

Atomic-scale growth mechanism of graphene on micrometer-sized AlN powders with curvature effect analysis

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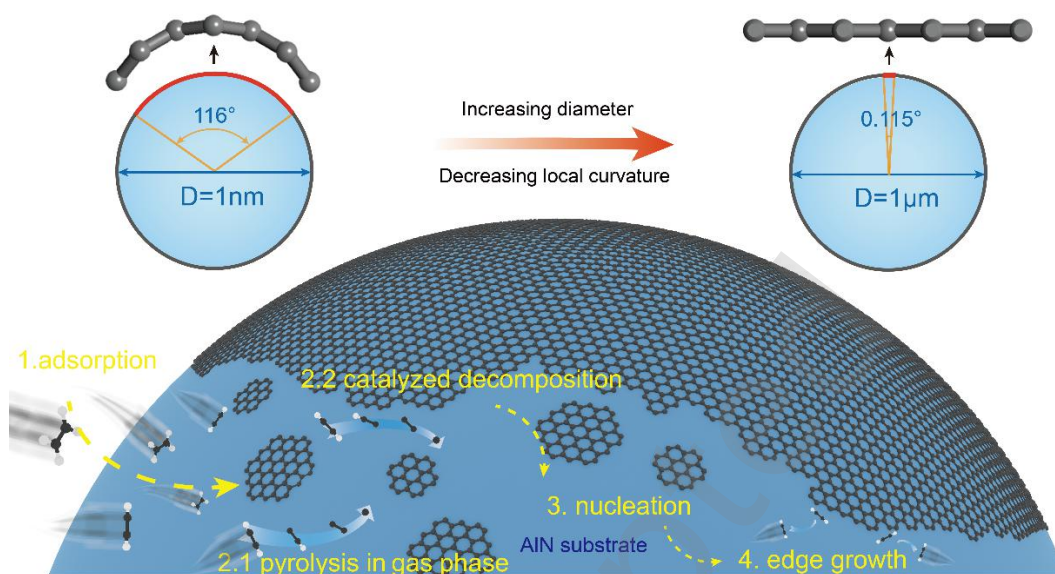
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As the particle diameter increases, the local surface curvature of micrometer-sized powders becomes very small. Carbon sources undergo adsorption, decomposition, nucleation, and edge growth on the surface of micrometer-sized AlN powders. Finally, continuous graphene films are formed.

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ABSTRACT: Aluminum nitride (AlN) powders show great potential for high-efficiency thermal management due to their high thermal conductivity and excellent electrical insulation. However, their practical thermal performance is often limited by interfacial thermal resistance and surface instability. Growing graphene on AlN powder surfaces is expected to simultaneously enhance interfacial heat transport and provide surface protection. The growth mechanism of graphene on micrometer-sized AlN powders remains unclear, which limits experimental control of synthesis. In this work, density functional theory is used to systematically study the formation and growth of graphene on AlN surfaces. Curvature energy analysis first shows that surface curvature no longer dominates the early growth of graphene in micrometer-sized powder systems. Based on this, the key reaction pathways and kinetic features under different carbon precursors are further revealed. The results show that: (i) Carbon precursors decompose both on the substrate surface and in the gas phase, supplying carbon active species for growth; (ii) The dominant nucleation species depends on the precursor, with C dominating in the C₂H₂ system and CH₂C dominating in the C₂H₄ system; (iii) During edge growth, CHCH is the dominant active species in both systems. The growth barrier along the armchair (AC) edge is much lower than that along the zigzag (ZZ) edge. This indicates that graphene growth exhibits a pronounced edge dependence. This work provides a mechanism of graphene growth on micrometer-sized aluminum nitride powders, providing theoretical guidance for its controlled preparation.

KEYWORDS: density functional theory, graphene, chemical vapor deposition, AlN, curvature

1 Introduction

With the rapid development of 5G communication, artificial intelligence, new energy vehicles, and high-power chip technologies, electronic devices are evolving toward miniaturization, high integration, and high power density. In this context, thermal management has gradually become one of the key factors limiting further performance improvement of electronic devices [1-3]. Developing high-thermal-conductivity ceramic-filled composites and constructing efficient thermal interfaces have become among the most promising strategies for thermal management in electronic devices [4-6].

Aluminum nitride (AlN) is a ceramic powder with excellent overall properties. Its theoretical thermal conductivity can reach 320 W/(m·K). It also has a low thermal expansion coefficient, excellent electrical insulation, a low dielectric constant, and a thermal expansion coefficient close to that of silicon. Therefore, AlN is one of the most competitive ceramic fillers for high-thermal-conductivity

composites [7, 8]. In practical applications, AlN is usually used as a micrometer-sized thermal conductive filler in thermal conductive composites or thermal interface materials [9]. However, two major problems seriously limit the performance of AlN powders. On the one hand, the contact between micrometer-sized AlN particles is insufficient. The interfacial bonding between particles is weak. Severe phonon mismatch also increases the interfacial thermal resistance. As a result, the actual thermal conductivity is much lower than the theoretical value [10, 11]. On the other hand, AlN powders are easily hydrolyzed and oxidized. Under high-temperature, high-humidity, and oxygen-containing conditions, the surface can react with water and oxygen to form products such as aluminum oxide and aluminum hydroxide. These reactions destroy the particle structure and increase interfacial defects. As a result, the thermal conductivity of the composites decreases significantly, which affects their long-term stability [12, 13]. Therefore, precise surface modification and structural regulation of AlN powders through interface engineering are

considered important strategies for improving their overall performance. These methods can reduce interfacial thermal resistance and enhance hydrolysis and oxidation resistance without changing the intrinsic properties of AlN [14].

In recent years, two-dimensional materials represented by graphene have provided new strategies for interface regulation [15]. Graphene has unique advantages in interface modification, heat transport regulation, and structural protection because of its ultrahigh intrinsic thermal conductivity, excellent mechanical stability, and atomically dense lattice structure [16-19]. Interface modification technologies based on graphene-skinned powder materials have been verified in many systems. These technologies show excellent universality and performance [20-22]. For thermal conductivity enhancement, graphene-skinned copper powders increase the effective graphene loading because of their high specific surface area. The phonon-electron coupling effect also greatly reduces the interfacial thermal resistance. Therefore, they show better thermal conductivity than pure copper powders [23]. Graphene-skinned alumina powders are prepared by fluidized bed-chemical vapor deposition. A continuous graphene film is formed on the particle surface. The fast interlayer heat transfer mechanism increases the thermal conductivity of the system by one order of magnitude compared with traditional alumina powders. A cross-scale three-dimensional thermal bridge framework constructed from these powders can effectively connect the heat transfer pathways inside composites. It also breaks the interfacial heat transfer barriers between particles. As a result, the trade-off between thermal conductivity enhancement and latent heat loss can be overcome [24]. For protective performance, continuous graphene films can form dense physical barrier layers. These layers can effectively suppress the diffusion and penetration of oxygen and water molecules. Bilayer graphene can further enhance the barrier effect. Its water vapor transmission rate is one order of magnitude lower than that of commercial barrier films. This technology has been successfully used for oxidation and moisture protection of metal substrates. It can also serve as a long-term water and oxygen barrier film for optoelectronic devices, thereby improving the stability and reliability of substrate materials under complex service conditions [25, 26].

These unique practical advantages endow graphene-skinned materials with irreplaceable application potential in advanced thermal management of high-end electronic devices and thermal energy storage in aerospace systems [27, 28]. Within this material framework, constructing graphene-skinned powder systems is expected to enable effective regulation of particle interfaces while preserving the intrinsic thermal conductivity of the fillers. Growing continuous graphene films on AlN powders provides efficient phonon transport pathways and reduces interfacial thermal resistance. At the same time, graphene acts as a physical barrier and protects AlN powders from environmental degradation. This approach enables both enhanced heat conduction and substrate protection. However, in graphene-skinned powder systems, these functions do not depend solely on the intrinsic properties of

graphene. They depend on whether a continuous and stable graphene film can form on the powder surface. Compared with physical mixing or post-coating methods, in-situ growth is more promising for constructing atomically continuous graphene films on AlN powder surfaces. This approach maximizes the preservation of graphene's intrinsic superior properties while providing effective protection for the AlN surface. The realization of these advantages fundamentally relies on a deep understanding of the growth mechanism of graphene on AlN powder surfaces.

The special structural characteristics of powders bring new and unknown challenges to the in-situ growth of graphene. The surfaces of micrometer-sized AlN powders are naturally curved. Therefore, one important issue has not been fully considered. It remains unclear whether the strain induced by curvature has a significant effect on the early growth of graphene. Systematic quantitative studies on this issue are still lacking. In this work, density functional theory (DFT) calculations are employed to systematically investigate the growth behavior of graphene on AlN powder surfaces. First, the competitive relationship among curvature energy, boundary energy, and adsorption energy at different scales is systematically analyzed. The dominant energetic factors during graphene formation on micrometer-sized AlN powders are revealed. On this basis, the adsorption and decomposition behaviors of C_2H_2 and C_2H_4 as carbon precursors on the AlN (000 $\bar{1}$) surface are systematically examined, along with their migration, nucleation, and edge growth processes. This work provides atomistic insights for the design of super graphene-skinned AlN powders and establishes a theoretical foundation for the development of high thermal conductivity composite materials.

2 Calculation and Methods

All density functional theory (DFT) calculations were performed using the Vienna ab initio Simulation Package (VASP). The projector augmented wave (PAW) method was employed to describe the electron-ion interactions [29], while the exchange-correlation effects were treated using the Perdew-Burke-Ernzerhof (PBE) functional within the generalized gradient approximation (GGA). The plane-wave cutoff energy was set to 450 eV. All structures were fully relaxed until the forces on each atom were less than 0.01 eV/Å, and the total energy convergence criterion was set to 1×10^{-4} eV. All calculations were carried out using a Γ -centered $1 \times 1 \times 1$ k-point mesh. The climbing image nudged elastic band (CI-NEB) method implemented in VASP was used to locate transition states. The DFT-D3 method was employed to account for van der Waals interactions [30]. A vacuum layer of 15 Å was introduced along the z-direction to eliminate spurious interactions between periodic images.

3 Results and discussion

3.1 Energetic Evaluation of Curvature Effects at Different Length Scales

In practical applications, aluminum nitride typically exists in the form of micrometer-sized powders, whose surfaces inevitably exhibit a certain degree of curvature. This geometric feature raises a critical question: whether curvature effects need to be explicitly considered when

investigating the growth mechanism of graphene on powder surfaces. This issue is not only crucial for the validity of the theoretical model, but also directly affects the consistency between computational results and experimental systems. Therefore, it is necessary to quantitatively evaluate the energy contribution induced by curvature at different length scales.

Figure 1(a) shows the curvature of graphene on the surfaces of graphene-skinned powders with different scales. It directly illustrates the curvature effect experienced by graphene. On nanoscale substrates, graphene layers must bend significantly to match the substrate surface. This produces large local bending angles and introduces additional curvature energy. When the particle size increases to the micrometer scale, the local surface curvature decreases significantly. In this case, graphene only undergoes slight bending, and the structural distortion caused by curvature becomes almost negligible.

Figure 1(b) presents the curvature energy (E_c) as a function of particle diameter, which was calculated based on the continuum elastic theory described by Eq. (1) [31]. Here, D is the particle diameter, and d is the distance between graphene and the substrate surface. A is a constant related to the Young's modulus. Detailed calculations are provided in the curvature energy calculation section of the Electronic Supplementary Material (ESM).

The results indicate that within the nanoscale regime,

the curvature energy decreases rapidly with increasing particle diameter. When the substrate diameter is approximately 1 nm, the curvature energy is comparable in magnitude to the adsorption energy involved in the nucleation process, and thus can significantly influence the initial nucleation behavior of graphene, making it non-negligible at this scale. However, as the diameter increases to several tens of nanometers, the curvature energy decays rapidly. When further extended to the micrometer scale, the curvature energy becomes nearly negligible, and its contribution to the geometric strain of the system can be reasonably neglected.

$$E_c = \frac{A}{(\frac{D}{2} + d)^2} \quad (1)$$

To further evaluate the effect of curvature on the early-stage formation of graphene, Fig. 1(c) shows the variation of formation energy under different curvature conditions [32, 33]. A formation energy decomposition model is used. The total formation energy is divided into adsorption energy (E_A), boundary energy (E_B), and curvature energy (E_c). The expression is given in Eq. (2). E_A describes the interaction between each carbon atom and the substrate. E_B represents the formation energy per unit length of the graphene edge. r_c is the radius of the existing carbon structure. Detailed calculations are provided in the formation energy calculation section of the ESM.

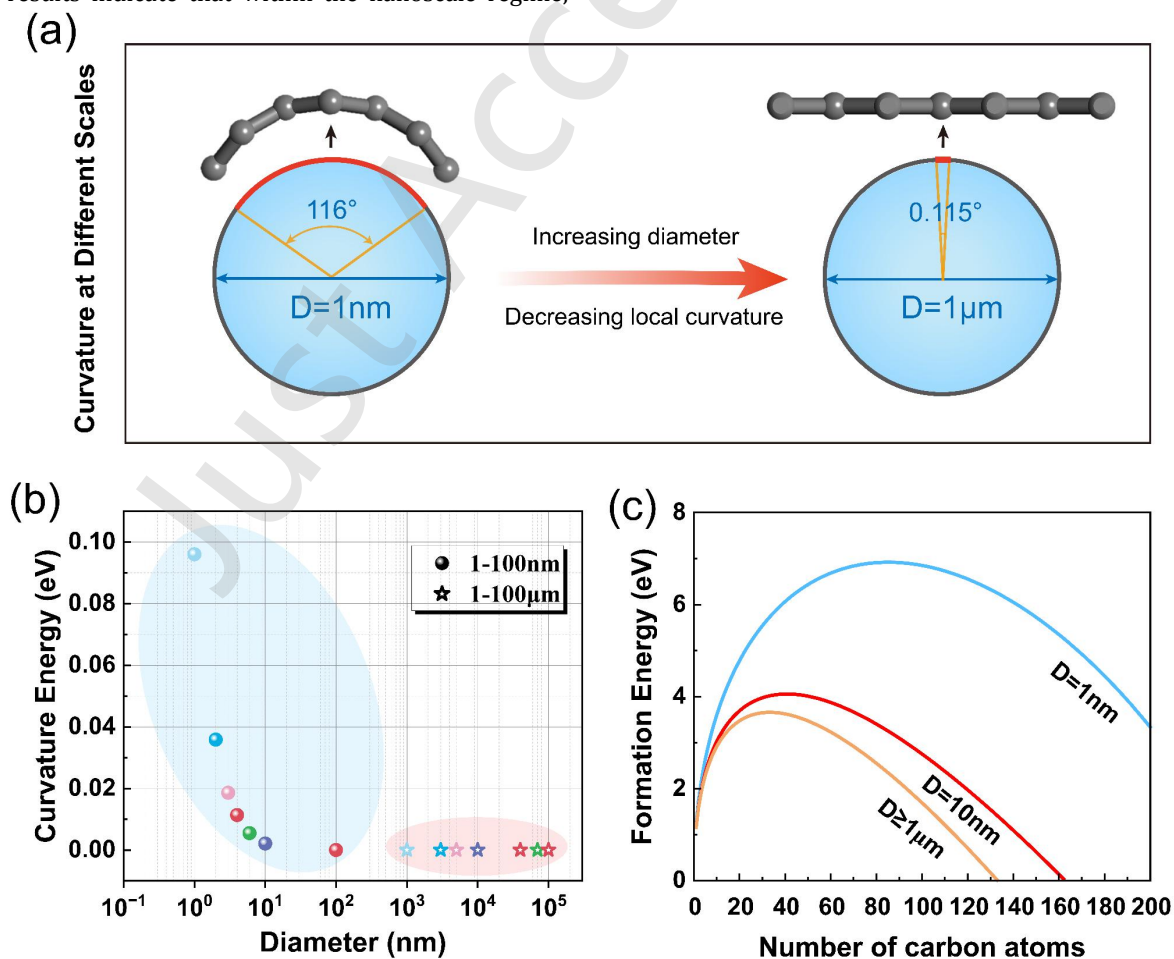


Figure 1. Curvature effect on graphene growth. (a) Curvature of graphene on graphene-skinned powder surfaces at different scales. (b) Calculated curvature energy as a function of particle diameter based on Eq. (1). (c) Formation energy of graphene on

substrate particles.

$$E_F = NE_A + 2\pi r_c E_B + NE_C \left(\frac{D}{2} + d \right) \quad (2)$$

The results show that the energy barrier is high at the nanoscale. This is unfavorable for the initial nucleation of graphene. As the particle diameter increases to about 10 nm, the barrier decreases significantly. At the micrometer scale, the formation energy curve shifts downward. A graphene-skinned fullerene-like structure is formed. In this case, the adsorption energy between graphene and the substrate is maximized. The contribution of curvature energy is minimized. The curvature energy becomes negligible compared to the other energy terms. The formation energy of the system is mainly dominated by adsorption energy and edge energy.

This result has clear experimental implications. For micrometer-sized AlN powders used in practice, the effect of surface curvature on the early-stage formation of graphene can be neglected. This indicates that graphene growth is mainly governed by surface reaction processes rather than geometric factors. Therefore, it is reasonable to use an ideal planar AlN surface as the model in subsequent studies. This approach significantly reduces the computational complexity. It also allows the obtained mechanisms to directly guide the controllable fabrication of graphene-skinned AlN powders in experiments.

3.2 Stability of Active Species Adsorbed on the AlN (000 $\bar{1}$) Surface

After confirming that curvature effects no longer dominate graphene formation on micrometer-sized AlN powders, the growth of graphene can be treated as a series

of surface reactions on a locally planar surface. In practical chemical vapor deposition (CVD) experiments, the choice of carbon precursor is a key factor that affects graphene growth. Acetylene (C_2H_2) and ethylene (C_2H_4) are two commonly used dual-carbon sources. These two precursors generate different carbon active species during the reaction process. As a result, they may have different effects on the growth of graphene.

In practical AlN powder systems, the surface consists of different crystallographic facets. Calculations of surface formation energies (see Fig. S1 in the ESM) show that the AlN (000 $\bar{1}$) facet possesses the lowest surface energy and is therefore thermodynamically the most stable. Based on this result, the AlN (000 $\bar{1}$) facet is selected as the representative surface. It captures the dominant interfacial characteristics of the system. It also helps establish a direct connection with experimental systems.

There is a basic prerequisite for studying the subsequent processes. The carbon active species must be stably adsorbed on the substrate surface, regardless of the carbon precursor. Only in this case can they participate in migration, nucleation, and edge growth. Therefore, this section systematically investigates the adsorption stability of C_xH_y active species generated from gas-phase pyrolysis and catalytic decomposition of the two carbon sources. It also defines the carbon species considered in this work.

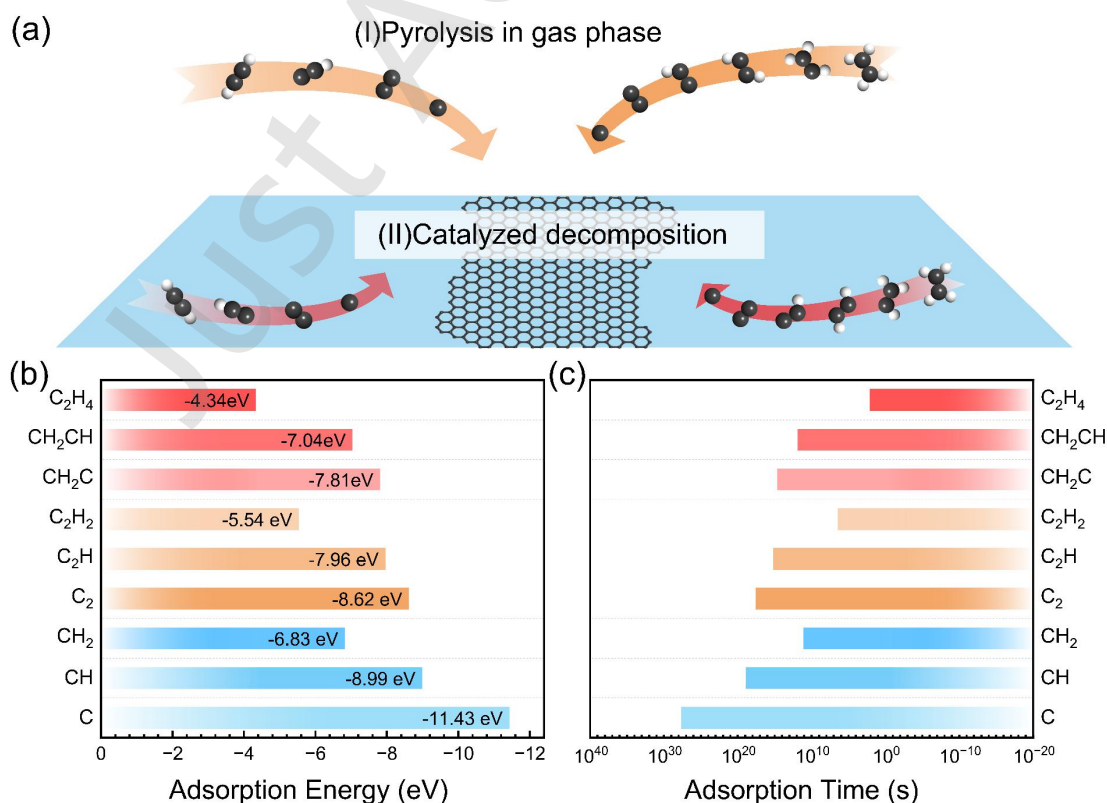


Figure 2. Adsorption behavior of carbon active species. (a) Origin of adsorbate species: schematic illustration of various C_xH_y active species generated from C_2H_2 and C_2H_4 . (b) Adsorption energies of different carbon active species on the AlN surface. (c)

First, the adsorption energies of different species on the substrate surface are calculated. They are defined as follows:

$$E_a = E_{tot} - E_{sub} - E_{C_xH_y} \quad (3)$$

E_{tot} is the total energy of the adsorbed system. E_{sub} is the energy of the substrate. $E_{C_xH_y}$ is the energy of the carbon active species. In the calculations, typical adsorption sites are considered, including top (T), bridge (B), and hollow (H) sites. These sites are used to identify the most stable adsorption configurations for each species. The most stable structures are shown in Fig. S2. The results are summarized in Fig. 2(b). As shown in Fig. 2(b), the adsorption energies of C_2H_2 , C_2H_4 , and their possible carbon active species on the substrate surface are all negative. This indicates that the total energy of the system decreases significantly after adsorption, which is thermodynamically stable. These results indicate that the carbon species can be effectively adsorbed and stably maintained on the substrate surface. They can therefore provide carbon sources for the subsequent nucleation and growth of graphene.

Based on these results, the adsorption time of each active species on the substrate surface is further calculated from the adsorption energy [34]:

$$\tau = \tau_0 \times e^{-\left(\frac{E_a}{kT}\right)} \quad (4)$$

$$\tau_0 = \frac{h}{kT} \quad (5)$$

Here, h is the Planck constant and k is the Boltzmann constant. T is the temperature. The calculated results are

shown in Fig. 2(c). The results show that the adsorption times of all carbon active species on the substrate surface are much longer than the characteristic time required for the subsequent growth of graphene. Even for C_2H_4 , which has the weakest adsorption, the residence time is longer than 10^2 s. It can therefore remain stably on the substrate surface and participate in subsequent reactions. These results indicate that both C_2H_2 and C_2H_4 can serve as effective carbon sources for graphene growth from the perspective of adsorption stability. Their differences are more likely to appear in the subsequent reaction pathways and growth kinetics.

3.3 Decomposition of Carbon Precursors

After confirming that active carbon species can stably adsorb on the substrate surface, the decomposition behavior of carbon precursors needs to be further investigated. This is because it determines the dominant active species involved in graphene growth. Therefore, the decomposition behaviors of C_2H_2 and C_2H_4 are systematically studied in both the gas phase and on the substrate surface. Compared with single-carbon precursors that mainly undergo stepwise dehydrogenation, dual-carbon sources contain both C-H and C-C bonds. Their decomposition involves multiple competing pathways. The energy barriers of these pathways are different. This difference determines the dominant active species in the subsequent reactions. It also affects the nucleation and growth of graphene.

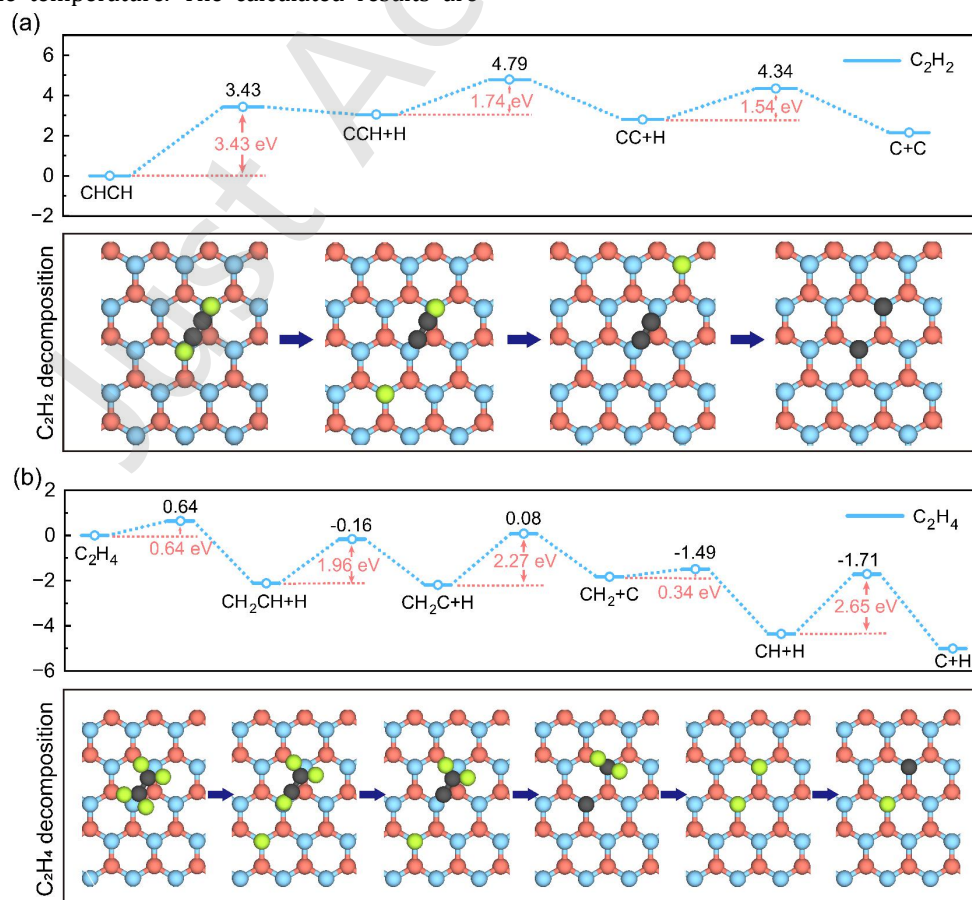


Figure 3. Decomposition of carbon precursors. (a) Decomposition energy barriers and schematic decomposition pathway of the carbon precursor C_2H_2 on the substrate surface. (b) Decomposition energy barriers and schematic decomposition pathway of the carbon precursor C_2H_4 on the substrate surface.

For acetylene (C_2H_2), the decomposition pathways are shown in Fig. S3 in the ESM. The optimal pathways in both the gas phase and on the substrate involve stepwise dehydrogenation followed by C-C bond breaking. However, the energy barriers are significantly different. On the substrate surface, the first dehydrogenation step is the rate-determining step. The barrier is 3.43 eV. In the gas phase, the highest barrier appears in the final C-C bond breaking step. The barrier reaches 8.70 eV. This difference indicates that the substrate has a catalytic effect. It can significantly promote the decomposition of C_2H_2 compared with gas-phase pyrolysis. Figure 3(a) shows the optimal pathway on the substrate. The first dehydrogenation barrier plays a key role. If this barrier cannot be overcome, C_2H_2 tends to remain in its original structure. It adsorbs on the substrate without further decomposition. Once the initial dehydrogenation is activated, the barriers of the subsequent steps decrease significantly. The decomposition process then becomes energetically accessible. The C-C bond can be further broken. Finally, single carbon atoms are formed.

For ethylene (C_2H_4), the decomposition pathways in the gas phase and on the substrate are more different, as shown in Fig. S4. In the gas phase, the optimal pathway involves stepwise removal of four hydrogen atoms, followed by C-C bond breaking. The highest energy barrier appears in the final step and is 8.70 eV. This indicates that complete decomposition in the gas phase is difficult. On the substrate surface, the decomposition pathway is different (Fig. 3(b)). The molecule preferentially undergoes dehydrogenation of two hydrogen atoms on the same side. Then the C-C bond

breaks. Finally, the remaining hydrogen atoms are removed. The maximum barrier of the whole process is 2.65 eV. Figure S4 also shows that after the first dehydrogenation step, the energy barriers for the formation of CHCH and CH_2C are comparable. This indicates that both intermediates have comparable formation probabilities. They may coexist during the reaction process.

Overall, the carbon active species involved in graphene growth do not only come from surface decomposition. They can also originate from thermal decomposition in the gas phase. Meanwhile, the differences in the decomposition behaviors of C_2H_2 and C_2H_4 in the gas phase and on the substrate indicate that the presence of the substrate not only reduces the overall decomposition barriers. It also regulates the distribution of intermediates to some extent. This further affects the subsequent nucleation and edge growth processes.

3.4 Population Distribution and Migration Behavior of Active Species on the Substrate Surface

However, decomposition energy barriers alone are not sufficient to determine the dominant carbon active species under real growth conditions. The decomposition pathways only determine which active species may be formed. Under high-temperature growth conditions (800-1600 K), the actual participating species also depend on their thermodynamic distribution and surface migration ability. Therefore, the equilibrium population distribution and migration behavior of active species are further considered to identify the key species governing graphene growth.

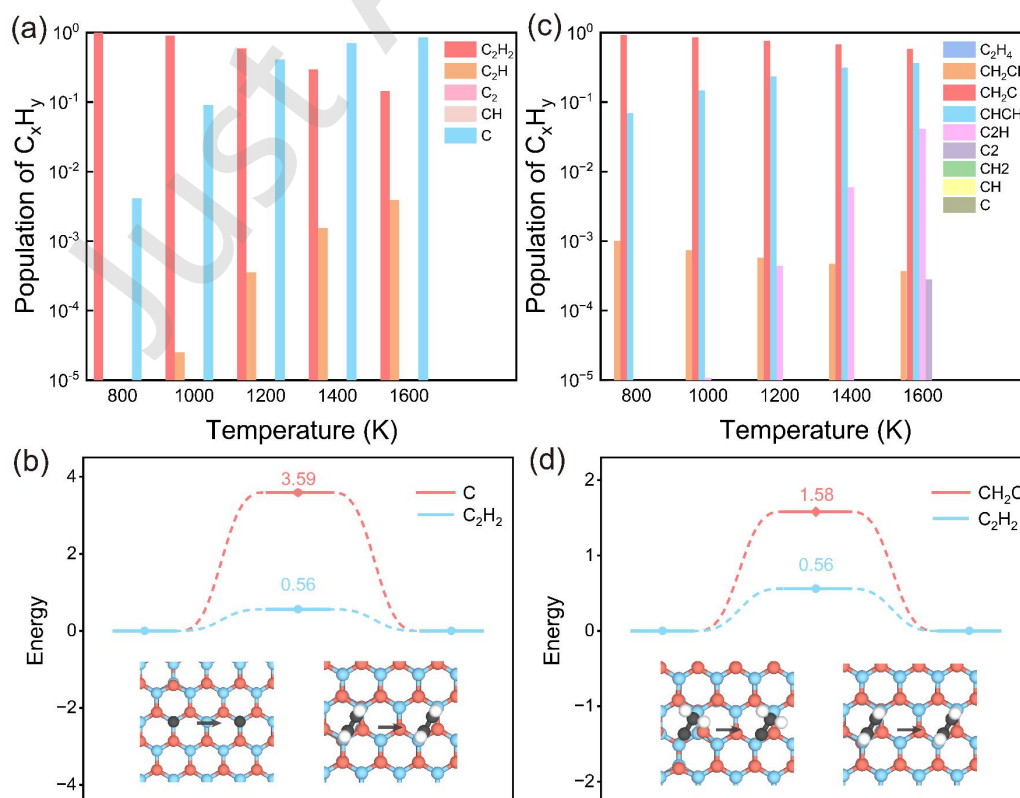


Figure 4. Distribution and migration of active species. (a) Distribution of active species derived from C_2H_2 on the AlN (000 $\bar{1}$) surface. (b) Migration energy barriers of C and C_2H_2 on the substrate surface. (c) Distribution of active species derived from C_2H_4 on the AlN (000 $\bar{1}$) surface. (d) Migration energy barriers of CH_2C and C_2H_2 on the substrate surface.

In this section, two sources of carbon species are considered: (i) Species generated by catalytic decomposition on the AlN (000 $\bar{1}$) surface. (ii) Species generated by gas-phase pyrolysis and then adsorbed on the substrate surface. Based on the thermodynamic calculation method described in Section 6 of the ESM, the equilibrium distributions of active species at different temperatures were obtained from their relative Gibbs free energies. Combined with surface migration barriers, their ability to participate in nucleation and growth processes is systematically evaluated.

Figure 4 shows the temperature-dependent distribution of active species derived from C_2H_2 and C_2H_4 on the AlN (000 $\bar{1}$) surface. For the C_2H_2 precursor (Fig. 4(a)), CHCH and C are the dominant species in the typical growth temperature range. When migration barriers are considered, a clear functional division between these two species is observed, as shown in Fig. 4(b). CHCH exhibits a low migration barrier of 0.56 eV, enabling efficient surface diffusion. In contrast, C has a high migration barrier of 3.59 eV. It is almost unable to undergo long-range migration on the surface. Therefore, C tends to accumulate in local regions. It promotes the formation of initial carbon clusters and mainly participates in the nucleation process. CHCH tends to supply carbon to the edges of existing carbon structures. It mainly governs the subsequent edge growth process.

In contrast, the C_2H_4 system (Fig. 4(b)) exhibits a different distribution of dominant species. Within the growth temperature range, CH_2C has the highest concentration, followed by CHCH. Their roles can be further distinguished by analyzing the migration barriers, as shown in Fig. 4(d). CH_2C has a migration barrier of 1.58 eV. Its diffusion ability is relatively limited. In contrast, CHCH has a low migration barrier of 0.56 eV. It shows strong mobility on the surface. Therefore, in the C_2H_4 system, CH_2C has a high concentration and weak mobility. It tends to form stable carbon clusters in local regions. It is the main species responsible for nucleation. CHCH has a lower migration barrier. It can easily migrate to graphene edges. It therefore dominates the edge growth process.

In summary, although different carbon precursors show differences, they exhibit a similar functional division during growth. When sufficient active species are present on the substrate surface, species with low mobility dominate the nucleation process. Species with high mobility dominate the edge growth process. This helps to understand the graphene growth process. It also provides guidance for experimental control of growth. The distribution of active species on the substrate surface can be tuned by adjusting the carbon precursor type and reaction conditions. This enables effective control of nucleation density and crystal growth behavior.

3.5 Nucleation of Carbon Active Species

After identifying the main active species responsible for nucleation from the two carbon precursors, we further investigate the stability of carbon clusters formed during graphene nucleation. The nucleation process is

systematically analyzed from the perspective of Gibbs free energy.

First, the formation energies of the ground-state structures formed by different active species on the surface are calculated. The formation energy is defined as:

$$E_N = E_{tot} - E_{sub} - N \times E_{Gr} - M \times E_H \quad (6)$$

In the equation, E_{tot} is the total energy of the substrate and the ground-state structure formed on the substrate surface. E_{sub} is the energy of the clean substrate. E_{Gr} is the energy of a single carbon atom in graphene. E_H is the energy of a single hydrogen atom on the substrate surface. N and M represent the number of carbon atoms and hydrogen atoms.

Based on classical nucleation theory, we study ground-state structures containing up to 16 carbon atoms. The formation energies of each structure are provided in the Electronic Supplementary Material (ESM). However, graphene growth occurs under finite temperature and pressure conditions. First-principles calculations alone cannot directly represent experimental conditions. Therefore, Gibbs free energy is introduced to account for the effect of environmental chemical potential on growth. The Gibbs free energy is defined as [35, 36]:

$$G_N = E_N - N \times \Delta\mu \quad (7)$$

$\Delta\mu$ is the chemical potential difference of carbon between different phases. It represents the thermodynamic driving force for graphene nucleation. It also determines the tendency of graphene nucleation and growth.

Figures 5(a-b) and (c-d) show the Gibbs free energy evolution of nucleation involving C and CH_2C as active species. Figures 5(a) and 5(c) present the original calculated results of the Gibbs free energy evolution for cluster formation on the substrate surface as functions of the number of carbon atoms in the cluster and the chemical potential. Figures 5(b) and 5(d) show the corresponding fitted curves.

We find that early carbon clusters prefer one-dimensional linear chain structures. Compared with two-dimensional ring structures containing the same number of carbon atoms, carbon chains have lower formation energy. Therefore, carbon active species tend to aggregate into chain-like configurations. Based on this result, we fit the energy of one-dimensional carbon chains as a function of atom number. The expressions for C and CH_2C are given as follows:

$$G_{1D-1} = 0.61 \times N + 0.35 - N \times \Delta\mu \quad (8)$$

$$G_{1D-2} = 1.02 \times N - 8.04 - N \times \Delta\mu \quad (9)$$

As the number of carbon atoms increases, one-dimensional carbon chains become unstable. In contrast, ring-like structures become more stable. Therefore, carbon clusters transform from one-dimensional chains to two-dimensional rings. Therefore, we fit the energy of two-dimensional carbon rings as a function of atom number:

$$G_{2D-1} = 1.90 \times \sqrt{N} - 0.15 - N \times \Delta\mu \quad (10)$$

$$G_{2D-2} = 1.70 \times \sqrt{N} - 6.09 - N \times \Delta\mu \quad (11)$$

Based on the calculations, the nucleation barrier and nucleation rate of graphene are obtained, as shown in Fig. 5(e) and 5(f). The detailed calculation methods for the nucleation rate are provided in the ESM. As the chemical potential increases, the nucleation barriers gradually decrease. The aggregation and structural transformation of carbon clusters also become easier. Figure 5(e) shows that the nucleation barriers of CH_2C are significantly lower than those of C across the entire $\Delta\mu$ range. Consistent with the trend of the nucleation barriers, the nucleation rates of CH_2C in Fig. 5(f) are higher than those of C across the entire $\Delta\mu$ range, and the difference can reach several orders of magnitude.

In summary, under the same chemical potential conditions, carbon clusters formed with CH_2C as the

nucleation active species have lower energies and higher thermodynamic stability. These clusters are less likely to decompose and can remain stable and continue to grow during the early stage of graphene growth. At the same time, the lower nucleation barriers of CH_2C lead to faster nucleation rates. As a result, a large number of stable graphene nuclei can form within a short time, thereby providing sufficient and stable initial sites for the subsequent continuous growth of graphene. Therefore, CH_2C exhibits superior thermodynamic and kinetic properties during the initial stage of graphene nucleation, making it more favorable for the efficient and stable early growth of graphene.

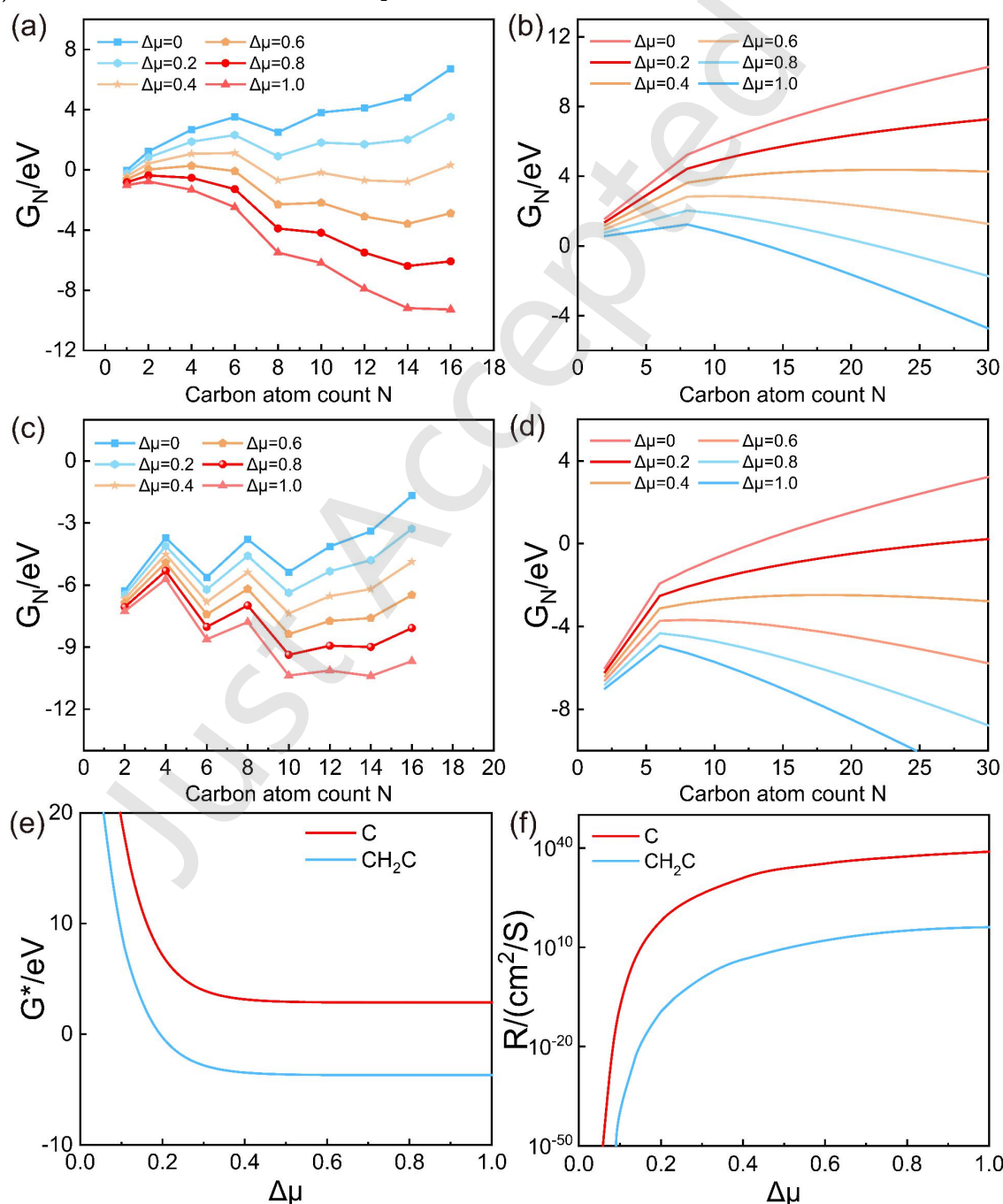


Figure 5. Comparison of the Gibbs free energy evolution and nucleation kinetic parameters for different carbon active species during the nucleation process. (a, c) Original results of the Gibbs free energy evolution for carbon clusters formed by C and

CH₂C as functions of the carbon atom number N and chemical potential $\Delta\mu$. (b, d) Fitted curves for the corresponding one-dimensional carbon chain stage and two-dimensional carbon ring stage. (e) Variations in the nucleation barriers of the two carbon active species with carbon chemical potential. (f) Variations in the nucleation rates of the two carbon active species with carbon chemical potential.

3.6 Edge Growth of Carbon Active Species

From the previous analysis, CHCH is identified as the dominant active species in both C₂H₂ and C₂H₄ systems. It shows high surface concentration and low migration barrier. Therefore, it is the main species involved in graphene edge growth. Based on this, we focus on the growth behavior of CHCH along different edges on the substrate surface [37].

Based on the elementary reaction processes involved in graphene growth, including adsorption, dehydrogenation, carbon insertion, and edge reconstruction, possible reaction pathways were constructed. Subsequently, the CI-NEB (Climbing Image Nudged Elastic Band) method was employed to optimize these pathways and determine the corresponding reaction barriers. The results (Fig. 6) show that CHCH exhibits significantly different growth behaviors on AC and ZZ edges. For the AC edge, the growth process can

be described as a three-step cycle involving carbon addition and continuous dehydrogenation. First, CHCH adsorbs and inserts into the H-passivated AC edge. It forms a new six-membered ring with edge carbon atoms. The energy barrier is 0.43 eV. This low barrier indicates that the formation of carbon six-membered rings is kinetically favorable. However, the initial edge is hydrogen-passivated. Therefore, dehydrogenation is required to stabilize the structure and reconstruct the sp² network. In the second step, CHCH migrates to the edge and removes one edge hydrogen atom. The barrier is 2.23 eV. This is the highest barrier in the AC edge growth pathway. Therefore, this is the rate-determining step. In the third step, another CHCH removes the remaining edge hydrogen atom. The barrier is 0.85 eV. At this stage, the edge is fully dehydrogenated and returns to a stable six-membered ring structure. One complete AC edge growth cycle is finished.

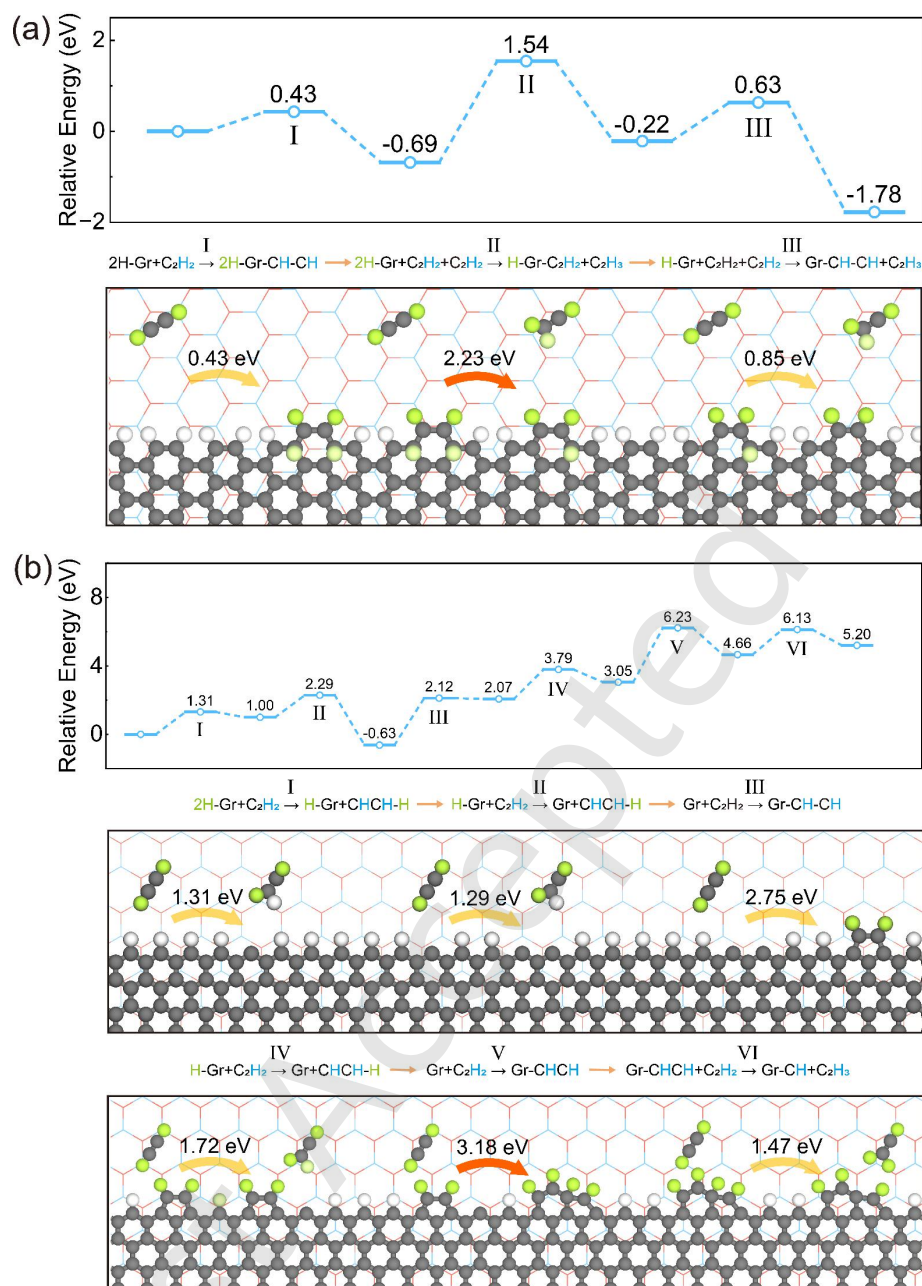


Figure 6. Edge growth kinetics (a) Growth behavior of CHCH along the AC edge. (b) Growth behavior of CHCH along the ZZ edge. The reaction pathways and corresponding energy barriers were obtained using the CI-NEB method.

By comparison, the ZZ edge has overlapping six-membered ring structures. Its growth process is more complex. Multiple steps are required to complete one full cycle. The growth starts with two consecutive dehydrogenation steps. Two CHCH species remove two edge hydrogen atoms. The corresponding barriers are 1.31 eV and 1.29 eV. These steps activate the edge and create conditions for carbon insertion. Then a new CHCH inserts into the graphene edge. A five-membered intermediate structure is formed. Next, another CHCH removes one edge hydrogen atom. The barrier is 1.72 eV. A key ring reconstruction step then occurs. A new CHCH inserts and reconstructs a complete six-membered ring structure. The barrier is 3.18 eV. This is the highest barrier in the ZZ edge growth pathway. Therefore, it is the rate-determining step. Finally, the remaining hydrogen atoms are removed with a barrier of 1.47 eV. This completes one full ZZ edge growth cycle.

Based on these results, CHCH-driven edge growth shows different behaviors on AC and ZZ edges. The AC edge has lower energy barriers and simpler steps. It is easier to grow and expand. The ZZ edge has higher barriers. Its growth is partially suppressed. This difference leads to anisotropic graphene growth. The AC edge grows preferentially. Its growth rate is higher than that of the ZZ edge. According to kinetic Wulff construction theory, the fast-growing AC edge gradually disappears. The slow-growing ZZ edge is preserved and determines the edge morphology of graphene (Fig.S7 in the ESM). This result is consistent with experimentally observed anisotropic graphene growth. It provides a clear atomic-scale explanation.

4 Conclusions

In summary, this work establishes a complete framework for the growth of graphene on micrometer-sized

AlN powders, including curvature energetics, carbon source decomposition, surface species distribution, migration behavior, and edge growth kinetics. The atomic-scale growth mechanism of graphene is revealed, and the influence of particle-size-dependent curvature effects on the growth behavior is systematically investigated. The results show that: (i) The contribution of surface curvature energy to the formation energy decreases rapidly with increasing particle diameter. At the micrometer scale, the influence of curvature effects on the initial nucleation and growth of graphene is greatly weakened. Graphene growth is mainly dominated by adsorption energy and edge energy. (ii) Carbon sources can provide carbon active species for graphene growth through both substrate-catalyzed decomposition and gas-phase pyrolysis pathways. The dominant nucleation active species differ significantly for different carbon sources, and their roles are jointly determined by equilibrium concentration and migration ability. (iii) Differences between the growth processes of the AC and ZZ edges of graphene lead to different growth barriers, which finally result in edge morphologies dominated by ZZ edges. This work clarifies the mechanism of curvature effects and the atomic-scale growth mechanism of graphene. It can provide theoretical support for optimizing experimental parameters, such as carbon source type, reaction temperature, and gas partial pressure, as well as for precisely controlling the nucleation density and microstructure of graphene.

Electronic Supplementary Material: Supplementary material (further calculation details and supplementary figures) is available in the online version of this article at <https://doi.org/10.26599/NR.2026.94909138>.

Data availability

All data needed to support the conclusions in the paper are presented in the manuscript and the Electronic Supplementary Material. Additional data related to this paper may be requested from the corresponding author upon request.

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Declaration of competing interest

All the contributing authors report no conflict of interests in this work.

Author contribution statement

Meiqi Su: Data curation, Investigation, Formal analysis, Methodology, Writing manuscript.
Chaojie Yu: Methodology, Writing – review & editing
Jianjian Shi: Writing – review & editing
Tao Yang: Writing – review & editing
Guangping Zhang: Supervision, Methodology, Resources, Writing – review & editing
Xiaoli Sun: Investigation, Conceptualization, Methodology, Supervision, Writing – review & editing
Zhongfan Liu: Funding acquisition, Project administration, Conceptualization, Writing – review & editing

Use of AI statement

None.

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Electronic Supplementary Material

Atomic-scale growth mechanism of graphene on micrometer-sized AlN powders with curvature effect analysis

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1. Details of Curvature Energy Calculation

Curvature energy quantifies the bending penalty experienced by each carbon atom in the graphene-coated structure. Ding et al. [1, 2] used a function of n proposed by Adams [3, 4] to calculate the curvature energy of fullerene spheres. By considering the surface atomic density, the number of atoms (n) in a fullerene is converted into the diameter of the sphere. This leads to an expression for the curvature energy of fullerene-like structures. The expression is further refined and improved. C60 is used for correction due to its highly symmetric spherical structure and high stability. All carbon atoms in C60 are equivalent. Considering the structural characteristics, the interlayer distance d between the substrate and graphene is incorporated into the formula. Based on this, the final expression for the curvature energy is obtained as follows:

$$E_C = \frac{A}{(\frac{D}{2} + d)^2} \quad (S1)$$

In the Eq. S1, the constant $A=0.0593$, D is the equivalent diameter of the substrate, d is the finite distance between graphene and the substrate.

2. Details of Formation Energy Calculation

$$E_A = \frac{E_{total} - E_{gr} - E_{sub}}{N} \quad (S2)$$

E_A represents the adsorption energy per carbon atom on the substrate. E_{total} is the total energy of graphene adsorbed on the AlN substrate. E_{gr} is the energy of graphene. E_{sub} is the energy of the substrate. N is the number of carbon atoms in graphene.

$$E_B = \frac{E_{total} - E_{sub} - NE_{gr} - ME_H}{2l} \quad (S3)$$

E_B represents the edge formation energy. M is the number of hydrogen atoms used for edge passivation. E_H is the energy of a hydrogen atom. l is the length of the graphene edge.

3. Details of Surface Energy Calculation

The surface formation energy is calculated as follows [5]:

For symmetric surfaces:

$$E_{surface} = \frac{E_{slab} - n \times E_{bulk}}{2A} \quad (S4)$$

For asymmetric surfaces:

$$E_{surface} = \frac{E_{slab}^{unrelax} - n \times E_{bulk}}{2A} + \frac{E_{slab}^{relax} - E_{slab}^{unrelax}}{A} \quad (S5)$$

E_{bulk} is the energy of the bulk system. $E_{slab}^{unrelax}$ and E_{slab}^{relax} are the energies of the slab before and after relaxation, respectively. A is the surface area. n is the ratio of the number of atoms between the slab and the bulk.

Using these expressions, the surface formation energies of different crystal facets can be obtained. As shown in Fig. S1, the AlN(000 $\bar{1}$) surface has the lowest formation energy. This indicates that it is the most stable surface.

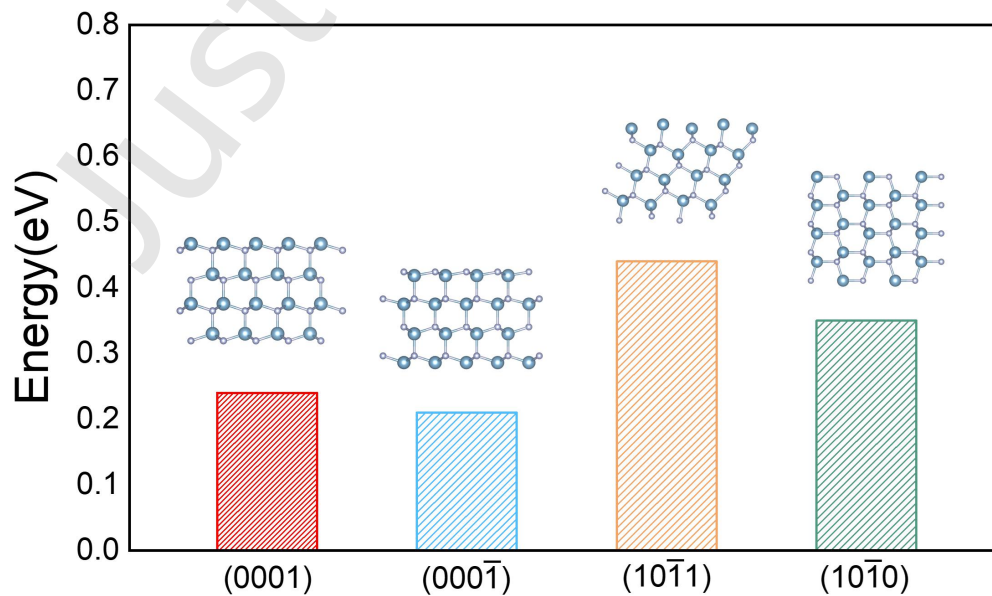


Figure S1. Surface formation energies of different crystal facets.

4. Most Stable Adsorption Sites

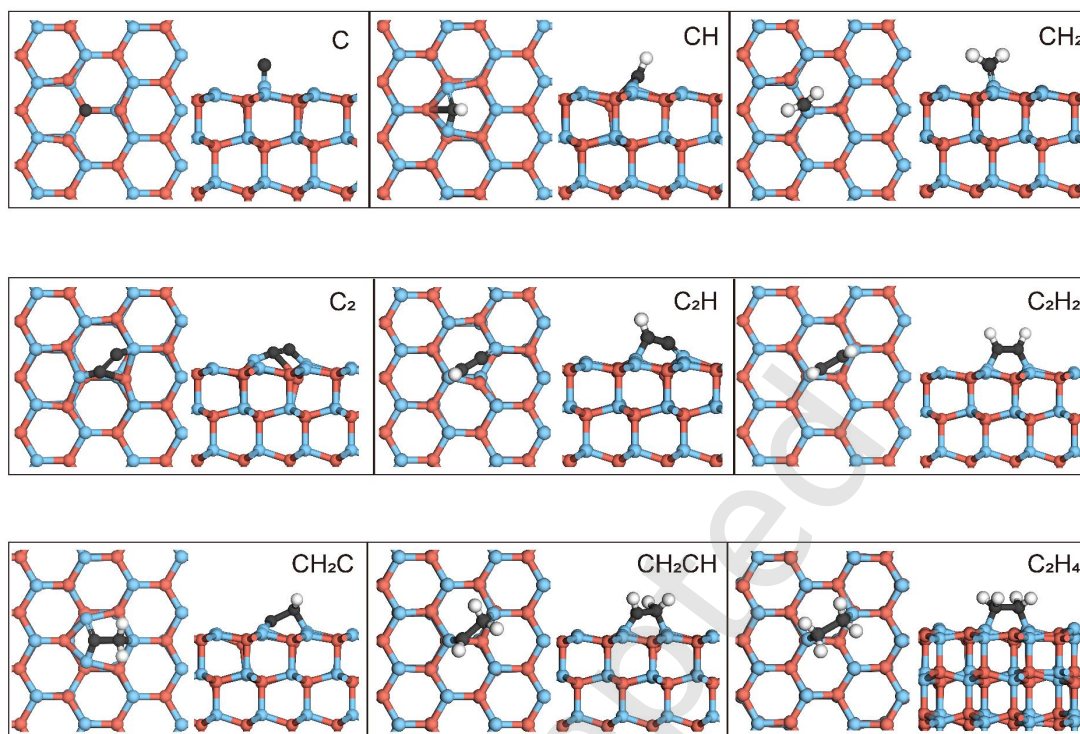


Figure S2. Most stable adsorption sites of different active carbon species on the AlN(000 $\bar{1}$) surface.

5. Decomposition Pathways and Energy Barriers of Carbon Precursors

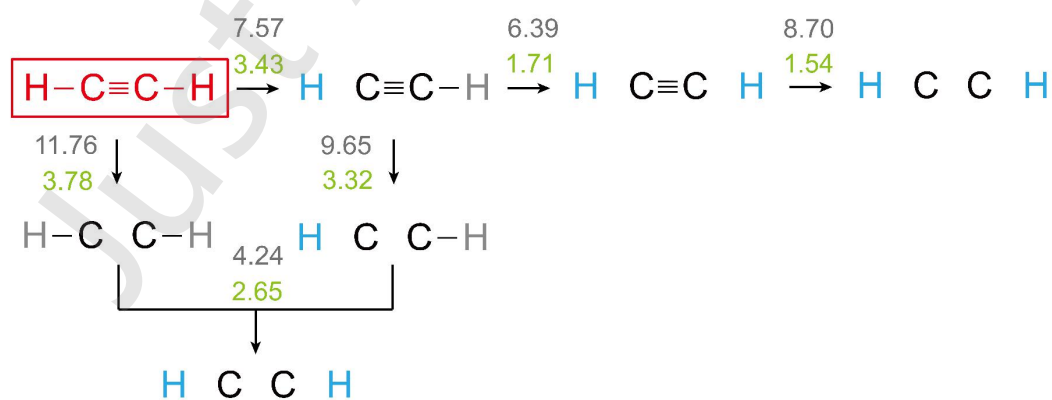


Figure S3. Decomposition energy barriers of the carbon precursor C_2H_2 in vacuum and on the AlN(000 $\bar{1}$) surface (gray: vacuum; green: substrate surface) [6].

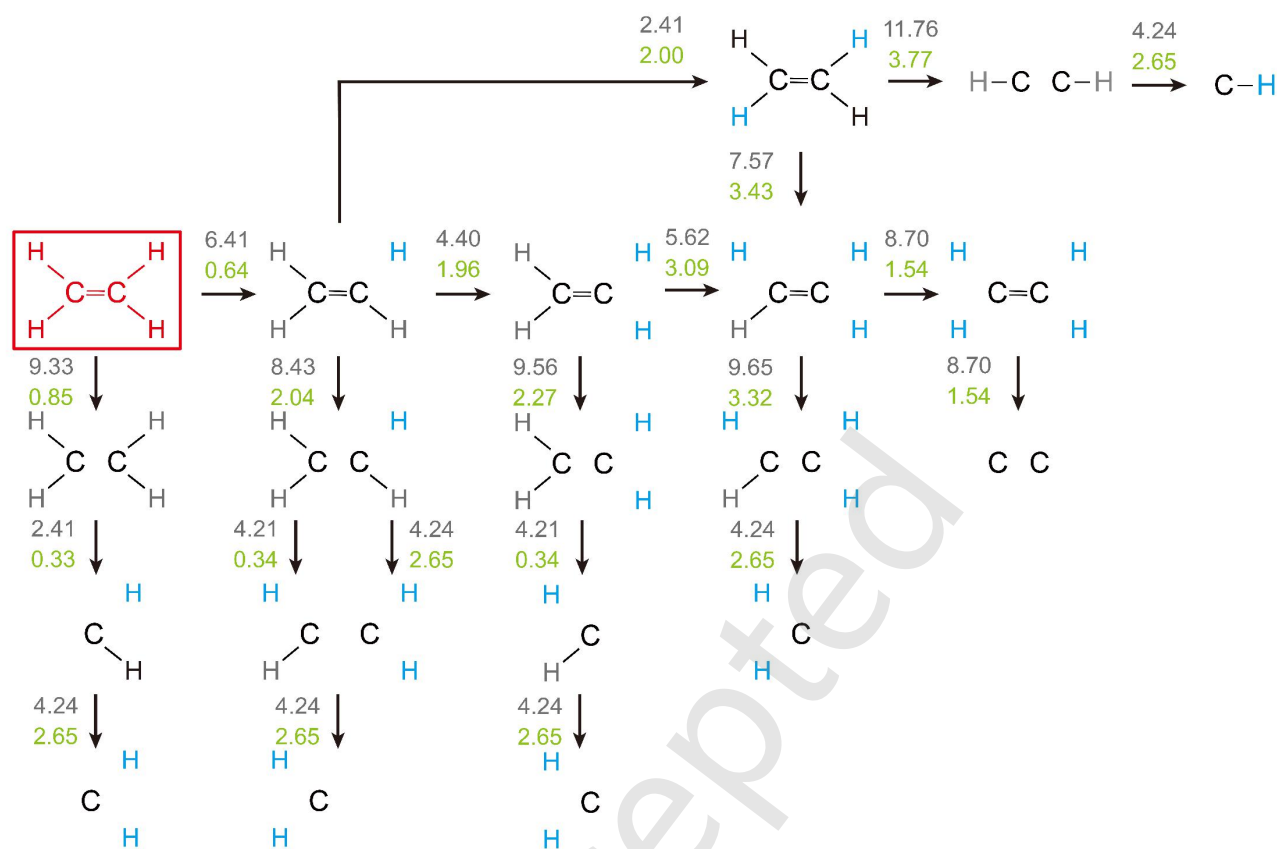


Figure S4. Decomposition energy barriers of the carbon precursor C_2H_4 in vacuum and on the $AlN(000\bar{1})$ surface (gray: vacuum; green: substrate surface).

6. Calculation of thermodynamic population distribution of active species

The relative Gibbs free energies of surface-adsorbed C_xH_y species were calculated to evaluate their thermodynamic stability under different growth conditions. The relative Gibbs free energy was defined as follows[7, 8]:

$$\Delta G_f = E_{tot} - E_{sub} + \Delta F_{vib} - x * \mu_C - y * \mu_H \quad (S6)$$

where E_{tot} and E_{sub} are the total energies of the adsorbed system and the clean substrate, respectively. x and y represent the stoichiometric numbers of carbon and hydrogen atoms in the C_xH_y species. ΔF_{vib} accounts for the vibrational contribution to the Gibbs free energy.

The vibrational contribution was calculated according to:

$$\Delta F_{vib} = h\omega \left(\frac{1}{2} + \frac{1}{e^{\beta h\omega} - 1} \right) - kT \left[\frac{\beta h\omega}{e^{\beta h\omega} - 1} - \ln(1 - e^{-\beta h\omega}) \right] \quad (S7)$$

where $\beta = 1/kT$, and ω represents the vibrational frequency of the adsorbed species.

The hydrogen chemical potential is calculated as:

$$\mu_H = E_{H_2} + kT \ln \left(\frac{kT}{P} \times g \times \xi_{trans} \times \xi_{rot} \times \xi_{vib} \right) \quad (S8)$$

where E_{H_2} is the DFT-calculated energy of the hydrogen molecule, k is the Boltzmann constant, P is the partial pressure of hydrogen, and g represents the electronic degeneracy. ξ_{trans} , ξ_{rot} , and ξ_{vib} denote the translational, rotational, and vibrational partition functions, respectively.

The carbon chemical potential is expressed as:

$$\mu_C = E_{C_xH_y} - \frac{y}{2} E_{H_2} - 2\mu_H^* + kT \ln \frac{P(C_xH_y)}{P(H_2)} \quad (S9)$$

$E_{C_xH_y}$ is the energy of the carbon active species, while μ_H^* represents the contribution of the hydrogen chemical potential associated with temperature and hydrogen partial pressure.

After obtaining the relative Gibbs free energies of different active species, the thermodynamic equilibrium population fractions of these species were calculated according to the Boltzmann distribution:

$$P_i = \frac{\exp(-\Delta G_i/k_B T)}{\sum_i \exp(-\Delta G_i/k_B T)} \quad (S10)$$

where P_i represents the thermodynamic equilibrium population fraction of species i , and ΔG_i is the relative Gibbs free energy of the corresponding species.

7. Details of nucleation rates Calculation

The nucleation rate is calculated based on classical nucleation theory[9, 10]. For the two-dimensional nucleation process, the fundamental expression is given by:

$$R = \omega \times Z \times n_1 \times \exp\left(-\frac{G^*}{kT}\right) \quad (S11)$$

where ω is the attachment rate of active species to a critical-sized cluster, Z is the Zeldovich factor, which corrects for the non-equilibrium concentration distribution around the critical nucleus, n_1 is the monomer density on the substrate surface, and G^* is the critical nucleation barrier.

Furthermore, the attachment rate ω can be expressed as:

$$\omega = n_{edge}^* \times p \times v \times \exp\left(\frac{E_b - E_{diff}}{kT}\right) \quad (S12)$$

Where n_{edge}^* is the number of available edge sites on the critical nucleus, p is the surface coverage of carbon species, v is the atomic attempt frequency, E_b is the activation energy for desorption, and E_{diff} is the surface diffusion barrier. Therefore, the attachment rate ω is collectively determined by the number of effective edge sites on the critical nucleus, the surface coverage of active species, the atomic attempt frequency, and the competition between desorption and diffusion.

8. Structural Evolution of Active Carbon Species during Nucleation

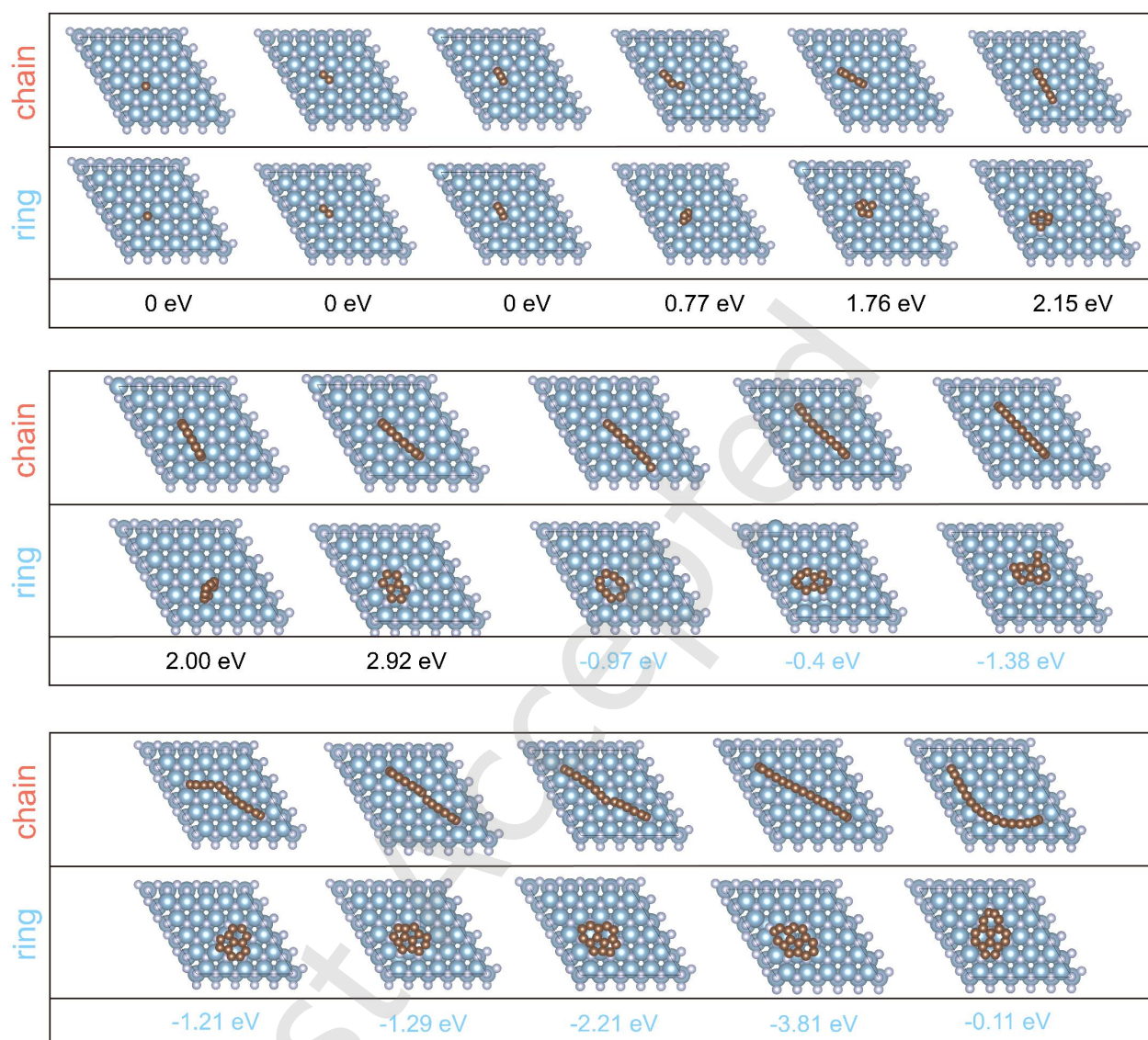


Figure S5. Most stable chain and ring structures and their relative energies for C during nucleation at different carbon atom numbers. The ring structure becomes more stable than the corresponding chain structure at $N = 9$.

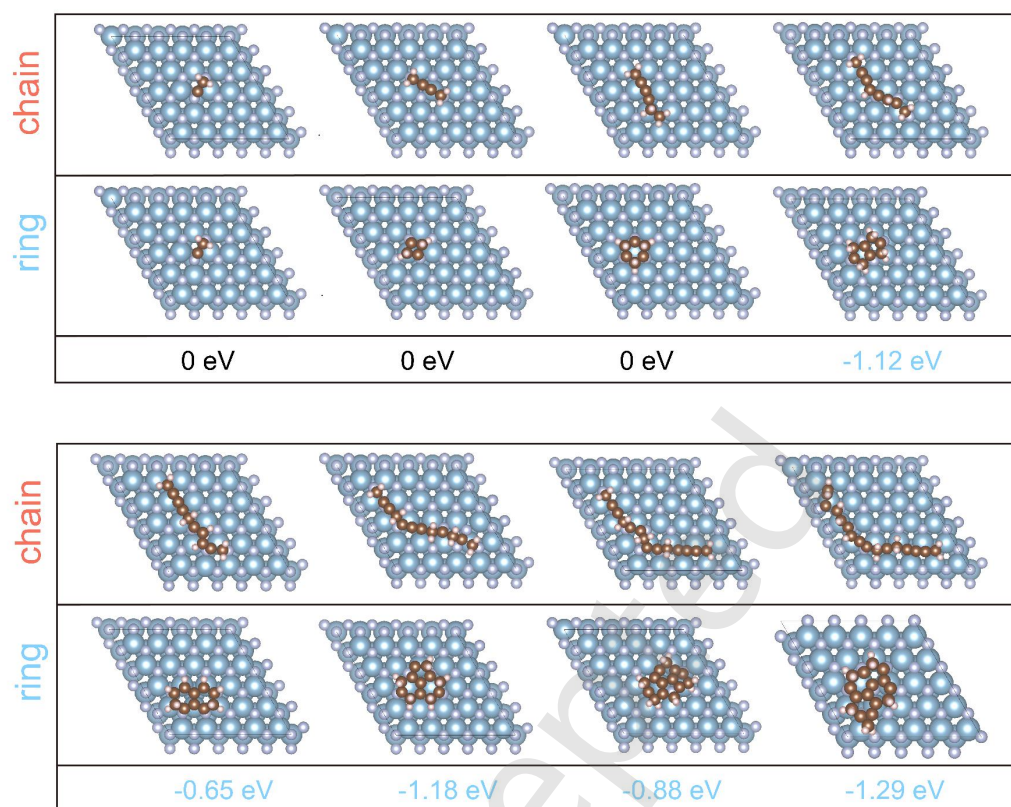


Figure S6. Most stable chain and ring structures and their relative energies for CH₂C during nucleation at different carbon atom numbers. The ring structure becomes more stable than the corresponding chain structure at N = 8.

9. Kinetic Wulff construction theory

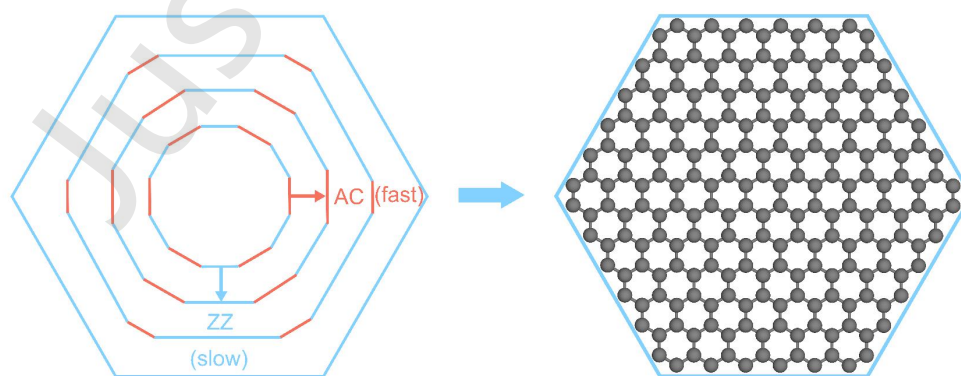


Figure S7. Schematic illustration of the Wulff construction for graphene growth[11]. Owing to the lower growth rate of zigzag (ZZ) edges compared with armchair (AC) edges, the final morphology is dominated by ZZ edges.

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