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

NiPd co-doped nitrogen-coordinated graphene as a high-efficiency electrocatalyst for oxygen reduction reaction: A first-principles determination

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Table S1 The Metal-N bond lengths (d_{M-N}), the Ni-Pd bond lengths (d_{Ni-Pd}) and charges of each atom using different supercell sizes.

	5×5	10×5
d_{Ni-N}(Å)	1.848/1.841/1.950	1.848/1.840/1.950
d_{Pd-N}(Å)	1.924/1.998/2.003	1.924/1.998/2.003
d_{Ni-Pd}(Å)	2.241	2.241
Charge_Ni	-0.63	-0.63
Charge_Pd	-0.41	-0.41
Charge_T_3	0.60	0.60
Charge_T_4	1.20	1.20
Charge_T_5	1.09	1.09
Charge_T_6	1.07	1.07
Charge_T_7	1.30	1.30
Charge_T_8	0.71	0.71
after O adsorption		
Charge_O	0.79	0.79
Charge_Ni Charge_Pd	-0.91	-0.91
Charge_T_3	0.61	0.61
Charge_T_4	1.21	1.21
Charge_T_5	1.06	1.06
Charge_T_6	0.66	0.66
Charge_T_7	1.14	1.14
Charge_T_8	0.61	0.61

Table S2 The Metal-N bond lengths ($d_{M\text{-}N}$) vs. sum of covalent radii ($r_M + r_N$) of the metal and N atoms, and the Ni-Pd bond lengths ($d_{Ni\text{-}Pd}$) vs. sum of covalent radii ($r_{Ni} + r_{Pd}$) of Ni and Pd atoms.

Model	$d_{Ni\text{-}N}$(Å)	$r_{Ni} + r_N$(Å)	$d_{Pd\text{-}N}$(Å)	$r_{Pd} + r_N$(Å)	$d_{Ni\text{-}Pd}$(Å)	$r_{Ni} + r_{Pd}$(Å)
$NiPdN_6$-G	1.88	1.95	1.98	2.10	2.24	2.63
NiN_4-G	1.88	1.95				
PdN_4-G			1.95	2.10		

Table S3 The formation energies (E_{f1} and E_{f2}), standard dissolution potential standard dissolution potential (U^0_{diss}), number of transferred electrons (N_e) during the dissolution, dissolution potential (U_{diss}), the binding energies (E_b) and the cohesive energy (E_{coh}) for each catalyst.

Model	E_{f1}(eV)	E_{f2}(eV)		U^0_{diss}(V)		N_e		U_{diss}(V)		E_b(eV)	E_{coh} (eV)
		Ni-PdN_6	Pd-NiN_6	Ni	Pd	Ni	Pd	Ni	Pd		
$NiPdN_6$-G	-5.46	-6.12	-4.51	-0.26	0.95	2	2	2.80	3.21	-5.65	-5.19
NiN_4-G	-4.45			-0.26		2		1.97		-8.21	-5.84
PdN_4-G	-2.33			0.95		2		2.12		-7.02	-4.54

Table S4 The free-energy (ΔG) for the different reaction intermediates and the overpotential (η) for all possible ORR pathways on $NiPdN_6$-G.

Path	Process	ΔG (eV)						η (V)
		$*O_2$	*OOH	*O+*OH	*OH+*OH	*O	*OH	
1	$1\rightarrow 2_i(B)\rightarrow 3(up)\rightarrow 4(up)$	4.36	4.06			1.83	1.00	0.40
2	$1\rightarrow 2_i(B)\rightarrow 3(down)\rightarrow 4(down)$	4.36	4.06			1.83	0.98	0.38
3	$1\rightarrow 0(T_2)\rightarrow 2_{ii}(T_2)\rightarrow 3(up)\rightarrow 4(up)$	4.36	4.06	3.83		1.83	1.00	0.40
4	$1\rightarrow 0(T_2)\rightarrow 2_{ii}(T_2)\rightarrow 3(down)\rightarrow 4(down)$	4.36	4.06	3.83		1.83	0.98	0.38
5	$1\rightarrow 0(T_2)\rightarrow {2'_{ii}}(T_2)\rightarrow 3'(T_2)\rightarrow 4(up)$	4.36	4.06	3.83	2.71		1.00	0.37
6	$1\rightarrow {2_{iii}}(T_2)\rightarrow 3'(T_2)\rightarrow 4(up)$	4.36	4.06		2.71		1.00	0.37
7	$1\rightarrow 0(T_3)\rightarrow 2_{ii}(T_3)\rightarrow 3(up)\rightarrow 4(up)$	4.36	4.06	4.24		1.83	1.00	0.40
8	$1\rightarrow 0(T_3)\rightarrow 2_{ii}(T_3)\rightarrow 3(down)\rightarrow 4(down)$	4.36	4.06	4.24		1.83	0.98	0.38
9	$1\rightarrow 0(T_3)\rightarrow {2'_{ii}}(T_3)\rightarrow 3'(T_3)\rightarrow 4(up)$	4.36	4.06	4.24	3.30		0.98	0.37
10	$1\rightarrow {2_{iii}}(T_3)\rightarrow 3'(T_3)\rightarrow 4(up)$	4.36	4.06		3.30		0.98	0.47
11	$1\rightarrow 0(T_8)\rightarrow 2_{ii}(T_8)\rightarrow 3(up)\rightarrow 4(up)$	4.36	4.06	4.22		1.83	1.00	0.40
12	$1\rightarrow 0(T_8)\rightarrow 2_{ii}(T_8)\rightarrow 3(down)\rightarrow 4(down)$	4.36	4.06	4.22		1.83	0.98	0.38
13	$1\rightarrow 0(T_8)\rightarrow {2'_{ii}}(T_8)\rightarrow 3'(T_8)\rightarrow 4(up)$	4.36	4.06	4.22	3.37		0.98	0.38
14	$1\rightarrow {2_{iii}}(T_8)\rightarrow 3'(T_8)\rightarrow 4(up)$	4.36	4.06		3.37		0.98	0.54

Table S5 The total energy (ΔE), the changes of the zero-point energy (ΔZPE), the temperature T and the changes of entropy (ΔS) of each system calculated by DFT in free-energy (ΔG) calculation.

	ΔE	ΔZPE-$T\Delta S$	ΔG (U=0)
*O_2	-440.158	0.003	4.36
*OOH	-444.211	0.341	4.06
*O(B)+*OH(T_2)	-444.298	0.204	3.83
*O(B)+*OH*(T_3)	-444.121	0.431	4.24
*O(B)+*OH(T_8)	-444.136	0.434	4.22
*OH(B)+*OH(T_2)	-449.260	0.641	2.71
*OH(B)+*OH(T_3)	-448.699	0.667	3.30
*OH(B)+*OH(T_8)	-448.668	0.707	3.37
*O	-435.348	0.071	1.83
*OH (up)	-439.852	0.334	1.00
*OH (down)	-439.988	0.460	0.98

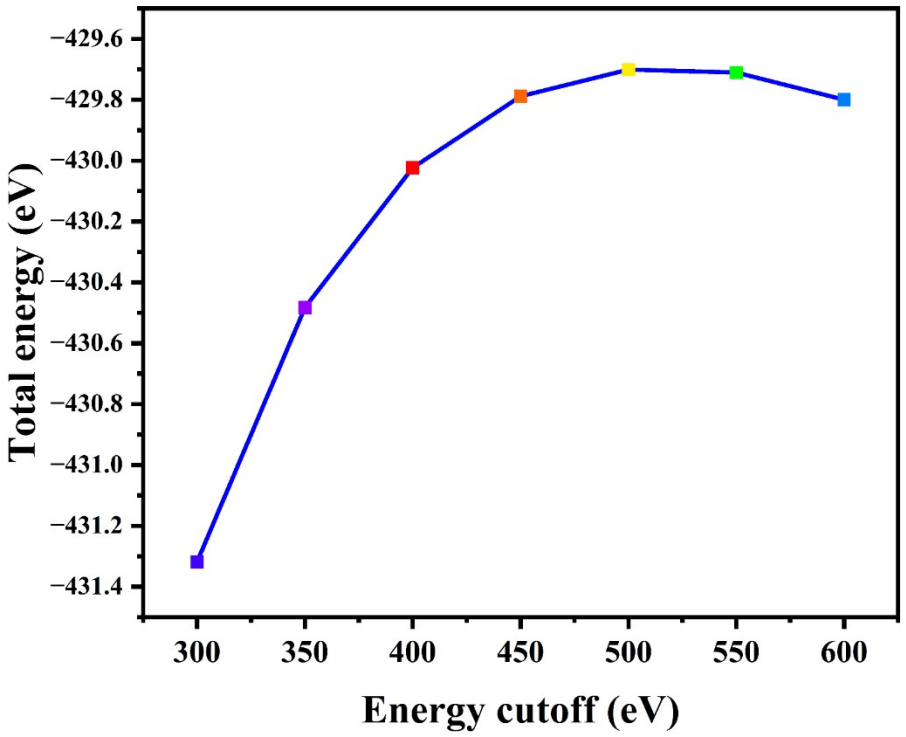

Fig. S1 Calculated total energies of $NiPdN_6$-G using different energy cutoff values.

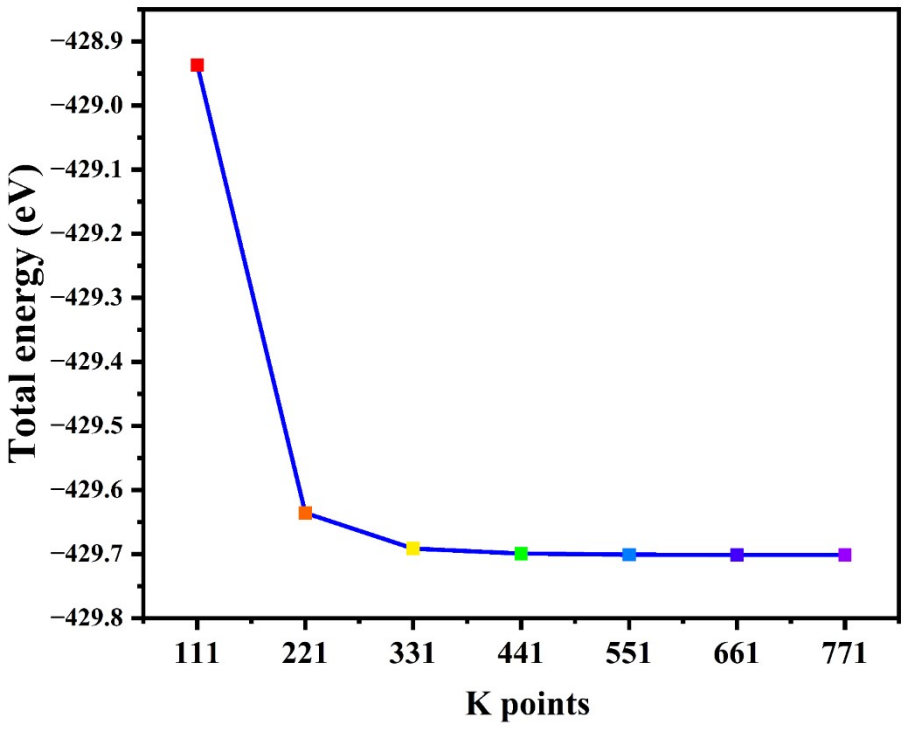

Fig. S2 Calculated total energies of $NiPdN_6$-G using different *k*-point meshes.

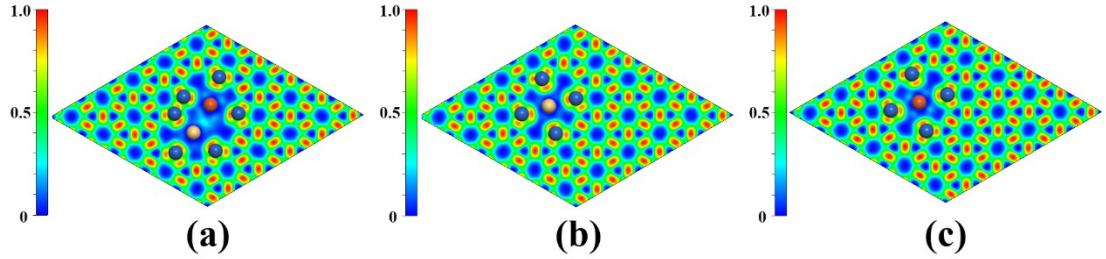

Fig. S3 The electron location functions (EFLs) for (a) $NiPdN_6$-G, (b) NiN_4-G and (c) PdN_4-G. Blue, yellow and orange spheres represent N, Ni and Pd atoms, respectively. Scale bar: ELF = 0, 0.5, and 1, corresponding to no electron (blue), the electron gas (green), and perfect electron (red), respectively.

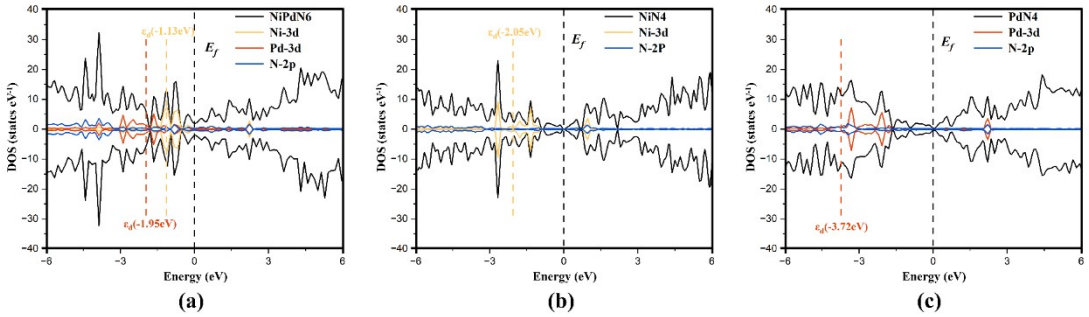

Fig. S4 Total DOS, projected Ni-3*d*, Pd-3*d* and N-2*p* states, and the metal *d*-band centers (ε_d) calculated from both spin up and spin down states of (a) $NiPdN_6$-G, (b) NiN_4-G and (c) PdN_4-G. Fermi level is set at 0 eV.

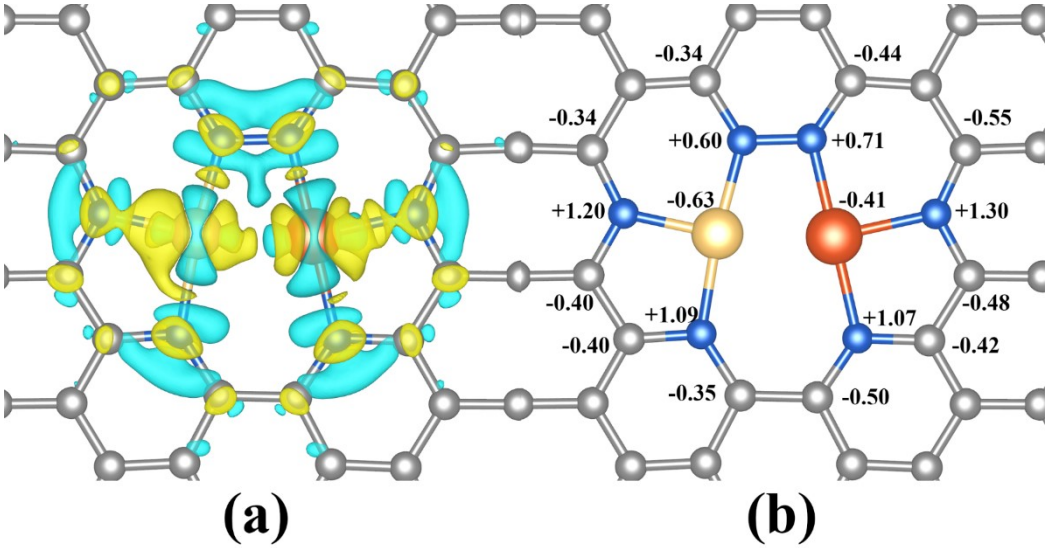

Fig. S5 (a) The charge density difference plot and (b) calculated Bader charges for

$NiPdN_6$-G catalyst. Yellow and cyan bubbles indicate electron accumulation and depletion, respectively. Blue, yellow and orange spheres represent N, Ni and Pd atoms, respectively. The '+' and '-' denote the gained and lost charges, respectively.

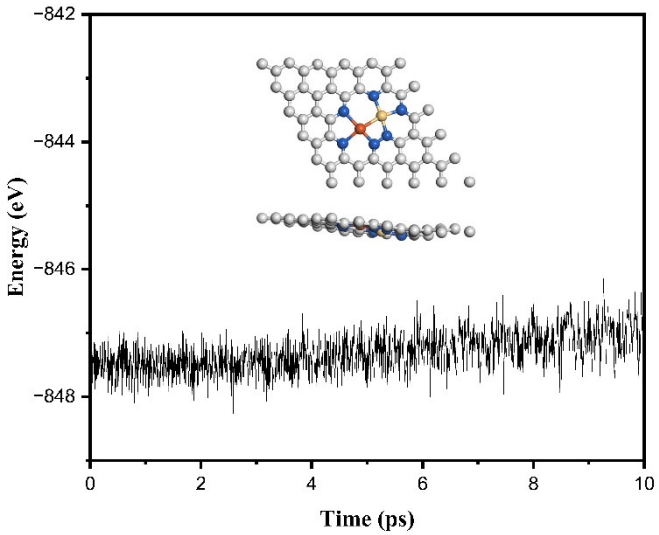

Fig. S6 The energy curve of $NiPdN_6$ structure is simulated *via* AIMD at 500 K, and the top-view and side-view of $NiPdN_6$ structure are both obtained at 10 ps.

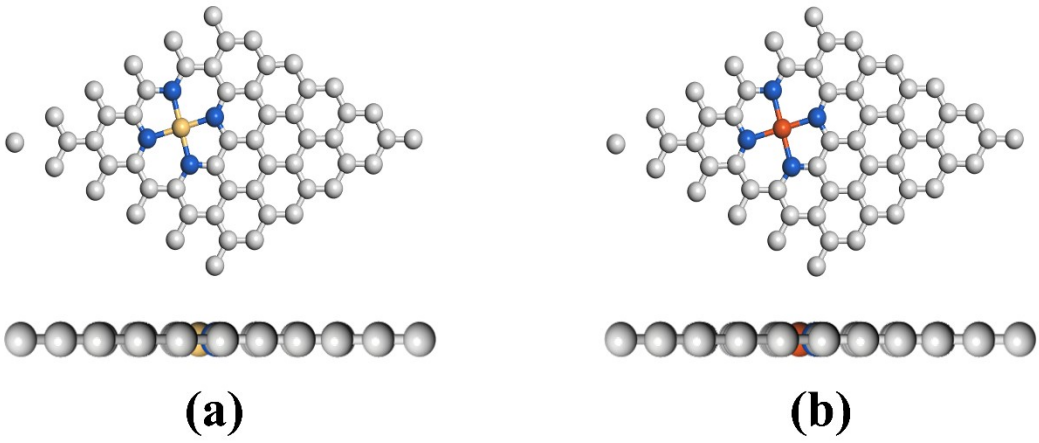

Fig. S7 The optimized structures of (a) NiN_4-G and (b) PdN_4-G. Grey, blue, yellow and orange spheres represent C, N, Ni and Pd atoms, respectively.

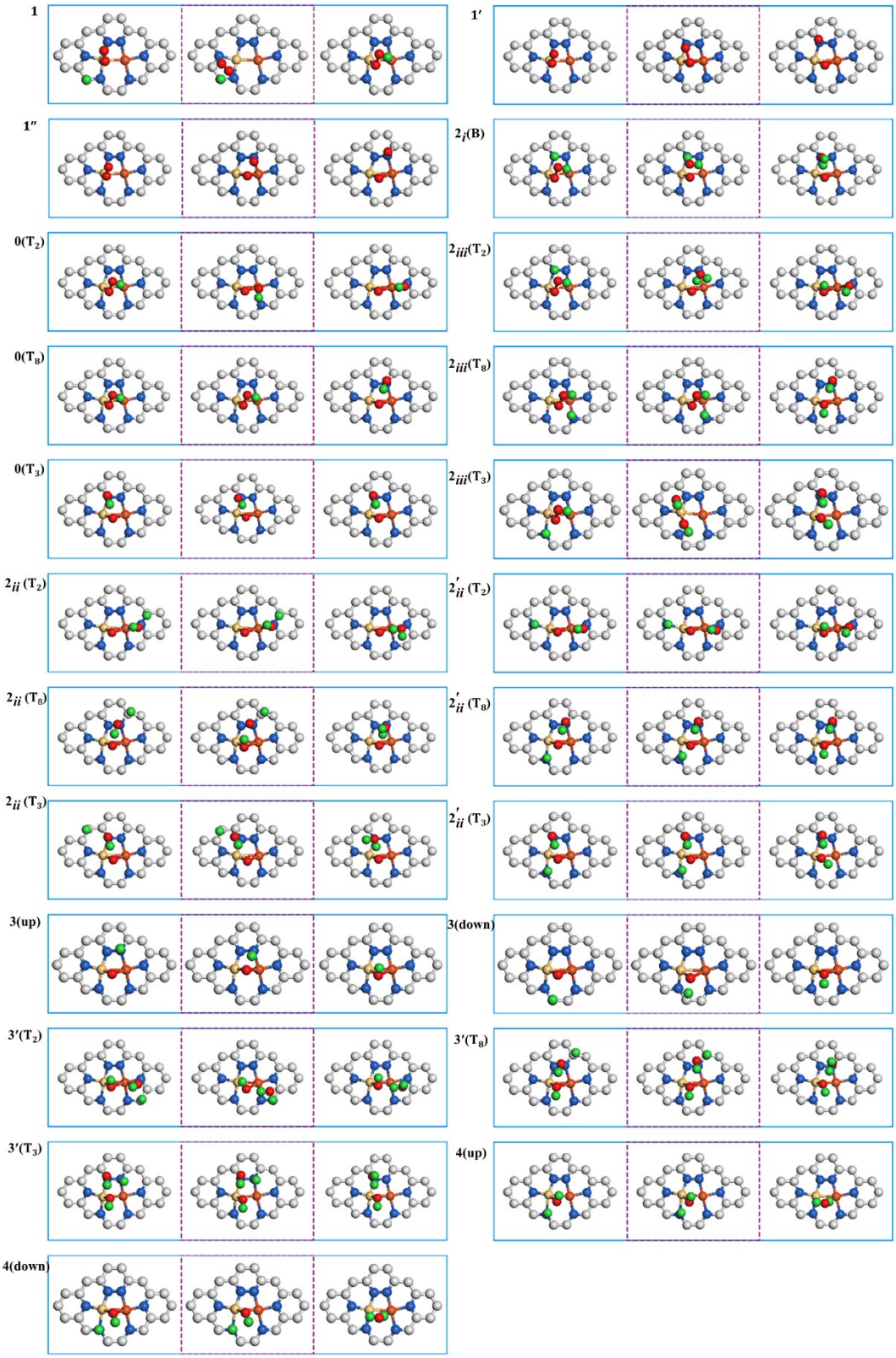

Fig. S8 Atomic structures of IS, TS, and FS for each step of ORR on $NiPdN_6$-G. The TS structures are marked by dashed boxes. Grey, blue, yellow, orange, red and green spheres represent C, N, Ni, Pd, O and H atoms, respectively.

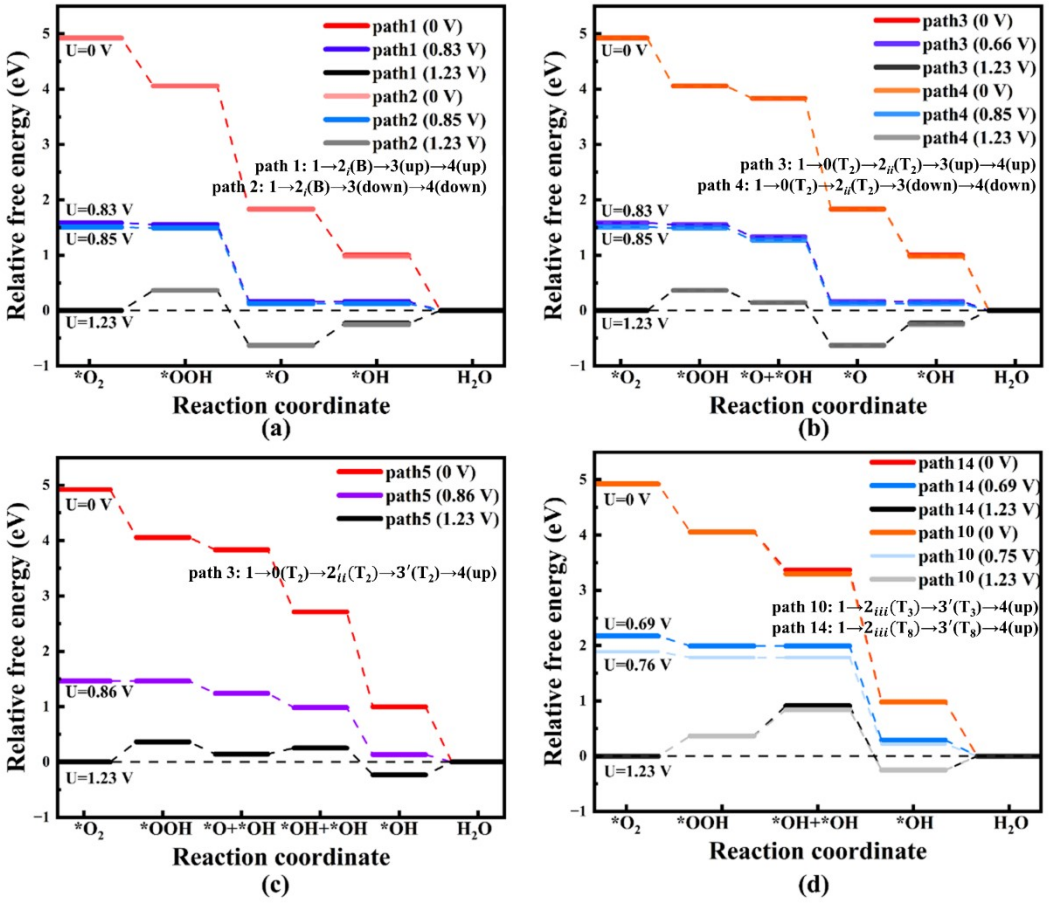

Fig. S9 Free-energy diagrams for ORR on $NiPdN_6$-G in (a) paths 1 and 2; (b) paths 3 and 4; (c) path 5; (d) paths 10 and 14.

The formation energy (E_{f1}) for evaluating the structural stability, was calculated by the following equation

$$E_{f_1} = E_{NiPdN_6\text{-}G} - E_{Ni} - E_{Pd} - 6\mu_N - 40\mu_C \text{ * MERGEFORMAT (S1)}$$

or

$$E_{f_1} = E_{MN_4\text{-}G} - E_M - 4\mu_N - 44\mu_C \text{ * MERGEFORMAT (S2)}$$

Where $E_{NiPdN_6\text{-}G}$ is the total energy of $NiPdN_6$-G DAC, while E_{MN_4-G} is the total energy of NiN_4-G or PdN_4-G SAC. E_{Ni} and E_{Pd} are the energies of isolated Ni and Pd atoms in vacuum, and E_M takes above value as appropriate. The chemicalpotentials of C and N atoms are denoted as μ_C and μ_N, which are derived from nitrogen gas and pristine graphene.

Besides E_{f1}, the formation energy (E_{f2}) was also calculated to evaluate the thermodynamic for $NiPdN_6$-G, as following equation

$$E_{f_{Ni}} = E_{NiPdN_6\text{-}G} - E_{PdN_6\text{-}G} - E_{Ni} \text{ * MERGEFORMAT (S3)}$$

and

$$E_{f_{Pd}} = E_{NiPdN_6\text{-}G} - E_{NiN_6\text{-}G} - E_{Pd} \text{ * MERGEFORMAT (S4)}$$

where $E_{f_2\text{-}Ni}$ and $E_{f_2\text{-}Pd}$ are the total energy of single Ni or Pd atom doped N-coordinated graphene.

The dissolution potential (U_{diss}) were also used to evaluate the electrochemical stabilities using the follow equation

$$U_{diss} = U^0_{diss}(metal,bulk) - \frac{E_{f_2}}{eN_e} \text{ * MERGEFORMAT (S5)}$$

Where $U^0_{diss}(metal,bulk)$ is the standard dissolution potential of bulk metal, N_e is the number of electrons during the dissolution, respectively.

The binding energy (E_b) between two metal atoms and substrate, and the cohesive energy (E_{coh}) were calculated respectively using the following equations

$$E_b = \frac{E_{NiPdN_6\text{-}G} - E_{Ni} - E_{Pd} - E_{N_6\text{-}G}}{2} \text{ * MERGEFORMAT (S6)}$$

$$E_{\mathrm{b}} = E_{\mathrm{MN_4\text{-}G}} - E_{\mathrm{M}} - E_{\mathrm{N_4\text{-}G}} \quad \backslash* \text{ MERGEFORMAT (S7)}$$

and

$$E_{\mathrm{coh}} = \frac{E_{\mathrm{Ni(bulk)}} + E_{\mathrm{Pd(bulk)}} - E_{\mathrm{Ni}} - E_{\mathrm{Pd}}}{2} \backslash* \text{ MERGEFORMAT (S8)}$$

$$E_{\mathrm{coh}} = E_{\mathrm{M(bulk)}} - E_{\mathrm{M}} \quad \backslash* \text{ MERGEFORMAT (S9)}$$

The charge density difference plots were calculated using the following equation:

$$\Delta\rho(r) = \rho(r)_{\mathrm{NiPdN_6\text{-}G}} - \rho(r)_{\mathrm{Ni+Pd}} - \rho(r)_{\mathrm{N_6\text{-}G}}$$

where $\rho(r)_{\mathrm{NiPdN_6\text{-}G}}$ is the charge density of $NiPdN_6$-G catalyst. $\rho(r)_{\mathrm{Ni+Pd}}$ is the charge densities of Ni and Pd atoms. $\rho(r)_{\mathrm{N_6\text{-}G}}$ is the charge density of the N-doped graphene.

References

1. W. Chen, J. Huang, J. Wei, D. Zhou, J. Cai, Z. D. He and Y. X. Chen, *Electrochem. Commun.*, 2018, **96**, 71-76.
2. H. A. Gasteiger, S. S. Kocha, B. Sompalli and F. T. Wagner, *Appl. Catal., B*, 2005, **56**, 9-35.