

Supporting Information

Healing Double Vacancy Defects on Graphene. Reconstruction by C₂ Adsorption.

Parisa Alamdari¹, Farhad Sharif^{1*}, Saeedeh Mazinani², German Sastre^{3*}, Hermenegildo Garcia³

¹ Department of Polymer Engineering and Color Technology, Amirkabir University of Technology, Tehran, Iran.

² New Technologies Research Center (NTRC), Amirkabir University of Technology, Tehran, Iran.

³ Instituto de Tecnología Química, Consejo Superior de Investigaciones Científicas–Universidad Politécnica de Valencia (CSIC-UPV), Avenida de los Naranjos s/n, Valencia 46022, Spain.

Effect of size of graphene unit cell.

To be sure that 4×4 supercells are large enough to prevent the interaction between cells, the formation energy of double carbon vacancy defects in 4×4 and 6×6 supercells were calculated and compared, not only with each other but also with those reported in literature for different size supercells. There are various methods in the literature for the calculation of vacancy formation energy. If the vacancy formation energy is defined as an average energy per vacant carbon atom in defected graphene structures, then the formation energy per vacant C atom, E_f for each configuration can be calculated from Equation SI-1:

$$E_f = \frac{1}{n} (E_{v_n} - \frac{N-n}{N} E_{gra}) \quad \text{Equation SI-1}$$

in which n is the number of vacant carbon atoms in the supercell, E_{v_n} is the total energy of defected graphene, N is the number of carbon atoms in the supercell, and E_{gra} is the total energy of defect free graphene supercell with the same size.

From Equation 1, the formation energy of DV in 4×4 and 6×6 supercells were calculated to be 3.88 and 3.94 eV, respectively in good agreement with the literature, ranging from 3.18 to 4.49 eV (S. T. Skowron, I. V. Lebedeva, A. M. Popov and E. Bichoutskaia, Chemical Society Reviews, 2015, 44, 3143-3176).

It should be noted that in order to correctly compare DV formation energies reported in literature, it is important to consider the differences in definitions of formation energy. In some cases, the defect formation energy is defined by Equation SI-2:

$$E_f = (E_{v_n} + n\mu - E_{gra}) \quad \text{Equation SI-2}$$

in which μ is the chemical potential, calculated by dividing the total energy of defect free graphene supercell by the number of atoms in the supercell. Indeed, by rearrangement of Equation SI-2, using Equation SI-1, the difference between the two definitions will be $\frac{1}{n}$ coefficient of Equation SI-1.

Furthermore, considering NEB (nudged elastic band), used in this study for barrier energy calculations, which are computationally expensive, using supercells larger than 4×4 was not affordable.

Differences between chemisorption and physisorption processes.

The chemical bond formation has been considered as the main criteria to clarify between physisorption and chemisorption.

When the reactant approaches the graphene surface, physisorption occurs. This leads to $C_{\text{graph}}-H_{\text{hydrocarbon}}$ distances of ca. 3 Å, and adsorption energies of ca. -100 kJ/mol.

Upon further approach to the graphene surface the latter is reconstructed through formation of $C_{\text{graph}}-C_{\text{hydrocarbon}}$ bonds whose distances are ca. 1.5 Å, and adsorption energies are -200 kJ/mol or stronger.

Physisorption to chemisorption process goes always from subfigures a→c (Figures 3 and 4 for ethylene, Figures 6 and 7 for acetylene).

Adsorption energies and $C_{\text{graph}}-C_{\text{hydrocarbon}}$ distances

Ethylene adsorption	Orientation	$C_{\text{graph}}-C_{\text{hydrocarbon}}$ d(G1/E1) (Å)	Adsorption energy (kJ/mol)	Figure
Physisorption	DVH	3.08	-93.6	3 ^a
	DVP	3.57	-91.9	4 ^a
Chemisorption	DVH	1.57	-199.8	3c
	DVP	1.51	-275.0	4c
Acetylene adsorption	Orientation	$C_{\text{graph}}-C_{\text{hydrocarbon}}$ d(G1/A1) (Å)	Adsorption energy (kJ/mol)	Figure
Physisorption	DVH	3.22	-90.8	6a
	DVP	3.40	-88.1	7a
Chemisorption	DVH	1.51	-933.2	6c
	DVP	1.46	-381.3	7c

Isomorphic substitution of carbon atom in DV graphene.

There are four distinct position around DV for carbon substitution with nitrogen, whose influence on the interaction of carbon dimers with DV could not be neglected. Before studying the carbon dimer interaction with doped DV structures, the total energy and stability of these four configurations were carefully calculated and compared.

Different positions around DV for carbon substitution with nitrogen

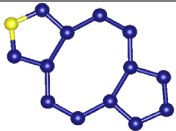
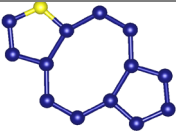
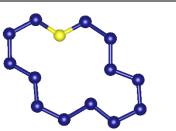

			
0	28.8	38.3	94.4
N _{G1}	N _{G2}	N _P	N _{G3}
Graphitic N in 1	Graphitic N in 2	Pyridinic N	Graphitic N in 3

Table S1. Geometries corresponding to the interaction of Ethylene with DV through DVH mechanism.

Ethylene-DVH											
X axis	Note	Distance in initial geometry (Å)	Y axis	Distance in final geometry (Å)							
Ethylene chemisorption - NEB calculation											
-			Energy (kJ/mol)	E1G1	E2G3	E1G2	E2G4	G1G2	G3G4	E1H2	G2H2
-	No interaction	Far	0	-	-	-	-	-	-	-	-
1	Physisorption (full opt, local min)		-93.6	3.08	3.16	3.28	3.33	1.79	1.79	1.10	2.88
2	TS1 _{NEB} (energy barrier = 56.9 kJ/mol)		-36.6	2.20	2.28	2.86	2.87	1.92	1.90	1.10	2.47
3	Chemisorption (full opt, local min)		-199.8	1.57	1.57	2.71	2.71	2.10	2.11	1.10	2.49
First C-C bond formation - E1-G2 distance is constrained (except in full optimizations)											
-		E1G2	Energy (kJ/mol)	E1G1	E2G3	E1G2	E2G4	G1G2	G3G4	E1H2	G2H2
3	Chemisorption (full opt, local min)	2.7	-199.8	1.57	1.57	2.71	2.71	2.10	2.11	1.10	2.49
4		2.6	-196.6	1.56	1.57	2.59	2.69	2.05	2.11	1.10	2.36
5		2.4	-173.5	1.56	1.57	2.38	2.65	1.90	2.07	1.10	2.15
6		2.2	-125.2	1.56	1.57	2.17	2.63	1.80	2.05	1.10	1.96
7	TS2 (energy barrier = 126.4 kJ/mol)	2	-73.4	1.58	1.57	2.01	2.64	1.82	2.07	1.10	1.79
-		1.9	-299.3	1.48	1.54	1.91	2.62	2.74	2.39	2.26	1.12
8	Local min (full opt of E1G2=1.9)	1.6	-367.5	1.51	1.54	1.58	2.56	2.60	2.44	2.10	1.12
Second C-C bond formation - E2-G4 distance is constrained (except in full optimizations)											
		E2G4/	Energy (kJ/mol)	E1G1	E2G3	E1G2	E2G4	G1G2	G3G4	E2H4	G4H4
8	Local min (full opt of E1G2=1.6)	2.6	-367.5	1.51	1.54	1.58	2.56	2.60	2.44	1.10	2.28
9		2.4	-358.9	1.52	1.54	1.57	2.38	2.59	2.36	1.11	2.08
10	TS3 (energy barrier = 38.0 kJ/mol)	2.2	-337.5	1.52	1.53	1.56	2.22	2.59	2.35	1.11	1.90
11		2	-510.5	1.51	1.48	1.58	2.01	2.63	2.83	2.37	1.11
-		1.8	-583.3	1.52	1.50	1.57	1.80	2.62	2.73	2.27	1.12
12	Healed DV (Full opt of E2G4=1.8)	1.56	-632.1	1.52	1.52	1.56	1.56	2.61	2.61	2.13	1.12

Table S2. Geometries corresponding to the interaction of Ethylene with DV through DVP mechanism.

Ethylene-DVP											
X axis	Note	Distance in initial geometry (Å)	Y axis	Distances in final geometry (Å)							
Ethylene chemisorption - NEB calculation											
-			Energy (kJ/mol)	E1G1	E2G2	E1G3	E2G4	G3G4	G3H3	G4H4	E1E2
-	No interaction	Far	0	-	-	-	-	-	-	-	-
1	Physisorption (full opt, local min)		-91.9	3.57	3.66	4.02	3.57	1.79	3.81	4.59	1.35
2	TS1 _{NEB} (energy barrier = 134.9 kJ/mol)		43.3	2.02	2.13	3.39	3.30	1.84	2.74	3.55	1.42
3	Chemisorption (full opt, local min)		-275.0	1.51	1.51	3.06	3.06	2.08	2.55	3.38	1.53
First C-H bond formation – H3G3 distance is constrained (except in full optimizations)											
-		H3G3	Energy (kJ/mol)	E1G1	E2G2	E1G3	E2G4	G3G4	G3H3	E1H3	E1E2
3	Chemisorption (full opt, local min)	2.6	-275.0	1.51	1.51	3.06	3.06	2.08	2.55	1.09	1.53
4		2.4	--274.9	1.51	1.51	3.03	3.09	2.08	2.38	1.10	1.52
5		2.2	-272.4	1.51	1.51	2.95	3.14	2.08	2.17	1.10	1.52
6		2.0	-267.4	1.51	1.51	2.87	3.13	2.10	2.01	1.11	1.52
7		1.8	-254.1	1.51	1.51	2.76	3.14	2.11	1.80	1.12	1.51
8		1.6	-229.1	1.51	1.50	2.64	3.11	2.15	1.59	1.15	1.50
9	TS2 (energy barrier = 80.3 kJ/mol)	1.4	-191.7	1.50	1.50	2.52	3.03	2.26	1.38	1.22	1.49
-		1.2	-208.7	1.31	1.51	2.80	2.52	2.15	1.22	2.48	1.48
10	Local min (full opt of H3G3=1.2)	1.1	-325.1	1.73	1.49	2.52	2.60	2.82	1.10	2.32	1.52
Second C-H bond formation – H4G4 distance is constrained (except in full optimizations)											
		H4G4	Energy (kJ/mol)	E1G1	E2G2	E1G3	E2G4	G3G4	G4H4	E2H4	E1E2
10	Local min (full opt of H3G3=1.2)	2.65	-325.1	1.73	1.49	2.52	2.60	2.82	2.65	1.11	1.52
11		2.5	-322.2	1.73	1.49	2.51	2.55	2.83	2.49	1.11	1.52
12		2.3	-309.8	1.69	1.49	2.51	2.51	2.83	2.28	1.11	1.51
13		2.1	-286.7	1.65	1.49	2.51	2.48	2.85	2.06	1.11	1.51
14		1.8	-240.9	1.57	1.49	2.51	2.46	2.86	1.80	1.13	1.50
15	TS2 (energy barrier = 136.0 kJ/mol)	1.6	-189.1	1.51	1.48	2.53	2.44	2.87	1.59	1.18	1.49
16		1.4	-395.3	1.46	1.47	3.01	2.89	2.79	1.38	2.00	1.35
-		1.2	-463.3	1.46	1.47	3.01	2.86	2.79	1.16	2.11	1.35
17	Local min (full opt of H4G4=1.2)		-471.1	1.46	1.47	3.00	2.85	2.79	1.09	2.14	1.34

Table S2. Continued. Geometries corresponding to the interaction of Ethylene with DV through DVP mechanism.

C-C bond formation – First E2G2, then E1G3 distances are constrained (except in full optimizations)											
-		E2G4 (E1G3)	Energy (kJ/mol)	E1G1	E2G2	E1G3	E2G4	G3G4	G3H3	G4H4	E1E2
17	Local min (full opt of H4G4=1.2)		-471.1	1.46	1.47	3.00	2.85	2.79	1.09	1.09	1.34
18		2.6	-456.7	1.46	1.46	2.92	2.59	2.80	1.10	1.08	1.34
19		2.4	-417.3	1.46	1.47	2.94	2.38	2.79	1.09	1.08	1.35
20		2.2	-350.4	1.47	1.48	2.98	2.17	2.80	1.10	1.08	1.35
21		2.0	-274.9	1.47	1.51	2.92	1.96	2.81	1.09	1.08	1.37
22		1.8	-253.5	1.41	1.53	2.63	1.80	2.80	1.08	1.11	1.44
23	TS3 (energy barrier = 223.0 kJ/mol)	1.6	-248.1	1.41	1.56	2.57	1.59	2.82	1.09	1.11	1.46
24		(2.4)	-249.2	1.42	1.55	2.38	1.68	2.75	1.08	1.12	1.45
25		(2.2)	-249.5	1.48	1.55	2.17	1.67	2.66	1.10	1.12	1.45
26		(2.0)	-265.9	1.50	1.55	2.01	1.65	2.64	1.11	1.12	1.46
27		(1.8)	-300.3	1.53	1.55	1.80	1.62	2.61	1.12	1.13	1.48
-		(1.6)	-321.0	1.56	1.56	1.59	1.61	2.59	1.13	1.13	1.49
28	Local min (full opt of E1G3 =1.6)		-321.4	1.55	1.56	1.61	1.61	2.59	1.13	1.13	1.49

Table S3. Geometries corresponding to the interaction of Acetylene with DV through DVH mechanism.

Acetylene-DVH										
X axis	Note	Distance in initial geometry (Å)	Y axis	Distances in final geometry (Å)						
Healing - NEB calculation										
-			Energy (kJ/mol)	A1G1	A2G2	A1G3	A2G4	G1G2	G3G4	A1A2
-	No interaction	Far	0	-	-	-	-	-		
1	Physisorption (full opt, local min)		-90.8	3.22	3.24	3.21	2.23	1.79	1.79	1.22
2	TS1 _{NEB} (energy barrier = 58.0 kJ/mol)		-32.8	2.26	2.61	2.25	2.60	1.94	1.94	1.25
3	Product (full opt, local min)		-933.2	1.51	1.51	1.51	1.51	2.51	2.51	1.55

Table S4. Geometries corresponding to the interaction of Acetylene with DV through DVP mechanism.

Acetylene-DVP										
X axis	Note	Distance in initial geometry (Å)	Y axis	Distances in final geometry (Å)						
Chemisorption - NEB calculation										
-			Energy (kJ/mol)	A1G1	A2G2	A1G3	A2G4	G1G2	G3G4	A1A2
-	No interaction	Far	0	-	-	-	-	-		
1	Physisorption (full opt, local min)		-88.1	3.40	3.47	3.53	3.70	1.79	1.79	1.21
2	TS1 _{NEB} (energy barrier =123.0 kJ/mol)		34.9	2.06	2.11	3.43	3.47	2.0	1.80	1.26
3	Chemisorption (full opt, local min)		-381.3	1.46	1.46	2.92	2.92	2.82	2.04	1.34
Two C-C bond formation- NEB calculation										
-			Energy (kJ/mol)	A1G1	A2G2	A1G3	A2G4	G1G2	G3G4	A1A2
3	Chemisorption (full opt, local min)		-381.3	1.46	1.46	2.92	2.92	2.82	2.04	1.34
4	TS2 _{NEB} (energy barrier = 154.7 kJ/mol)		-226.6	1.46	1.50	2.53	2.03	2.82	2.43	1.42
5	Product (Full opt, , local min)		-587.8	1.55	1.55	1.55	1.55	2.83	2.83	1.49

Table S5. Geometries corresponding to the interaction of Acetylene with NP through DVH mechanism.

Acetylene-NP-DVH										
X axis	Note	Distance in initial geometry (Å)	Y axis	Distances in final geometry (Å)						
Healing - NEB Calculation										
-			Energy (kJ/mol)	A1G1	A2G3	A1G2	A2N	G1G2	G3N	A1A2
-	No interaction	Far	0	-	-	-	-	-	-	-
1	Physisorption (full opt, local min)		-89.6	3.35	3.07	3.43	3.42	1.89	2.36	1.22
2	TS1 _{NEB} (energy barrier = 14.0 kJ/mol)		-75.6	2.83	2.33	2.96	2.85	1.99	2.42	1.23
3	Product (full opt, local min)		-911.6	1.51	1.51	1.51	1.53	2.50	2.48	1.55

Table S6. Geometries corresponding to interaction of Acetylene with NP1 through DVP mechanism (Acetylene is chemisorbed on G1 and G2)

Acetylene-NP-DVP										
X axis	Note	Distance in initial geometry (Å)	Y axis	Distances in final geometry (Å)						
Chemisorption – NEB Calculation										
-			Energy (kJ/mol)	A1G1	A2G2	A1G3	A2N	G1G2	G3N	A1A2
-	No interaction	Far	0	-	-	-	-			
1	Physisorption (full opt, local min)		-89.3	3.38	3.37	4.82	4.49	1.87	2.35	1.21
2	TS1 _{NEB} (energy barrier = 103.7 kJ/mol)		14.4	2.22	2.09	3.47	3.37	2.12	2.39	1.25
3	Chemisorption (full opt, local min)		-448.4	1.46	1.45	2.65	2.81	2.86	2.53	1.35
C-C and C-N bond formation - NEB Calculation										
			Energy (kJ/mol)	A1G1	A2G2	A1G3	A2N	G1G2	G3N	A1A2
3	Chemisorption (full opt, local min)		-448.4	1.46	1.45	2.65	2.81	2.86	2.53	1.35
4	TS2 _{NEB} (energy barrier = 7.4 kJ/mol)		-441.0	1.47	1.44	2.30	2.64	2.86	2.61	1.37
5	Product (full opt, local min)		-572.0	1.56	1.55	1.55	1.58	2.80	2.76	1.48

Table S7. Geometries corresponding to interaction of Acetylene with N_p^2 through DVP mechanism (Acetylene is chemisorbed on G1 and G2)

Acetylene-NP-DVP										
X axis	Note	Distance in initial geometry (Å)	Y axis	Distances in final geometry (Å)						
Chemisorption – NEB Calculation										
-			Energy (kJ/mol)	A1G1	A2G2	A1G3	A2N	G1G2	G3N	A1A2
-	No interaction	Far	0	-	-	-	-			
1	Physisorption (full opt, local min)		-88.7	3.57	3.51	3.60	3.17	1.86	2.34	1.21
2	TS1 _{NEB} (energy barrier = 28.5 kJ/mol)		-59.5	3.24	3.50	2.22	2.99	1.91	2.44	1.24
3	Chemisorption (full opt, local min)		-405.4	2.96	2.98	1.48	1.49	1.88	2.64	1.33
C-C and C-N bond formation - NEB Calculation										
			Energy (kJ/mol)	A1G1	A2G2	A1G3	A2N	G1G2	G3N	A1A2
3	Chemisorption (full opt, local min)		-405.4	2.96	2.98	1.48	1.49	1.88	2.64	1.33
4	TS2 _{NEB} (energy barrier = 153.3 kJ/mol)		-252.1	2.60	1.97	1.43	1.54	2.39	2.73	1.41
5	Product (full opt, local min)		-572.0	1.56	1.55	1.55	1.58	2.80	2.76	1.48

Table S8. Geometries corresponding to the interaction of Acetylene with N_{G1} through DVH mechanism.

Acetylene-NG1-DVH										
X axis	Note	Distance in initial geometry (Å)	Y axis	Distances in final geometry (Å)						
Healing – NEB Calculation										
-			Energy (kJ/mol)	A1G1	A1G2	A2G3	A2G4	G1G2	G3G4	A1A2
-	No interaction	Far		-/	-	-	-			
1	Physisorption (full opt, local min)		-88.2	3.56	3.56	3.33	3.33	1.66	1.69	1.21
2	TS _{1NEB} (energy barrier = 104.2 kJ/mol)		16.0	2.62	2.90	1.90	2.55	1.78	2.00	1.26
3	Product (full opt, local min)		-853.3	1.51	1.51	1.51	1.51	2.48	2.51	1.55

Table S9. Geometries corresponding to the interaction of Acetylene with N_{G1} through DVP mechanism.

Acetylene-NG1-DVP										
X axis	Note	Distance in initial geometry (Å)	Y axis	Distances in final geometry (Å)						
Chemisorption – NEB Calculation										
-			Energy (kJ/mol)	A1G1	A2G2	A1G3	A2G4	G1G2	G3G4	A1A2
-	No interaction	Far	0	-	-	-	-			
1	Physisorption (full opt, local min)		-88.2	3.48	3.51	3.65	3.64	1.66	1.69	1.21
2	TS1			No data						
3	Chemisorption (full opt, local min)		-355.6	2.91	2.91	1.46	1.46	1.77	2.80	1.34
Two C-C bond formation - NEB Calculation										
			Energy (kJ/mol)	A1G1	A2G2	A1G3	A2G4	G1G2	G3G4	A1A2
3	Chemisorption (full opt, local min, starting point of scan)		-355.6	2.91	2.91	1.46	1.46	1.77	2.80	1.34
4	TS2 _{NEB} (energy barrier = 153.2 kJ/mol)		-202.4	2.02	2.50	1.43	1.42	2.46	2.83	1.42
5	Product (full opt of A1G1=1.8)		-496.9	1.56	1.56	1.55	1.55	2.77	2.82	1.48

Table S10. Geometries corresponding to the interaction of Acetylene with NG₂ through DVH mechanism.

Acetylene-NG ₂ -DVH										
X axis	Note	Distance in initial geometry (Å)	Y axis	Distances in final geometry (Å)						
Healing – NEB Calculation										
-			Energy (kJ/mol)	A1G1	A1G2	A2G3	A2G4	G1G2	G3G4	A1A2
-	No interaction	Far								
1	Physisorption (full opt, local min)		-88.6	3.43	3.45	3.34	3.39	1.64	1.70	1.21
2	TSl _{NEB} (energy barrier = 97.0 kJ/mol)		8.4	2.24	2.65	2.22	2.64	1.81	1.92	1.25
3	Product (full opt, local min)		-866.5	1.51	1.51	1.51	1.51	2.50	2.51	1.56

Table S11. Geometries corresponding to the interaction of Acetylene with NG₂ through DVP mechanism.

Acetylene-NG ₂ -DVP										
X axis	Note	Distance in initial geometry (Å)	Y axis	Distances in final geometry (Å)						
Chemisorption – NEB Calculation										
-			Energy (kJ/mol)	A1G1	A2G2	A1G3	A2G4	G1G2	G3G4	A1A2
-	No interaction	Far								
1	Physisorption (full opt, local min)		-87.8	3.66	3.71	3.52	3.51	1.64	1.70	1.21
2	TS1			No data						
3	Chemisorption (full opt, local min)		-349.1	2.91	2.93	1.46	1.46	1.72	2.79	1.34
Two C-C bond formation - NEB Calculation										
			Energy (kJ/mol)	A1G1	A2G2	A1G3	A2G4	G1G2	G3G4	A1A2
3	Chemisorption (full opt, local min)		-349.1	2.91	2.93	1.46	1.46	1.72	2.79	1.34
4	TS _{2NEB} (energy barrier = 117.1 kJ/mol)		-232.0	2.56	2.07	1.43	1.50	2.46	2.83	1.40
5	Product (full opt, local min)		-504.2	1.57	1.55	1.56	1.56	2.79	2.83	1.48

Table S12. Geometries corresponding to interaction of Acetylene with S_G through DVH mechanism.

DVG-S-Acetylene										
X axis		Distance in initial geometry (Å)	Y axis	Distances in final geometry (Å)						
Healing – NEB Calculation										
-	Note		Energy (kJ/mol)	A1G1	A1G2	A2G3	A2S	G1G2	G3S	A1A2
-	No interaction	-	0							
1	Physisorption (full opt, local min)		-152.4	3.30	3.29	3.4	3.85	1.84	2.09	1.21
2	TS1 (energy barrier = 49.0 kJ/mol)		-103.4	2.96	3.19	1.94	2.94	2.00	2.32	1.26
3	Product (full opt, local min, starting point of scan)		-809.6	1.50	1.51	1.49	1.85	2.50	2.62	1.52

Table S13. Geometries corresponding to the interaction of Acetylene with S_G through DVP mechanism.

Acetylene-GS-DVP										
X axis	Note	Distance in initial geometry (Å)	Y axis	Distances in final geometry (Å)						
Chemisorption – Neb Calculation										
-			Energy (kJ/mol)	A1G1	A2G2	A1G3	A2S	G1G2	G3S	A1A2
-	No interaction	-	0	-	-	-	-	-	-	-
1	Physisorption (full opt, local min)		-150.8	3.49	3.48	3.49	4.03	1.82	2.09	1.21
2	TS1			No data						
3	Chemisorption (full opt, local min, starting point of scan)		-508.6	1.47	1.46	2.82	2.90	2.81	2.25	1.34
C-C bond formation – A1G3 distance is constrained (except in full optimizations)										
		A1G3	Energy (kJ/mol)	A1G1	A2G2	A1G3	A2S	G1G2	G3S	A1A2
3	Chemisorption (full opt, local min, starting point of scan)	2.8	-508.6	1.47	1.46	2.82	2.90	2.81	2.25	1.34
4		2.6	-504.1	1.47	1.46	2.59	2.89	2.82	2.31	1.35
5		2.4	-491.3	1.48	1.45	2.38	2.90	2.81	2.40	1.36
6	TS2 (energy barrier = 29.7 kJ/mol)	2.2	-478.9	1.49	1.43	2.17	2.92	2.81	2.56	1.38
7		2	-479.7	1.50	1.40	2.01	2.92	2.83	2.81	1.41
8		1.8	-492.5	1.53	1.40	1.80	2.91	2.82	2.97	1.44
-		1.6	-496.7	1.56	1.39	1.59	2.87	2.82	3.09	1.46
9	Local min (full opt of A1G3=1.6)	1.6	-499.9	1.55	1.39	1.65	2.88	2.82	3.08	1.45
C-S bond formation – A2S distance is constrained (except in full optimizations)										
		A2S	Energy (kJ/mol)	A1G1	A2G2	A1G3	A2S	G1G2	G3S	A1A2
9	Local min (full opt of A1G3=1.6, starting point of scan)		-499.9	1.55	1.39	1.65	2.88	2.82	3.08	1.45
10		2.6	-486.9	1.55	1.40	1.64	2.59	2.83	2.97	1.45
11	TS3 (energy barrier = 30.5 kJ/mol)	2.4	-469.4	1.55	1.42	1.62	2.38	2.84	2.91	1.45
12		2.2	-472.8	1.55	1.47	1.60	2.17	2.84	2.78	1.47
13		2	-493.5	1.55	1.51	1.60	2.01	2.84	2.69	1.48
-		1.8	-505.8	1.55	1.54	1.59	1.80	2.84	2.65	1.49
14	Product (full opt of A2S=1.8, local min)		-507.2	1.55	1.53	1.59	1.84	2.84	2.65	1.49

Discussion on the energy barriers of all reaction paths described in Table 1 and Table 2

Tables 1 and 2, from the main manuscript, are reproduced below for the sake of comparison.

- Barrier I in Eth-DV-DVH is lower than Barrier I in Eth-DV-DVP (56.9 versus 134.9 kJ/mol) due to the less stable transition state of the former resulting from the stress-induced seven-membered ring formation which is folded not planar.
- Barrier II in Eth-DV-DVH is higher than Barrier II in Eth-DV-DVP (126.4 versus 80.3 kJ/mol). After ethylene chemisorption, due to larger distances between G1G3 and G2G4 in comparison with G1G2 and G3G4, stress induces in structure by approaching hydrogen to G3 breaks the G3G4 reconstruction and facilitate hydrogen transfer in Eth-DV-DVP. However, by approaching hydrogen to G4 in Eth-DV-DVH, the G3 also approaches G4 and makes it more stabilized.
- Barrier III in Eth-DV-DVH is lower than Barrier II in Eth-DV-DVH (38.0 versus 126.4 kJ/mol). The second hydrogen transfer and C-C bond formation in Eth-DV-DVH is more facilitated, due to the presence of stabilized undercoordinated carbon for second hydrogen transfer and C-C bond formation.
- Barrier III in Eth-DV-DVP is higher than Barrier II in Eth-DV-DVP (136.0 versus 80.3 kJ/mol). After first hydrogen transfer to G3, reconstruction between G3 and G4 is broken. This makes undercoordinated G4 extremely reactive which is then stabilized by attracting E1. The stabilization effect of E1 on G4 makes the second hydrogen transfer to G4 more difficult and the barrier for second hydrogen transfer increases in comparison with first hydrogen transfer.
- Barrier I in Ace-DV-DVH is comparable with barrier I in Eth-DV-DVH (58.0 versus 56.9 kJ/mol). Acetylene is more reactive than ethylene. When DV reconstruction break due to Acetylene adsorption through DVH, acetylene can further fill the DV. However, ethylene is chemisorbed on DV.
- Barrier I in Ace-DV-DVP is lower than barrier I in Eth-DV-DVP: (123.0 versus 134.9 kJ/mol). Acetylene is more reactive than ethylene.
- Barrier II in Ace-DV-DVP is higher than Barrier I in Ace-DV-DVP (154.7 versus 123.0 kJ/mol). As reactants, acetylene is more reactive than chemisorbed acetylene.
- Barrier I in Ace-N_p-DVH is lower than Barrier I in Ace-DV-DVH (14.0 versus 58.0 kJ/mol). As shown in table 3, nitrogen has less stabilization effect on G4 in N_p, in comparison with stabilization effect of G₃ on G₄ in DV (NG₄ =2.36 versus G₃G₄=1.79 Å). Therefore, G₃ in N_p is extremely reactive in comparison with G₃ in DV.
- Barrier I in Ace-N_p-DVP is lower than Barrier I in Ace-DV-DVP (103.8 versus 123.0 kJ/mol). In both cases, acetylene interacts with reconstructed G1G2, but the reconstruction length in N_p is higher than that of DV (G1G2 (N_p) = 1.91 versus G1G2 (DV) =1.79 Å). Therefore, N_p is more reactive than DV toward acetylene interaction.
- Barrier II in Ace-N_p-DVP is lower than Barrier II in Ace-DV-DVP (7.4 versus 154.7 kJ/mol). As shown in table 3, nitrogen has less stabilization effect on G4 in N_p, in comparison with stabilization effect of G₃ on G₄ in DV (HG₄ =2.36 versus G₃G₄=1.79 Å). Therefore, G₃ in N_p is extremely reactive in comparison with G₃ in DV.
- Barrier I in Ace-N_{G1}-DVP is higher than barrier I in Ace-DV-DVH (104.2 versus 58.0 kJ/mol). As shown in Table 3, the G1G2 in N_{G1} is 1.69 Å, but G1G2 in DV is 1.79 Å, moreover electron donating effect of nitrogen more stabilized G1 and G2, symmetrically.
- Barrier I in Ace-N_{G2}-DVP is higher than barrier I in Ace-DV-DVH (97.0 versus 58.0 kJ/mol). As shown in Table 3, the G1G2 in N_{G2} is 1.70 but G1G2 in DV is 1.79, moreover electron donating effect of nitrogen more stabilized G1 and G2, unsymmetrically.
- Barrier I in Ace-N_{G1}-DVP is comparable with barrier I in Ace-N_{G2}-DVP (104.2 versus 97.0 kJ/mol). As shown in Table 3, the G1G2 in N_{G1} is 1.69 and G1G2 in N_{G2} is 1.70, moreover stabilization effect of nitrogen on G1 and G2 in N_{G1} is symmetrical, however, stabilization effect of nitrogen on G1 and G2 in N_{G2} is unsymmetrical.

- Barrier II in Ace- N_{G1} -DVP is comparable with barrier II in Ace-DV-DVP (153.2 versus 154.7 kJ/mol). G3G4 in both cases are very similar and nitrogen of N_{G1} is far enough to not affect the amount of barrier IIs.
- Barrier II in Ace- N_{G2} -DVP is lower than barrier II in Ace- N_{G1} -DVP (117.1 versus 153.2 kJ/mol). A1 carbon of acetylene is more influenced by electron donating effect of nitrogen of N_{G2} in comparison with N_{G1} , due to two carbon space between nitrogen and A1 in N_{G1} and three carbon space between nitrogen and A1 in N_{G2} .
- Barrier I in Ace- S_G -DVH is slightly lower than barrier I in Ace-DV-DVH (49.0 versus 58.0 kJ/mol). As shown in table 3, G1G2 and G3S in S_G are 1.96 Å and 1.94 Å respectively, however G1G2 and G3G4 in DV are both equal to 1.79 Å. On the other hand, large size of sulfur in comparison with carbon induces some stress in defective graphene structure.

Table 1. Energies (kJ/mol) of the different steps of the reaction of ethylene with DV.

GBM	Approach	Physisorption	Barrier I	Chemisorption	Barrier II	Local Min	Barrier III	Local Min	Barrier IV	Local Min
DV	DVH*	-93.6 ^a	56.9 ^b	-199.8 ^c	126.4 ^d	-367.5 ^e	38.0 ^f	-632.1 ^g	-	-
DV	DVP**	-91.9 ^a	134.9 ^b	-275.0 ^c	80.3 ^d	-325.1 ^e	136.0 ^f	-471.1 ^h	223.0 ⁱ	-321.4 ^j

* The geometries corresponding to this path shown in Figure 3, (a) to (g)

** The geometries corresponding to this path shown in Figure 4, (a) to (j)

Table 2. Energies (kJ/mol) of the different steps of the reaction of acetylene with DVs (* = No data)

GBM	Approach	Physisorption	Barrier I	Chemisorption	Barrier II	Local Min	Barrier III	Product
DV	DVH*	-90.8 ^a	58.0 ^b	-	-	-	-	-933.2 ^c
N_P	DVH	-89.6	14.0	-	-	-	-	-911.6
N_{G1}	DVH	-88.2	104.2	-	-	-	-	-853.3
N_{G2}	DVH	-88.6	97.0	-	-	-	-	-866.5
S_G	DVH	-152.4	49.0	-	-	-	-	-809.6
DV	DVP**	-88.1 ^a	123.0 ^b	-381.3 ^c	154.7 ^d	-	-	-587.8 ^e
N_P^1	DVP	-89.3	103.7	-448.4	7.4	-	-	-572.0
N_P^2	DVP	-88.7	28.5	-405.4	153.3	-	-	-572.0
N_{G1}	DVP	-88.2	*	-355.6	153.2	-	-	-496.9
N_{G2}	DVP	-87.8	*	-349.1	117.1	-	-	-504.2
S_G	DVP	-150.8	*	-508.6	29.6	-499.9	30.5	-507.2

* The geometries corresponding to this path shown in Figure 6, (a) to (c)

** The geometries corresponding to this path shown in Figure 7, (a) to (e)

¹ Acetylene is chemisorbed on G1 and G2

² Acetylene is chemisorbed on G3 and N

Table 3. Effect of doping on weakening or strengthening DV reconstruction. G_1 , G_2 , G_3 and $G_4/N/S$ as in Figure 8.

GBM	G_1G_2 (Å)	G_3 ($G_4/N/S$) (Å)
DV	1.79	1.79
N_{G1}	1.66	1.69
N_{G2}	1.70	1.71
N_P	1.91	2.36
S_G	1.96	1.94

Free energy calculations:

For the sake of assessing how much energies are affected by entropic contributions, we have calculated free energies for two processes, whose choice was made as follows. Between ethylene and acetylene we chose acetylene since the two additional hydrogens of ethylene make interaction with DV more complicated. Among the two possibilities with acetylene, giving as product either hexagonal rings (Figure 6, DVH) or a hydrogenated Stone-Wales defect (Figure 7, DVP), we chose the latter and, from the doping suggested (Figure 8) we considered N_p . This is of special importance since the presence of the pyridinic nitrogen significantly facilitates SW formation, and also because the formation of N-doped non-hexagonal rings is of practical interest. Therefore we studied the free energy change: a) from acetylene physisorption on N_p to acetylene chemisorption through DVP; and b) from acetylene chemisorption leading to the N-doped SW formation.

We have considered Gibbs free energy, defined under constant pressure, and Helmholtz free energy, defined under constant volume. The Gibbs free energy can be calculated by the minimization according to¹:

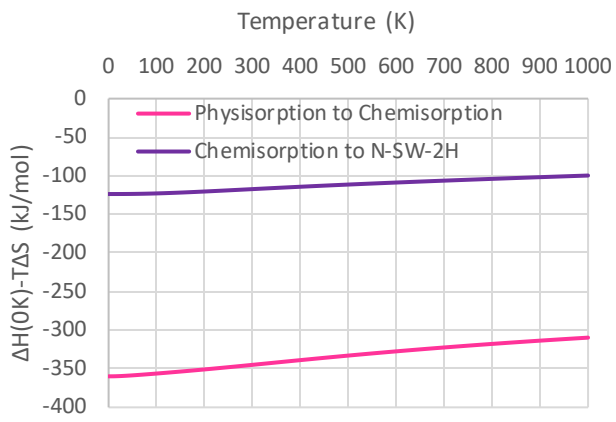
$$G(T, p) = \min_V [U(V) + F_{phonon}(V, T) + pV] \quad \text{Equation 3}$$

in which, $U(V)$ is the total energy corresponding to ground state at an equilibrium volume, $F_{phonon}(V, T)$ is the crystal vibration energy including zero point energy related to temperature. To calculate the Gibbs free energy of each state (reactants and products) it is essential to calculate the energy corresponding to at least five volume points. For each volume point and for just one state (physisorption, chemisorption or healed DV) of the studied systems i.e. acetylene interacting with N_p , with 34 atoms, 204 displacements were created using the finite displacement method as implemented in Phonopy software². Therefore, at least 1020 single point energy calculations should be done. Indeed, only for one ΔG calculation using quasi-harmonic approximation (QHA) phonon calculations, at least 2040 single point energy calculations are required. According to Table 1 and Table 2, in this study 13 reactions, including 34 states have been considered. Therefore, to calculate ΔG s for all reaction steps at least 34680 single point calculations would be required, which is not computationally affordable and that is why only two free energy calculations were selected, as stated above.

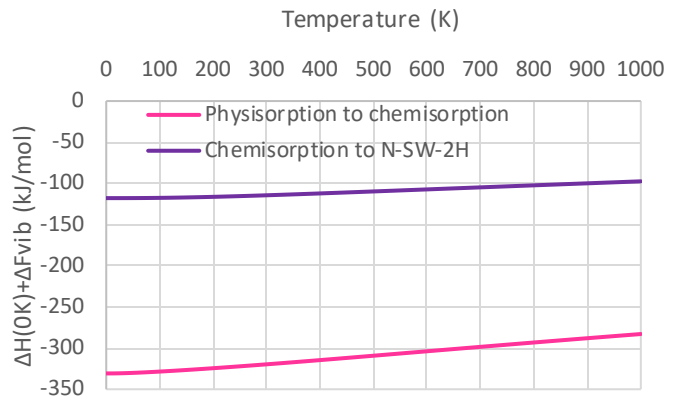
Hence, the free energy changes from acetylene physisorption on N_p to acetylene chemisorption through DVP and the subsequent N-doped SW formation were studied using the finite displacement method indicated above. All variables were selected similar to the reported electronic structure calculations using Quantum Espresso and the free energy calculations for fully relaxed geometries corresponding to numbers 1, 3 and 5 of Table S6 were conducted. We approximate the Gibbs free energy as the sum of total energy and vibrational free energy by estimating pV and TS^{conf} to be negligible from Equation 4 as follows³:

$$G = E + F^{vib} - TS^{conf} + pV \approx E + F^{vib} \quad (\text{Electron and phonon contribution}) \quad \text{Equation 4}$$

Considering the possibility to estimate the electron contribution of free energy at elevated temperatures from calculated energy at 0 K using Quantum Espresso, $\Delta H(0K) - T\Delta S$ and $\Delta H(0K) + \Delta F^{vib}$ versus temperature were calculated as follows.



$\Delta H(0K)-T\Delta S$ versus T plot



$\Delta H(0K)+\Delta F^{vib}$ versus T plot

- [1] Y.-L. Jiang and X.-B. Yang, Solid State Commun. 2021, **337**, 114452.
- [2] A. Togo and I. Tanaka, Scripta Materialia, 2015, **108**, 1-5.
- [3] M. Geng and H. Jónsson, J. Phys. Chem. C 2018, **123**, 464-472.