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CH_4, CO_2 和 H_2O 在非金属原子修饰石墨烯表面的吸附

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CH_4, CO_2 and H_2O Adsorption on Nonmetallic Atom-Decorated Graphene Surfaces

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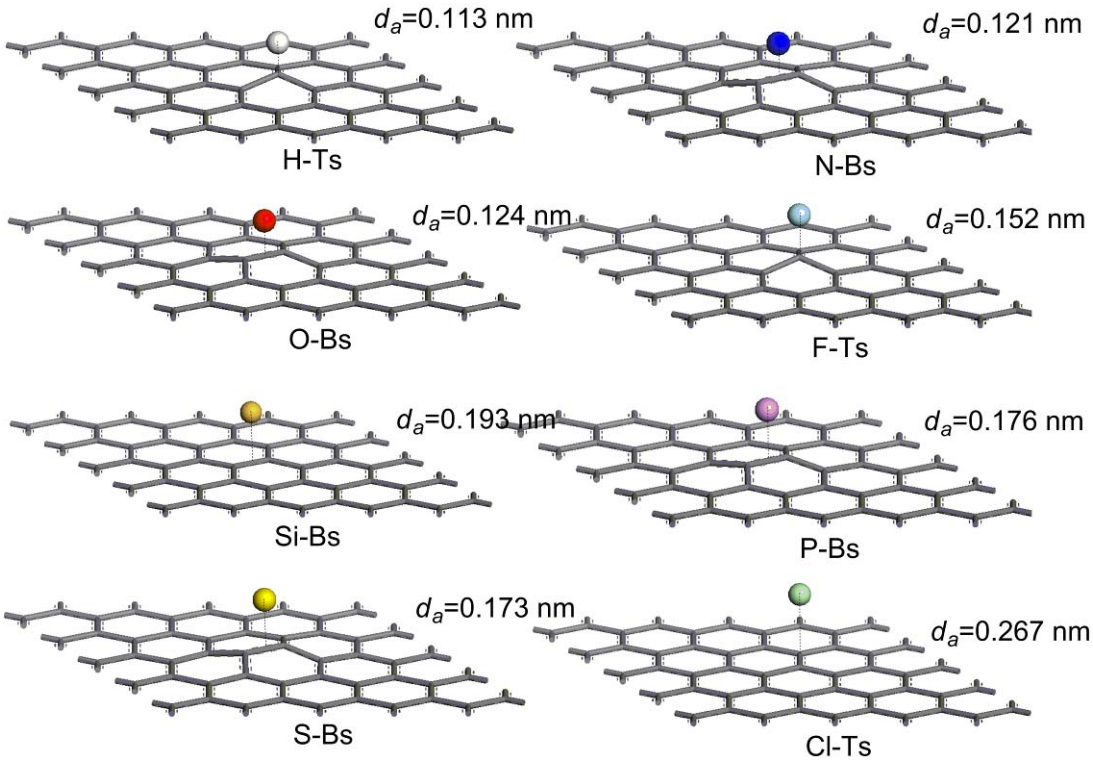

图 S1　X 吸附在 Gr 上的能量最稳定构型

Fig.S1　The most energetically favorable optimized structures for X adsorption on Gr

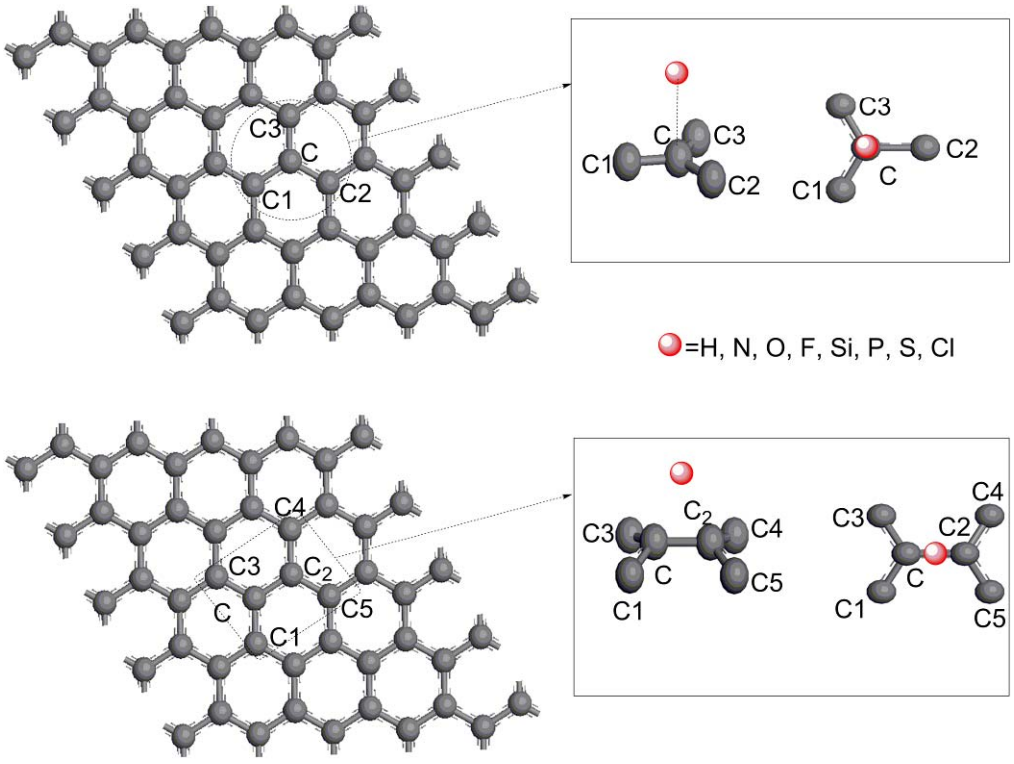

图 S2　X 吸附在 Gr 上的键长键角示意图

Fig.S2　The bond lengths and angles for X adsorption on Gr

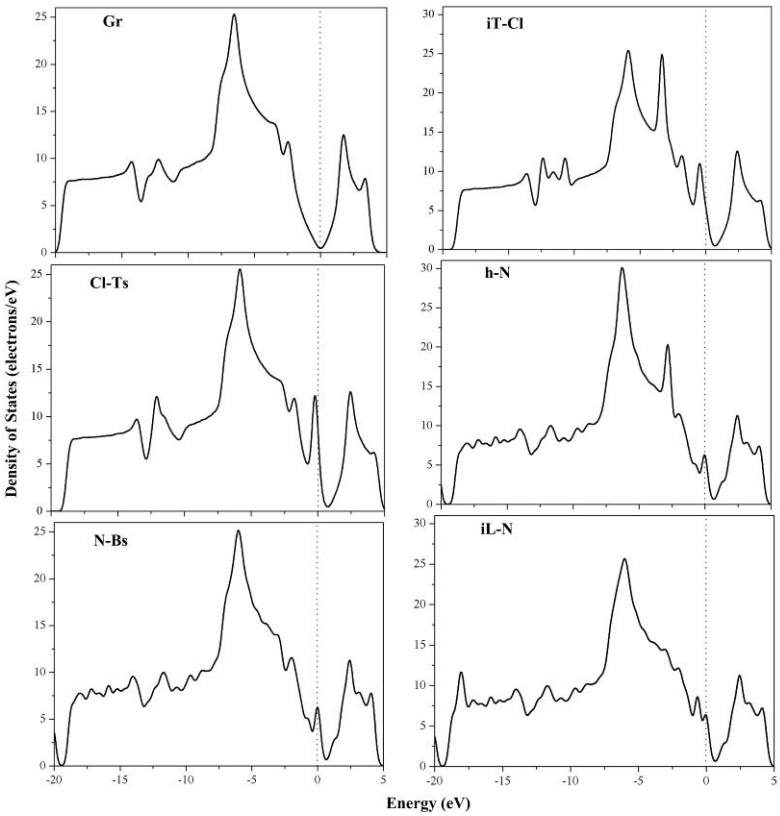

图 S3　Gr, Cl-T_s, N-B_s, iT-Cl, h-N 和 iL-N 体系的态密度

Fig.S3　The density of states for Gr, Cl-T_s, N-B_s, iT-Cl, h-N and iL-N

The vertical dashed is Fermi level of the system, which is set to zero.

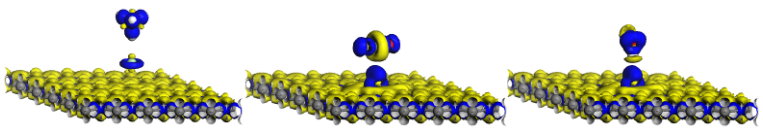

图 S4　iT-Cl, h-N 和 iL-N 的差分电荷密度图

Fig.S4　The electronic density difference images for iT-Cl, h-Nand iL-N

The blue region means the electron accumulation, while yellow region shows the electron loss.

表 S1　X 吸附在 Gr 上的键长 l_{Bond}（nm）

Table S1　The bond lengths l_{Bond}（nm）for X adsorption on Gr

System		l_{Bond}										
Atoms	Sites	C-C1	C-C2	C-C3	C2-C4	C2-C5	X-C	X-C1	X-C2	X-C3	X-C4	X-C5
H	Ts	0.147	0.147	0.147	-	-	0.113	0.204	0.204	0.204	-	-
N	Bs	0.144	0.154	0.144	0.144	0.144	0.144	0.243	0.144	0.243	0.243	0.243
O	Bs	0.145	0.149	0.145	0.145	0.145	0.145	0.241	0.145	0.241	0.241	0.241
F	Ts	0.147	0.147	0.147	-	-	0.152	0.232	0.232	0.232	-	-
Si	Bs	0.142	0.144	0.142	0.142	0.142	0.206	0.271	0.206	0.271	0.271	0.271
P	Bs	0.144	0.147	0.144	0.144	0.144	0.191	0.275	0.191	0.272	0.272	0.275
S	Bs	0.145	0.148	0.145	0.145	0.145	0.188	0.276	0.188	0.276	0.276	0.276
Cl	Ts	0.141	0.141	0.141	-	-	0.267	0.305	0.305	0.305	-	-
Gr		0.141	0.141	0.141	0.141	0.141	-	-	-	-	-	-

表 S2　X 吸附在 Gr 上的键角 A (度,°)

Table S2　The bond Angles A (Degree,°) for X adsorption on Gr

System		A(Degree,°)					
Atoms	Sites	C1-C-C2	C1-C-C3	C4-C2-C5	C-C2-C4	X-C-C1	X-C-C2
H	Ts	115.839	115.857	-	-	101.925	101.932
N	Bs	117.079	119.533	119.533	117.279	112.974	57.558
O	Bs	118.432	119.418	119.418	118.405	112.836	59.058
F	Ts	115.533	115.544	-	-	102.374	102.381
Si	Bs	119.345	121.295	121.295	119.320	100.799	69.567
P	Bs	119.317	120.182	120.182	117.527	109.782	67.283
S	Bs	118.382	118.605	118.605	118.361	110.974	66.930
Cl	Ts	119.951	119.952	-	-	91.262	91.283
Gr		120.000	120.000	120.000	120.000	-	-

表 S3　X 吸附在 Gr 上的二面角 D (度,°)

Table S3　The dihedral angles D (Degree,°) for X adsorption on G

System		D(Degree，°)			
Atoms	Sites	C1-C-C2-C5	C1-C-C2-C4	X-C3-C-C1	X-C-C2-C4
H	Ts	-	-	-	-
N	Bs	152.593	0.153	143.378	103.856
O	Bs	158.097	0.003	136.117	100.955
F	Ts	-	-	-	-
Si	Bs	177.717	-0.010	109.815	91.132
P	Bs	158.598	-1.944	126.567	98.757
S	Bs	155.509	-0.006	130.206	102.129
Cl	Ts	-	-	-	-
Gr		180.000	0.000	-	-

表 S4　X 吸附在 Gr 上的吸附能(Δ*E*/eV），吸附平衡距离(d_a/nm)和 Mulliken 电荷转移(Q_a/ a.u.）. "-"表示不存在稳定构型

Table S4　Adsorption energies (Δ*E*/eV), equilibrium distances (d_a/nm）and Mulliken charge (Q_a/ a.u.) for X adsorption on Gr. "-" denoting absence of stable structure

System		ΔE	d_a	Q_a
Atoms	Sites			
	Bs	-	-	-
H	Cs	-0.38	0.232	-0.26
	Ts	-2.05	0.113	0.38
	Bs	-4.50	0.121	-0.41
N	Cs	-	-	-
	Ts	-	-	-
	Bs	-4.68	0.124	-0.46
O	Cs	-2.37	0.190	0.79
	Ts	-3.84	0.141	-0.63
	Bs	-2.61	0.196	-0.57
F	Cs	-2.38	0.226	-0.63
	Ts	-2.97	0.152	-0.42
	Bs	-1.78	0.193	0.54
Si	Cs	-1.27	0.182	0.74
	Ts	-1.76	0.199	0.59
	Bs	-2.14	0.176	0.21
P	Cs	-	-	-
	Ts	-	-	-
	Bs	-2.27	0.173	0.00
S	Cs	-0.81	0.278	-0.40
	Ts	-1.91	0.191	-0.27
	Bs	-1.45	0.269	-0.54
Cl	Cs	-1.39	0.291	-0.53
	Ts	-1.46	0.267	-0.53

表 S5　CH_4 在 X 修饰的石墨烯上的吸附能（Δ*E*/eV），吸附平衡距离（d_g/nm），X 到石墨烯的距离（$d_a^{'}$/nm），Mulliken 电荷（Q_g/a.u.）

Table 5　Adsorption energies (Δ*E*/eV), equilibrium distances (d_g/nm), X-Graphene equilibrium distances ($d_a^{'}$/nm）and Mulliken charge (Q_g/a.u.）for CH_4 adsorption on X-decorated graphene

Systems	Atoms	ΔE	d_g	$d_a^{'}$	Q_g
Orientations					
iT	H	-0.086	0.307	0.114	0.01
xP		-0.121	0.267	0.113	0.00
rT		-0.124	0.264	0.114	0.02

iT	N	-0.089	0.311	0.121	-0.03
xP		-0.100	0.304	0.121	0.01
rT		-0.047	0.283	0.121	0.00
iT	O	-0.084	0.314	0.125	-0.02
xP		-0.054	0.291	0.124	-0.02
rT		-0.065	0.287	0.124	0.00
iT	F	-0.099	0.315	0.152	-0.01
xP		-0.057	0.278	0.151	0.00
rT		-0.066	0.273	0.151	0.00
iT	Si	-0.108	0.324	0.195	-0.01
xP		-0.046	0.315	0.194	0.00
rT		-0.089	0.309	0.194	-0.01
iT	P	-0.090	0.352	0.174	-0.02
xP		-0.059	0.308	0.178	0.00
rT		-0.099	0.303	0.177	0.01
iT	S	-0.084	0.341	0.174	-0.01
xP		-0.094	0.300	0.174	-0.01
rT		-0.108	0.296	0.173	-0.01
iT	Cl	-0.138	0.328	0.265	-0.01
xP		-0.105	0.321	0.265	0.01
rT		-0.074	0.305	0.259	-0.01

表 S6　CO_2 在 X 修饰的石墨烯上的吸附能（ΔE/eV），吸附平衡距离（d_g/nm），X 到石墨烯的距离（d_a'/nm），Mulliken 电荷（Q_g/a.u.）

Table S6　Adsorption energies (ΔE/eV）, equilibrium distances (d_g/nm), X-Graphene equilibrium distances (d_a'/nm）and Mulliken charge (Q_g/a.u.）for CO_2 adsorption on X-decorated graphene

Systems / Orientations	Atoms	ΔE	d_g	d_a'	Q_g
h	H	-0.093	0.211	0.113	-0.02
v		-0.142	0.316	0.113	0.02
h	N	-0.223	0.221	0.120	-0.07
v		-0.073	0.408	0.112	-0.01
h	O	-0.201	0.285	0.125	-0.01
v		-0.054	0.412	0.124	0.00
h	F	-0.191	0.233	0.152	-0.01
v		-0.022	0.367	0.150	0.00
h	Si	-0.114	0.293	0.192	-0.03
v		-0.033	0.417	0.195	0.01

h	P	-0.131	0.287	0.175	-0.01
v		-0.030	0.394	0.177	0.01
h	S	-0.129	0.280	0.172	0.00
v		-0.111	0.401	0.174	0.01
h	Cl	-0.189	0.267	0.254	-0.04
v		-0.071	0.444	0.265	0.01

表 S7　H_2O 在 X 修饰的石墨烯上的吸附能（ΔE/eV），吸附平衡距离（d_g/nm），X 到石墨烯的距离（$d_a^{'}$/nm），Mulliken 电荷（Q_g/a.u.）

Table S7　Adsorption energies (ΔE/eV）, equilibrium distances (d_g/nm), X-Graphene equilibrium distances ($d_a^{'}$/nm）and Mulliken charge (Q_g/a.u.）for H_2O adsorption on X-decorated graphene

Systems / Orientations	Atoms	ΔE	d_g	$d_a^{'}$	Q_g
rV	H	-0.317	0.187	0.115	0.06
iV		-0.327	0.186	0.115	0.08
pV		-0.324	0.187	0.115	0.09
rL		-0.313	0.190	0.115	0.07
iL		-0.308	0.190	0.115	0.08
rV	N	0.025	0.348	0.121	0.00
iV		-0.267	0.266	0.121	-0.02
pV		-0.467	0.265	0.121	-0.07
rL		-0.464	0.266	0.120	-0.08
iL		-0.450	0.265	0.120	-0.09
rV	O	0.010	0.292	0.124	0.00
iV		-0.180	0.271	0.125	-0.01
pV		-0.304	0.275	0.125	-0.06
rL		-0.300	0.271	0.125	-0.06
iL		-0.290	0.270	0.125	-0.06
rV	F	-0.330	0.269	0.156	-0.03
iV		-0.244	0.273	0.154	0.00
pV		-0.245	0.274	0.152	0.00
rL		-0.312	0.272	0.156	-0.03
iL		-0.297	0.273	0.156	-0.03
rV	Si	-0.190	0.270	0.199	0.05
iV		-0.127	0.310	0.193	-0.01
pV		-0.189	0.284	0.200	0.05
rL		-0.209	0.261	0.201	0.05
iL		-0.133	0.326	0.195	-0.01

rV	P	-0.142	0.284	0.197	0.03
iV		-0.197	0.302	0.178	-0.01
pV		-0.235	0.304	0.175	-0.03
rL		-0.171	0.281	0.178	0.01
iL		-0.210	0.302	0.178	-0.01
rV	S	-0.133	0.262	0.174	0.03
iV		-0.149	0.299	0.175	0.00
pV		-0.173	0.298	0.176	0.02
rL		-0.224	0.289	0.174	-0.01
iL		-0.197	0.296	0.175	0.00
rV	Cl	-0.442	0.332	0.263	-0.03
iV		-0.366	0.309	0.273	-0.01
pV		-0.448	0.294	0.278	-0.02
rL		-0.428	0.299	0.267	-0.04
iL		-0.434	0.298	0.273	-0.04