Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Graphene-hBN non-van der Waals vertical heterostructures for four electron oxygen reduction reaction

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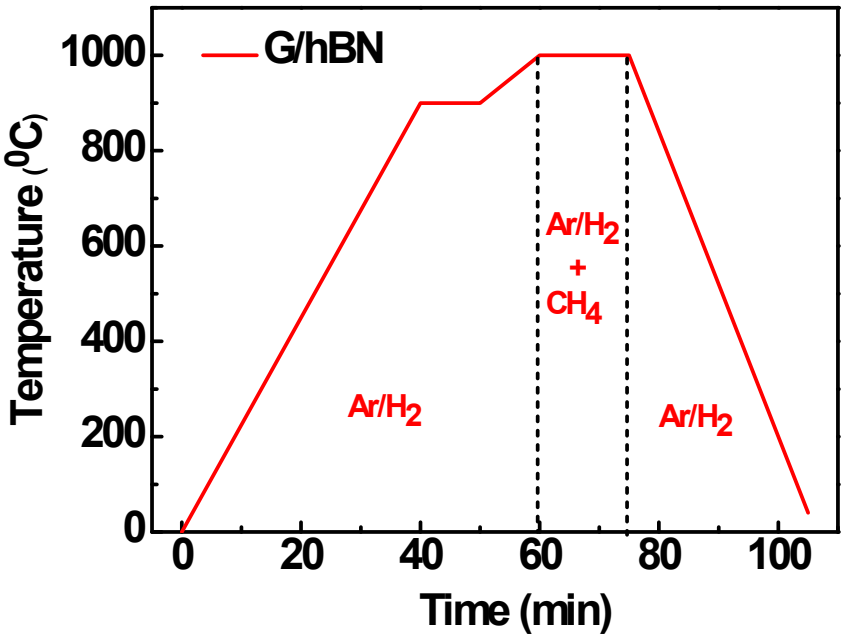

Fig. S1 Temperature-time profile for CVD growth of G/hBN.

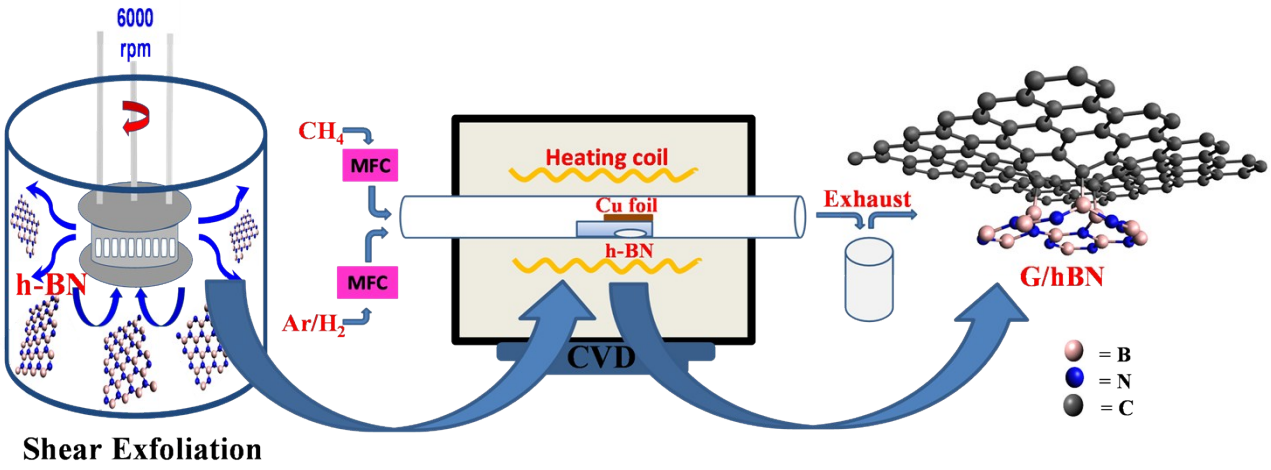

Fig. S2 Schematic sketch of synthesis process of G/hBN hybrid domains.

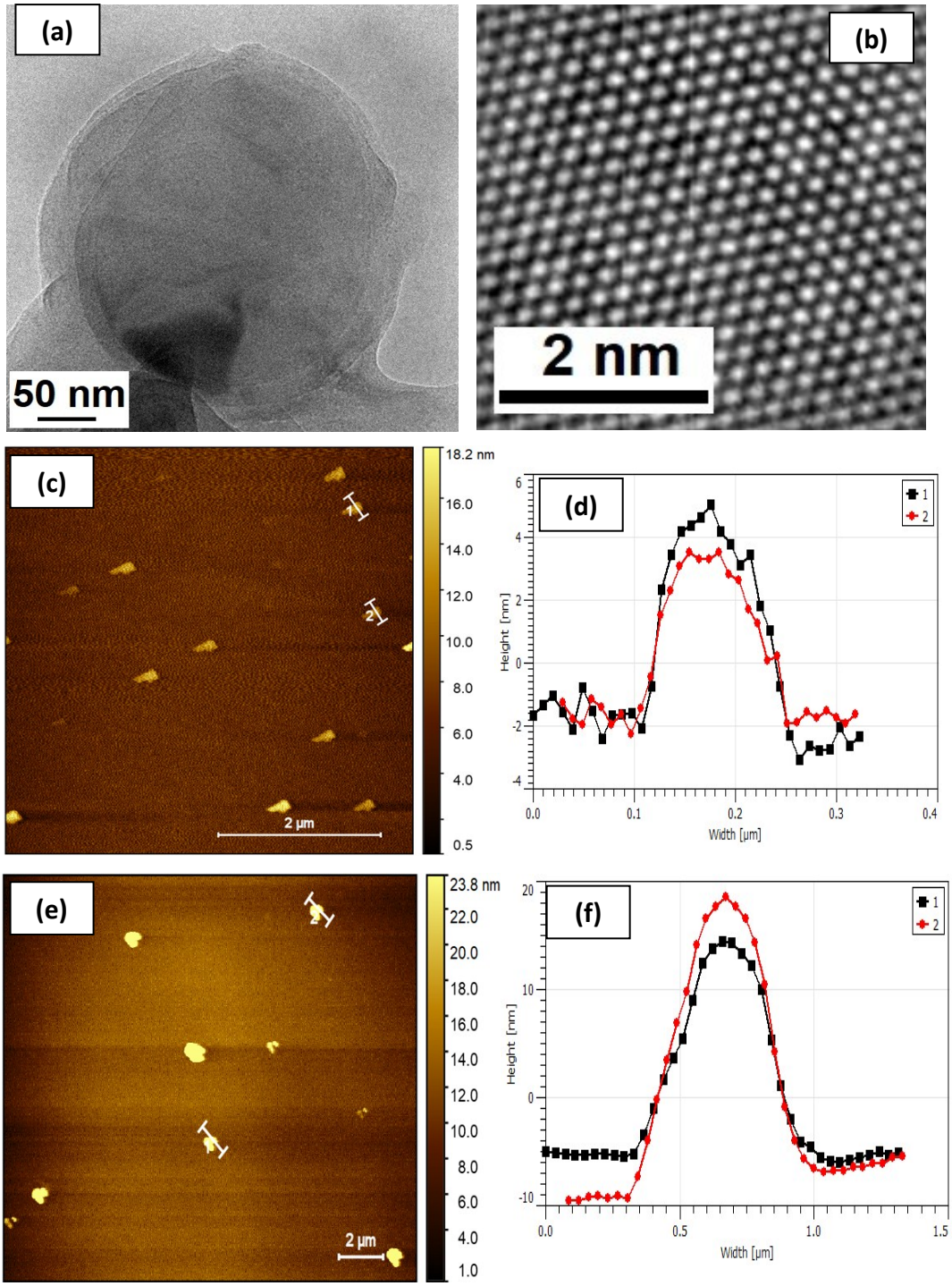

Fig. S3 (a) TEM and (b) HR-TEM images of exfoliated hBN. Fig. c and Fig. e shows the AFM images of the exfoliated hBN and as-obtained G/hBN sample respectively. The corresponding height profiles of the sheets along the marked lines are shown in Fig. d (hBN) and Fig. f (G/hBN).

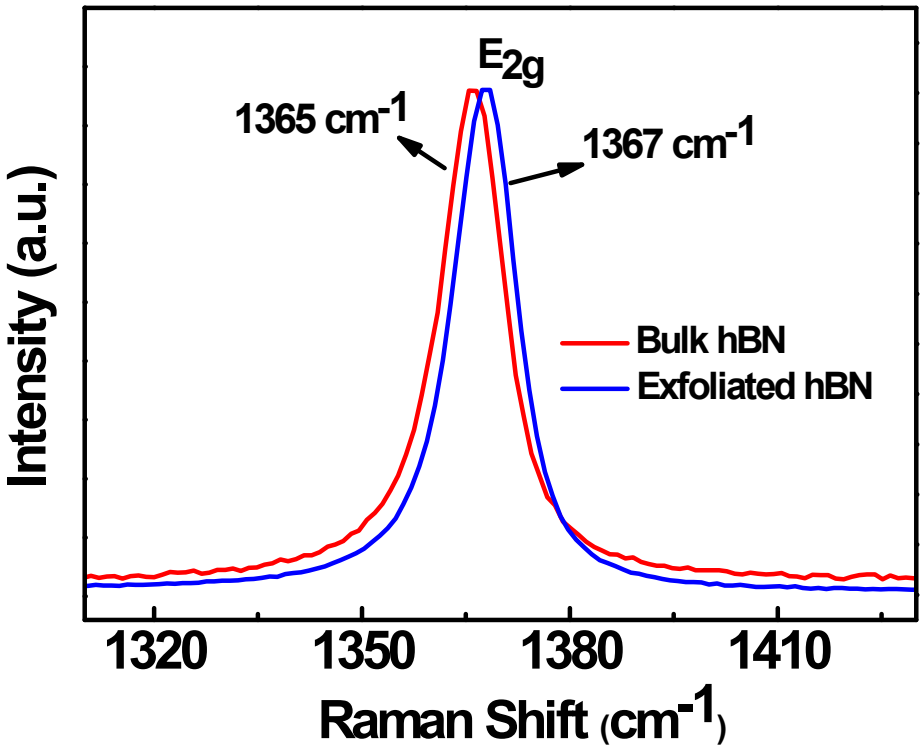

Fig. S4 Raman spectra of bulk hBN and exfoliated hBN.

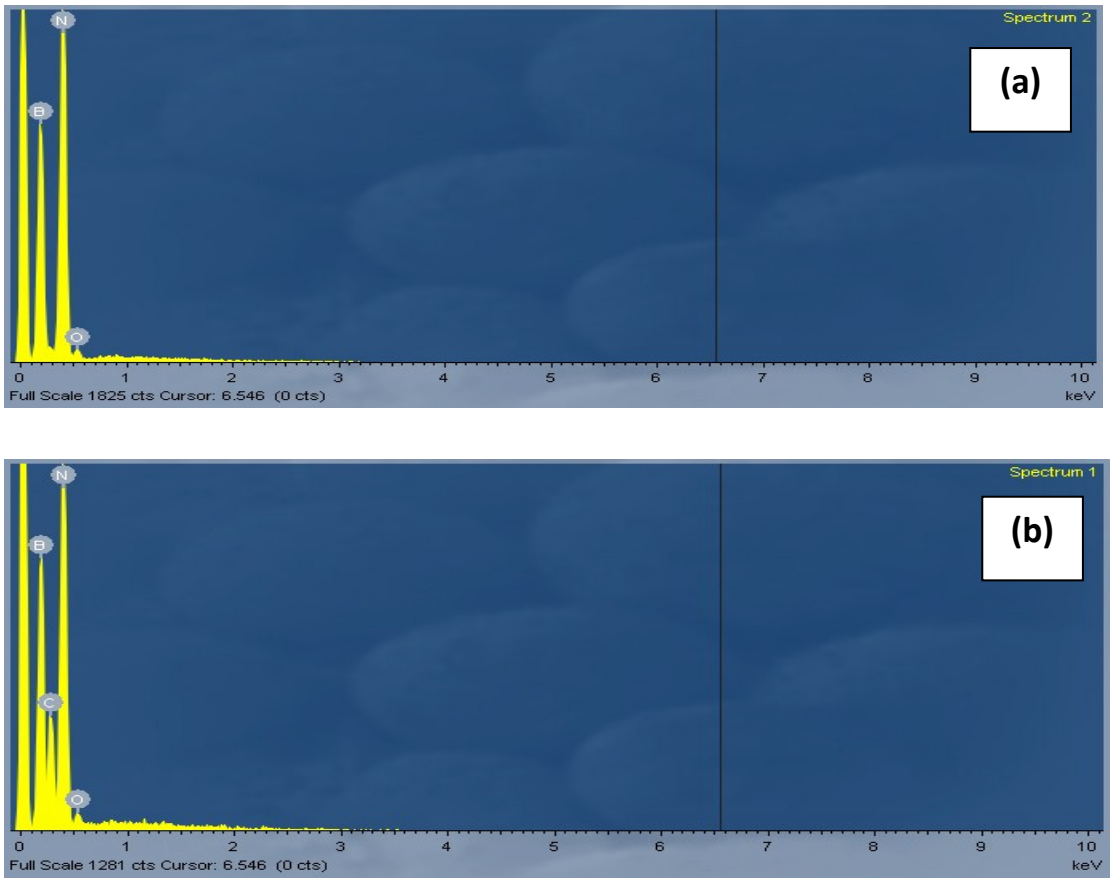

Fig. S5 EDAX spectra of (a) exfoliated hBN and (b) as-obtained G/hBN.

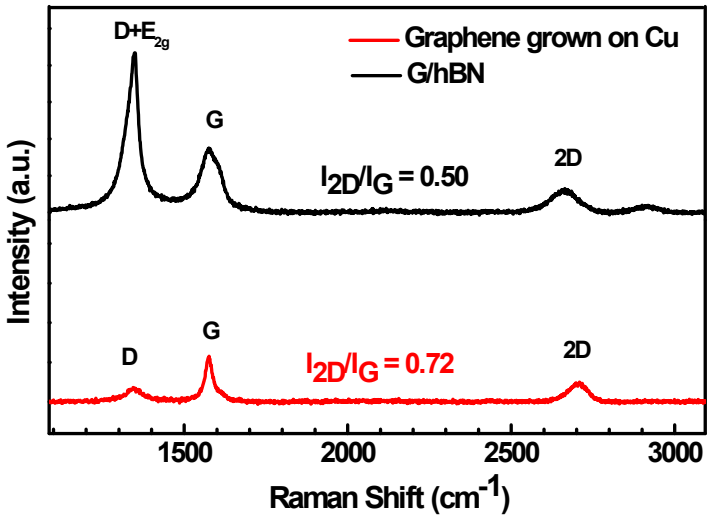

Fig. S6 Micro-Raman spectra of G/hBN and graphene deposited on the Cu foil which is used to cover the boat (Graphene grown on Cu).

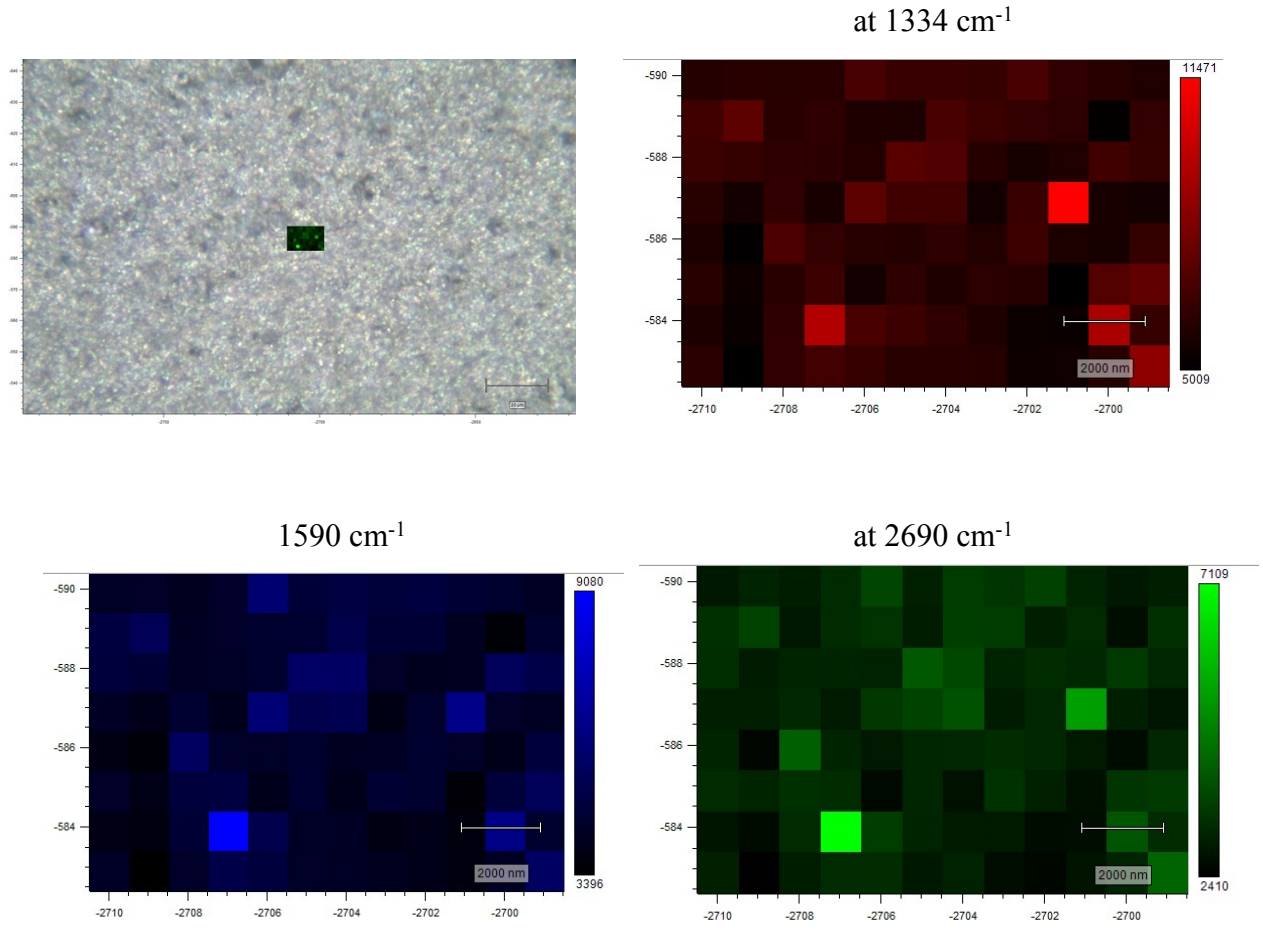

Fig. S7 Raman mapping image of G/hBN at different wavenumbers.

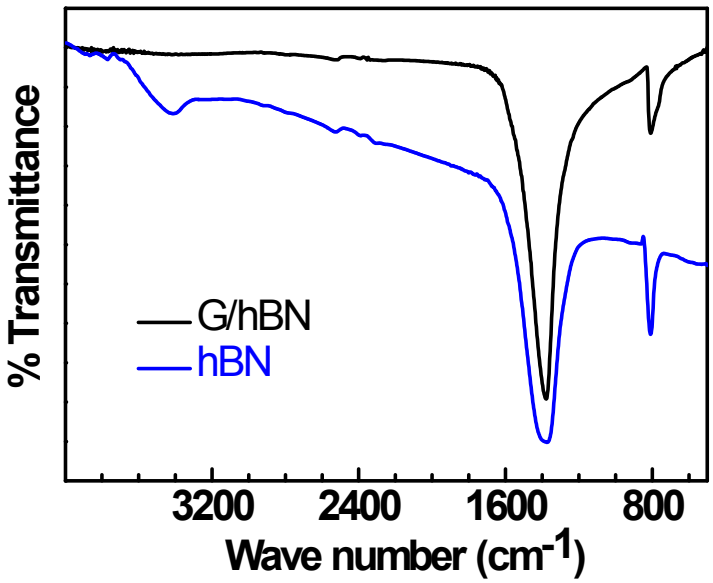

Fig. S8 The FT-IR spectra of exfoliated hBN and as-obtained G/hBN material.

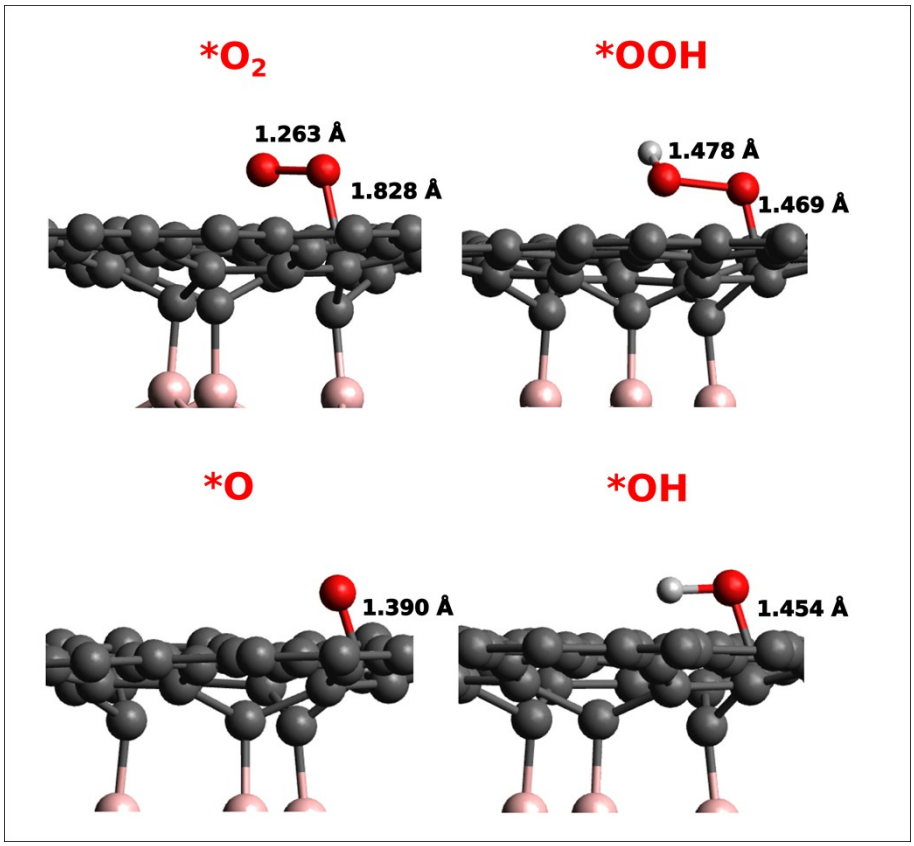

Fig. S9 Relaxed intermediates noting O-O and C-O bond distances for individual steps in the 4 e ORR.

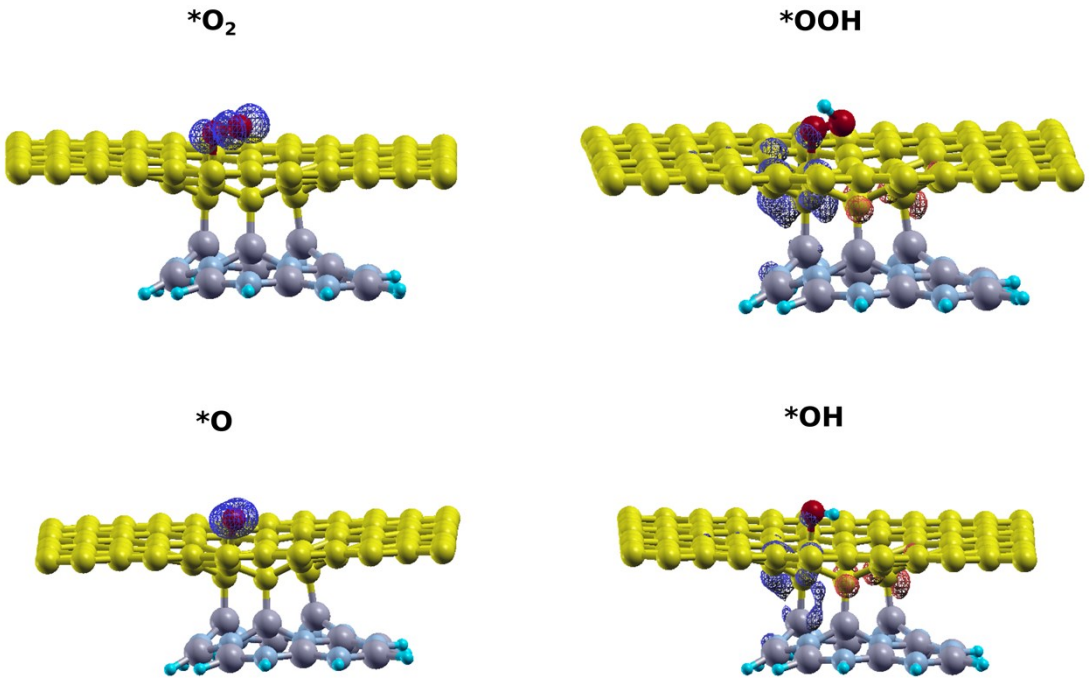

Fig. S10 Local Density of States (LDOS) with up (red) and down (blue) polarisations for all four intermediates, where $*O_2$ and *O are plotted with an isovalue of 0.01 e/ Å^3 and *OOH and *OH are plotted with an isovalue of 0.0005 e/Å^3. (C-yellow, B-purple, N-dark blue, H-sky blue, O-Red).

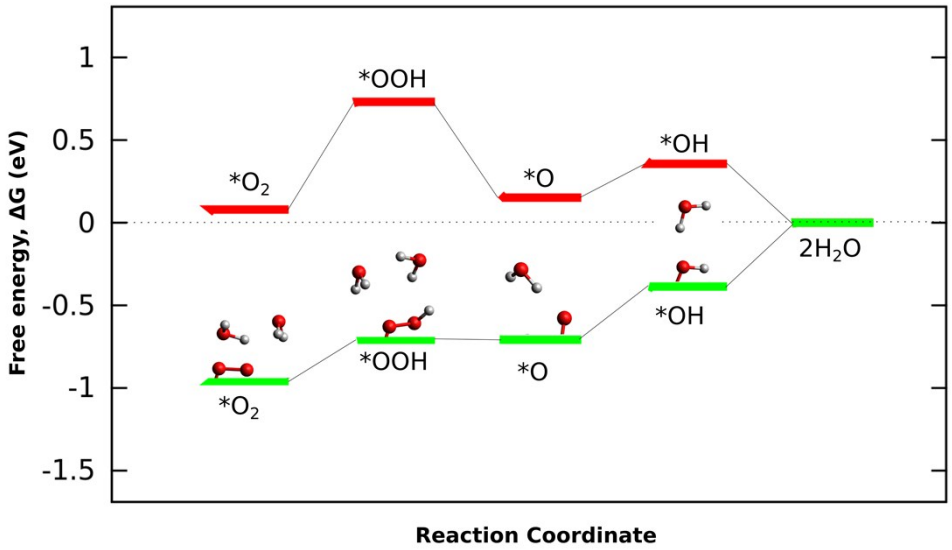

Fig. S11 Reaction pathways without (red) and with (green) water.

Table S1: XPS elemental compositions (% atomic concentration) of hBN and G/hBN, as determined from the full-range XPS spectra (Fig. 3a).

Samples	Content (At%)				
	B	**N**	**C**	**O**	**Si**
hBN	40.07 ± 0.11	40.89 ± 0.11	14.65 ± 0.16	4.13 ± 0.11	0.25 ± 0.05
G/hBN	20.34 ± 0.09	19.24 ± 0.08	55.65 ± 0.12	4.52 ± 0.08	0.26 ± 0.05

Table S2: A comparative chart showing the ORR activities of various doped graphene systems (B or N doped or co-doped) and the present work.

Catalysts	Medium	Synthesis Method	Catalyst loading (mg/cm^2)	E_{onset} (mV *vs* RHE)	Current density (J_L) ($mAcm^{-2}$)	Number of electron transfers	References
B, N co-doped graphene	0.1 M KOH	Hydrothermal and thermal annealing procedure	~0.1	794#	~5.5@0.164 V#	3.8	R1
3D B,N doped-graphene Foam	0.1M KOH	Chemical vapor deposition (CVD) method	Not available	804#	~3.8@0.464 V#	3.4-3.8	R2
N-doped reduced graphene oxide	0.1 M KOH	Wet chemical reaction	Not available	764#	~3.0@0.164 V#	2.6	R3
N-doped 3D graphene network	0.1 M KOH	CVD	~0.1	864#	~5.5@0.164 V#	3.7	R4
N-doped graphene	0.1 M KOH	CVD	~0.0635	784#	~0.8@0.164 V#	3.6-4.0	R5
B incorporated graphene	1.0 M KOH	Spin-on dopant method	Not available	823#	~0.45 at 0.723 V#	Not available	R6
N-doped graphene (HNG)	0.1 M KOH	Hydrothermal reduction	~0.1	764#	Not available	3.0	R7
N-doped graphene (NG)	0.1 M KOH	Pyrolysing GO in presence of melamine	~0.1	811#	Not available	2.5-3.4	R8
Boron doped graphene	0.1 M KOH	Thermal annealing	~0.052	915#	~0.3@0.464 V#	3.5	R9
B, N co-doped graphene (BNG)	0.1 M KOH	Microwave-hydrothermal synthesis	Not Available	730	~0.6@0.2 V	~2.0	R10
Two-step boron, nitrogen co-doping of graphene (B,N-graphene)	0.1 M KOH	Thermal annealing method	0.282	860#	~5.01@0.364 V#	3.8-3.9	R11
Single-step boron, nitrogen doping of graphene (*h*-BN/graphene)	0.1 M KOH	Thermal annealing method	0.282	744#	~2.42@0.364 V#	3.4-3.5	R11
Graphene-hBN non-van der Waals vertical heterostructures (G/hBN)	0.1 M KOH	CVD	0.282	780	~4.5@0.3 V	3.6-3.8	Present Work
G/hBN on Au electrode	0.1 M KOH	CVD	0.282	930	--	--	Present work

converted potentials (with respected to RHE) from the reported potentials in the reference.
E (vs. RHE) = E (vs. Ag/AgCl) + 0.059pH + 0.197
E (vs. RHE) = E (vs. SCE) + 0.059pH + 0.244
Note: For the actual reported potential values please refers the respective cited reference.

Table S3: DFT calculated energies and free energies for intermediates formed in the 4 electron transfer ORR (all energies are in eV).

Intermediates	**ΔE (normalised to final energy)**	**ZPE**	**-TΔS**	**ΔG(normalised to final energy)**	**ΔG - eU (U = 0 V)**	**ΔG - eU (U = 1.23 V)**
$*O_2$	4.658567	0.0	0.0	4.998567	4.998567	0.078567
*OOH	3.6815505	0.19	0.21	4.4215505	4.4215505	0.7315505
*O	3.053443	0.03	-0.47	2.613443	2.613443	0.153443
*OH	0.9382335	0.10	0.21	1.5882335	1.5882335	0.3582335
* + $2H_2O$	0	0.13	-0.47	0	0	0

The relaxed coordinates for *OOH intermediate:

B 6.51982510 12.67896329 6.28805915

B 9.02879381 12.72220175 6.20623285

B 7.80809579 10.89900411 5.22597219

N 6.54355859 11.28704043 5.89022633

N 9.05455474 11.29390286 5.89128665

N 7.75191952 13.38928649 6.28708751

N 10.26427413 13.42128931 6.38906769

N 11.51064499 11.35950497 6.12720373

B 11.52815339 12.76693371 6.31616208

B 10.31840482 10.58436183 5.91399408

B 5.41051520 10.46239507 6.19498055

B 6.27726832 8.13683443 5.28672137

B 9.44606585 8.20337569 5.19489434

N 5.45701872 9.04180918 6.06022820

N 10.38809585 9.11520374 5.85474409

N 6.68522273 6.88428416 5.91722603

N 9.19848180 6.90091068 5.84603094

N 11.58961412 7.00303943 6.38939286

B 11.56075424 8.43069996 6.33834613

B 10.39279432 6.23270904 6.31372066

B 7.93876645 6.23214361 6.07729807

H 7.94230455 5.11772819 6.58464181

H 4.42731400 10.96081789 6.72499995

H 5.47607548 13.22296086 6.61057805

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H 12.54853473 9.03668598 6.71984725

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