

Supplementary Information

1. The stable configuration of a linear carbon chain owning ten carbon atoms and the corresponding adsorption energy per carbon atom (figure 1). In this calculation, the Cu (111) facet was simulated by a 4-layer slab of 4×8 supercell, which contains 128 copper atoms.

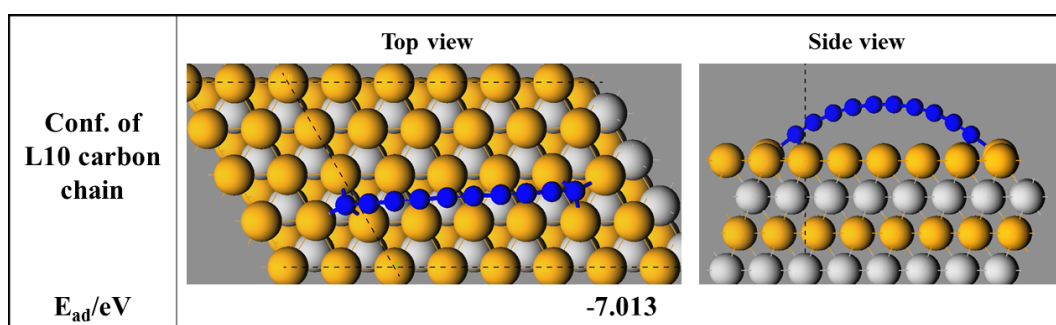


Figure 1. Top and side view of the L10 carbon chain, and corresponding adsorption energy.

2. The scheme designed to add extra carbon atoms, the adsorption sites used (figure 2), and the calculated results (figure 3) of the HCP central Y-type carbon species. To illustrate this series of Y-type carbon species represent the similar nucleation tendency as those owning a FCC central carbon atom, comparison between the adsorption energies per carbon atom in them are given in figure 4.

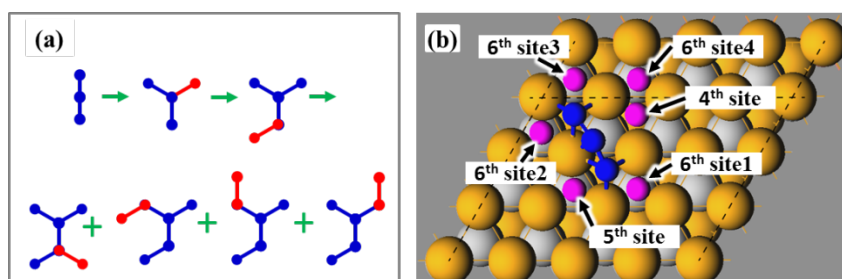


Figure 2. The scheme designed to import additional carbon atoms, and the adsorption sites have been used of the HCP central Y-type carbon species.

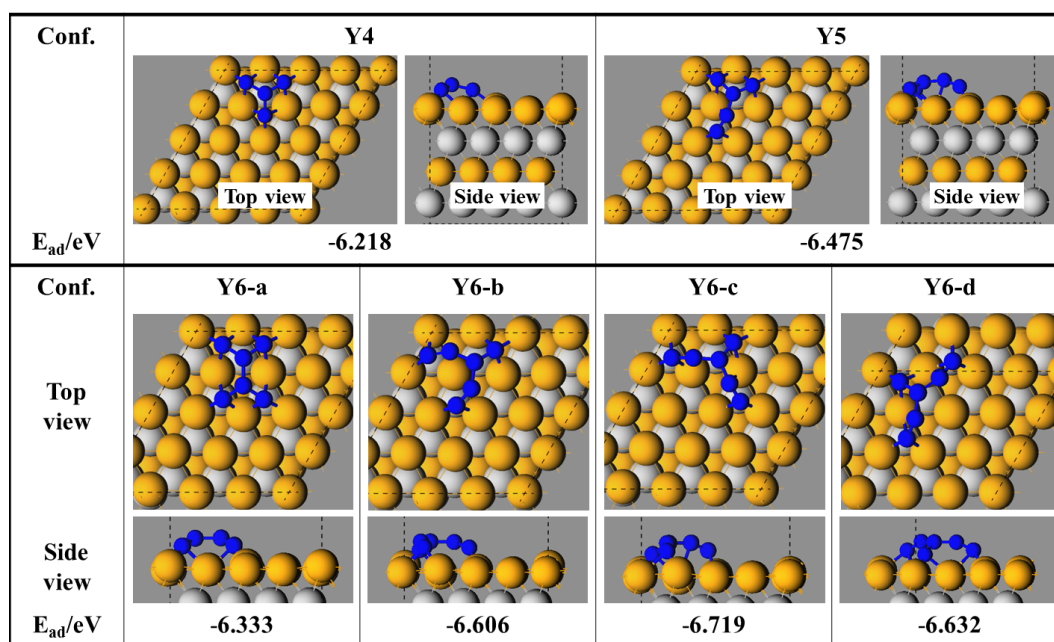


Figure 3. The stable configurations and corresponding adsorption energies per carbon atom obtained of the HCP central Y-type carbon species.

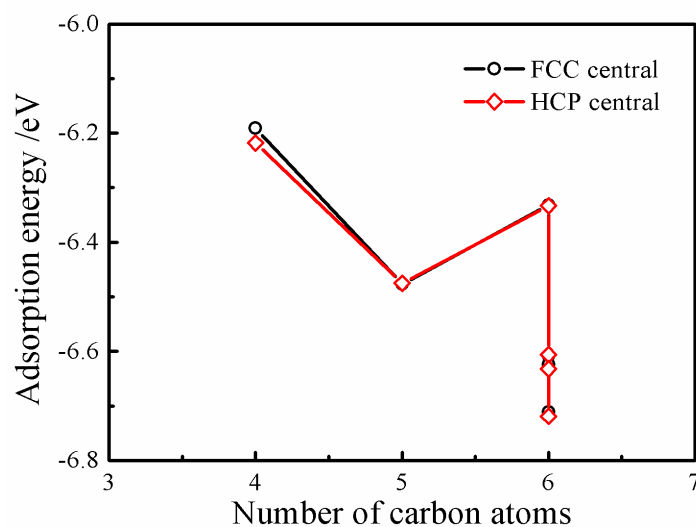


Figure 4. Comparison between the adsorption energies per carbon atom in the FCC and HCP central Y-type carbon species.

3. The scheme, used adsorption sites, final stable configurations and adsorption energies of the circular carbon species starting from C3-a are given in figure 5. The comparisons between the adsorption energies per carbon atom in this serial of configurations and that in the serials starting from C3-b are given in figure 6.

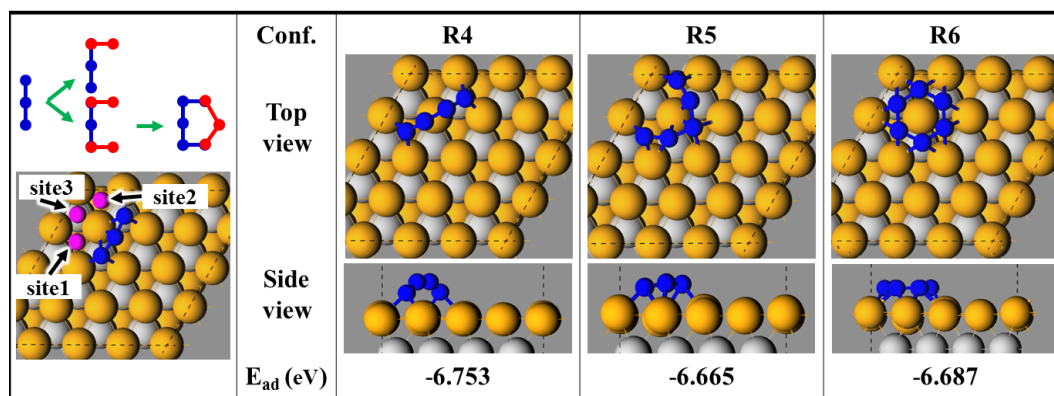


Figure 5. The scheme, used adsorption sites, final stable configurations and adsorption energies of the circular carbon species starting from C3-a.

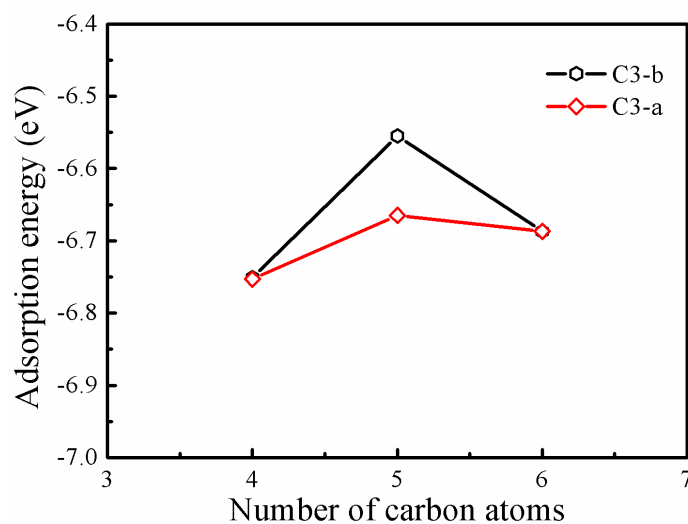


Figure 6. Comparisons between the adsorption energies per carbon atom in configurations starting from C3-a and C3-b.

4. The calculated results of the arrangements by adding carbon atoms on the two ends of a linear carbon chain R4 (main body). Both the stable configurations and adsorption energies are given. Distinguished to the linear nucleation process in the main body, these configurations are labeled by R*.

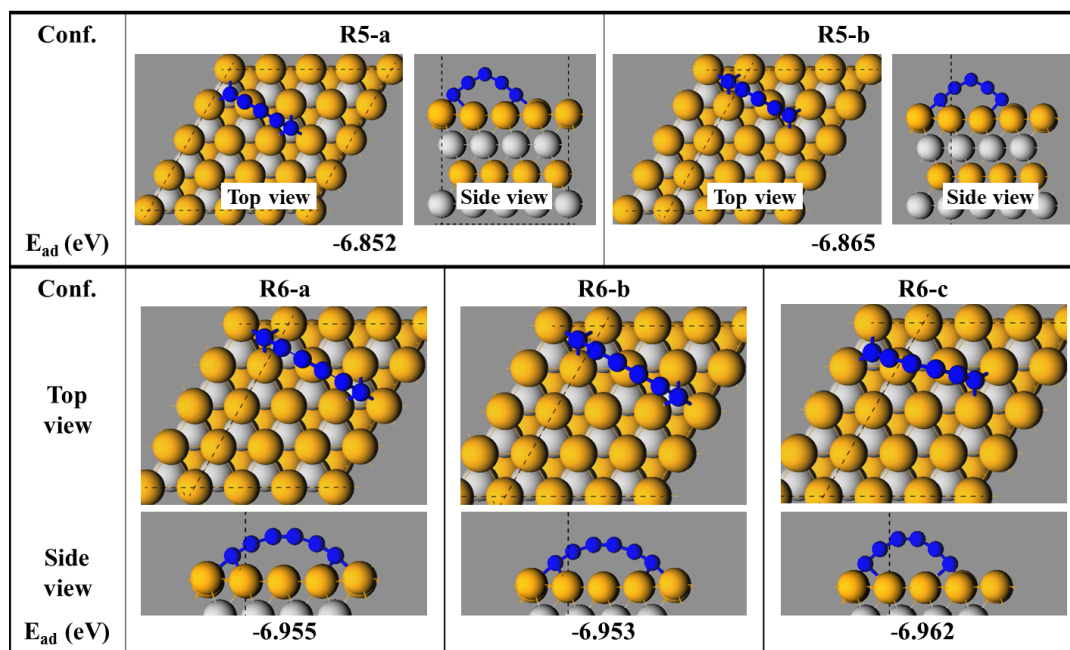


Figure 7. The stable configurations and corresponding adsorption energies obtained when we add extra carbon atoms on the two ends of a linear carbon chain R4.

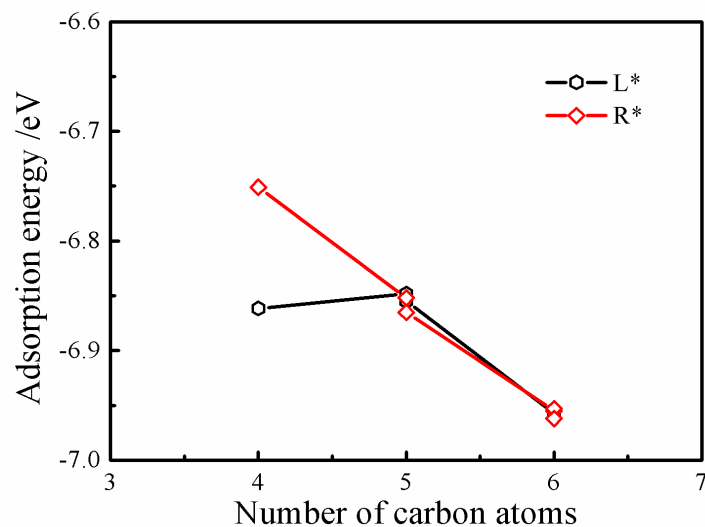


Figure 8. Comparison between the adsorption energies per carbon atom in the linear chains L* (given in the main body) and R* (here).

5. Analyses on the driving force and the energetic preference of the linear growth. Figure 9 gives the deformation electro densities (with isovalue 0.05 electrons \AA^{-3} for more clear) of standard C-C bonds composed of sp, sp² and sp³ carbon atoms. Figure 10 gives those of the linear and Y-type carbon species on the

copper surface. Table 1 shows the bond lengths of them.

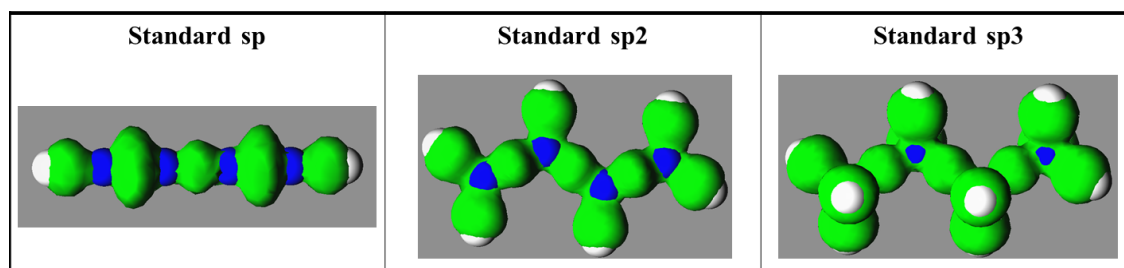


Figure 9. The deformation electro densities of standard C-C bonds composed of sp, sp2 and sp3 carbon atoms. Isovalue is set as 0.05 electrons \AA^{-3} .

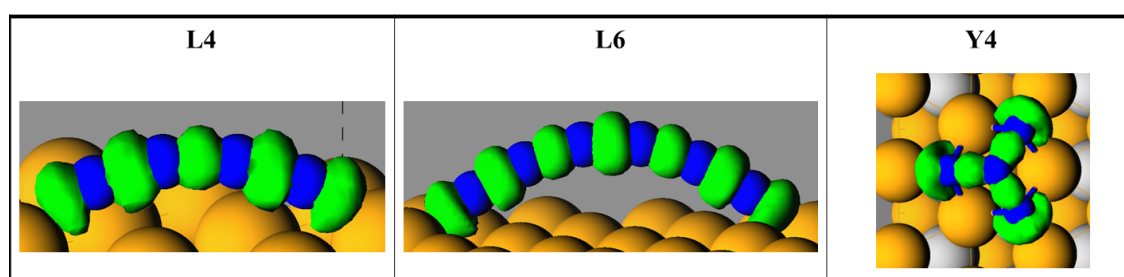


Figure 10. The deformation electro densities of the linear and Y-type carbon species. Isovalue is set as 0.05 electrons \AA^{-3} .

Table 1. The bond lengths in above configurations, S stand for standard.

	Bonds lengths (\AA) — from left to right				
S-sp	1.222	1.302	1.222		
S-sp2	1.347	1.451	1.347		
S-sp3	1.529	1.531	1.529		
L4	1.297	1.357	1.297		
L6	1.299	1.338	1.271	1.338	1.299
Y4	1.441				

Clearly, the shapes of the deformation electro densities of the linear carbon species on Cu surface (L4 and L6) are similar as the standard sp carbon chain, i. e they are all linear without branches and the fat&thin changing corresponding to 3&1 bond order are similar as standard sp carbon chain. The lengths of bond in L4 (1.297 \AA) and in

L6 (1.299 Å and 1.271 Å) corresponds to the triple bond (1.222 Å) in the standard sp carbon chain. The fact that they are longer than the standard length is due to the formation of stronger C-Cu bond between the end carbon atoms and the copper surface than the C-H bond in the standard sp carbon chain. Additionally, the influences of copper surface on other carbon atoms, like the next end carbon atoms and the middle carbon atom in L5*, can also impact the bond length of C-C bond on copper surface. The maps of deformation electro densities also reveal that even the end carbon atom has formed three C-Cu bonds with the nearest three copper atoms, only one of them is strong.

The shape of the deformation electro densities of the Y-type carbon species Y4 is very similar to that in the standard sp² carbon chain. And also due to the stronger C-Cu bond between the end carbon atoms and the copper surface than the C-H bond, the C-C bond length in Y4 (1.441 Å) is longer than that in the standard sp² carbon chain (1.347 Å).

6. The results of another growth path which shows not be dominated in graphene nucleation process.

Firstly, one carbon atom is assigned on site 7th site, which is just atop a copper atom. After geometry optimizations, it slides aside and forms a 3-membered ring with two carbon atoms in the linear chain. Unlike the feature of the 5- or 6-membered carbon rings in Figure 7 (main body) that all the Ring-carbon atoms are almost at grade, one carbon atoms in this 3-membered ring is obvious higher than other two ones. Then, starting from the obtained configuration, another carbon atom is added on 8th site with the purpose to form a 4-membered ring with carbon atoms labeled 1, 2 and 3 (as they form an arc shape). But finally, the configuration L6+2, in which a new 3-membered ring is formed, is obtained. And still, the arch is also the main feature, which is similar as the linear chain L6. Additionally, the absorption energy per carbon atom in it shows about 0.11 eV higher than that in the corresponding configurations in Figure 7 (main body), which shows it is not energetically preferred. These results indicate this growth path should not be dominated in the nucleation process of

graphene.

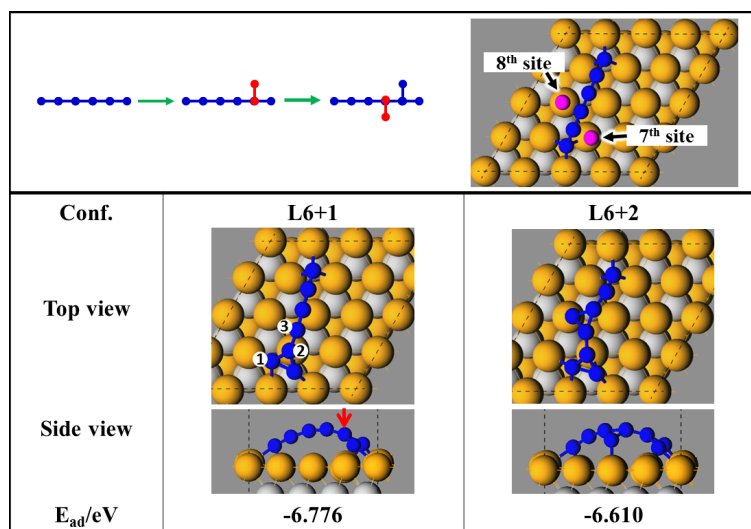


Figure 11. The scheme, adsorption sites, corresponding optimized configurations and adsorption energies for the attempts to form Y-type from linear chain L6.

7. The stable configurations and adsorption energies of two graphene islands: a twelve- and an eighteen-membered one. They are labeled as I12 and I18, respectively, and both the top and side views of them are given in Figure 11. The distances between the nearest carbon atoms are 4.333 and 4.008 Å in I12 and I18, respectively, as illustrated in Figure 13. To evaluate the errors caused by interactions between adjacent carbon atoms, we have calculated the energy differences between the two configurations shown in Figure 14. In configuration 2 C2, the nearest distance between two dimers is 3.994 Å, and this induces about 0.1 eV error in energy. So, in configurations I12 and I18, this error should be smaller as it will be averaged by more carbon atoms.

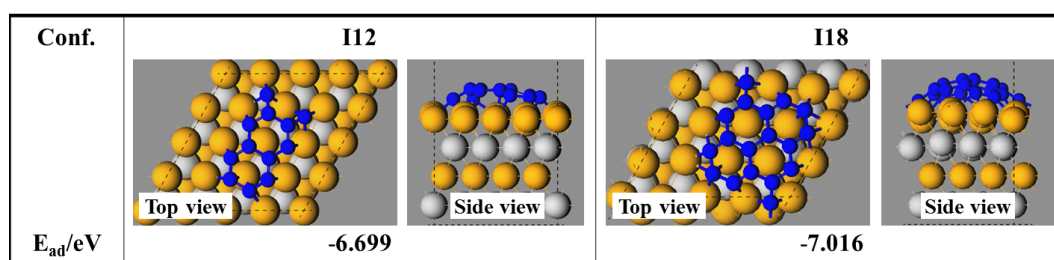


Figure 12. The stable configurations and adsorption energies per carbon atom of a twelve- and an eighteen-membered graphene island.

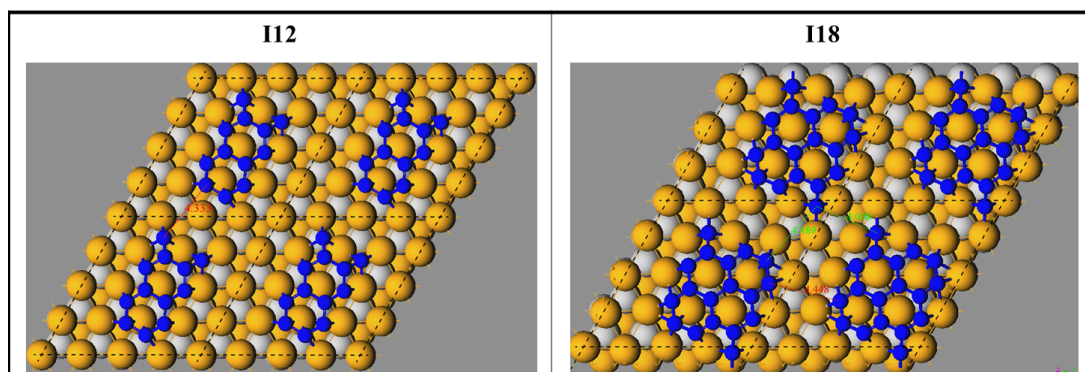


Figure 13. The 8×8 supercells for I12 and I18 to characterize the nearest C-C distances in adjacent carbon species.

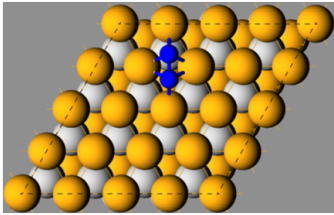
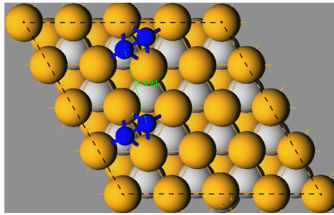
	C2	2 C2
Conf.		
Nearest distance (Å)		3.994
E_{ad} (eV)	-6.674	-6.770

Figure 14. The configurations calculated to evaluate the errors caused by interactions between adjacent carbon atoms.