

## Tailoring nitrogen doping in metal-free mesoporous carbons derived from aminotriazine for superior oxygen reduction reaction

Jefrin M. Davidraj<sup>1</sup>, CI Sathish<sup>1\*</sup>, Premkumar Selvarajan<sup>2</sup>, Mohammed Fawaz<sup>1</sup>, Vibin Perumalsamy<sup>1</sup>, Xiaojiang Yu<sup>3</sup>, Mark BH Breese<sup>3</sup>, Jiabao Yi<sup>1\*</sup> and Ajayan Vinu<sup>\*1</sup>

<sup>1</sup>Global Innovative Centre for Advanced Nanomaterials (GICAN), School of Engineering, The University of Newcastle, Callaghan, New South Wales 2308, Australia

<sup>2</sup>Department of Physics, School of Advanced Sciences, Vellore Institute of Technology, Vellore, India.

<sup>3</sup> Singapore Synchrotron Light Source, National University of Singapore, Singapore, 119260

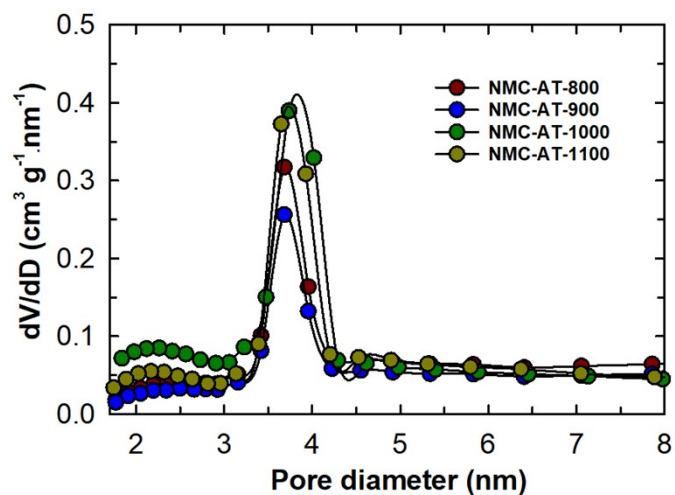
Correspondence E-mail: [sathish.ci@newcastle.edu.au](mailto:sathish.ci@newcastle.edu.au), [jiabao.yi@newcastle.edu.au](mailto:jiabao.yi@newcastle.edu.au)  
[ajayan.vinu@newcatle.edu.au](mailto:ajayan.vinu@newcatle.edu.au)

**Table S1:** Summary of XPS deconvolutions

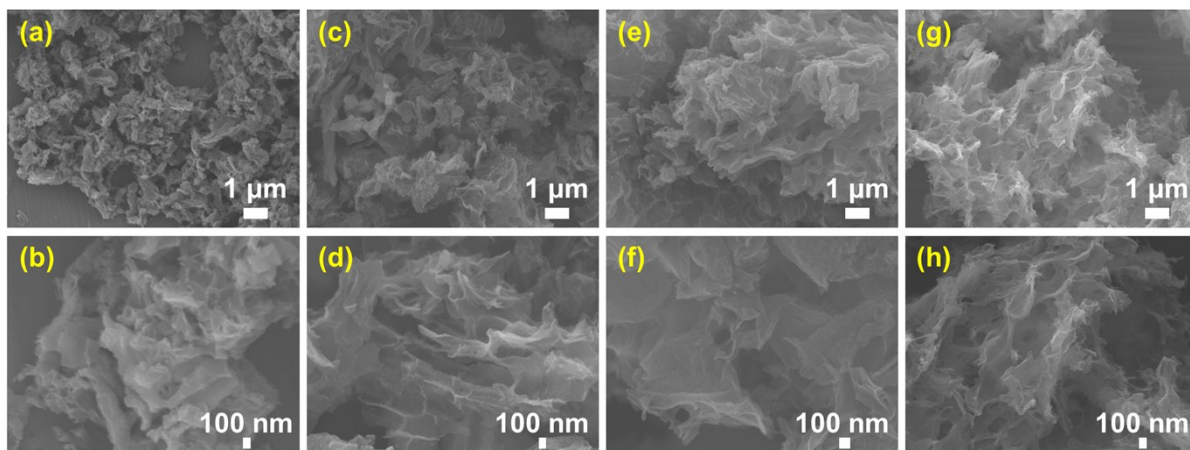
Sample	C 1s				N 1s		
	C=C	C-N	C=N	C-O	Pyridinic N	Pyrrolic N	Graphitic N
NMC-AT-800	41.03	50.06	8.91		47.69	49.08	3.23
NMC-AT-900	52.28	36.37	11.35		41.85	49.56	8.59
NMC-AT-1000	65.36	26.89	7.75		42.43	47.60	9.97
NMC-AT-1100	54.4	16.83	20.39	8.38	31.11	37.7	31.19

**Table S2:** Comparison of the ORR activity of different N-doped carbon electrocatalysts with NMC-AT-1000 catalyst

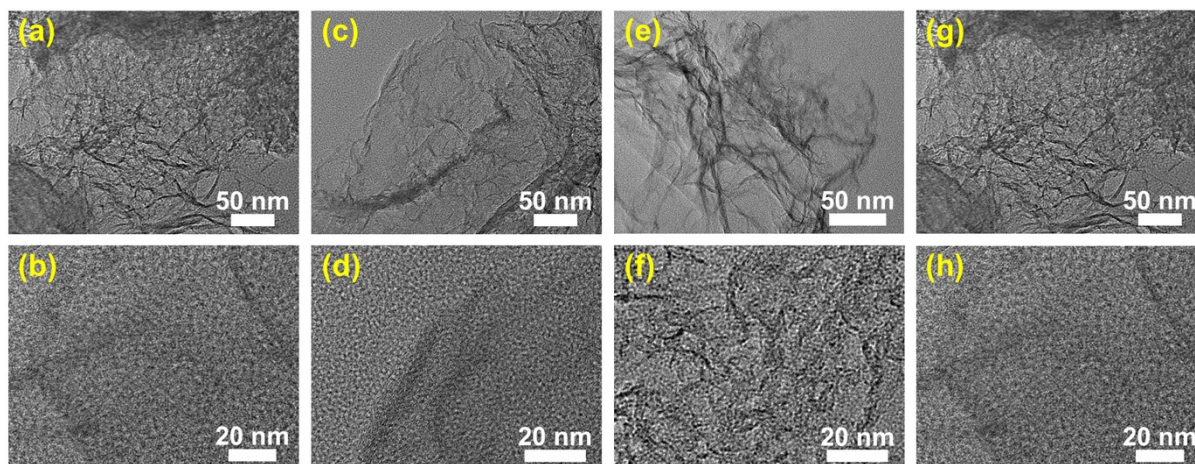
S.No	Electrocatalyst	On-Set potential (V)	Current density (mA/cm <sup>2</sup> )	Electron transfer number	Reference
1	3D-NG@SiO <sub>2</sub> -2-900	0.91	4	3.9	[1]
2	NPGC-950	0.91	4.8	3.8	[2]
3	NG900	0.89	4.5	3.2	[3]
4	N-RGO-800	0.86	5.0	3.8	[4]
5	N-G-1000	0.83	5.1	3.9	[5]
6	N-hG6	0.83	5.2	3.9	[6]
7	NMC-AT-1000	0.87	5.1	4.02	<b>This work</b>



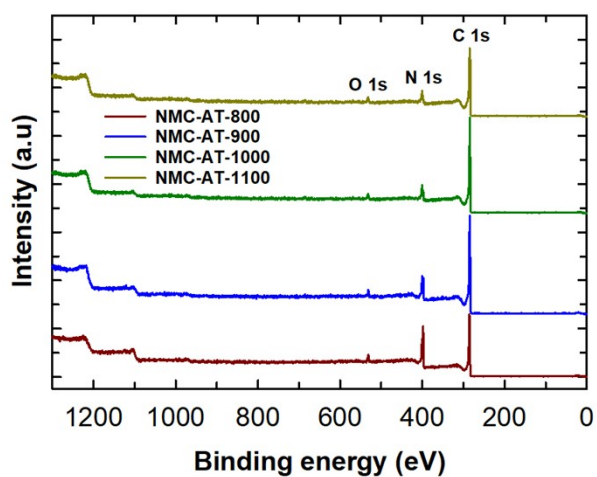
**Fig. S1** Pore size distribution of NMC-AT samples.



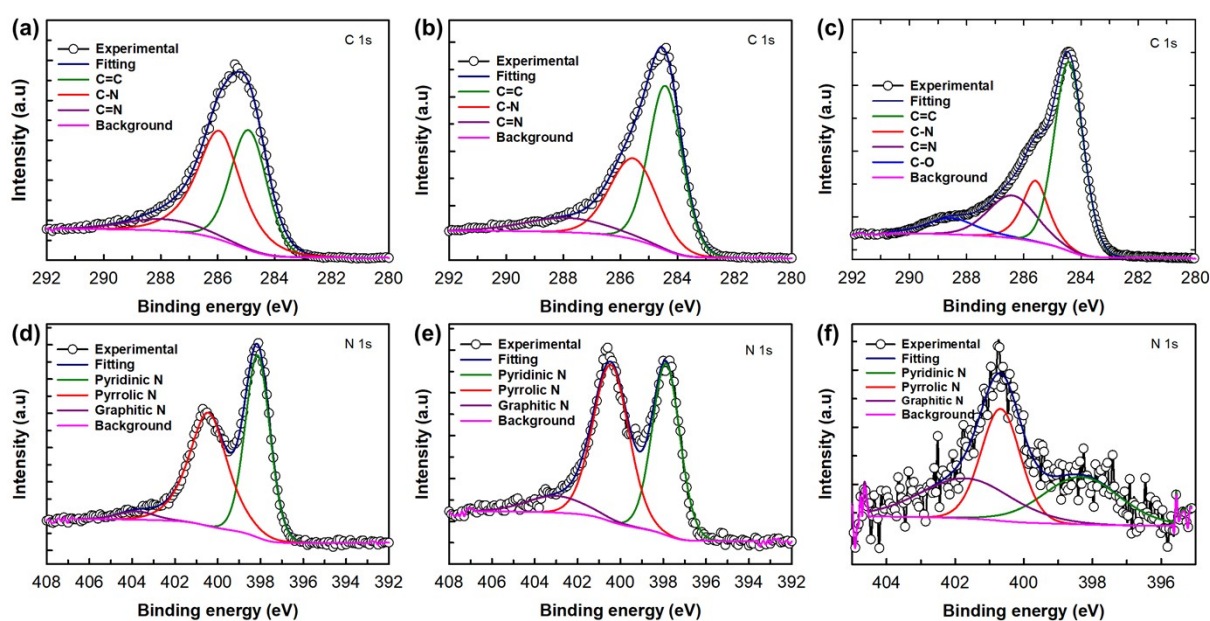
**Fig. S2** Low and high magnification SEM images of (a & b) NMC-AT-800, (c & d) NMC-AT-900, (e & f) NMC-AT-1000, and (g & h) NMC-AT-1100 samples



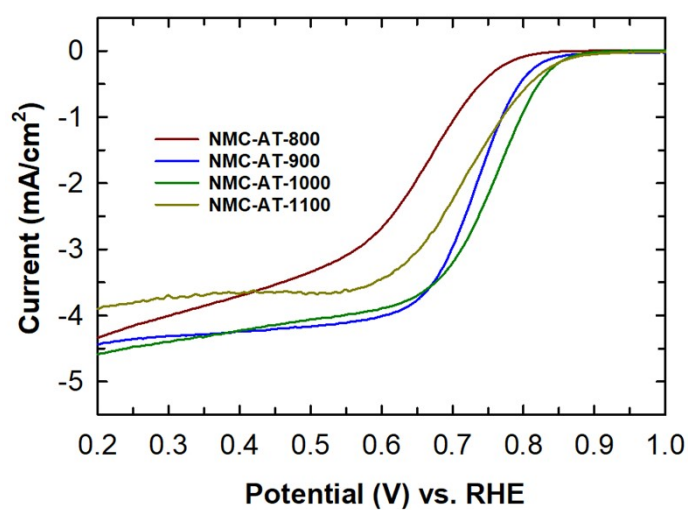
**Fig. S3** Low and high magnification TEM images of (a & b) NMC-AT-800, (c & d) NMC-AT-900, (e & f) NMC-AT-1000, and (g & h) NMC-AT-1100 samples.



**Fig. S4** Survey spectrum of NMC-AT samples



**Fig S5** XPS deconvolutions of C 1s and N 1s spectra (a & d) NMC-AT-800, (b & e) NMC-AT-900, and (c & f) NMC-AT-1100 samples.



**Fig. S6** LSV curves of the NMC-AT samples at a scan rate of 5 mV/s.

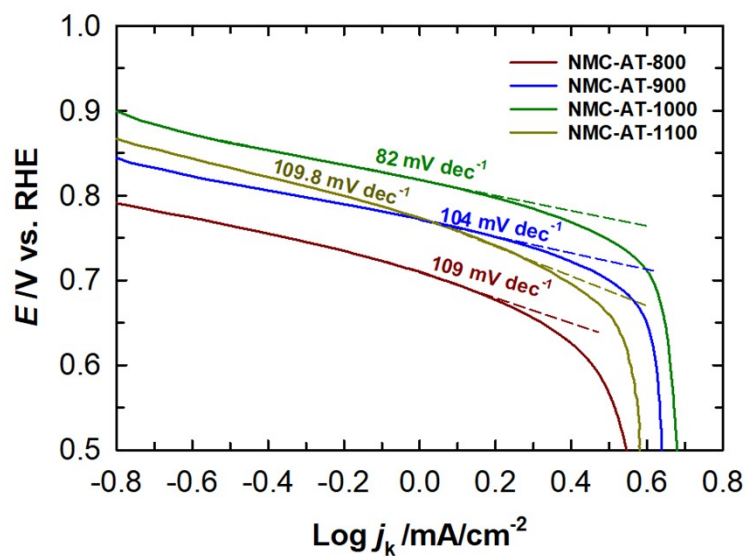


Fig. S7 Tafel slope of NMC-AT samples.

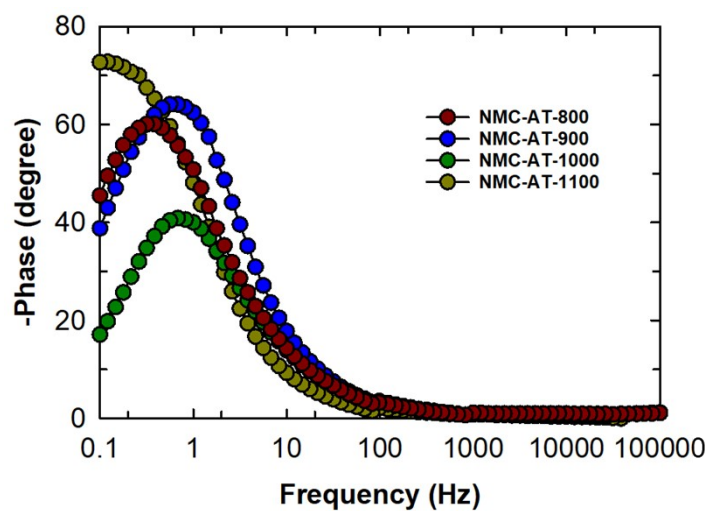


Fig. S8 Bode-plot of NMC-AT samples.

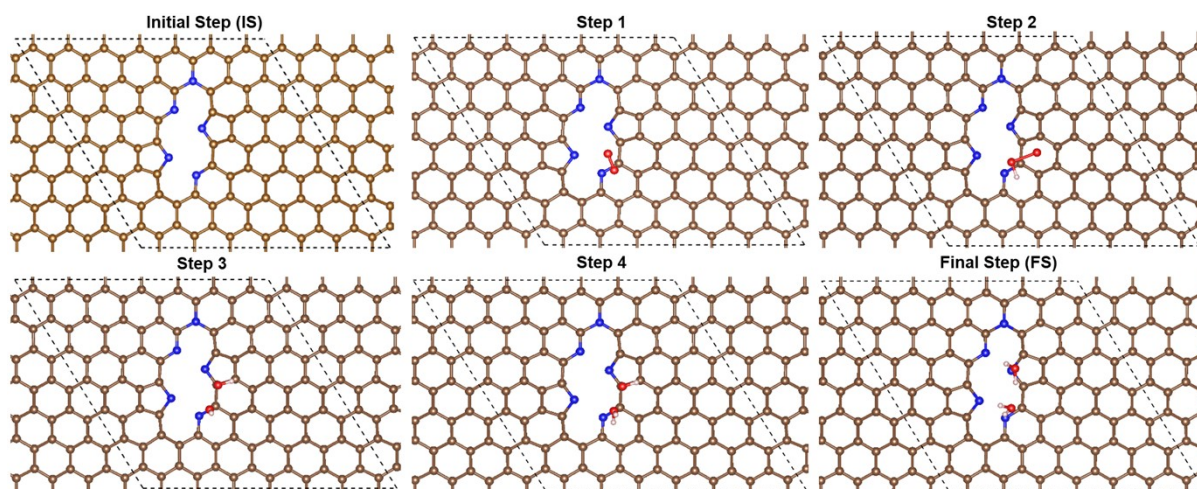


Fig. S9 Electrochemical ORR four-electron pathway of NMC-AT sample.

## References:

- [1] X.W. Lu, Z.F. Li, X.Y. Yin, S.W. Wang, Y.R. Liu, Y.X. Wang, Controllable synthesis of three-dimensional nitrogen-doped graphene as a high performance electrocatalyst for oxygen reduction reaction, *International Journal of Hydrogen Energy* 42(27) (2017) 17504-17513. <https://doi.org/10.1016/j.ijhydene.2017.02.090>.
- [2] B. Men, Y.Z. Sun, M.J. Li, C.Q. Hu, M. Zhang, L.N. Wang, Y. Tang, Y.M. Chen, P.Y. Wan, J.Q. Pan, Hierarchical Metal-Free Nitrogen-Doped Porous Graphene/Carbon Composites as an Efficient Oxygen Reduction Reaction Catalyst, *Acs Appl Mater Inter* 8(2) (2016) 1415-1423. <https://doi.org/10.1021/acsami.5b10642>.
- [3] Y.Y. She, J.F. Chen, C.X. Zhang, Z.G. Lu, M. Ni, P.H.L. Sit, M.K.H. Leung, Nitrogen-doped graphene derived from ionic liquid as metal-free catalyst for oxygen reduction reaction and its mechanisms, *Applied Energy* 225 (2018) 513-521. <https://doi.org/10.1016/j.apenergy.2018.05.015>.
- [4] H. Miao, S.H. Li, Z.H. Wang, S.S. Sun, M. Kuang, Z.P. Liu, J.L. Yuan, Enhancing the pyridinic N content of Nitrogen-doped graphene and improving its catalytic activity for oxygen reduction reaction, *International Journal of Hydrogen Energy* 42(47) (2017) 28298-28308. <https://doi.org/10.1016/j.ijhydene.2017.09.138>.
- [5] X.Y. Lu, D. Wang, L.P. Ge, L.H. Xiao, H.Y. Zhang, L.L. Liu, J.Q. Zhang, M.Z. An, P.X. Yang, Enriched graphitic N in nitrogen-doped graphene as a superior metal-free electrocatalyst for the oxygen reduction reaction, *New Journal of Chemistry* 42(24) (2018) 19665-19670. <https://doi.org/10.1039/c8nj04857f>.
- [6] Y. Bian, H. Wang, J. Hu, B. Liu, D. Liu, L. Dai, Nitrogen-rich holey graphene for efficient oxygen reduction reaction, *Carbon* 162 (2020) 66-73. <https://doi.org/10.1016/j.carbon.2020.01.110>.