# Supporting Information

# Formation of Carbon Clusters in the Initial Stage of Chemical Vapor Deposition Graphene Growth on Ni(111) surface

*Junfeng Gao[1,2,#], Qinghong Yuan[1,#],  Hung Hu[1], Jijun Zhao[2*], Feng Ding[1*]*

1) Institute of Textiles and Clothing, Hong Kong Polytechnic University, Hong Kong, China

2) Key Laboratory of Materials Modification by Laser, Ion and Electron Beams (Dalian University of Technology), Ministry of Education, Dalian 116024, China

*E-mail: feng.ding@rice.edu or zhaojj@dlut.edu.cn

# these authors contributed equally to this work

**RECEIVED DATE**

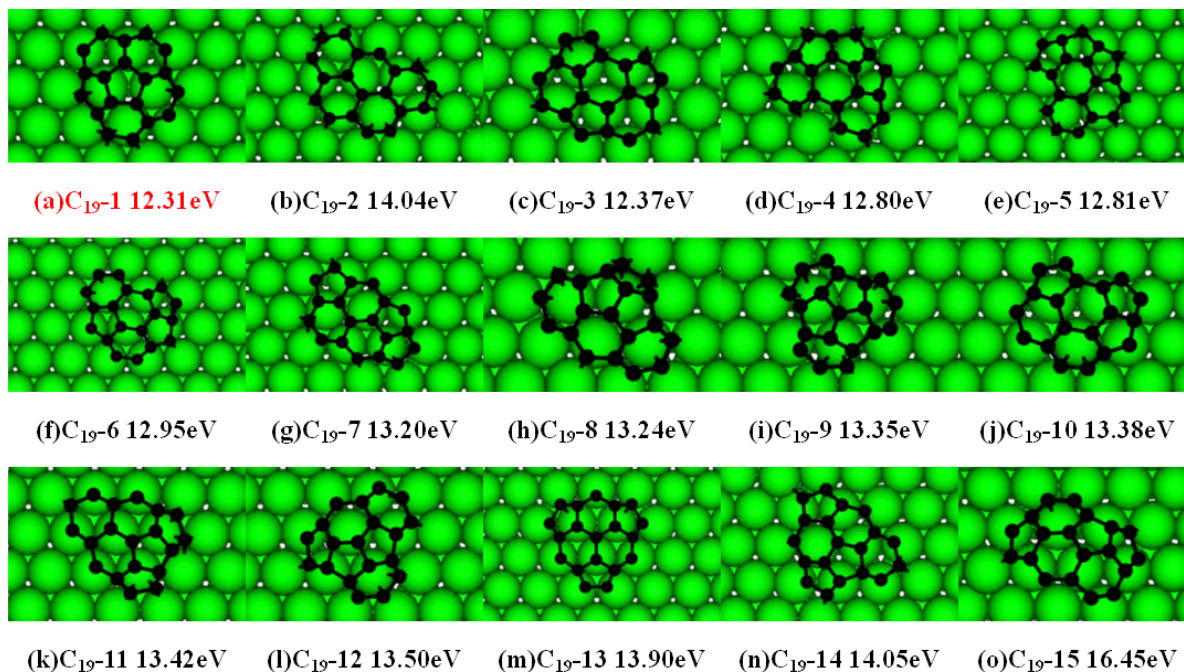**S1    Some of the $C_{19}$ isomers explored and their formation energies**



(a)$C_{19}$-1 12.31eV    (b)$C_{19}$-2 14.04eV    (c)$C_{19}$-3 12.37eV    (d)$C_{19}$-4 12.80eV    (e)$C_{19}$-5 12.81eV

(f)$C_{19}$-6 12.95eV    (g)$C_{19}$-7 13.20eV    (h)$C_{19}$-8 13.24eV    (i)$C_{19}$-9 13.35eV    (j)$C_{19}$-10 13.38eV

(k)$C_{19}$-11 13.42eV    (l)$C_{19}$-12 13.50eV    (m)$C_{19}$-13 13.90eV    (n)$C_{19}$-14 14.05eV    (o)$C_{19}$-15 16.45eV

**Figure S1**. Structures and formation energies of fifteen isomers of supported $C_{19}$@Ni(111). The lowest isomer $C_{19}$-1(a) is highlight by a red color. $C_{19}$-2 (b) that contains only hexagons is 1.73eV higher than $C_{19}$-1(a).

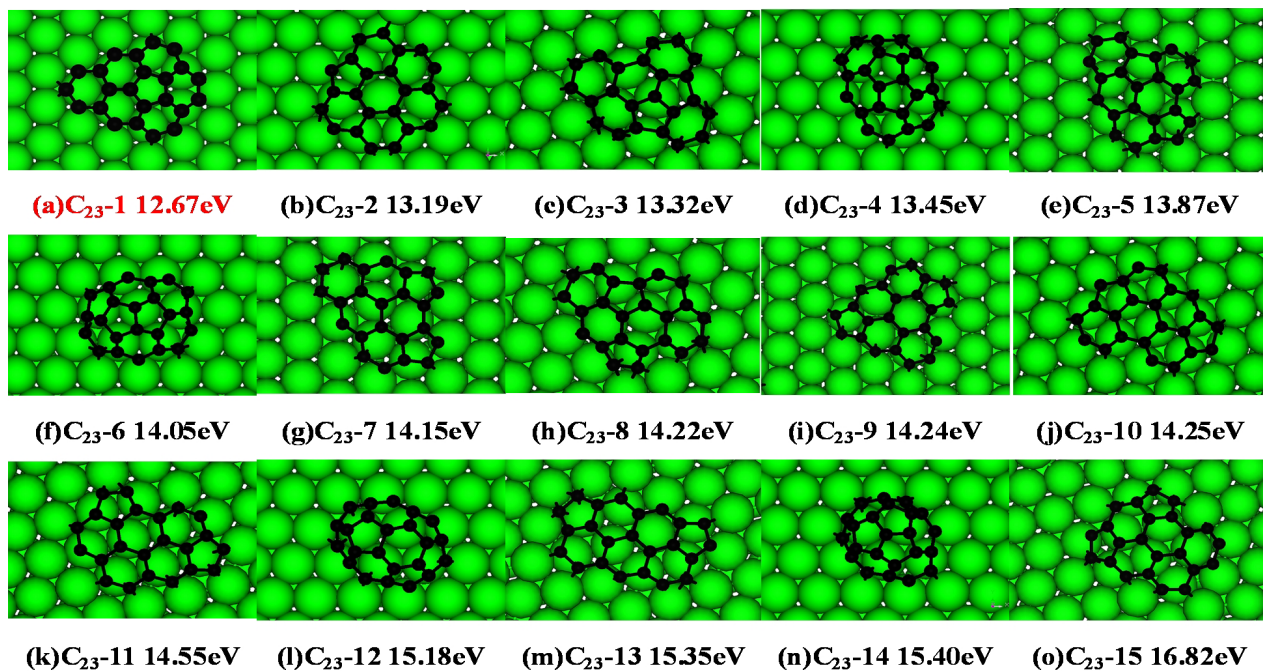## S2        Some of the isomers of $C_{23}$ explored and their formation energies



| | | | | |
|---|---|---|---|---|
| (a)$C_{23}$-1 12.67eV | (b)$C_{23}$-2 13.19eV | (c)$C_{23}$-3 13.32eV | (d)$C_{23}$-4 13.45eV | (e)$C_{23}$-5 13.87eV |
| (f)$C_{23}$-6 14.05eV | (g)$C_{23}$-7 14.15eV | (h)$C_{23}$-8 14.22eV | (i)$C_{23}$-9 14.24eV | (j)$C_{23}$-10 14.25eV |
| (k)$C_{23}$-11 14.55eV | (l)$C_{23}$-12 15.18eV | (m)$C_{23}$-13 15.35eV | (n)$C_{23}$-14 15.40eV | (o)$C_{23}$-15 16.82eV |

**Figure S2.** Structures and formation energies of fifteen $C_{23}$ isomers on Ni(111) surface. The lowest isomer $C_{23}$-1(a) is highlight by a red color.
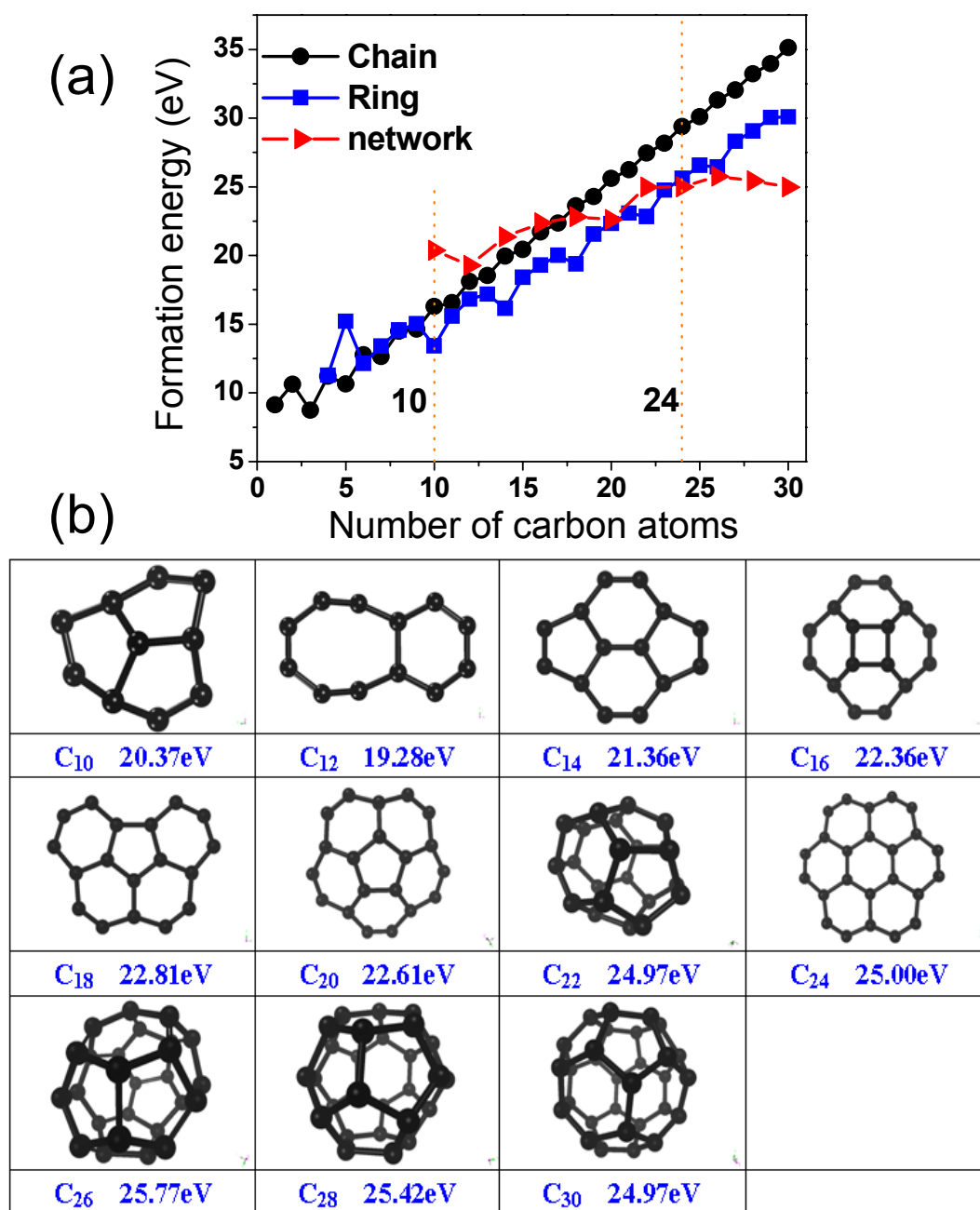
## S3    The formation of free C clusters



**Figure S3.** Formation energies of free-standing carbon clusters (a) and some lowest energy sp$^2$ network isomers (b).

To shed light on the differences between free-standing carbon clusters and those supported by a Ni(111) surface, the formation energy and structures were systematically calculated using the ***ab inito*** method (see method part in the main text) and shown in figure S3. It is obviously that the formation energies of free-standing carbon clusters are much higher than the corresponding C clusters supported by a metal surface due to the absence of metal passivation. Also the formation energy of a chain presents an odd-even stagger oscillation, with its amplitude decreasing as cluster size increases. It can be interpreted by the different electronic states of end atoms in odd and even chains. For a chain with an odd number of carbon atoms, the ground electronic state is a singlet, whereas for the even-numbered chain, the ground state is a triplet.[1] There is a 4n+2 periodicity in the curve of ring formation energy vs. the number of C atoms. This oscillation in the ring can be explained by rules of Hückel.[2,3]

For free C clusters, the chain is the most stable structure at small size (N < 6). The chain formation energy then catches that of ring in the range of 5 < N < 9. Eventually the mono-cyclic ring becomes a more stable structure in the size range of 9 < N < 24. When the number of carbon atoms reaches 24, bowl shaped $sp^2$ networks and fullerenes dominate the ground state geometry. The results presented here are in good agreement with previous work.[3,4]

**S4. The calculation of C chain end formation energy**

As a one dimensional structure, the formation energy of a C chain on Ni(111) surface increases linearly with cluster size N, as shown in figure 5. Its formation energy $E_{ch}$ can be fitted as:

$$E_{ch} = \lambda N + \xi \ (eV),$$

where the fitted slope is $\lambda = 0.81$ eV/atom, which is the energy difference between a C atom in the chain and a C atom in graphene on a Ni(111) surface. The second term, $\xi$, which can be interpreted as the formation energy of the two Ni(111) passivated chain ends, is 0.40 eV. Thus the formation energy of every chain end is only 0.2 eV/end on a Ni(111) surface. Similarly, we can obtain the end formation energy of a freestanding chain end as 3.5 eV/end by linearly fitting the data shown in figure S3.

## REFERENCES

(1)     Fan, X.; Liu, L.; Lin, J.; Shen, Z.; Kuo, J.-L. *ACS Nano* **2009**, *3*, 3788.

(2)     Pitzer, K. S.; Clementi, E. *J. Amer. Chem. Soc.* **1959**, *81*, 4477.

(3)     Jones, R. O. *J. Chem. Phys*. **1999**, *110*, 5189.

(4)     Jones, R. O.; Seifert, G. *Phys. Rev. Lett.* **1997**, *79*, 443.