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

Supporting Information

Charge-compensated co-doping of graphdiyne with boron and nitrogen to form metal-free electrocatalysts for oxygen reduction reaction

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Supplementary Figures

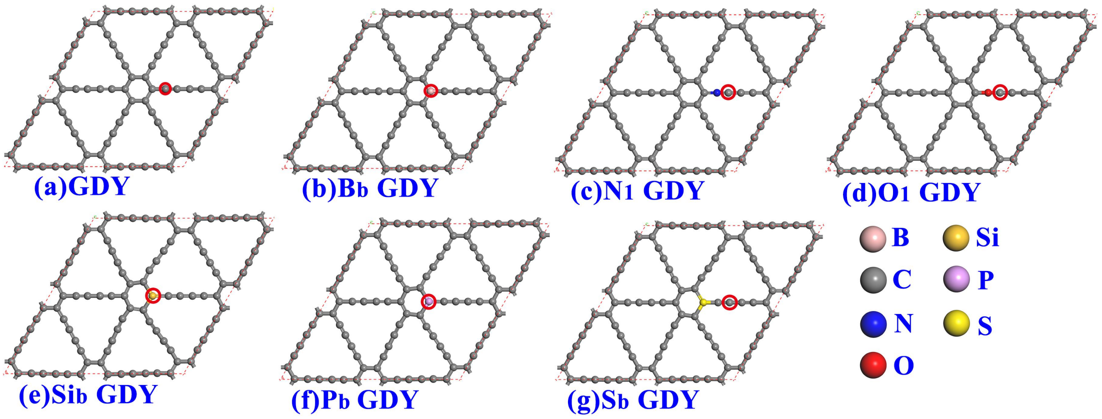


Figure S1. The optimized structures of single atom doped GDY supercells. (a) GDY, (b) B_b-GDY, (c) N_1-GDY, (d) O_1 -GDY, (e) Si_b -GDY, (f) P_b -GDY, and (g) S_b -GDY. The most active sites are indicated by red circles.

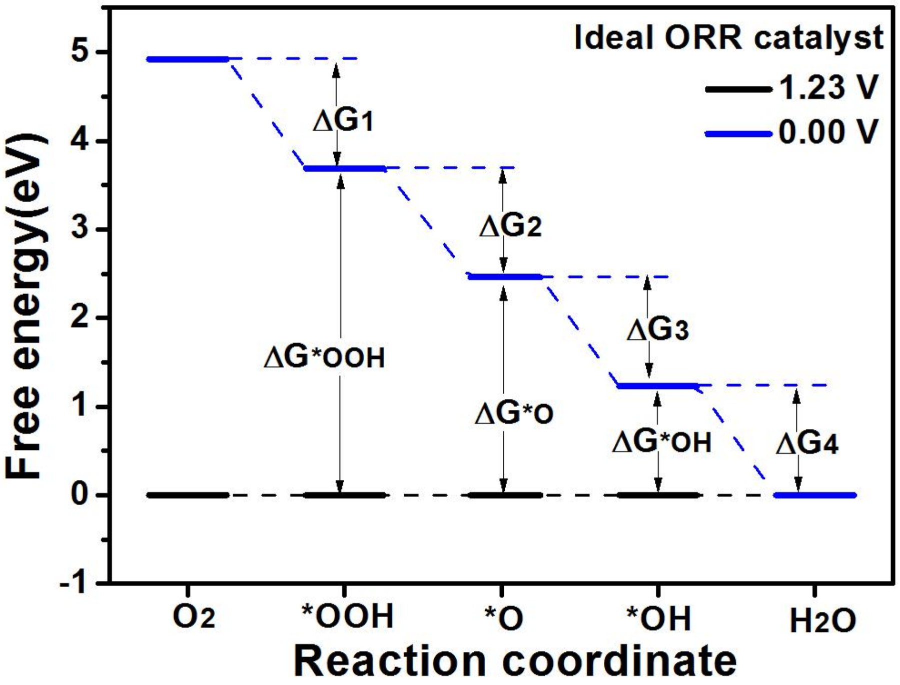
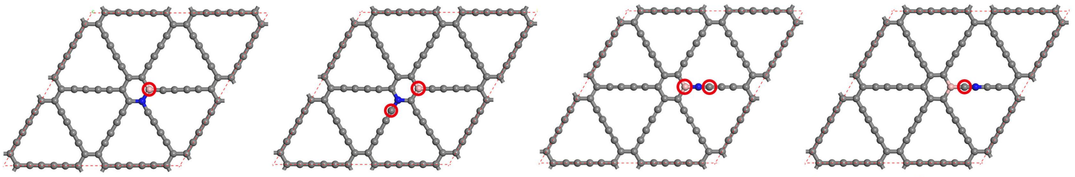
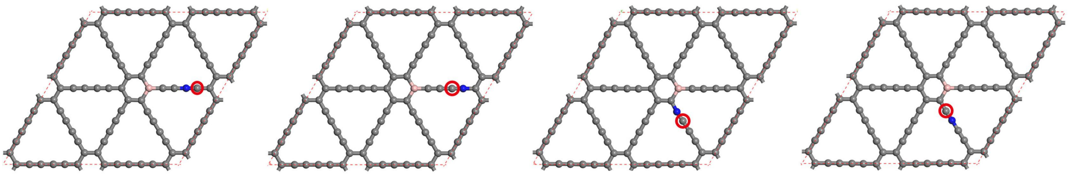


Figure S2 Free-energy diagram for ideal electrocatalytic ORR at zero electrode potential and equilibrium potential (U_0 = 1.23 V). The free-energy change of all four steps should be the same ($\Delta G_1 = \Delta G_2 = \Delta G_3 = \Delta G_4$).

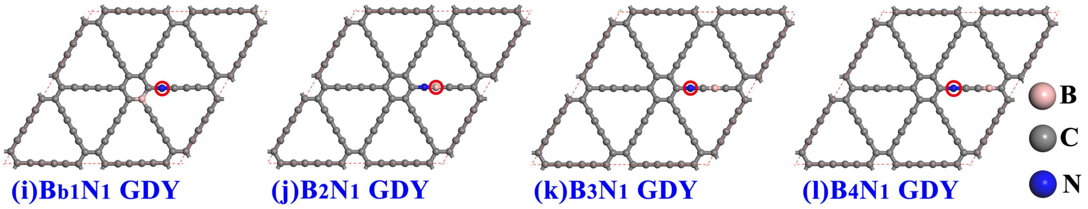
In the ideal situation (**Fig. S2**), the reaction free energies of all the steps should be identical ($\Delta G_1 = \Delta G_2 = \Delta G_3 = \Delta G_4$), corresponding to the maximum potential of 1.23 V (equilibrium potential, U_0 =4.92 eV/4e =1.23 V) allowed in a fuel cell. According to the definition of Gibbs adsorption free energy, the ideal ORR catalyst process the Gibbs adsorption free energies that $\Delta G_{*\mathrm{OOH}}$ = 3.69 eV, $\Delta G_{*\mathrm{O}}$ = 2.46 eV, and $\Delta G_{*\mathrm{OH}}$ = 1.23 eV.



(a)B_bN_{b1} GDY **(b)B_bN_{b2} GDY** **(c)B_bN_1 GDY** **(d)B_bN_2 GDY**



(e)B_bN_3 GDY **(f)B_bN_4 GDY** **(g)$B_bN_{1\text{-}1}$ GDY** **(h)$B_bN_{1\text{-}2}$ GDY**



(i)$B_{b1}N_1$ GDY **(j)B_2N_1 GDY** **(k)B_3N_1 GDY** **(l)B_4N_1 GDY**

Figure S3. The optimized structures of boron and nitrogen compensating doped GDY supercells. (a) B_bN_{b1} -GDY, (b) B_bN_{b2} -GDY, (c) B_bN_1 -GDY, (d) B_bN_2 -GDY, (e) B_bN_3 -GDY, (f) B_bN_4 -GDY, (G) $B_bN_{1\text{-}1}$ -GDY, (h) $B_bN_{1\text{-}2}$ -GDY, (i) $B_{b1}N_1$ -GDY, (j) B_2N_1 -GDY, (k) B_3N_1 -GDY, and (l) B_4N_1 -GDY. The most active sites are indicated by red circles.

Supplementary Tables

Table S1 Zero point energy (*ZPE*) corrections and entropic contributions (at 298.15 K) to the free energies for the ORR on different doped GDY systems.

Systems	Species	*O	$*O_2$	*OH	*OOH	O_2	H_2	H_2O
GDY	ΔZPE	0.08	0.19	0.39	0.32	0.10	0.27	0.56
	$T\Delta S$	0.05	0.09	0.07	0.18	0.64	0.41	0.67
P_b -GDY	ΔZPE	0.08	0.15	0.35	0.44	0.10	0.27	0.56
	$T\Delta S$	0.05	0.12	0.06	0.18	0.64	0.41	0.67
N_1 -GDY	ΔZPE	0.09	0.19	0.34	0.46	0.10	0.27	0.56
	$T\Delta S$	0.05	0.06	0.06	0.18	0.64	0.41	0.67

Table S2 The formation energies of (E_{for}) of single atom doped GDY systems.

Systems	GDY	B_b	B_1	B_2	N_b	N_1	N_2	O_b	O_1	O_2
E_{for} (eV)	0	0.41	1.08	1.24	1.12	0.07	0.39	2.97	0.91	2.29
Systems	GDY	Si_b	Si_1	Si_2	P_b	P_1	P_2	S_b	S_1	S_2
E_{for} (eV)	0	2.12	3.53	3.68	2.24	3.26	3.58	4.30	4.58	5.29

Table S3 Gibbs adsorption free energy values (eV) of oxygenated intermediates and overpotentials of ORR on various doped GDY structures.

Systems	ΔG_{*OOH}(eV)	ΔG_{*O}(eV)	ΔG_{*OH}(eV)	ΔG_{*OOH}-ΔG_{*O}(eV)	η^{ORR} (V)
GDY(1)	5.35	2.40	1.62	2.95	1.66
B_b (B)	4.41	1.35	1.23	3.06	1.00
N_l (2)	3.48	2.00	0.03	1.48	1.19
O_l (2)	0.78(×)	-2.47	-1.54	3.25	2.77
Si_b (Si)	2.34	0.45	-1.27	1.89	2.50
P_b (P)	2.64	-0.56	-0.91	3.20	2.14
S_b (2)	3.98(×)	0.48	-0.73	3.50	1.96
B_bN_{b1}(B)	4.33	1.47	1.03	2.86	0.79
B_bN_{b2}(B)	4.56	1.66	1.32	2.90	0.89
B_bN_{b2}(1)	4.82	1.68	1.24	3.14	0.79
B_bN_1(B)	4.30	1.81	0.96	2.49	0.61
B_bN_1(2)	4.26	2.10	0.94	2.16	0.57
B_bN_2(1)	3.99	1.31	0.59	2.68	0.64
B_bN_3(4)	3.71	1.06	0.28	2.65	0.95
B_bN_4(3)	3.93	1.42	0.51	2.51	0.72
B_bN_{1-1}(2)	3.88	1.22	0.46	2.66	0.77
B_bN_{1-2}(1)	4.01	1.49	0.54	2.52	0.69
$B_{b1}N_1$(N)	3.14	2.28	-0.36	0.86	1.59
B_2N_1(B)	3.75	2.25	0.34	1.50	0.89
B_3N_1(N)	3.48	4.27	-0.04	-0.79	2.02
B_4N_1(N)	3.44	4.14	-0.01	-0.70	1.93

×: no stable adsorption configuration from optimization.

Table S4 The formation energies of (E_{for}) of optimized boron and nitrogen compensating doped GDY systems.

Systems	GDY	B_bN_{b1}	B_bN_{b2}	B_bN_1	B_bN_2	B_bN_3	B_bN_4
E_{for} (eV)	0	-0.28	0.73	-1.16	-0.24	0.06	-0.25
Systems	GDY	B_bN_{1-1}	B_bN_{1-2}	$B_{b1}N_1$	B_2N_1	B_3N_1	B_4N_1
E_{for} (eV)	0	-0.26	-0.14	-0.26	-1.61	0.14	-0.55

Table S5 The ORR over potentials (η^{ORR}) for the different catalysts.

Systems	U (V)	References
B_bN_1(2)-GDY	0.57	Present work
B_bN_1(B)-GDY	0.61	Present work
B_bN_2(1)-GDY	0.64	Present work
pre^{ORR}-GDY	0.49	Present work
Pt (111)	0.45	Nørskov et al. 2004 [1]
B-N-doped C_3N	0.60	He et al. 2018 [2]
B-C-doped C_3N	0.98	He et al. 2018 [2]
Cu @MoS_2	0.63	Wang et al. 2017 [3]
P-doped graphene	0.96	Bai et al. 2016 [4]
N,P co-doped graphene	0.48	Zhang et al. 2015 [5]
B-doped graphene	0.38	Wang et al. 2016 [6]
N-doped GDY	1.17	Das et al. 2016 [7]
B doped R-graphyne	1.01	Das et al. 2016 [8]

Supplementary notes

Note S1

The ORR is considered to proceed along the 4e$^-$ processes, as below:

$$*+O_2(g)+H^++e^- \leftrightarrow *OOH \tag{S1}$$

$$*OOH+H^++e^- \leftrightarrow *O+H_2O(l) \tag{S2}$$

$$*O+H^++e^- \leftrightarrow *OH \tag{S3}$$

$$*OH+H^++e^- \leftrightarrow H_2O(l)+* \tag{S4}$$

where * stands for an adsorption site on catalysts. *l* and *g* refer to liquid and gas phases, respectively.

At electrode potential U, the ΔG for each step can be calculated by the following relations.

$\Delta G_1= G_{*OOH}- G(O_2) - G(*) -G(H^+ + e^-)$

$=\{\Delta G_{*OOH} + G(*) + [2G(H_2O) - 3/2G(H_2)]\} -\{4.92 + 2G(H_2O) - 2G(H_2)\}- G(*) - 1/2G(H_2) +eU$

$= \Delta G_{OOH*}- 4.92 + eU$ (S5)

$\Delta G_2=G_{*O}+ G(H_2O) -G_{*OOH} -G(H^+ + e^-)$

$= \{\Delta G_{*O} + G(*) + [G(H_2O) - 1G(H_2)]\}+ GH_2O -\{\Delta G_{OOH*} + G(*) + [2G(H_2O) - 3/2G(H_2)]\} -1/2G(H_2) +eU$

$= \Delta G_{*O}- \Delta G_{*OOH} + eU$ (S6)

$\Delta G_3=\Delta G_{*OH}-G_{*O} -G(H^+ + e^-)$

$=\{\Delta G_{*OH} + G(*) + [G(H_2O) - 1/2G(H_2)]\}-\{\Delta G_{*O} + G(*) + [G(H_2O) - G(H_2)]\}-1/2G(H_2) +eU$

$=\Delta G_{*OH}- \Delta G_{*O} + eU$ (S7)

$$\Delta G_4 = G^* + G(\mathrm{H_2O}) - G_{*\mathrm{OH}} - G(\mathrm{H^+} + \mathrm{e^-})$$

$$= G(*) + G(\mathrm{H_2O}) - \{\Delta G_{\mathrm{OH*}} + G(*) + [G(\mathrm{H_2O}) - 1/2G(\mathrm{H_2})]\} - 1/2G(\mathrm{H_2}) + \mathrm{e}U$$

$$= -\Delta G_{*\mathrm{OH}} + \mathrm{e}U \qquad \text{(S8)}$$

Note S2

The details for the derivation of Gibbs reaction free energy (ΔGads) from the adsorption free energy. The * stands for an adsorption site on catalysts.

$$*+2H_2O \leftrightarrow *OOH+3/2\ H_2 \quad \text{(S9)}$$

$$*+H_2O \leftrightarrow *O+H_2 \quad \text{(S10)}$$

$$*+H_2O \leftrightarrow *OH+1/2\ H_2 \quad \text{(S11)}$$

$$\Delta G_{*OOH}= G_{*OOH} +3/2\ G(H_2) - G^* - 2G\ (H_2O) \quad \text{(S12)}$$

$$\Delta G_{*O} = G_{*O} + G\ (H_2) - G^* - G\ (H_2O) \quad \text{(S13)}$$

$$\Delta G_{*OH} = G_{*OH} +1/2\ G\ (H_2) - G^* - G\ (H_2O) \quad \text{(S14)}$$

Note S3

For single-heteroatom-doped GDY monolayers (i.e., B, N, O, Si, P, and S- doped GDY), the relationships among ΔG_{*OOH}, ΔG_{*O}, and ΔG_{*OH} are caculated as below.

$$\Delta G_{*OOH} = 0.97\Delta G_{*OH} + 3.51 \tag{S15}$$

$$\Delta G_{*O} = 1.05\Delta G_{*OH} + 0.62 \tag{S16}$$

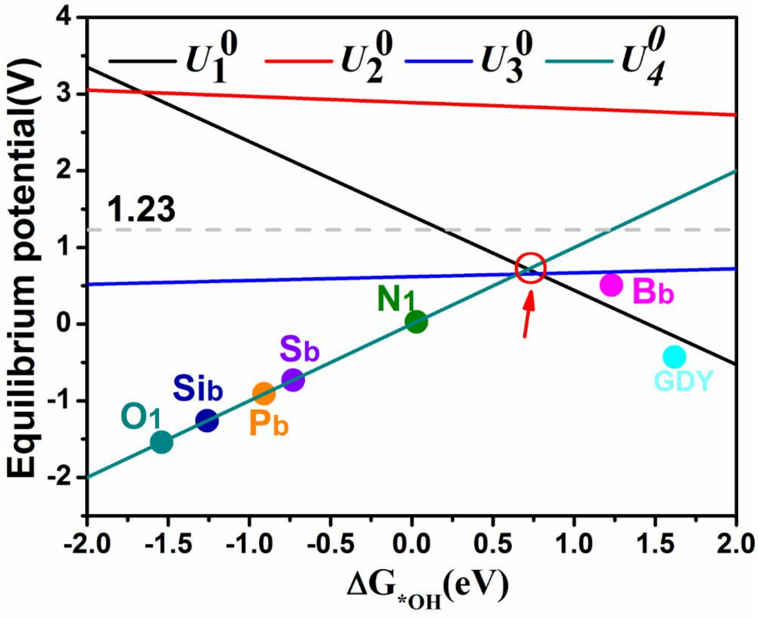


Figure S4. Thermodynamic volcano relation for ORR activity as a function of ΔG_{*OH} in various single-heteroatom-doped GDY structures. Coloured data points are the calculated standard equilibrium potential for the potential-determining step. The lines of different styles and colors are the U_i^0 *vs* ΔG_{*OH} dependence predicted by reactions 1-4 which are derived according to the scaling relations between the adsorption free energy of various intermediates. The gray dash line indicates the level of the equilibrium potential for the overall four-electron reduction of ORR in aqueous solution (1.23 V)..

Thus, the equilibrium potential U_i^0 for the potential-determining step can be related to ΔG_{*OH} as below.

$$eU_1^0 = 4.92 - \Delta G_{*OOH} = 4.92 - 0.97\ \Delta G_{*OH} - 3.51 = 1.41 - 0.97\Delta G_{*OH} \tag{S17}$$

$$eU_2^0 = \Delta G_{*OOH} - \Delta G_{*O} = 0.97\ \Delta G_{*OH} + 3.51 - 1.05\Delta G_{*OH} - 0.62$$

$$= -0.08\ \Delta G_{*\mathrm{OH}} + 2.89 \tag{S18}$$

$$\mathrm{e}U_3^0 = \Delta G_{*\mathrm{O}} - \Delta G_{*\mathrm{OH}} = 1.05\Delta G_{*\mathrm{OH}} + 0.62 - \Delta G_{*\mathrm{OH}}$$

$$= 0.05\ \Delta G_{*\mathrm{OH}} + 0.62 \tag{S19}$$

$$\mathrm{e}U_4^0 = \Delta G_{*\mathrm{OH}} \tag{S20}$$

Figure S4 show the thermodynamic volcano relation for ORR activity as a function of $\Delta G_{*\mathrm{OH}}$ in various single-heteroatom-doped GDY structures. According to eqs S25 and S28, the volcano top can be calculated, where $U_1^0 = U_4^0 = \Delta G_{*\mathrm{OH}}$. It is noticed that $\mathrm{B_b}$-dope GDY and $\mathrm{N_l}$-doped GDY are closest to the volcano top, which is in line with the Gibbs adsorption free energies. Thus, we select B,N co-doped to develop efficient metal-free electrocatalysts.

Note S4

The volcano plots of ORR process are calculated as below.

$\eta^{ORR} = \max\ [\Delta G_1, \Delta G_2,\ \ \Delta G_3,\ \ \Delta G_4]/e+1.23V$

$= \max\{\Delta G_{OOH*} - 4.92, \Delta G_{*O} - \Delta G_{*OOH}, \Delta G_{*OH} - \Delta G_{*O}, -\Delta G_{*OH}\}/e+1.23V$

$= \max\{\Delta G_{*OH} - 1.48, -0.22\ \Delta G_{*OH} - 2.16, -0.22\ \Delta G_{*OH} - 1.28, -\Delta G_{*OH}\}/e+1.23V$ (S21)

The equations describing the ORR process for the volcano plot are therefore:

$-\eta^{ORR} = \Delta G_{*OH}/e - 1.23 \qquad \Delta G_{*OH} \leq 0.74eV$ (S22)

$-\eta^{ORR} = -\Delta G_{*OH}/e + 0.25 \qquad \Delta G_{*OH} \geq 0.74eV$ (S23)

Note S5

We can predict the ORR free energy diagram of an optimal pre$^{\mathrm{ORR}}$-GDY (**Figure S5**), since $\Delta G_{*\mathrm{OH}} = 0.74$ eV, $\eta^{\mathrm{ORR}} = 0.49$ V. Thus, $\Delta G_{*\mathrm{OH}} = 0.74$ eV, $\Delta G_{*\mathrm{OOH}} = \Delta G_{*\mathrm{OH}} + 3.44 = 4.18$ eV, $\Delta G_{*\mathrm{O}} = 0.78\Delta G_{*\mathrm{OH}} + 1.28 = 1.86$ eV.

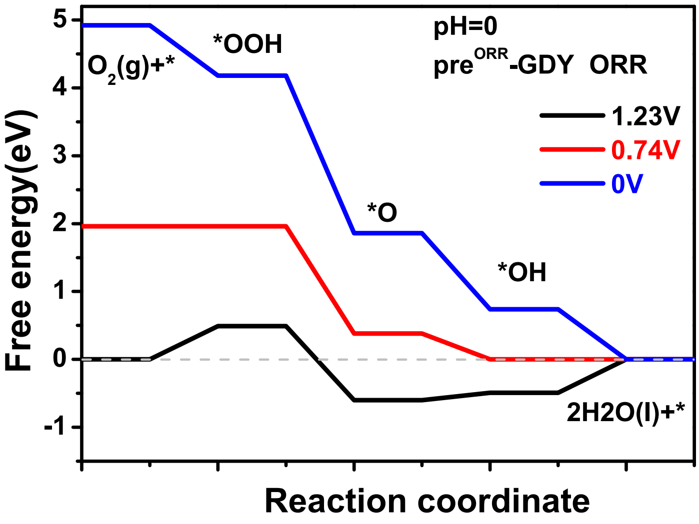


Figure S5. Free energy diagram for ORR on pre$^{\mathrm{ORR}}$-GDY.

References

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