Fractal-Theory-Based Control of the Shape and Quality of CVD-Grown 2D Materials

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The precise control of the shape and quality of 2D materials during chemical vapor deposition (CVD) processes remains a challenging task, due to a lack of understanding of their underlying growth mechanisms. The existence of a fractal-growth-based mechanism in the CVD synthesis of several 2D materials is revealed, to which a modified traditional fractal theory is applied in order to build a 2D diffusion-limited aggregation (2D-DLA) model based on an atomic-scale growth mechanism. The strength of this model is validated by the perfect correlation between theoretically simulated data, predicted by 2D-DLA, and experimental results obtained from the CVD synthesis of graphene, hexagonal boron nitride, and transition metal dichalcogenides. By applying the 2D-DLA model, it is also discovered that the single-domain net growth rate (SD-NGR) plays a crucial factor in governing the shape and quality of 2D-material crystals. By carefully tuning SD-NGR, various fractal-morphology high-quality single-crystal 2D materials are synthesized, achieving, for the first time, the precise control of 2D-material CVD growth. This work lays the theoretical foundation for the precise adjustment of the morphologies and physical properties of 2D materials, which is essential to the use of fractal-shaped nanomaterials for the fabrication of new-generation neural-network nanodevices.

2D materials, including graphene, hexagonal boron nitride (h-BN), and transition metal dichalcogenides (TMDs), have attracted considerable interests from the materials science community, due to their remarkable electrical,^[1] optical,^[2] mechanical,^[3] and thermal properties.^[4] Because the physical properties

and performances of nanodevices highly depend on the shape and quality of 2D materials,^[5] various routes have been explored to synthesize high-quality controllable-shaped 2D materials. This has led to the development of different synthesis methods including mechanical exfoliation,^[6] liquid-phased exfoliation,^[7] and chemical vapor deposition (CVD).^[8] CVD has been shown to be the most performant synthetic method, and is currently the most widely used for large-scale fabrication of high-quality 2D materials.^[9] Tremendous efforts have been made to control the CVD synthetic process, for example, growing large single crystals of graphene by limiting the growth process to one nucleus,^[10] fabricating wafer-scale single crystals of h-BN on liquid-gold substrates,^[11] or depositing 2D transition-metal chalcogenides via adding molten salt.^[12] However, to achieve the precise control of the growth process of 2D materials, it is essential to take into account its underlying physical mechanisms. Many attempts have been made to explore the

atomic mechanism and grow higher-quality materials by considering the oxygen effect,^[13] the hydrogen etching,^[14] the edge-energy equilibrium,^[15] the classical Wulff structure,^[16] and the phase-field approach in the past years.^[17] However, due to a large number of influenced factors and the underlying intricate nanoscale physical mechanisms, the precise control of the shape and quality of CVD-grown 2D materials, till now, is still regarded as a formidable challenge.

Our study shows that dendritic-structured patterns commonly appear during the CVD growth processes of various 2D materials. To understand this phenomenon, we investigate the growth mechanisms in the framework of the fractal theory.^[18] Although, in the past, this theory has provided an explanation for the sound of irregular or fragmented natural structures and self-similar patterns with the unfolding symmetry,^[19] this theory has never been applied, to our knowledge, to the interpretation of growth mechanisms of CVD-grown 2D materials. Here, we demonstrate, both experimentally and theoretically, the existence of fractal growth mechanisms in the CVD growth process of graphene, h-BN, and molybdenum disulfide (MoS₂). Based on the classic diffusion-limited aggregation (DLA),^[20] a typical model of the fractal theory, we develop an

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unconventional 2D-DLA model to precisely describe the micro-dynamics involved in the CVD growth of 2D materials; we then validate our model by showing a perfect match between numerical-simulated results and CVD experimental data. Additionally, by analyzing the micromechanisms of 2D-DLA, we find that the single-domain net growth rate (SD-NGR), defined as the single-crystal domain-size increase per unit growth time, serves as a determining factor of the shape and quality of the crystals in CVD-grown graphene, h-BN, MoS₂, and, likely, many other 2D materials. By adjusting the SD-NGR in the CVD process, we synthesize nanomaterials of various fractal morphologies and different crystal qualities in a controllable manner.

In CVD processes, we find that most 2D materials such as graphene, h-BN, and MoS₂ regularly form specific *n*-fold (*n* = 2, 3, 4, and 6) symmetry-shaped patterns with self-similar edges that are typical characteristics of classical fractal geometries (Figure S1, Supporting Information).^[18] Based on this observation and the published literature on graphene fractal etching,^[21] we attempt to analyze the micromechanisms underlying the CVD synthesis of 2D materials, using fractal theory. As a significant component of this theory, the DLA model, which describes the molecular dynamics associated with, for example, the random walking of atoms in Brownian motion,^[22] as well as their clustering and aggregation,^[23] has not yet been applied to the direct CVD synthesis of 2D materials due to the differences between the release modes of the source atoms and the types of covalent bonds. Here, we develop a modified DLA model (Table S1, Figure S2, Supporting Information), the 2D-DLA, specifically designed for the CVD growth of 2D materials, taking into account the various condensed modes unique lattice structures, thermal energy influences, and gases chemical reactions involved in CVD processes.^[24]

Graphene, the “mother” of 2D materials and an ideal platform for the investigation of fundamental growth mechanisms of 2D materials,^[25] is selected as the prototype for our study. First, we use the 2D-DLA model to simulate the CVD growth process of graphene in six sequential phases (Figure 1a): (I) stochastic releasing; (II) nucleation, (III) docking; (IV) recrystallization; (V) hexagonization; (VI) film forming. At the beginning of phase I, carbon atoms are stochastically released from the peripheral, 2D-released mode, and the interior quasi-3D-released mode of the effective area that experimentally corresponds to the surface of the copper substrate (Figure S3, Supporting Information). Once the atoms have been released or have landed, they start to move, in Brownian motion, within the effective area. Phase II is defined by the fact that a single atom is attached to the defect of the substrate and behaves as the nucleus does.^[26] In phase III, once a free atom governed by the Brownian motion accidentally gets close enough to another atom or nucleus, it bonds and becomes stationary. In phase IV, based on the principle of minimum energy^[27] and under the influence of the hydrogen chemical and thermal energies, the metastable stationary atoms may depart from the lattice as free atoms. However, stable stationary atoms remain at their positions, whereas free atoms tend to go to the more stable sites resulting in an increase in the proportion of stable atoms in the graphene lattice. In the last two phases, V and VI, the distinct hexagon-shaped graphene domains emerge, grow epitaxially, and eventually form the graphene film.

In a 2D-DLA simulation, a fractal-tree shape (a typical fractal pattern, see Figure S4, Supporting Information) is formed when the atom-releasing process is limited to the 2D-released mode (Figure 1b). To assess the robustness of the 2D-DLA model, when applied to the real case scenario of CVD growth of graphene, we design a specific, 2D-released composite-structured substrate, which involves covering this copper substrate (99.8%, Alfa-Aesar) with a small-sized (25 mm²) squared sapphire chip (C-axis, Alfa-Aesar) that limits the active carbon atoms to diffuse only from the edges of the sapphire chip, instead of stochastically generating from the covered copper surface (Figure S5, Supporting Information). Using this sapphire-copper (Al₂O₃/Cu) substrate, we synthesize another similar tree-branch-shaped graphene domain by CVD, under gas using 10 sccm of CH₄ and 20 sccm of H₂, *T* = 1030 °C (Figure 1c), applications with the goal of building carbon-based nano-neural-network structures.^[28] We find that our 2D-DLA model is able to precisely simulate the CVD growth of graphene based on the morphology of CVD-grown graphene (Figure 1c) and the simulation results (Figure 1b) obtained with this model. In addition to the particular 2D-released situation as mentioned earlier, we confirm the applicability of 2D-DLA under regular synthetic conditions by altering the quasi-3D-released mode, which leads to quasi-hexagonal star-shaped simulation results (Figure 1d). As expected, an almost identical graphene domain was synthesized by CVD under the conditions with growth environment of CH₄ = 10 sccm, H₂ = 10 sccm, and *T* = 1030 °C (Figure 1e). It is worth noticing the presence of several unexpected holes in the pattern of simulation results as well as an activation of the D-peak by the defects, revealed by the Raman spectrum of the CVD-grown graphene. To obtain higher-quality, defect-free graphene, we analyze the 2D-DLA model; we find out that when the release rate of the active carbon atoms is significantly decreased (using the 2D-DLA model), the holes disappear and the shapes of simulated patterns tend to be regular hexagons (Figure 1f). In light of these findings, we lower the rate at which active carbon atoms are generated by increasing the ratio of H₂/CH₄ to 50 sccm: 5 sccm under the same growth temperature of 1030 °C; this allows us to obtain a high-quality, defect-free, hexagonal graphene domain by the CVD growth (Figure 1g).

After further analysis, we find that the SD-NGR, under the effect of condensation and etching in the recrystallization phase, acts as a determining factor of the shape and quality of the domains in CVD-grown 2D materials. During the recrystallization phase of graphene's CVD synthesis (Figure 2a), free-active carbon atoms, produced by the decomposition of methane catalyzed by copper substrates, or secondary carbon atoms from the etching process, tend to locate at lower-energy empty sites and become covalently bonded atoms (condensation process). At the same time, due to the external excitation energy (*E*_{T,H}) supplied by high temperature of the furnace and the chemical activities of hydrogen, metastable single-bond atoms and parts of double-bond atoms may escape from the lattice, becoming secondary active carbon atoms or leaving as gaseous hydrocarbon (C_xH_y) (etching process). During the CVD synthesis, controlling the growth temperature or gas mass-flow ratios of hydrogen and methane allows us to adjust the level of *E*_{T,H} in the region from the double-bond-atom energy level (*E*₂) to the triple-bond-atom

Figure 1. 2D-DLA model combining fractal-theory-based DLA and the physical mechanisms of graphene's CVD growth. a) Schematic of 2D-DLA processes. b) A fractal-tree pattern formed by 2D-DLA simulation in 2D-released mode. c) CVD-synthesized graphene in the low ratio of H_2/CH_4 with the specific Al_2O_3/Cu substrate, which differs from regular shapes of graphene (scale bar: 10 μm). d) A pattern of 2D-DLA simulation with the quasi-3D-released mode, where defected holes can be noticed in the simulation result. e) Common-shape graphene synthesized by CVD (scale bar: 50 μm). f) Sixfold symmetry structures of a quasi-hexagonal shape obtained from 2D-DLA simulation for enhanced recrystallization processes. g) Perfect hexagonal graphene domain fabricated under a higher ratio of H_2/CH_4 (scale bar: 50 μm).

energy level (E_3). Changes of $E_{T,H}$ influence the relative intensity of the etching process and the condensation process by altering the possibilities of metastable atoms escaping from the lattice, and eventually determine the SD-NGR in the recrystallization phase (Figure 2b). As the SD-NGR decreases, more atoms tend to stay in lower energy states, rather than metastable energy states (e.g., single-bond-atom or double-bond-atom states). In this case, the etching effect is improved, and the shape of the domain gradually changes to a standard hexagon. In addition to affecting the shape of the domains, the SD-NGR also impacts on the quality of the crystal by taking part in both the

formation and the removal of defects during the growth process (Figure 2c). When we lower the SD-NGR by increasing the ratio of the flow of H_2/CH_4 or the growth temperature, a larger $E_{T,H}$ is exerted, which raises the possibility of removing or repairing the defects generally formed during the graphene's growth process, which ultimately improves the quality of the graphene crystals (Figure 2d).

Based on the descriptions of the microprocesses, we hypothesize that the SD-NGR, a pivotal parameter influencing the shape and quality of the domains, itself depends on multiple factors including gas mass flow ratios, growth temperature,

Figure 2. Precise control of the graphene shapes and qualities by utilizing the SD-NGR. a) Schematic of domain-shaped changes from star to hexagon under the influence of SD-NGR, which is determined by condensation and etching processes. b) Energy diagram of the free-atom level (FA), the single-bond-atom level (SA), the double-bond-atom level (DA), the triple-bond-atom level (TA) and external-excited energy level ($E_{T,H}$) which is determined by the growth temperature and ratio of H_2/CH_4 . c) Schematic of the improvement process of crystal qualities by removing defects from extra atoms and repairing vacancy defects in the recrystallization process. d) Energy diagram of defected and perfect structure status. $E_{T,H}$ provides the energy for the defected structure to get over the potential barrier and become perfect graphene. e) Raman mappings and spectra of star-shaped graphene synthesized at the lower ratio of H_2/CH_4 (scale bar: 60 μm). f) Raman characteristics of hexagonal-shaped graphene with a higher gas-rate ratio in CVD (scale bar: 20 μm). g,h) Raman mappings and spectra of different crystal-quality graphene synthesized at 1000 and 1070 °C, respectively (scale bar: 100 μm). i) Raman mappings and spectra typify low nucleation density brings large leaf-like graphene petals (blue point area) (scale bar: 60 μm). j) Magnified view of high nucleation density results in the forming of small hexagon-shaped graphene (scale bar: 20 μm).

and nucleation densities. First, by adjusting the gas-flow ratio of H_2/CH_4 at a set growth temperature, we can adjust the SD-NGR by influencing the generation rates of active carbon atoms that determine the relative intensities of the condensation and etching processes. This leads to the synthesis of uniformly distributed petal-shaped graphene for a relatively large value of SD-NGR (Figure 2e); however, high-quality hexagonal domains of graphene are obtained using a much smaller value of SD-NGR (Figure 2f). In addition to the gas environment, the growth temperature is another factor influencing the SD-NGR as it affects the energy level of $E_{T,H}$ to further adjust the etching effect intensity. To verify this statement, we synthesize a sublayer of graphene at two different growth temperatures, 1000 and 1070 °C, under similar gas conditions (CH_4 : H_2 = 10 sccm: 20 sccm). Raman mappings and spectra (with D-peak) reveal the existence of a number of defects in

the hexagonal-star domain fabricated at 1000 °C (Figure 2g), whereas perfect, defect-free hexagonal domains of graphene are obtained at the higher temperature of 1070 °C (Figure 2h).

Additionally, using the 2D-DLA model allows us to investigate the influence of nucleation densities on the shape and quality of single domains. Under the same growth conditions of the gas environment and the furnace's temperature, in terms of two different nucleus density substrates, the total amount of active carbon atoms being generated on the copper-substrate surface, per unit time is equal. Therefore, higher values of nucleation densities lead to fewer active carbon atoms being captured by each nucleus on average, resulting in smaller values of the SD-NGRs, leading to the formation of high-quality, hexagonal-shaped domains. Similarly, a CVD-growth experiment conducted on a chemically electropolished copper substrate with a rough, nonuniform surface under CH_4 : H_2 = 20 sccm:

Figure 3. SEM images of a series of 2D-material patterns with typical fractal shapes in the precisely controlled CVD growth. a) A fractal-tree-shaped graphene domain with specific growth substrate structures (scale bar: 10 μm). b) Petal-shaped graphene for a low gas-flow ratio of hydrogen and methane (scale bar: 50 μm). c) Perfect hexagonal-shaped graphene domains in a high ratio of H_2/CH_4 in the copper substrate (scale bar: 50 μm). d) Self-similar structures h-BN under the gas-flow ratio of $\text{H}_2/\text{Ar} = 10$ sccm: 10 sccm (scale bar: 10 μm). e) Quasi-hexagonal domains for a medium gas-flow ratio of H_2/Ar (scale bar: 20 μm). f) Regular triangular-shaped h-BN domains in a high ratio of H_2/Ar (scale bar: 20 μm). g–i) Fractal-shaped MoS_2 domains fabricated in the condition of argon gas flow from 30, 17, and 5 sccm, respectively (scale bar: 10 μm).

20 sccm, $T = 1030^\circ\text{C}$ reveals that areas with much lower nucleus densities have poor-quality, large, leaf-shaped graphene (Figure 2i), whereas areas with higher nucleus densities exhibit tiny regular hexagonal graphene domains of high-quality crystals (Figure 2j). This phenomenon leads us to conclude that the graphene of superior quality graphene can also be obtained for high nucleation densities and at extremely low values of SD-NGR, and also for low nucleation densities values generally obtained during the CVD growth process.

In light of these findings, we broaden the equivalent SD-NGR effect to other 2D materials such as h-BN and MoS_2 , due to their analogous lattice structures, electronic gas distribution modes, and synthetic methods. Under the guidance of 2D-DLA, we synthesize graphene at a low gas-flow ratio of hydrogen and methane ($\text{CH}_4/\text{H}_2 = 10$ sccm: 20 sccm, $T = 1030^\circ\text{C}$), for 10 min, on a custom-designed $\text{Al}_2\text{O}_3/\text{Cu}$ substrate, using a CVD growth process (Figure S6, Supporting Information). We obtain fractal, tree-shaped graphene domains (Figure 3a). When changing to a general copper substrate and a flow rate ratio $\text{CH}_4/\text{H}_2 = 5$ sccm: 20 sccm under the same growth temperature of 1030°C during the CVD synthesis, we find that after 10 min graphene domains exhibiting a quasi-sixfold

symmetry petal shape and with typical fractal characteristics are being formed (Figure 3b). To lower the SD-NGR in the synthesis process, we increase the H_2/CH_4 to 60 sccm: 5 sccm, keep the temperature at 1030°C , and extend the time of the CVD growth process to 50 min. This leads to the formation of perfect, hexagonal-shaped domains with a sixfold symmetry (Figure 3c). Similarly to the way we control the shape of the graphene domains during the CVD process, we grow various fractal-shaped single crystals of h-BN by adjusting the gas-flow rate ratios of hydrogen and carrier gas argon (Ar) (Figure S9, Supporting Information), under the source-region temperature of 90°C and sufficient amount of borazine source (97%, Sigma-Aldrich). We synthesize several fractal-shaped h-BN domains by CVD with the growth temperature of 1050°C , including the self-similar structure under the gas-flow ratio of $\text{H}_2/\text{Ar} = 10$ sccm: 10 sccm (Figure 3d), the quasi-hexagonal domains with 10 sccm argon and 7 sccm hydrogen (Figure 3e), as well as the most stable triangular-shaped h-BN with a triad symmetry, with $\text{H}_2/\text{Ar} = 20$ sccm: 5 sccm (Figure 3f). Furthermore, we assume that the 2D-DLA model is suitable for the synthesis of TMD materials, the third-generation 2D materials. We select MoS_2 , one representative TMD material, and conduct

Figure 4. Electrical transport property measurements of graphene-based FET. a) The 3D-view schematic of the FET structure. b) Side view of the measurement circuit, dielectric thickness ≈ 300 nm SiO_2 , channel length ≈ 10 μm , and width ≈ 20 μm . c) Resistance (R) versus back-gate voltage (V_g) from -15 to $+15$ V. Three graphene samples of different crystal qualities were obtained, for three different SD-NGR settings: $80 \mu\text{m}^2 \text{min}^{-1}$ (black), $50 \mu\text{m}^2 \text{min}^{-1}$ (blue), and $20 \mu\text{m}^2 \text{min}^{-1}$ (red). d) Holes mobilities μ of 20 sets of graphene samples with SD-NGR from 1 to $100 \mu\text{m}^2 \text{min}^{-1}$.

experiments at various gas-flow rates of Ar, at a fixed temperature (180°C) for the precursor sulfur source (99%, Sigma-Aldrich). We obtain three different shapes for the domains by CVD with growth temperature of 800°C (Figure S10, Supporting Information), under Ar gas-flow ratios of either 30, 17, or 5 sccm: spherical fractal-tree shape (Figure 3g), quasi-sixfold symmetry star shape (Figure 3h), and a standard threefold symmetry triangular MoS_2 single crystal (Figure 3i).

Electrical transport is a crucial physical property to consider when evaluating the performance of electronics and other nanodevices, and is directly related to the crystal quality of 2D thin films.^[29] Therefore, in order to be able to precisely adjust the electronic properties by controlling the crystal quality of graphene under the guidance of fractal-theory-based 2D-DLA model, we fabricate a series of graphene field-effect transistors (G-FETs) using graphene samples of various crystal qualities (Figure 4a and the Supporting Information). Samples are synthesized individually for several SD-NGR values of CVD and transferred on top of h-BN/ SiO_2 /Si substrates (Figure 4b). The electrical transport of CVD-grown graphene samples with three values of SD-NGR is measured using I - V curves by a physical property measurement system (PPMS) (Figure 4c). The transport of carriers in G-FET can be described using a drift-diffusive model, and the total resistance of the device can be expressed as

$$R_{\text{Total}} = R_s + \frac{L_G}{W_G} \frac{1}{q\mu n} \quad (1)$$

where R_s denotes the contact resistance between the source (or drain) and the graphene, L_G and W_G , the length and width of the graphene channel, μ and n , the mobility and concentration of the carriers (electrons or holes), and q , the electron charge. The term $L_G/q\mu n W_G$ represents the resistance of the graphene channel under the gate control. Calculated values of holes mobilities are 463, 554, and $1035 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$, respectively (Supporting Information). To demonstrate the accurate control of the graphene crystal qualities and electronic properties, we measure 20 sets of G-FET Dirac curves from various SD-NGR graphene samples and calculate their carrier mobilities.^[30] A statistical distribution implies that the carrier mobilities increase with decreasing SD-NGR (Figure 4d). h-BN capacitors and MoS_2 FETs are also fabricated using CVD-grown samples (Figure S12, Supporting Information). More details on the measurement of physical properties will be included in future work.

In this study, we combine a traditional fractal-theory-based DLA model with the CVD-growth process of 2D materials to develop a novel 2D-DLA model that explains some of the intricate micromechanisms underlying the synthesis of 2D materials using CVD. Based on a comparative analysis of this new 2D-DLA model with experimental results, we isolate SD-NGR as a key factor affecting the shape of the domains and the crystal quality of 2D materials. We synthesize several representative single-crystal 2D materials of different shapes and crystal qualities, and demonstrate the perfect match between our 2D-DLA model and the CVD experimental results. Finally, we

fabricate graphene-FET nanodevices to show the significance, accuracy, and reliability of our 2D-DLA model, when applied to the fabrication of high-performance 2D electronics. This work provides a new approach to elucidate the physical mechanisms of the CVD-growth process of 2D materials, at the nanoscale, using the fractal-growth theory; it provides an interesting alternative to further improve the performance of existing 2D materials, and a tool to explore new low-dimensional materials. Moreover, the precise control of the growth process of 2D materials opens new avenues to design new-generation, low-dimensional, nanomaterial-based artificial intelligence nanodevices.

Experimental Section

Synthesis of 2D Materials: Details on the synthetic and transfer methods used for graphene, h-BN, and MoS₂ can be found in Section S6–S9 (Supporting Information).

Measurements: Raman spectra and mappings of graphene and MoS₂ were obtained by confocal Raman spectroscopy (WITec Alpha 300R, Ulm, Germany) with the 488 nm laser wavelength, 10 mW laser energy power, and 300 nm resolution. Scanning electron microscopy (SEM) images were obtained by ZEISS MERLIN. The Dirac *I*–*V* curves were measured using a physical property measurement system (PPMS, Quantum Design).

Numerical Simulations: Numerical molecular dynamics simulations were conducted on the Supercomputer of Cray XC40 SHAHEEN II at KAUST.

Supporting Information

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

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Conflict of Interest

The authors declare no conflict of interest.

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