

Electronic Supporting Information

Effect of Acetylene Bond on Hydrogen Adsorption in Diamond-like Carbon Allotropes: from First Principles to Atomic Simulation †

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The supporting information includes three sections. Section 1 describes the mechanical properties of diamond-like carbon allotropes (DLCAs). Section 2 describes the computation details about grand canonical Monte Carlo (GCMC) simulations and hydrogen adsorption properties on DLCAs. Section 3 lists the references cited in the supporting information.

Section 1. Mechanical properties of DLCAs

Birch-Murnaghan equation:¹

$$\frac{\Delta E}{V_0} = a_0 + a_1 f^4 + a_2 f^2 + a_3 f^3 \quad (S1)$$

Where $f = \frac{1}{2} \left[\left(\rho / \rho_0 \right)^{2/3} - 1 \right]$, $a_2 = \frac{9}{2} B$, B denotes bulk modulus, ρ_0 , ρ and V_0 denote original and present density, original volume of materials, respectively.

The elastic moduli (shear modulus and Young's modulus) can be also estimated by the Voigt-Reuss-Hill approximation.²

$$E = \frac{9BG}{3B + G}, \quad G = \frac{1}{2}(G_V + G_R)$$

Where E denotes the Young's modulus, G denotes the shear modulus;

$$G_V = \frac{1}{5} [(c_{11} - c_{12}) + 3c_{44}], \quad G_R = \left[\frac{4}{5} (c_{11} - c_{12})^{-1} + \frac{3}{5} c_{44}^{-1} \right]^{-1}$$

where c_{ij} ($i = 1-6, j = 1,6$) denotes the elastic constant computed via VASP with LDA-PAW potentials.³

The $\Delta E/V$ - f relationships of DA_PA_W, TND-1_PA_W and TND-2_PA_W are shown in Fig.S1-S3.

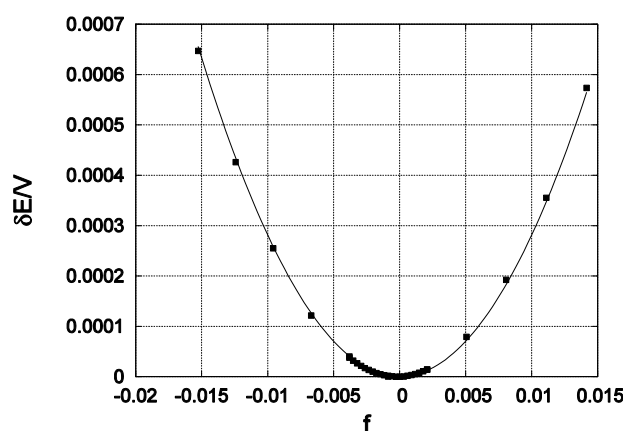


Fig.S1 $\Delta E/V$ - f relationship used to calculate bulk modulus of DA_PA_W.

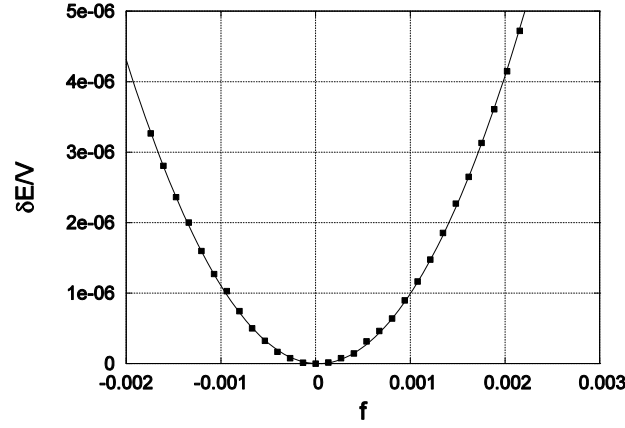


Fig.S2 $\delta E/V$ - f relationship used to calculate bulk modulus of TND-1_PAW.

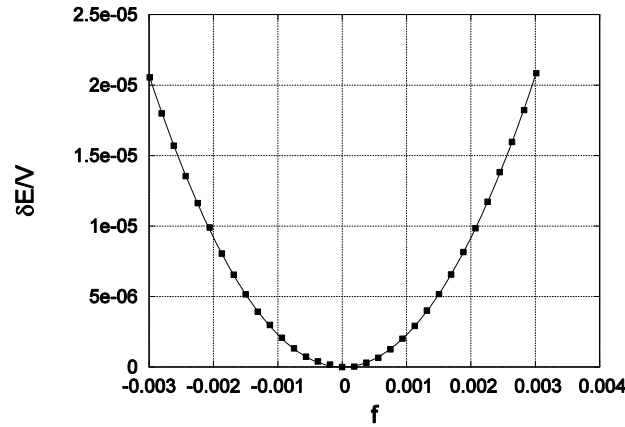


Fig.S3. $\delta E/V$ - f relationship used to calculate bulk modulus of TND-2_PAW.

Section 2. Gas adsorption properties of DLCAs

The chemical potentials of gas sorbates at different temperatures and pressures were converted to fugacities by the Peng-Robinson equation of state (PREOS).⁴ The absolute adsorbed amounts (N_{abs}) obtained by GCMC simulations are converted to excess adsorbed amounts (N_{exc}), using the following equation

$$N_{exc} = N_{abs} - \rho_{bulk} \cdot V_{free} \quad (S3)$$

where N_{abs} is the amount of absolute adsorbed molecules, V_{free} represents the pore volume of adsorbent, and ρ_{bulk} is the density of the sorbate calculated using PREOS at a given temperature and pressure. The numbers of unit cells in each DLCAs was adjusted to be at least twice the Morse cut-off distance, and periodic boundary conditions were applied in all three dimensions to eliminate boundary effects. The DLCAs were treated as rigid with frozen atoms during simulation. During calculation of the nonbonding interactions for GCMC, only the Morse potentials are considered for H_2 adsorption and cutoff radius of potentials is 12 Å. A total of 10^7 steps were used; the first half of these moves was used for equilibration, and the remaining steps were used for calculating the ensemble averages. Four types of moves (translation, random insertion, rotation and deletion) were used. Every possible move was given equal probability.

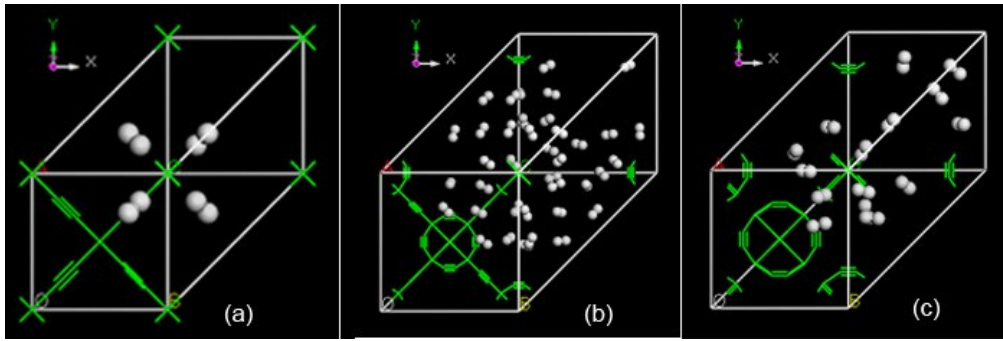


Fig. S4 Various final hydrogen adsorption geometries based on calculation with Dmol3 module. (a) $4\text{H}_2@DA_PAW$, (b) $38\text{H}_2@TND-1_PAW$, (c) $15\text{H}_2@TND-2_PAW$. Green lines refer to carbon atoms in DLCAs, and white balls refer to hydrogen atoms. We can find that none of hydrogen molecule enters into C16 node comprising acetylene bonds in TND-1_PAW or TND-2_PAW.

Fig.S4 shows the different final hydrogen adsorption geometries based on calculation with Dmol3 module. It is speculated that the highest amounts of hydrogen adsorbed in DLCAs are 4, 38 and 15 H_2 molecules per primitive cell for DA_PAW, TND-1_PAW and TND-2_PAW, respectively. For $4\text{H}_2@DA_PAW$, $38\text{H}_2@TND-1_PAW$ and $15\text{H}_2@TND-2_PAW$ systems, their adsorbed hydrogen molecules were inserted into the structures of DLCAs by the simulated annealing method. Then their geometries were optimized with Dmol3 module. We can find that none of hydrogen molecule enters into C16 node comprising acetylene bonds in TND-1 or TND-2 because the pore size of the node is about 4 Å and it is too small to store any hydrogen molecule. Those invalid pores occupied the partial space of them, resulting in their hydrogen storage capacities decrease to a certain comparing with that of DDA_PAW.

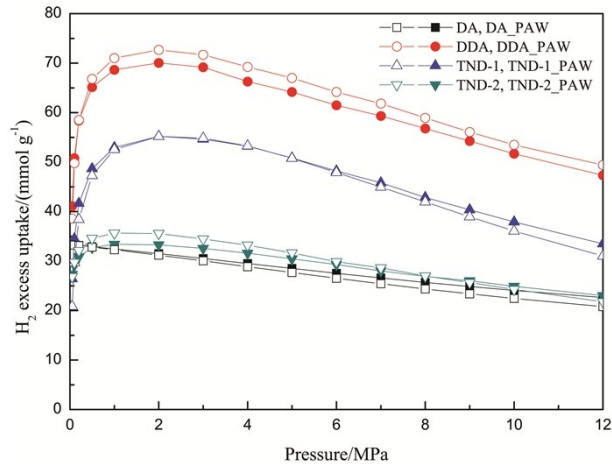


Fig.S5 Simulated excess H₂ isotherms in the original and optimized DLCAs at 77K.

Fig.S5 shows the comparison of simulated excess H₂ isotherms in the original and optimized DLCAs at 77K. The excess H₂ isotherm in each DLCA material shows slight difference in this condition between the optimized and original structures, indicating that slight structural variance of each DLCA material takes almost no effect on its H₂ adsorption properties. Therefore, hydrogen adsorption capacities only in the optimized DLCAs at ambient temperatures were calculated later.

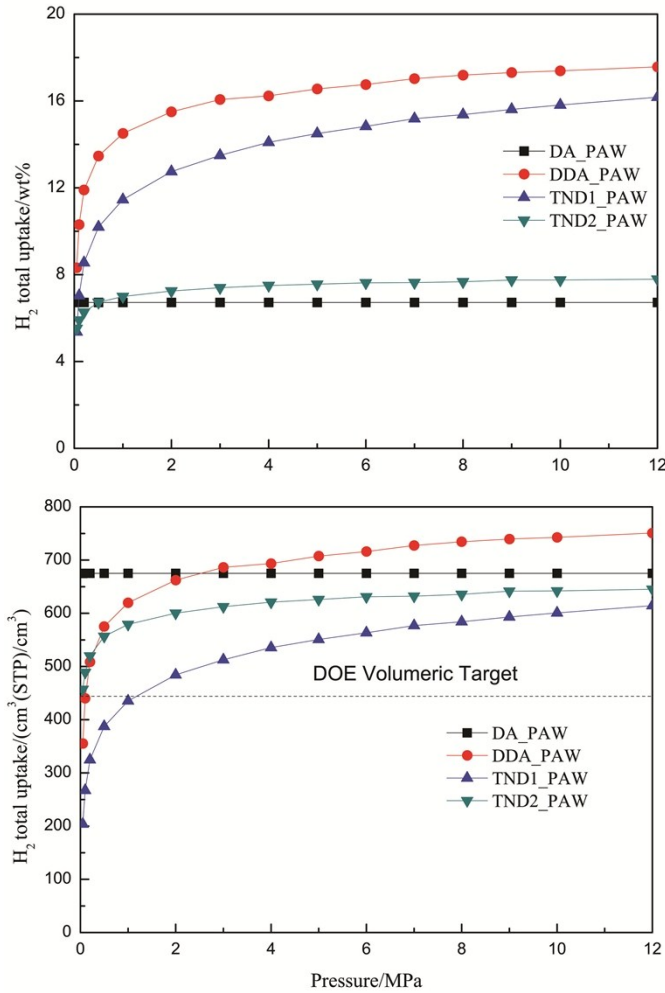


Fig. S6 Simulated H₂ total gravimetric and volumetric isotherms in optimized DLCAs at 77K

Fig. S6 shows the simulated total gravimetric and volumetric H₂ uptakes in optimized DLCAs at 77K. The maximum total H₂ uptakes in all DLCAs at this temperature totally hit the DOE gravimetric and volumetric targets (5.5wt% and 444 cm³(STP)cm⁻³, respectively).

Section 3. References

1. F. Birch, *Physical Review*, 1947, **71**, 809-824.
2. R. Hill, *Proc. Phys. Soc. A*, 1952, **65**, 349.
3. L. Huang, Z. Xiang and D. Cao, *Journal of Materials Chemistry A*, 2013, **1**, 3851-3855.
4. D.-Y. Peng and D. B. Robinson, *Ind. Eng. Chem. Fund.*, 1976, **15**, 59-64.