Supplementary Information

TM atoms on the B/N doped defective graphene as

catalyst for oxygen reduction reaction: a theoretical study

Xiaoming Zhang,[1] Shansheng Yu[1*], Hong Chen[2], Weitao Zheng[1*]

[1]Department of Materials Science, Key Laboratory of Mobile Materials, MOE, and State Key Laboratory

of Superhard Materials, Jilin University, Changchun 130012, PR China.

[2] Department of Control Science & Engineering, Jilin University, Changchun 130012, PR China.
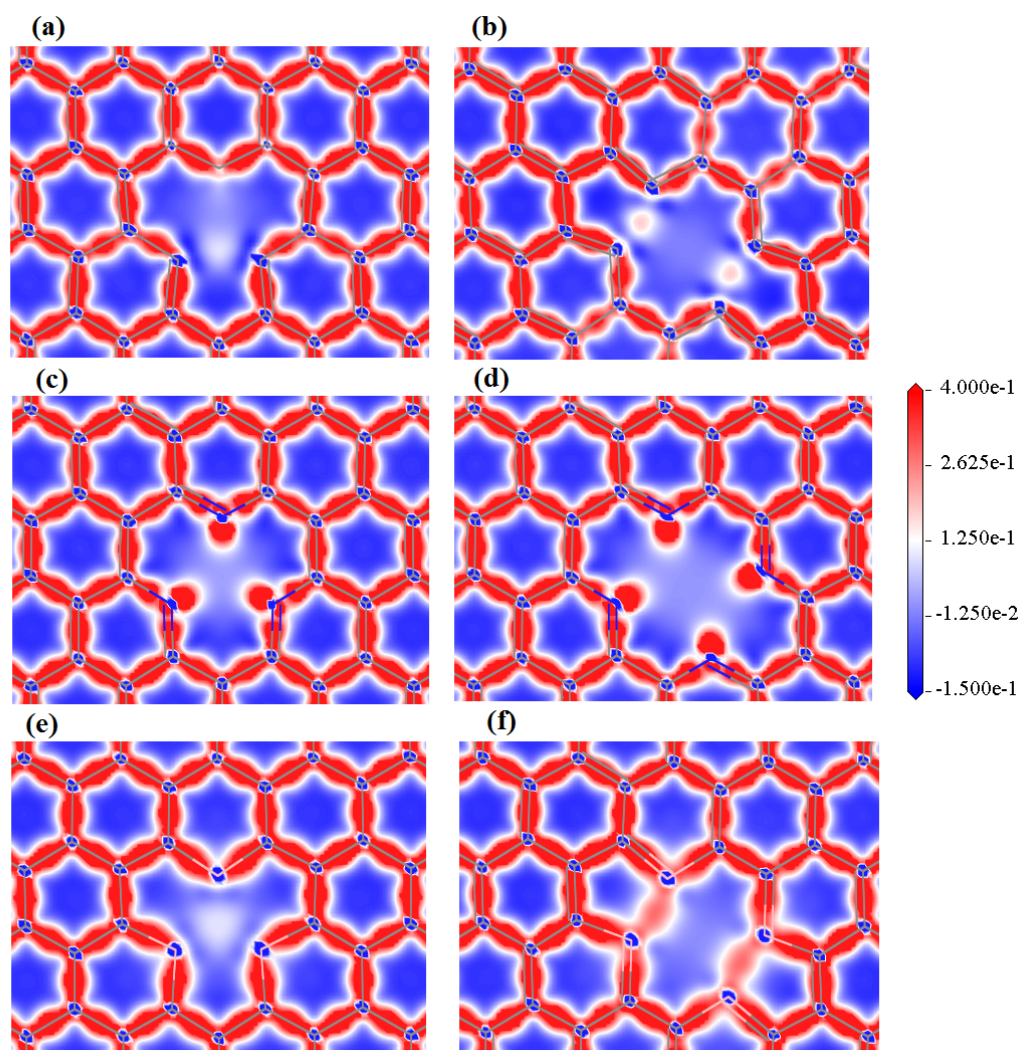
Fig S 1 Deformation electron density for six V1, (a); V2, (b); VN1, (c); VN2, (d); VB1, (e) and VB2 (f). The red color represents electron accumulation, while the blue color represents electron depletion. The intensity of color depends on the amount of electron change: the darkest red marks the most accumulation; the darkest blue marks the most depletion. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Table S 1 The formation energy, bond length, hirshfeld charge and hirshfeld spin of dangling atoms.

	E_{form}	l1	Charge	Spin
V1	7.63, 7.85[1]	2.10	0.01, -0.01	0.07, 0.67
VN1	3.51, 3.53[1]	2.61	-0.11	0.00
VB1	4.16	2.18	0.09	0.00
V2	7.84, 8.51[1]	1.80	0.01	0.00
VN2	4.00, 3.99[1]	2.62	-0.11	0.00
VB2	6.59	1.85	0.07	0.00

Table S 2 Hirshfeld charge of TM-vacancy complex

TM	V1		VN1		VB1		V2		VN2		VB2	
	TM	C1	TM	N1	TM	B1	TM	C1	TM	N1	TM	B1
Sc	0.61	-0.14	0.71	-0.15	0.67	-0.02	0.57	-0.12	0.67	-0.15	0.68	-0.02
Ti	0.51	-0.13	0.55	-0.13	0.51	0.00	0.55	-0.12	0.44	-0.13	0.49	-0.00
V	0.47	-0.11	0.40	-0.11	0.40	0.01	0.42	-0.10	0.34	-0.13	0.42	0.00
Cr	0.54	-0.12	0.50	-0.13	0.45	0.01	0.51	-0.11	0.44	-0.15	0.51	-0.01
Mn	0.32	-0.08	0.28	-0.09	0.32	0.01	0.28	-0.08	0.27	-0.11	0.28	0.02
Fe	0.26	-0.06	0.27	-0.08	0.29	0.02	0.21	-0.07	0.20	-0.10	0.20	0.04
Co	0.21	-0.05	0.19	-0.09	0.18	0.03	0.13	-0.06	0.18	-0.09	0.17	0.05
Ni	0.23	-0.04	0.24	-0.09	0.20	0.05	0.05	-0.05	0.09	-0.08	0.08	0.06
Cu	0.38	-0.09	0.31	-0.13	0.34	0.01	0.39	-0.10	0.37	-0.13	0.33	0.02
Zn	0.34	-0.10	0.37	-0.13	0.31	0.04	0.36	-0.08	0.41	-0.13	0.40	0.01
Pd	0.56	-0.08	0.38	-0.13	0.45	0.01	0.46	-0.10	0.47	-0.14	0.46	0.02
Pt	0.42	-0.05	0.22	-0.11	0.32	0.04	0.29	-0.07	0.28	-0.11	0.31	0.05

Table S 3 The binding energy, deformation energy and interaction energy of various TM-vacancy complexes.

TM-monovacancy complexes

	TM-V1			TM-VN1			TM-VB1		
TM	E_b	E_{defor}	E_{inter}	E_b	E_{defor}	E_{inter}	E_b	E_{defor}	E_{inter}
Sc	-7.04	1.03	-8.07	-6.37	0.74	-7.11	-3.38	0.05	-3.43
Ti	-8.27	0.84	-9.11	-6.29	0.80	-7.09	-3.24	0.04	-3.28
V	-7.41	0.86	-8.27	-5.73	0.63	-6.36	-2.50	0.18	-2.67
Cr	-6.28	0.86	-7.14	-3.97	0.77	-4.74	-1.85	0.01	-1.87
Mn	-6.44	0.74	-7.18	-4.24	0.63	-4.87	-2.12	0.84	-2.96
Fe	-7.73	0.89	-8.62	-5.38	0.52	-5.90	-3.31	0.98	-4.29
Co	-8.14	0.68	-8.82	-5.21	0.54	-5.75	-3.95	1.14	-5.09
Ni	-6.76	0.54	-7.30	-4.49	0.56	-5.05	-3.94	1.13	-5.07
Cu	-3.54	0.86	-4.40	-3.00	0.48	-3.48	-2.24	0.05	-2.30
Zn	-1.40	1.80	-3.20	-1.58	0.53	-2.11	-0.62	0.02	-0.64

Pd	-4.25	0.66	-4.91	-1.70	0.14	-1.84	-2.48	1.49	-3.96
Pt	-3.95	0.80	-4.75	-1.25	0.13	-1.38	-2.28	1.82	-4.10

TM-divacancy complexes

	TM-V1			**TM-VN2**			**TM-VB1**		
TM	E_b	E_{defor}	E_{inter}	E_b	E_{defor}	E_{inter}	E_b	E_{defor}	E_{inter}
Sc	-6.04	2.88	-8.92	-8.56	0.62	-9.18	-5.39	0.32	-5.70
Ti	-7.50	2.63	-10.13	-8.34	0.56	-8.90	-5.37	0.31	-5.67
V	-6.69	2.35	-9.05	-7.63	0.68	-8.31	-4.69	0.36	-5.04
Cr	-5.19	2.61	-7.80	-6.66	0.53	-7.19	-3.22	0.54	-3.76
Mn	-5.43	2.69	-8.12	-6.76	0.61	-7.37	-3.46	0.50	-3.96
Fe	-6.12	2.54	-8.67	-7.90	0.58	-8.48	-4.77	0.74	-5.52
Co	-6.62	2.72	-9.34	-8.31	0.53	-8.83	-5.19	0.74	-5.92
Ni	-6.27	3.08	-9.35	-7.68	0.56	-8.24	-4.93	1.01	-5.94
Cu	-4.86	2.96	-7.82	-4.93	0.43	-5.35	-3.46	1.02	-4.48
Zn	-2.52	2.85	-5.37	-3.60	0.48	-4.08	-1.12	0.57	-1.69
Pd	-3.23	2.77	-6.00	-4.31	0.67	-4.98	-3.18	1.81	-4.99
Pt	-2.92	3.32	-6.24	-3.65	0.90	-4.55	-3.02	2.15	-5.17

Table S 4 The TM-C(B/N) bond length change after O_2, OOH, HOOH and OH adsorbed on V1 and VN2 complexes.

TM-VN2

TM	l_{TM-N}	∇l_{TM-N}	∇l_{TM-N}	∇l_{TM-N}	∇l_{TM-N}	∇l_{TM-N}
	bare	O_2	OOH	HOOH	OH	O
Sc	2.10	0.09*2	0.06*2	0.20*2	0.06*4	0.02*4
		0.08*2	0.08*2	0.25*2		
Ti	2.05	0.03*2	0.01*3	0.07*2	0.02*4	0.04*4
		0.06*2	0.05	0.11*2		
V	2.00	0.03*2	0.03*3	0.07*2	0.01*2	0.05*4
		0.06*2	0.08	0.13*2	0.03*2	
Cr	1.95	0.05*2	0.03*2	0.08	0.03*4	0.06*4
		0.06*2	0.04*2	0.10		
				0.17*2		
Mn	1.93	0.06*2	0.02*2	0.18*2	0.03*2	0.04*4
		0.08*2	0.05*2	0.10	0.04*2	
				0.11		
Fe	1.91	0.01	0.01	0.09*2	0.01*2	0.03*4
		0.02*3	0.02*3	0.17	0.02*2	
				0.19		
Co	1.91	0.01*4	0.01*4	0.01*4	0.00*2	0.02*4
					0.01*2	
Ni	1.89	0.00*4	0.02*4	-0.00*4	0.02	0.02*2
					0.03*3	-0.02
						0.00
Cu	1.94	0.00*4	0.04*4	0.01	0.10*3	0.02*2

				0.00*3	0.11	-0.03
						0.00
Zn	1.97	0.07*2	0.12*3	0.31*2	0.16*3	0.02*2
		0.08*2	0.33	0.31*2	0.17	0.04
						-0.04
Pd	1.99	-0.01*4	-0.01*4	-0.01*2	-0.01	0.01*2
				0.02*2	-0.00	0.00
					0.01*2	-0.02
Pt	2.01	-0.00*4	0.01*4	-0.00*4	0.01*2	0.03
					0.02	0.02
					0.03	0.00*2

Table S 5 The adsorption energies, E_{ads} , of reactants and intermediate products of oxygen reduction reaction on the V1 and VN2 graphene surfaces.

TM-VN2

	$E_{ads}(O_2)$	$E_{ads}(OOH)$	$E_{ads}(HOOH)$	$E_{ads}(O)$	$E_{ads}(OH)$
Sc	-2.87	-3.76	-5.20	-5.22	-5.10
Ti	-4.34	-4.00	-6.28	-7.55	-5.35
V	-3.42	-3.29	-5.08	-7.33	-4.61
Cr	-1.99	-2.21	-3.56	-6.06	-3.54
Mn	-1.46	-1.97	-2.71	-5.01	-3.23
Fe	-1.02	-1.88	-2.03	-4.20	-2.95
Co	-0.80	-1.54	-1.55	-2.92	-2.62
Ni	-0.16	-0.50	-0.50	-2.39	-1.46
Cu	-0.25	-0.58	-0.50	-2.47	-1.58
Zn	-0.45	-1.30	-1.32	-2.45	-2.57
Pd	-0.04	-0.14	0.11	-2.37	-1.39
Pt	0.09	1.67	-0.19	-2.31	-1.38

[1]   S. Kattel, P. Atanassov, B. Kiefer, The Journal of Physical Chemistry C 116 (2012) 8161-8166.