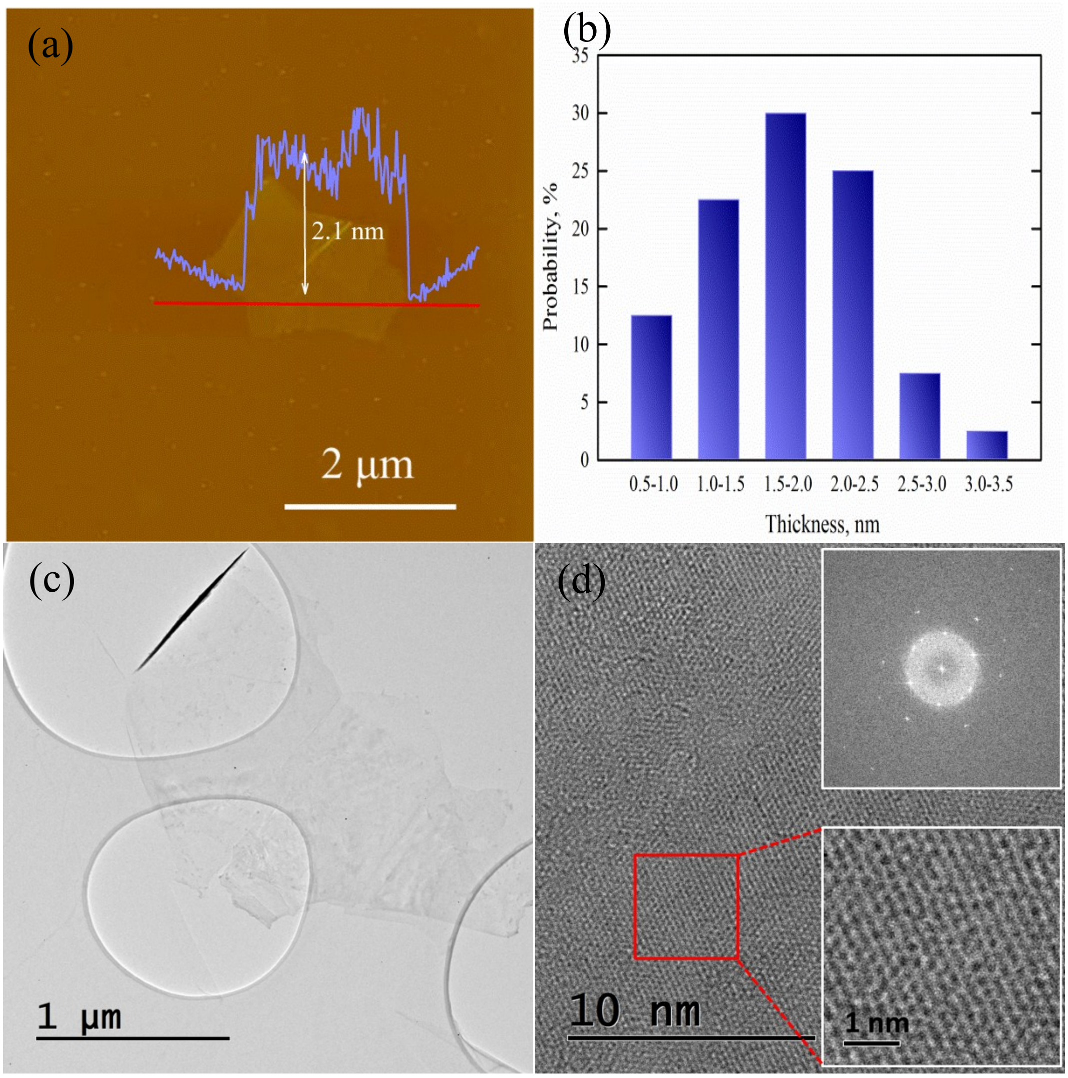


Fig. S1 a) Typical AFM image of C-Graphene with a height profile (blue curve) taken along the red line. The sample was prepared by spin coating of C-Graphene suspension on freshly cleaved mica. b) The thickness distribution of about 80 pieces of C-Graphene sheets obtained from the AFM height profile. c) Typical bright field TEM image of C-Graphene. d) High-resolution TEM image of C-Graphene. The upper right inset is a FFT of the whole image. The lower right inset is the zoom-in high-resolution TEM image.

S2 Manipulating the properties of nitrogen-doped graphene

Table S1 The effect of electrolyte compositions on the elemental composition of the graphene obtained.*

NH_3•H_2O /$(NH_4)_2SO_4$ concentration in the electrolyte, M	**Electrolyte composition, M**			**Elemental composition of graphene obtained, at%**		
	NH_3•H_2O	**NH_4^+**	**OH^-**	**C**	**O**	**N**
0.0/1.0	$1.00*10^{-7}$	2.00	9.00×10^{-13}	91.83	8.17	0.00
0.5/1.0	0.50	2.00	4.50×10^{-6}	86.70	11.34	1.96
1.0/1.0	1.00	2.00	9.00×10^{-6}	86.58	10.80	2.62
2.0/1.0	2.00	2.00	1.80×10^{-5}	83.83	12.50	3.63
5.0/1.0	5.00	2.00	4.50×10^{-5}	83.40	11.66	4.95
1.0/0.5	1.00	1.00	1.80×10^{-5}	84.35	13.00	2.66
1.0/0.2	1.00	0.40	4.50×10^{-5}	83.63	13.87	2.49
0.5 M KOH + 1 M $(NH_4)_2SO_4$	0.50	2.00	6.00×10^{-6}	88.07	10.10	1.83

* The exfoliation was carried out by applying 7.5 V voltage at 25 ^{o}C.

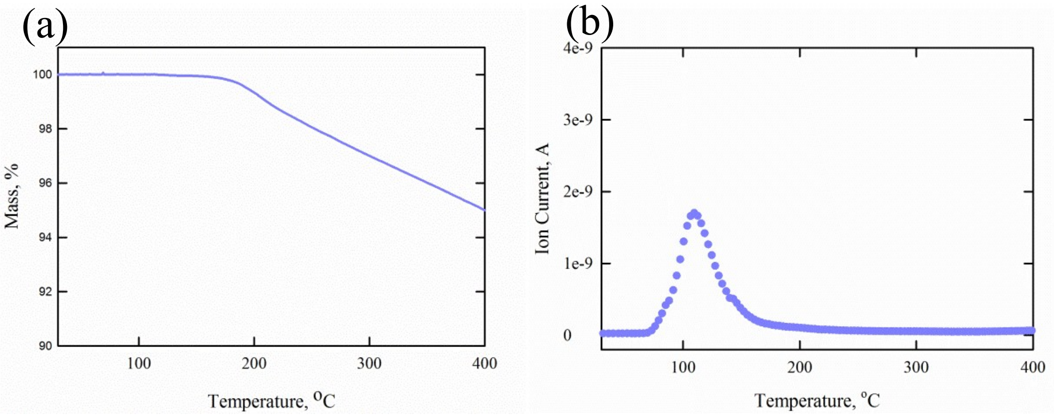


Fig. S2 a) Thermogravimetric analysis curve of N-Graphene. b) *in situ* mass spectrum of NH_3 from N-Graphene. Thermogravimetric analysis experiment was carried out on a STA 449 C analyzer (Netzsch, Germany) at a heating rate of 10 ^{o}C min^{-1} under argon flow (80 sccm). An *in situ* mass spectrometer was connected to the STA 449 C analyzer to investigate the composition of the exhaust gas.

The graphene samples were dried at 120 ^{o}C for 24 hours under vacuum before thermogravimetric analysis and XPS test. The evolution of NH_3 finished before 190 ^{o}C, while the weight loss of N-Graphene up to 190 ^{o}C is only 0.41 wt%. According to the XPS results, the nitrogen content in N-Graphene is about 5.5 wt%. Therefore, the error of XPS results due to the physically absorbed NH_3 is less than 6.1%. This is an acceptable error. Therefore, the nitrogen contents obtained from XPS are reliable.

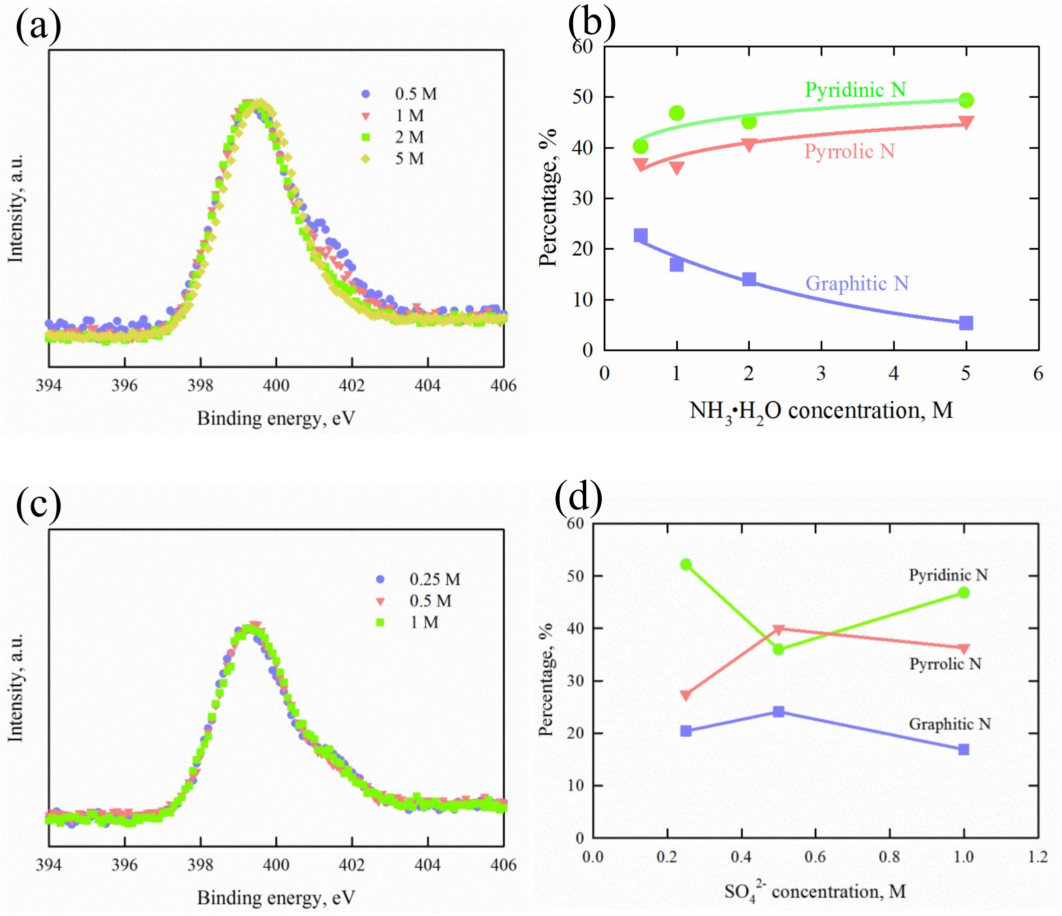


Fig. S3 The effect of electrolyte compositions on the nitrogen configurations. N 1s spectra of nitrogen-doped graphene obtained in electrolytes with different $NH_3•H_2O$ concentrations (a) and corresponding relative contents of different nitrogen configurations (b). N 1s spectra of nitrogen-doped graphene obtained in electrolytes with different SO_4^{2-} concentrations (c) and corresponding relative contents of different nitrogen configurations (d).

Table S2 The effect of exfoliation temperatures on the elemental composition of the graphene obtained.*

Temperature, ^{o}C	**C, at%**	**O, at%**	**N, at%**
25	83.46	12.43	4.12
60	81.91	9.51	8.58

* The exfoliation was carried out by applying 15 V voltage using 5M $NH_3 \bullet H_2O$ and 1M $(NH_4)_2SO_4$ mixed aqueous solution as electrolyte.

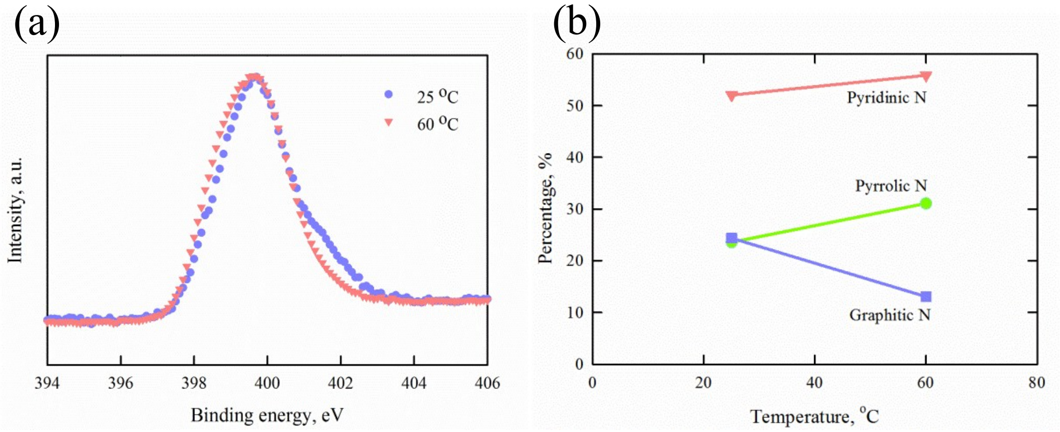


Fig. S4 The effect of exfoliation temperatures on the nitrogen configurations. N 1s spectra of nitrogen-doped graphene obtained with different exfoliation temperatures (a) and corresponding relative contents of different nitrogen configurations (b).

Table S3 The effect of exfoliation voltages on the elemental composition of the graphene obtained.*

Applied voltage, V	**C, at%**	**O, at%**	**N, at%**
4	91.61	4.35	4.03
7.5	83.40	11.66	4.95
15	83.46	12.43	4.12

* The exfoliation was carried out by utilizing 5M $NH_3 \bullet H_2O$ and 1M $(NH_4)_2SO_4$ mixed aqueous solution as electrolyte at 25 ^oC.

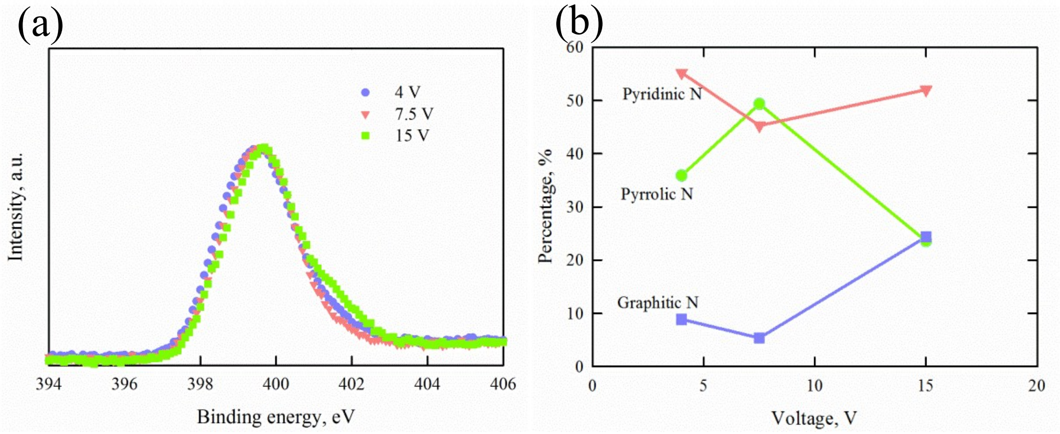


Fig. S5 The effect of exfoliation voltages on the nitrogen configurations. N 1s spectra of nitrogen-doped graphene obtained with different exfoliation voltages (a) and corresponding relative contents of different nitrogen configurations (b).

The concentration of $NH_3 \bullet H_2O$ in the electrolyte affects both the nitrogen doping level and nitrogen atom configurations in obtained graphene (Table S1 and Fig. S3). The increase of $NH_3 \bullet H_2O$ concentration increases the nitrogen content and reduces the relative content of graphitic nitrogen, but has little effect on the oxygen content. The concentration of SO_4^{2-} has no clear effect on the nitrogen contents and binding configurations but can affect the exfoliation rate obviously. Moreover, the nitrogen content can be significantly increased at high exfoliation temperature (Table S2). The exfoliation voltage has no obvious effect on the nitrogen contents and nitrogen configurations, but the oxygen content can be reduced at lower exfoliation voltage at the expense of reduced exfoliation rate (Table S3 and Fig. S5). Therefore, the properties of nitrogen-doped graphene, such as nitrogen contents, nitrogen binding configurations and oxygen contents, can be manipulated by carefully tuning the exfoliation conditions.

S3 Bonding configurations of C, N and O for C-Graphene and N-Graphene

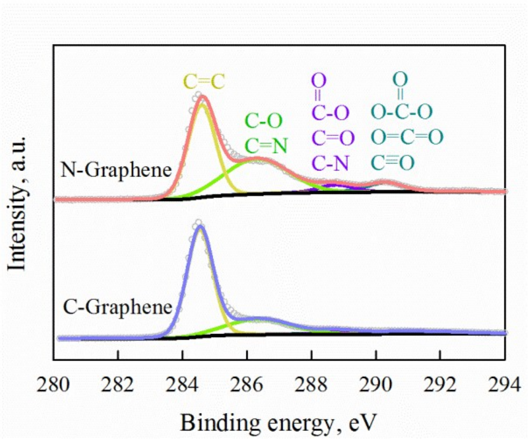


Fig. S6 High-resolution C 1s XPS spectra of C-Graphene and N-Graphene.

The high-resolution C 1s spectra can be deconvoluted into four components: peak I (284.6 eV), graphitic carbon; peak II (286.1-286.3 eV), carbon in phenolic, alcohol, ether or C=N groups; peak III (288.4-288.9 eV), carbon in ketone, quinone, carboxyl, ester or C-N group; peak IV (290.5-291.2 eV), carbon in carbonate groups and/or adsorbed CO and CO_2 (Fig. S5).[1-4] Peak I of N-Graphene is obviously weaker than that of C-Graphene (Table S4), indicating that nitrogen incorporation results in more defects. The relative strength of peak II is greater in N-Graphene (Table S4) and this is consistent with incorporation of nitrogen into the graphene structure and the formation of C=N bonds.

Table S4 Contents of functional groups in C 1s from XPS spectra.

Sample	Contents, at%				Relative contents, %			
	Peak I	Peak II	Peak III	Peak IV	Peak I	Peak II	Peak III	Peak IV
C-Graphene	61.5	21.4	1.9	7.0	67.0	23.3	2.1	7.6
N-Graphene	39.6	33.8	3.8	6.2	47.5	40.5	4.6	7.4

Table S5 Contents of functional groups in N 1s from XPS spectra.

Sample	Contents, at%			Relative contents, %		
	Peak I	Peak II	Peak III	Peak I	Peak II	Peak III
C-Graphene	-	-	-	-	-	-
N-Graphene	2.4	2.2	0.3	49.3	45.3	5.4

Table S6 Contents of functional groups in O 1s from XPS spectra.

Sample	Contents, at%			Relative contents, %		
	Peak I	Peak II	Peak III	Peak I	Peak II	Peak III
C-Graphene	3.4	3.1	1.7	41.4	37.6	21.0
N-Graphene	1.9	6.6	3.1	16.8	56.5	26.7

S4 Stability of C-Graphene and N-Graphene in different solvents

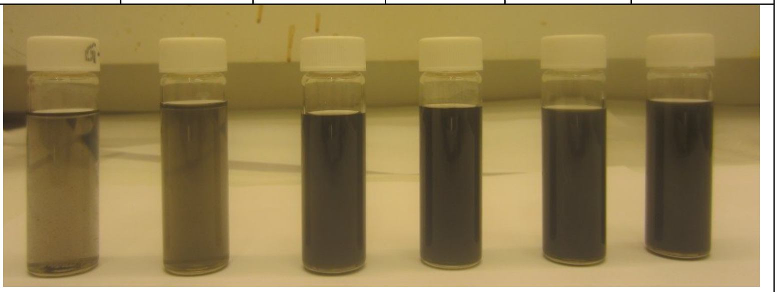
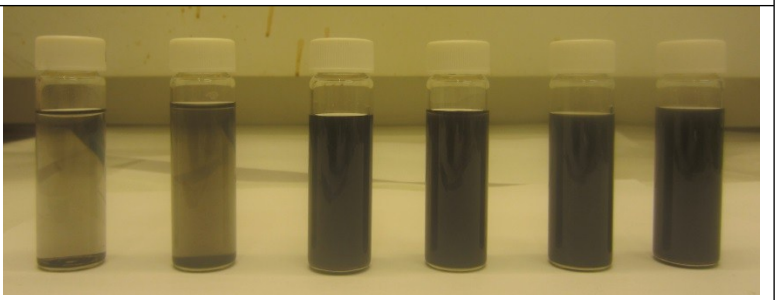
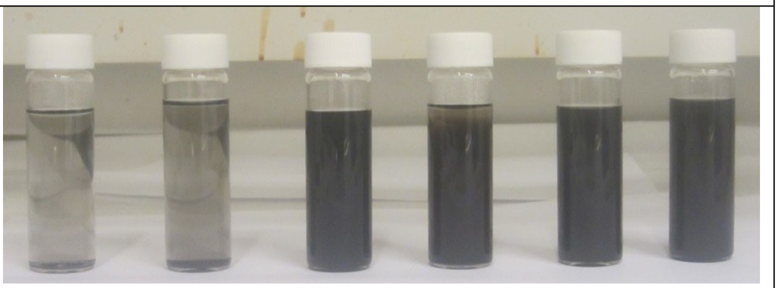
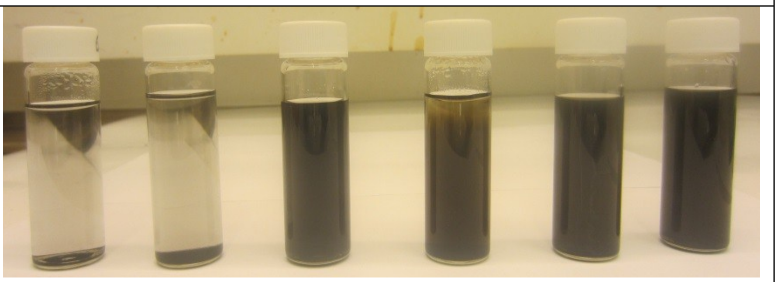
<table>
<tr><th rowspan="2"></th><th colspan="3">C-Graphene</th><th colspan="3">N-Graphene</th></tr>
<tr><th>Water</th><th>Ethanol</th><th>NMP*</th><th>Water</th><th>Ethanol</th><th>NMP</th></tr>
<tr><td>Directly after centrifugation.</td><td colspan="6"></td></tr>
<tr><td>1 day</td><td colspan="6"></td></tr>
<tr><td>10 days</td><td colspan="6"></td></tr>
<tr><td>100 days</td><td colspan="6"></td></tr>
</table>

Fig. S7 Photographs of C-Graphene and N-Graphene in different solvents.

* N-Methyl-2-pyrrolidone

S5 Catalytic performances of C-Graphene and N-Graphene towards ORR

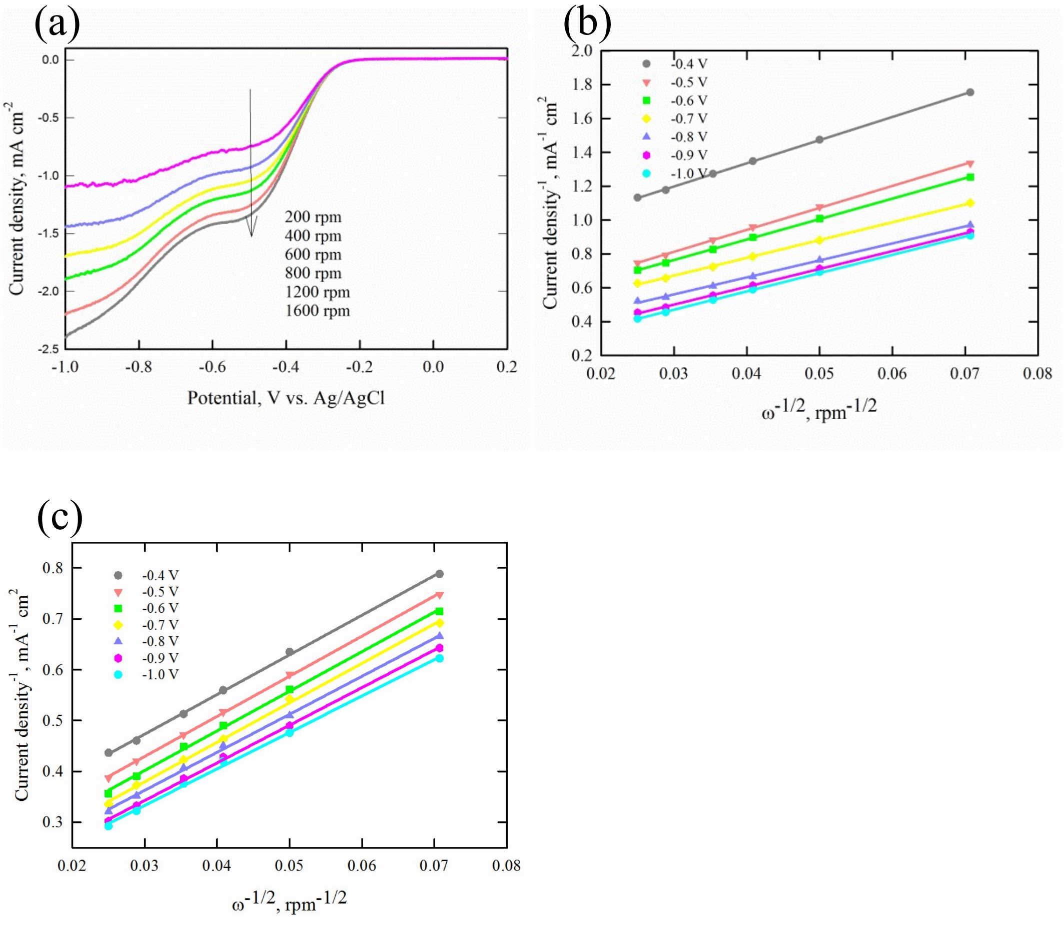


Fig. S8 a) RDE voltammograms of C-Graphene in 0.1 M oxygen saturated KOH at a scan rate of 10 mV s^{-1} and various rotating rates. Koutecky-Levich plots of C-Graphene (b) and N-Graphene (c) at different electrode potentials.

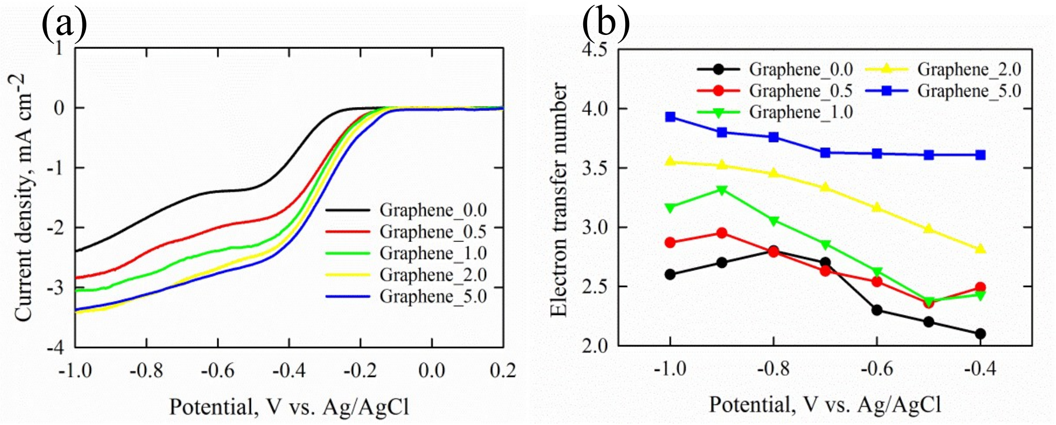


Fig. S9 a) RDE voltammograms of nitrogen-doped graphene with different doping levels in 0.1 M oxygen saturated KOH at a scan rate of 10 mV s^{-1} and a rotating rate of 1600 rpm. b) The electron transfer number of nitrogen-doped graphene with different doping levels as a function of potential. Graphene_0.0 (C-Graphene), Graphene_0.5, Graphene_1.0, Graphene_2.0, Graphene_5.0 (N-Graphene) were exfoliated in 1 M $(NH_4)_2SO_4$ mixed with 0, 0.5, 1.0, 2.0 and 5.0 M $NH_3 \cdot H_2O$, respectively, at 25 ^{o}C by applying 7.5 V voltage. The nitrogen doping levels of Graphene_0.0 (C-Graphene), Graphene_0.5, Graphene_1.0, Graphene_2.0, Graphene_5.0 (N-Graphene) are 0.00, 1.96, 2.62, 3.63 and 4.95 at%, respectively (Table S1).

Table S7 Catalytic performance of nitrogen-doped graphene prepared by different methods.

Preparation method	Preparation T, °C	Nitrogen content, at%	Onset potential V vs Ag/AgCl	Electron transfer number (potentials V vs Ag/AgCl)	Ref.
CVD*	1000	4	about-0.15	3.6-4.0 (-0.4 to-0.8)	Qu et al.[5]
Pyrolysis of GO and urea	800	7.86	-0.10	3.6-4 (-1.0 to -0.5)	Lin et al.[4]
Electrochemical exfoliation of graphite in NH_4NO_3 solution	room T	1.3	<-0.20	3.4-3.7 (-0.40 to -0.55)	Gondosiswanto et al.[6]
Electrochemical reduction of GO in NH_3•H_2O	room T	3.3	-0.10	3.90-4.05 (-0.5 to -1.0)	Ma et al[7]
Treat GO with NH_3•H_2O	90	6.0	-0.13	3.75 (-0.6)	Xing et al[8]
Pyrolysis of GO and melamine	950	5.7	about -0.18	about 3.42 (-0.6)	Xing et al[8]
Annealing GO in NH_3	600	6.8	about -0.18	about 3.23 (-0.6)	Xing et al[8]
CVD	800	4.95	-0.08	3.9 (-0.4)	Ito et al[9]
CVD	400 to 600	2.7	-0.20	3.5-4.0 (-0.4 to -0.6)	Yasuda et al[10]
CVD	400 to 600	2.0	-0.20	1.9-2.1 (-0.4 to -0.6)	Yasuda et al[10]
Hydrothermal reaction	180	7.78	about -0.15	2.6 (-0.5)	Zhang et al[11]
Electrochemical exfoliation of graphite in NH_3•H_2O and $(NH_4)_2SO_4$ solution	**room T**	**4.95**	**-0.08**	**3.6-3.9 (-0.4 to -1.0)**	**This work**

* Chemical vapor deposition

References

[1] Z. R. Yue, W. Jiang, L. Wang, S. D. Gardner and C. U. Pittman Jr, Carbon 1999, 37, 1785.

[2] J.-H. Zhou, Z.-J. Sui, J. Zhu, P. Li, D. Chen, Y.-C. Dai and W.-K. Yuan, Carbon 2007, 45, 785.

[3] U. Zielke, K. J. Hüttinger and W. P. Hoffman, Carbon 1996, 34, 983.

[4] Z. Lin, G. Waller, Y. Liu, M. Liu and C.-P. Wong, Advanced Energy Materials 2012, 2, 884.

[5] L. Qu, Y. Liu, J.-B. Baek and L. Dai, ACS Nano 2010, 4, 1321.

[6] R. Gondosiswanto, X. Lu and C. Zhao, Aust. J. Chem. 2015, 68, 830.

[7] F.-X. Ma, J. Wang, F.-B. Wang and X.-H. Xia, Chem. Commun. 2015, 51, 1198.

[8] T. Xing, Y. Zheng, L. H. Li, B. C. C. Cowie, D. Gunzelmann, S. Z. Qiao, S. Huang and Y. Chen, ACS Nano 2014, 8, 6856.

[9] Y. Ito, H. J. Qiu, T. Fujita, Y. Tanabe, K. Tanigaki and M. Chen, Adv. Mater. 2014, 26, 4145.

[10] S. Yasuda, L. Yu, J. Kim and K. Murakoshi, Chem. Commun. 2013, 49, 9627.

[11] Y. Zhang, K. Fugane, T. Mori, L. Niu and J. Ye, J. Mater. Chem. 2012, 22, 6575.