Supplementary informations

Hydrazine selective decomposition over metal free carbonaceous materials

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The present supplementary information document contains in figure S1 and S2 the optimized graphitic surfaces obtained by DFT optimization and the charge density Laplacian analysis iso-surfaces plot of PG, SV, DV, SW,VSW1 and VSW2, respectively. Table S1 and S2 reports the energetic for NH_3 probe molecule on the individuated active sites, respectively for SV and DV. In Figure S3 to S6 the hydrogen diffusion and recombination pathways and energy profiles are showed. Finally, figure S7 presents the difference between the second symmetric and asymmetric dehydrogenation step.

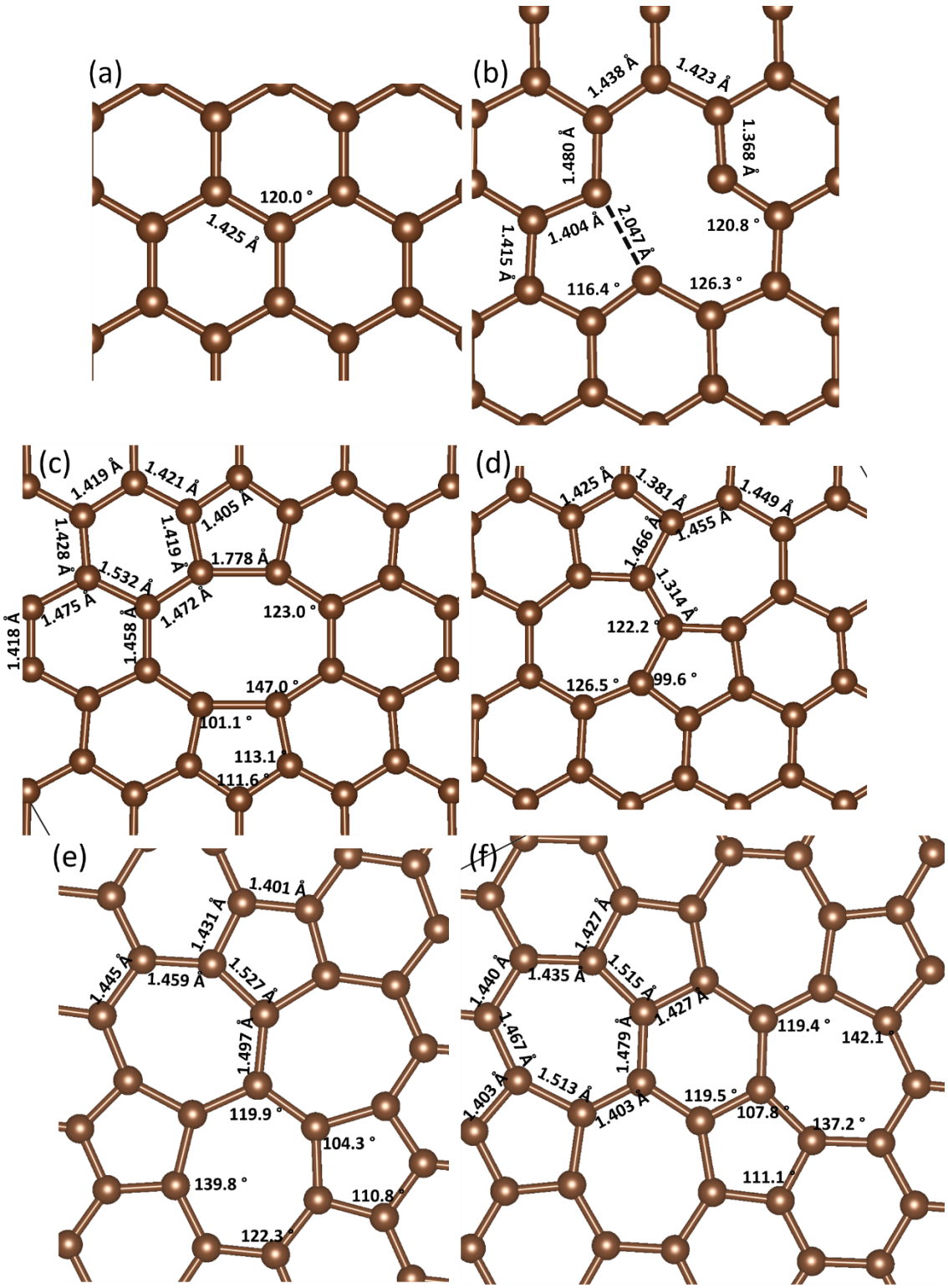


Figure S1: Top view of the optimized graphitic surfaces: a) pristine graphene b) SV c) DV d) SW e) VSW1 f) VSW2. Inset, distances (Å) and angles (°) of interest. Carbon atoms are brown.

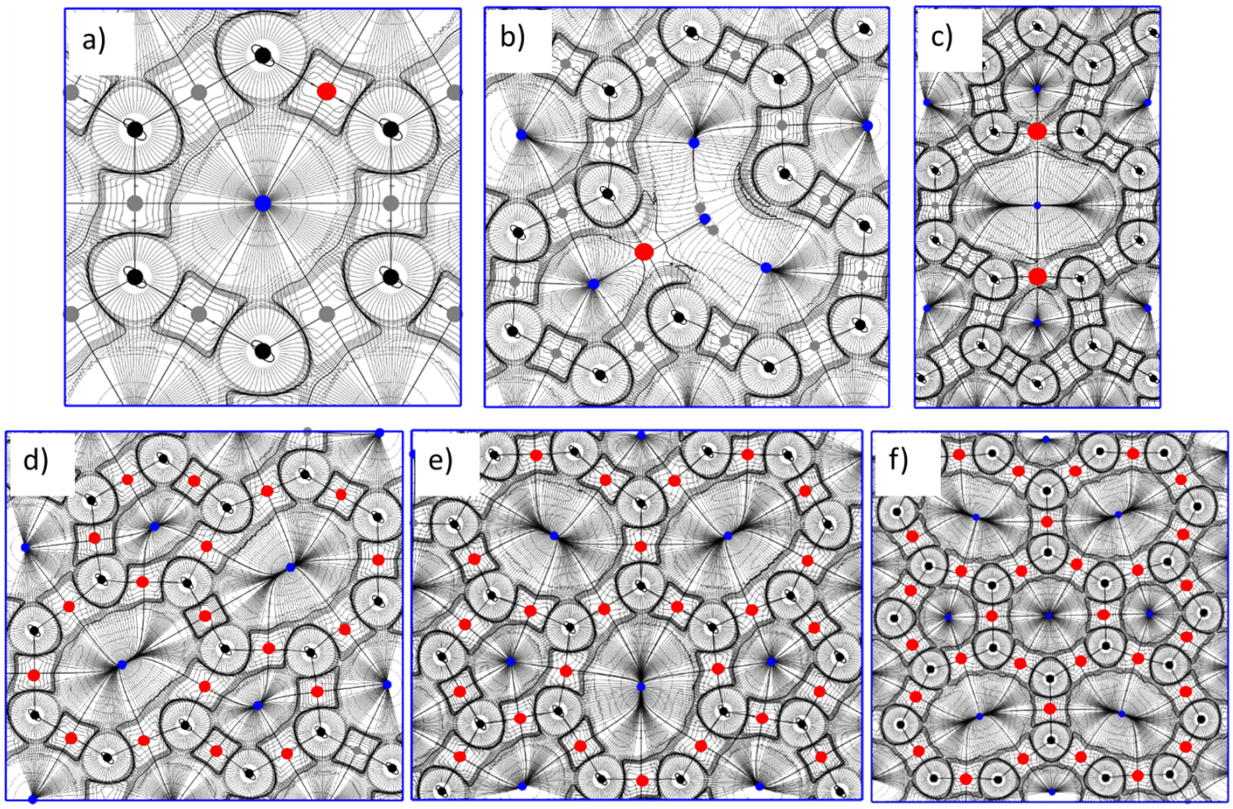


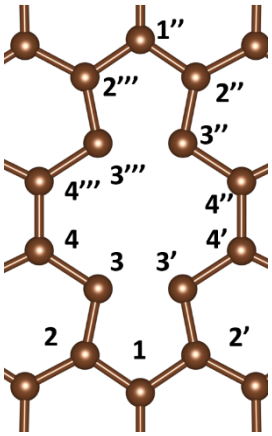
Figure S2: Charge density Laplacian analysis iso-surfaces plot of: a) PG, b) SV, c) DV, d) SW, e) VSW1 and f) VSW2. Red circles indicate where the Bond Critical Point analysis was performed for our purposes. Black circles indicate nuclear charge density maxima, grey Bond Critical Points and blue Ring Critical Points.

Table S1 NH_3 proble molecule, adsorption energetic for SV. From all the tested configurations, only the stable one are reported. The symmetric counterparts (e.g. X-C_3' Y-C_3 to Y-C_3' X-C_3) returned the same adsorption value within the computational precision due to the symmetry effect. The labels refer to Figure 3 in main paper.

Chemisorption (eV)	Dissociative (eV)
C_3 -1.17	H_2N-C_3 H-C_3' -2.05
C_3' -1.17	H_2N-C_3 H-C_7 -2.05
C_7 -1.01	H_2N-C_3' H-C_7 -2.05

Table S2 NH_3 proble molecule, adsorption energetic for DV. From all the tested configurations, only the stable one are reported. The symmetric counterparts (e.g. X-C_3' Y-C_3 to Y-C_3' X-C_3) returned the same adsorption value within the computational precision due to the symmetry effect. Where a '/' is present, an endothermic adsorption was obtained.

Chemisorption	Dissociative
/	H_2N-C_3 H-C_3' -1.59 eV



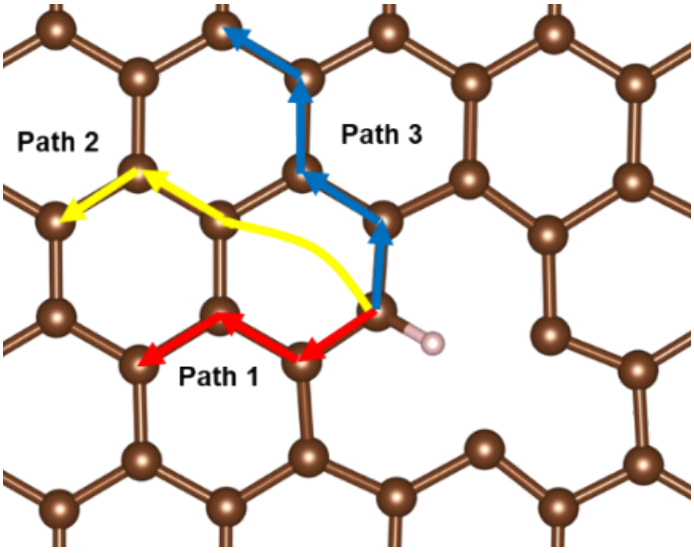


Figure S3: Out of vacancy atomic hydrogen diffusion pathways.

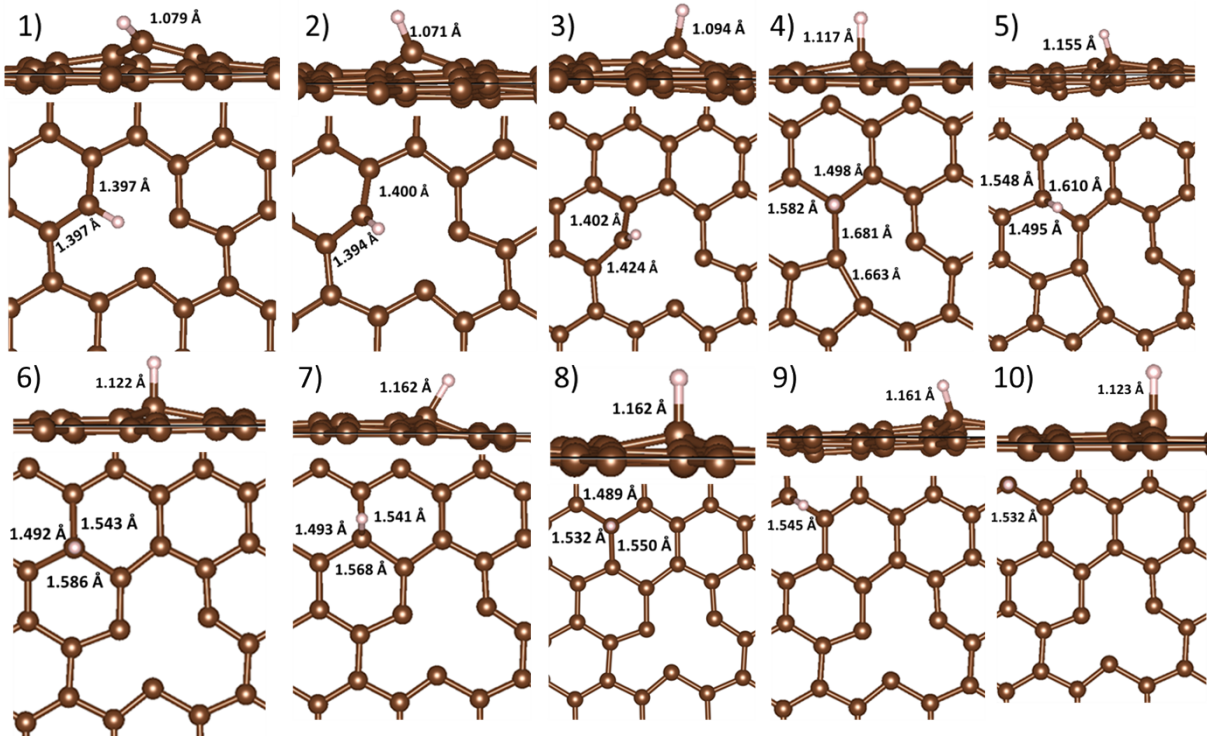


Figure S4: Top and side view of the most favourable steps of hydrogen diffusion process. Inset, distances (Å) and angles (°) of interest. Carbon atom is labelled in brown and hydrogen in white.

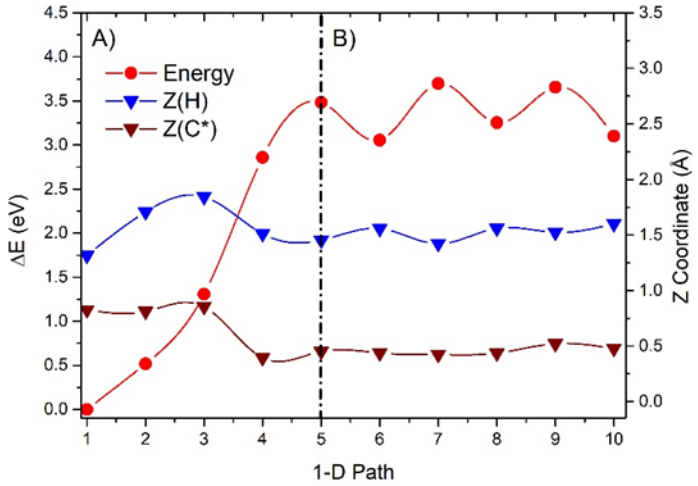


Figure S5: Hydrogen diffusion on SV system. A, left side) Vacancy influence B, right side) Graphene-like behaviour. Red profile: hydrogen diffusion energy profile. Blue profile: H z-coordinate fluctuations. Brown profile: C atom bonded with H z-coordinate fluctuations.

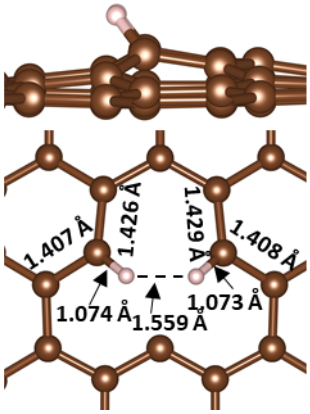


Figure S6: Hydrogen recombination on SV system. Inset, distances (Å) and angles (°) of interest. Carbon atom is labelled in brown and hydrogen in white

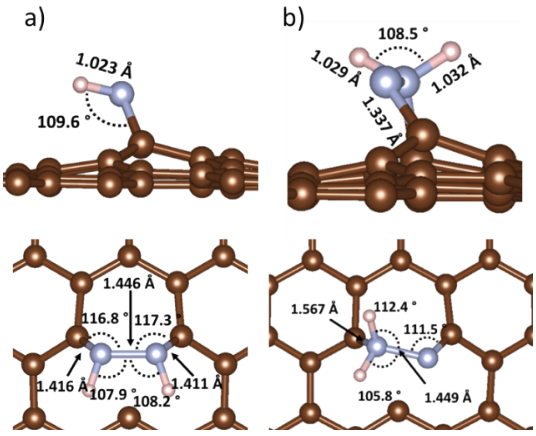


Figure S7: Top and side view of second de-hydrogenation step: a) Symmetric decomposition and b) Asymmetric decomposition. Inset are distances (Å) and angles (°) of interest. Carbon atom is labelled in brown, nitrogen in blue and hydrogen in white. $\Delta E_{\text{Asymm--Symm}}$ = 0.739 eV