

Supporting Information

The Active Structure of *p*-block SnNC Single-Atom Electrocatalysts for Oxygen Reduction Reaction

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Computational details

The detailed pathways for classical 4e⁻ pathway in ORR was adopted in our work as the following five steps:



Therefore, considering the effect of electrode potential (U), the equation of reaction free energy of reaction SR1-SR5 is given:

$$\Delta G_1 = G_{O_2^*} - G_{O_2} - G_* \quad (S1a)$$

$$\Delta G_2 = G_{OOH^*} - G_{O_2^*} - 1/2G_{H_2} + eU \quad (S1b)$$

$$\Delta G_3 = G_{O^*} + G_{H_2O} - G_{OOH^*} - 1/2G_{H_2} + eU \quad (S1c)$$

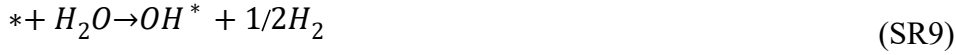
$$\Delta G_4 = G_{OH^*} - G_{O^*} - 1/2G_{H_2} + eU \quad (S1d)$$

$$\Delta G_5 = G_* + G_{H_2O} - G_{OH^*} - 1/2G_{H_2} + eU \quad (S1e)$$

Owing to the high-spin ground state of the O₂ molecule, the energy of triplet O₂ molecule is poorly described in DFT computations, consequently, the free energy of O₂ molecule (G_{O_2}) is derived as $G_{O_2} = 2G_{H_2O} - 2G_{H_2} + 4.92 \text{ eV}$.

To calculate the adsorption free energy of oxygen intermediates (O₂^{*}, OOH^{*}, O^{*} and OH^{*}), the reaction free energy of eqs SR6-SR9 are calculated.





After that, the Gibbs reaction free energy of eqs SR6-SR9 can be defined as:

$$\Delta G_{O_2^*} = 2G_{H_2} + G_{O_2^*} - 2G_{H_2O} - G_* \quad (S2a)$$

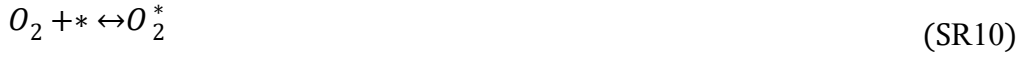
$$\Delta G_{OOH^*} = 3/2G_{H_2} + G_{OOH^*} - 2G_{H_2O} - G_* \quad (S2b)$$

$$\Delta G_{O^*} = G_{O^*} + G_{H_2} - G_{H_2O} - G_* \quad (S2c)$$

$$\Delta G_{OH^*} = G_{OH^*} + 1/2G_{H_2} - G_{H_2O} - G_* \quad (S2d)$$

The detailed pathways for conventional O₂ dissociative mechanism (O* mechanism)

in ORR on the SnNC surface was adopted in our work as the following six steps:



Therefore, considering the effect of electrode potential (U), the equation of reaction free energy of reaction SR10-SR15 is given:

$$\Delta G_1 = G_{O_2^*} - G_{O_2} - G_* \quad (S3a)$$

$$\Delta G_2 = G_{O^*} + G_{O^*} - G_{O_2^*} \quad (S3b)$$

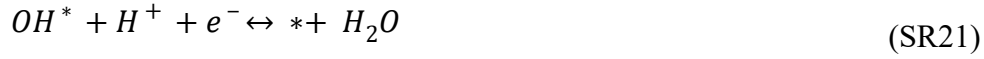
$$\Delta G_3 = G_{O^*} + G_{OH^*} - G_{O^*} + G_{O^*} - 1/2G_{H_2} + eU \quad (S3c)$$

$$\Delta G_4 = G_{O^*} + G_{H_2O} - G_{O^*} + G_{OH^*} - 1/2G_{H_2} + eU \quad (S3d)$$

$$\Delta G_5 = G_{OH^*} - G_{O^*} - 1/2G_{H_2} + eU \quad (S3e)$$

$$\Delta G_6 = G_* + G_{H_2O} - G_{OH^*} - 1/2G_{H_2} + eU \quad (S3f)$$

The detailed pathways for O₂ dissociative mechanism (2OH* mechanism) in ORR on the SnNC surface was adopted in our work as the following six steps:



Therefore, considering the effect of electrode potential (U), the equation of reaction free energy of reaction SR16-SR21 is given:

$$\Delta G_1 = G_{O_2^*} - G_{O_2} - G_* \quad (S4a)$$

$$\Delta G_2 = G_{O^* + O^*} - G_{O_2^*} \quad (S4b)$$

$$\Delta G_3 = G_{O^* + OH^*} - G_{O^* + O^*} - 1/2G_{H_2} + eU \quad (S4c)$$

$$\Delta G_4 = G_{2OH^*} - G_{O^* + OH^*} - 1/2G_{H_2} + eU \quad (S4d)$$

$$\Delta G_5 = G_{OH^*} + G_{H_2O} - G_{2OH^*} - 1/2G_{H_2} + eU \quad (S4e)$$

$$\Delta G_6 = G_* + G_{H_2O} - G_{OH^*} - 1/2G_{H_2} + eU \quad (S4f)$$

The detailed pathway for conventional 2e⁻ mechanism on the SnNC surface in ORR was adopted in our work as the following three steps:



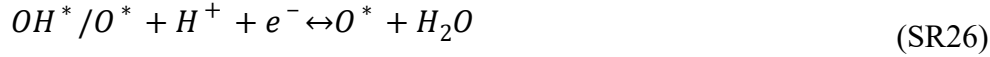
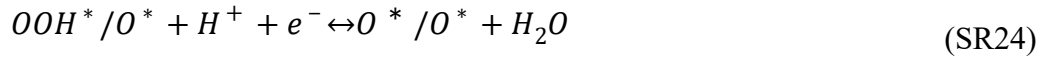
Therefore, considering the effect of electrode potential (U), the reaction free energy of SR1'-SR3' can be calculated by:

$$\Delta G_1 = G_{O_2^*} - G_{O_2} - G_*$$
 (S5a)

$$\Delta G_2 = G_{OOH^*} - G_{O_2} - 1/2G_{H_2} + eU$$
 (S5b)

$$\Delta G_3 = G_{H_2O_2} + G_* - G_{OOH^*} - 1/2G_{H_2} + eU$$
 (S5c)

The detailed pathways for classical associative pathway on SnN₃C₁-O, SnN₁C₃-O in ORR was adopted in our work as the following five steps:



Therefore, considering the effect of electrode potential (U), the equation of reaction free energy of reaction SR22-SR26 is given:

$$\Delta G_1 = G_{O_2^*/O^*} - G_{O_2/O^*} - G_*$$
 (S6a)

$$\Delta G_2 = G_{OOH^*/O^*} - G_{O_2^*/O^*} - 1/2G_{H_2} + eU$$
 (S6b)

$$\Delta G_2 = G_{O^*/O^*} + G_{H_2O} - G_{OOH^*/O^*} - 1/2G_{H_2} + eU$$
 (S6c)

$$\Delta G_3 = G_{OH^*/O^*} - G_{O^*/O^*} - 1/2G_{H_2} + eU$$
 (S6d)

$$\Delta G_4 = G_{O^*} + G_{H_2O} - G_{OH^*/O^*} - 1/2G_{H_2} + eU$$
 (S6e)

The detailed pathway for 2e⁻ mechanism on SnN₃C₁-O, SnN₁C₃-O in ORR was adopted in our work as the following three steps:





Therefore, considering the effect of electrode potential (U), the reaction free energy of SR22'-SR24' can be calculated by:

$$\Delta G_1 = G_{O_2^*/O^*} - G_{O_2/O^*} - G_* \quad (S7a)$$

$$\Delta G_2 = G_{OO H^*/O^*} - G_{O_2^*/O^*} - 1/2G_{H_2} + eU \quad (S7b)$$

$$\Delta G_3 = G_{H_2O_2} + G_{O^*} - G_{OO H^*/O^*} - 1/2G_{H_2} + eU \quad (S7c)$$

The calculated reaction free energy for all of the elementary reactions can then be used to plot the ORR free energy diagram. According to Norskov and coworkers, the highest potential at which all the reaction steps are downhill in free energy is called the thermodynamic limiting potential (U_L) and the difference between the equilibrium potential of $U = 1.23$ V and the limiting potential is called the theoretical overpotential (η). The theoretical limiting potential is determined by $U_L = -\max(\Delta G_1, \Delta G_2, \Delta G_3, \Delta G_4)/e$, and the maximum U_L of 1.23 V corresponds to zero overpotential. Besides, the elementary step with a maximum free energy change for the standard equilibrium potential has been termed the potential-determining step (PDS), which represents the unfavorable thermodynamics reaction step on the SnNC surface.

The change in reaction free energy under implicit solvation model is calculated as the following equation.

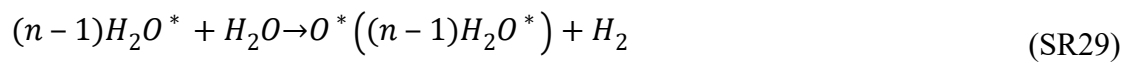
$$\Delta G_{imp} = \Delta E + \Delta E_{imp} + \Delta E_{ZPE} - T\Delta S + \Delta G_{pH} + \Delta G_U \quad (SR27)$$

Where ΔE , ΔE_{sol} , ΔE_{ZPE} , $T_{\Delta S}$ donate the change in electronic energy, implicit solvation correction, zero-point energy, entropy change at $T = 298.15K$, respectively. Additionally, ΔG_{pH} represents the change of free energy with the variation of H^+ concentration ($pH = 0$ under acid medium). $\Delta G_U = -eU$ is used to express the change of free energy caused by electrode potential (U).

The adsorption energies of the ORR intermediates in the presence of explicit water layer are calculated by replacing one water molecule from the first water layer with the adsorbate. The energy of the water molecule in the water layer structure is assumed to be the average energy of a water molecule in the water layer without adsorbate, defined as the following equation.

$$E^{WL}(H_2O) = \frac{1}{n}(E(nH_2O^*) - E(*)) \quad (SR28)$$

Where $E^{WL}(H_2O)$ and n are the average energy of a water molecule in the water layer and the number of water molecules in the water layer, respectively. $E(nH_2O^*)$ and $E(*)$ are the total energy of the catalyst surface with and without water bilayers, respectively. Whenever one adsorbate is placed on the catalyst surface, one water molecule is removed from the water layer. Consequently, the adsorption energies of ORR intermediates in equation S2a-2d in the main manuscript need a slight modification. For example, the adsorption energy of O^* intermediate as the presence of water can be rewritten as the following Equation.



$$\Delta G^{WL}(O^*) = G(O^* ((n-1)H_2O^*)) + G(H_2) - E((n-1)H_2O^*) - G(H_2O) \quad (SR30)$$

Where $\Delta G^{WL}(O^*)$ is the free adsorption energy of O^* intermediate with the presence of the explicit water layers. $G(O^*(n-1)H_2O^*)$ is the total free energy of the catalyst surface with O^* adsorbate at the active site and the explicit water layers (one water molecule in the first layer is removed and replaced by O^* adsorbate, so there are only $n-1$ water molecules left). $G(H_2)$ and $G(H_2O)$ are the free energy of hydrogen and water molecule, respectively. $E((n-1)H_2O^*)$ is calculated from the following Equation.

$$E((n-1)H_2O^*) = E(nH_2O^*) - E^{WL}(H_2O) \quad (\text{SR31})$$

It is assumed that the energy of a water molecule that is removed from the water layer is equal to the average energy of a water molecule in the water layer without the adsorbate. In this approach, the total number of adsorbates plus water molecules is kept constants in all cases to avoid the situation where inserted adsorbates push water molecules away from their stable position in a well-developed water layer.

Table S1. The calculated binding energies of Sn single atom on different structure (E_b), cohesive energies of Sn metal as reference to its bulk forms (E_{coh}) as well as the energy difference between E_b and E_{coh} (ΔE_b).

materials	E_b^1	ΔE_b^3	E_{coh}^2
Sn	-	-	-3.34
SnN₄	-5.10	-1.76	-
SnN₃C₁	-5.45	-2.11	-
SnN₂C₂-hex	-4.79	-1.45	-
SnN₂C₂-pen	-5.73	-2.39	-
SnN₂C₂-oppo	-5.95	-2.61	-
SnN₁C₃	-4.86	-1.52	-
SnC₄	-4.32	-0.98	-

1E_b is binding energy of single Sn atom on the graphene, which is calculated through

$E_b = E_{M+substrate} - E_{substrate} - E_M$, where the $E_{M+substrate}$, $E_{substrate}$ and E_M are the energies of Sn-N-C complex, pure substrate and metal atom (Sn).

${}^2E_{coh}$ is the cohesive energy of metal, which is calculated by,

$E_{coh} = (E_{M(bulk)} - nE_M)/n$, where the $E_{M(bulk)}$, n is the energy of metal crystal and the number of metal atom in the crystal, respectively.

${}^3\Delta E_b$ is the energy difference between E_b and E_{coh} .

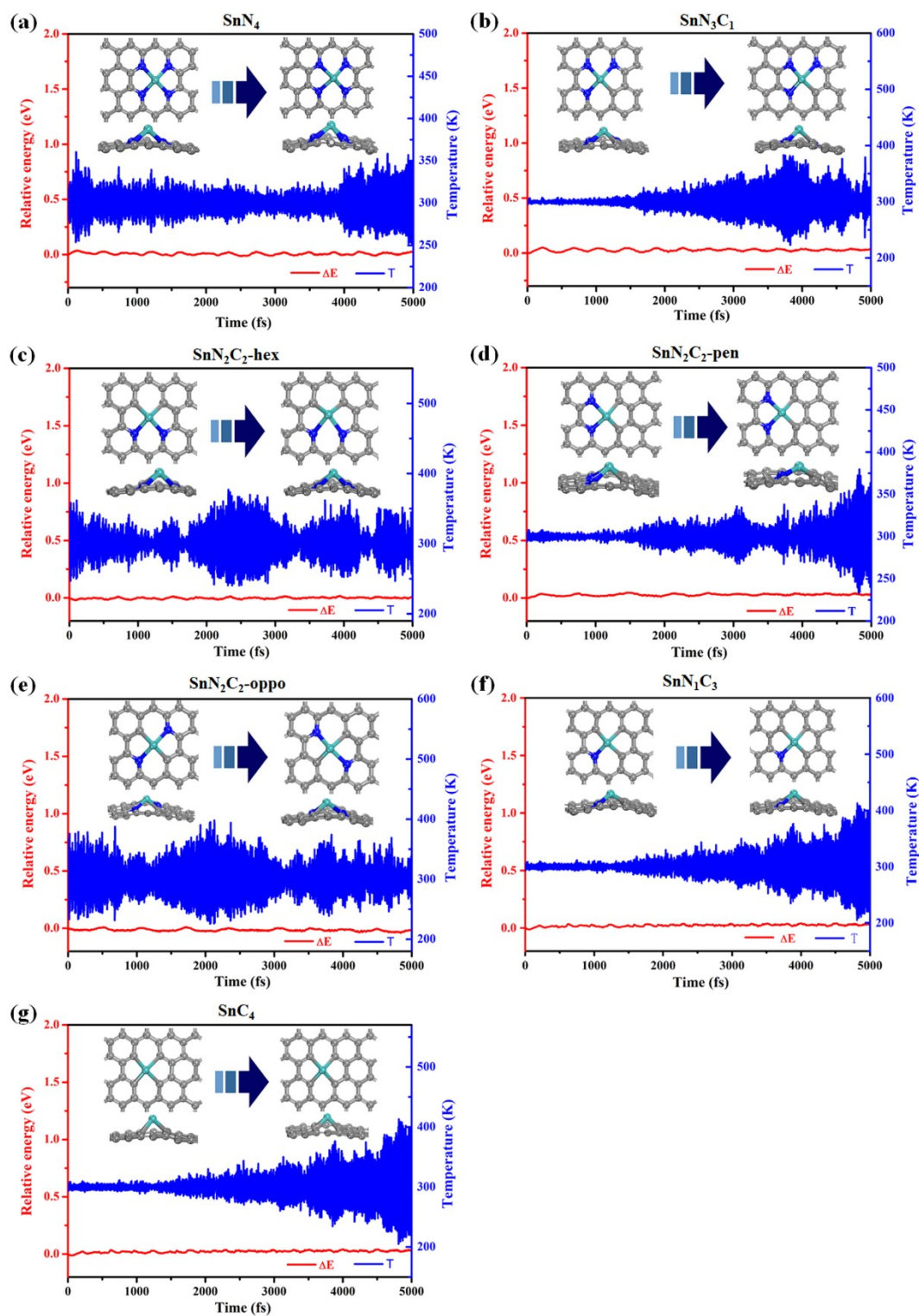


Figure S1. The AIMD simulation, the time step is 1fs and AIMD simulation is performed at 300K for 5 ps. SnN_4 (a), SnN_3C_1 (b), SnN_2C_2 -hex (c), SnN_2C_2 -pen (d), SnN_2C_2 -oppo (e), SnN_1C_3 (f), SnC_4 (g). Here, the relative energy of the initial

configuration is set to zero for reference.

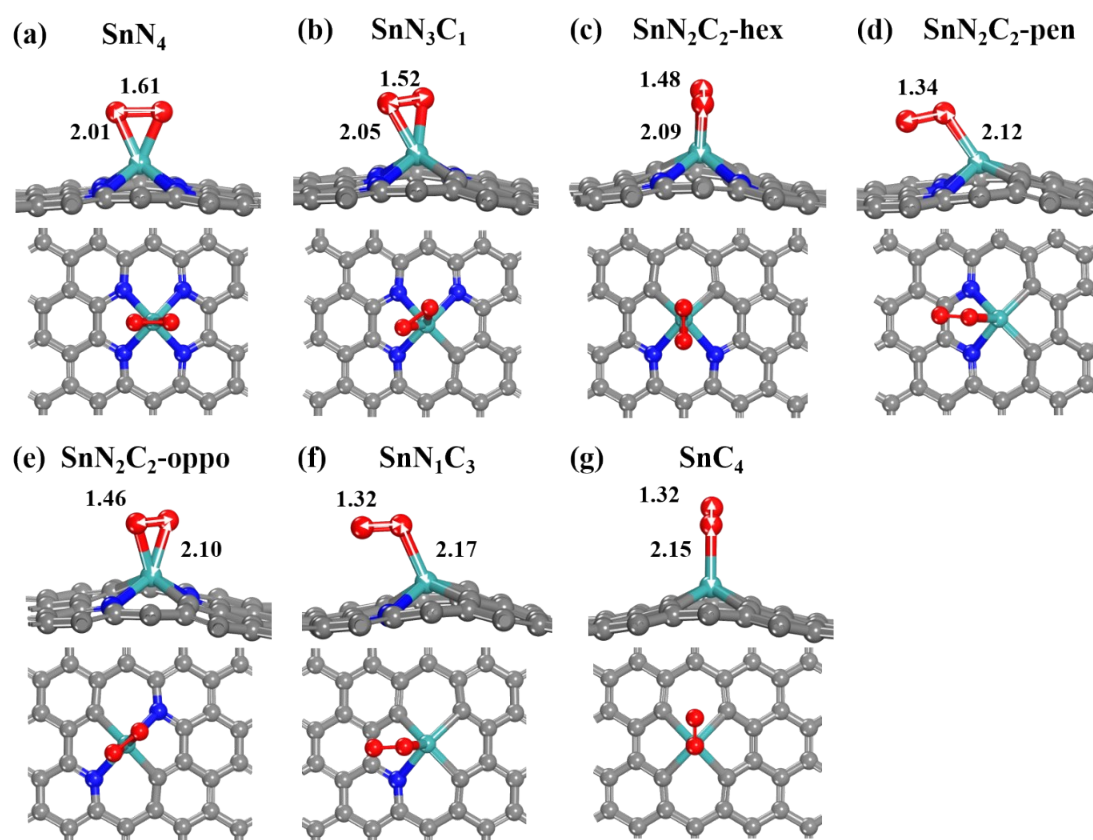


Figure S2. Top and side view of atomic structure of relaxed geometries for O_2 adsorbed on the center Sn atom of the SnN_4 (a), SnN_3C_1 (b), SnN_2C_2 -hex (c), SnN_2C_2 -pen (d), SnN_2C_2 -oppo (e), SnN_1C_3 (f), and SnC_4 (g). The gray, blue, cyan and red balls represent C, N, Sn and O atoms, respectively.

Table S2. Reaction energetics and corresponding Gibbs free activation barrier (G_{act}) of O_2^* protonation forming OOH^* or dissociation forming O^*+O^* on SnNC catalysts at $T = 298.15$ K, $pH = 0$, and $U = 0$ V.

Elementary reactions	SnN_2C_2 -hex	SnN_2C_2 -pen	SnN_2C_2 -oppo
$O_2^* \rightarrow O^*+O^*$	-2.20	-2.40	-1.77

<i>Gact</i>	1.36	1.71	1.45
$O_2^*+H^++e^- \rightarrow OOH^*$	-0.99	-0.96	-1.11
<i>Gact</i>	0.60	0.90	0.62
Elementary reactions	SnN ₄	SnC ₄	SnN ₃ C ₁
$O_2^* \rightarrow O^*+O^*$	-0.32	-1.38	-1.87
<i>Gact</i>	0.63	0.79	0.92
$O_2^*+H^++e^- \rightarrow OOH^*$	-0.37	-1.03	-1.84
<i>Gact</i>	2.53	1.91	1.41
Elementary reactions	SnN ₁ C ₃		
$O_2^* \rightarrow O^*+O^*$	-1.69		
<i>Gact</i>	1.00		
$O_2^*+H^++e^- \rightarrow OOH^*$	-2.76		
<i>Gact</i>	1.12		

Table S3. Reaction energetics (eV) of OOH* protonation forming O*+H₂O or dissociation forming O*+OH* on SnN₂C₂-hex, SnN₂C₂-pen, SnN₂C₂-oppo, SnN₃C₁-O and SnN₁C₃-O at $T = 298.15$ K, $pH = 0$, and $U = 0$ V.

Elementary reactions	SnN ₂ C ₂ -hex	SnN ₂ C ₂ -pen	SnN ₂ C ₂ -oppo
$OOH^*+H^++e^- \rightarrow O^*+H_2O(l)$	-2.08	-1.73	-2.75
$OOH^* \rightarrow O^*+OH^*$	-0.17	-0.29	0.00
Elementary reactions	SnN ₃ C ₁ -O	SnN ₁ C ₃ -O	
$OOH^*+H^++e^- \rightarrow O^*+H_2O(l)$	-1.38	-1.17	
$OOH^* \rightarrow O^*+OH^*$	-0.86	0.72	

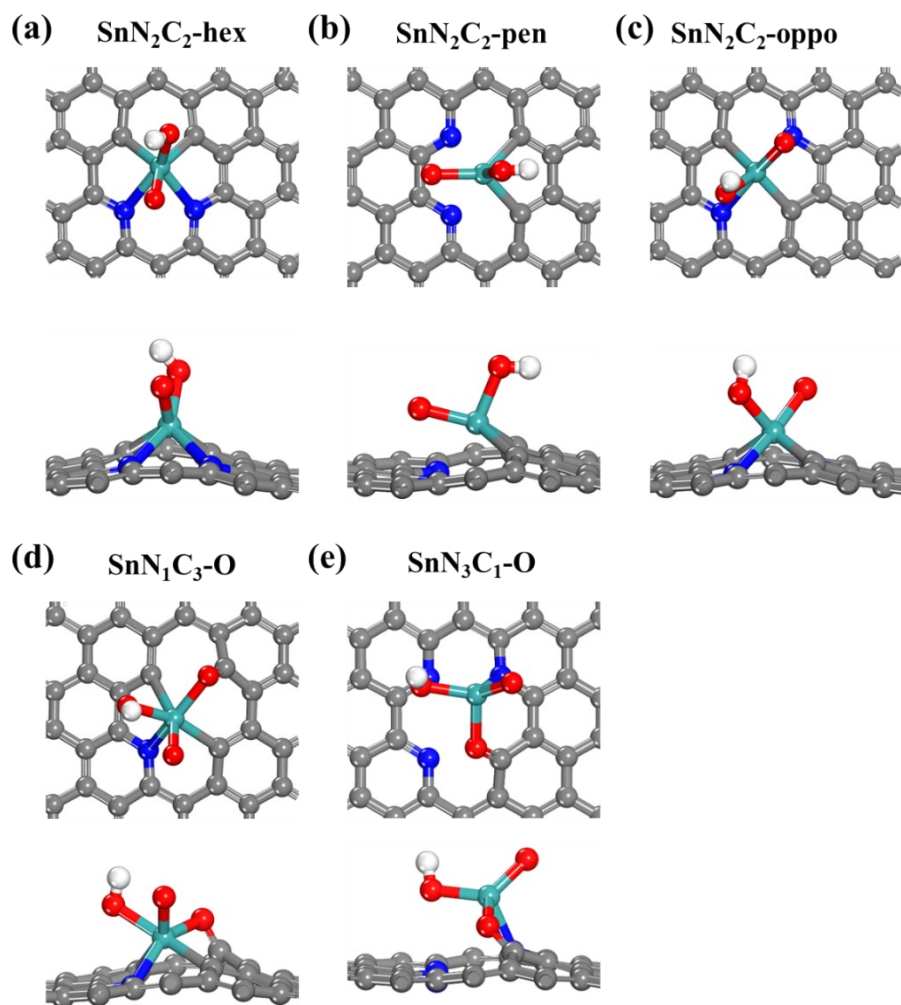


Figure S3. Top and side view of atomic structure of relaxed geometries for O^*-OH^* adsorbed on the center Sn atom of the SnN_2C_2 -hex (a), SnN_2C_2 -pen (b), SnN_2C_2 -oppo (c), SnN_1C_3 -O (d), and SnN_3C_1 -O (e). The gray, blue, cyan and red balls represent C, N, Sn and O atoms, respectively.

Table S4. Reaction energetics (eV) of OOH^* protonation forming $\text{O}^*+\text{H}_2\text{O}$ or H_2O_2 ($4e^-$ or $2e^-$ pathway) on SnN_2C_2 -hex, SnN_2C_2 -pen, SnN_2C_2 -oppo, SnN_3C_1 -O and SnN_1C_3 -O at $T = 298.15$ K, $pH = 0$, and $U = 0$ V.

Elementary reactions	SnN_2C_2 -hex	SnN_2C_2 -pen	SnN_2C_2 -oppo
$\text{OOH}^*+\text{H}^++e^- \rightarrow \text{O}^*+\text{H}_2\text{O}(\text{l})$	-2.08	-1.73	-2.75

$\text{OOH}^* + \text{H}^+ + \text{e}^- \rightarrow \text{H}_2\text{O}_2 + ^*$	-0.34	-0.03	0.18
Elementary reactions	$\text{SnN}_3\text{C}_1\text{-O}$	$\text{SnN}_1\text{C}_3\text{-O}$	
$\text{OOH}^* + \text{H}^+ + \text{e}^- \rightarrow \text{O}^* + \text{H}_2\text{O}(\text{l})$	-1.38	-1.17	
$\text{OOH}^* + \text{H}^+ + \text{e}^- \rightarrow \text{H}_2\text{O}_2 + ^*$	0.46	1.11	

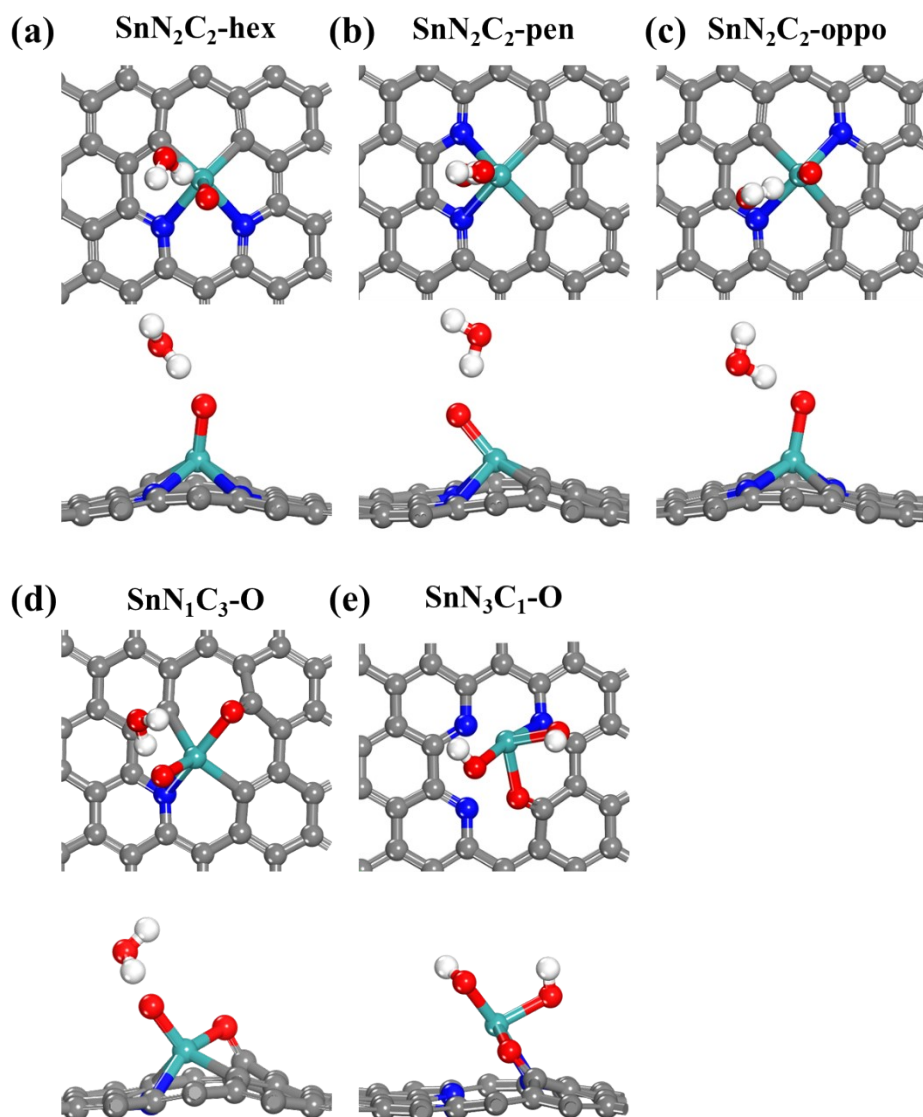


Figure S4. Top and side view of atomic structure of relaxed geometries for spontaneously dissociated H_2O_2 on the center Sn atom of the $\text{SnN}_2\text{C}_2\text{-hex}$ (a), $\text{SnN}_2\text{C}_2\text{-pen}$ (b), $\text{SnN}_2\text{C}_2\text{-oppo}$ (c), $\text{SnN}_1\text{C}_3\text{-O}$ (d), and $\text{SnN}_3\text{C}_1\text{-O}$ (e). The gray, blue, wathet and red balls represent C, N, Sn and O atoms, respectively.

(a) OH*-assisted associative pathway

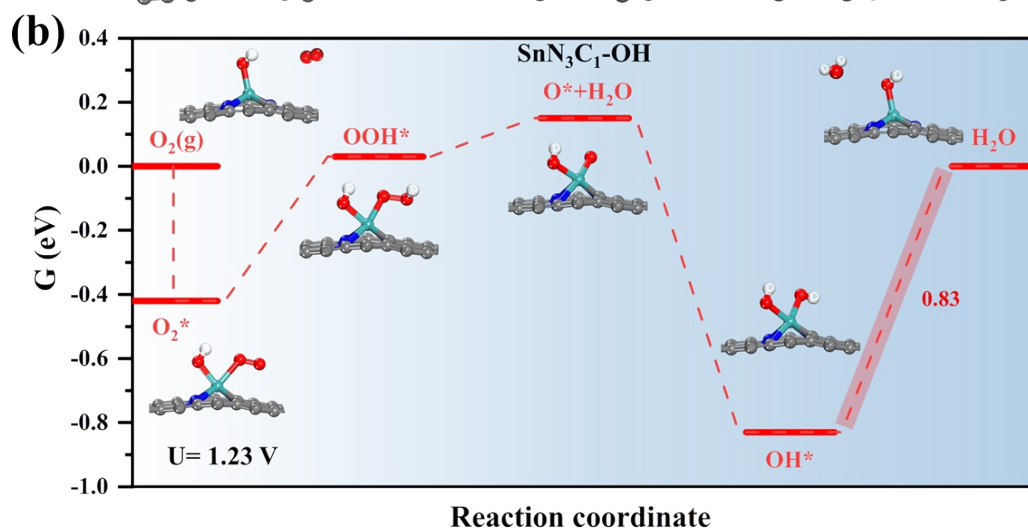
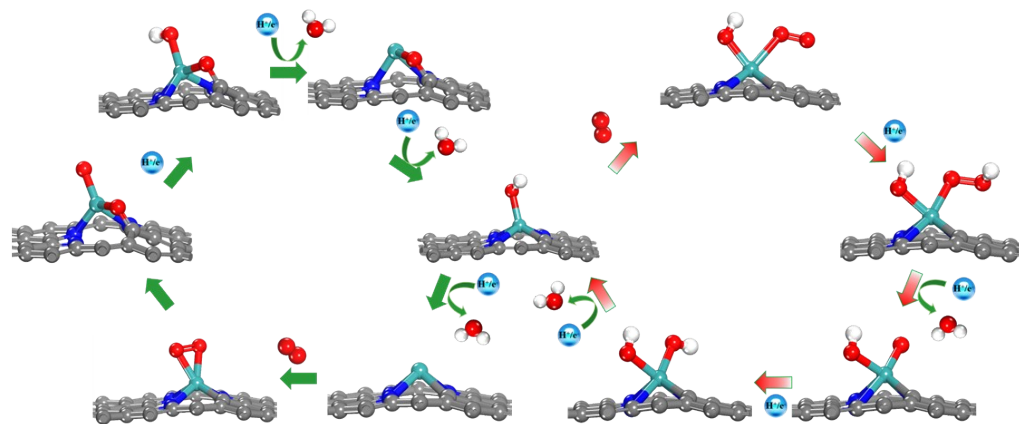


Figure S5. The OH*-assisted associative pathway (red) on the SnN₃C₁ (a) and the corresponding Gibbs free energy diagram at $U = 1.23$ V (b).

(a) O^{*}-assisted associative pathway

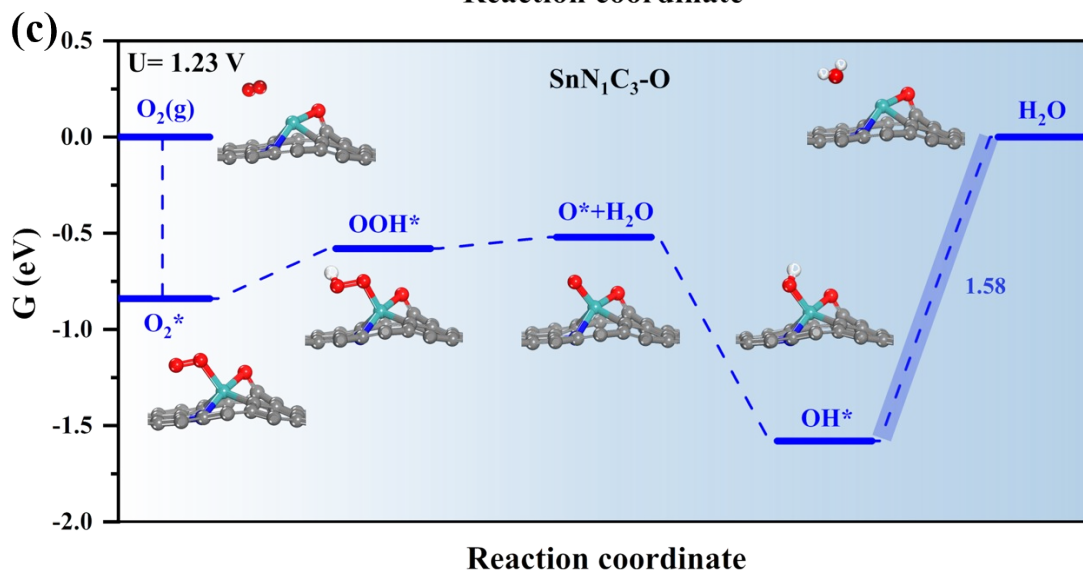
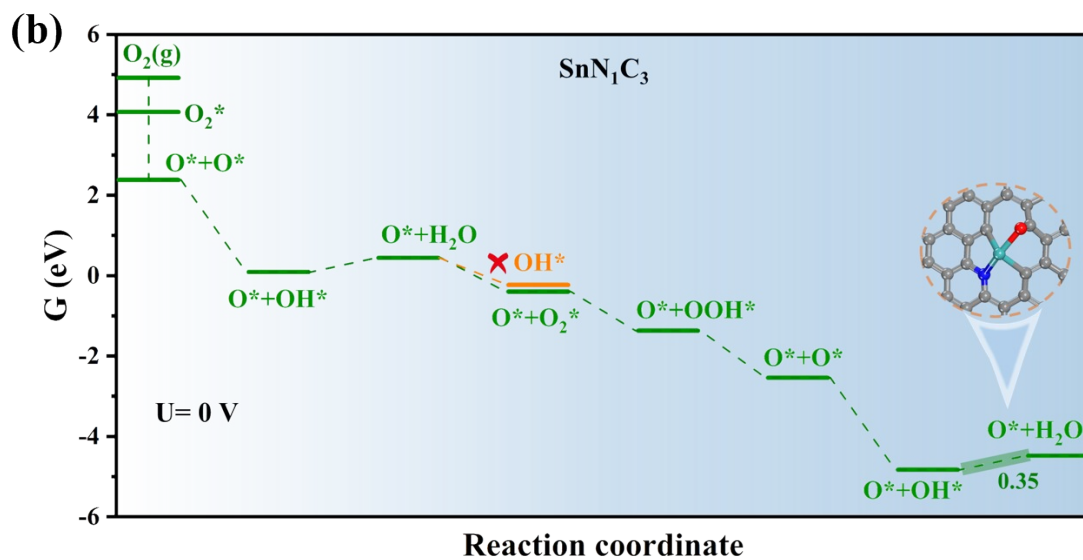
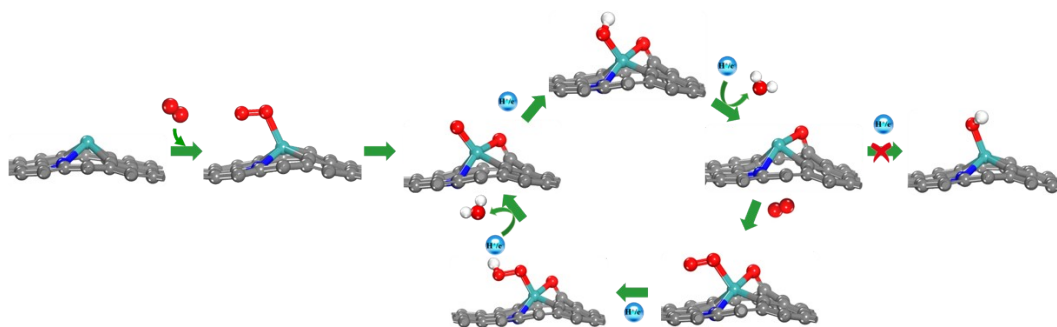


Figure S6. The O^{*}-assisted associative pathway on the SnN₁C₃ (a) and the corresponding Gibbs free energy diagram at $U = 0$ V (b) and $U = 1.23$ V (c).

Table S5. Reaction energetics (eV) for the 4e⁻ transfer processes during ORR on SnN₂C₂-hex, SnN₂C₂-pen and SnN₂C₂-oppo at $T = 298.15$ K, $pH = 0$, and $U = 1.23$ V.

Elementary reactions	SnN ₂ C ₂ -hex	SnN ₂ C ₂ -pen	SnN ₂ C ₂ -oppo
$O_2(g)+* \rightarrow O_2^*$	-0.08	-0.41	-0.47
$O_2^*+H^++e^- \rightarrow OOH^*$	0.24	0.27	0.12
$OOH^*+H^++e^- \rightarrow O^*+H_2O(l)$	-0.85	-0.50	-1.52
$O^*+H^++e^- \rightarrow OH^*$	-0.13	-0.45	0.82
$OH^*+H^++e^- \rightarrow H_2O^*$	0.81	1.09	1.05

Table S6. Reaction energetics (eV) for the 4e⁻ transfer processes during ORR on SnN₄ and SnC₄ at $T = 298.15$ K, $pH = 0$, and $U = 1.23$ V.

Elementary reactions	SnN ₄	Elementary reactions	SnC ₄
$O_2(g)+* \rightarrow O_2^*$	0.04	$O_2(g)+* \rightarrow O_2^*$	-0.40
$O_2^* \rightarrow O^*+O^*$	-0.32	$O_2^* \rightarrow O^*+O^*$	-1.38
$O^*+O^*+H^++e^- \rightarrow OH^*+O^*$	-0.52	$O^*+O^*+H^++e^- \rightarrow OH^*+O^*$	-1.06
$OH^*+O^*+H^++e^- \rightarrow 2OH^*$	-0.66	$OH^*+O^*+H^++e^- \rightarrow H_2O(l)+O^*$	1.30
$2OH^*+H^++e^- \rightarrow OH^*+H_2O$	1.28	$O^*+H^++e^- \rightarrow OH^*$	0.42
$OH^*+H^++e^- \rightarrow H_2O+*$	0.18	$OH^*+H^++e^- \rightarrow H_2O+*$	1.12

Table S7. Reaction energetics (eV) for the 4e⁻ transfer processes during ORR on SnN₃C₁-O and SnN₁C₃-O at $T = 298.15$ K, $pH = 0$, and $U = 1.23$ V, respectively.

Elementary reactions	SnN ₃ C ₁ -O	SnN ₁ C ₃ -O
$O_2(g) \rightarrow O_2^*$	-0.34	-0.84
$O_2^*+H^++e^- \rightarrow OOH^*$	0.40	0.26
$OOH^*+H^++e^- \rightarrow O^*+H_2O(l)$	-0.15	0.06
$O^*+H^++e^- \rightarrow OH^*$	-0.00	-1.06
$OH^*+H^++e^- \rightarrow H_2O^*$	0.09	1.58

Table S8. Reaction energetics (eV) for the 4e⁻ transfer processes during ORR on SnN₃C₁-O at $T = 298.15$ K, $pH = 0$, and $U = 1.23$ V in different media, vacuum, implicit solvation, explicit solvation.

Elementary reactions	vacuum	implicit	explicit
$O_2(g) \rightarrow O_2^*$	-0.34	-0.62	0.05
$O_2^* + H^+ + e^- \rightarrow OOH^*$	0.40	0.48	0.18
$OOH^* + H^+ + e^- \rightarrow O^* + H_2O(l)$	-0.15	-0.32	-1.25
$O^* + H^+ + e^- \rightarrow OH^*$	-0.00	0.24	0.43
$OH^* + H^+ + e^- \rightarrow H_2O^*$	0.09	0.21	0.59

Table S9. The zero-point energy (ZPE) and the entropy change (T^*S) of free molecules and the ORR intermediates for the 7 SnNC catalysts.

Gas molecules						
T=298.15K	H ₂ O	ZPE	0.56	H ₂	ZPE	0.27
		TS	0.67		TS	0.41
The different catalysts (SnNC)						
		SnN ₂ C ₂ -hex	SnN ₂ C ₂ -pen	SnN ₂ C ₂ -oppo	SnN ₃ C ₁ -O	SnN ₁ C ₃ -O
O ₂ *	ZPE	0.13	0.11	0.12	0.13	0.11
	TS	0.14	0.10	0.18	0.12	0.09
OOH*	ZPE	0.45	0.43	0.38	0.46	0.45
	TS	0.19	0.22	0.11	0.20	0.18
O*	ZPE	0.10	0.10	0.10	0.12	0.11
	TS	0.03	0.03	0.03	0.04	0.04
OH*	ZPE	0.35	0.33	0.36	0.37	0.36
	TS	0.12	0.10	0.10	0.11	0.11
		SnN ₄			SnC ₄	
O ₂ *	ZPE	0.12	O ₂ *	ZPE	0.11	
	TS	0.17		TS	0.10	
O*+O*	ZPE	0.15	O*+O*	ZPE	0.15	

	TS	0.12		TS	0.12	
O*+OH*	ZPE	0.44	O*+OH*	ZPE	0.45	
	TS	0.14		TS	0.15	
2OH*	ZPE	0.71	O*	ZPE	0.10	
	TS	0.20		TS	0.03	
OH*	ZPE	0.33	OH*	ZPE	0.42	
	TS	0.13		TS	0.05	

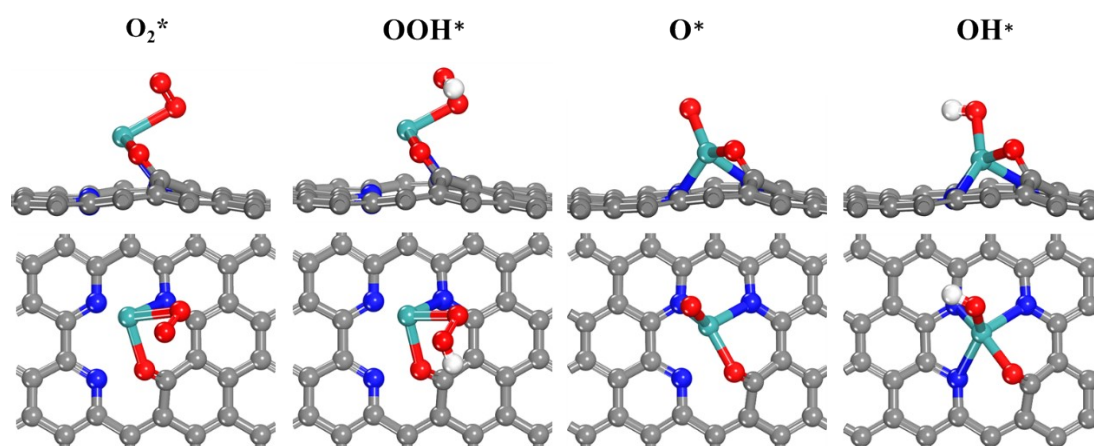


Figure S7. Top and side view of relaxed geometries for O_2^* , OOH^* , O^* and OH^* adsorption on the center Sn atom of SnN_3C_1-O under implicit solvation model.

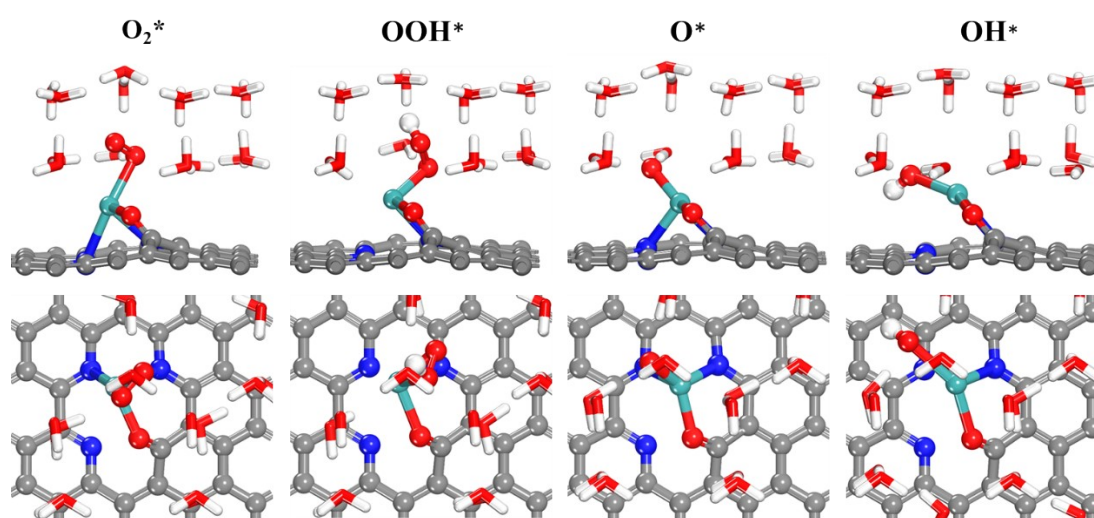


Figure S8. Top and side view of relaxed geometries for O_2^* , OOH^* , O^* , and OH^* adsorption on the center Sn atom of SnN_3C_1-O under explicit solvation model.

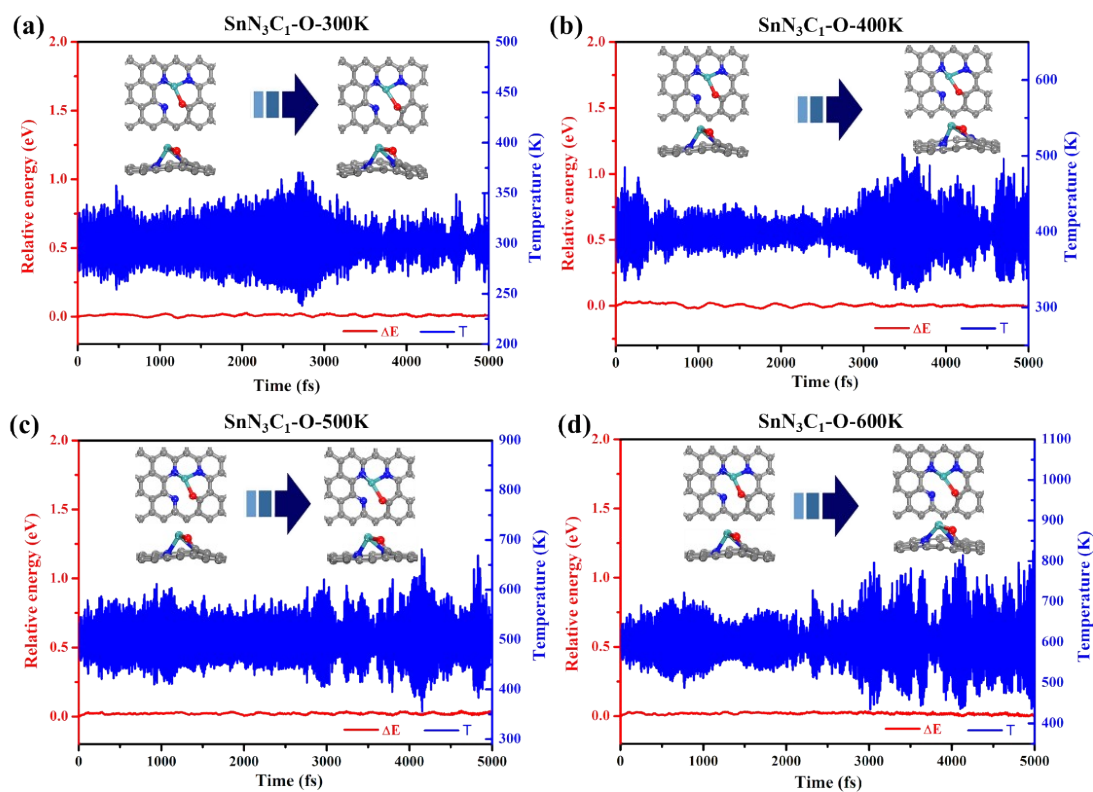


Figure S9. In the AIMD simulation, the time step is 1fs and AIMD simulation of $\text{SnN}_3\text{C}_1\text{-O}$ catalyst is performed at 300K (a), 400K (b), 500K (c), and 600K (d) for 5 ps. Here, the electronic energy of the initial configuration is set to zero for reference.