The edge termination controlled kinetics in graphene chemical vapor deposition growth†

Haibo Shu,ab Xiaoshuang Chenb and Feng Ding*ab

Understanding the kinetics of graphene chemical vapor deposition (CVD) growth is crucial for desired graphene growth. Depending on the partial pressure of hydrogen in the carrier gas, the temperature and the type of substrate, both armchair (AC) and zigzag (ZZ) edges of graphene can be either passivated by a metal surface or terminated by hydrogen atoms. Owing to the large barrier for incorporating C atoms, the growth rate of H terminated graphene edges is significantly slower than that of metal surface passivated ones. Based on this understanding, various behaviours and the kinetics of graphene growth at different temperatures, H2 pressure and on various catalyst surfaces are satisfactorily explained and the strategy of growing edge-controlled graphene domains is predicted.

1. Introduction

Graphene has attracted great attention since 2004 (ref. 1) due to its exceptional physical properties, such as extremely high carrier mobility, excellent thermal conductivity, extraordinary mechanical strength, etc. These properties ensure that graphene has great potential for a large number of applications, such as high performance field effect transistors (FETs), energy generation and storage, sensors, composite materials, metal free catalysts, etc. To realize these applications, especially those in high performance electronics, it is critical to synthesize large-area graphene with controlled crystallinity, edge type, and number of layers. Among numerous methods of graphene synthesis, the transition metal catalyzed chemical vapour deposition (CVD) method is broadly recognized as the most promising approach to achieve this target. Various transition metals, such as Au, Cu, Ni, Co, Pd, Pt, Rh, Ir, Ru and their alloys, have been used as catalysts for CVD growth. To facilitate the experimental design for preferred graphene growth, many theoretical approaches have been carried out recently2–14 but the understanding of graphene growth at an atomic level is still very limited.

Recently, more and more experimental evidences suggest that the shape, quality, and the number of layers of CVD-grown graphene strongly depend on the H2 content in the gas flow. For example, graphene domains grown on a Cu surface present versatile shapes. Under low H2 pressure or high CH4 : H2 ratio, the graphene domains normally present a fractal-like branched shape.15–18 In contrast, with high H2 flow, most graphene domains present a regular hexagonal shape with zigzag edges.19–24 The graphene domains grown on a Au surface are known to have similar behaviours as those formed on a Cu surface.25–26 Differently, graphene domains grown on an active catalyst such as Ni, Co, Pt, Ru, and Rh surfaces are mostly in a regular hexagonal shape.27–30

It is known that the fractal-like graphene shape must be understood based on the diffusion limited growth in which the edge of crystal is highly active for atom/molecule adsorption and the feedstock supply near the edge is limited.31 In contrast, a regular graphene edge can be explained based on the orientation dependent growth rates by applying the well-known theory of kinetic Wulff construction (KWC)28 that the fast growing edges will quickly disappear.

To understand the versatile experimental observations during graphene CVD growth, we systematically explored the termination of graphene edges on various catalyst surfaces (Au, Cu, Ni, Co) and the incorporation process of carbon onto these edges. Our results demonstrate two modes of graphene CVD growth: if a graphene edge is passivated by a metal surface (M–G), the addition of C atoms is fast because of the high activity of the edge. On the other hand, if a graphene edge is terminated by H atoms (H–G), the addition of C atoms is slow because of the edge inertness. Moreover, our study has revealed a mechanism
for controlling the edge structure of graphene domains by adjusting the growth parameters.

2. Computational details

In this study, density functional theory (DFT) total energy calculations were performed using the Vienna ab initio Simulation Package (VASP).33,34 The exchange–correlation energy was described in the generalized gradient approximation (GGA) using the PBE functional.35 By considering the energies concerned in this study as mainly being attributed to the chemical binding between the graphene edge and the catalyst surface, the GGA method should be sufficient. The energy cutoff for the plane-wave expansion was set to 400 eV, using the projector augmented wave (PAW) potentials36 to describe the electron–ion interactions. The geometry optimization was performed using the conjugate gradient scheme until the force acting on each atom was less than 0.01 eV Å⁻¹.

To investigate the structural stability of the graphene edges on the transitional metal (TM) surfaces (Au, Cu, Ni, and Co), a four-layer metal slab with fixed bottom layer atoms was used to represent the metal surfaces, then the pristine and H-terminated graphene nanoribbons (GNRs) were put on the metal surfaces (see Fig. 1 and Fig. S1 in the ESI†). The repeated slabs were separated by ~12 Å to eliminate their interactions, and the allowed lattice mismatch of GNR–metal interfaces in the constructed slab models was smaller than 3%. The unit cells of the surface slabs are 4.43 Å × 15.34 Å and 17.71 Å × 2.56 Å for the AC and ZZ graphene edges on the Cu(111) surface, respectively. Similar models were used to investigate the stability of GNRs on Au, Ni, and Co surfaces. The unit cells of AC-GNRs on Au, Ni, and Co surfaces are 8.65 Å × 14.98 Å, 4.32 Å × 14.95 Å, and 4.34 Å × 17.55 Å, respectively. For the ZZ-GNRs on Au, Ni, and Co surfaces, their unit cells are 23.07 Å × 4.99 Å, 21.58 Å × 2.49 Å, and 26.05 Å × 2.51 Å, respectively. The corresponding k-point meshes are 6 × 2 × 1 for the metal-supported AC edges and 2 × 6 × 1 for the metal-supported ZZ edges. The above settings were obtained on the basis of a series of tests for the energy convergence with respect to the k-point mesh setting and the thickness of the vacuum layer (see the ESI, Fig. S2 and S3†) and the calculated results showed that the settings used in the present calculations can supply enough accuracy.

The stability of the graphene edges was evaluated by calculating their formation energies. For the freestanding graphene edges, their formation energies are defined as,

\[ E_f = [2E(w) - E(2w)]/2L, \]

where \( w \) and \( L \) are the ribbon width and the length of unit cell along the periodic direction, and \( E(w) \) and \( E(2w) \) are the energies of GNRs with the width of \( w \) and \( 2w \). Here the width \( w \) used of AC and ZZ GNRs is 9.84 Å and 11.36 Å, respectively and the length \( L \) of the unit cell along AC and ZZ directions is 4.26 Å and 2.46 Å, respectively. The formation energies of H-passivated graphene edges were calculated by

\[ E_f = E(G) + [E(H) - E(G) - n_H E_H]/2L, \]

where \( E(H), E(G) \) and \( E_H \) are the energies of the H-passivated GNR, the freestanding GNR, and the H atom in a hydrogen molecule, respectively. \( E(G) \) is the formation energies of freestanding GNR. \( n_H \) is the number of H atoms in the H-passivated GNR. For the metal-supported GNR, their formation energies are calculated by

\[ E_f = [2E_f(w) - E_f(2w) - E_M]/2L, \]

where \( E_f(w) \) and \( E_f(2w) \) are the energies of metal-supported GNRs with the width of \( w \) and \( 2w \) respectively, and \( E_M \) is the

| Table 1 | Formation energies of armchair (AC) and zigzag (ZZ) graphene edges (in eV nm⁻¹) in vacuum, terminated by H atoms and on metal surfaces. Here the energy of the H₂ molecule is used as the reference. The atomic structures of these graphene edges are shown in Fig. 1. |
|---------|------------------|------------------|------------------|------------------|------------------|
|         | None             | H                | Au               | Cu               | Co               | Ni               |
| AC      | 10.01            | 0.20             | 8.73             | 7.38             | 5.26             | 5.38             |
| ZZ      | 11.84            | 0.90             | 7.84             | 5.52             | 3.98             | 3.61             |
total energy of the metal substrate. The models for calculating the formation energies of metal-supported GNRs are shown in Fig. S4. Such a computational model can eliminate the effect of van der Waals interactions between the GNR and metal substrate on the formation energies of graphene edges.

Ab initio molecular dynamics (MD) simulations were carried out to investigate the role of graphene edges in the incorporation of carbon atoms on a Cu(111) surface. In the calculations, we used the models with the surface slabs of 8.85 Å × 15.34 Å for the growth of AC-edges and 17.71 Å × 7.67 Å for the growth of ZZ-edges. As it is hugely time consuming to run a MD simulation for a large system (there are 120 and 123 atoms in the models of AC and ZZ edges), a Gamma-only k-point was used in the calculations for the Brillouin-zone integration. MD simulations were performed in the canonical ensemble (NVT) at 1500 K with a 1.0 fs time step.

3. Results and discussion

Firstly, let’s consider the structural stability of various graphene edges. An unpassivated graphene edge (Fig. 1a and b) possesses very high formation energies due to the formation of dangling bonds at the edge and therefore is very unstable. As listed in Table 1, the formation energies are as high as 10.01 and 11.84 eV nm⁻¹ for the armchair (AC) and zigzag (ZZ) graphene edges, respectively. In contrast, the hydrogenation of unpassivated edges (Fig. 1c and d) leads to a notable reduction of the formation energies and a notable enhancement of the stability. It can be found that their formation energies are only 0.20 and 0.90 eV nm⁻¹ for AC and ZZ edges, respectively. If a freestanding graphene edge is placed on a metal surface (Fig. 1e and f), the edge will be bent to the metal surface and will be passivated spontaneously. On the Co(0001) or Ni(111) surfaces, the graphene edge is more stable than that on the Cu(111) or Au(111) surface due to their high activity on the metal surfaces.

From the above discussion, we can conclude that, during the graphene CVD growth, an unpassivated edge is not stable and it should be either passivated by the metal surface (M–G) or be terminated by the H atoms (H–G). Next let’s turn to the competition between the two types of edges under the condition of CVD growth. Considering the high temperature of graphene CVD growth, the free-energy difference between a H–G and a M–G edge can be written as:

\[ \Delta G = \Delta E_f + \Delta F_{vib} - N_H \times \mu_H(T, P) \]

where \( \Delta E_f \) is the difference of formation energy between the H–G and the M–G edges, \( \Delta F_{vib} \) is the vibrational free energy of H.
Fig. 4 The incorporation of C atoms at the H-passivated (a) armchair and (b) zigzag graphene edges on the Cu(111) surface to form a new hexagon. The green and black balls represent H and C atoms in graphene and the blue and red balls represent the attached C atoms and the Cu atoms, respectively. The formation energies, calculated by using the energy of the H₂ molecule as the reference, in eV are shown under each panel.

atmospheres at the H–G edge, \( N_{\text{H}} \) is the number of H atoms, and \( \mu_\text{H} \) is the chemical potential of the H₂ gas as a function of H₂ partial pressure \( p \) and temperature \( T \) (see the details in the ESI†).

Fig. 2 shows the thermodynamic diagrams of graphene AC and ZZ edges on Au, Cu, Co and Ni surfaces as functions of \( T \) and \( p \). It can be found that the termination type of graphene edges in CVD growth highly depends on the \( T, p \) and the type of metal substrates.

On the widely used metal substrate, the Cu(111) surface, the phase transition from H–G to M–G requires a H₂ pressure of \( \sim 10^{-2} \) Torr for the ZZ edge and a H₂ pressure of \( \sim 10^{-5} \) Torr for the AC edge in the temperature range of 1200–1400 K (typical CVD growth temperature, see Table S1 of the ESI†). Such a result reveals that graphene edges are mostly passivated by the metal surface in the low-pressure CVD growth (LPCVD) and H-terminated graphene edges may occur in the atmospheric pressure CVD growth (APCVD) on the Cu surface. When the H₂ pressure lies between \( 10^{-2} \) and \( 10^{-5} \) Torr, the ZZ edge tends to be passivated by the metal surface and the AC edge tends to be H-terminated. Hence, the diagram can be divided into three regions: (i) the M–G edges dominating the growth at high \( T \) and low \( p \); (ii) the H–G edges dominating the growth at low \( T \) and high \( p \); and (iii) the AC edges are terminated by H but the ZZ edges are passivated by the metal surface at medium \( T \) and \( p \).

On the Au, Ni, and Co surfaces, similar characteristics as those for Cu are presented but the transition from H–G to M–G occurs at very different \( T \) and \( p \). In the range of the typical graphene CVD growth temperature (1200–1400 K), the edge phase transition from H–G to M–G on the Au(111) surface requires the H₂ pressure below \( \sim 10^{-6} \) to \( 10^{-7} \) Torr, which is nearly impossible unless the pressure of H₂ is very carefully controlled. This implies that, during graphene CVD growth on a Cu surface at typical growth conditions, the graphene edges should be terminated by H atoms. On Ni(111) and Co(0001) surfaces, the H₂ pressure of edge phase transition increases to \( \sim 0.1 \) Torr for the AC edge and \( \sim 100 \) Torr for the ZZ edge. In view of experimental growth conditions (see Table S1†), the H₂ pressure is generally kept in the range of \( 10^{-4}–10^{-5} \) Torr and the growth temperature is mostly maintained at \( \sim 1300 \) K. Therefore, the graphene growth on Ni(111) and Co(0001) surfaces is mostly dominated by the M–G edges.

It is worth mentioning that the C solubility in Ni and Co at the temperature of graphene CVD growth is high. The diffusion of C atoms into the metal substrates may lead to the formation of surface carbide. In order to understand how the carbide affects the graphene edge–metal surface interaction, the formation energies of graphene edges on Ni(111) and Co(0001) with surface carbide have been calculated (see the details in the ESI†). We find that the formation energies of the armchair/zigzag graphene edge on the NiₓC and CoₓC surface carbides are 5.62/4.21 and 5.66/4.37 eV nm⁻¹, respectively (see Table S2 of ESI†). These formation energies are about 10% higher than those on pure Ni and Co surfaces, which implies that there is a minor influence of the C solubility inside the catalyst the formation of graphene edges. Consequently, the H₂ pressure for the phase transition of graphene edges from H–G to M–G was slightly changed for both AC and ZZ edges but their order of stability remains (see the ESI, Fig. S8†). Hence, we can conclude that the C solubility is a secondary factor for the edge phase diagram and growth kinetics of graphene on Ni and Co substrates.

The carbon addition from the metal surface to the graphene edges dominates the kinetics of graphene CVD growth. According to the theory of kinetic Wulff construction (KWC) (see the ESI, Fig. S9†), the edge that grows slowest dominates the circumference of a graphene domain. For a H–G edge, as all the dangling bonds are saturated, the addition of more C atoms to the edge requires the strong C–H bond to be broken and thus it is normally very difficult to be achieved. In contrast, for a M–G edge, each edge atom of graphene contacts with a few metal atoms and thus the addition of C atoms from the metal surface to the graphene edge should be much easier. Such a difference can be clearly seen in the MD simulation shown in Fig. 3. At 1500 K and in 10 ps, the dispersed C atoms easily attach to the edge of both AC and ZZ M–G edges on a Cu(111) surface (Fig. 3a and c). Although there is not enough
time to heal the defects formed during the C addition, the relatively high activity of the M–G edge is clearly demonstrated. In sharp contrast, there is no C atom attached to the H–G edge in another simulation performed under exact same condition, which clearly presents the inertness of the H–G edge (Fig. 3b and d).

To fully understand the evolution of the graphene domain in the CVD growth, the knowledge of the growth rate of various types of graphene edges, such as AC, ZZ and the titled ones, is required. In previous studies, it is well established that, a kink site (either AC kink or ZZ kink) of a M–G edge acts as an active site for the sinking of new C atoms and thus the edge with more kinks grows faster.\textsuperscript{42-46} For the two edges without any kinks, the ZZ edge grows slower than the AC edge because of its large kink height.\textsuperscript{42} From this analysis, we can simply draw a conclusion that the ZZ edges should be the ones that grow slowest. As a consequence of the KWC, the regular graphene domain with M–G edges should have a hexagonal shape with zigzag edges, which is in agreement with many experimental observations.\textsuperscript{19-30}

In the range of high H\textsubscript{2} pressure on metal surfaces, both AC and ZZ edges are hydrogen terminated. During growth, incorporating C atoms to the H-terminated edges is very difficult due to the inertness of the H–G edge. As an example, the atomic structures and threshold barriers for the incorporation of C atoms at the H terminated AC and ZZ edges on Cu(111) surface are shown in Fig. 4a and b, respectively (see the ESI\textsuperscript{†} for the computational details). For the H-terminated AC edge, a repeatable cycle of graphene growth requires the addition of two C atoms in sequence to produce a new hexagon at an AC site. Fig. 4a shows the lowest-energy path of forming a new hexagon at the AC edge. It can be found that the incorporation of the second C atom is the threshold step with a threshold energy of 4.55 eV. For the ZZ edge, to form the first hexagon on the continuous edge requires the addition of three C atoms and the threshold step appears during the addition of the second C atom with a threshold energy of 4.68 eV (Fig. 4b), which is just a bit higher than that of the AC edge growth. Although the threshold energies are very similar for the growth of both AC and ZZ edges, the requirement of three atoms to form a hexagonal ring at the ZZ edge implies that the growth rate of the ZZ edge $R_{ZZ} \sim [(\cdot - \cdot) / \cdot]^{3}$ must be much slower than that of the AC edge $R_{AC} \sim [(\cdot - \cdot) / \cdot]^{2}$ because the supersaturation level of active carbon, $(\cdot - \cdot) / \cdot$, is normally far less than 1, where $\cdot$ and $\cdot$ are the concentration of C atoms during growth and under equilibrium, respectively. $R_{AC} > R_{ZZ}$ implies that H-terminated graphene edges also prefer the ZZ type during growth and the shape of a growing graphene domain should be a hexagon as well (Fig. 5).

The above analysis indicates that both metal-passivated and H-terminated graphene domains tend to have a hexagonal shape with six ZZ edges in the parameter region of (i)—high T and low p (Fig. 5) and (iii)—low T and high p (Fig. 5). Now let’s turn to region (ii) in the diagram, where the AC edge is terminated by H and the ZZ edge is passivated by the catalyst surface. For graphene growth on the Cu(111) surface at a typical CVD temperature ($\sim$1300 K), the H\textsubscript{2} partial pressure ranges from $10^{-2}$ to $10^{-5}$ Torr. Because the metal-supported ZZ edge grows

![Fig. 5](https://example.com/fig5.png)  
Fig. 5  The diagram of graphene AC and ZZ edges on the Cu(111) surface and the corresponding possible shapes of graphene domains grown in each region—metal passivated fractal-like domains or regular ZZ edged hexagons in (i), H terminated AC edged hexagon domains in (ii) and hydrogen terminated ZZ edged hexagon domain in (iii).
faster than the H-passivated AC edge (Fig. 3), a growing graphene domain should be dominated by the edge type that grows fastest, which is the H terminated AC edge. As a consequence, the growing graphene domains in this region should have a hexagonal shape with six H terminated AC edges (Fig. 5).

Conversely, an active M–G edge tends to quickly adsorb all carbon atoms that approach it. However, the growth rate would highly depend on the diffusion of the active carbon species on the catalyst surface if the carbon supply is not sufficient. Among the known catalysts for graphene growth, Cu and Au are two less active ones and the barrier of decomposing feedstock, such as CH$_4$, on them was proved high and thus the carbon supply for graphene growth may be not sufficient. Hence, it is possible to observe the diffusion limited growth (DLG) behaviour and fractal-like graphene domains on Cu and Au surfaces at region (i)—where temperature $T$ is high and H$_2$ partial pressure $p$ is low (Fig. 5). On other transition metals which are more active, such as Ni, Co, Fe, Pt, Pd, Ru, Rh, and Ir, the observation of the DLG would be very difficult because of the high rates of feedstock decomposition on these metal surfaces.

4. Conclusions

In summary, our theoretical investigation on the diagram and growth kinetics of graphene edges in chemical vapor deposition (CVD) growth on four typical metal surfaces (Au(111), Cu(111), Ni(111), and Co(0001)) demonstrates that temperature, $T$, and H$_2$ partial pressure $p$, dependent growth behavior includes three parameter regions. At high $T$ and low $p$, both AC and ZZ edges are metal passivated and grow fast. At high $p$ and low $T$, both AC and ZZ graphene edges are H terminated and grow slowly. Beyond, the steady state shape of the graphene domain in CVD growth are predicated to be ZZ edged hexagons for both AC and ZZ graphene edges are H terminated and grow slowly. However, the growth rate would highly depend on the diffusion of the active carbon species on the catalyst surface if the carbon supply is not sufficient. Among the known catalysts for graphene growth, Cu and Au are two less active ones and the barrier of decomposing feedstock, such as CH$_4$, on them was proved high and thus the carbon supply for graphene growth may be not sufficient. Hence, it is possible to observe the diffusion limited growth (DLG) behaviour and fractal-like graphene domains on Cu and Au surfaces at region (i)—where temperature $T$ is high and H$_2$ partial pressure $p$ is low (Fig. 5). On other transition metals which are more active, such as Ni, Co, Fe, Pt, Pd, Ru, Rh, and Ir, the observation of the DLG would be very difficult because of the high rates of feedstock decomposition on these metal surfaces.

Acknowledgements

This work was supported in part by Hong Kong RGC-GRF grants (B-Q35N and B-Q26K), NSFC grant (21273189 and 11404309). Computational resources from the Shanghai and Tianjin Supercomputer Centers are acknowledged.

Notes and references


