Tailoring the Electronic Structure and Chemical Activity of Iron via Confining into Two Dimensional Materials

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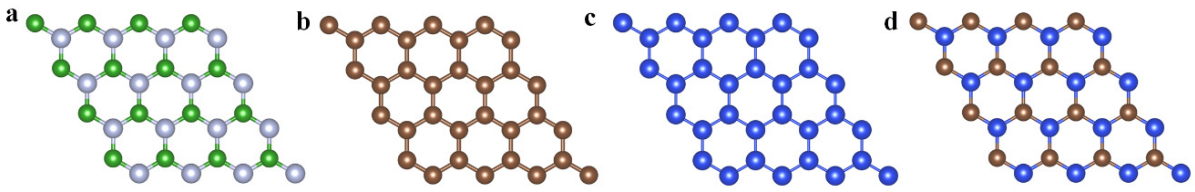

Figure S1. The structures of 2D materials (a) h-BN; (b) graphene; (c) silicene; (d) silicon-carbon (boron, nitrogen, carbon, silicon atoms are given in green, gray, brown, blue).

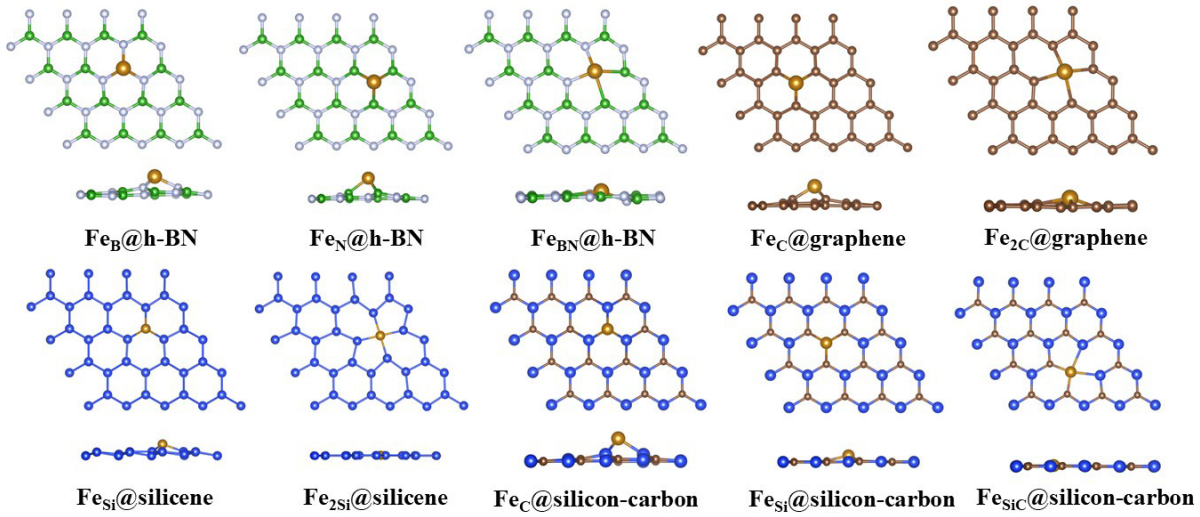

Figure S2. The top and side view of the most stable structures of the Fe doped 2D materials (h-BN, graphene, silicene, silicon-carbon).

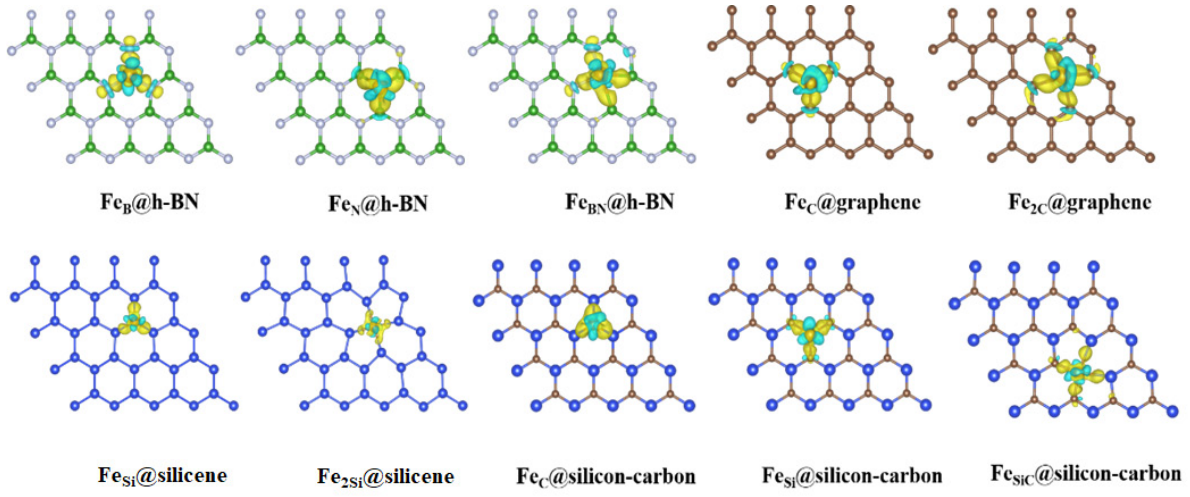

Figure S3. The Fe atomic electronic density of 10 doped materials.

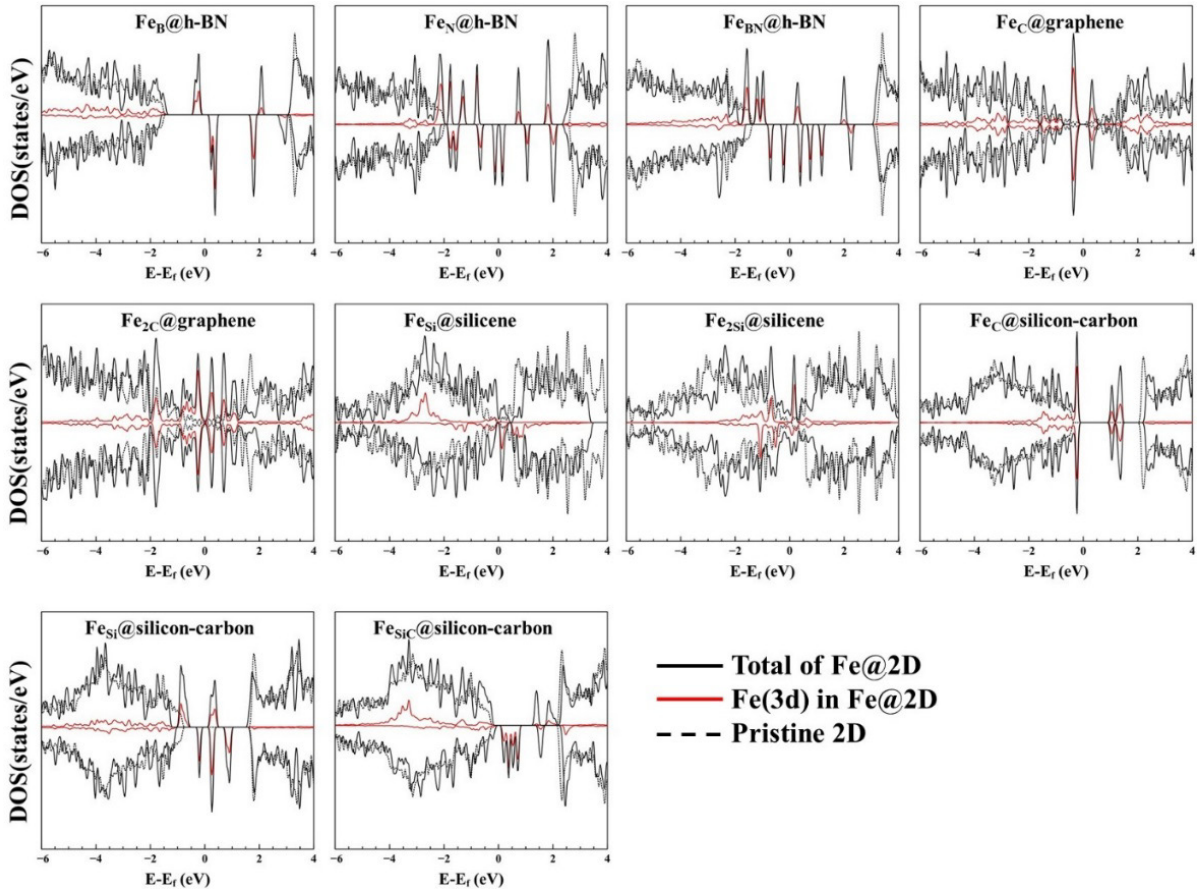

Figure S4. DOS of doped structures near Fermi energy level; the total electron density state of doped materials, showed by black line, the 3d orbit electron density state of iron atom in doped materials, showed by red line, and the electron density state of 2D materials, showed by black dash line.

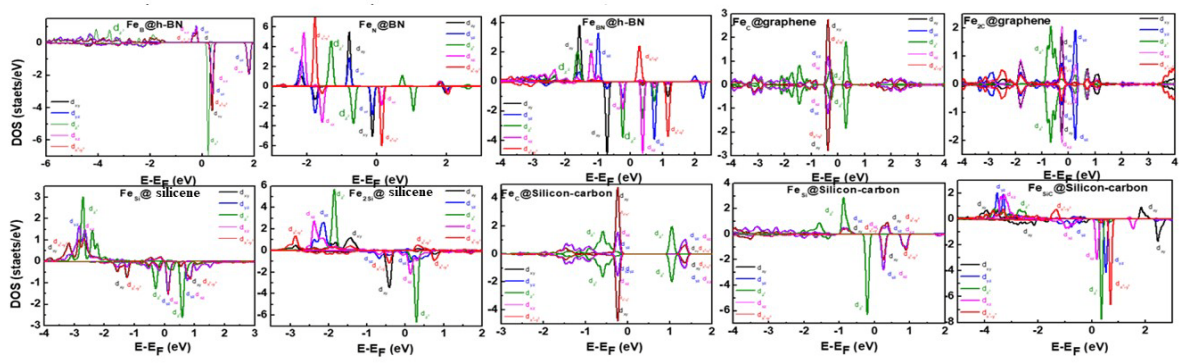

Figure S5. The d_{xy}, d_{yz}, d_{xz}, $d_{x^2-y^2}$, d_{z^2} electron density states of Fe@2D.

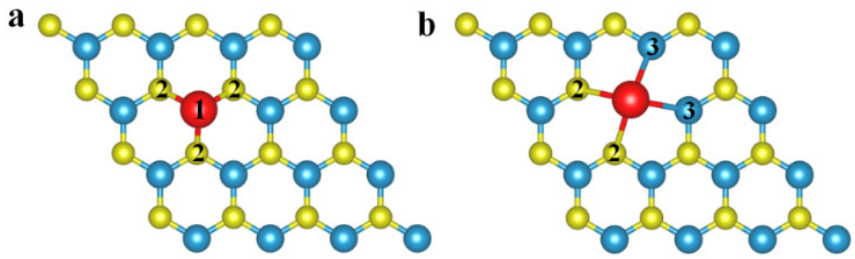

Figure S6. The possible adsorption sites of CO, H, C and O on Fe@2D (a) on-Fe (1 site) and on-Y (2 sites) of Fe_X@2D(CN=3); (b) on-Fe (1 sites), on-X (2 sites) and on-Y (3 sites) of Fe_{XY}@2D(CN=4).

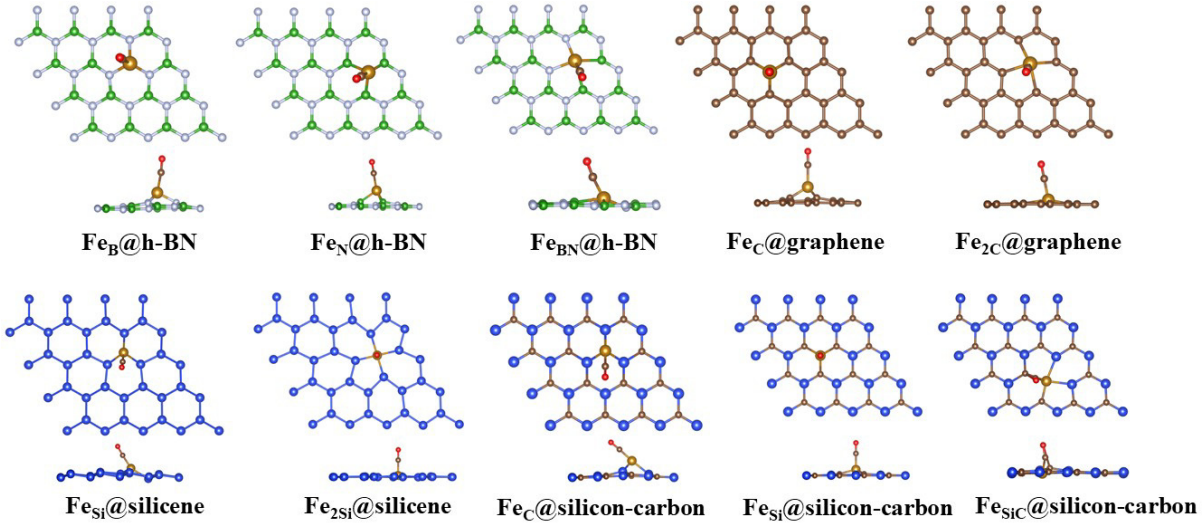

Figure S7. The adsorption structures of CO on Fe@2D.

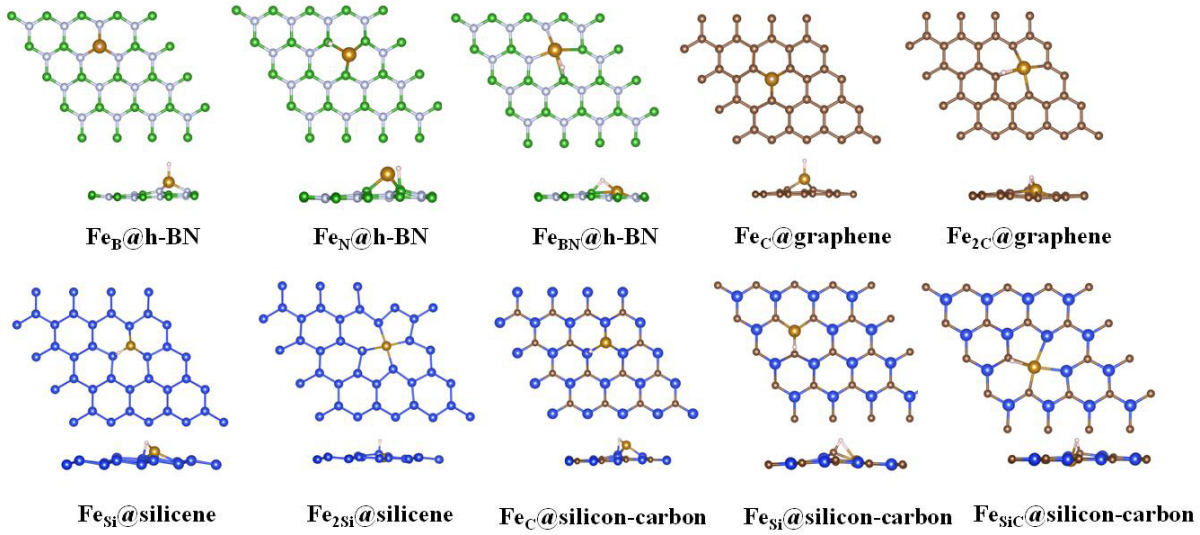

Figure S8. The adsorption structures of H on Fe@2D.

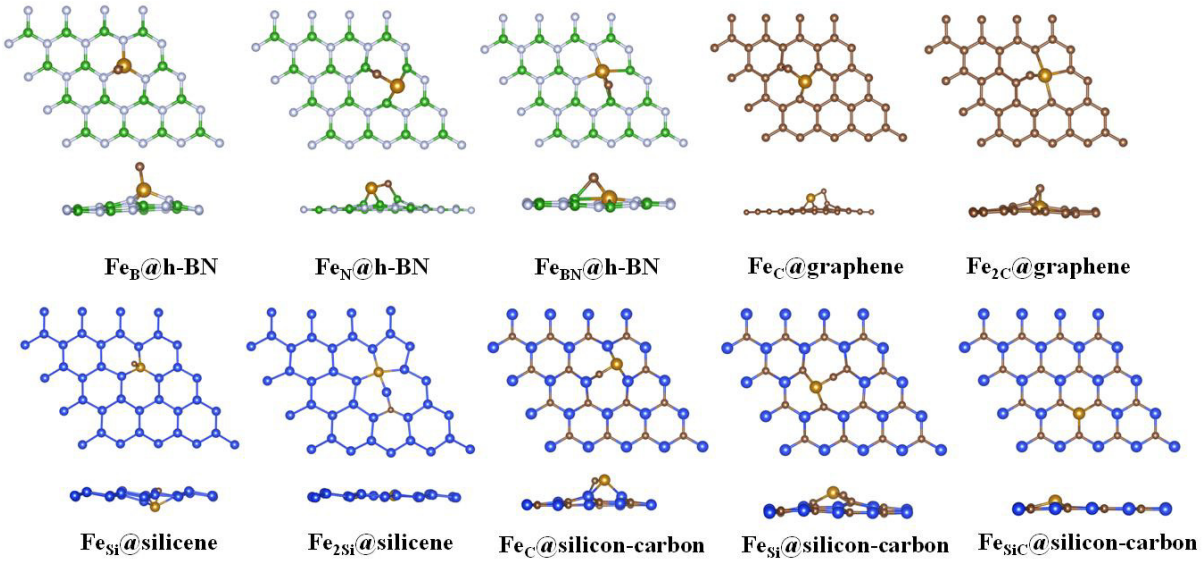

Figure S9. The adsorption structures of C on Fe@2D.

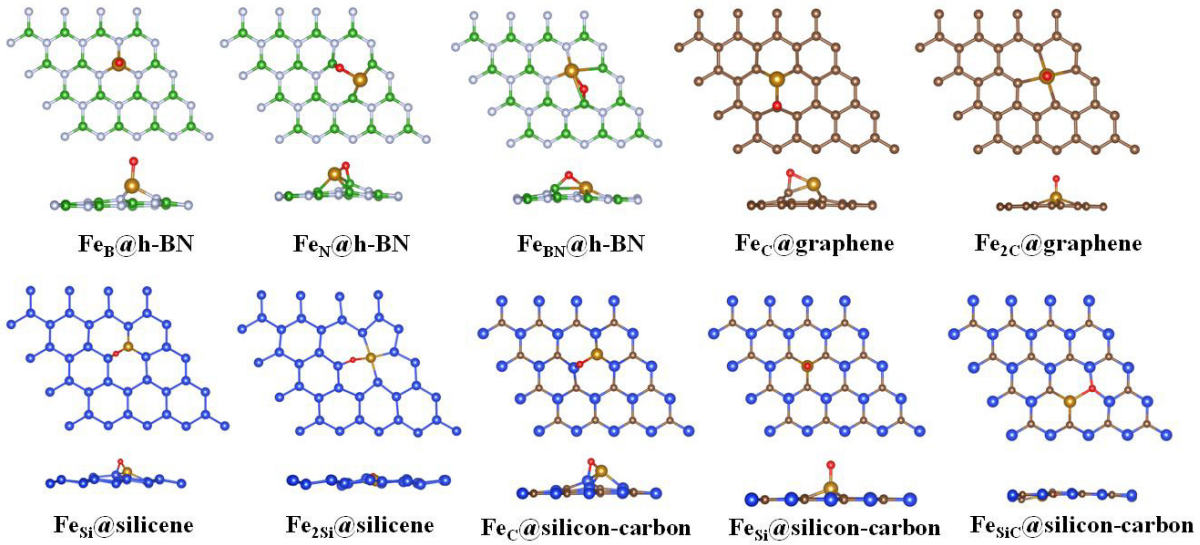

Figure S10. The adsorption structures of O on Fe@2D.

Table S1. Calculated iron atomic d orbital position of bonding (E_{bond}) and antibonding (E_{anti}).

		d_{xy}	$d_{x^2-y^2}$	d_{xz}	d_{yz}	d_{z^2}
Fe_B@h-BN	E_{bond}	-3.57	-3.58	-3.76	-3.75	-2.95
	E_{anti}	-0.32	-0.32	-0.37	-0.34	-0.89
Fe_N@h-BN	E_{bond}	-1.47	-1.35	-2.09	-2.17	-1.42
	E_{anti}	0.18	-0.17	0.11	0.76	0.49
Fe_{BN}@h-BN	E_{bond}	-2.28	-3.13	-1.85	-2.04	-1.79
	E_{anti}	0.24	1.66	-0.10	0.44	-0.07
Fe_C@graphene	E_{bond}	-2.31	-2.31	-3.11	-3.11	-2.25
	E_{anti}	0.60	0.60	1.14	1.14	0.60
Fe_{2C}@graphene	E_{bond}	-2.23	-3.20	-1.56	-2.01	-1.35
	E_{anti}	1.11	2.48	0.67	0.68	0.21
Fe_{Si}@silicene	E_{bond}	-2.23	-2.23	-1.85	-1.85	-1.66

	E_{anti}	-0.50	-0.49	-0.47	-0.47	-0.69
Fe_{2Si}@silicene	E_{bond}	-1.24	-1.98	-0.99	-1.06	-0.75
	E_{anti}	0.33	0.83	0.08	0.17	-0.40
Fe_C@silicon-carbon	E_{bond}	-1.04	-1.04	-1.59	-1.59	-1.10
	E_{anti}	0.45	0.45	1.01	1.01	0.57
Fe_{Si}@silicon-carbon	E_{bond}	-4.14	-4.14	-2.48	-2.48	-2.02
	E_{anti}	0.04	0.03	0.08	0.08	-0.32
Fe_{SiC}@silicon-carbon	E_{bond}	-3.51	-2.07	-2.06	-2.09	-2.04
	E_{anti}	0.88	-0.51	-0.75	-0.57	-0.93

Table S2. Calculated catalyst performance of doped materials, the adsorption energy of CO, H, C and O on doped materials of different sites (in eV).

Before	E_{ads-CO}	E_{ads-H}	E_{ads-C}	E_{ads-O}
Fe_B@h-BN-Fe	-1.40	-0.47	-2.48	-0.30
Fe_B@h-BN-N	-1.22	0.25	-1.81	2.32
Fe_N@h-BN-Fe	-1.90	-0.25	-2.26	0.24
Fe_N@h-BN-B	-1.60	-0.43	-2.49	-1.05
Fe_{BN}@h-BN-Fe	-2.17	-0.61	-2.62	-0.13
Fe_{BN}@h-BN-B	-1.98	-0.61	-2.67	-1.38
Fe_{BN}@h-BN-N	-1.08	-0.32	-2.38	2.00
Fe_C@graphene-Fe	-1.44	-0.20	-2.21	0.49
Fe_C@graphene-C	-1.43	0.44	-1.62	1.07

Fe_{2C}@graphene-Fe	-1.71	-0.21	-2.22	0.00
Fe_{2C}@graphene-C	-1.68	-0.27	-2.33	0.12
Fe_{Si}@silicene-Fe	-1.85	-0.34	-7.03	-0.41
Fe_{Si}@silicene-Si	-1.99	-0.52	-6.26	-0.99
Fe_{2Si}@silicene-Fe	-1.92	-0.04	-2.05	-0.22
Fe_{2Si}@silicene-Si	0.01	-0.30	-7.52	-0.97
Fe_{C}@silicon-carbon-Fe	-2.14	-0.41	-4.35	0.26
Fe_{C}@silicon-carbon-Si	-0.60	-0.41	-5.73	-0.81
Fe_{Si}@silicon-carbon-Fe	-1.03	-0.09	-6.30	0.53
Fe_{Si}@silicon-carbon-C	-1.03	-0.58	-5.45	0.71
Fe_{SiC}@silicon-carbon-Fe	-1.35	-0.10	-8.24	-1.59
Fe_{SiC}@silicon-carbon-C	-1.50	-0.94	-6.69	1.02
Fe_{SiC}@silicon-carbon-Si	-0.24	0.00	-4.61	-1.61

Table S3. Calculated catalyst performance of doped materials, the adsorption energy of CO, H, C and O on doped materials of stable adsorption site (in eV).

	E_{ads-CO}	Bond(C-O)	E_{ads-H}	E_{ads-C}	E_{ads-O}
Fe_{B}@h-BN	-1.40	1.163	-0.47	-2.48	-0.30
Fe_{N}@h-BN	-1.90	1.171	-0.43	-2.49	-1.05
Fe_{BN}@h-BN	-2.17	1.176	-0.61	-2.67	-1.38
Fe_{C}@graphene	-1.44	1.157	-0.20	-2.21	0.49
Fe_{2C}@graphene	-1.71	1.167	-0.27	-2.33	0.00

Fe_{Si}@silicene	-1.99	1.171	-0.52	-7.03	-0.99
Fe_{2Si}@silicene	-1.92	1.170	-0.30	-7.52	-0.97
Fe_{C}@silicon-carbon	-2.14	1.172	-0.41	-5.73	-0.81
Fe_{Si}@silicon-carbon	-1.03	1.162	-0.58	-6.30	0.53
Fe_{SiC}@silicon-carbon	-1.50	1.201	-0.94	-8.24	-1.61

Table S4. Calculated catalyst performance, the adsorption energy of CO, H, C and O on the different surface of Fe and 2D materials (in eV).

	E_{ads-CO}	E_{ads-H}	E_{ads-C}	E_{ads-O}
Fe(100)	-1.78	-0.39	-8.44	-1.00
Fe(110)	-1.96	-0.77	-8.12	-0.92
Fe(111)	-1.97	-0.60	-7.91	-0.61
Fe(211)	-1.82	-0.56	-7.76	-0.42
Fe(310)	-1.65	-0.32	-8.24	-0.08
h-BN(B-X)	0.00	2.43	-0.92	3.71
h-BN(N-X)	0.00	3.17	-0.92	3.71
graphene(C-X)	0.00	1.50	-1.43	3.47
silicene(Si-X)	0.30	-0.41	-4.87	0.50
silicon-carbon(C-X)	0.00	1.30	-3.65	1.45
silicon-carbon (Si-X)	0.00	1.10	-3.08	1.45

Table S5. Calculated the energy of CO, H, C and O (in eV).

	Formula	E/eV
CO	$E_{CO} = E_{CO}$	-14.79
H	$E_H = 1/2E_{H2}$	-3.40
C	$E_C = E_C$	-1.39
O	$E_O = E_{H_2O} - E_{H_2}$	-7.43

Table S6. The Bader charge and valence of the Fe atom (Q) on sulfides, oxides and doped materials.

	Q	Oxidation Number
FeO	1.28	II
Fe_2O_3	1.62	III
FeS	0.67	II
Fe_B@h-BN	1.28	II
Fe_N@h-BN	-0.06	0
Fe_{BN}@h-BN	0.80	II
Fe_C@graphene	0.73	II
Fe_{2C}@graphene	0.84	II
Fe_{Si}@silicene	0.30	0
Fe_{2Si}@silicene	0.30	0
Fe_C@silicon-carbon	-0.59	0
Fe_{Si}@silicon-carbon	0.87	II
Fe_{SiC}@silicon-carbon	0.90	II