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Supporting Information

On the Hydrogen Evolution Reaction Activity of Graphene-hBN van der Waals Heterostructures

Sumit Bawari, Nisheal M. Kaley, Shubhadeep Pal, Thazhe Veettil Vineesh, Shamasree Ghosh, Jagannath Mondal,* and Tharangattu N. Narayanan*

[1]Tata Institute of Fundamental Research - Hyderabad, Sy. No. 36/P, Gopanapally Village,

Serilingampally Mandal, Hyderabad - 500 107, India.

(Corresponding authors: jmondal@tifrh.res.in and tnn@tifrh.res.in or tn_narayanan@yahoo.com)

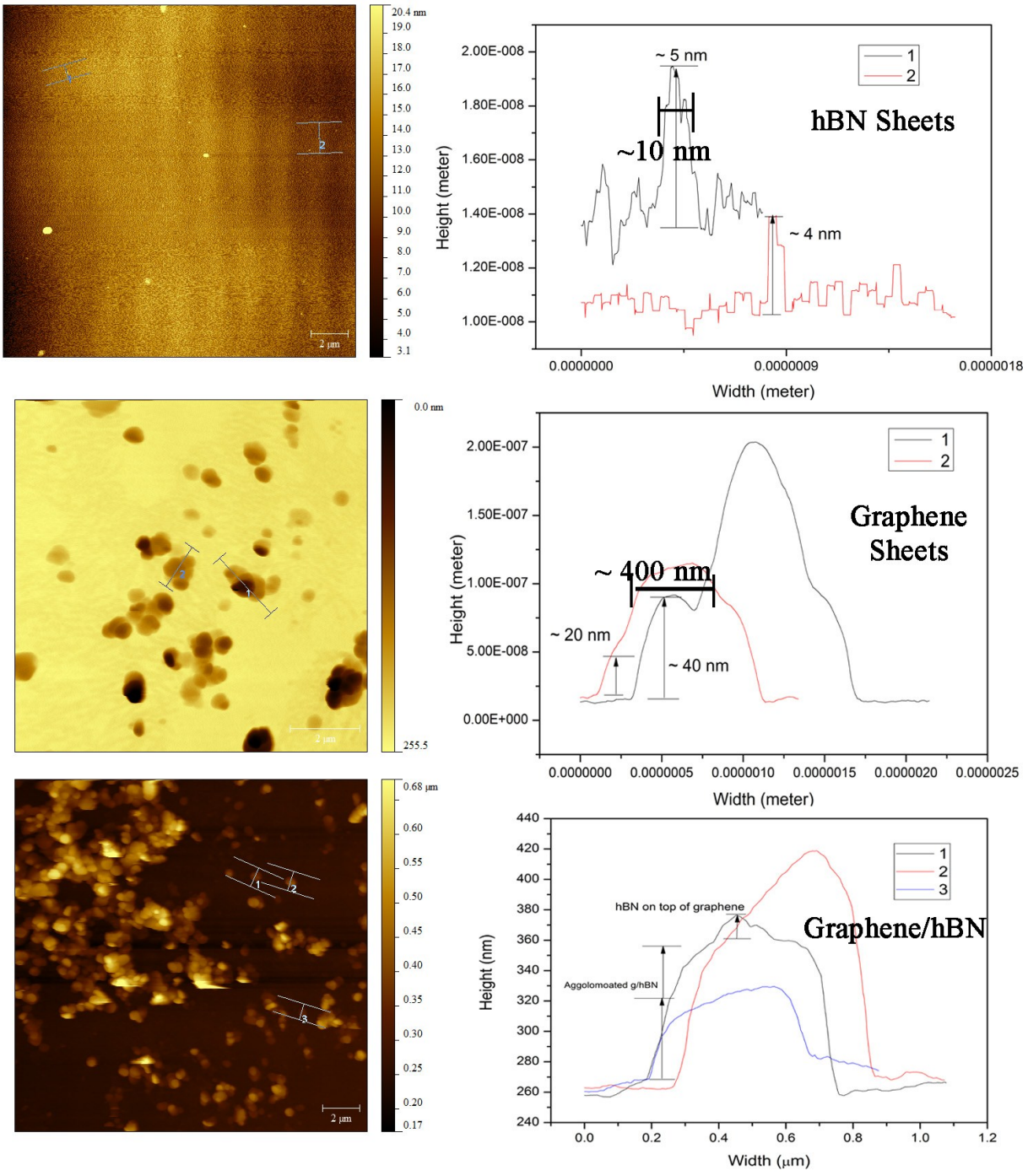

Figure S1: AFM images and corresponding line scans of hBN, SEG and SEG-hBN.

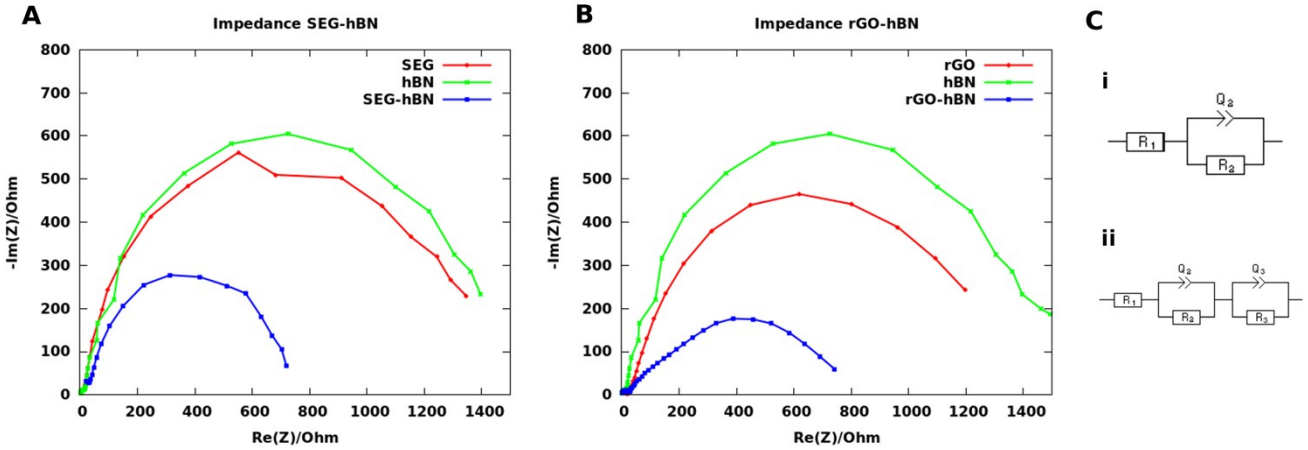

Figure S2: Nyquist plots for: A) SEG, hBN and hBN on graphene (G-hBN), and B) rGO, hBN, and hBN on rGO, at ~ -500 mV vs RHE in 0.5 M H_2SO_4 solution. C) The fitted Randles circuits.

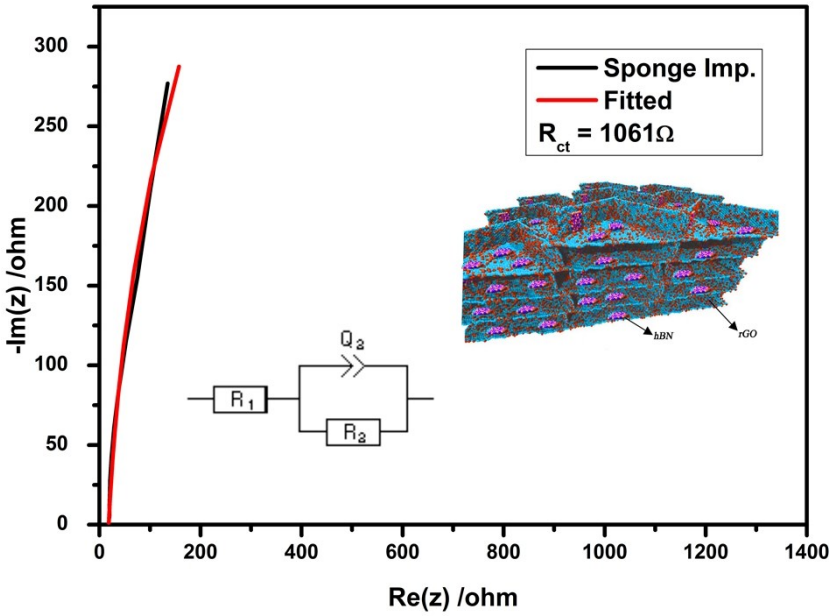

Figure S3: : Nyquist plot for 3D rGO-hBN (schematic is shown inset). The fitted Randles circuit is also shown. R_1 (R_s): Solution resistance and R_2 (R_{ct}): Charge transfer resistance.

Table S1: Summary of the EIS analyses:

Sample	R_S(Solution resistance)[Ω]	R_{ct} (Charge transfer resistance)[Ω]
SEG	11	1394
hBN	13	1495
SEG-hBN	29	702
rGO	36	1222
rGO-hBN	20	362
3D rGO-hBN	20	1061

Table S2: ΔG_H values for different locations on Graphene, hBN and the lowest ΔG_H locations on the Graphene/hBN interface.

Location	ΔG_H(eV)
Pure Graphene	1.18
hBN(on Nitrogen)	3.33
hBN(on Boron)	2.21
G/hBN(Nitrogen shadow site)[AA]	1.06
G/hBN(Boron shadow site)[AA]	1.10
hBN/G(close to hBN edge)[AA]	1.09

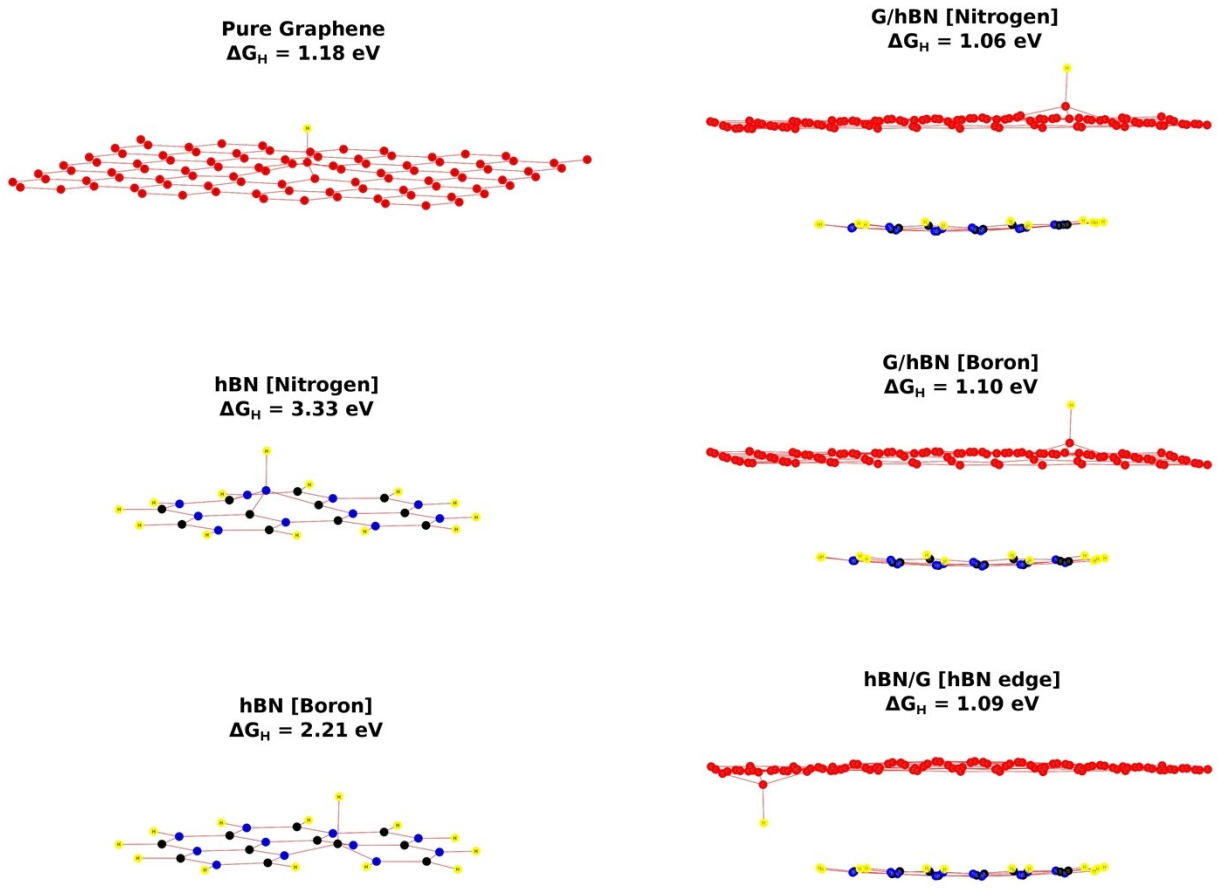

Figure S4: ΔG_H values for different locations on Graphene, hBN and the lowest ΔG_H locations on the Graphene/hBN interface.

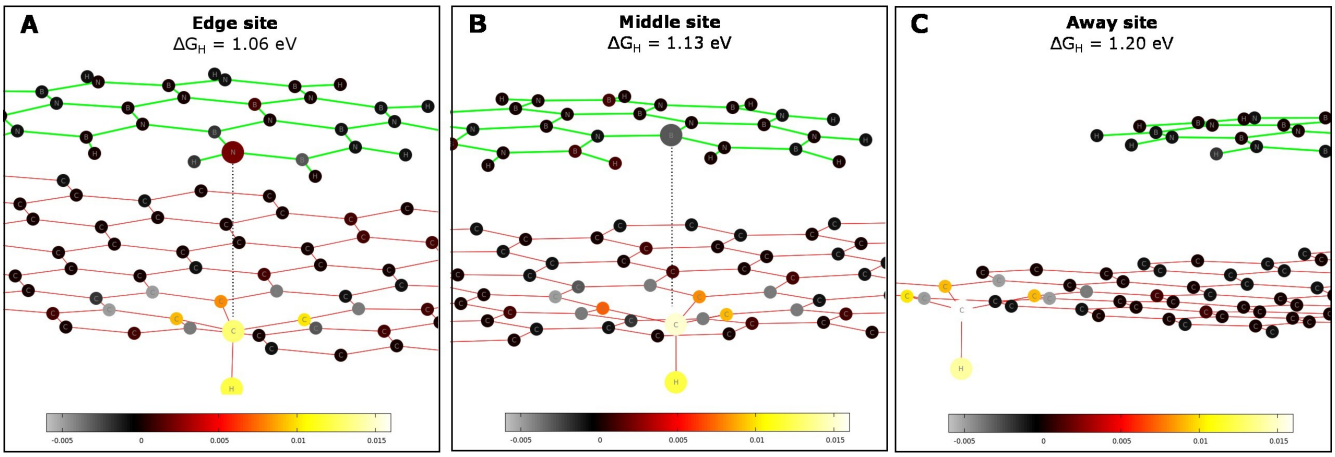

Figure S5: Difference in hirshfeld charge density before and after hydrogenation, plotted for three locations below the hBN edge(A), hBN center(B) and away from the hBN sheet(C) with increasing ΔG_H values. The edge site has the most charge transferred from Nitrogen and lowest ΔG_H.

Table S3: XYZ coordinates of hydrogenated G/hBN AA system :

B	4.68968053	10.43726903	7.55295844	1
B	7.21585843	10.52393219	7.59549545	1
B	6.03102378	8.29868161	7.72603430	1
N	4.73527962	8.98732009	7.67029791	2
N	7.27064449	9.06254452	7.69119859	2
N	5.91906276	11.15853365	7.55290168	2
N	8.44885708	11.26475524	7.52034527	2
N	9.74660282	9.19577039	7.51470334	2
B	9.73069211	10.62871112	7.45829558	1
B	8.56166823	8.37883361	7.64314994	1
B	3.50480797	8.21625509	7.61493574	1
B	4.83984496	6.07560918	7.73761992	1
B	7.36424349	6.14499625	7.76177236	1
N	3.59047029	6.79231838	7.67575064	2
N	6.08326440	6.84042211	7.78035153	2
N	8.61590052	6.90807651	7.71113984	2
N	4.91775353	4.63463879	7.72388052	2
N	7.39471874	4.67484599	7.75845677	2
N	9.86071446	4.75805975	7.66261440	2
B	9.87185339	6.18840910	7.64014869	1
B	8.66202537	3.97538816	7.68945983	1
B	6.14997863	3.91911481	7.71283116	1
H	6.15718158	2.70897288	7.64500899	3
H	2.42701109	8.75964333	7.49515474	3
H	3.63417050	11.02276522	7.43447448	3
H	10.75456989	11.27054560	7.35659261	3
H	10.94033761	6.75728723	7.54458719	3
H	8.71578748	2.76596935	7.63315768	3
H	10.66732052	8.72212435	7.46039523	3
H	10.76791894	4.26401530	7.56724919	3
H	4.03911654	4.08830446	7.63705586	3
H	2.70831044	6.25237877	7.58491050	3
H	5.87480403	12.18816031	7.42332465	3
H	8.40968476	12.29729162	7.42218869	3
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C	-0.10714006	0.65907356	4.68693092	4
C	-0.10676716	2.08613360	4.67437000	4
C	1.12953237	2.79924222	4.65827346	4
C	3.60214349	-0.05557146	4.69889046	4
C	2.36572456	0.65757049	4.68753525	4
C	2.36562222	2.08544493	4.66268411	4
C	3.60164897	2.79969875	4.63191570	4
C	6.07514123	-0.05169478	4.69280339	4
C	4.83842349	0.66007970	4.68346479	4
C	4.83801781	2.08672413	4.64217553	4
C	6.07390742	2.80231687	4.59425355	4
C	8.54753409	-0.04899624	4.67569115	4

C	7.31091023	0.66362694	4.66748882	4
C	7.31069038	2.09070944	4.61697557	4
C	8.54664179	2.80681256	4.57748680	4
C	11.02143464	-0.04989492	4.64607382	4
C	9.78433755	0.66534839	4.64364652	4
C	9.78409896	2.09084884	4.60545596	4
C	11.02154074	2.80582459	4.59311551	4
C	13.49466583	-0.05350403	4.61447253	4
C	12.25828820	0.66154253	4.61592050	4
C	12.25829383	2.08928781	4.60195281	4
C	13.49536962	2.80045537	4.59183980	4
C	1.12978813	4.22652280	4.63932293	4
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C	-0.10268563	6.36741840	4.65533458	4
C	1.12996347	7.08156913	4.59113762	4
C	3.60112724	4.22649219	4.57075427	4
C	2.36500319	4.94053068	4.58480080	4
C	2.36460927	6.36730707	4.53878153	4
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C	6.06881559	7.08002908	4.40223048	4
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C	7.30752929	4.94068154	4.47314070	4
C	7.30267932	6.36698706	4.41886611	4
C	8.53744151	7.08630665	4.36631501	4
C	11.02278477	4.23191896	4.56085943	4
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C	9.78482811	6.36731669	4.41953722	4
C	11.03063470	7.08791464	4.47556789	4
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C	12.25993816	4.94197158	4.59225466	4
C	12.26393295	6.36953590	4.58054290	4
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C	3.59853873	8.50747611	4.42656969	4
C	2.36444819	9.22230922	4.48101982	4
C	2.36480569	10.64913212	4.46173895	4
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C	6.08230916	11.36016952	4.34259867	4
C	8.51818978	8.49171054	4.27328156	4
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C	12.25975639	9.21535801	4.47153693	4
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C	6.07379862	15.65093513	4.39184424	4
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C	11.02049436	15.65477048	4.35867027	4
C	13.49213878	12.79578620	4.39781422	4
C	12.25833561	13.51255969	4.40289531	4
C	12.25764255	14.93935699	4.36098617	4
C	13.49406312	15.64962216	4.31839339	4
H	9.85519880	9.20527981	2.82718624	3