Electronic Supplementary Information

Theoretical study of Au–N_X–C catalysts for H_2O_2 electrosynthesis via two-electron oxygen reduction reaction

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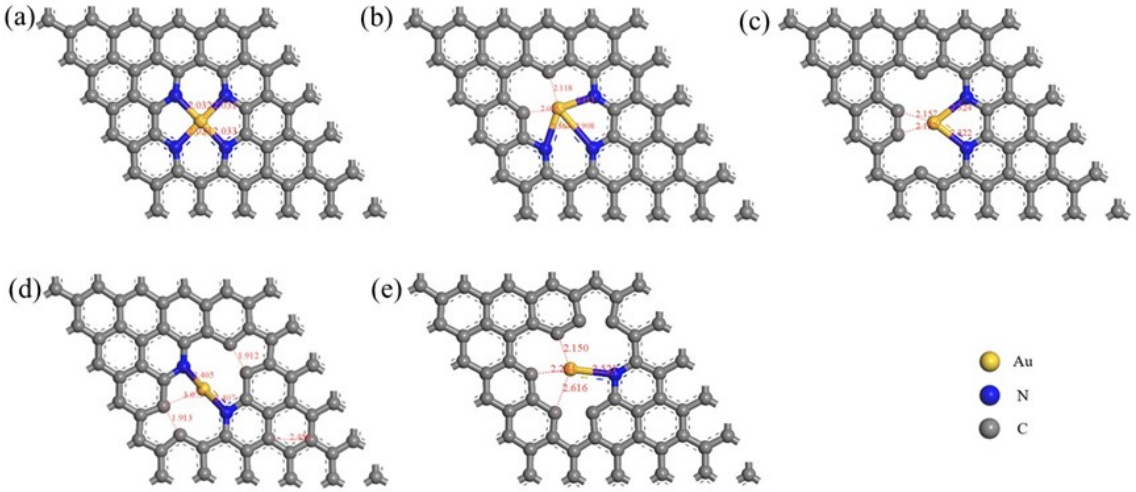

Figure S1 top view of Au–N_X–C (X = 1, 2, 3, 4) embedded graphene depicting the bond distance: (a) Au–N_4–C, (b) Au–N_3–C, (c) Au–N_2–C_{ortho}, (d) Au–N_2–C_{para}, (e) Au–N_1–C.

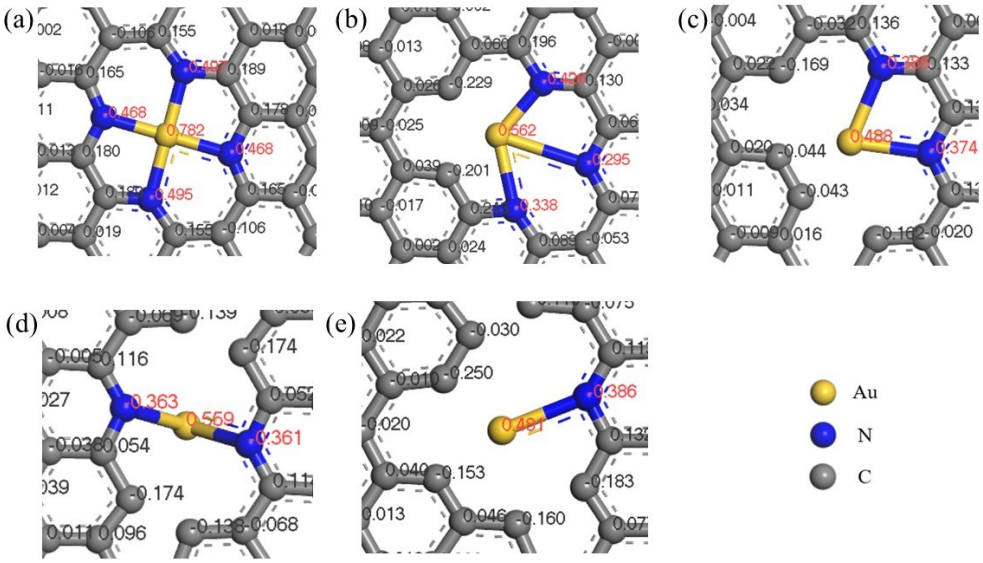

Figure S2 Charge population of Au–N_X–C: (a) Au–N_4–C, (b) Au–N_3–C, (c) Au–N_2–C_{ortho}, (d) Au–N_2–C_{para}, and (e) Au–N_1–C.

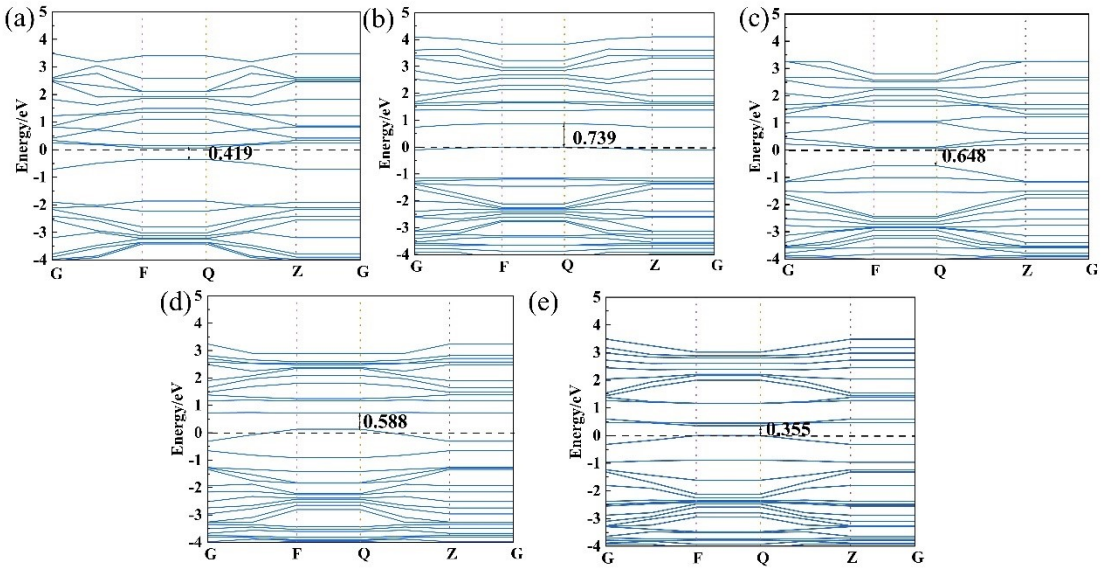

Figure S3 Energy band diagram of Au–N_X–C, (a) Au–N_4–C, (b) Au–N_3–C, (c) Au–N_2–C_{ortho}, (d) Au–N_2–C_{para}, and (e) Au–N_1–C.

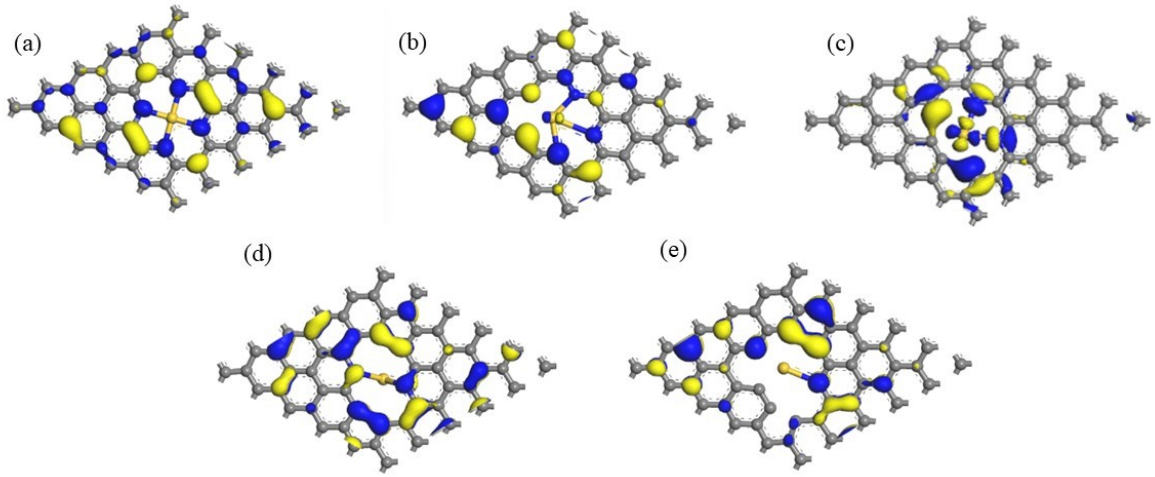

Figure S4 Highest occupied molecular orbitals in (a) Au–N_4–C, (b) Au–N_3–C, (c) Au–N_2–C_{ortho}, (d) Au–N_2–C_{para}, and (e) Au–N_1–C.

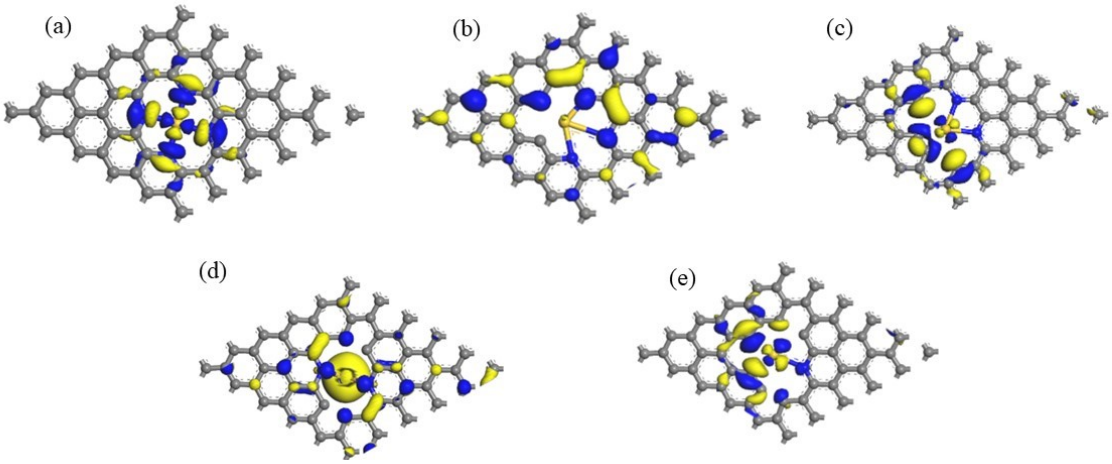

Figure S5 Lowest unoccupied molecular orbitals in (a) Au–N_4–C, (b) Au–N_3–C, (c) Au–N_2–C_{ortho}, (d) Au–N_2–C_{para}, and (e) Au–N_1–C.

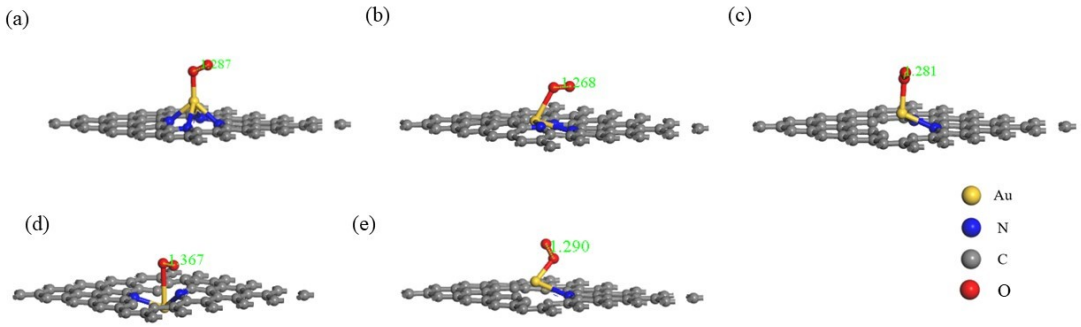

Figure S6 Side view of the optimized configuration of O_2 adsorption on Au–N_X–C: (a) Au–N_4–C, (b) Au–N_3–C, (c) Au–N_2–C_{ortho}, (d) Au–N_2–$C_{para,}$; and (e) Au–N_1–C.

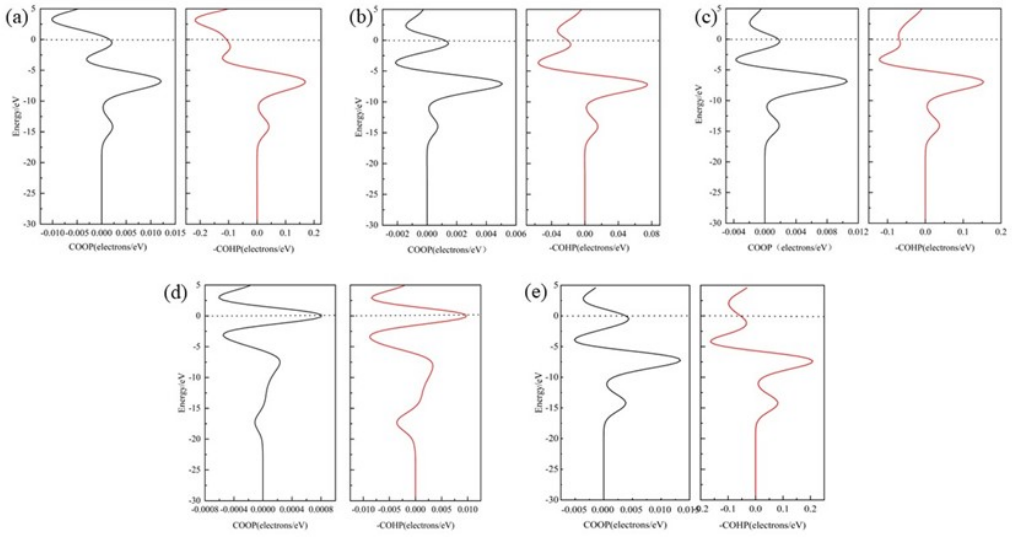

Figure S7 Crystal orbital overlap population (COOP) and crystal orbital Hamilton population (COHP) of Au–N_X–C: (a) Au–N_4–C, (b) Au–N_3–C, (c) Au–N_2–C_{ortho}, (d) Au–N_2–C_{para}, and (e) Au–N_1–C.

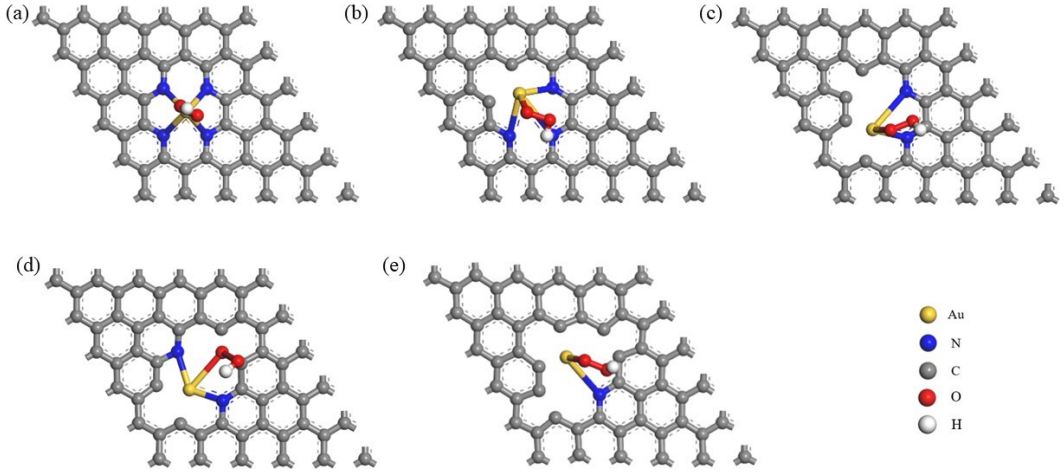

Figure S8 The structure-optimized model of OOH adsorbed on Au–N_x–C: (a) Au–N_4–C, (b) Au–N_3–C, (c) Au–N_2–C_{ortho}, (d) Au-N_2-C_{para}, and (e) Au-N_1-C.

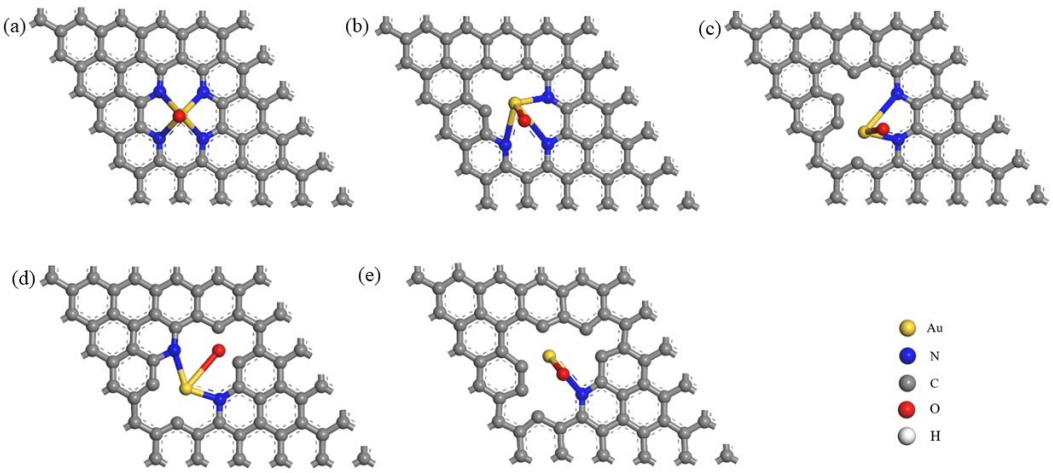

Figure S9 The structure-optimized model of O adsorbed on Au–N_x–C: (a) Au–N_4–C, (b) Au–N_3–C, (c) Au–N_2–C_{ortho}, (d) Au–N_2–C_{para}, and (e) Au–N_1–C.

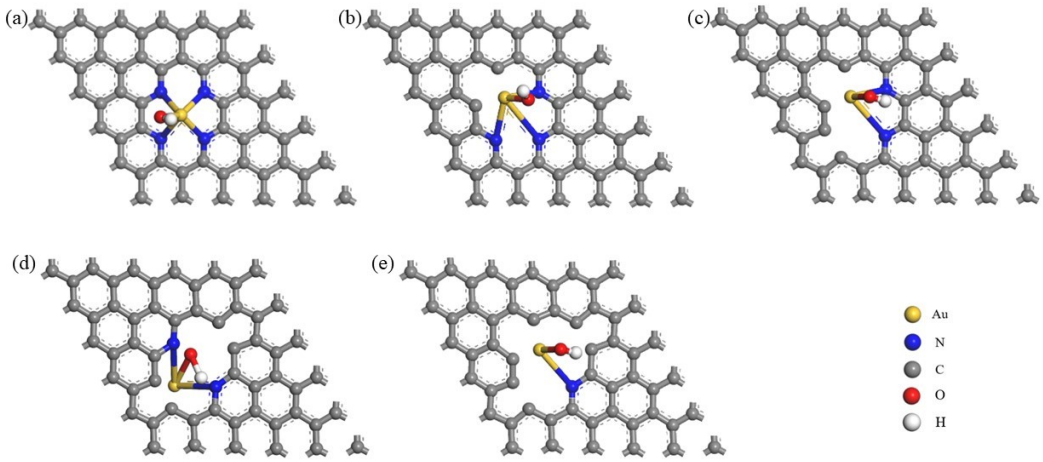

Figure S10 The structure-optimized model of *OH adsorbed on Au–N_x–C: (a) Au–N_4–C, (b) Au–N_3–C, (c) Au–N_2–C_{ortho}, (d) Au–N_2–C_{para}, and (e) Au–N_1–C.

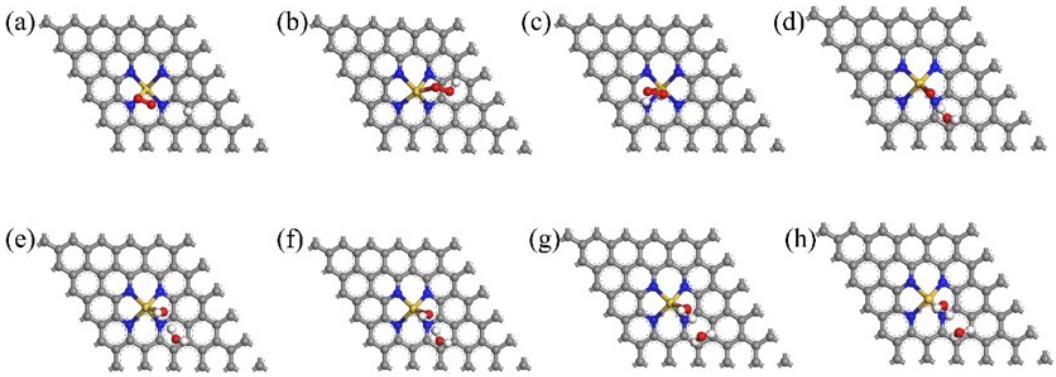

Figure S11 $4e^-$ ORR pathway of the OOH dissociation on Au–N_4–C: (a) O_2* + H^+ + e^-, (b) OOH*, (c) OOH* + H^+ + e^-, (d) H_2O + O*, (e) O* + H^+ + e^- + H_2O, (f) OH* + H_2O, (g) OH* + H^+ + e^- + H_2O, (h) $2H_2O$.

Table S1 The calculation process for free energy on Au-N_4-C at different electrode potentials

	U=0V		
	ΔE+ TΔS+ΔZPE (eV)	ΔG_U (eV)	ΔG (eV)
O_2*	4.92	0	4.92
OOH*	2.130	0	2.130
O*	2.128	0	2.128
OH*	2.127	0	2.127
H_2O*	0	0	0
	U=1.23V		
O_2*	4.92	1.23*4	0
OOH*	2.130	1.23*3	-1.560
O*	2.128	1.23*2	-0.331
OH*	2.127	1.23*1	0.897
H_2O*	0	1.23*0	0
	U=0.68V		
O_2*	4.92	0.68*2	3.560
OOH*	2.130	0.68*1	1.450
H_2O_2	3.560	0.68*0	3.560

Table S2 The calculation process for free energy on Au-N_3-C at different electrode potentials

	U=0V		
	ΔE+ TΔS+ΔZPE (eV)	ΔG_U (eV)	ΔG (eV)
O_2*	4.92	0	4.92
OOH*	4.742	0	4.742
O*	4.428	0	4.428
OH*	4.265	0	4.265
H_2O*	0	0	0
	U=1.23V		
O_2*	4.92	1.23*4	0
OOH*	4.742	1.23*3	-0.178
O*	4.428	1.23*2	1.968
OH*	4.265	1.23*1	3.035
H_2O*	0	1.23*0	0
	U=0.68V		
O_2*	4.92	0.68*2	3.560
OOH*	4.742	0.68*1	4.062
H_2O_2	3.560	0.68*0	3.560

Table S3 The calculation process for free energy on Au-N_2-C_{ortho} at different electrode potentials

	U=0V		
	ΔE+ TΔS+ΔZPE (eV)	ΔG_U (eV)	ΔG (eV)
O_2*	4.92	0	4.92
OOH*	4.098	0	4.098
O*	3.641	0	3.641
OH*	3.645	0	3.645
H_2O*	0	0	0
	U=1.23V		
O_2*	4.92	1.23*4	0
OOH*	4.098	1.23*3	-0.822
O*	3.641	1.23*2	1.181
OH*	3.645	1.23*1	2.415
H_2O*	0	1.23*0	0
	U=0.68V		
O_2*	4.92	0.68*2	3.560
OOH*	4.098	0.68*1	3.398
H_2O_2	3.560	0.68*0	3.560

Table S4 The calculation process for free energy on Au-N_2-C_{para} at different electrode potentials

	U=0V		
	ΔE+ TΔS+ΔZPE (eV)	ΔG_U (eV)	ΔG (eV)
O_2*	4.92	0	4.92
OOH*	5.489	0	5.489
O*	5.459	0	5.459
OH*	5.454	0	5.454
H_2O*	0	0	0
	U=1.23V		
O_2*	4.92	1.23*4	0
OOH*	4.098	1.23*3	0.569
O*	3.641	1.23*2	2.999
OH*	3.645	1.23*1	4.224
H_2O*	0	1.23*0	0
	U=0.68V		
O_2*	4.92	0.68*2	3.560
OOH*	5.489	0.68*1	4.789
H_2O_2	3.560	0.68*0	3.560

Table S5 The calculation process for free energy on Au-N_1-C at different electrode potentials

	U=0V		
	ΔE+ TΔS+ΔZPE (eV)	ΔG_U (eV)	ΔG (eV)
O_2*	4.92	0	4.92
OOH*	4.455	0	4.455
O*	2.668	0	2.668
OH*	2.620	0	2.620
H_2O*	0	0	0
	U=1.23V		
O_2*	4.92	1.23*4	0
OOH*	4.455	1.23*3	-0.465
O*	2.668	1.23*2	0.208
OH*	2.620	1.23*1	1.390
H_2O*	0	1.23*0	0
	U=0.68V		
O_2*	4.92	0.68*2	3.560
OOH*	4.455	0.68*1	3.775
H_2O_2	3.560	0.68*0	3.560