Support Information

Modulating Oxygen Reduction Activity of Heteroatoms doped Carbon Catalysts via Triple Effect: Charge, Spin Density and Ligand effect

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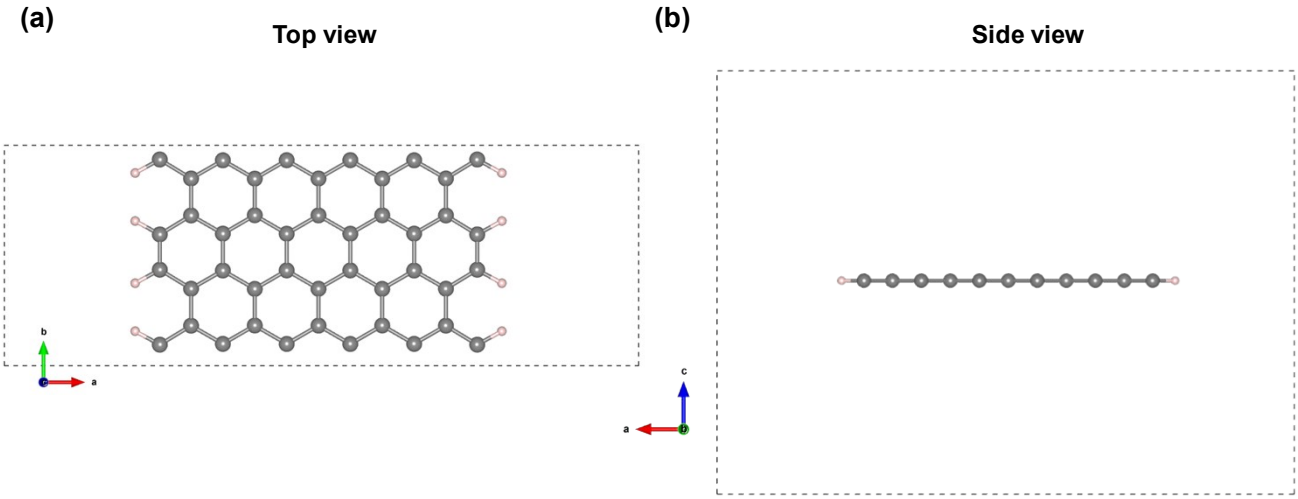


Figure S1: The model of the graphene sheet: (a) top view, (b) side view.

Table S1. Experimental entropic contributions at standard conditions: T=298 K and P=1 bar as listed in follow table. The calculated DFT total energies (E) are for single molecule in gas phase. The zero point energies (ZPE) of single molecule and adsorbents were calculated in gas phase and adsorbed state, respectively. The entropy corrections for the adsorbents on the surface are considered.[1] Here, we use the entropy of gas-phase water calculated at 0.035 bar because this is the equilibrium pressure at T=298 K.[2-3] This means that the free energy of gas-phase water at these conditions is equal to the free energy of liquid water. Energies unit are in eV.

	E^{DFT}/eV	ZPE/eV	$T\Delta S^{exp}$/eV
H_2O(l)	-14.22	0.56	0.22 0.67 (0.035 bar)
H_2(g)	-6.76	0.27	0.40
***OH**	—	0.39	0.07
***O**	—	0.09	0.05
***OOH**	—	0.46	0.16

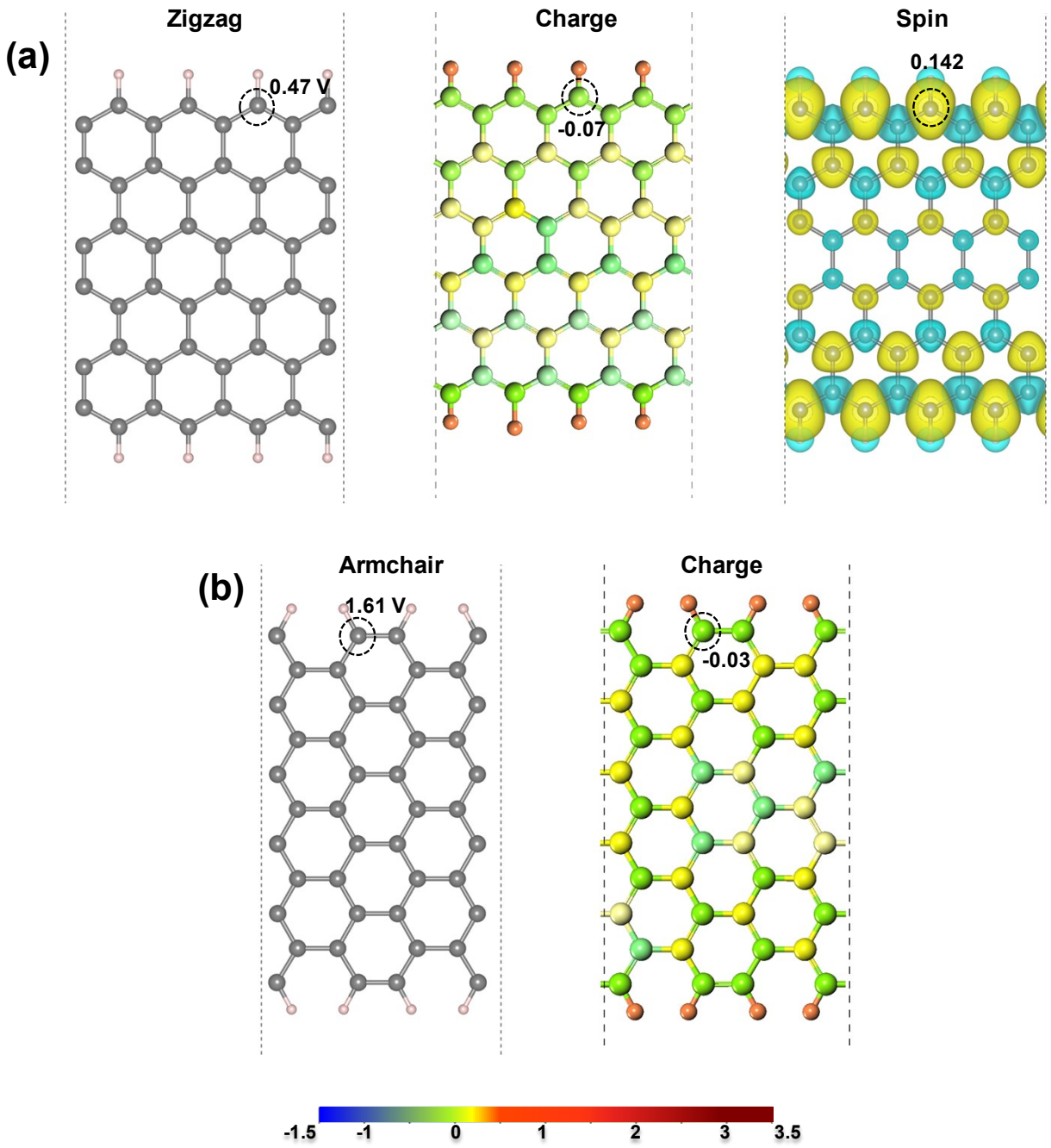


Figure S2. Bader charge and spin density distribution of pure graphene frameworks: (a) zigzag (b) armchair structure. For the charge distribution, the colors of the balls represent the value of Bader charge, which increases gradually from the blue color to red color. For the spin density distribution, yellow and blue iso-surfaces correspond to positive and negative spin density, respectively, the iso-surface levels are 0.0005 eÅ^{-3}. The ORR overpotentials, Bader charge and spin value of the carbon active sites are also listed on them. Here, the spin density is electron density applied to free radicals. It is defined as the total electron density of electrons of one spin minus the total electron density of the electrons of the other spin and mapping it in 3D-space, which is qualitative description method. According to the spin density 3D-space range of atom, gathered spin density on the center atom and given quantitative data of spin density of this atom be called spin density value.

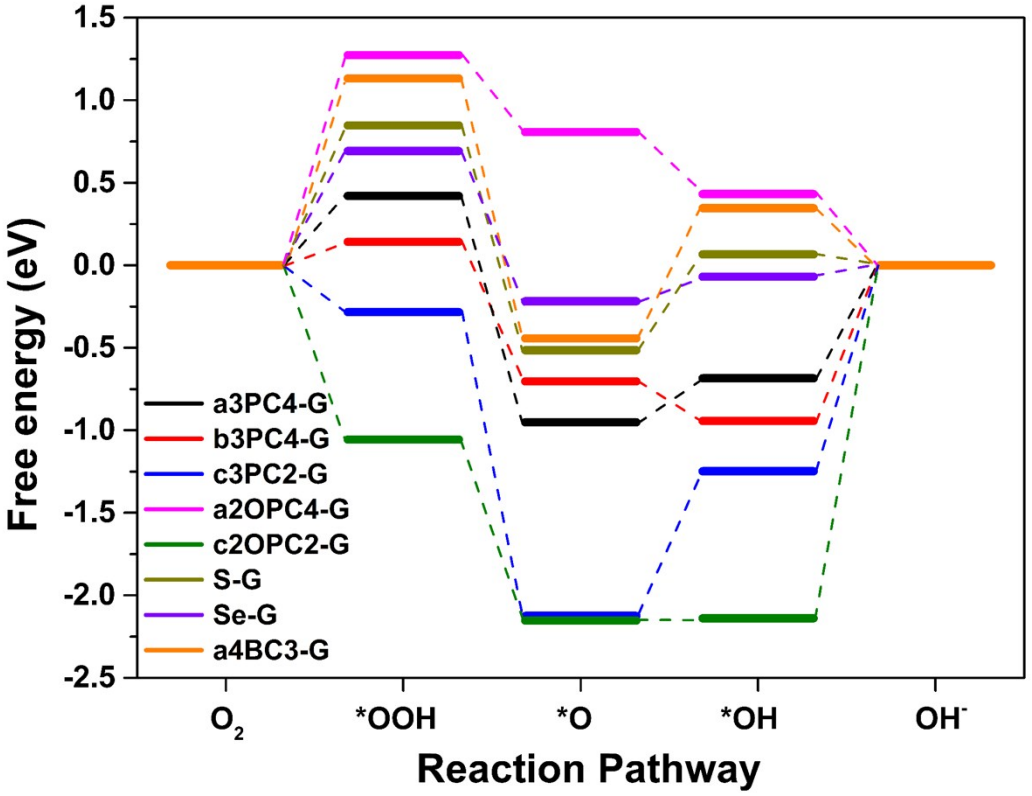
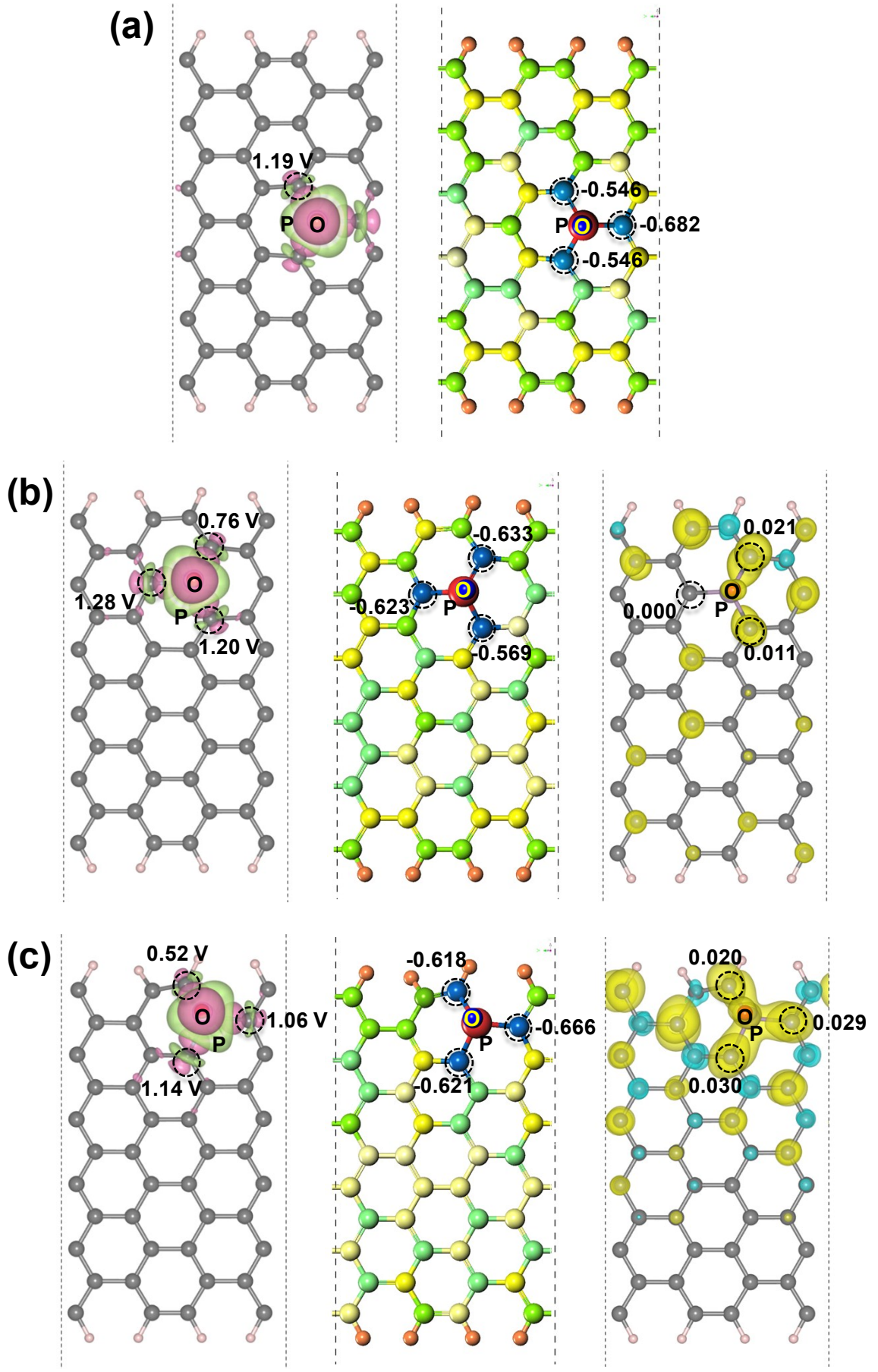
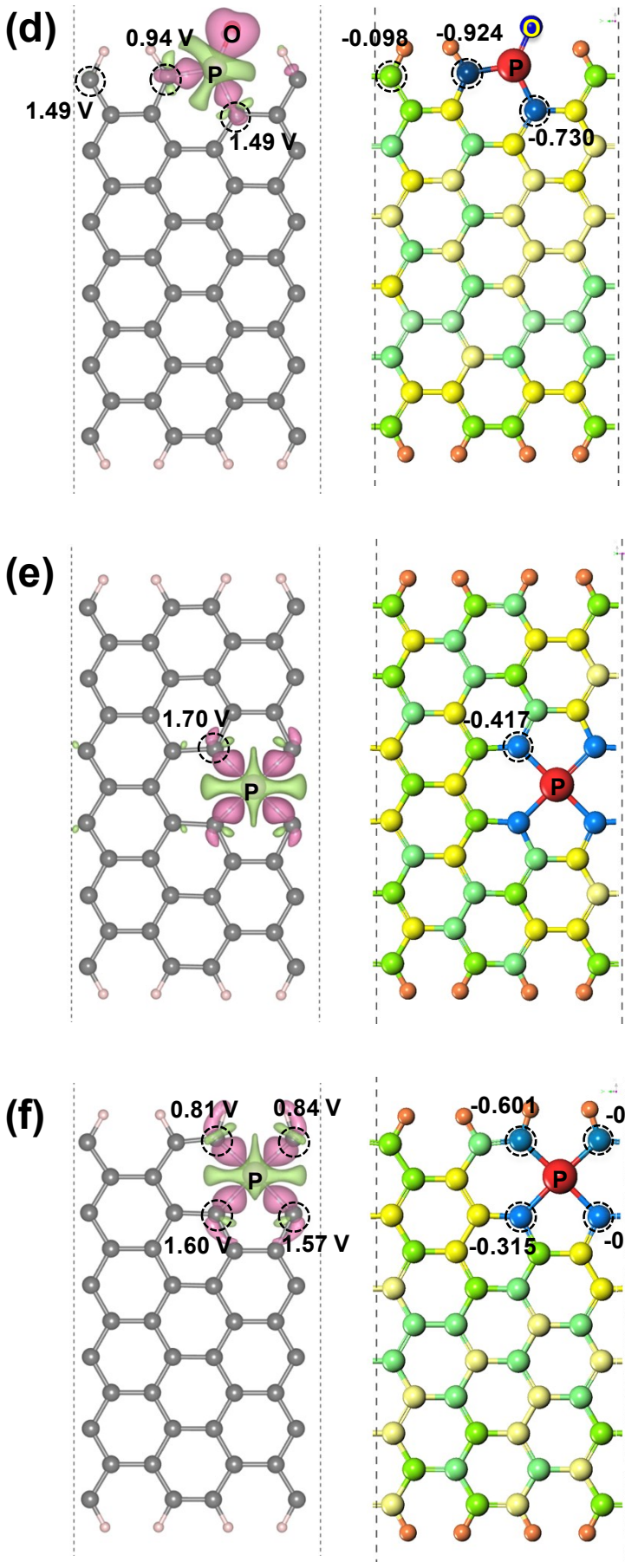
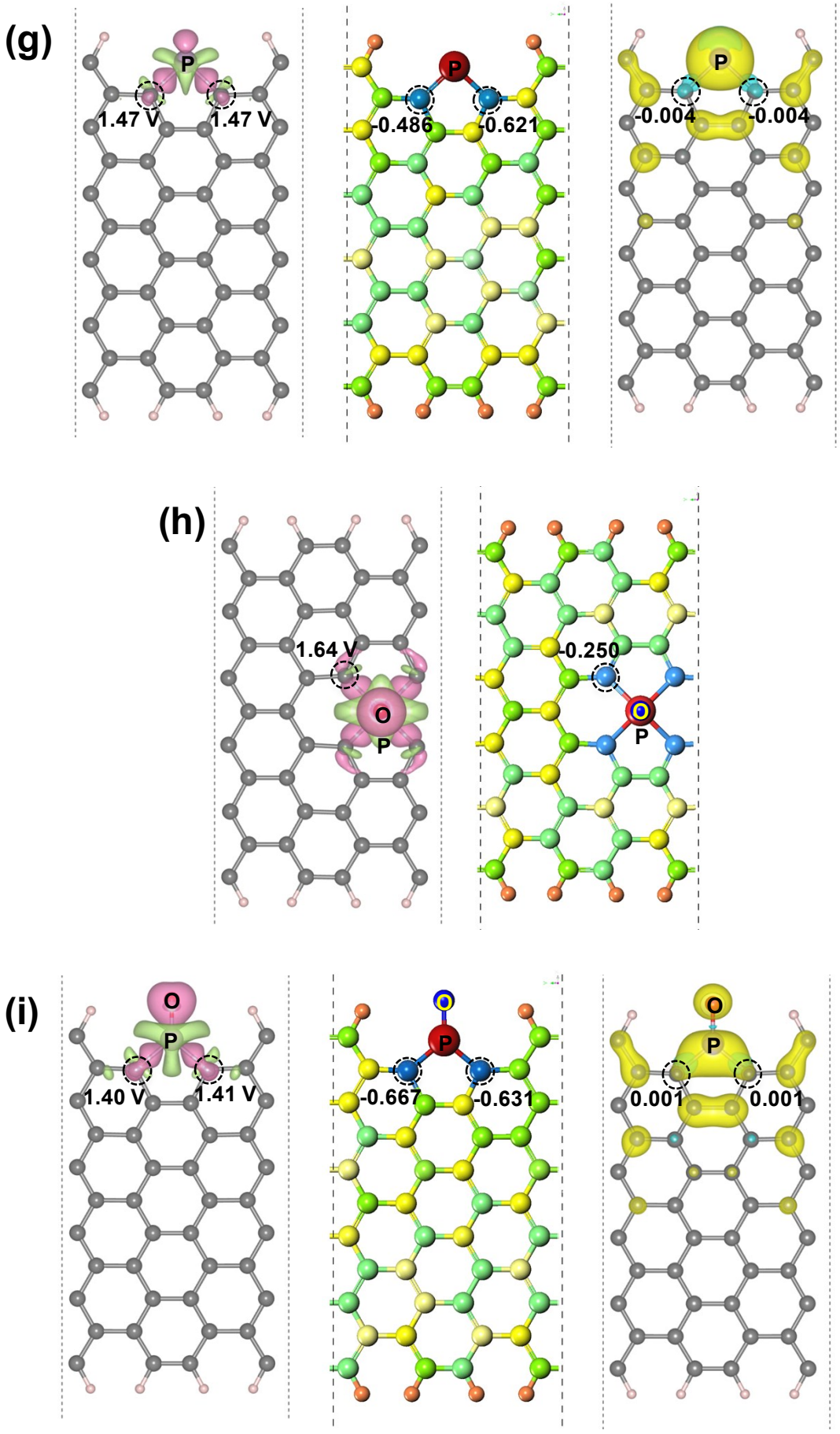
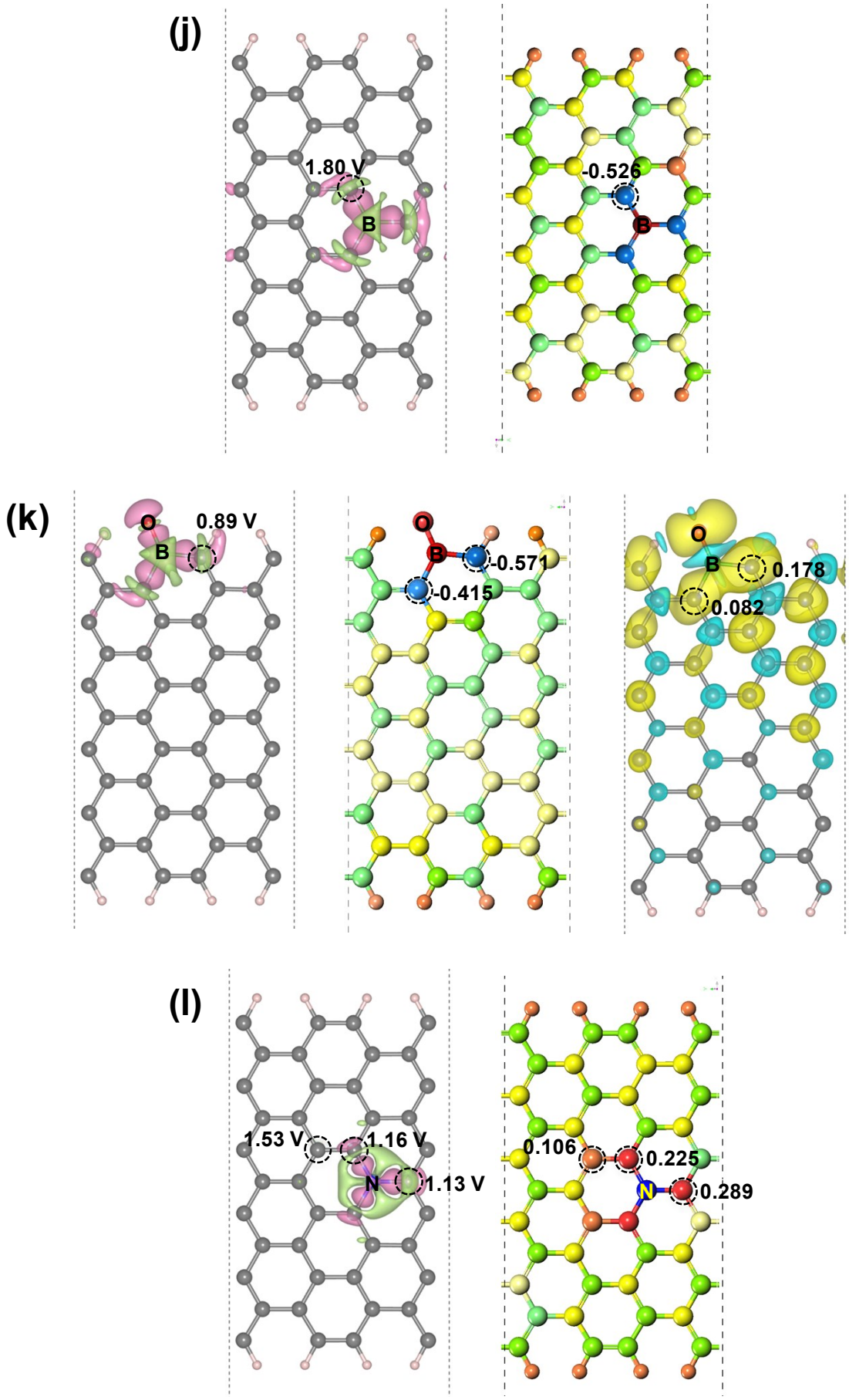


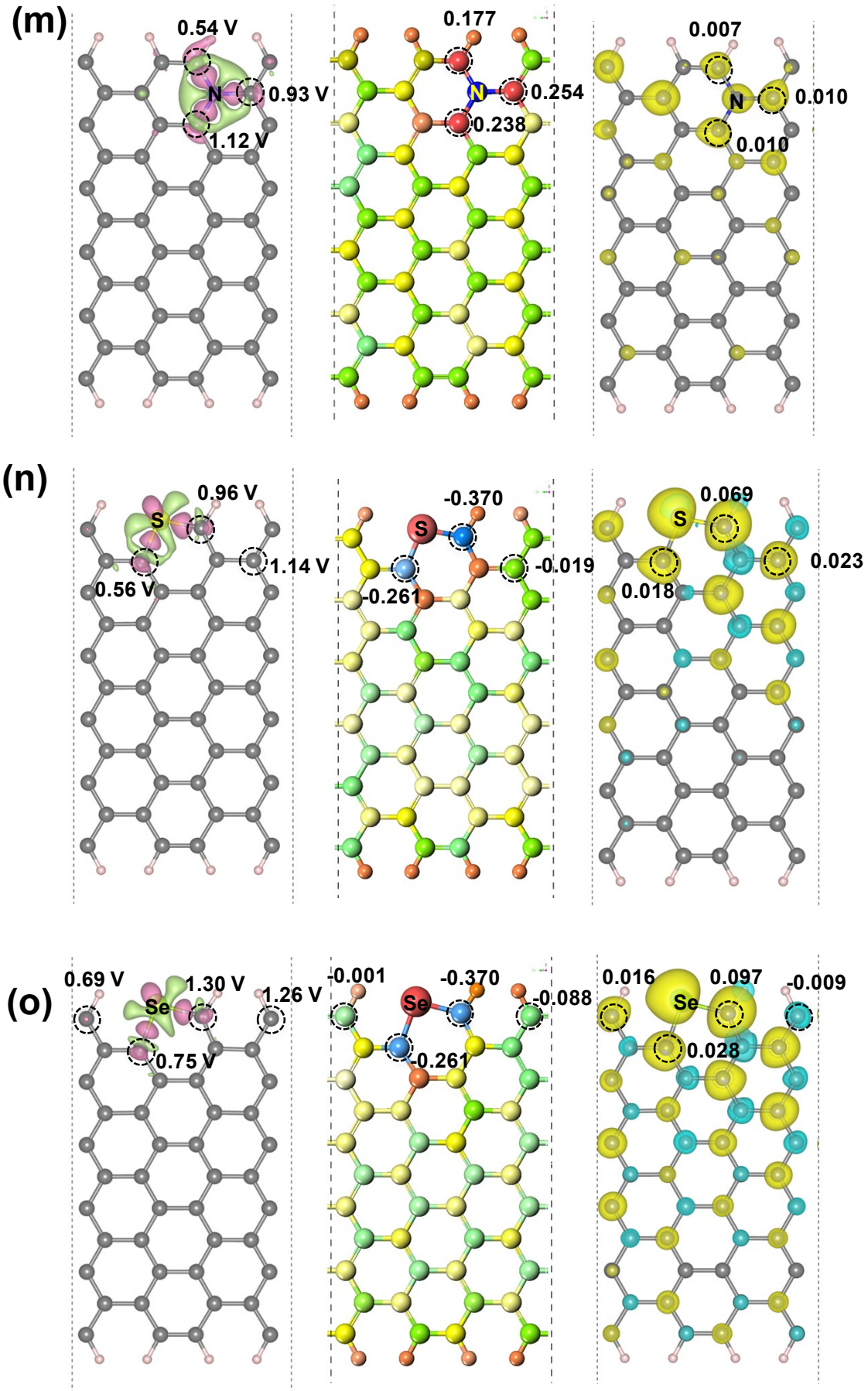
Figure S3. Free energy diagram of the dopant active sites for the different doped-graphene configurations at the equilibrium potential U^{NHE} = 0.455 V vs NHE.


(a)
1.19 V
P
O
-0.546
P
O
-0.682
-0.546
(b)
0.76 V
O
1.28 V
P
1.20 V
-0.633
-0.623
P
-0.569
0.021
O
0.000
P
0.011
(c)
0.52 V
O
1.06 V
P
1.14 V
-0.618
O
-0.666
P
-0.621
0.020
O
P
0.029
0.030


(d)
0.94 V
O
P
1.49 V
1.49 V
-0.098
-0.924
P
-0.730
(e)
1.70 V
P
-0.417
P
(f)
0.81 V
0.84 V
P
1.60 V
1.57 V
-0.601
-0.525
P
-0.315
-0.472


(g)
P
1.47 V
1.47 V
P
-0.486
-0.621
P
-0.004
-0.004
(h)
1.64 V
O
P
-0.250
O
P
(i)
O
P
1.40 V
1.41 V
P
-0.667
-0.631
O
P
0.001
0.001


(j)
1.80 V
B
-0.526
B
(k)
O
B
0.89 V
O
B
-0.571
-0.415
O
B
0.178
0.082
(l)
1.53 V
1.16 V
N
1.13 V
0.106
0.225
N
0.289


(m)
0.54 V
N
0.93 V
1.12 V
0.177
N
0.254
0.238
0.007
N
0.010
0.010
(n)
0.96 V
S
1.14 V
0.56 V
-0.370
S
-0.019
-0.261
0.069
S
0.023
0.018
(o)
0.69 V
1.30 V
Se
1.26 V
0.75 V
-0.001
-0.370
Se
-0.088
-0.261
0.016
0.097
Se
-0.009
0.028

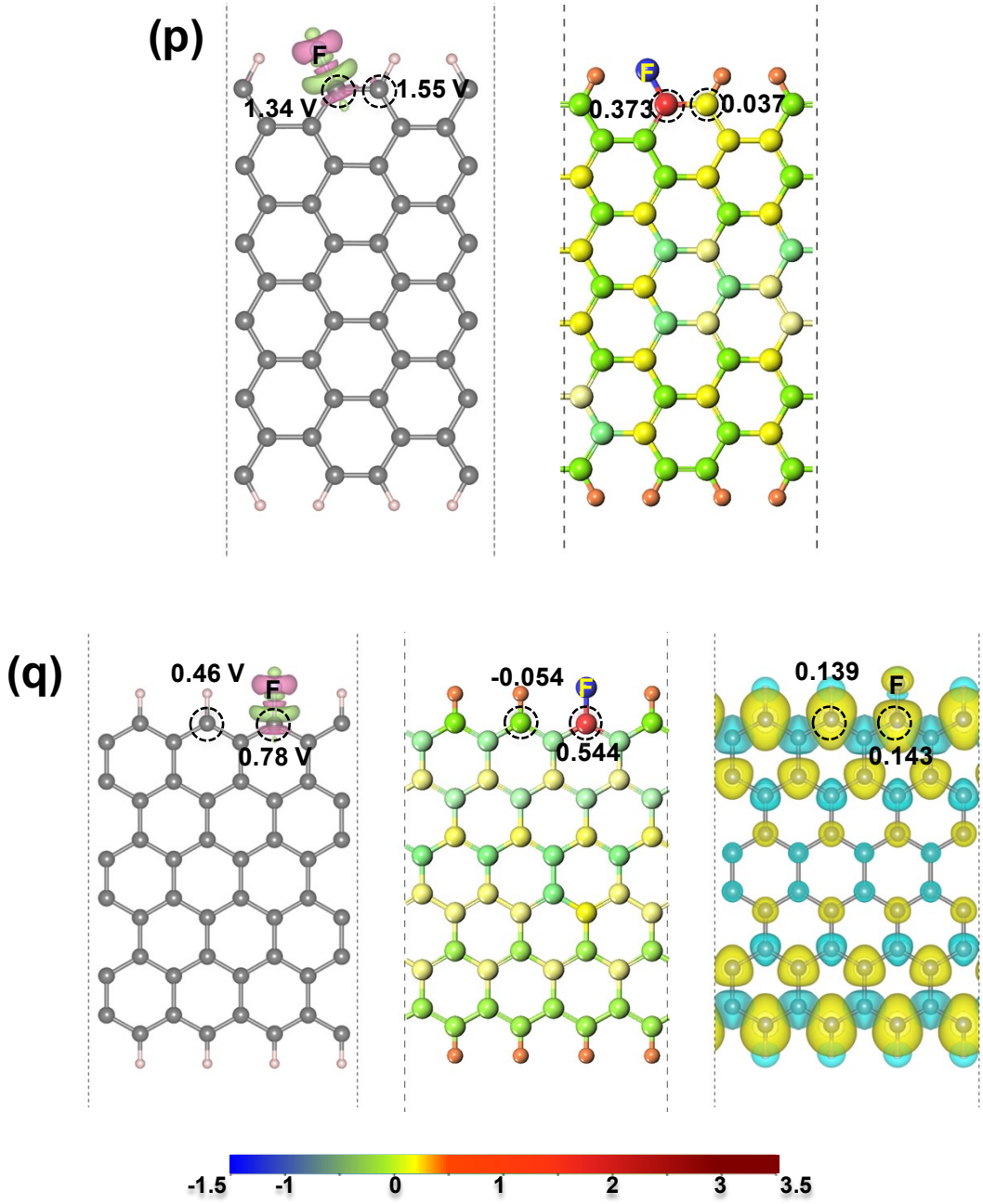


Figure S4. The difference charge density, Bader charge and spin density distribution for the heteroatom-doped graphene models: (a) a1OPC3-G, (b) b1OPC3-G, (c) c1OPC3-G, (d) d1OPC2-G, (e) a3PC4-G, (f) b3PC4-G, (g) c3PC2-G, (h) a2OPC4-G, (i) c2OPC2-G, (j) a4BC3-G, (k) b4OBC2-G, (l) a5NC3-G, (m) b5NC3-G, (n) S-G (o) Se-G, (p) a6FC1-G and (q) b6FC1-G. For the difference charge density, the red and blue indicate the accumulation and loss of charge, respectively, the iso-surface levels are 0.007 $eÅ^{-3}$. For the charge distribution, the colors of the balls represent the value of Bader charge, which increases gradually from the blue color to red color. For the spin density distribution, yellow and blue iso-surfaces correspond to positive and negative spin density, and the iso-surface levels are 0.0005 $eÅ^{-3}$. The ORR overpotentials, Bader charge and spin density values of the explored carbon active sites are also listed on them.

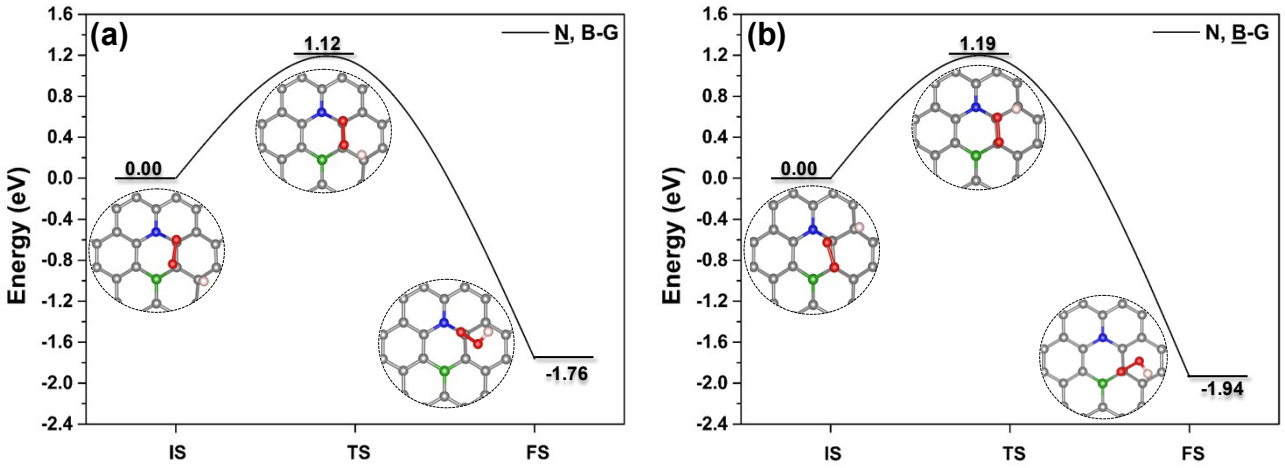


Figure S5. The energy profile of *O_2 protonation and information *OOH on N, B-G surface, in which the adsorption site of *OOH is the carbon atom bonded to the N atom (marked as N, B-G) (a), and the carbon atom bonded to the B atom (marked as N, B-G) (b).

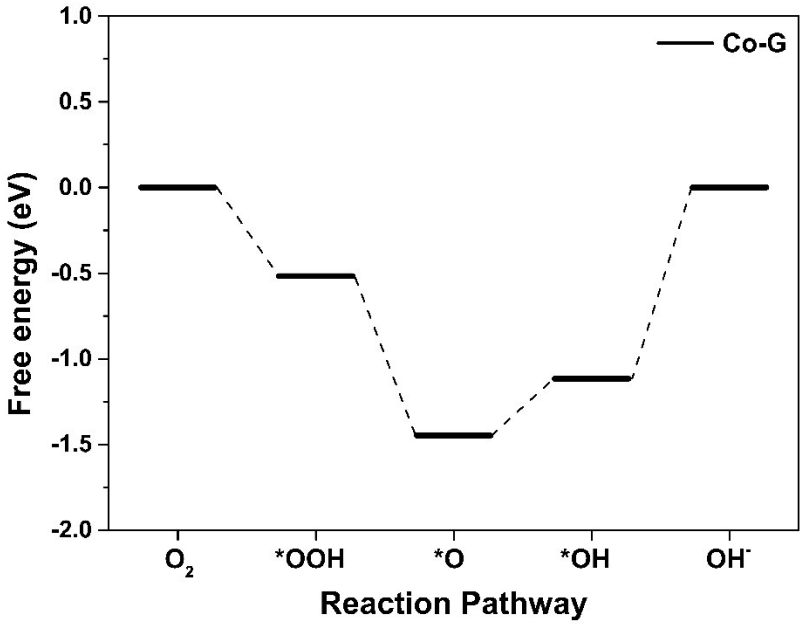


Figure S6. Free energy diagram of the Co active sites for Co-G configuration at the equilibrium potential U^{NHE} = 0.455 V vs NHE.

Supplementary References

(S1) Li, M.; Zhang, L.; Xu, Q.; Niu, J.; Xia, Z. *J. Catal.* **2014,** *314*, 66-72.

(S2) Bajdich, M.; Garcia-Mota, M.; Vojvodic, A.; Norskov, J. K.; Bell, A. T. *J. Am. Chem. Soc.* **2013,** *135* (36), 13521-30.

(S3) Norskov, J. K.; Rossmeisl, J.; Logadottir, A.; Lindqvist, L.; Kitchin, J. R.; Bligaard, T.; Jonsson, H. *J. Phys. Chem. B* **2004,** *108* (46), 17886-17892.