Morphology-Control Growth of Graphene Islands by Nonlinear Carbon Supply

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Controlling the morphology of graphene and other two-dimensional (2D) materials in chemical vapor deposition (CVD) growth is crucial because the morphology reflects the crystal quality of as-synthesized nanomaterials in a certain way, and consequently it indirectly represents the physical properties of 2D materials such as band gap, selective ion transportation, and impermeability. However, precise control of the morphology is limited by the complex formation mechanism and sensitive growth-environment factors of graphene. Therefore, the CVD synthesis of single-crystal hexagonal-shaped graphene islands with specific sizes is challenging. Herein, an unconventional nonlinear carbon supply growth strategy is proposed to realize controllable CVD growth of desired hexagonal graphene islands with specific sizes on Cu substrates. Large-area graphene films of isolated islands with desired densities, sizes, and distances between the islands were successfully synthesized. Subsequently, the direct growth of a planar-tunnel-junction structure based on two parallel gapped graphene islands was achieved by specific adjustment of the growth and etching processes of graphene CVD synthesis. We therefore demonstrated that the nonlinear carbon supply growth strategy is a reliable method for the synthesis of high-quality graphene and can facilitate the direct growth of graphene-based nanodevices in the future.
1. Introduction

The artificially controlled synthesis of two-dimensional (2D) materials, such as graphene, is crucial because the crystal quality of the resulting material directly influences its performance in electronic nanodevices.\cite{1-4} In particular, the morphology of graphene islands is an intuitive indicator of the crystal quality of as-synthesized graphene materials. Macroscopically characterized hexagonal morphology can indirectly be used to determine the high crystal quality of as-grown graphene islands.\cite{5-8} Currently, several studies were conducted on the morphology control for synthesizing high-quality 2D materials using the chemical vapor deposition (CVD) method. Most of these studies successfully synthesized graphene with various island morphologies and controlled the corresponding crystal qualities by regulating the CVD parameters (e.g., reaction-chamber temperature/pressure, gas flow ratio, etching-assisted growth, multistage carbon supply, etc.) and by modifying the substrates used for CVD growth via electrochemical polishing, oxygen pretreatment, and single crystallization.\cite{9-19} In addition, some approaches successfully achieved specific-sized hexagonal-shaped graphene islands on Cu substrate.\cite{20-22} However, in conventional carbon supply CVD growth, it is not easy to maintain the island shape and produce any-sized hexagonal graphene islands owing to its environmentally sensitive nature and complex mechanisms involved in the continuous growth process.\cite{23-25} It is still challenging to achieve the continuously controllable growth of high-quality hexagonal graphene with varying island sizes.

In our work, we achieve the controllable synthesis of high-quality hexagonal graphene islands with various sizes using an unconventional nonlinear carbon supply growth method. First, the island morphology formation mechanism was investigated based on the nucleation-epitaxy growth mode of graphene CVD synthesis. Subsequently, a nonlinear carbon supply mode
was proposed and experimentally demonstrated as a reliable approach to prepare hexagonal graphene islands with a specific size. Density functional theory (DFT) was used to examine the changes in the shape of the graphene islands for increasing size. Furthermore, by dynamically adjusting graphene growth parameters in the unconventional carbon-supply mode, various types of graphene-based planar-tunnel-junction structures were fabricated, comprising parallel graphene islands with a specific gap (edge-to-edge or corner-to-corner), which are considered a direct-growth platforms for further investigation of the tunneling effect in graphene systems. This direct-growth approach differs from conventional lithography fabrication methods, by preventing chemical contact and contamination, and is thought to be more conducive to improving nanodevice performance and preserving the intrinsic properties of 2D materials. Additionally, a large-area discontinuous quasi-monolayer graphene film with a specific gap spacing between each graphene island was synthesized by precisely tuning the growth-etching dynamic equilibrium, which is expected to provide the foundation for future research on large-area integrated graphene-based tunneling nanoelectronics. This study may circumvent the conventional approach of graphene CVD synthesis by using a constant carbon supply and providing a new approach for reliable and controlled synthesis of high-quality hexagonal graphene. Furthermore, the application of this method to prepare large-area, high-quality, discontinuous gapped graphene films may provide an ideal platform for future physical studies on graphene-based quantum tunneling effects.

2. Results and Discussion

2.1. Graphene Island Morphology under Various Carbon-Supply Modes

The CVD growth of graphene on metal substrates, such as Cu, is based on the catalytic decomposition of methane into active carbon atoms on the metal surface, in which the carbon
atoms nucleate and grow under a continuous carbon supply, eventually forming graphene islands.[26, 27] A key factor affecting the size and shape of the graphene islands on the Cu surface is the dynamic competition between the growth and etching processes, which has been investigated in previous studies.[28-31] Based on a detailed analysis of the growth mechanism, it was observed that the graphene island exhibits different morphologies as the crystal size changes during the growth process under the conventional constant carbon supply growth mode (Figure 1a). During the early stage of the growth process, when the external carbon supply is excessive, the graphene islands exhibit a circular shape (Stage I). As the size of the graphene islands increases, the amount of carbon required to further increase the size of the graphene island increases until equilibrium is reached with the externally supplied carbon. Within this particular range, the graphene islands grow to have an ideal hexagonal morphology (Stage II). However, petal-shaped graphene islands often appear during the later stage of the CVD growth process, i.e., when the external carbon supply is relatively insufficient to cover the entire perimeter of the hexagonal graphene island (Stage III). This suggests that the morphology of the as-synthesized graphene islands was significantly influenced by the real-time carbon supply during the graphene growth process in the CVD system.

Furthermore, according to the analysis of the graphene growth model and from the observations of the $^{13}$C-labeled graphene growth experiments, a relationship between the graphene-island radius and growth time in the constant-carbon-supply growth mode was observed (Figures 1b, c). Based on theoretical calculations and further mechanism investigations (Figure 1d and Figure S1), an unconventional carbon-supply mode for hexagonal graphene formation was proposed, which differs from the conventional constant-carbon-supply mode by means of incorporating a nonlinear increasing carbon-supply mode. This growth strategy can
more easily maintain the single-crystal hexagonal island morphology at various grain sizes by CVD growth than the traditional constant-carbon-supply mode.

2.2. Synthesis of Hexagonal Graphene Islands Using the Nonlinear Carbon Supply Mode

Based on the analysis of the graphene island growth mechanism, the morphology of the graphene islands using different carbon supply modes was experimentally investigated. Notably, during the experiments, the hydrogen gas flowrate was kept constant, and the carbon supply of the CVD system was controlled by regulating the methane flowrate (Figure S2 and Table S1). During the traditional constant carbon supply growth mode, when the carbon supply is much larger than the actual graphene growth requirements (called an oversupply mode), graphene islands exhibit a round morphology with high nucleus densities. The optical images exhibited small liquid drop-like graphene islands with smooth edges (Figure 2a). However, in the undersupply mode, in which the carbon supply is insufficient compared with the actual carbon supply requirements for hexagonal graphene islands growth, graphene preferentially grows along the six-degree symmetric axial direction. Thus, a petal-like island morphology forms, occasionally together with a hexagonal star morphology, which is the most commonly observed graphene morphology obtained using conventional CVD growth (Figure S3). Petal-shaped graphene islands with fractal edges were observed on the Cu substrate by optical microscopy (Figure 2b).

In contrast with the traditional constant carbon supply growth experiments, nonlinear carbon supply experiments were conducted by controlling the methane gas flow ratios during the CVD growth process. Using the nonlinear carbon supply growth mode, graphene islands with an ideal hexagonal morphology and sharp edges were successfully synthesized (Figures 2c, d).
addition to the morphology study, the relationship between the crystal quality of as-grown 2D materials and the carbon-supply modes was investigated by collecting the Raman spectra from the as-grown hexagonal- and petal-shaped graphene islands from the controlled experiments of conventional- and nonlinear-carbon supply CVD growth (Figure S4). Smaller area and lower intensity of D peak signal were observed from the Raman mappings of the hexagonal-shaped graphene islands compared to that of the petal-shaped islands, indicating a relatively high crystal quality of as-grown graphene in the nonlinear carbon supply mode. To investigate the edge structure, the as-synthesized graphene island was transferred onto an Au grid for high-resolution transmission electron microscopy (HR-TEM) imaging at a low voltage of 80 kV (Figure 2e). An atomic sharp edge with a zigzag atom arrangement was observed in the TEM images (Figure 2f). Furthermore, the density of graphene islands on the Cu substrate and their sizes could be adjusted by varying the parameters of the nonlinear carbon supply mode (i.e., methane flowrate, hydrogen flowrate and temperature). The resulting graphene islands were aligned and had a hexagonal shape with the high crystal quality (Figures 2g–i and Figure S5). Notably, in all cases, the as-synthesized hexagonal graphene islands exhibited extremely sharp and straight edges, which suggests that the edges of these hexagonal islands have a zigzag atomic arrangement consistent with the earlier claim.\textsuperscript{[32-34]}

2.3. DFT Simulations of Graphene Islands

Based on DFT simulations, the total energies of petal- and hexagonal-shaped graphene islands were compared, and the favorable shape was determined as a function of the island size. The total energy of per C atom was calculated as $E = (E_{\text{graphene@slab}} - E_{\text{slab}})/n$, where $E_{\text{graphene@slab}}$ and $E_{\text{slab}}$ are the total energies of the Cu(111) slab with and without the graphene island (containing $n$ C atoms), respectively. A circular-shaped island with 12 C atoms was regarded as
nucleus, for which we obtain $E = -7.32$ eV (Figure 3a). For the small (43 C atoms), medium (77 C atoms), and large (189 C atoms) petal-shaped graphene islands shown in Figure 3b–d, we obtain $E = -7.28$ eV, -8.59 eV, and -8.65 eV (Figure S6). For the small (24 C atoms), medium (66 C atoms), and large (181 C atoms) hexagonal-shaped graphene islands shown in Figure 3e–g, we obtain $E = -8.28$ eV, -8.82 eV, and -9.04 eV (Figure S7). In addition, results for circular-shaped graphene islands are provided in Figure S8. According to Figure 3h, the hexagonal-shaped graphene islands are energetically favorable for any size, indicating that they will be formed when the external environment (e.g., carbon supply) is sufficient during the growth of graphene in the CVD process. Otherwise, undesired shapes are possible to be formed.

2.4. Formation of Graphene-based 2D Planar-Tunnel-Junction Structures

Precise control over the growth of sub-monolayer graphene islands was achieved by regulating the dynamic carbon supply process during graphene growth, which led to the successful preparation of graphene-based 2D planar-tunnel-junction structures consisting of parallel hexagonal graphene islands.\textsuperscript{[32, 35, 36]} Under specific growth conditions, tunnel-junction-structured graphene islands formed with a small edge-to-edge gap, which is adjustable from the nanometer to micrometer scale (Figures 4a, b). The high-resolution scanning electron microscopy (SEM) images exhibited the straight–sharp edges of parallel graphene islands with a gap of ~1.15 µm (Figure 4c). Raman spectra collected from the graphene and Cu region exhibited sharp G and 2D peaks ($I_G/I_{2D} = \sim 0.57$), and an absence of a D peak, indicating that the as-synthesized graphene was a high-quality monolayered single crystal (Figure 4d). This is consistent with our previous claim that hexagonal graphene island usually has high crystal quality. Furthermore, graphene-based junction structures with various gap distances were successfully synthesized and characterized by Raman microscope and SEM (Figure 4e, Figures
S9, S10, and Table S2). This unique graphene-based structure, consisting of well-aligned hexagonal islands, could be used as a graphene-based tunneling transistor. By not following the traditional nanofabrication processes such as ultraviolet lithography, electron beam lithography, plasma etching, and patterning, the synthesized graphene-based 2D planar-tunnel-junction structures were free of chemical contamination and unexpected damage, resulting in improved device performance. Moreover, the results are beneficial for evaluating the intrinsic properties of the material.[37, 38]

In addition to these parallel edge-to-edge tunnel structures, it was also possible to fabricate corner-to-corner tunneling structures with specific spacing between the two graphene islands. The extremely sharp–straight edges and clean surface of the as-synthesized graphene islands were observed and confirmed by SEM (Figure 4f). The true component analysis of the Raman mapping clearly indicated that the graphene and Cu regions were separated by a distinct grain boundary (Figure 4g). Raman mapping of the 2D peak intensity exhibited good uniformity and high crystal quality of the as-synthesized single-crystal graphene islands (Figure 4h). The corner-to-corner spacing of 2.23 µm was determined by line scan analysis of the 2D peak intensity across the corners (Figure 4i). By precisely tuning the parameters and controlling the processes of graphene CVD growth, different types and structures of graphene-based planar-tunnel junctions can be realized on a Cu substrate.

2.5. Production of Small-Gapped Quasi-Monolayer Graphene Films

A novel large area of discontinuous quasi-monolayer graphene films (i.e., with small gaps between islands) was fabricated using the developed carbon supply-controlled growth mode. Various types of discontinuous graphene films with different graphene island sizes and
average gap distances were synthesized by precisely controlling and regulating the growth parameters. An optical image shows that nearly every graphene island had a channel gap with its neighbors, and the gap size was adjustable from microns to nanometers (Figures 5a–c). The statistical analysis of the size of the graphene island in the discontinuous films indicated that for larger graphene islands, the gaps formed were larger and the graphene size distribution was relatively more dispersed. However, for smaller graphene islands, the graphene size distribution was relatively more uniform, and the gap size was much smaller (~ nanometer level), and the edges were straighter in appearance (Figure 5d–f). Moreover, a similar phenomenon was observed in the non-hexagonal graphene film.

We found that when graphene islands grow to a certain size when using the nonlinear carbon supply mode, the growing and etching effects can reach dynamic equilibrium by controlling the growth condition, leading to a weak growth-time dependency for the size of the graphene islands. Consequently, in these statues, the gap distances between adjacent islands are nearly unaffected by the growth time in the CVD system. Based on this mechanism, discontinuous large-area graphene films with specific gaps between adjacent islands were controllably fabricated by regulating the nonlinear carbon supply. Since the graphene islands seem to be imperfect hexagonal shaped with a constant gap distance, there is still considerable room to study and improve this approach. The characteristic graphene films have great potential for applications in large-area, highly-integrated graphene-based tunneling electronics along its development (Figure S11).

3. Conclusion
In this study, the formation mechanism of graphene islands with different morphologies was investigated and an unconventional nonlinear carbon supply mode for the synthesis of high-quality single-crystal hexagonal graphene with specific sizing was proposed. In contrast to the conventional carbon supply CVD growth, this nonlinear carbon supply method enables the controllable synthesis of hexagonal-shaped graphene islands with desired sizes. The Graphene-based planar tunnel junction structures were directly synthesized with edge-to-edge and corner-to-corner gap-aligned graphene islands by precise regulation of the CVD growth parameters. Furthermore, the dynamic equilibrium of the growth and etching processes was controlled, leading to the fabrication of large-area discontinuous quasi-monolayer graphene films with gaps between individual islands. These fabricated films serve as a prototype for highly integrated 2D material-based tunnel junctions. This study provides a novel strategy for controlling the synthesis of high-quality hexagonal graphene using an unconventional nonlinear carbon supply by CVD growth, and in the future, will serve as the foundation for the direct synthesis of 2D materials for applications in highly integrated electronics.
4. Experimental Methods

CVD Growth of Graphene Film: The 25 μm-thick polycrystalline Cu foils (99.999 wt%, Alfa Aesar) were polished and then pressed onto the pretreated c-plane sapphire substrate. A long-term annealing was conducted at 1070 °C in H₂ (99.999%, 50 sccm) and Ar (99.999%, 50 sccm) at a pressure of ~ 1 atm to fabricate single-crystal Cu foils. Subsequently, graphene was synthesized on the Cu surface in a CVD system at 1030 °C using a mixture of CH₄ (0.05–20 sccm) and H₂ (10 sccm). After graphene growth, the sample was removed from the furnace and cooled to room temperature under the same gas conditions.

Optical Characterization: Optical images, Raman spectra, and mappings of graphene on Cu substrates were obtained by confocal Raman spectroscopy (Alpha 300 R, WITec) at a laser wavelength of 488 nm.

Electron Microscopy Characterization: SEM (Quattro, FEI) was used to characterize the surface morphology of synthesized graphene islands. HR-TEM images were acquired using a transmission electron microscope (Titan Cs Image, FEI) equipped with an electron beam monochromator and double Cs corrector operated at 80 kV.

DFT Simulations: We employed spin-degenerate density functional theory using the Vienna ab initio simulation package (projector-augmented wave method).[39] The cut-off energy of the plane-wave basis was set to 500 eV. The electronic exchange-correlation potential was modeled in the generalized gradient approximation of Perdew-Burke-Ernzerhof.[40] Van der Waals corrections were included through the zero-damping method of Grimme.[41] Graphene was attached to a two-layer (111) slab cleaved from face-centered cubic Cu and augmented in the out-of-plane direction with a vacuum slab of 12 Å thickness. The energetically favorable stacking was taken from previous work[34] to construct 8 × 8 × 1 and 12 × 12 × 1 supercells. Models of petal-, hexagonal-, and circular-shaped graphene islands with small, medium, and large sizes were built. The Cu atomic coordinates were fixed, whereas the C atomic coordinates were relaxed. Using a 2 × 2 × 1 Γ-centered k-mesh for the Brillouin sampling, the total energies were converged to 10⁻⁵ eV and the Hellmann–Feynman forces were converged to 10⁻² eV/Å.
Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Figure 1. (a) Schematic of the graphene island formation process during CVD growth. (b) Atomic illustration of the variation in size of the hexagonal graphene islands. (c) True component Raman mapping of as-grown isotope-C\textsuperscript{13} labeled graphene islands with commonly seen petal shape. The line scan of the 2D peak intensity of graphene is presented. (d) Relationship between the radius and growth time based on theoretical calculations and experimental results. The C\textsuperscript{12} and C\textsuperscript{13} growth periods were represented by blue and green stars, respectively.
Figure 2. (a) Optical images of round-shaped liquid drop-like graphene islands with smooth edges synthesized under lower constant carbon supply CVD growth mode. (b) Optical images of petal-shaped graphene islands with fractal edges synthesized under constant oversupply of carbon by CVD. (c–d) Optical and SEM images of as-synthesized hexagonal-shaped graphene islands. (e–f) Low- and high-resolution TEM images of the edge structure of the hexagonal island. (g–i) Optical images of various sizes and densities of hexagonal-shaped graphene islands synthesized under the unconventional nonlinear carbon supply growth mode.
**Figure 3.** Atomic structures of (a) the graphene nucleus, (b) small-, (c) medium-, and (d) large-sized petal-shaped graphene islands, and (e) small-, (f) medium-, and (g) large-sized hexagonal-shaped graphene islands on Cu(111). All the images are viewed in the <0001> direction. The Cu and C atoms are shown in brown and black. (h) Total energy per C atom of the graphene islands.
Figure 4. (a–b) Schematic of the graphene-based 2D planar tunnel-junction structure. (c) False-color SEM image of the typical tunnel-junction structure consisting of two aligned hexagonal graphene islands with a gap size of ~1.15 µm. (d) Raman spectra of graphene and Cu collected from the marked regions in (c). No noticeable D peak can be observed in the graphene spectrum. (e) Raman mappings of various as-synthesized gapped graphene islands with different gap distances. The line profile (along the marked line) is plotted below each image. (f) SEM image of the corner-to-corner planar tunnel-junction structure. (g) True component Raman mapping of graphene and Cu signals of the corner-to-corner structure. (h) Raman mapping of the 2D peak intensity of the region in (g). (i) Line profile of the Raman signal intensity of the 2D peak along the marked line plotted in (h).
Figure 5. (a–c) Optical microscopy images of the as-synthesized small-gapped quasi-monolayer graphene film with various graphene island sizes and gap distances. Enlarged inverted color image of the selected gap areas: (a) 1.54 µm gap size with an inset scale bar of 4 µm, (b) 0.71 µm gap size with an inset scale bar of 2 µm, and (c) 0.22 µm gap size with an inset scale bar of 0.5 µm. (d–f) Statistical size distributions of graphene islands under different nonlinear carbon supply growth processes.
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Toc text:
An unconventional nonlinear-carbon-supply growth strategy for synthesizing hexagonal graphene with specific sizes is presented. The dynamic adjustment of the carbon supply and precise control of the growth and etching processes resulted in the direct growth of graphene-based tunnel-junction structures and small-gapped quasi-monolayer films. This study provides a foundation for directly synthesizing 2D materials for applications in highly integrated electronics.

Toc figure: