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

Supporting Information

O_2 and H_2O_2 Transformation Steps for Oxygen Reduction Reaction Catalyzed by Graphitic Nitrogen-doped Carbon Nanotubes in Acidic Electrolyte from First Principles Calculations

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Table S1 The values of energy variations and transition states energy gaps for the whole ORR paths.

Initial	TS	Final	E_{gap} of TS / eV	E_{bar} / eV	E_{rea} / eV
Oxygen Adsorption					
OO23 (v)	OTS0-1	OO23	0	0.309	-0.341
OO1 (v)	OTS0-2	OO1	0	0.113	0.105
The First Electron					
OO23	OTS1-1	OOH3	0	0.286	-2.204
OO23	OTS1-2	O(OH)32	0	1.474	-4.283
OO1	-	OOH1	-	0	-2.357
The Second Electron					
OOH3	OTS2-1	H_2O_2	0	0.313	-1.839
OOH3	-	O3	-	0	-4.143
OOH3	OTS2-2	OH(OH)23	0.052	0.191	-4.177
OH(OH)23	OTS2-3	H_2O_2	0	3.072	2.253
OOH1	OTS2-4	H_2O_2	0.09	0.553	-1.660
OOH1	OTS2-5	O1	0.05	0.231	-3.949
OOH3	OTS2-6	OH(OH)35	0.065	1.803	-3.937
OH(OH)35	OTS2-7	H_2O_2	0	3.117	2.333
O(OH)32	OTS2-8	O3	0.105	1.592	-1.595
O(OH)32	-	OH(OH)23	-	0	-1.591
The Third Electron					
O3	-	OH3	-	0	-2.036
O1	-	OH1	-	0	-1.957
OH(OH)23	OTS3-1	OH3	0	1.032	-2.357
OH(OH)35	OTS3-2	OH3	0	0.573	-2.256
The Fourth Electron					
OH3	OTS4-1	H_2O	0.021	0.729	-2.061
OH1	OTS4-2	H_2O	0.042	0.845	-1.875

$E_{bar} = E(TS) - E(Initial)$; $E_{rea} = E(Final) - E(Initial)$; $E_{gap} = E(Condution\ Edge) - E(Valence\ Edge)$

Table S2 The values of energy variations and transition states energy gaps for the whole HPRR paths.

Initial	TS	Final	Gap of TS / eV	E_{bar} / eV	E_{rea} / eV
Hydrogen Peroxide Adsorption					
H_2O_2	PTS0-1	OH(OH)23	0	0.819	-2.253
H_2O_2	PTS0-2	OH(OH)35	0	0.784	-2.333
OOH&H_3O	-	OOH(H)38	-	0	-1.534
The First Electron					
OOH(H)38	-	OH3	-	0	-6.086
OOH(H)38	-	O(H)38	-	0	-4.561
O(H)38	PTS1-1	OH3	0	0.672	-1.368
OH(OH)23	OTS3-1	OH3	0	1.032	-2.357
OH(OH)35	OTS3-2	OH3	0	0.573	-2.256
The Second Electron					
O(H)38	PTS2-1	H_2O	0.218	0.690	-3.138
O(H)38	-	OH(H)38	-	0	-1.768
OH(H)38	PTS2-2	H_2O	0.208	0.843	-1.530
OH3	OTS4-1	H_2O	0.021	0.729	-2.061

$E_{bar} = E(TS) - E(Initial)$; $E_{rea} = E(Final) - E(Initial)$; $E_{gap} = E(Condution\ Edge) - E(Valence\ Edge)$

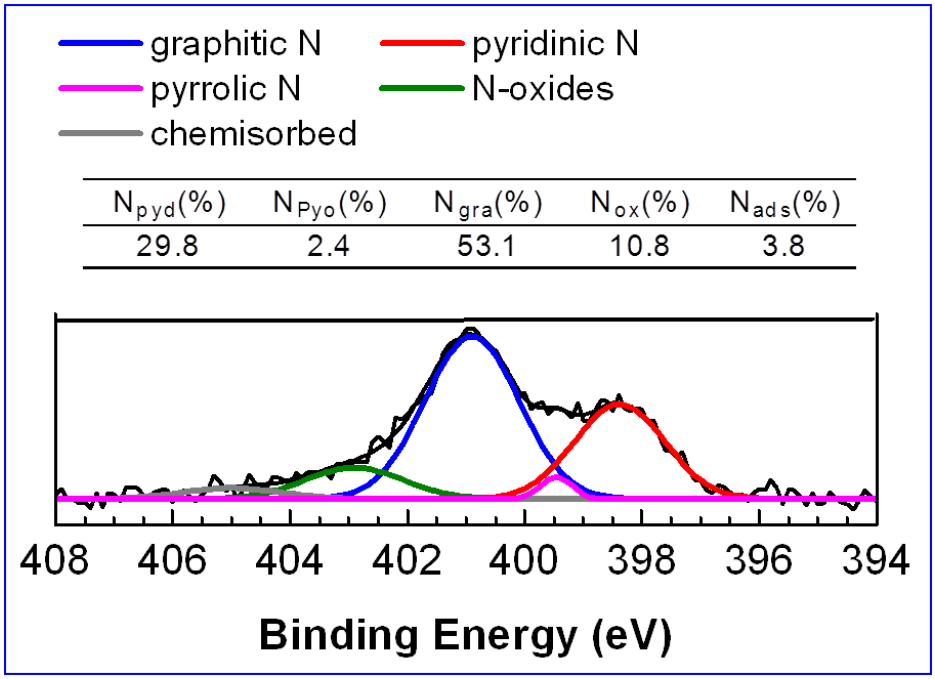

Fig. S1 The N 1s XPS analysis of NCNTs[s1].

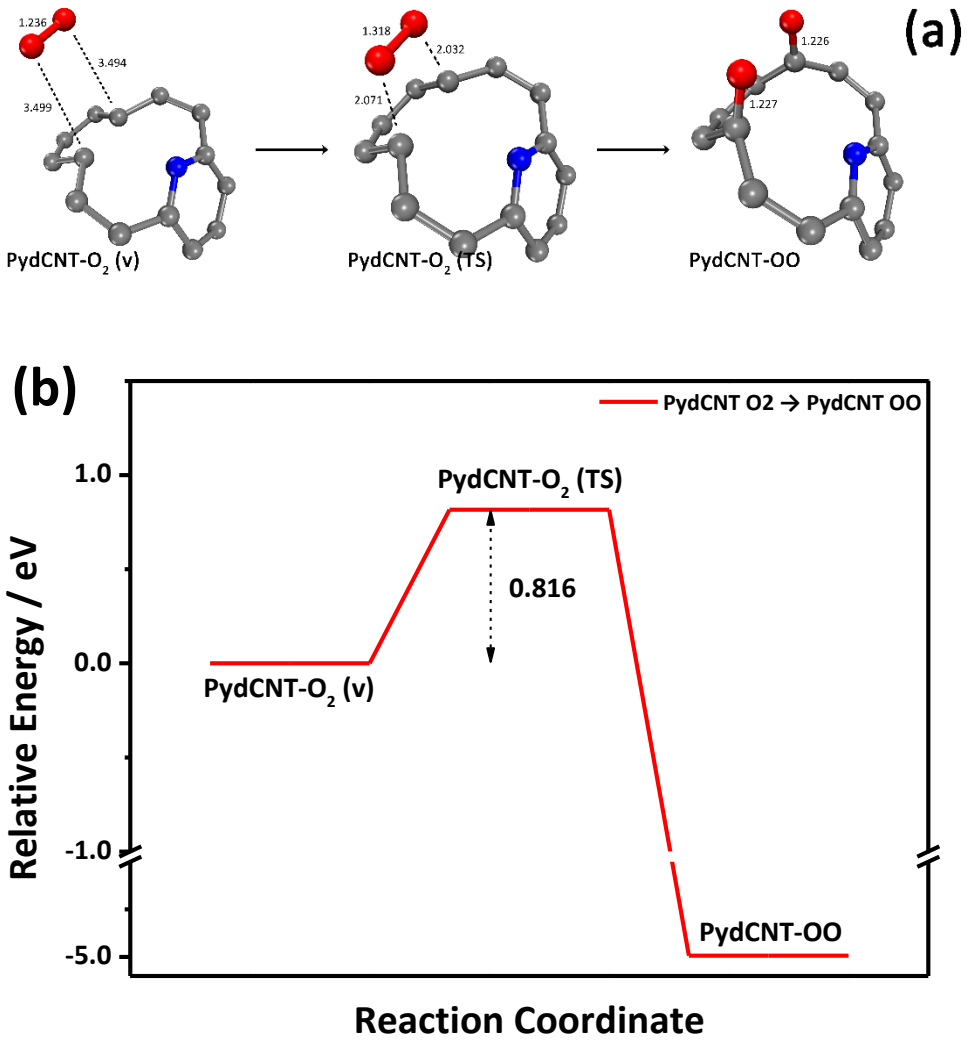

Fig. S2 (a) The configuration variation and (b) the energy evolution for the oxygen adsorption over pyridinic nitrogen doped CNTs.

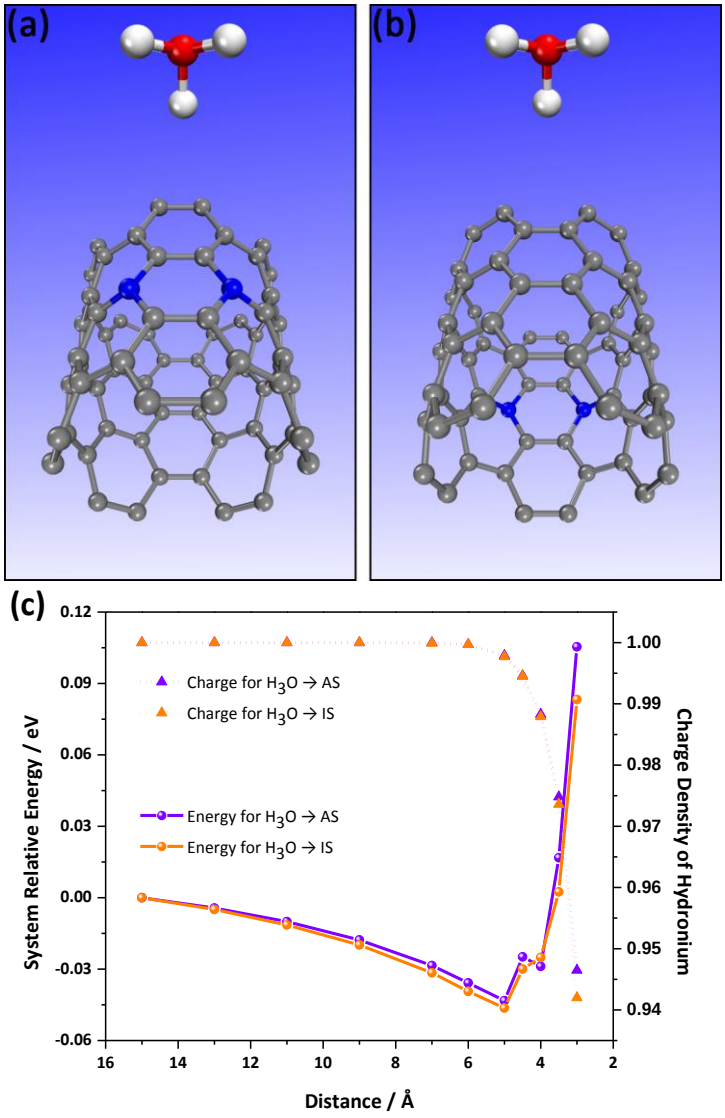

Fig. S3 (a, b) Sketches of migration orientations. The red ball is oxygen and the white ball is hydrogen. (c) Evolutions of system energy and hydronium charge, where distance is the length between hydronium and nanotube surface ranging from 15 Å to 3 Å. Two situations are considered, where hydronium gets close to AS and IS, respectively. AS means the area around nitrogen atoms while IS means the opposite surface to nitrogen.

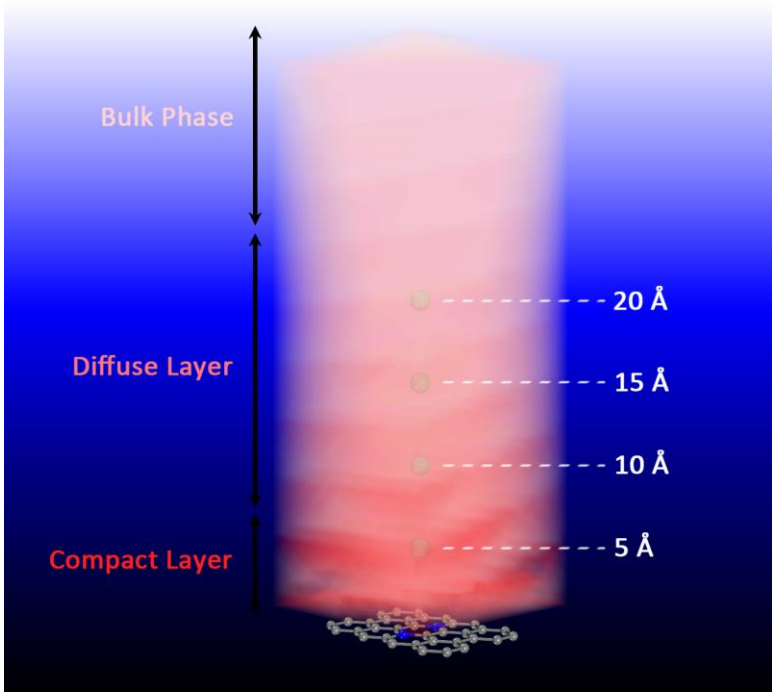

Fig. S4 The COSMO field over graphitic N-doped graphene with one electron. The color map ranging from red to white stands for the positive potential (screening charge) from 0.2 to 0. Distance values mean the positions over active sites of graphene.

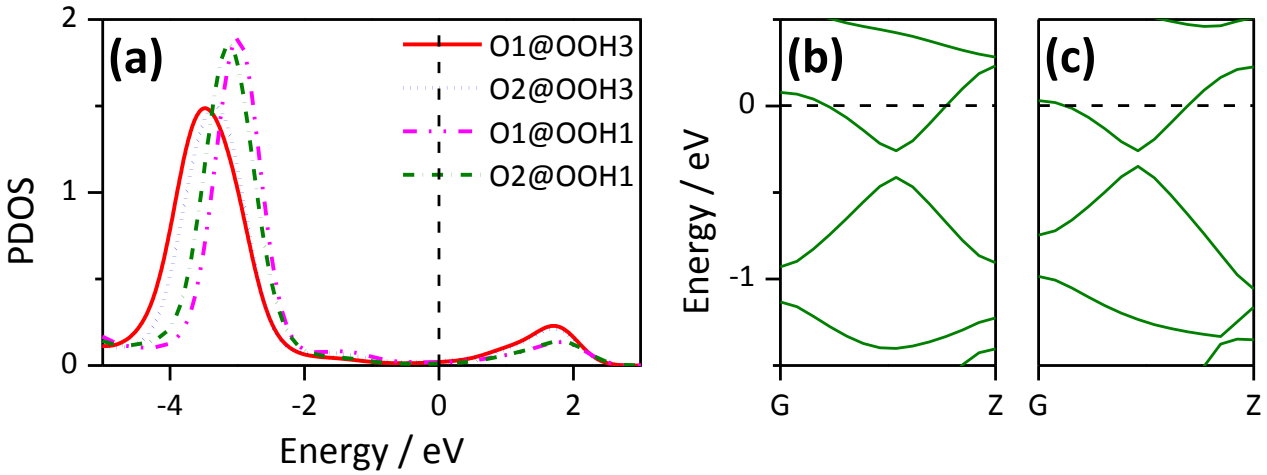

Fig. S5 (a) PDOS of oxygen atoms in different intermediates. Band structures of (b) OOH3 and (c) OOH1.

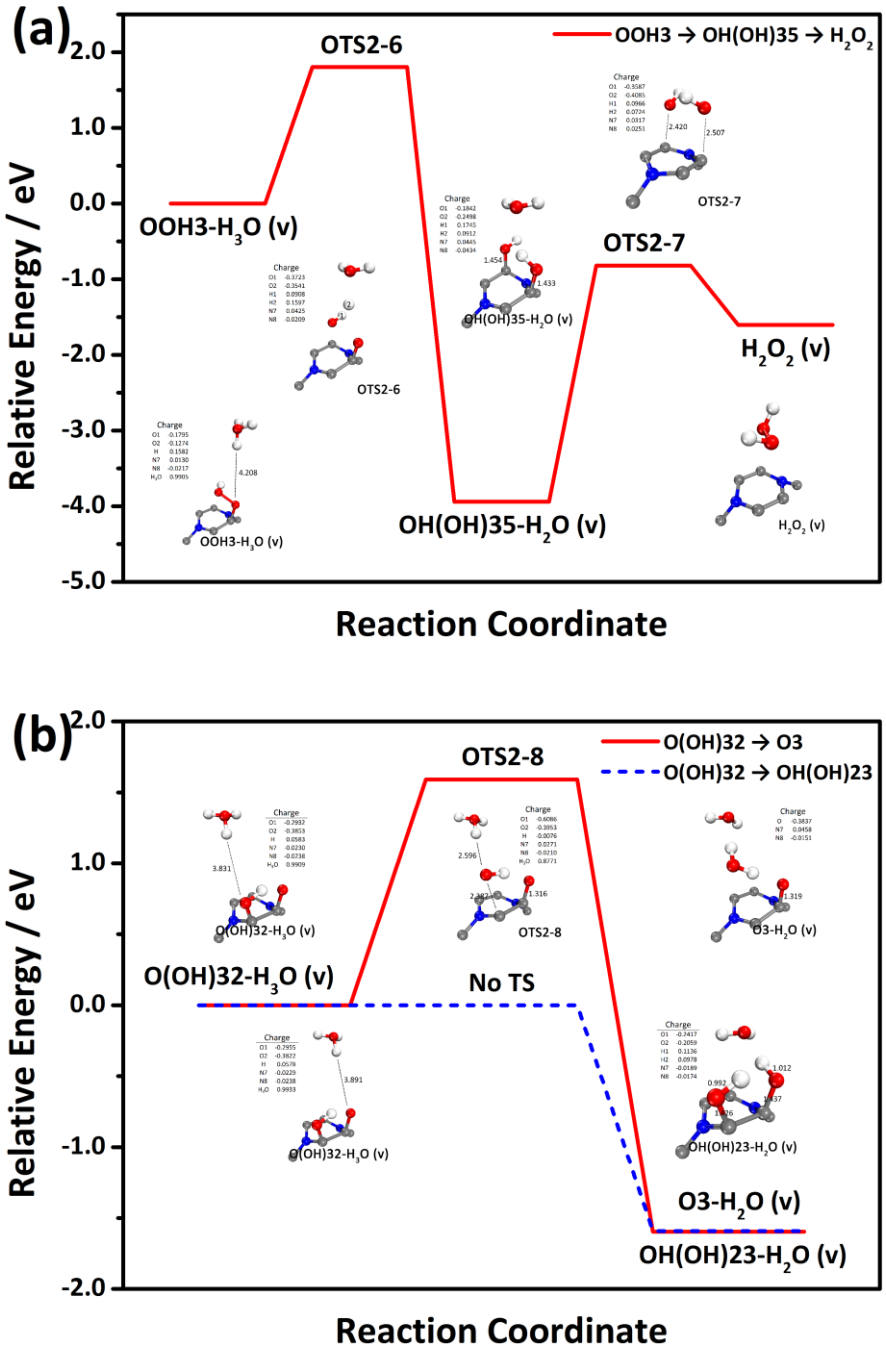

Fig. S6 Unlikely energy evolutions for the second electron reaction in ORR from the initial systems (a) OOH3 and (b) O(OH)32.

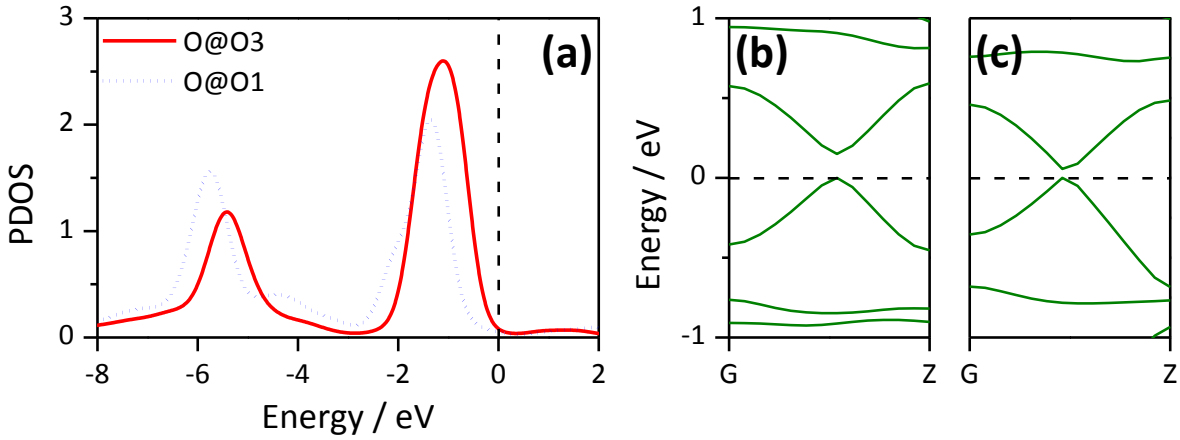

Fig. S7 (a) PDOS of oxygen atoms in O3 and O1. Band structures of (b) O3 and (c) O1.

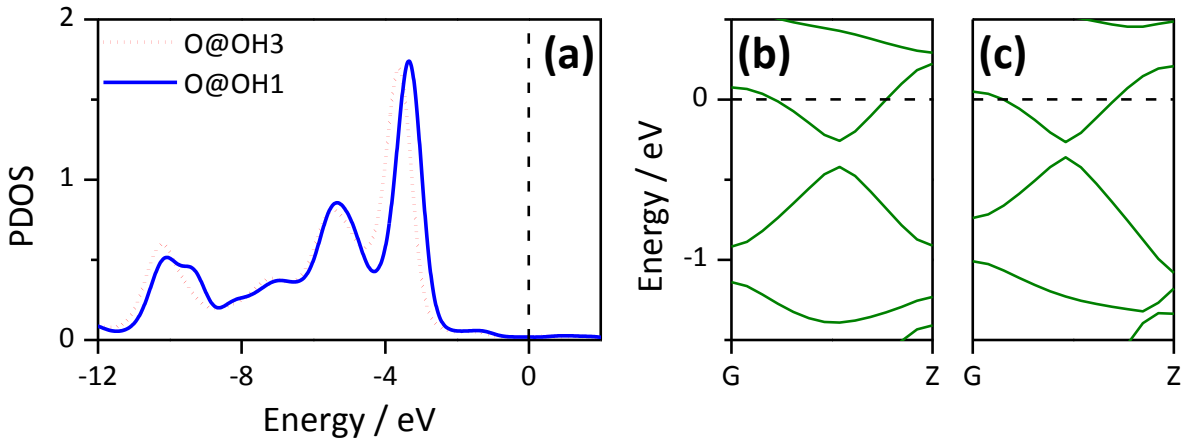

Fig. S8 (a) PDOS of oxygen atoms in OH3 and OH1. Band structures of (b) OH3 and (c) OH1.

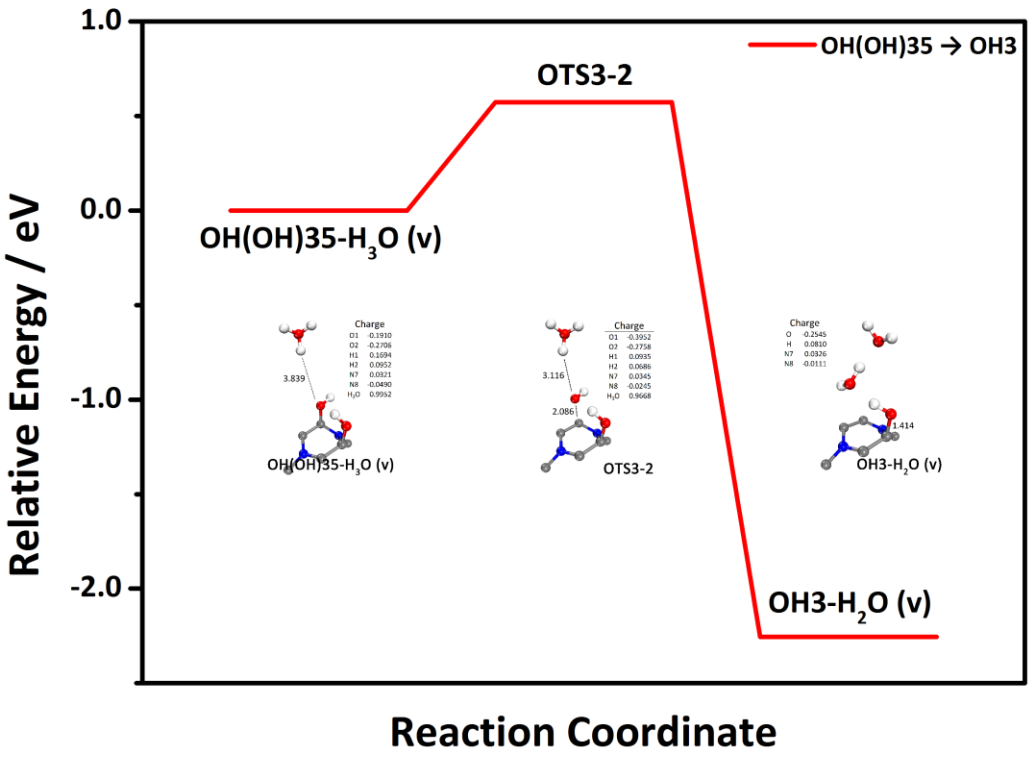

Fig. S9 Unlikely energy evolutions for the third electron reaction in ORR from the initial system OH(OH)35.

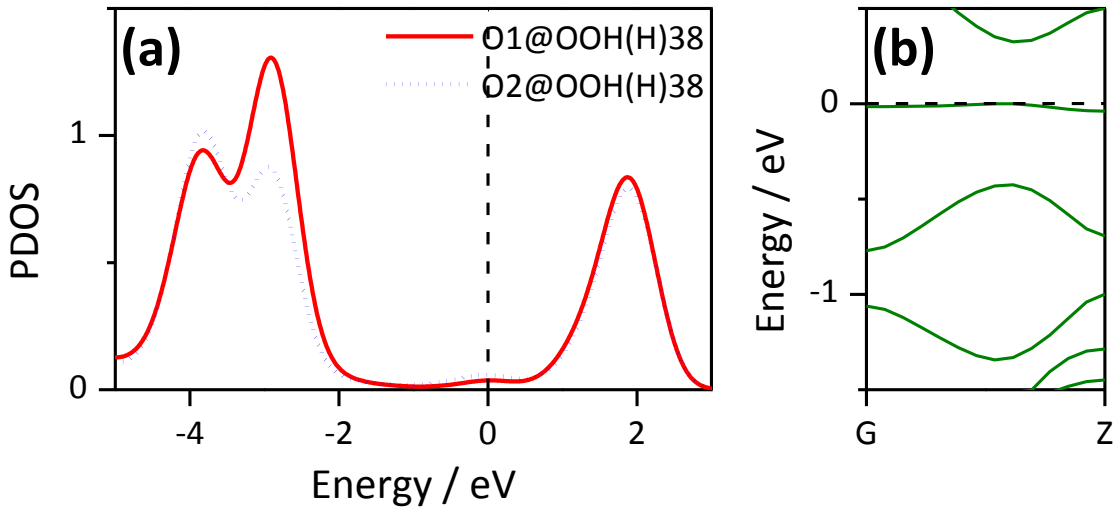

Fig. S10 (a) PDOS of oxygen atoms in OOH(H)38. (b) The band structure of OOH(H)38.