Supplementary Information

First-principles studies of enhanced oxygen reduction reactions on graphene- and nitrogen-doped graphene-coated platinum surfaces

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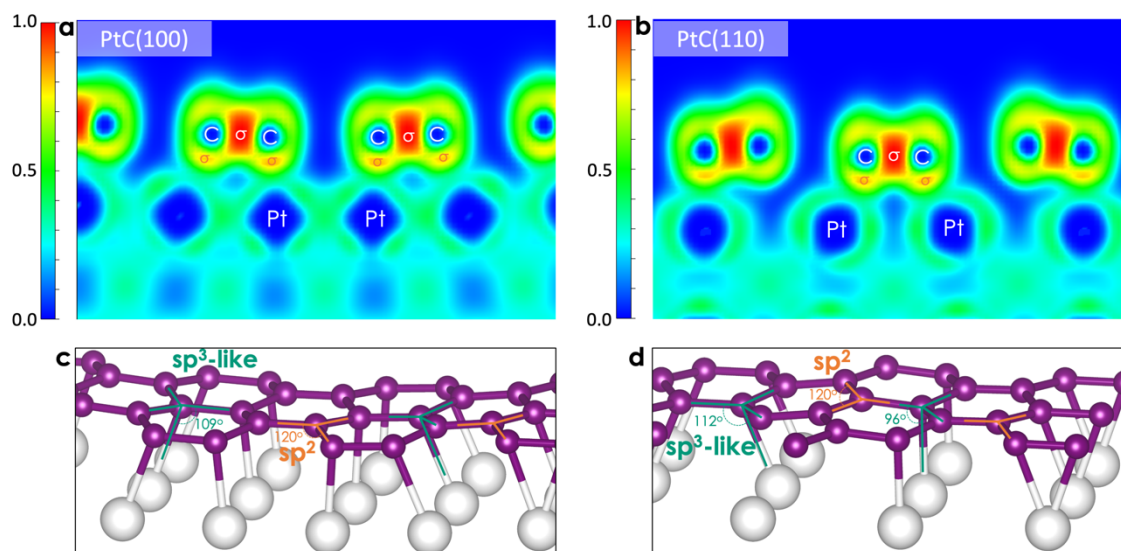
Figure S1: The calculated electron localization function (ELF) between Pt and C atoms of (a) Pt(100)@C and (b) Pt(110)@C systems (where blue regions represent no bonding feature while red regions represent electron pairing with covalent bond feature). The covalent bonds between nearest atoms are denoted by σ. Accordingly, the strong localized electrons observed between C-C atoms as evidence of covalent bonds. Similarly, there are pretty high localized electron regions observed between Pt-C atoms, which indicates some character of the covalent bond between Pt-C even though its strength is weaker as compared to C-C bonds.
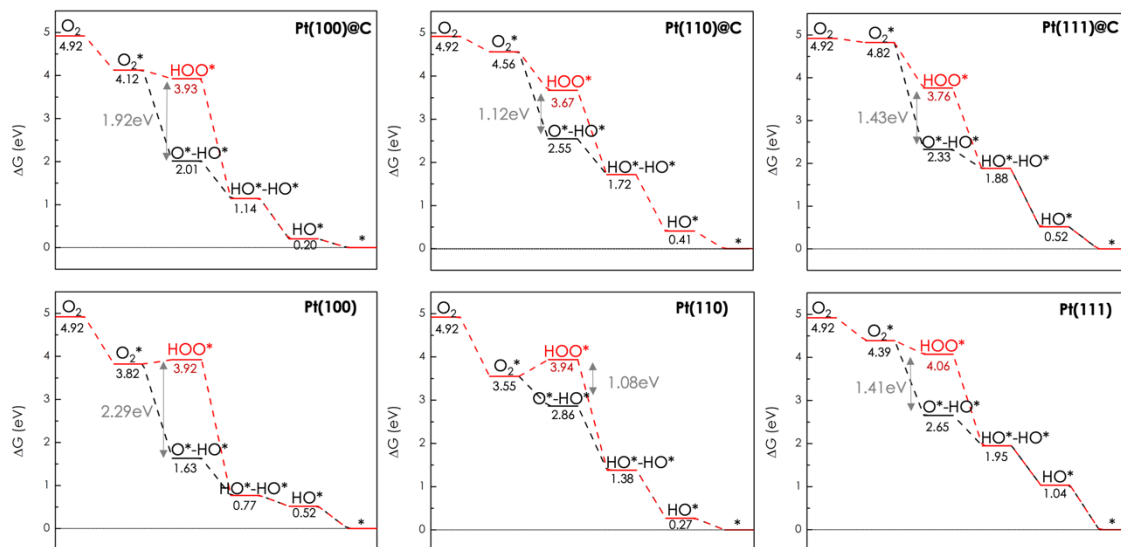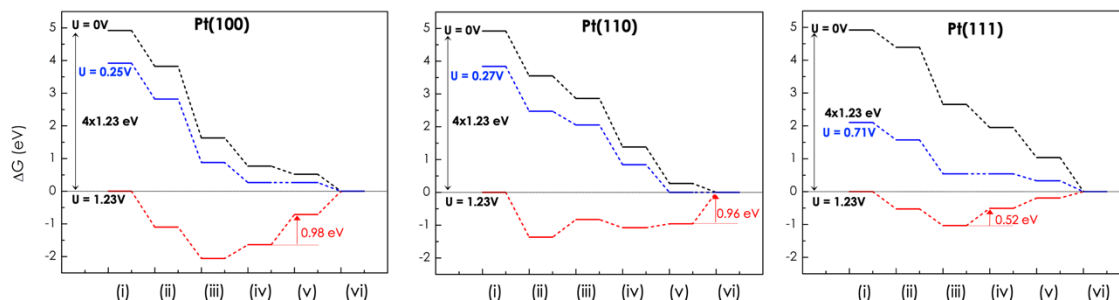
Fig. S2: Free energy diagram at $U_{\text{RHE}} = 0$ V of ORR on Pt(100), Pt(110), Pt(111), and corresponding graphene-coated surfaces, involving *O-*OH (in black) or *OOH (in red).

In Figure S2, we show the free energy diagram at $U_{\text{RHE}} = 0$ V of ORR on Pt(100), Pt(110), Pt(111), and respective graphene-coated surfaces. A consistent observation is the systematic instability of the *OOH intermediate compared to *O-*OH by a minimum of 1.0 eV. Let us assume that all mechanisms involve only *OOH. The oxygen reduction reaction (ORR) on Pt(100) and Pt(110) would be highly inefficient due to the endergonic nature of the first hydrogenation reaction to *OOH. On Pt(111) surface, the first hydrogenation step is predicted to be the rate-determining step (RDS). At an electrode potential of 1.23 V, the activation free energy of this step is 0.90 eV.

On Pt(100)@C and Pt(110)@C, the reaction is downhill at zero electrode potential. This indicates that these graphene-coated surfaces should be significantly more

reactive than the corresponding bare Pt surfaces. On Pt(100)@C, the first hydrogenation (*O$_2$ to *OOH) and the last hydrogenation (*OH to H$_2$O) steps have near identical activation free energies (1.03 eV). They are both considered the RDS. The Pt(110)@C surface has an activation free energy of 0.82 eV for the last hydrogenation step. On the Pt(111)@C surface, the last hydrogenation step is the RDS, with an activation free energy of 0.71 eV. Again, in comparison to the Pt(111) surface, Pt(111)@C is marginally more reactive.

In summary, assuming the *OOH intermediate and considering the RDS activation free energy, the catalytic activity is ranked as Pt(111)@C > Pt(110)@C $\approx$ Pt(111) $\approx$ Pt(100)@C $\gg$ Pt(100) > Pt(110).

Fig. S3: Free energy diagram of ORR on Pt(100), Pt(110), and Pt(111) at different electrode potentials: $U_{\mathrm{RHE}} = 0$ V (black line), $U_{\mathrm{RHE}} = 1.23$ V (red line), and limiting potential U_{L}. *O-*OH is the intermediate.

In Figure S3, we show the free energy diagram of ORR on Pt(100), Pt(110), and Pt(111) at different electrode potentials: $U_{\mathrm{RHE}} = 0$ V, 1.23 V, and U_{L}. Here, *O-*OH is the intermediate. Comparing Figure S3 and Figure 6(b) enables a clear distinction between the bare Pt surfaces and Pt@C surfaces.

Table S1: The calculated data of electronic energy (E_{elec}), zero-point energy correction (E_{ZPE}), vibrational heat capacity (C_p), and adsorbate entropy (S) at T = 298.15 K from DFT method is collected for all considered systems, including Pt(100), Pt(110), Pt(111), Pt(100)@C, Pt(110)@C, Pt(111)@C, Pt(111)@C/N, and isolated gas. The substrate is denoted as *, where species are adsorbed.

Intermediates	E_{elec} (eV)	E_{ZPE} (eV)	C_p (eV)	TS (eV)	G (eV)
Pt(100)					
*	-508386.3516				-508386.3516
O$_2$*	-509517.3709	0.139	0.069	0.156	-509517.3189
HOO*	-509533.4633	0.407	0.061	0.121	-509533.1163
O*-HO*	-509535.7969	0.427	0.064	0.103	-509535.4089
HO*-HO*	-509552.8716	0.758	0.080	0.135	-509552.1686
HO*	-508969.4489	0.358	0.045	0.081	-508969.1270
Pt(110)					
*	-508376.7283				-508376.7283
O$_2$*	-509508.0503	0.133	0.049	0.097	-509507.9653
HOO*	-509523.8521	0.420	0.054	0.102	-509523.4801
O*-HO*	-509524.8314	0.380	0.069	0.171	-509524.5534
HO*-HO*	-509542.5405	0.673	0.069	0.133	-509541.9315
HO*	-508960.0638	0.353	0.048	0.088	-508959.7508
Pt(111)					
*	-457553.4876				-457553.4876
O$_2$*	-458683.9862	0.148	0.063	0.111	-458683.8862
HOO*	-458700.4599	0.415	0.074	0.143	-458700.1139
O*-HO*	-458701.8402	0.402	0.092	0.174	-458701.5202
HO*-HO*	-458718.7104	0.693	0.108	0.213	-458718.1224
HO*	-458136.0043	0.316	0.050	0.107	-458135.7453
Pt(100)@C					
*	-514404.2707				-514404.2707
O$_2$*	-515535.0904	0.184	0.047	0.076	-515534.9354
HOO*	-515551.4077	0.458	0.083	0.166	-515551.0327

O*-HO*	-515553.3823	0.464	0.049	0.076	-515552.9453
HO*-HO*	-515570.4868	0.809	0.063	0.097	-515569.7118
HO*	-514987.7247	0.391	0.041	0.067	-514987.3597
Pt(110)@C					
Intermediates	E_{elec} (eV)	E_{ZPE} (eV)	C_p (eV)	TS (eV)	G (eV)
*	-516404.5780				-516404.5780
O_2*	-517534.9622	0.186	0.047	0.076	-517534.8052
HOO*	-517552.0013	0.451	0.062	0.107	-517551.5953
O*-HO*	-517553.1459	0.456	0.05	0.078	-517552.7179
HO*-HO*	-517570.1855	0.789	0.076	0.126	-517569.4465
HO*	-516987.8275	0.389	0.043	0.069	-516987.4645
Pt(111)@C					
Intermediates	E_{elec} (eV)	E_{ZPE} (eV)	C_p (eV)	TS (eV)	G (eV)
*	-462064.4389				-462064.4389
O_2*	-463194.5585	0.181	0.048	0.077	-463194.4065
HOO*	-463211.7332	0.461	0.082	0.174	-463211.3642
O*-HO*	-463213.2392	0.468	0.050	0.078	-463212.7992
HO*-HO*	-463229.8776	0.789	0.076	0.129	-463229.1416
HO*	-462647.5811	0.394	0.041	0.066	-462647.2121
Pt(111)@C/N					
Intermediates	E_{elec} (eV)	E_{ZPE} (eV)	C_p (eV)	TS (eV)	G (eV)
*	-462196.4021				-462196.4021
O_2*	-463326.5289	0.146	0.070	0.144	-463326.4569
HOO*	-463343.8115	0.466	0.079	0.147	-463343.4135
O*	-462762.4885	0.092	0.027	0.044	-462762.4135
HO*	-462779.1639	0.386	0.044	0.073	-462778.8069
Isolated gas					
Gas	E_{elec} (eV)	E_{ZPE} (eV)	C_p (eV)	TS (eV)	G (eV)
H_2	-31.749223	0.267	0.091	0.403	-31.7952
H_2O (l)	-599.18683	0.564	0.104	0.670	-599.1898
O_2					-1129.8692

The details procedure of applied potential on the Gibbs free energy difference could be approximated by:

$$\Delta G_U = \Delta G - neU$$

where n is the number of electrons transferred in each reaction step, e is the electron's elementary charge, and U is the applied electrode potential. Specifically, the applied potential to Gibbs free energy of reaction steps with the corresponding number of electrons transferred is as follows:

Steps	Intermediates	Number of electrons tranffered (n)
(i)	$G_{O2} + 2G_{H2} - 2G_{H2O} - neU$	4
(ii)	$G_{*O2} + 2G_{H2} - (2G_{H2O} + G_{*}) - neU$	4
(iii-a)	$G_{*O\text{-}*OH} + 3/2G_{H2} - (2G_{H2O} + G_{*}) - neU$	3
(iii-b)	$G_{*OOH} + 3/2G_{H2} - (2G_{H2O} + G_{*}) - neU$	3
(iv-a)	$G_{*OH\text{-}*OH} + G_{H2} - (2G_{H2O} + G_{*}) - neU$	2
(iv-b)	$G_{*O} + G_{H2} - (G_{H2O} + G_{*}) - neU$	2
(v)	$G_{*OH} + 1/2G_{H2} - (G_{H2O} + G_{*}) - neU$	1
(vi)	$G_{H2O} + G_{*} - (G_{H2O} + G_{*}) - neU$	0