

**Supporting Materials for**  
**New insights into phase transition behavior and electrochemistry**  
**corrosion of three-dimensional biphenylene**

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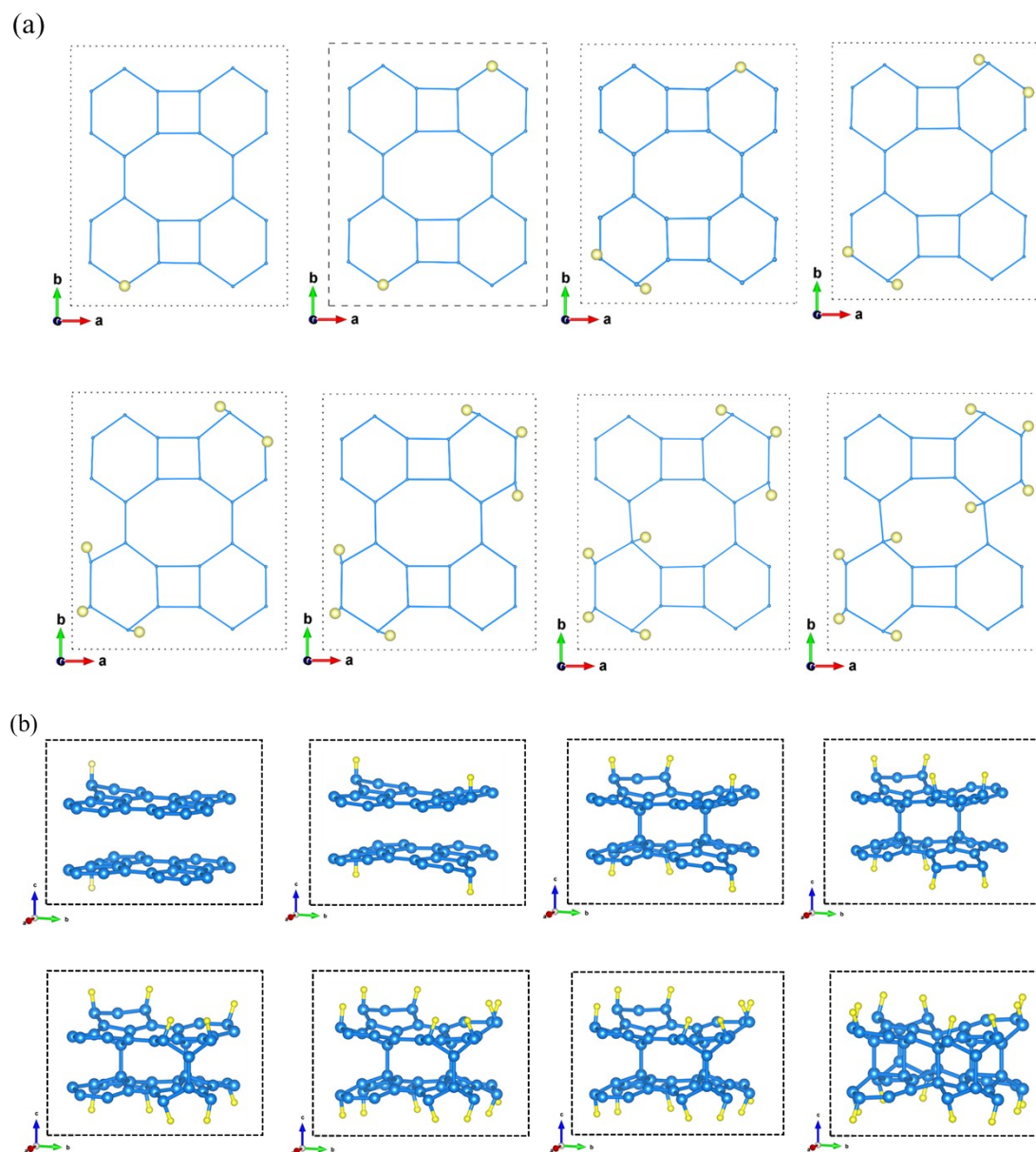
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## 1 · Hydrogen atom configuration of biphenylene adsorption



**Figure S1.** (a) Energy points corresponding to the structures of H atoms adsorbed on monolayers of biphenylene; (b) Energy points corresponding to the structures of H atoms on bilayers of bilayers of bilaterally hydrogenated biphenylene. H atoms adsorbed on opposite sides are indicated in yellow, and C-C bonds between adjacent layers are indicated in blue.

## 2. Gibbs free energy calculation $\Delta G$

Chemically induced phase transition” is essentially a nanoscale phenomenon, and the transition pressure largely depends on the film thickness. Although theory suggests that surface-induced transformation can reach 10-30 layers (3-10 nm), there is currently little experimental evidence, limited to bilayers (or 3-4 layers assisted by metal substrates). Therefore, we believe that the nucleation kinetics of the biphenyl vinylene to diamond-like film is worth exploring. For this nucleation dynamic process, we strictly followed the previous literature<sup>[1-3]</sup>.

The transformation barrier energy can be calculated from Gibbs energy difference between structures of multilayered biphenylene absorbed by  $n$  hydrogen atoms with interlayer C-C bonds and without interlayer C-C bonds. For few layered biphenylene chemisorbed with  $n$  H atoms, the conjunction of the layers occurred almost immediately, with no interface hindrance. The formula of  $\Delta G$  is:

$$\Delta G = \Delta E^{bulk}(N - 2)n + \Delta E^{surf}n + \gamma + \rho\Delta V \quad (S1)$$

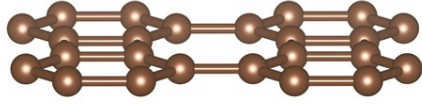
### 2.1 Bulk term $\Delta E^{bulk}$

This term can be directly calculated by subtraction the energy of biphenylene ( - 8.3302 eV/atom ) from the energy of BP-DLC (-8.7898 eV/atom). Nucleated structure contains  $N - 2$  inner layers which every layer consists of approximately  $n/2$   $sp^3$ -carbon atoms connected with upper layer and  $n/2$  atoms connected with down layer. Thus

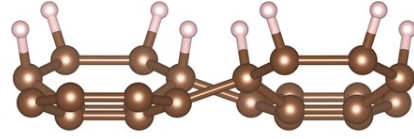
$$\Delta E^{bulk} = (- 8.3301 + 8.78985) \cdot (N - 2) \cdot n = 0.45968 \cdot (N - 2) \cdot n . \quad (S2)$$

### 2.2 Surface term $\Delta E^{surf}$

(a)



(b)

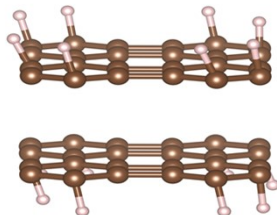


**Figure S2.** Atomic structure of a) pristine biphenylene and b) hydrogenated biphenylene.

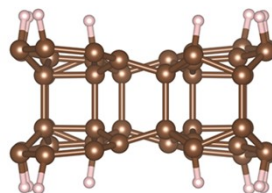
This term means a surface contribution to phase transformation, implicitly including the surface strain caused by the buckling tendency due to the functionalization of one side. The term contains a difference in binding energy of surface absorbed by H atoms connected to next layer with not connected ones, so it cannot be directly calculated.

As shown in Figure S2, the buckling caused by hydrogen atoms is almost negligible, so in this case, this value is very close to the normalized per chemisorbed H energy difference between hydrogenated bilayer clathrate structure and single biphenylene layer functionalized only from one side. Indeed, the subtraction from the energy of hydrogenated bilayered diamane (Figure S3a) the energy of corresponding two isolated graphone layers (Figure S3b) gives surface energy difference  $\Delta E^{surf} = -0.75$  whereas our best fitting yields value of  $-0.74$  eV.

(a)



(b)



**Figure S3.** Atomistic structures of a) two isolated hydrogenated biphenylene layers and b) bilayered diamane.

Adding all terms above together,  $\Delta G$  can be expressed as

$$\Delta G = -0.74 \cdot n. \quad (\text{S3})$$

### 2.3 Interface term $\gamma$

The third term,  $\gamma$ , evaluates the energy of nucleus interface in the internal layers and strain in multilayer biphenylene around nucleus. A direct calculation of interface energy in the internal layers is rather difficult. However, we can take into account that an interface between formed diamond nucleus (sp<sup>3</sup>-hybridized bonds) and biphenylene (sp<sup>2</sup>-hybridized bonds) has the same nature both for the surface and for the internal layers. Therefore,  $\gamma$  term can be evaluated from the simplified model of hydrogenated single biphenylene sheet which includes both sp<sup>3</sup> (C-H) and sp<sup>2</sup> (C-C) hybridized bonds in its structure. The dependence of binding energy of adsorbed hydrogen on the number of H atoms on the both side of graphene monolayer is shown. The trend follows the equation  $\varepsilon_b n = \varepsilon_\infty n - \gamma' \sqrt{n}$ , which consists of the “bulk” contribution,  $\varepsilon_\infty$ , proportioned to a nucleus area (i.e. the number of H atoms,  $n$ ), and interface term proportioned to number of interface atoms  $n \sim \sqrt{n}$  with coefficient  $\gamma' = 1.01 \text{ eV}$ . [10] For the considered case of multilayer biphenylene it should be multiplied by number of internal layers,  $N - 2$ .

A strain in multilayer graphene around nucleus mainly originates from difference in the corresponding interplane distance in biphenylene and diamond-like carbon. Elastic energy caused by this stress can be estimated using

continuum model and, therefore, contribution to the Equation 3 can be expressed in the following way:

$$\gamma = 1.01(N - 2)\sqrt{n} + \frac{1}{2}C \iint h\varepsilon^2 dxdl \quad (S4)$$

where  $h = 3.4 \cdot N \text{ \AA}$  is a film thickness,  $C$  is the elastic modulus of graphite in  $c$  direction,  $x$  is the distance from the edge of diamond nucleus to  $+\infty$ ,  $l$  is a perimeter of

strained area  $\left( l \approx 2\pi R = \frac{2.5}{\sqrt{2}}\pi\sqrt{n} \right)$ , where  $2.5 \text{ \AA}$  is distance between neighbored

adatoms) and  $\varepsilon$  is a strain  $\varepsilon = (\varepsilon_{max} - \varepsilon_p)\exp\left(-\frac{x}{H}\right)$ , where  $\varepsilon_{max}$  is the relative difference between lattice constants of diamond-like and biphenylene in  $c$  direction.

Exponent in the equation represents the decay of the strain in the lattice with increasing of the distance  $x$  from the nucleus. By analyzing the geometry of investigated structures and for best fitting of calculated dependencies  $H$  was estimated as  $3.125 \cdot N \cdot \text{\AA}$ . the interface term has the following form:

$$\gamma = 1.01(N - 2)\sqrt{n} + 0.375N^2\sqrt{n}(0.6911 - \varepsilon_p) \quad (S5)$$

#### 2.4 Enthalpy term $H_{elastic}$

In  $H_{elastic}$  the first part is the elastic energy change under the external pressure which can be represented only as the elastic energy of graphene with  $sp^3$ -hybridized region in this work, since diamond is much harder than graphite,  $\varepsilon$  of nucleus is very small. If we mark the equilibrium volume of graphite region as  $V_0^G$ , then

$$V_0^G = hS = h\pi R^2 = 3.4N\text{\AA}\pi\left(\frac{1}{2}\sqrt{\frac{n}{2}}2.5\right)^2\text{\AA}^2 = 8.3Nn\text{\AA}^3 \quad (S6)$$

The elastic energy change:

$$H_{elastic} = -\frac{1}{2}\varepsilon_p pV_0^G - (\varepsilon_{max} - \varepsilon_p)pV_0^G \quad (S7)$$

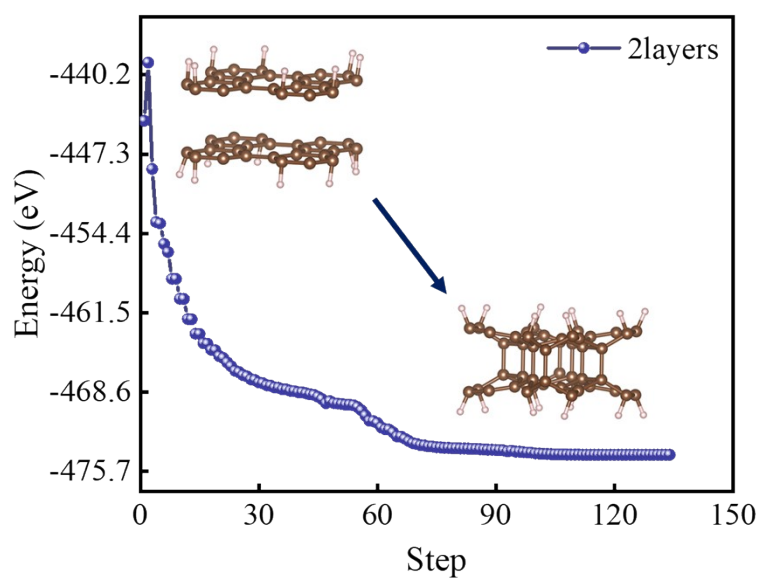
Finally, analytical equations for Gibbs free energy difference between N-layered biphenylene contained n chemisorbed H atoms on both surfaces with and without chemically bounded layers can be presented in the following forms:

$$\begin{aligned} \Delta G &= 0.4597(N-2)n - 0.74n + 1.01(N-2)\sqrt{n} + 0.375(0.6911 - \varepsilon_p)^2 N^2 \sqrt{n} - 1.718Nnp\varepsilon_p \\ &\quad np(0.6911 - \varepsilon_p) \end{aligned} \quad (S8)$$

All coefficients to the final Equation S7 or Equation 5 for both hydrogenated and structures are presented in the Table S1

Table S1. Numerical values of the parameters in the Equation 5.

	$\Delta E^{bulk}$ , eV	$\Delta E^{surf}$ , eV	$\gamma'$ , eV	$\gamma^G$ , eV	$V^G$ , Å <sup>3</sup>
H	0.4597	-0.74	1.01	2.79	3.436Nn

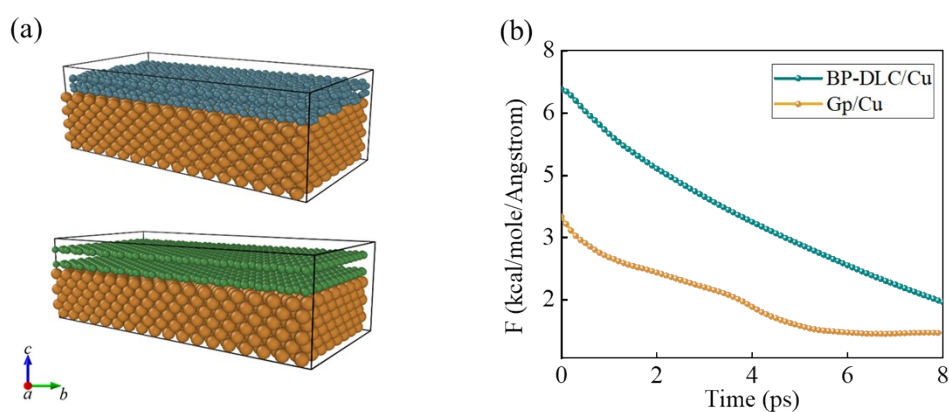


**Figure S4.** Hydrogenation of bilayer biphenyl network structures induces energy changes.



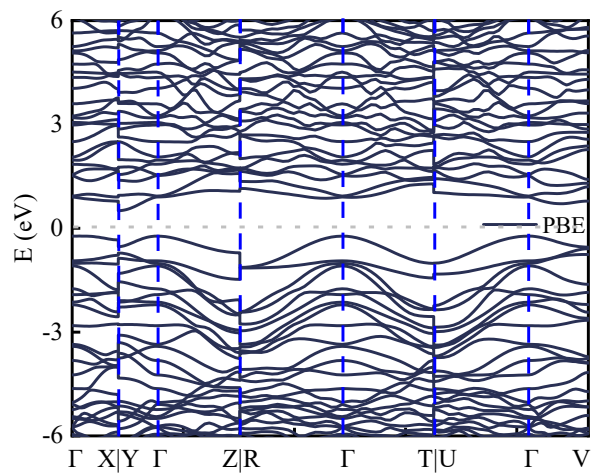
### 3. Exfoliation behavior of BP-DLC with graphene

We used the molecular dynamics software lammps to simulate the exfoliation between graphene and diamond-like film and Cu substrate under dry conditions as well as 30° exfoliation angle conditions, all exfoliation forces increase rapidly at the beginning and reach a maximum value, then decrease until a steady state of constant magnitude is reached, and comparison with graphene reveals that the exfoliation force required for the diamond-like film is much larger than that of graphene, and the bonding performance of the structure to the substrate is much higher than that of graphene through the pegging effect and the inherent van der Waals force interactions between the film and the substrate.



**Figure S5.** a) BP-DLC with Gp/Cu stripping model b) Peel force comparison.

### 3. Electronic band structure of BP-DLC



**Figure S6.** Band structure of BP-DLC around the Fermi level.

## 4. References

- [1] Rajasekaran S , Abild-Pedersen F , Ogasawara H ,et al. Interlayer Carbon Bond Formation Induced by Hydrogen Adsorption in Few-Layer Supported Graphene. *Physical Review Letters*, 2013, 111(8):697-711.
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- [3] S.V. Erohin, Q.Y. Ruan, P.B. Sorokin, B.I. Yakobson, Nano-thermodynamics of chemically induced graphene–diamond transformation, *Small* 2 (2020) 2004782.