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SUPPORTING INFORMATION

Theoretical and Experimental Studies of Highly Active Graphene Nanosheets to determine Catalytic Nitrogen Sites Responsible for the Oxygen Reduction Reaction in Alkaline Media

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Table 1S Bond distances (*d*, Å) for the R7 model structures, from geometries optimized at PM6 and PBE0/6-31+G(d) levels of theory, together with their deviation (Dv), percent error (%ε), mean unsigned error (MUE), and maximum absolute error (MAE); taking the PBE0 results as reference.

	d	PBE1PB	PM6	Dv	%ε
R7	4-1	1.424	1.439	0.014	1.012
	2-1	1.424	1.438	0.015	1.024
	3-1	1.417	1.408	-0.009	0.613
R7a	4-1	1.404	1.422	0.018	1.262
	2-1	1.404	1.422	0.018	1.270
	3-1	1.423	1.431	0.008	0.565
R7b	2-1	1.366	1.398	0.032	2.371
	3-1	1.311	1.325	0.015	1.120
R7c	2-1	1.406	1.432	0.026	1.815
	3-1	1.406	1.432	0.026	1.823
R7a(OH)	1-5	1.436	1.440	0.004	0.260
	1-2	1.483	1.514	0.031	2.094
	O-H	0.970	0.979	0.008	0.869
	1-3	1.507	1.507	0.000	0.024
	1-4	1.505	1.511	0.007	0.434
R7a(H)	1-5	1.116	1.137	0.021	1.867
	1-2	1.486	1.512	0.025	1.715
	1-3	1.517	1.516	0.000	0.028
	1-4	1.510	1.514	0.004	0.234
R7a(O)	1-5	1.253	1.238	-0.015	1.172
	1-2	1.849	1.808	-0.041	2.224
	1-3	1.511	1.529	0.019	1.235
	1-4	1.503	1.523	0.020	1.326
MUE				**0.02**	**1.15**
MAE				**0.04**	**2.37**

Table 2S Bond distances (*d*, Å) for the R19 model structures, from geometries optimized at PM6 and PBE0/6-31+G(d) levels of theory, together with their deviation (Dv), percent error (%ε), mean unsigned error (MUE), and maximum absolute error (MAE); taking the PBE0 results as reference.

	d	**PBE1PB**	**PM6**	**Dv**	**%ε**
R19	1-2	1.415	1.417	0.001	0.083
	1-3	1.425	1.448	0.022	1.557
	1-4	1.416	1.417	0.001	0.071
	2-5	1.425	1.448	0.022	1.553
	2-6	1.416	1.417	0.001	0.075
R19a	3-5	1.374	1.371	-0.003	0.215
	3-6	1.377	1.372	-0.006	0.408
	4-3	1.409	1.409	0.000	0.000
	1-2	1.426	1.463	0.037	2.601
	8-9	1.367	1.395	0.028	2.064
R19b(OH)	4-10	1.517	1.523	0.007	0.440
	4-3	1.474	1.494	0.020	1.351
	4-O	1.433	1.438	0.004	0.297
	O-H	0.970	0.981	0.011	1.111
	7-6	1.396	1.438	0.041	2.970
	11-8	1.333	1.369	0.036	2.737
	1-2	1.418	1.436	0.018	1.291
MUE				**0.015**	**1.107**
MAE				**0.041**	**2.970**

Table 3S Bond angles (*a*) for the R7 model structures, from geometries optimized at PM6 and PBE0/6-31+G(d) levels of theory, together with their deviation (Dv), percent error (%ε), mean unsigned error (MUE), and maximum absolute error (MAE); taking the PBE0 results as reference.

	a	**PBE1PB**	**PM6**	**Dv**	**%ε**
R7	4-1-2	120.0	120.0	0.002	0.00
	4-1-3	120.0	120.0	0.008	0.01
R7a	4-1-2	120.8	120.9	0.052	0.04
	4-1-3	119.6	119.6	-0.023	0.02
R7b	2-1-3	118.2	118.9	0.688	0.58
R7c	2-1-3	109.9	109.3	-0.572	0.52
R7a(OH)	2-O-H	108.2	112.8	4.618	4.27
R7a(H)	2-1-5	106.0	104.8	-1.213	1.14
R7a(O)	2-1-5	104.7	99.6	-5.083	4.86
MUE				**1.362**	**1.271**
MAE				**5.083**	**4.856**

Table 4S Bond angles (*a*) for the R19 model structures, from geometries optimized at PM6 and PBE0/6-31+G(d) levels of theory, together with their deviation (Dv), percent error (%ε), mean unsigned error (MUE), and maximum absolute error (MAE); taking the PBE0 results as reference.

	a	**PBE1PB**	**PM6**	**Dv**	**%ε**
R19	4-1-2	120.0	120.0	0.006	0.01
	7-3-1	120.0	120.0	0.005	0.00
	1-2-6	120.0	120.0	-0.005	0.00
R19a	4-3-5	119.3	119.6	0.276	0.23
	12-1-2	111.0	109.4	-1.545	1.39
	7-6-13	119.3	119.7	0.382	0.32
	14-8-9	119.0	119.2	0.188	0.16
R19a(OH)	4-3-5	118.0	119.1	1.091	0.92
	4-O-H	108.2	112.4	4.196	3.88
	11-8-9	119.0	119.3	0.224	0.19
	7-6-13	119.2	117.8	-1.318	1.11
	12-1-2	110.7	110.2	-0.431	0.39
MUE				**0.806**	**0.717**
MAE				**4.196**	**3.876**

Table 5S Entropy-Temperature (T*ΔS, kcal mol^{-1}), Zero-point correction (ΔZPE, kcal mol^{-1}), and Gibbs free energies (ΔG, kcal mol^{-1}) for the adsorption processes occurring on pristine graphene, and the a1 site (refer to Fig. 10) on N-GN using gas model.

	$^3O_2$			$^{\bullet}$OOH			^3O			$^{\bullet}$OH			$^{\bullet}$H		
	T*ΔS	ΔZPE	ΔG	T*ΔS	ΔZPE	ΔG	T*ΔS	ΔZPE	ΔG	T*ΔS	ΔZPE	ΔG	T*ΔS	ΔZPE	ΔG
Pristine G	1.94	-5.61	-5.61	-9.87	2.20	12.61	-6.68	-14.81	-7.76	-8.35	-17.97	-9.60	-5.54	-22.35	-17.12
a1	0.46	-10.06	-8.81	-9.45	-33.79	-23.77	-6.60	-62.15	-55.20	-7.24	-55.70	-48.26	-5.27	-49.58	-44.58

Table 6S Entropy-Temperature (T*ΔS, kcal mol^{-1}), Zero-point correction (ΔZPE, kcal mol^{-1}), and Gibbs free energies (ΔG, kcal mol^{-1}) for the adsorption processes occurring on pristine graphene, and the a1 site (refer to Fig. 10) on N-GN using implicit solvent model.

	$^3O_2$			$^{\bullet}$OOH			^3O			$^{\bullet}$OH			$^{\bullet}$H		
	T*ΔS	ΔZPE	ΔG	T*ΔS	ΔZPE	ΔG	T*ΔS	ΔZPE	ΔG	T*ΔS	ΔZPE	ΔG	T*ΔS	ΔZPE	ΔG
Pristine G	1.94	-5.95	-5.95	-9.87	3.11	13.52	-6.68	-27.72	-20.67	-8.35	-17.55	-9.18	-5.54	-24.58	-19.36
a1	0.46	-10.78	-9.53	-9.45	-33.10	-23.07	-6.60	-73.22	-66.27	-7.24	-55.43	-47.99	-5.27	-52.61	-47.62

Figure 7S Density of states for a N-GN graphitic periodic model and the density of states obtained for a N-GN graphitic cluster model.