Supplementary Information

Lithium-Grafted Si-doped γ-Graphyne as Reversible Hydrogen Storage Host Material

Nidhi Duhan[1] and T. J. Dhilip Kumar[1*]

[1]*Department of Chemistry, Indian Institute of Technology Ropar, Rupnagar 140001, India*

*Email: dhilip@iitrpr.ac.in

1. Structural stability of SiG nanolayer:

- Firstly, thermal stability of Si-doped γ-Graphyne nanolayer is established by performing AIMD simulations at a finite temperature of 400K for 10ps using a (NVT) canonical ensemble. The system is first equilibrated for 4ps at the same temperature. The energy vs time steps plot and the corresponding structure of the SiG nanolayer is as shown in Figure S1. The narrow range of fluctuations in total energy and the undistorted structure characterize the thermal stability of the nanolayer.
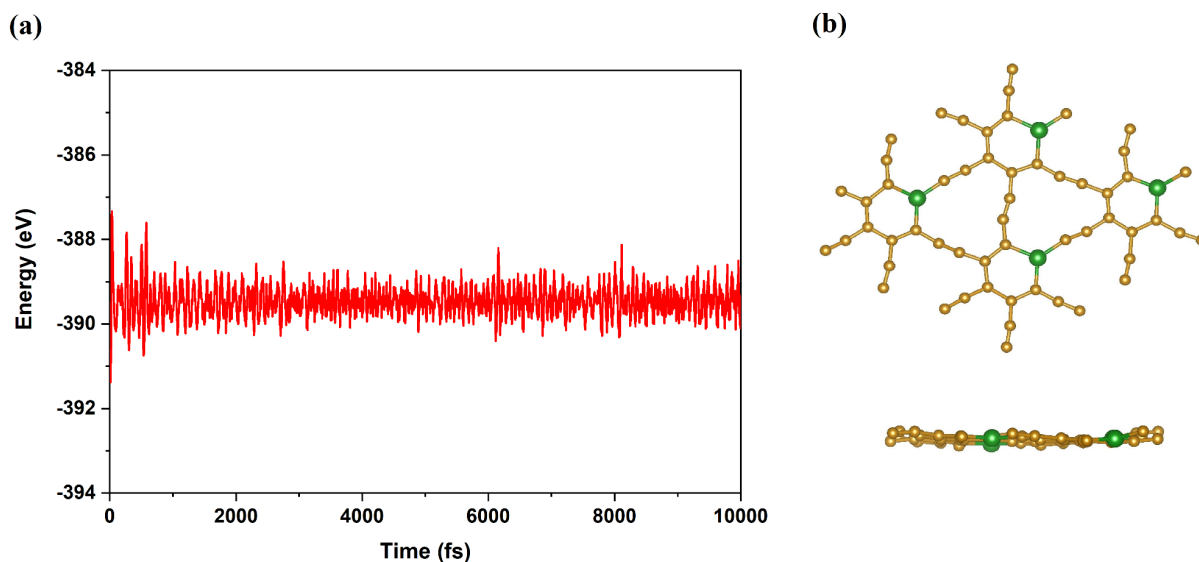
(a)   (b)

FiG. S1: (a) Variation in the total energy of Si-doped γ-Graphyne system with time in course of AIMD simulations for 10 ps at 400 K and (b) top and side view of the resulting structure after simulation.

- Next, the Phonon dispersion is studied using Phonopy code to estimate the extent of imaginary frequencies associated with the system, if any. The frequency vs kpath spectrum (Figure S2) indicates the presence of a small dip near the Γ-point representing imaginary frequencies < 10 cm^{-1}. The presence of high negative frequencies point towards instability of the given system. However, the small number of negative frequencies (< 10 cm^{-1}) is justified in literature, based on the small size of the system.[1,2]

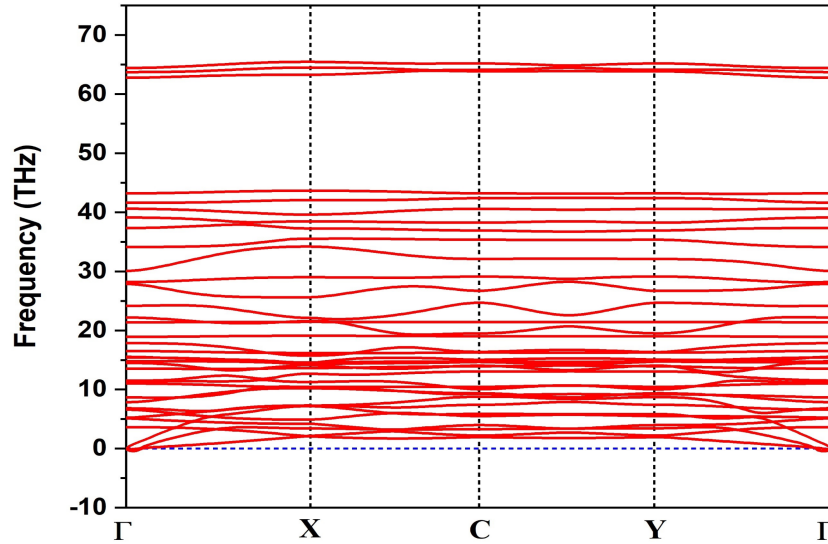**FIG. S2:** Phonon dispersion spectrum of a 2 × 2 × 1 supercell of Si-doped γ-Graphyne following kpath as Γ-X-C-Y-Γ.

- Further, we investigated the mechanical properties of the SiG nanolayer. The elastic constants (C_{ij}) are determined by implementing the energy-strain method. The independent elastic constants calculated are tabulated below as Table S1. It is noted that the Born–Huang criteria to confirm mechanical stability, i.e. C_{11} x C_{22} > C_{12} x C_{12} and C_{ij} >0, is fulfilled depicting the mechanical stability of the nanolayer.[3]

TABLE S1: The elastic constants of SiG nanolayer.

Elastic Constants (C_{ij})	Value (N/m)
C_{11}	163.84
C_{12}	77.95
C_{16}	11.48
C_{22}	182.26
C_{26}	3.83
C_{66}	43.25

- **Formation Energy:**

The formation energy of the Si-doped γ-Graphyne calculated using the following equation is 0.51 eV/atom:

$$E_f = (E(A_mB_n)-mE(A)-nE(B))/(m+n) \quad …S1$$

where, A_mB_n is a compound; m and n are the number of A and B in the formula; $E(A_mB_n)$, $E(A)$, and $E(B)$ are the energies of compound A_mB_n, and energies of constituent elements in their standard states.[4] While this formation energy is quite high, it is comparable to that of single-layer SiC (E_f = 0.50 eV/atom), which has indeed been fabricated successfully.[5,6]

A comparison of formation energy of different 2D materials has been provided in Table S2. This analysis supports the stability of SiG monolayer.

Table S2: Comparison of formation energy of different 2D materials.

2D monolayer	Formation Energy (eV/atom)
SiG	0.51
Graphene	0.88
B-doped Graphene	0.89
N-doped Graphene	0.90
Si-doped Graphene	0.93
P-doped Graphene	0.91
AlN	0.51

2. Qualitative Charge Analysis:

For qualitative analysis of charge transfer, the charge density difference ($\Delta\rho$) is calculated using equation S1 and it is mapped graphically using the visualization tool VESTA as shown in Figure S3. Here, the blue color represents the depletion of charge density whereas the yellow color illustrates charge accumulation. It is clear from the figure that Li donates a significant amount of charge to the nanolayer.

$$\Delta\rho = \rho_{LiSiG} - (\rho_{SiG} + \rho_{Li}) \quad \dots \text{S2}$$

Here, ρ_{LiSiG}, ρ_{SiG}, and ρ_{Li} are the charge densities of Li functionalized SiG nanolayer, bare SiG nanolayer, and Li atom, respectively.
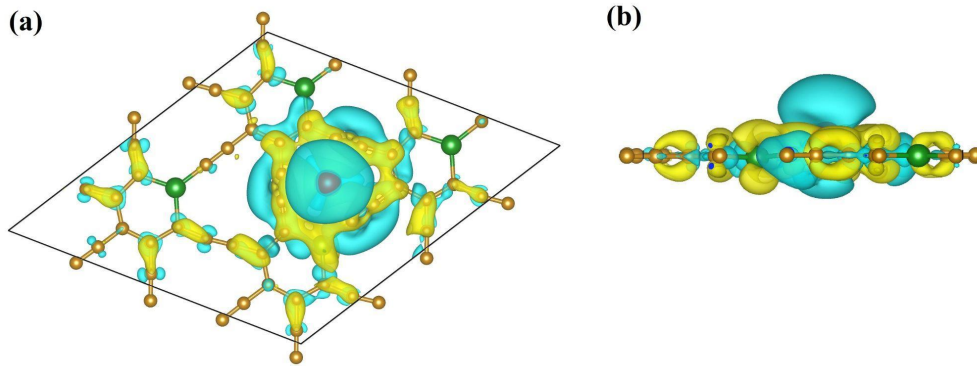
FIG S3: (a) Top and (b) side view of the difference in charge density between Li-loaded and pristine SiG nanolayer. (Blue region: Depletion of charge density, Yellow region: Elevated charge density.)

3. K-points convergence:

K-point convergence is an important aspect to consider while performing periodic calculations. The k-point mesh is an important parameter that controls the Brillouin Zone integration and can play a huge role in getting accurate results, especially for metals. Keeping that in mind, we have converged k-points with respect to energy to carry out the studies. Figure S4 presents the k-point convergence graph.
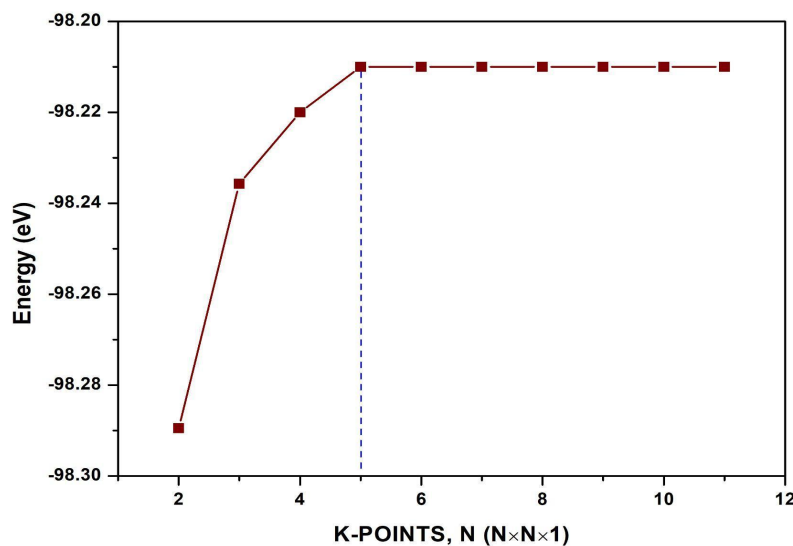

Figure S4. The variation of total energy of the monolayer with k-points. (N=5 shows convergence)

References:

1. Mahata, A.; Garg, P.; Rawat, K. S.; Bhauriyal, P.; Pathak, B. A free-standing platinum monolayer as an efficient and selective catalyst for the oxygen reduction reaction. J. Mater. Chem. A **2017**, 5, 5303–5313.
2. Zhang, Z.; Liu, X.; Yakobson, B. I.; Guo, W. Two-Dimensional Tetragonal TiC Monolayer Sheet and Nanoribbons. J. Am. Chem. Soc **2012**, 134, 19326–19329.
3. Mouhat, F.; Coudert, F. m. c.-X. Necessary and sufficient elastic stability conditions in various crystal systems. Phys. Rev. B **2014**, 90, 224104.
4. Ren, X.; Wang, B.; Zhu, J.; Liu, J.; Zhanga, W.; Wen, Z. The doping effect on the catalytic activity of graphene for oxygen evolution reaction in a lithium–air battery: a first-principles study. Phys. Chem. Chem. Phys. 2015, **17**, 14605-14612.
5. Lin, S. S. Light-Emitting Two-Dimensional Ultrathin Silicon Carbide. J. Phys. Chem. C, 2012, **116**, 3951–3955.
6. Zhuang, H. L.; Singh, A. K.; Hennig, R. G. Computational discovery of single-layer III-V materials. Phys. Rev. B, 2013, **87**, 165415