Supplementary Materials for

Ultra-low friction mechanism of highly sp3-hybrid amorphous carbon controlled by interfacial molecules adsorptions

Jing Shi,1,2 Tiandong Xia,3 Chengbing Wang,4,* Kun Yuan,5,6,* Junyan Zhang1,*

1 State Key Laboratory of Solid Lubrication, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, China
2 University of Chinese Academy of Sciences, Beijing 100049, China
3 School of Materials Science & Engineering, Lanzhou University of Technology, Lanzhou 730050, China
4 School of Materials Science & Engineering, Shaanxi University of Science and Technology, Xi’an 710021, China
5 College of Chemical engineering & Technology, Tianshui Normal University, Tianshui 741001, China
6 Institute for Chemical Physics & Department of Chemistry, School of Mechanical Engineering, Xi’an Jiaotong University, Xi’an, 710049, China

* Corresponding author. Email: wangcb@sust.edu.cn (Chengbing Wang)
* Corresponding author. Email: tsnuyk@yeah.net (Kun Yuan)
* Corresponding author. Email: zhangjunyan@licp.cas.cn (Junyan Zhang)
E-mail: jingjing_shi@126.com (Jing Shi)
**XPS spectra calculations**  XPS C{l}s spectra were decomposed by Gussian fitting into three constituent peaks corresponding to sp² carbon (284.6 eV), sp³ carbon (285.3 eV), and C-O bonding (286.4 eV). From the deconvoluted spectra, we proceeded to estimate the sp3-C fraction from the XPS spectra by applying an area ratio calculation method of each constituent peak. The relative content of sp³-C bonding is calculated by:

\[
\%sp^3C = \frac{A(sp^3C)}{\sum A\{ (sp^3C) + (sp^2C) + (C-O) \} } \times 100%
\]

where \( A(sp^3C) \) is the peak area of sp³-C, and \( \Sigma A\{ (sp^3C)+(sp^2C)+(C-O) \} \) is the sum of peaks areas under sp³C, sp²C and C-O. According to this formula, the sp³-C fractions derived from the C 1s spectra of a-C and a-C:H are 45.48% and 54.49%, respectively.

**Adsorption coordinates details.**  Adsorption coordinates details includes: (1) O₂@C_D (G1-4), O₂@C_T (G1-4), H₂O@C_D (G1-4), H₂O@C_T (G1-4), CO₂@C_D (G1-3), N₂@C_T (G1-3), CO₂@C_T (G1 and G2), (2) adsorption coordinates details of O₂, H₂O, N₂ and CO₂ molecules on C_G surfaces, (3) schematic illustrations of orbital interactions between CO₂ and cyclohexan, and (4) computed adsorption modes with and without BSSE corrected adsorption energies of O₂, H₂O, N₂ and CO₂ molecules on C_G.

The O₂ had chemical and physical adsorption modes on C_D surface. The chemical adsorption was shown in Figure 7, and the physical adsorptions (G2~5) were shown below in Figure S1. According to their adsorption energies, O₂ molecules were mostly chemical adsorbed on C_D surface. But the O₂@C_T were totally in physical modes (G1~4) as shown in Figure S2, which had no obvious adsorption energy differences. Similarly, the physical adsorption modes (G1~4) of H₂O on C_D and C_T were shown in Figure S3 and Figure S4, respectively. But the adsorption of N₂ and CO₂ molecules were different. The CO₂ molecules were physically adsorbed on C_D (Figure S5), and were respectively adsorbed in parallel orientation and perpendicular orientation on C_T.
surface (Figure S7). Similarly, the N$_2$ molecules’ adsorption mode on C$_T$ was in physical mode (Figure S6).

The weak interaction between the adsorbed CO$_2$ and a-C(:H) and the stabilization of sp$^3$-C···π and CH···π was indicated by the change of electron density change. And the Figure S8 further demonstrates this stabilization from perspective of orbital interaction. The cyclohexane (C1, C2 and C3 atoms) could be used as the prototype of a-C surface. The second order perturbation energy was calculated to be 4.5kJ/mol and 15.2kJ/mol for a-C: H and a-C, respectively. Due to this, friction force during the sliding to overcome the adsorption energy was much lower than the calculated values (11.35kJ/mol for a-C and 38.17kJ/mol for a-C: H). Within each step-length distance of 2.338Å, the orbital interaction was stabilized due to the presence of inter-vertical delocalized π$_4^3$ bonds in N$_2$ and CO$_2$. That is to say, the molecule desorption process was weakened.

The graphitic stacks were sporadically exists both in a-C and a-C: H, which was represented by C$_G$ clusters. Figure S9 and Table S1 indicate that the various species (O$_2$, H$_2$O, N$_2$ and CO$_2$) on C$_G$ were weak interactions.

**Fig. S1** - Lateral (left) and top (right) views of O$_2$ adsorption modes (G2~5) on C$_G$ clusters (Grey: carbon; red: oxygen, other instructions for understanding this figure can be found in the legend of Fig. 1.)
Fig. S2 - Lateral (left) and top (right) views of O\textsubscript{2} adsorption modes (G1~4) on C\textsubscript{T} clusters (Grey: carbon; red: oxygen; white: hydrogen, other instructions for understanding this figure can be found in the legend of Fig. 1.)

Fig. S3 - Lateral (left) and top (right) views of H\textsubscript{2}O adsorption modes (G1~4) on C\textsubscript{D} clusters (Grey: carbon; red: oxygen; white: hydrogen, other instructions for understanding this figure can be found in the legend of Fig. 1.)
**Fig. S4** - Lateral (left) and top (right) views of H$_2$O adsorption modes (G1~4) on C$_T$ clusters (Grey: carbon; red: oxygen; white: hydrogen, other instructions for understanding this figure can be found in the legend of Fig. 1.)

**Fig. S5** - Lateral (left) and top (right) views of CO$_2$ parallel adsorption modes (G1~3) on C$_D$ clusters (Grey: carbon; red: oxygen, other instructions for understanding this figure can be found in the legend of Fig. 1.)
**Fig. S6** - Lateral (left) and top (right) views of N$_2$ parallel adsorption modes (G1~3) on C$_T$ clusters (Grey: carbon; blue: nitrogen, other instructions for understanding this figure can be found in the legend of Fig. 1.)

**Fig. S7** - Lateral (left) and top (right) views CO$_2$ adsorption on C$_T$ clusters. The (a) G1 is parallel orientation (PLO), and (b) is perpendicular orientation (PDO) (Grey: carbon; red: oxygen; white: hydrogen, other instructions for understanding this figure can be found in the legend of Fig. 1.)
**Fig. S8** - Illustration of the orbital interaction between CO$_2$ and cyclohexan. The C1, C2 and C3 represent for danglinglized cyclohexane.

**(a) (b) (c) (d)**

**Fig. S9** - Adsorption coordinates of (a) O$_2$, (b) H$_2$O, (c) N$_2$ and (d) CO$_2$ on C$_G$ surfaces. (Grey: carbon; red: oxygen; white: hydrogen; blue: nitrogen, other instructions for understanding this figure can be found in the legend of Fig. 1.)

**Tab. S1** - Computed adsorption modes with ($\Delta E_{cp}$) and without ($\Delta E$) BSSE corrected adsorption energies of O$_2$, H$_2$O, N$_2$ and CO$_2$ molecules on C$_G$.

<table>
<thead>
<tr>
<th>Modes(Multiplicity)</th>
<th>Adsorption</th>
<th>$\Delta E_{cp}$(kJ/mol)</th>
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<tbody>
<tr>
<td>C$_G$-O$_2$-G1</td>
<td>Physical</td>
<td>-7.86</td>
</tr>
<tr>
<td>C$_G$-H$_2$O-G1</td>
<td>Physical</td>
<td>-15.82</td>
</tr>
<tr>
<td>C$_G$-N$_2$-G1</td>
<td>Physical</td>
<td>-10.57</td>
</tr>
<tr>
<td>C$_G$-CO$_2$-G1</td>
<td>Physical</td>
<td>-15.21</td>
</tr>
</tbody>
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