Electronic Supplemental Information

Density functional theory study of oxygen evolution reaction mechanism on rare earth Sc-doped graphene

Yiwen Liu [1], Mengqi Liao [1], Yuting Hu [1], Tae Gwan Lee [2], Ravindranadh Koutavarapu [3,*], Shaik Gouse Peera [2,*], Chao Liu [1,*]

[1] Faculty of Materials Metallurgy and Chemistry, Jiangxi University of Science and Technology, Ganzhou 341000, China; 2856056456@qq.com (Y. Liu)

[2] Department of Environmental Science and Engineering, Keimyung University, Daegu 42601, Republic of Korea; wateree@kmu.ac.kr (T.G. Lee)

[3] Department of Robotics Engineering, College of Mechanical and IT Engineering, Yeungnam University, Gyeongsan 38541, Republic of Korea

* Correspondence: ravindra_physicist@ynu.ac.kr (R. Koutavarapu); gouse@kmu.ac.kr (S.G. Peera); liuchao198967@126.com (C. Liu)

Table S1

	ScC_3	$ScNC_2$	ScN_2C	ScN_3	ScC_4	$ScNC_3$
ΔE_f	3.94	2.09	0.81	-0.20	5.26	3.245
	ScN_2C_2-h	ScN_2C_2-o	ScN_2C_2-p	ScN_3C	ScN_4	
ΔE_f	1.37	1.38	1.45	-0.28	-1.60	

Formation energy (ΔE_f, eV) of various ScN_xC_{3-x}@SACs and ScN_xC_{4-x}@SACs structures.

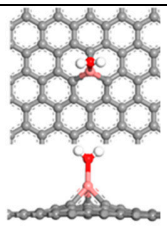
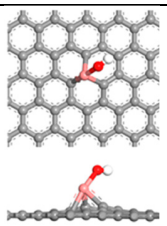
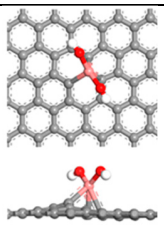
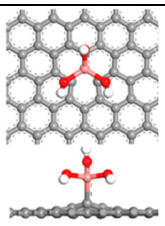
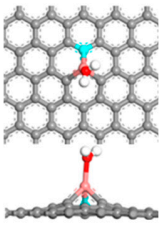
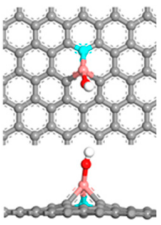
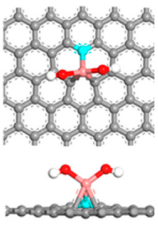
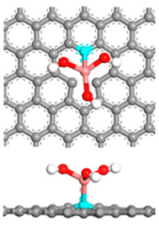
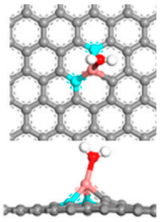
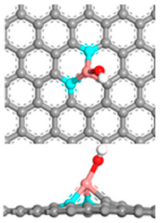
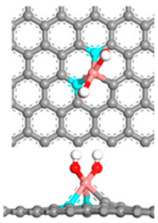
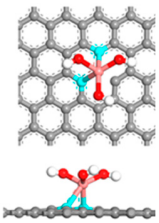
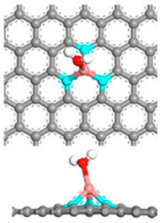
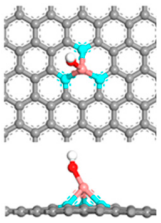
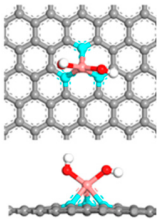
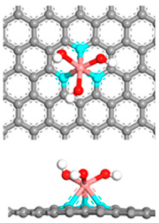
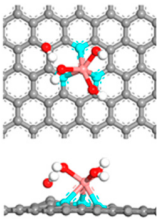
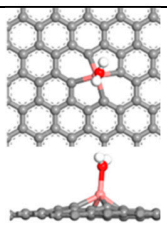
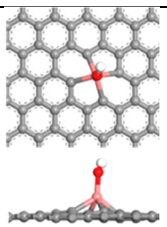
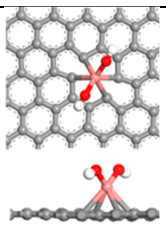
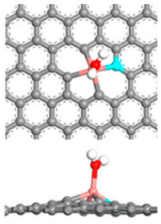
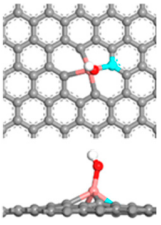
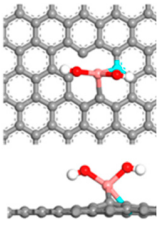
Table S2

Q(Sc), Q(N) and Q(C) refer to the charge on Sc atom, N and C atoms adjacent to Sc atom, respectively. $Q(C_N)$ and $Q(C_C)$ represent the charge of the outer C atoms of N, C atoms connected to Sc atom. The positive and negative numbers represent electrons lost and gained, respectively, based on the analysis of Mulliken charge (Q in e).

	Q(Sc)	Q(C)	Q(N)	$Q(C_N)$	$Q(C_C)$
ScC_3	0.975	1.050			0.254
$ScNC_2$	1.107	-0.736	-0.510	0.290	0.194
ScN_2C	1.266	-0.376	-1.042	0.589	0.115
ScN_3	1.424		-1.610	0.911	
ScC_4	1.114	-1.508			0.300
$ScNC_3$	1.167	-1.153	-0.485	0.293	-0.712
ScN_2C_2-h	1.237	-0.731	-0.527	0.639	0.114
ScN_2C_2-o	1.255	-0.791	-1.028	0.643	0.115
ScN_2C_2-p	1.248	-0.780	-1.044	0.532	0.220
ScN_3C	1.368	-0.386	-1.629	0.888	0.072
ScN_4	1.533		-2.208	1.136	

Table S3

The adsorption configurations of different number of OH^- and H_2O on various types of ScN_xC_{3-x}@SACs and ScN_xC_{4-x}@SACs.

	*H_2O	*OH	*2OH	*3OH	*4OH	*5OH
ScC_3						
$ScNC_2$						
ScN_2C						
ScN_3						
ScC_4						
$ScNC_3$						

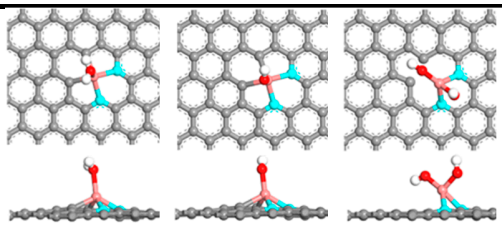
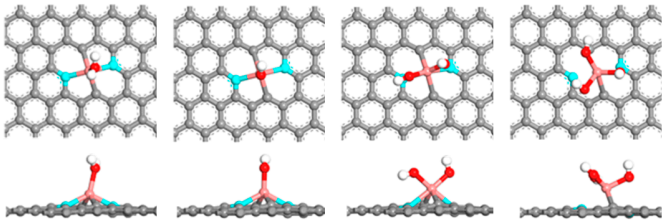
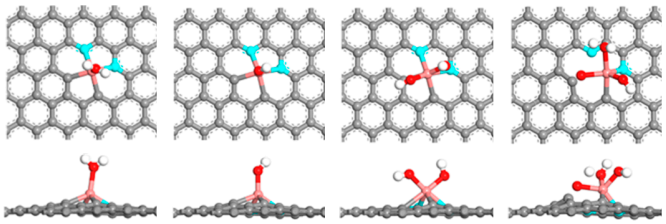
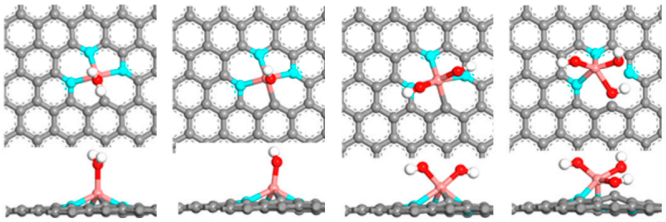
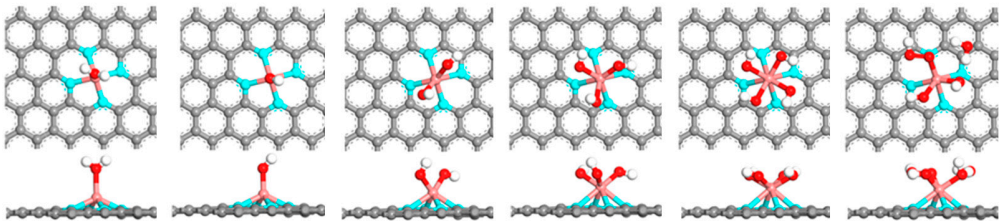
ScN_2C_2-h	
ScN_2C_2-o	
ScN_2C_2-p	
ScN_3C	
ScN_4	

Table S4

Adsorption energy data (ΔE_{ads}, eV) of H_2O and different number of OH^- on ScN_xC_{3-x}@SACs and ScN_xC_{4-x}@SACs.

	ΔE_{ads}*H_2O	ΔE_{ads}*OH	ΔE_{ads}*2OH	ΔE_{ads}*3OH	ΔE_{ads}*4OH
ScC_3	-0.851	-3.45	-3.58	-2.89	
$ScNC_2$	-0.912	-3.58	-3.71	-2.98	
ScN_2C	-0.966	-4.29	-3.12	-2.42	
ScN_3	-0.999	-4.75	-3.96	-2.44	
ScC_4	-0.938	-3.42	-3.72		
$ScNC_3$	-0.942	-3.38	-3.10		
ScN_2C_2-h	-0.990	-3.70	-2.86		
ScN_2C_2-o	-0.970	-3.56	-2.35	-1.76	
ScN_2C_2-p	-0.966	-3.59	-2.28	-5.03	
ScN_3C	-1.030	-3.99	-2.60	-3.44	
ScN_4	-1.052	-4.50	-2.88	-1.89	-1.13

Table S5

The adsorption configurations of $*O_2$ on ScN_3 and ScN_4 with different number of OH^-.

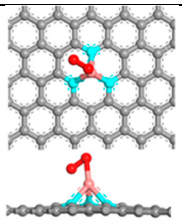
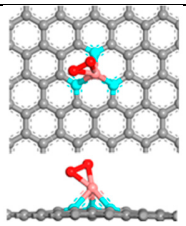
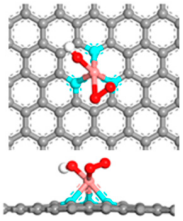
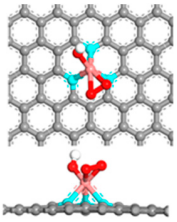
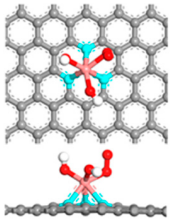
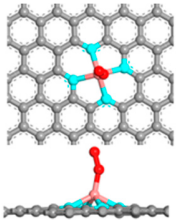
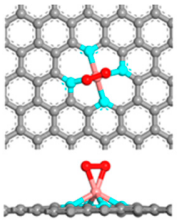
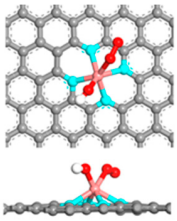
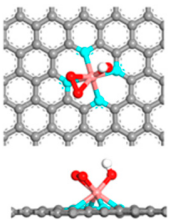
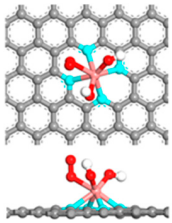
	$*O_{2(\text{end on})}$	$*O_{2(\text{side on})}$
ScN_3		
$Sc(OH)N_3$		
$Sc(OH)_2N_3$		
ScN_4		
$Sc(OH)N_4$		
$Sc(OH)_2N_4$		

Table S6

Adsorption energy (ΔE_{ads}, eV) of ScN_3 and ScN_4 with different number of OH ligands for adsorbed O_2.

	$\Delta E_{ads}{}^{*}O_{2(\text{end on})}$	$\Delta E_{ads}{}^{*}O_{2(\text{side on})}$		$\Delta E_{ads}{}^{*}O_{2(\text{end on})}$	$\Delta E_{ads}{}^{*}O_{2(\text{side on})}$
ScN_3	-3.52	-3.64	ScN_4	-1.75	-2.80
$Sc(OH)N_3$	-1.26	-2.09	$Sc(OH)N_4$	-0.42	-0.88
$Sc(OH)_2N_3$	-0.05		$Sc(OH)_2N_4$	0.25	

Table S7

The adsorption configurations of *OH, *OOH, *O, $*H_2O$ and $*O_2$ on $Sc(OH)_2N_3$ and $Sc(OH)_2N_4$.

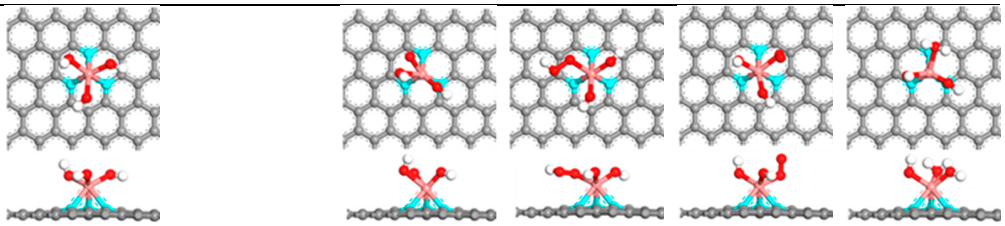
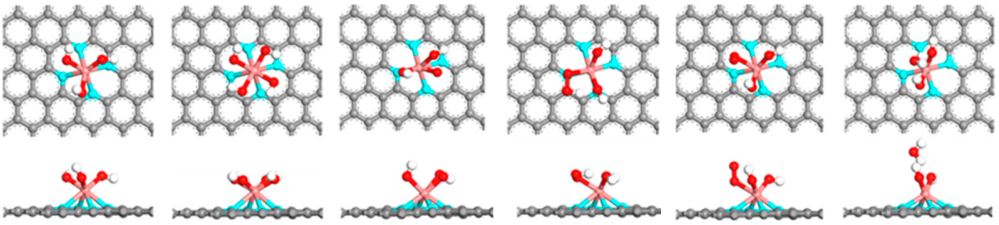
	*OH	*2OH	*O	*OOH	$*O_2$	$*H_2O$
$Sc(OH)_2N_3$						
$Sc(OH)_2N_4$						

Table S8

Adsorption energy data (ΔE_{ads}, eV) of reactive species on $Sc(OH)_2N_4$ and $Sc(OH)_2N_3$.

	$\Delta E_{ads}{}^{*}OH$	$\Delta E_{ads}{}^{*}O$	$\Delta E_{ads}{}^{*}OOH$	$\Delta E_{ads}{}^{*}O_{2(\text{end on})}$	$\Delta E_{ads}{}^{*}H_2O$
$Sc(OH)_2N_3$	-2.44	-2.98	-1.21	-0.05	-0.70
$Sc(OH)_2N_4$	-1.89	-2.67	-0.94	0.25	-0.51

Table S9

Free energy change (ΔG, eV) of ScN_3 and ScN_4 to produce $Sc(OH)_2N_3$ and $Sc(OH)_2N_4$.

	$\Delta G_{*+OH^-\rightarrow *OH}$	$\Delta G_{*OH+OH^-\rightarrow *2OH}$
ScN_3	-2.19	-1.36
ScN_4	-1.98	-0.28

Table S10

Free energy changes of ΔG_x (x=1-4, eV) and overpotential (η, V) of $Sc(OH)_2N_3$ and $Sc(OH)_2N_4$.

	ΔG_1	ΔG_2	ΔG_3	ΔG_4	η
$Sc(OH)_2N_3$	0.08	1.43	0.15	-0.06	1.03
$Sc(OH)_2N_{4(pathway\ 1)}$	0.57	1.50	0.17	-0.34	0.80
$Sc(OH)_2N_{4(pathway\ 2)}$	0.57	1.20	-0.13	-0.34	1.10

Table S11

Free energy change (ΔG, eV) of H_2O_2 formation.

	$\Delta G_{*OOH+OH^-\rightarrow *O+H_2O_2}$	$\Delta G_{*2OH+OH^-\rightarrow *OH+H_2O_2}$
$Sc(OH)_2N_3$	3.58	
$Sc(OH)_2N_4$	3.56	2.23

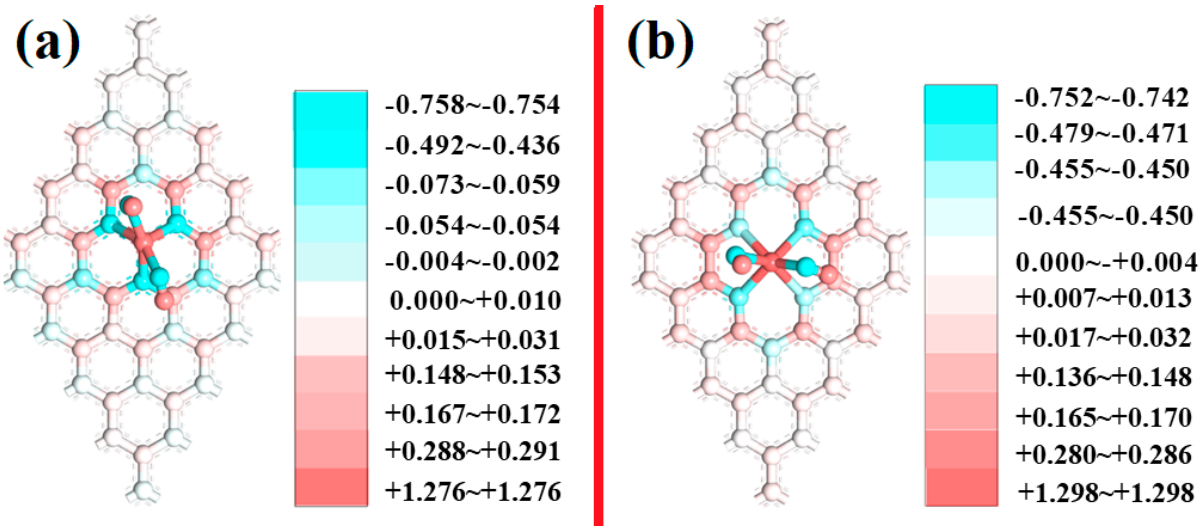


Fig. S1. The Mulliken charge analysis of (a) $Sc(OH)_2N_3$ and (b) $Sc(OH)_2N_4$.

Table S12

Q(Sc) and Q(N) refer to the charge on Sc atom and N atom adjacent to Sc atom, respectively. $Q(C_N)$, $Q(O_{Sc})$ and $Q(H_O)$ represent the charge of the outer C atoms of N atoms connected to Sc atom, the O atoms connected to Sc atom and the H atoms connected to O atoms. The positive and negative numbers represent electrons lost and gained, respectively, based on the analysis of Mulliken charge (Q in e).

	Q(Sc)	Q(N)	$Q(C_N)$	$Q(O_{Sc})$	$Q(H_O)$
$Sc(OH)_2N_3$	1.276	-1.388	0.962	-1.512	0.579
$Sc(OH)_2N_4$	1.298	-1.855	1,218	-1.492	0.566