Electronic Supplementary Material (ESI) for RSC Advances.

Supplementary Information

Halogenation of graphene triggered by heteroatom doping

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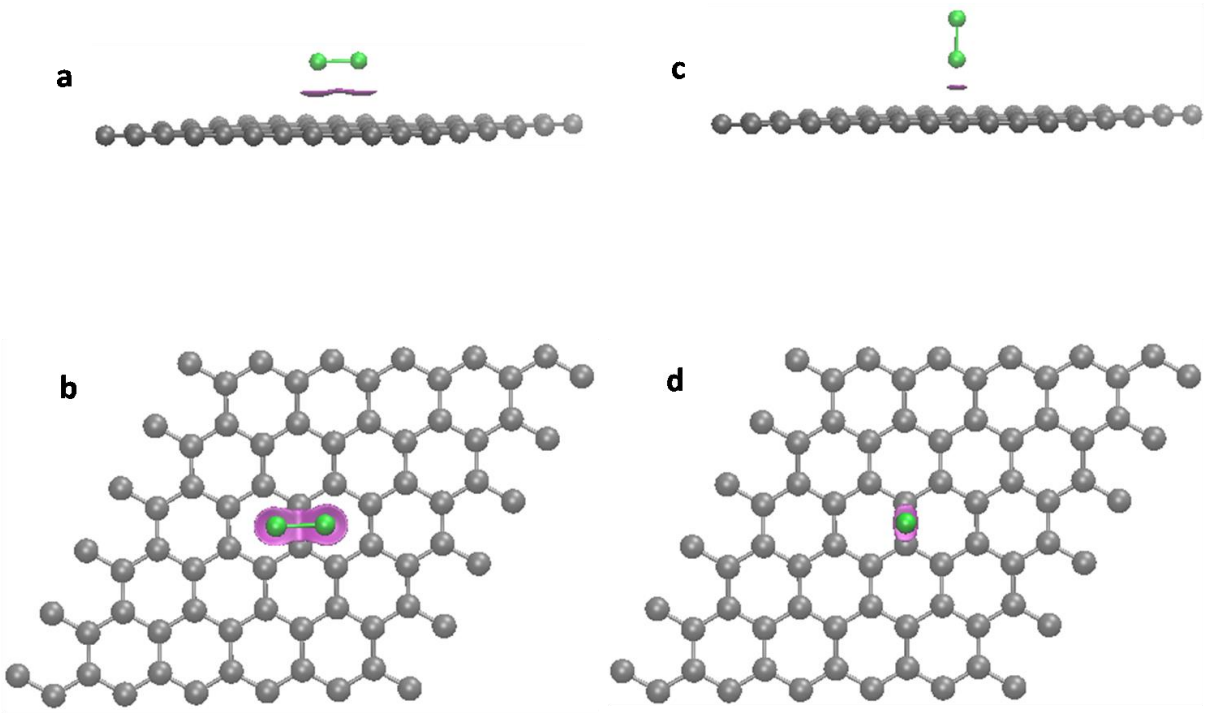

Figure S1. Non-covalent bonding analysis plot **(a)** Side view of the interacted halogen graphene system at adsorption site A. **(b)** Front view of the interacted halogen-graphene system at adsorption site A. **(c)** Side view of the interacted halogen-graphene system at adsorption site I. **(d)** Front view of the interacted halogen-graphene system at adsorption site I. Gray sphere, green sphere and purple membrane-like sheet represent carbon atoms, halogen atoms and intermolecular bonding force between halogen and pristinic graphene respectively.

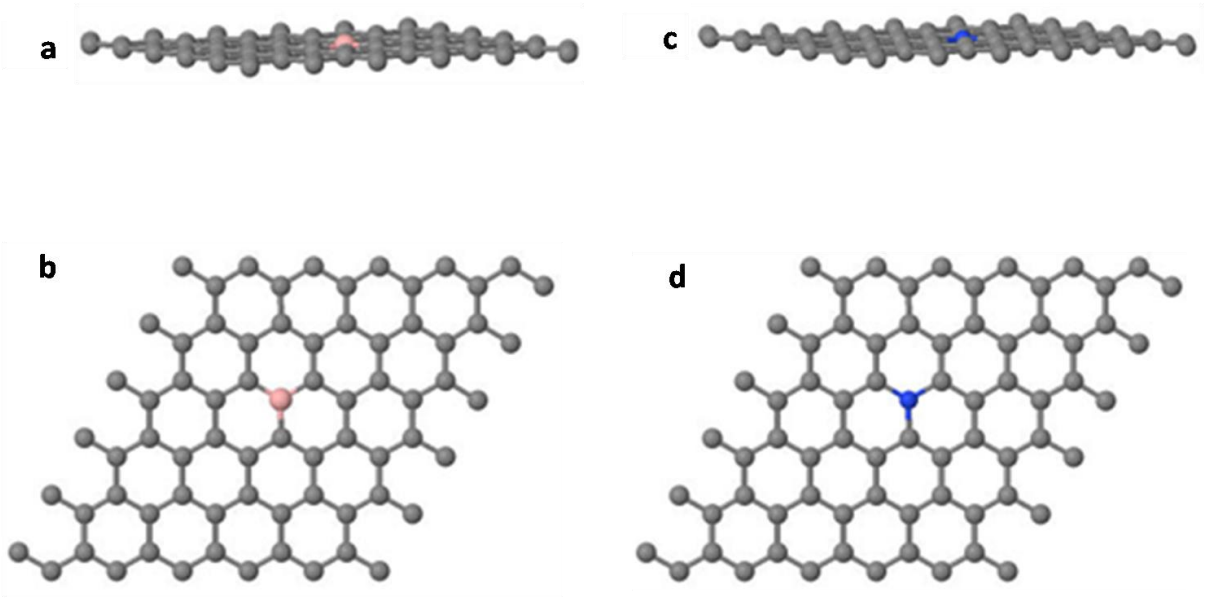

Figure S2. Optimized structure of doped-graphene system. **(a)** Side view of the boron-doped graphene system. **(b)** Front view of the boron-doped graphene system **(c)** Side view of the nitrogen doped graphene system. **(d)** Front view of the nitrogen-doped graphene system. Gray, pink and blue spheres represent carbon, boron and nitrogen atoms respectively.

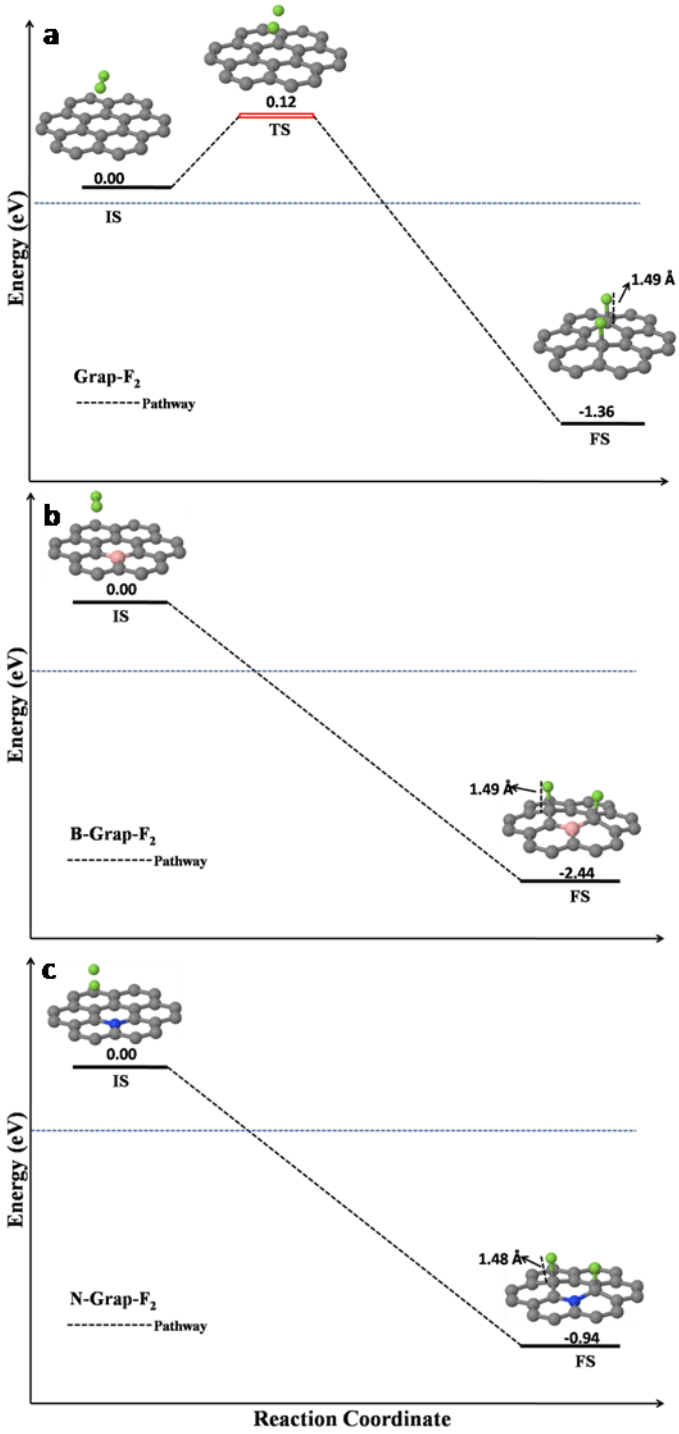

Figure S3. Reaction pathways of F_2 on (a) pristine graphene (b) B-doped graphene and (c) N doped graphene.

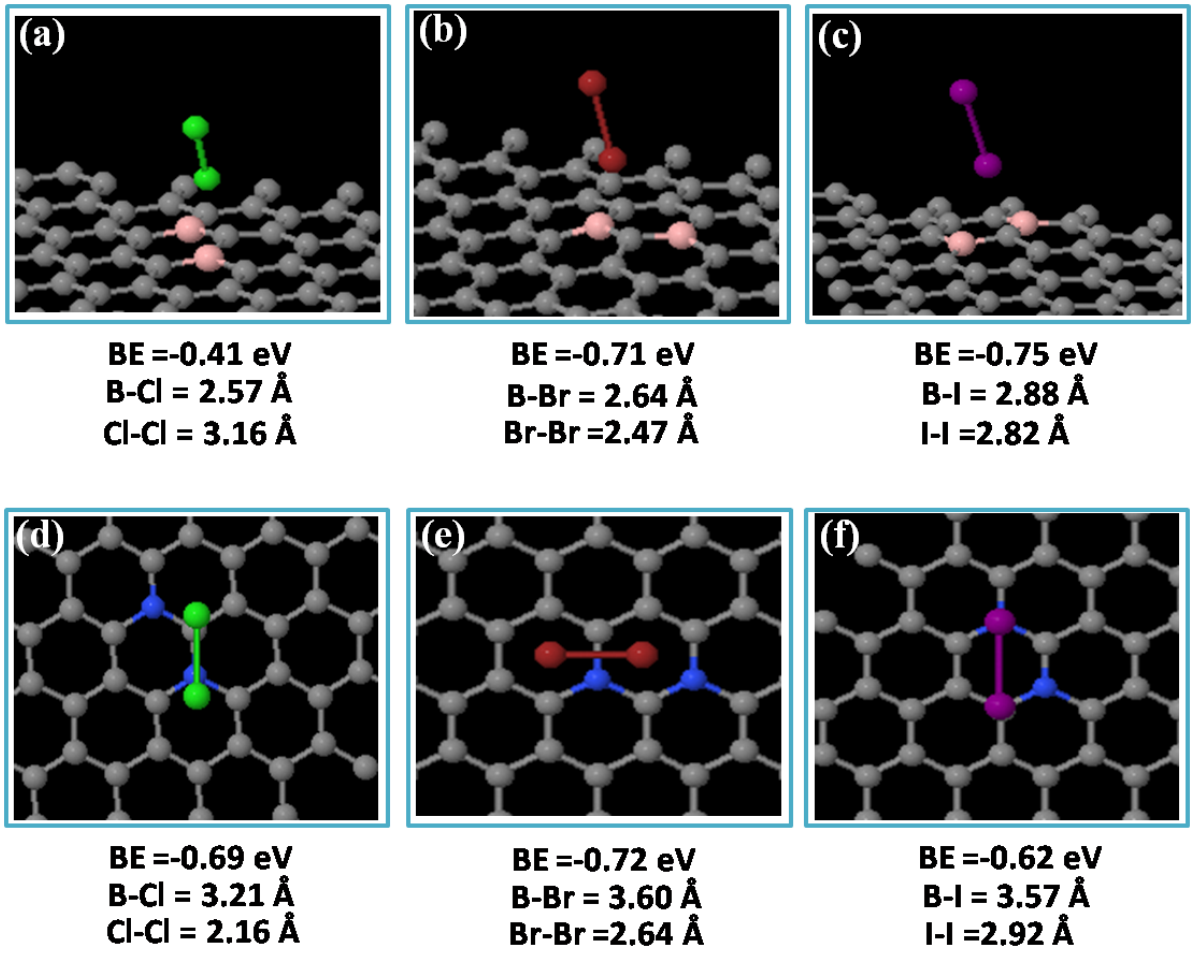

Figure S4. Optimized structure of diatomic halogens adsorbed on 2B-doped graphene and 2N-doped graphene at most stable binding sites. (a) Cl_2 (b) Br_2 (c) I_2 adsorbed on 2B-doped graphene; (d) Cl_2 (e) Br_2 (f) I_2 adsorbed on 2N-doped graphene. Gray, pink, blue, light green, green, brown and purple spheres represent carbon, boron, nitrogen, fluorine, chlorine, bromine and iodine atoms respectively.

Table S1. The Charge (Q, e) of adsorbed halogen molecules on pristine and doped graphene.

Graphene-Halogen System										
		Parallel						**Perpendicular**		
X_2	Charge	A	B	C	D	E	F	G	H	I
F_2	Q (|e|)	-0.245	-0.243	-0.237	-0.244	-0.241	-0.242	-0.226	-0.214	-0.219
Cl_2	Q (|e|)	-0.110	-0.116	-0.116	-0.108	-0.112	-0.109	-0.073	-0.011	-0.073
Br_2	Q (|e|)	-0.102	-0.106	-0.109	-0.110	-0.130	-0.113	-0.072	-0.086	-0.089
I_2	Q (|e|)	-0.007	-0.035	-0.034	-0.055	-0.041	-0.031	-0.049	-0.077	-0.065
Boron-Doped Graphene-Halogen System										
		Parallel						**Perpendicular**		
X_2	Charge	A	B	C	D	E	F	G	H	I
F_2	Q (|e|)	-0.161	-0.163	-	-0.163	-	-0.159	-	-1.128	-
Cl_2	Q (|e|)	-0.005	-0.004	-0.002	-0.004	-0.003	-0.006	-0.133	-0.148	-0.136
Br_2	Q (|e|)	-0.011	0.001	0.011	0.009	0.149	0.003	-0.070	-0.118	-0.116
I_2	Q (|e|)	0.085	0.057	0.073	0.069	0.084	0.077	-0.011	-0.124	0.096
Nitrogen-Doped Graphene-Halogen System										
		Parallel						**Perpendicular**		
X_2	Charge	A	B	A	B	A	B	A	B	A
F_2	Q (|e|)	-	-	-	-	-	-	-	-	-
Cl_2	Q (|e|)	-0.464	-0.497	-0.498	-0.505	-0.494	-0.490	-0.352	-0.352	-0.333
Br_2	Q (|e|)	-0.262	-0.260	-0.257	-0.258	-0.292	-0.261	-0.196	-0.204	-0.205
I_2	Q (|e|)	-0.160	-0.188	-0.179	-0.196	-0.193	-0.183	-0.127	-0.194	-0.175

Table S2. The height of the halogen molecules above the doped/undoped-graphene at various adsorption sites.

Graphene-Halogen System										
		Parallel						Perpendicular		
X_2	Units	A	B	C	D	E	F	G	H	I
F_2	Å	3.08	3.01	3.04	2.98	3.05	2.98	2.91	2.44	2.58
Cl_2	Å	3.61	3.48	3.49	3.71	3.55	3.46	3.41	3.00	3.08
Br_2	Å	3.75	3.60	3.60	3.57	3.62	3.57	3.51	3.00	3.24
I_2	Å	3.98	3.80	3.75	3.76	3.82	3.75	3.54	3.13	3.22
Boron-Doped Graphene-Halogen System										
		Parallel						Perpendicular		
X_2	Units	A	B	C	D	E	F	G	H	I
F_2	Å	3.07	3.02	-	3.00	-	2.98	-	2.04	-
Cl_2	Å	3.63	3.49	3.47	3.52	3.57	3.49	2.91	2.86	2.95
Br_2	Å	3.77	3.63	3.62	3.62	3.41	3.61	2.92	2.92	2.97
I_2	Å	4.02	3.74	3.77	3.77	3.81	3.67	3.08	2.96	3.09
Nitrogen-Doped Graphene-Halogen System										
		Parallel						Perpendicular		
X_2	Units	A	B	A	B	A	B	A	B	A
F_2	Å	-	-	-	-	-	-	-	-	-
Cl_2	Å	3.49	3.30	3.26	3.33	3.41	3.44	3.49	3.38	3.19
Br_2	Å	3.66	3.47	3.44	3.40	3.46	3.46	3.76	3.56	3.50
I_2	Å	3.98	3.70	3.68	3.68	3.69	3.61	3.58	3.27	3.33

Table S3. The bond distance of the halogen molecules adsorbed on doped and undoped graphene at various adsorption sites.

Graphene-Halogen System										
		Parallel						Perpendicular		
X_2	Units	A	B	C	D	E	F	G	H	I
F_2	Å	1.69	1.67	1.66	1.68	1.67	1.67	1.67	1.70	1.69
Cl_2	Å	2.05	2.05	2.05	2.05	2.05	2.04	2.02	2.02	2.02
Br_2	Å	2.39	2.40	2.39	2.39	2.39	2.39	2.38	2.31	2.37
I_2	Å	2.74	2.74	2.74	2.74	2.74	2.74	2.71	2.74	2.71
Boron-Doped Graphene-Halogen System										
		Parallel						Perpendicular		
X_2	Units	A	B	C	D	E	F	G	H	I
F_2	Å	1.66	1.64	-	1.65	-	1.65	-	1.72	-
Cl_2	Å	1.99	1.99	1.99	1.99	1.99	1.99	2.05	2.05	2.05
Br_2	Å	2.31	2.31	2.31	2.31	2.31	2.31	2.38	2.39	2.38
I_2	Å	2.68	2.68	2.69	2.69	2.69	2.68	2.75	2.76	2.75
Nitrogen-Doped Graphene-Halogen System										
		Parallel						Perpendicular		
X_2	Units	A	B	A	B	A	B	A	B	A
F_2	Å	-	-	-	-	-	-	-	-	-
Cl_2	Å	2.24	2.28	2.28	2.29	2.28	2.28	2.19	2.18	2.16
Br_2	Å	2.56	2.56	2.55	2.55	2.53	2.55	2.56	2.56	2.54
I_2	Å	2.85	2.88	2.88	2.87	2.88	2.87	2.82	2.83	2.85