Electronic Supplementary Information

Synergy of sp-N and sp^2-N Codoping Endows Graphdiyne with Comparable Oxygen Reduction Reaction Performance to Pt

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Table S1. Detailed energy information of ORR on NGDY.

System	Position	Q (|e|)	η^{ORR} (V)	ΔG_O (eV)	ΔG_{OOH} (eV)	ΔG_{OH} (eV)
Pristine GDY	βC^1	0.071	1.204	2.753	4.894	1.547
	αC^1	0.014	0.949	2.108	4.639	1.250
βN^1-GDY	αC^1	0.166	1.745	0.234	3.021	-0.515
	βC$^{1'}$	0.113	0.556	1.599	4.246	0.918
	αC$^{1'}$	0.063	0.515	1.471	4.205	0.756
αN^1-GDY	βC^1	0.17	1.381	0.714	3.343	-0.151
	αC$^{1'}$	0.136	0.851	1.100	3.715	0.379
	βC$^{1'}$	0.004	1.140	2.243	4.830	1.409
N^2-GDY	βC^1	0.104	0.969	2.156	4.659	1.346
	βC$^{1'}$	0.083	1.074	2.590	4.764	1.457
	αC^1	0.073	0.721	1.203	4.122	0.694
	αC$^{1'}$	0.031	0.820	1.918	4.510	1.177
m-N^{2}N^2	αC^1	0.061	0.819	1.055	4.047	0.644
	βC^1	0.111	0.926	2.021	4.616	1.381
	βC$^{1'}$	0.083	1.044	2.498	4.734	1.395
	αC$^{1'}$	0.028	0.889	1.827	4.579	1.451
p-N^{2}N^2	αC^1	0.074	0.747	1.277	4.128	0.794
	βC^1	0.092	1.033	1.983	4.723	1.357
	βC$^{1'}$	0.083	1.151	2.599	4.841	1.555
	αC$^{1'}$	0.022	0.917	1.774	4.607	1.239
N^{2}βN^1	αC$^{1'}$	0.181	1.883	-0.232	2.823	-0.653
	βC^1	0.161	1.060	0.900	3.985	0.730
	aC1	0.133	1.081	0.309	3.565	0.159
oN^{2}βN^1	aC1	0.139	1.327	-0.099	2.906	-0.097
	βC$^{1'}$	0.115	0.481	1.587	4.171	0.816
	αC$^{1'}$	0.053	0.916	0.963	3.990	0.649
mN^{2}βN^1	αC^1	0.154	1.760	-0.036	2.998	-0.530
	βC$^{1'}$	0.111	0.695	1.506	4.199	0.971
	αC$^{1'}$	0.060	0.698	1.211	3.927	0.679
pN^{2}βN^1	αC^1	0.162	1.589	0.222	3.102	-0.359
	βC$^{1'}$	0.116	0.579	1.662	4.269	0.901
	αC$^{1'}$	0.050	0.865	1.238	4.207	0.873
mN^{2}mN^{2}βN^1	αC^1	0.139	1.784	-0.088	3.058	-0.554
	βC$^{1'}$	0.110	0.754	1.446	4.180	0.971
	αC$^{1'}$	0.061	0.891	1.220	4.090	0.881
oN^{2}oN^{2}βN^1	αC^1	0.139	1.590	-0.083	2.978	-0.360
	βC$^{1'}$	0.118	0.519	1.546	4.087	0.711
	αC$^{1'}$	0.044	1.156	0.704	3.910	0.630
oN^{2}pN^{2}βN^1	αC^1	0.142	1.444	0.160	3.174	-0.214
	βC$^{1'}$	0.118	0.589	1.616	4.223	0.975
	αC$^{1'}$	0.048	0.999	1.002	4.175	0.771
oN^{2}mN^{2}βN^1	αC^1	0.134	1.765	-0.167	3.047	-0.535
	βC$^{1'}$	0.114	0.502	1.524	4.153	0.796
	αC$^{1'}$	0.054	0.909	0.977	4.031	0.656

Table S2. Detailed values of *ZPE* and *TS* for every intermediate.

Species	*E* (eV)	*ZPE* (eV)	*TS* (eV)
H_2	-6.764	0.27	0.41
H_2O	-14.219	0.56	0.67
*O	-	0.142	0.03
*OH	-	0.441	0.05
*OOH	-	0.514	0.12

The gas phase values were from Ref. S1, while the values for the adsorbed species were taken from DFT calculations. Gas phase H_2O at 0.035 bar was used as the reference state because at this pressure gas phase H_2O is in equilibrium with liquid water room temperature. The same values for the adsorbed species for all the models were used, as vibrational frequencies have been found to depend much less on the surface than the bond strength.

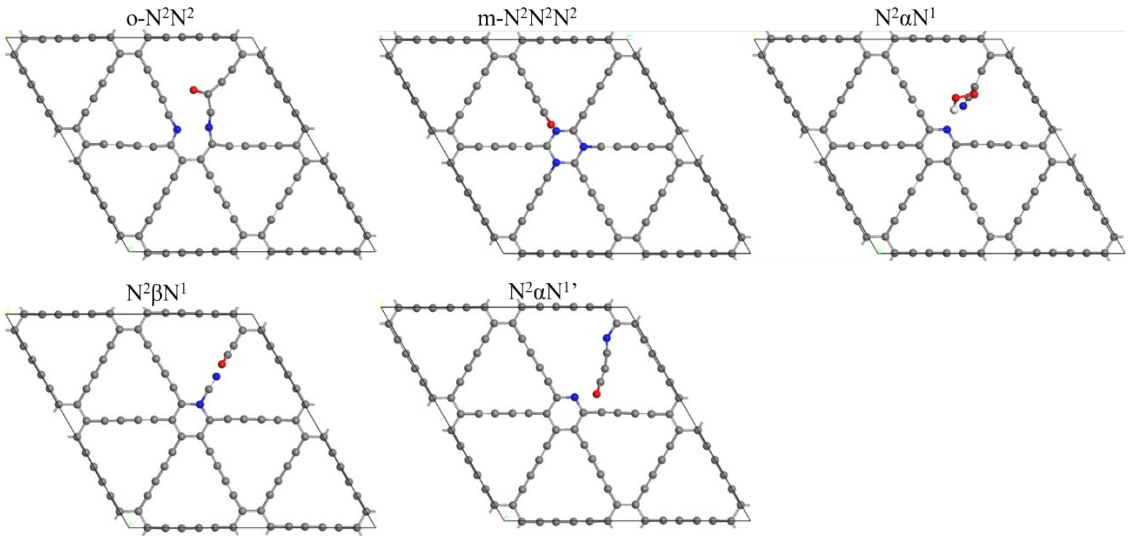

Figure S1. Illustration of structural breakings of some NGDY during ORR process.

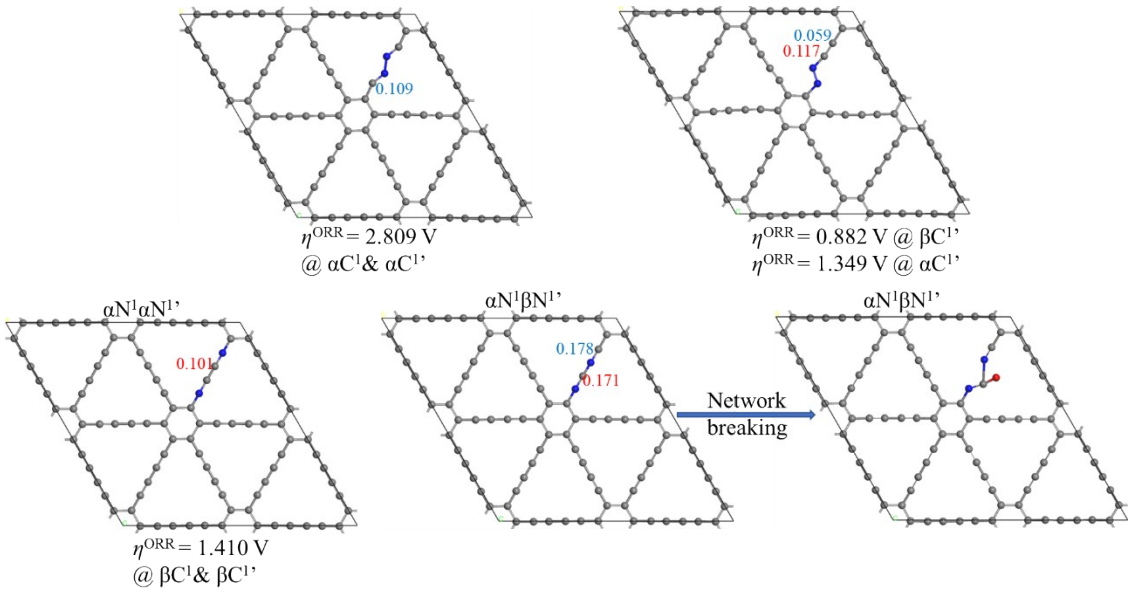

Figure S2. Illustration of several double-N^1 doped NGDY and their η^{ORR} values.

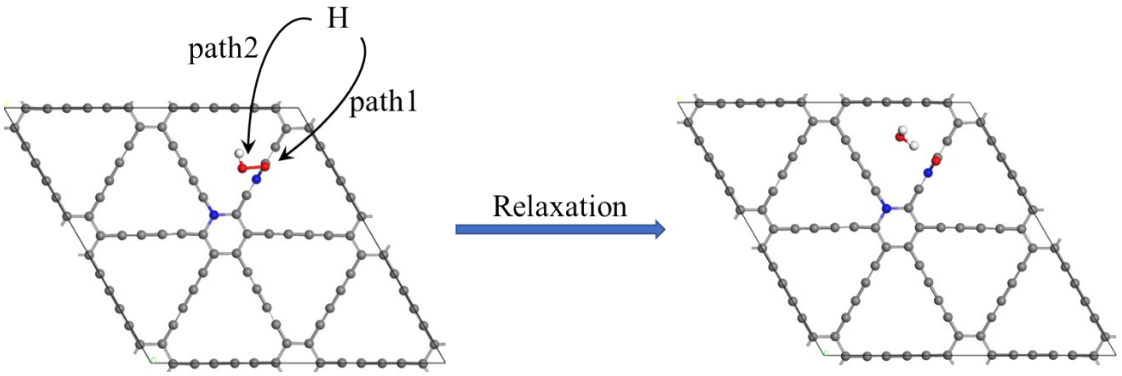

Figure S3. Illustration of O_2 dissociation upon second H addition.

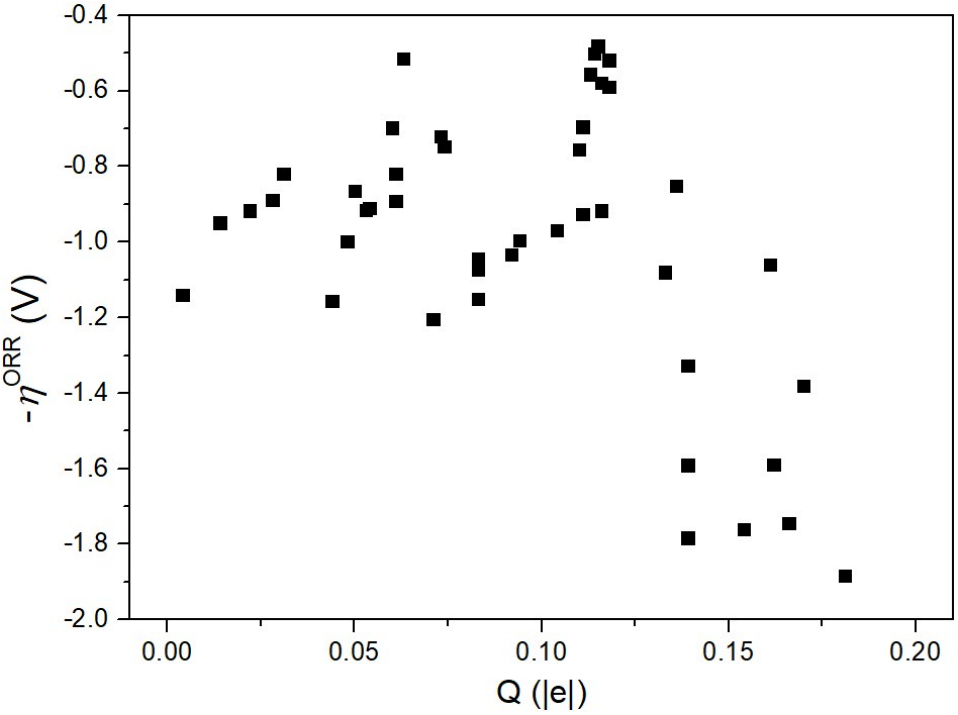

Figure S4. $-\eta^{ORR}$ as a function of Q.

Reference

1. P. W. Atkins, Physical Chemistry, sixth ed., Oxford University Press, Oxford (1998).