Supplementary Materials for

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

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XPS spectra calculations XPS C*1s* spectra were decomposed by Gussian fitting into three constituent peaks corresponding to sp^2 carbon (284.6 eV), sp^3 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 sp^3-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 sp^3-C, and ΣA{(sp^3C)+(sp^2C)+(C-O)} is the sum of peaks areas under sp^3C, sp^2C and C-O. According to this formula, the sp^3-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) O_2@C_D (G1-4), O_2@C_T (G1-4), H_2O@C_D (G1-4), H_2O@C_T (G1-4), CO_2@C_D (G1-3), N_2@C_T (G1-3), CO_2@C_T (G1 and G2), (2) adsorption coordinates details of O_2, H_2O, N_2 and CO_2 molecules on C_G surfaces, (3) schematic illustrations of orbital interactions between CO_2 and cyclohexan, and (4) computed adsorption modes with and without BSSE corrected adsorption energies of O_2, H_2O, N_2 and CO_2 molecules on C_G.

The O_2 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, O_2 molecules were mostly chemical adsorbed on C_D surface. But the O_2@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 H_2O on C_D and C_T were shown in Figure S3 and Figure S4, respectively. But the adsorption of N_2 and CO_2 molecules were different. The CO_2 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_2O, N_2 and CO_2) on C_G were weak interactions.

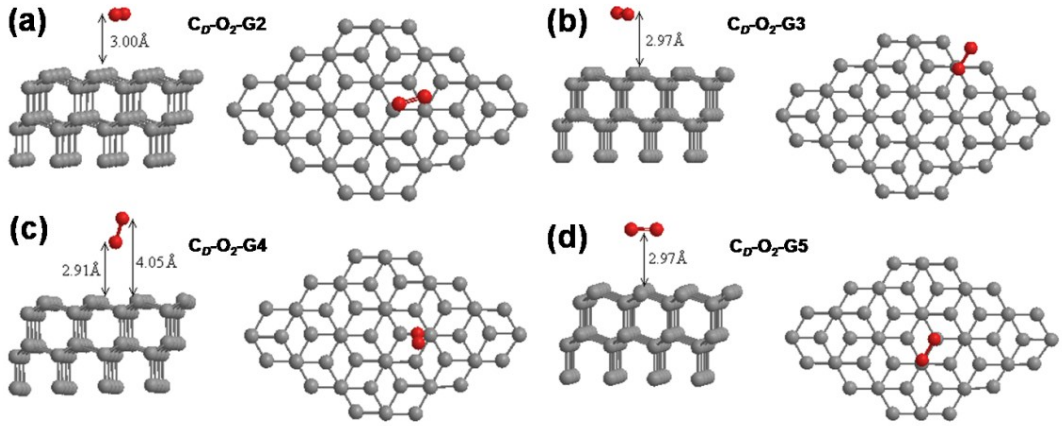

Fig. S1 - Lateral (left) and top (right) views of O_2 adsorption modes (G2~5) on C_D clusters (Grey: carbon; red: oxygen, other instructions for understanding this figure can be found in the legend of Fig. 1.)

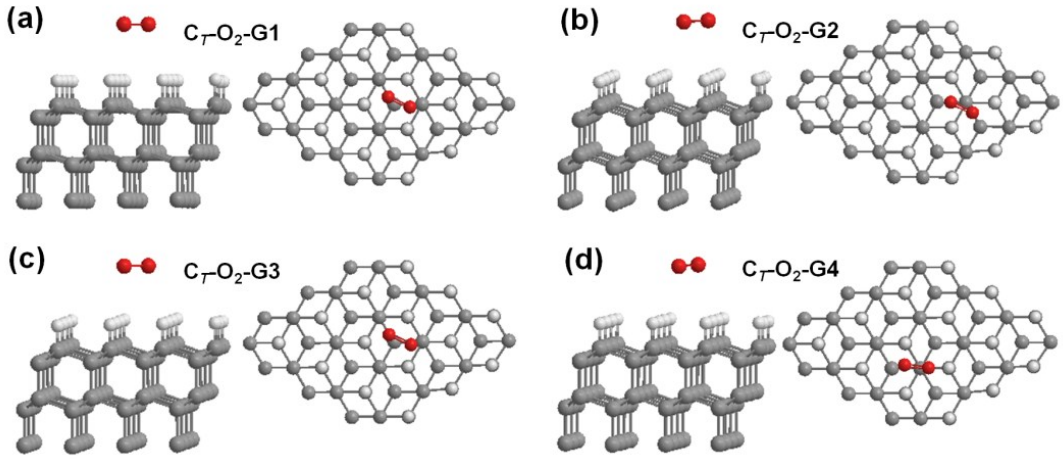

Fig. S2 - Lateral (left) and top (right) views of O_2 adsorption modes (G1~4) on C_T clusters (Grey: carbon; red: oxygen; white: hydrogen, other instructions for understanding this figure can be found in the legend of Fig. 1.)

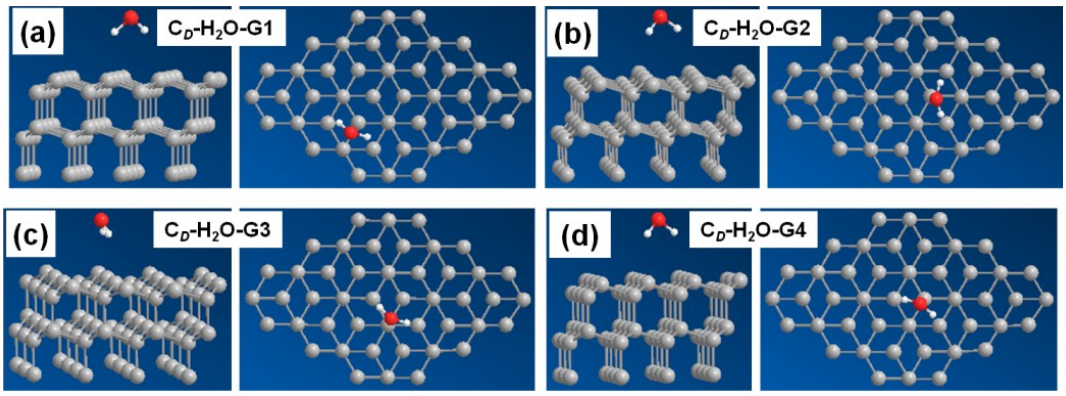

Fig. S3 - Lateral (left) and top (right) views of H_2O adsorption modes (G1~4) on C_D clusters (Grey: carbon; red: oxygen; white: hydrogen, other instructions for understanding this figure can be found in the legend of Fig. 1.)

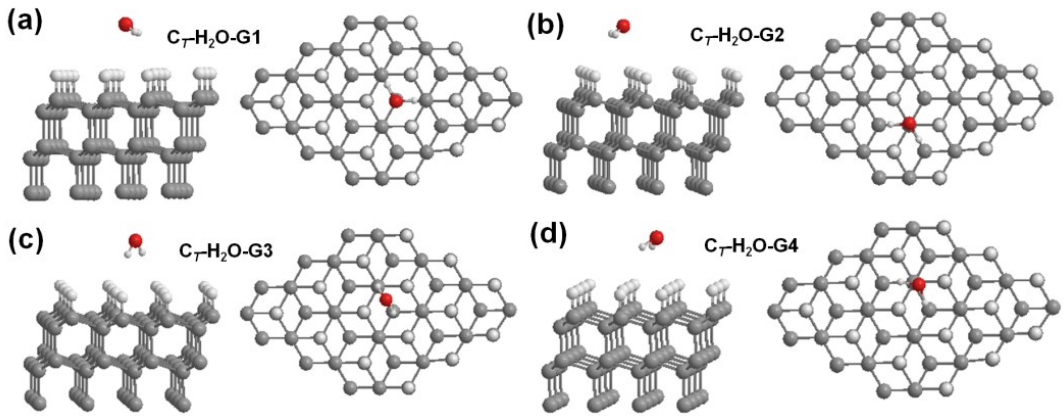

Fig. S4 - Lateral (left) and top (right) views of H_2O adsorption modes (G1~4) on C_T clusters (Grey: carbon; red: oxygen; white: hydrogen, other instructions for understanding this figure can be found in the legend of Fig. 1.)

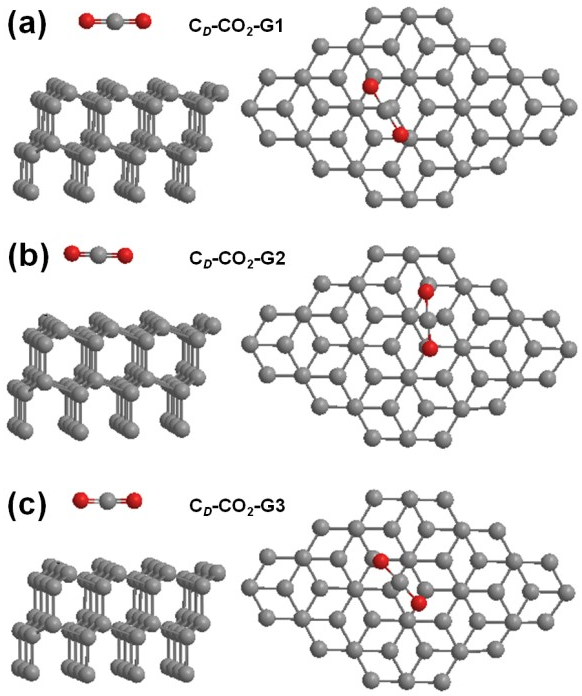

Fig. S5 - Lateral (left) and top (right) views of CO_2 parallel adsorption modes (G1~3) on C_D clusters (Grey: carbon; red: oxygen, other instructions for understanding this figure can be found in the legend of Fig. 1.)

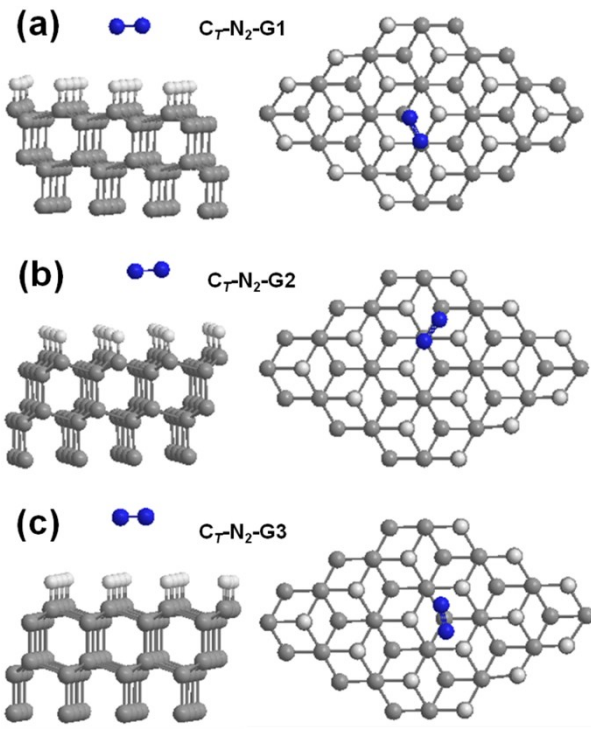

Fig. S6 - Lateral (left) and top (right) views of N_2 parallel adsorption modes (G1~3) on C_T clusters (Grey: carbon; blue: nitrogen, other instructions for understanding this figure can be found in the legend of Fig. 1.)

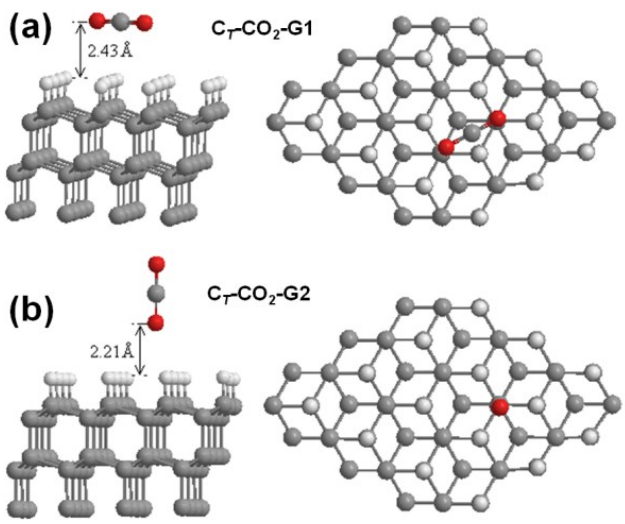

Fig. S7 - Lateral (left) and top (right) views CO_2 adsorption on C_T clusters. The (a) G1 is parallel orientation (PLO), and (b) is perpendicular orientation (PDO) (Grey: carbon; red: oxygen; white: hydrogen, other instructions for understanding this figure can be found in the legend of Fig. 1.)

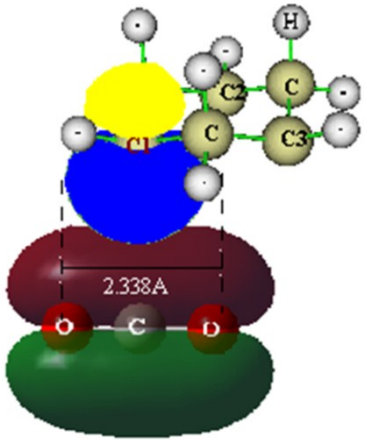

Fig. S8 - Illustration of the orbital interaction between CO_2 and cyclohexan. The C1, C2 and C3 represent for danglinglized cyclohexane.

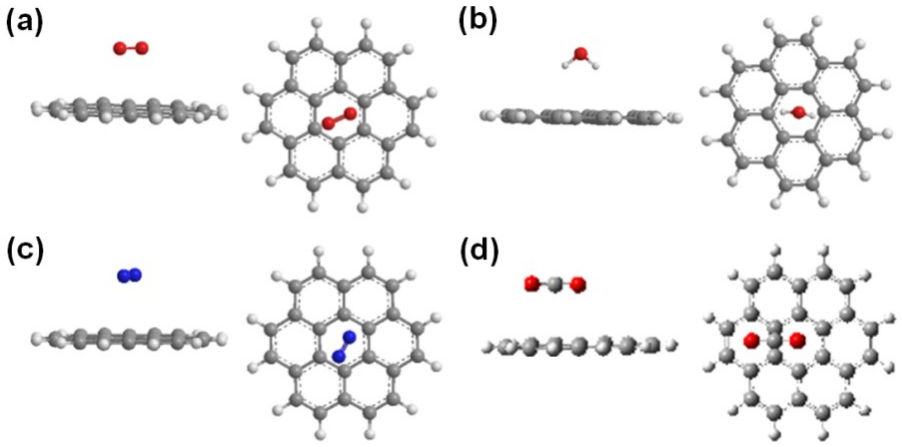

Fig. S9 - Adsorption coordinates of (a) O_2, (b) H_2O, (c) N_2 and (d) CO_2 on C_G surfaces. (Grey: carbon; red: oxygen; white: hydrogen; blue: nitrogen, other instructions for understanding this figure can be found in the legend of Fig. 1.)

Tab. S1 - Computed adsorption modes with (ΔE_{cp}) and without (ΔE) BSSE corrected adsorption energies of O_2, H_2O, N_2 and CO_2 molecules on C_G.

Modes(Multiplicity)	**Adsorption**	**ΔE_{cp}(kJ/mol)**
C_G-O_2-G1	Physical	-7.86
C_G-H_2O-G1	Physical	-15.82
C_G-N_2-G1	Physical	-10.57
C_G-CO_2-G1	Physical	-15.21