Supporting Information

The catalytic activity and mechanism of oxygen reduction reaction on single atom doped graphene: a DFT method

Xiaoming Zhang[a], Zhangxun Xia[a], Huanqiao Li[a], Shansheng Yu[b], Suli Wang[a], Gongquan Sun[a]**

[a]Division of Fuel Cells and Battery, Dalian National Laboratory for Clean Energy, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian, China 116023

[b]Department of Materials Science, Jilin University, Changchun 130012, China

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**Corresponding author: Gongquan Sun, e-mail: gqsun@dicp.ac.cn & Suli Wang, e-mail: suliwang@dicp.ac.cn*

Figures and Tables

Table S 1 The adsorption energy of various convergence test for important parameters (Orbital cut-off quality and k-point set) and slab size

Slab size	ΔE_{ads}^{DFT}	k-point	ΔE_{ads}^{DFT}	Cut-off	ΔE_{ads}^{DFT}
p(3x3)	-0.61	5x5x1	-0.61	4.8	-0.58
p(4x4)	-0.61	6x6x1	-0.61	5.0	-0.57
p(5x5)	-0.61	7x7x1	-0.61	5.2	-0.61
p(6x6)	-0.63	8x8x1	-0.61	5.4	-0.58

Table S 2 The bond length of X-C ($l_{X\text{-}C}$), height of X atoms above graphene plane (h_X), Mulliken charge of X atoms (Q_X) and adjacent C atoms (Q_C) as well as p electrons band center of X atoms (ε_p) in X-SV catalysts

Catalyst	*Atomic radius* (Å)*	$l_{x\text{-}c}$ *(Å)*	$l_{c\text{-}c}$ *(Å)*	h_x *(Å)*	*xp**	Q_x *(e)*	Q_c *(e)*	ε_{sp} *(eV)*
B@Gra#	0.88	1.48	1.41	0.00	2.00	0.01	-0.13	5.97
C@Gra#	0.77	1.42	1.42	0.00	2.50	0.00	0.00	-1.33
N@Gra#	0.70	1.41	1.42	0.00	3.00	-0.30	0.14	-4.23
O@Gra#	0.73	1.49	1.39	0.00	3.50	-0.51	0.22	-5.78
Al@Gra	1.43	1.86	1.41	1.66	1.50	1.10	-0.56	5.58
Si@Gra	1.17	1.77	1.41	1.38	1.80	0.87	-0.47	4.25
P@Gra	1.10	1.77	1.40	1.33	2.10	0.61	-0.37	1.90
S@Gra	1.04	1.75	1.40	1.18	2.50	0.54	-0.31	-0.37
Ga@Gra	1.35	1.87	1.41	1.67	1.60	0.36	-0.30	6.29
Ge@Gra	1.22	1.89	1.41	1.68	1.80	0.10	-0.22	4.69
As@Gra	1.20	1.92	1.40	1.67	2.00	0.03	-0.18	3.02
Se@Gra	1.19	1.90	1.40	1.53	2.40	0.11	-0.16	1.18
In@Gra	1.67	2.28	1.41	2.24	1.70	0.48	-0.34	5.98
Sn@Gra	1.40	2.17	1.41	2.21	1.80	0.47	-0.35	6.00
Sb@Gra	1.40	2.13	1.40	2.10	1.90	0.49	-0.34	4.37
Te@Gra	1.42	2.09	1.40	1.95	2.10	0.53	-0.33	2.70
Tl@Gra	1.70	2.69	1.40	2.50	1.80	0.45	-0.28	6.03
Pb@Gra	1.46	2.31	1.41	2.40	1.90	0.59	-0.39	6.22
Bi@Gra	1.50	2.26	1.40	2.29	1.90	0.62	-0.53	-0.89

* A.E. N.N. Greenwood, Chemistry of the Elements, second ed. Butterworth-Heinemann,Oxford (1997)

Table S 3 The bond length of X-C ($l_{X\text{-}C}$), height of X atoms above graphene plane (h_X), Mulliken charge of X atoms (Q_X) and adjacent C atoms (Q_C) as well as p electrons band center of X atoms (ε_p) in X-SV catalysts

Catalyst	*Atomic radius(Å)*	$l_{x\text{-}c}$ *(Å)*	$l_{c\text{-}c}$ *(Å)*	h_x *(Å)*	*xp*	Q_x *(e)*	Q_c *(e)*	ε_{sp} *(eV)*
Al@Gra#	1.43	1.94	1.40, 1.38	0.00	1.61	1.31	-0.52	6.53
Si@Gra#	1.17	1.89	1.43, 1.39	0.00	1.90	1.16	-0.48	6.05
P@Gra#	1.10	1.85	1.45, 1.39	0.00	2.19	0.91	-0.39	3.61
S@Gra#	1.04	1.87	1.45, 1.37	0.00	2.58	0.58	-0.28	-0.99
Ga@Gra#	1.53	1.96	1.40, 1.38	0.00	1.81	0.40	-0.25	6.27
Ge@Gra#	1.22	1.94	1.41, 1.38	0.00	2.01	0.44	-0.26	5.64
As@Gra#	1.21	1.92	1.42, 1.38	0.00	2.18	0.46	-0.26	5.05
Se@Gra	1.17	1.98	1.42, 1.38	0.69	2.55	0.28	-0.20	2.23
In@Gra	1.67	2.18	1.40, 1.40	1.46	1.78	0.66	-0.32	6.28
Sn@Gra	1.58	2.27	1.41, 1.40	1.65	1.96	0.49	-0.31	5.67
Sb@Gra	1.41	2.19	1.41, 1.39	1.53	2.05	0.51	-0.32	4.89
Te@Gra	1.37	2.13	1.42, 1.38	1.38	2.10	0.60	-0.32	3.31
Tl@Gra	1.71	2.69	1.42, 1.40	2.12	2.04	0.46	-0.25	6.10
Pb@Gra	1.75	2.40	1.41, 1.40	1.89	2.33	0.57	-0.33	5.92
Bi@Gra	1.82	2.31	1.41, 1.39	1.81	2.02	0.60	-0.45	-0.28

Table S 4 The binding energies between X atoms and defective graphene with or without considered water solution.

Without water	ΔE_b			ΔE_b			ΔE_b	
	SV	*DV*		*SV*	*DV*		*SV*	*DV*
B@Gra	-13.01		*Ga@Gra*	-4.30	-4.54	*Tl@Gra*	-0.23	0.10
C@Gra	-15.61		*Ge@Gra*	-6.46	-5.71	*Pb@Gra*	-1.90	-1.60
N@Gra	-12.14		*As@Gra*	-6.81	-5.73	*Bi@Gra*	-1.93	-1.41
O@Gra	-7.97		*Se@Gra*	-5.49	-4.93			
Al@Gra	-5.44	-5.80	*In@Gra*	-2.66	-2.07			
Si@Gra	-8.25	-7.88	*Sn@Gra*	-4.68	-3.08			
P@Gra	-8.45	-7.72	*Sb@Gra*	-5.25	-3.45			
S@Gra	-6.94	-6.16	*Te@Gra*	-4.10	-3.29			
With water	ΔE_b			ΔE_b			ΔE_b	
	SV	*DV*		*SV*	*DV*		*SV*	*DV*
B@Gra	-12.99		*Ga@Gra*	-4.35	-4.56	*Tl@Gra*	-0.28	0.01
C@Gra	-15.58		*Ge@Gra*	-6.44	-5.68	*Pb@Gra*	-1.90	-1.65
N@Gra	-12.13		*As@Gra*	-6.80	-5.69	*Bi@Gra*	-1.95	-1.46
O@Gra	-7.99		*Se@Gra*	-5.55	-4.98			
Al@Gra	-5.46	-5.79	*In@Gra*	-2.68	-2.66			
Si@Gra	-8.24	-7.85	*Sn@Gra*	-4.67	-4.17			
P@Gra	-8.44	-7.66	*Sb@Gra*	-5.29	-4.65			
S@Gra	-6.95	-6.09	*Te@Gra*	-4.27	-4.36			

Table S 5 The free energy of O*, OH* and OOH* on various X-SV/DV catalysts

Catalyst	ΔG_{OH*}	ΔG_{OOH*}	ΔG_{O*}
N-SV	1.21	4.45	2.44
Al-SV	-1.18	2.25	1.28
Ga-SV	-0.23	3.14	2.00
Ge-SV	-0.16	3.27	1.67
In-SV	-0.27	3.20	1.60
Te-SV	0.76	4.03	2.40
Al-DV	-0.34	3.15	2.22
Si-DV	-0.46	3.05	1.56
Ga-DV	0.26	3.59	2.76
Ge-DV	-0.11	3.30	2.00
In-DV	-0.24	3.11	2.21
Sn-DV	-0.05	3.38	2.00
Sb-DV	0.64	4.10	2.15
Tl-DV	0.13	3.51	2.45

Table S 6 The reaction free energy for each step of the ORR elementary reaction on various X-SV/DV catalysts with pH=13 and U^{NHE}=0.44 V

	Al-SV	*Si-DV*	*In-SV*	*Ge-SV*	*Te-SV*	*Sb-DV*	*N-SV*
ΔG_1	*-1.44*	*-0.64*	*-0.49*	*-0.42*	*0.34*	*0.41*	*0.76*
ΔG_2	*0.26*	*-0.27*	*-0.37*	*-0.37*	*-0.40*	*-0.72*	*-0.78*
ΔG_3	*-1.23*	*-0.79*	*-0.64*	*-0.61*	*-0.40*	*-0.28*	*0.00*
ΔG_4	*2.41*	*1.69*	*1.50*	*1.39*	*0.47*	*0.59*	*0.02*
	Al-DV	*In-DV*	*Ga-SV*	*Ge-DV*	*Sn-DV*	*Tl-DV*	*Ga-DV*
ΔG_1	*-0.55*	*-0.58*	*-0.55*	*-0.40*	*-0.31*	*-0.18*	*-0.10*
ΔG_2	*0.31*	*0.33*	*0.10*	*-0.06*	*-0.15*	*0.17*	*0.40*
ΔG_3	*-1.33*	*-1.12*	*-1.00*	*-0.88*	*-0.82*	*-1.09*	*-1.27*
ΔG_4	*1.57*	*1.47*	*1.46*	*1.34*	*1.28*	*1.10*	*0.97*

Table S 7 The calculated ΔG_{OH*} based DFT, ΔG_{OOH*} based on ΔG_{OH*} and their linear relationship on remaining 20 catalysts

	ΔG_{OH*}	$\Delta G_{OOH*} = \Delta G_{OH*} * 0.91 + 3.4$
B-SV	*1.16*	*4.46*
C-SV	*2.38*	*5.57*
O-SV	*-0.58*	*2.87*
Si-SV	*-1.28*	*2.24*
P-SV	*-0.46*	*2.98*
S-SV	*1.75*	*4.99*
As-SV	*1.04*	*4.35*
Se-SV	*1.45*	*4.72*
Sn-SV	*0.44*	*3.80*
Sb-SV	*1.37*	*4.65*
Tl-SV	*0.26*	*3.64*
Pb-SV	*0.98*	*4.29*
Bi-SV	*1.45*	*4.72*
P-DV	*0.35*	*3.72*
S-DV	*2.32*	*5.51*
As-DV	*0.52*	*3.87*
Se-DV	*2.17*	*5.37*
Te-DV	*1.93*	*5.16*
Pb-DV	*0.61*	*3.96*
Bi-DV	*1.61*	*4.87*

Table S 8 The calculated ΔG_{OH*} based DFT and their corresponding energy barrier for 14 catalysts

	ΔG_{OH*}	*Energy barrier*
N-SV	*1.21*	*0.76*
Al-SV	*-1.2*	*2.41*
Ga-SV	*-0.23*	*1.46*
Ge-SV	*-0.16*	*1.39*
In-SV	*-0.27*	*1.50*
Te-SV	*0.76*	*0.47*
Al-DV	*-0.34*	*1.57*
Si-DV	*-0.46*	*1.69*
Ga-DV	*0.26*	*0.97*
Ge-DV	*-0.11*	*1.34*
In-DV	*-0.24*	*1.47*
Sn-DV	*-0.05*	*1.28*
Sb-DV	*0.64*	*0.59*
Tl-DV	*0.13*	*1.10*

Table S 9 The calculated ΔG_{OH*} based DFT, ΔG_1 and ΔG_4 based on ΔG_{OH*} and the linear relationship between ΔG_{OH*} and ΔG_{OOH*}, as well as their corresponding energy barrier for remaining 20 catalysts

	ΔG_{OH*}	ΔG_1	ΔG_4	*average value of* ΔG_2 *and* ΔG_3	*Max energy barrier*
B-SV	*1.16*	*0.76*	*0.07*	*-0.42*	*0.76*
C-SV	*2.38*	*1.87*	*-1.15*	*-0.36*	*1.87*
O-SV	*-0.58*	*-0.81*	*1.81*	*-0.50*	*1.81*
Si-SV	*-1.28*	*-1.45*	*2.51*	*-0.53*	*2.51*
P-SV	*-0.46*	*-0.71*	*1.69*	*-0.49*	*1.69*
S-SV	*1.75*	*1.30*	*-0.52*	*-0.39*	*1.30*
As-SV	*1.04*	*0.66*	*0.19*	*-0.42*	*0.66*
Se-SV	*1.45*	*1.03*	*-0.22*	*-0.40*	*1.03*
Sn-SV	*0.44*	*0.11*	*0.79*	*-0.45*	*0.79*
Sb-SV	*1.37*	*0.96*	*-0.14*	*-0.41*	*0.96*
Tl-SV	*0.26*	*-0.05*	*0.97*	*-0.46*	*0.97*
Pb-SV	*0.98*	*0.60*	*0.25*	*-0.43*	*0.60*
Bi-SV	*1.45*	*1.03*	*-0.22*	*-0.40*	*1.03*
P-DV	*0.35*	*0.03*	*0.88*	*-0.45*	*0.88*
S-DV	*2.32*	*1.82*	*-1.09*	*-0.37*	*1.82*
As-DV	*0.52*	*0.18*	*0.71*	*-0.45*	*0.71*
Se-DV	*2.17*	*1.68*	*-0.94*	*-0.37*	*1.68*
Te-DV	*1.93*	*1.46*	*-0.70*	*-0.38*	*1.46*
Pb-DV	*0.61*	*0.26*	*0.62*	*-0.44*	*0.62*
Bi-DV	*1.61*	*1.18*	*-0.38*	*-0.40*	*1.18*

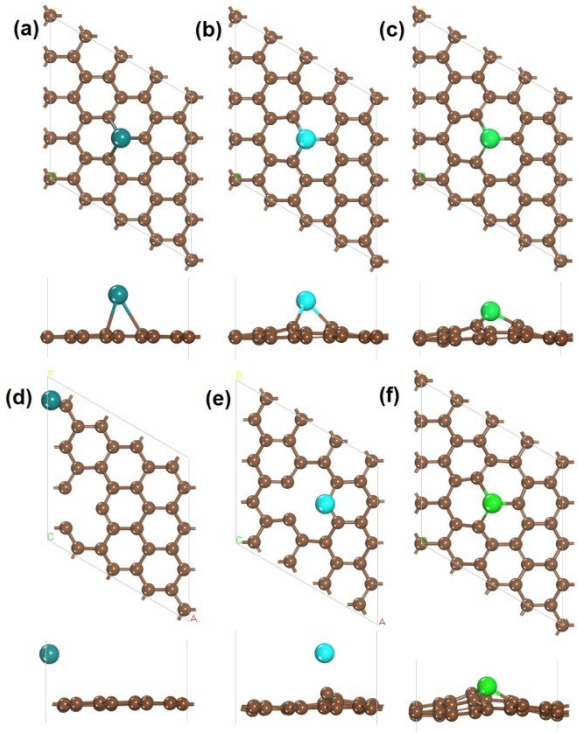

Figure S 1 The geometry structure of Tl-SV (a, d), In-SV (b, e) and Ga-SV (c, f) before (a, b, c) and after (d, e, f) first-principles molecular dynamics.

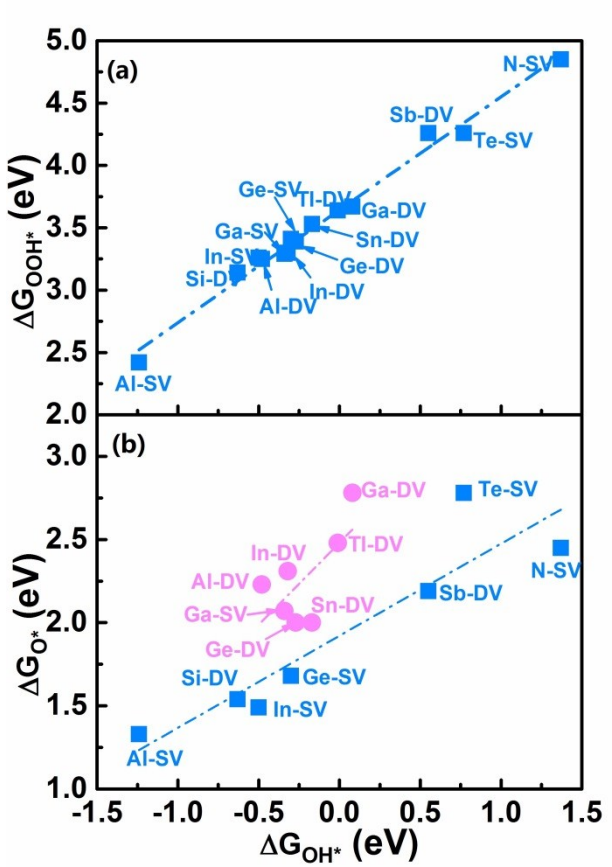

Figure S 2 The scaling relationship between ΔG_{OH^*} and ΔG_{OOH^*} (a) as well as ΔG_{OH^*} and ΔG_{O^*}

(b).

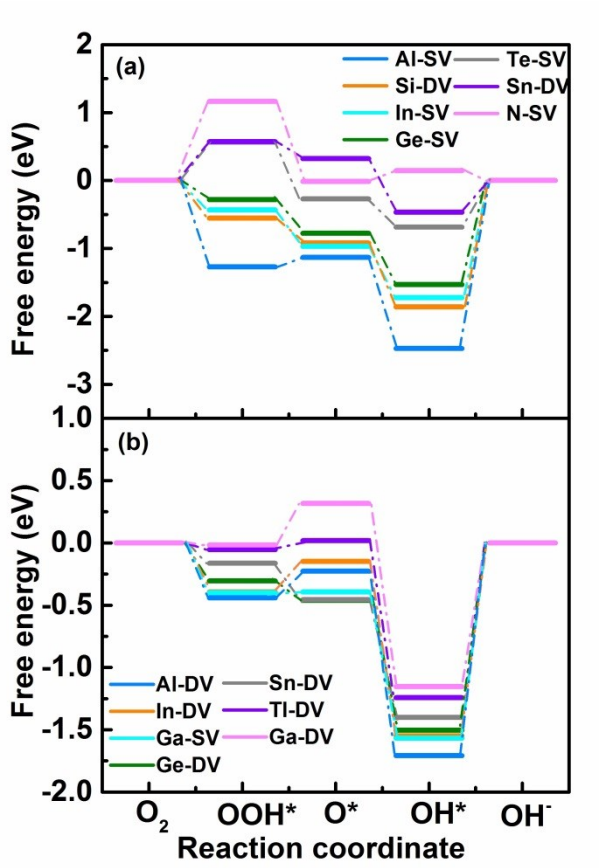

Figure S 3 The schematic Gibbs free energy diagrams of ORR for X-SV/DV with (a) or without (b) liner relationship.

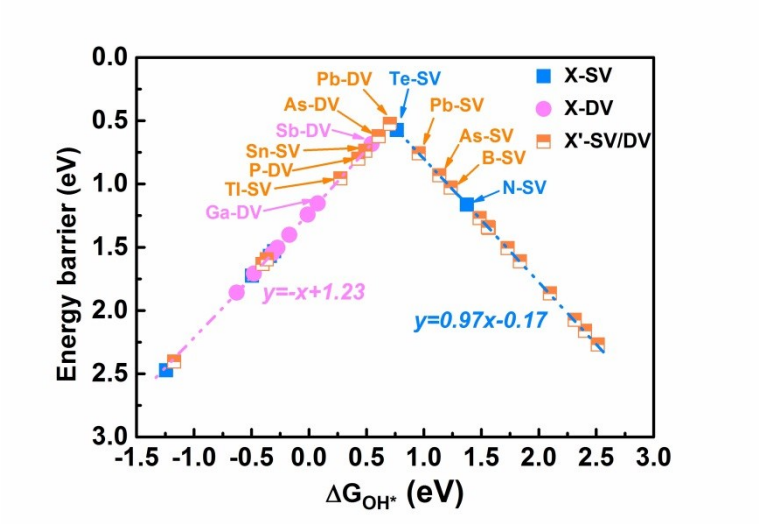

Figure S 4 The "volcanic curve" relationship between ΔG_{OH^*} and energy barrier for all 34 catalysts.