Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Doped ordered mesoporous carbons as novel, selective electrocatalysts for the reduction of nitrobenzene to aniline

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Supporting information

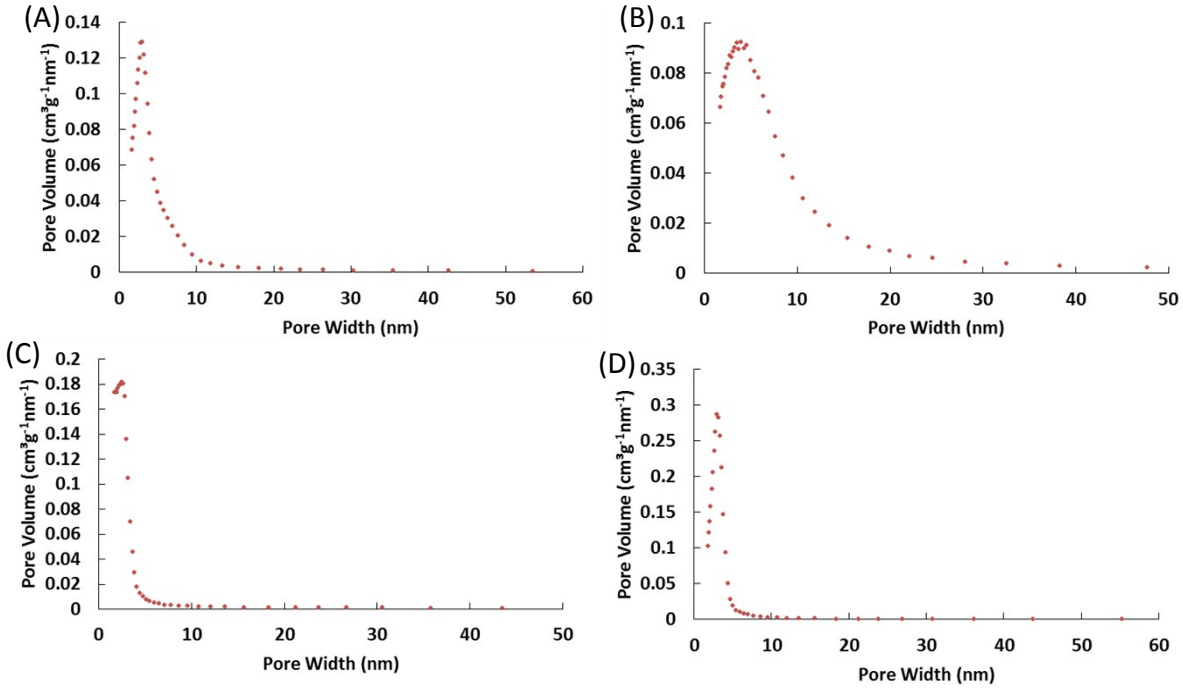

Figure S1. Pore size distribution curves of NOMC (A), BOMC (B), POMC (C) and OMC (D).

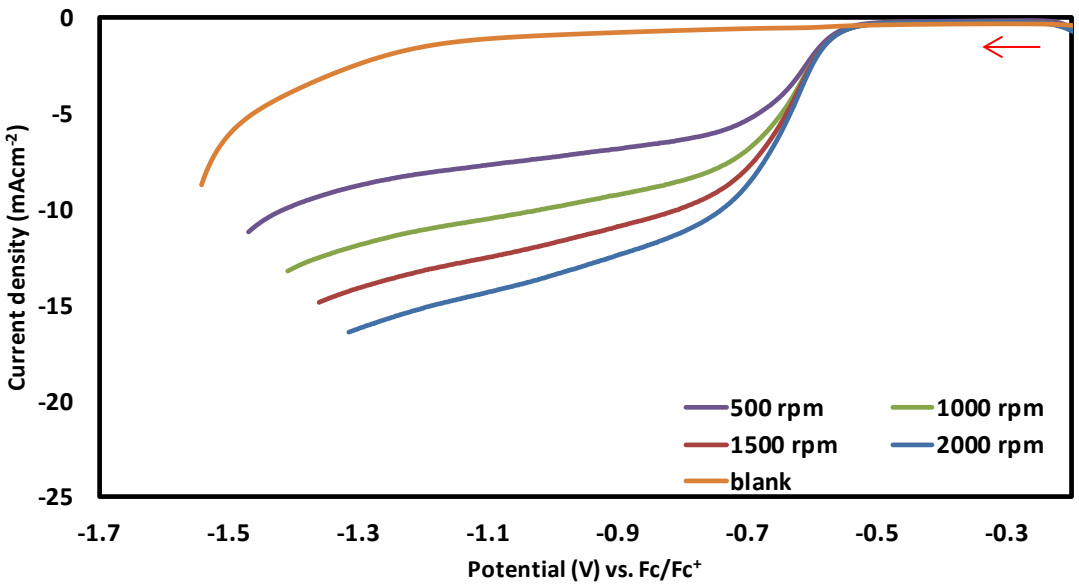

Figure S2. LSV plots of NOMC recorded in 5 mM nitrobenzene in 0.3 M $HClO_4$ in ethanol at a scan rate of 5 mVs^{-1} at different rotation rates and corrected for the iR drop.

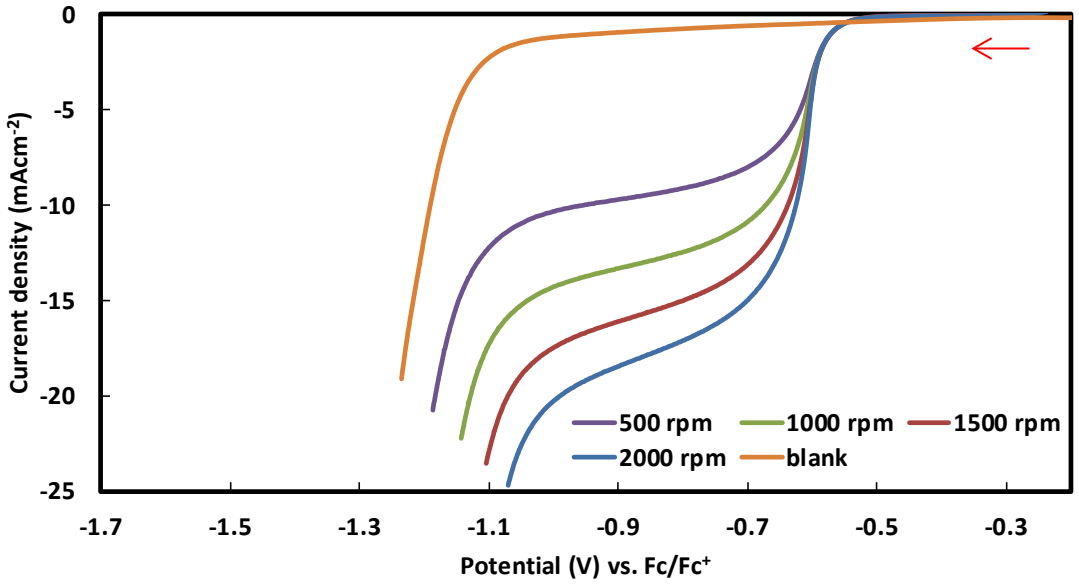

Figure S3. LSV plots of BOMC recorded in 5 mM nitrobenzene in 0.3 M $HClO_4$ in ethanol at a scan rate of 5 mVs^{-1} at different rotation rates and corrected for the iR drop.

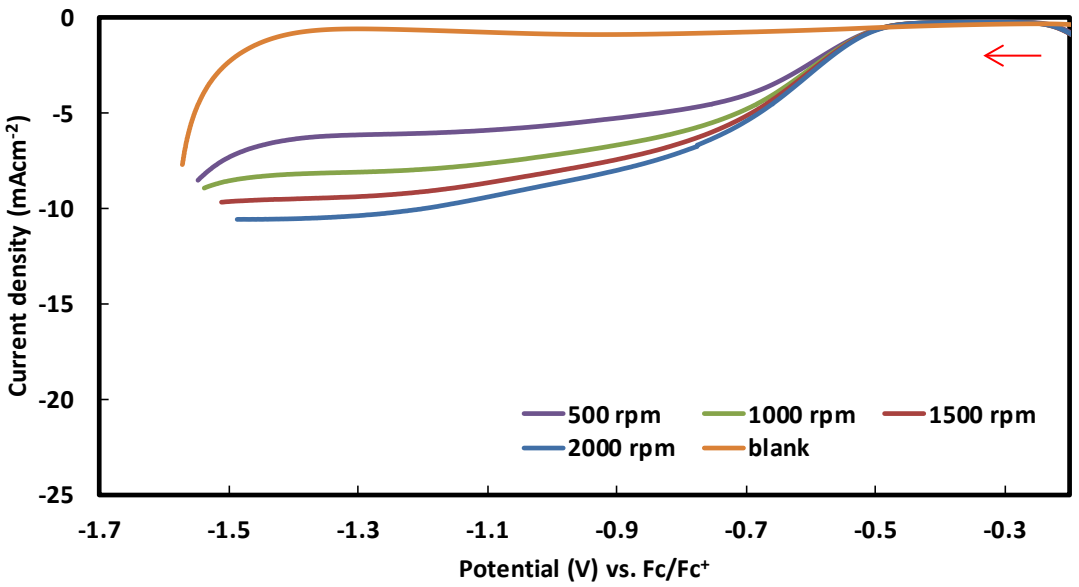

Figure S4. LSV plots of POMC recorded in 5 mM nitrobenzene in 0.3 M $HClO_4$ in ethanol at a scan rate of 5 mVs^{-1} at different rotation rates and corrected for the iR drop.

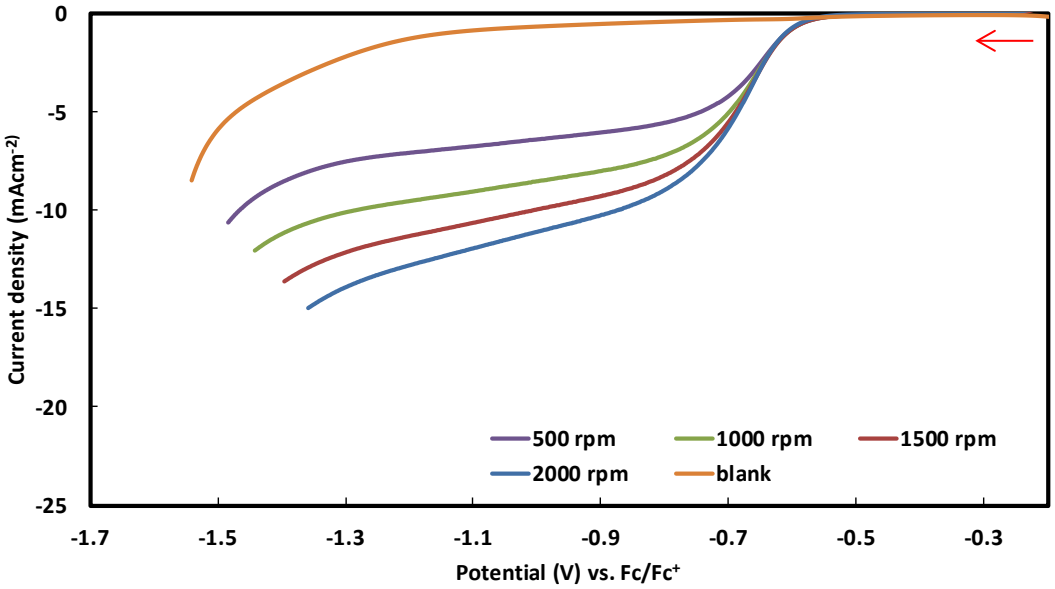

Figure S5. LSV plots of OMC recorded in 5 mM nitrobenzene in 0.3 M $HClO_4$ in ethanol at a scan rate of 5 mVs^{-1} at different rotation rates and corrected for the iR drop.

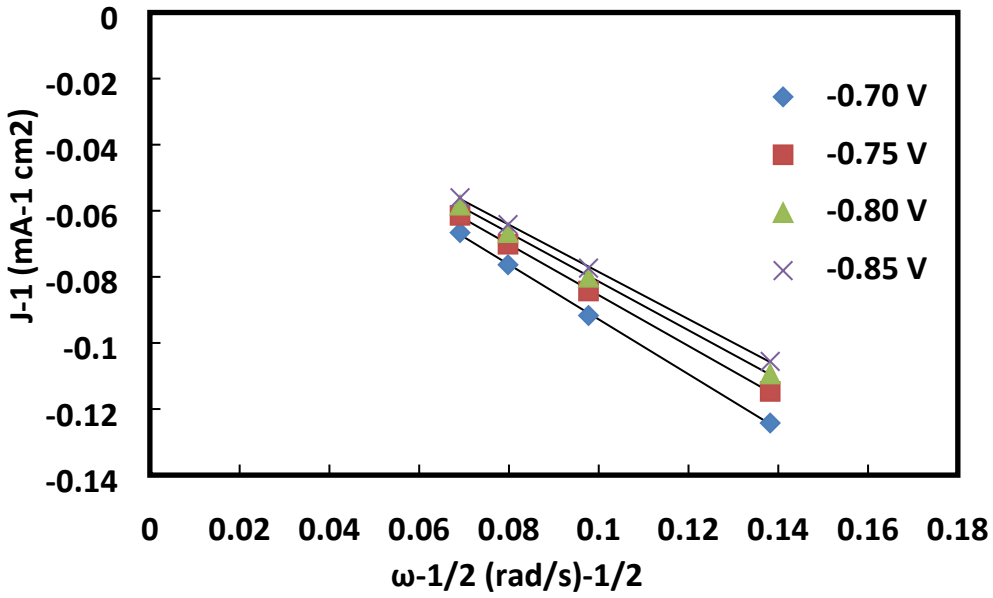

Figure S6. Koutécky-Levich plots (J^{-1} vs. $\omega^{-1/2}$) of BOMC at a potential interval from -0.70 to -0.85 V vs. Fc/Fc^{+}.

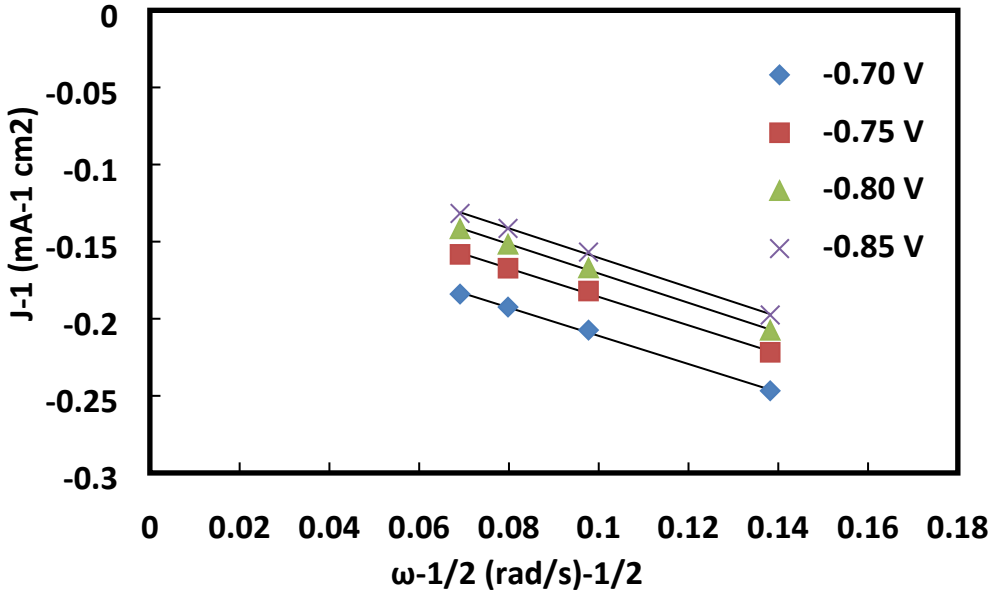

Figure S7. Koutécky-Levich plots (J^{-1} vs. $\omega^{-1/2}$) of POMC at a potential interval from -0.70 to -0.85 V vs. Fc/Fc^{+}.

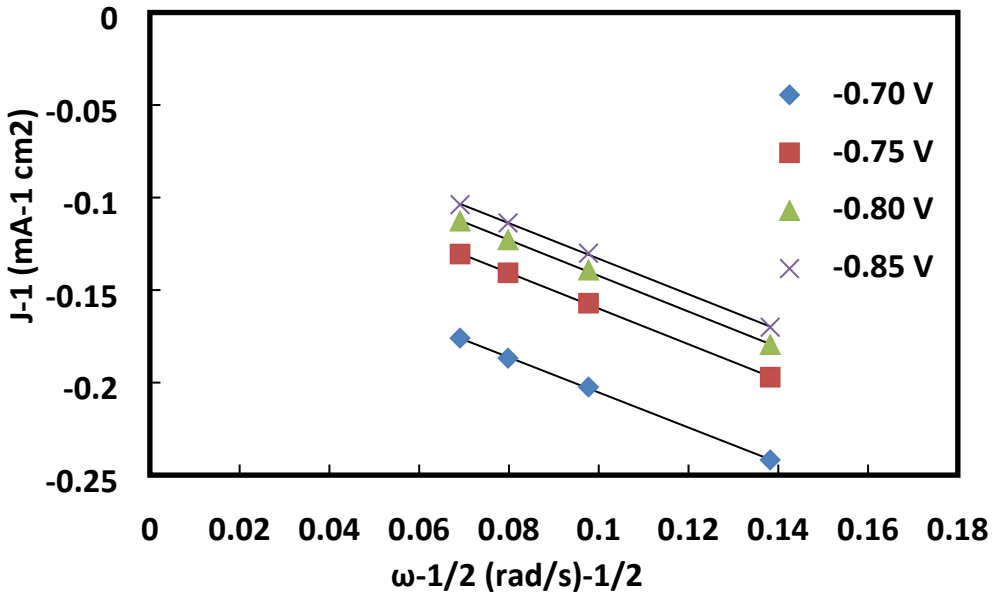

Figure S8. Koutécky-Levich plots (J^{-1} vs. $\omega^{-1/2}$) of OMC at a potential interval from -0.70 to -0.85 V vs. Fc/Fc^{+}.

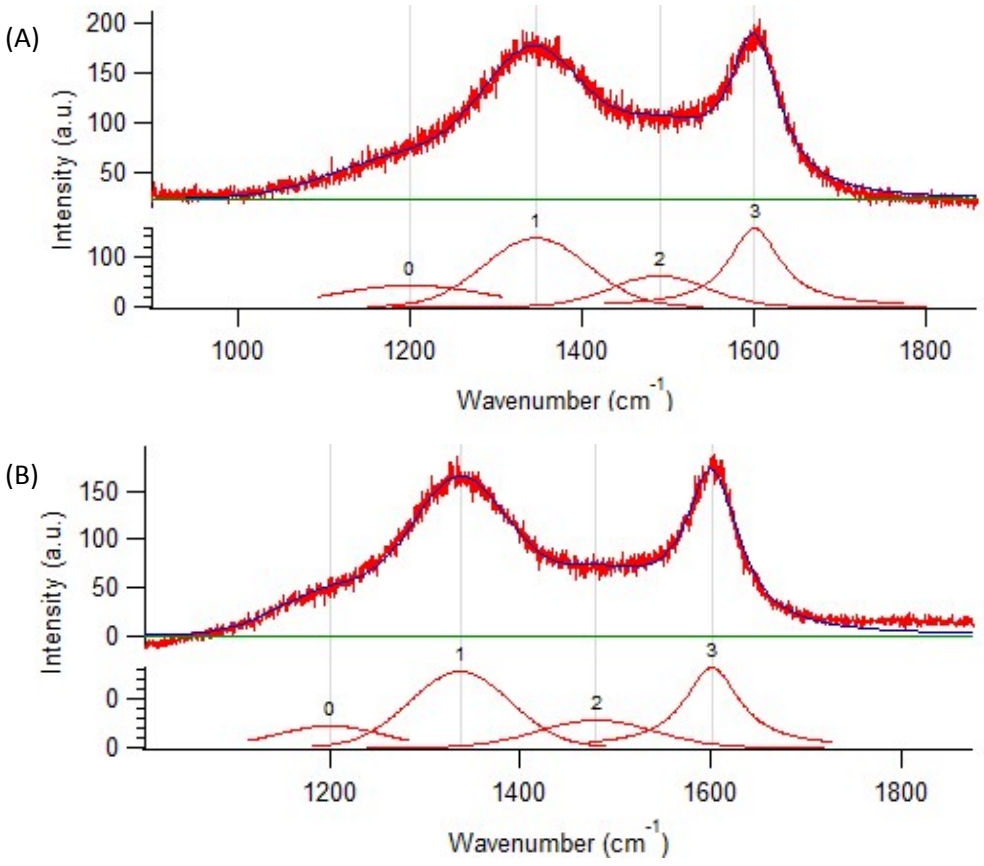

Figure S9. Deconvoluted Raman spectra of NOMC (A) and OMC (B).

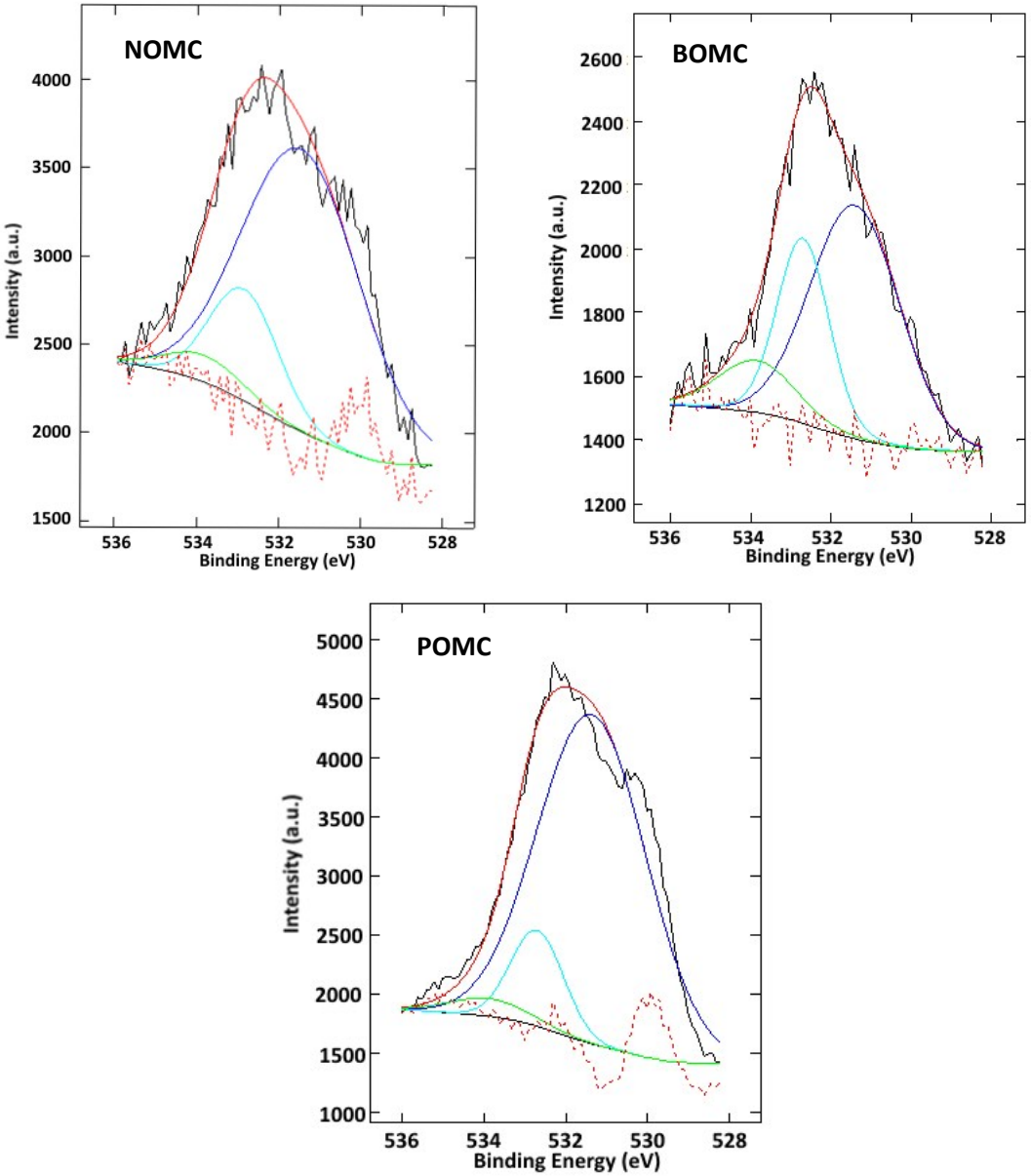

Figure S10. Deconvoluted high resolution O 1s XPS signals of NOMC, BOMC and POMC.

Element	Na (as Na_2O)	Si (as SiO_2)	P (as P_2O_5)	Ca (as CaO)	Fe (as Fe_2O_3)	Ni (as NiO)	Cu (as CuO)	Sr (as SrO)
wt%	1.039	0.213	2.947	0.104	0.012	0.007	0.004	0.005

Table S1. XRF elemental analysis of POMC. Note: the remaining 95.7 wt% of the material should consist of C (mainly), O and N, which cannot be measured by XRF.

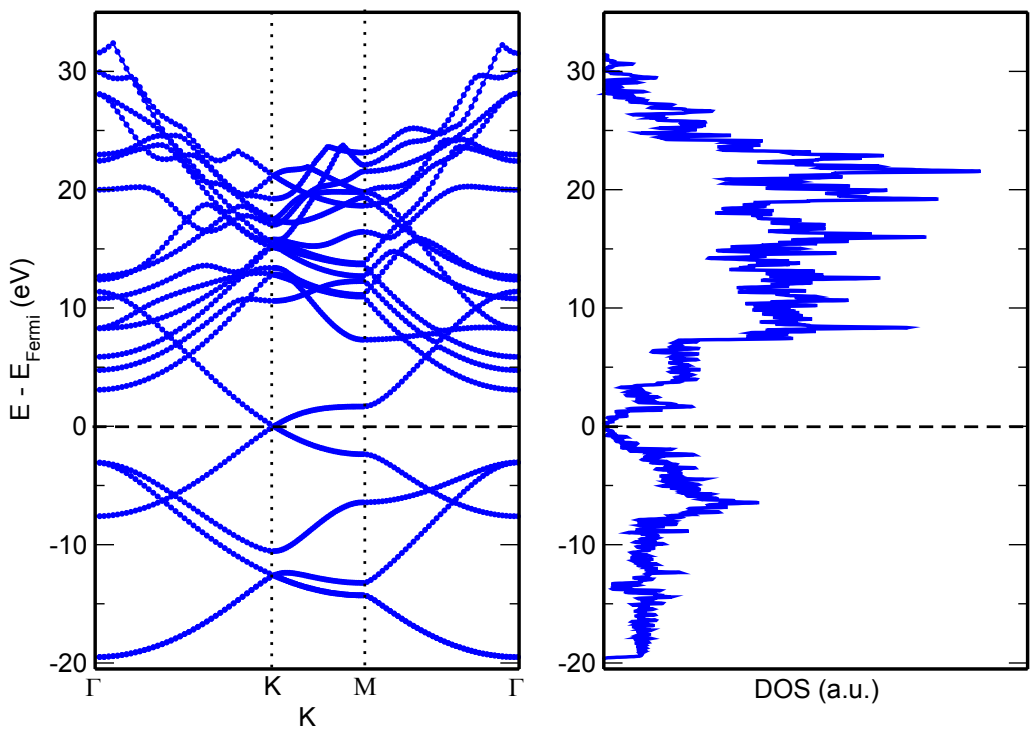

Figure S11. Bands structure and density of states of graphene (used to simulate the OMC surface).

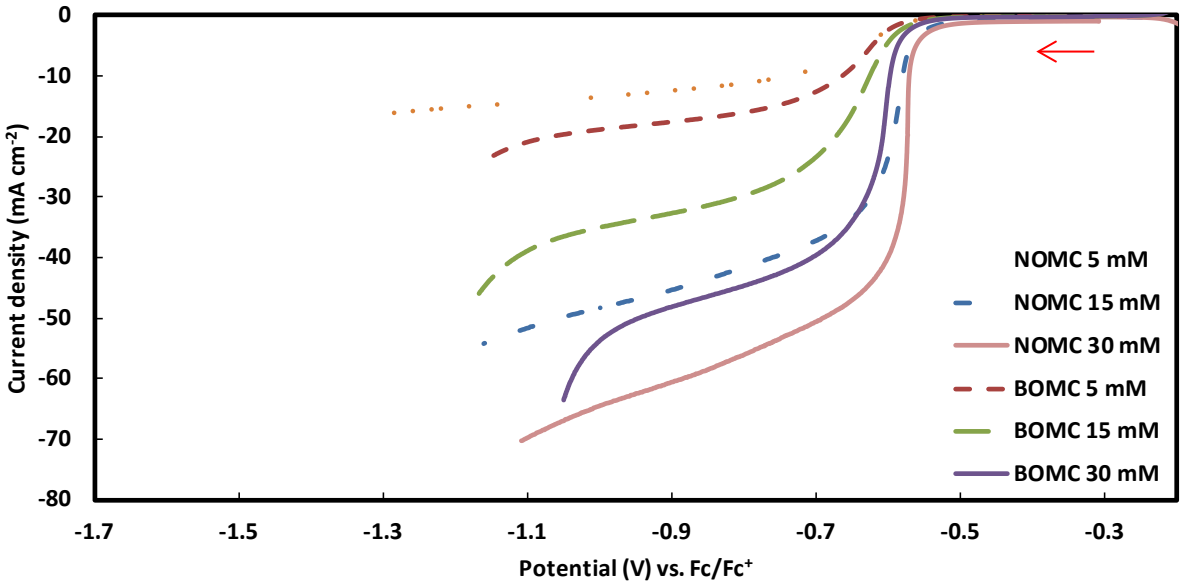

Figure S12. LSV plots of NOMC and BOMC, recorded at different concentrations of nitrobenzene (5, 15 and 30 mM) in 0.3 M $HClO_4$ in absolute ethanol at a scan rate of 5 mVs^{-1}, with a rotation speed of 2000 rpm and corrected for the iR drop.

Entry	ΔE_{ads} (no VDW) (eV)	ΔE_{ads} (VDW) (eV)	d_{mol-G} (no VDW) (Å)	d_{mol-G} (VDW) (Å)	d_{NO} (no VDW) (Å)	d_{NO} (VDW) (Å)
1	-0.099	-0.302	3.266	2.887	1.252-1.252	1.255-1.255
2	-0.086	-0.265	3.269	2.903	1.252-1.251	1.253-1.254
3	-0.090	-0.271	3.468	2.934	1.251-1.251	1.254-1.254
4	-0.028	-0.489	3.923	3.127	1.244-1.244	1.245-1.245
5	-0.060	-0.528	3.837	3.040	1.245-1.245	1.249-1.250
6	-0.047	-0.537	4.110	2.957	1.243-1.245	1.247-1.249
7	-0.070	-0.523	3.345	2.929	1.243-1.244	1.243-1.243
8	-0.054	-0.510	3.373	2.936	1.244-1.244	1.243-1.243

Table S2. Adsorption energy (ΔE_{ads}), space separation between nitrobenzene and monolayer (d_{mol-G}) and N-O distance between O and N atoms of nitro group (d_{NO}) of nitrobenzene adsorbed on N-doped graphene for all configurations reported in Figure S13 calculated including (VDW) or neglecting (no VDW) van der Waals interactions (DFT-D2 method). It should be noted that the interaction between nitrobenzene and the electrocatalyst surface is weak (being mainly based on van der Waals interactions) and, therefore, it should be considered as a physisorption.

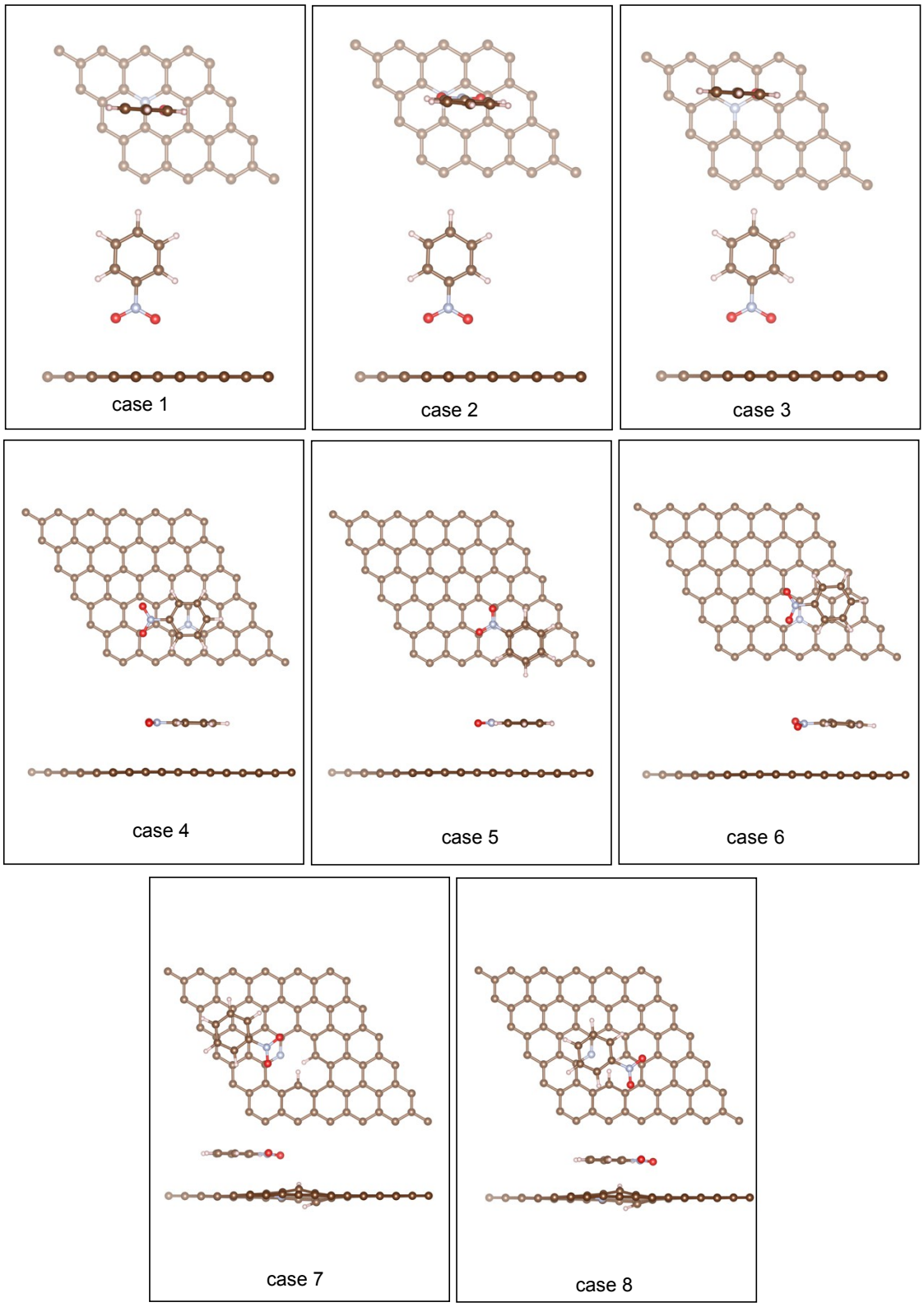

Figure S13. Balls and sticks representation (top and side views) of physisorption of nitrobenzene on N-doped graphene with N atoms in graphitic configuration (cases from 1 to 6) or pyridinic configuration (cases 7 and 8). Brown spheres represent C atoms, grey spheres N atoms and white spheres H atoms.