Supporting information

Etching-Controlled Growth of Graphene by Chemical Vapor Deposition

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1 Experiment parameters

Table S1. The experiment parameters of the etching-controlled growth of graphene on Cu surface by low pressure chemical vapor deposition.

Experiment number (#)	The flow rate ratio of CH_4 to H_2 (sccm)	Growth pressure (Pa)	Growth temperature (℃)	Growth time (min)
1	0.5:15	60	1020	30
2	0.5:20	85		
3	0.5:25	120		
4	0.5:30	160		
5	0.5:35	190		
6	05:40	240		
7	0.5:45	310		
8	0.5:50	410		

2 Supplementary SEM and optical microscope characterizations

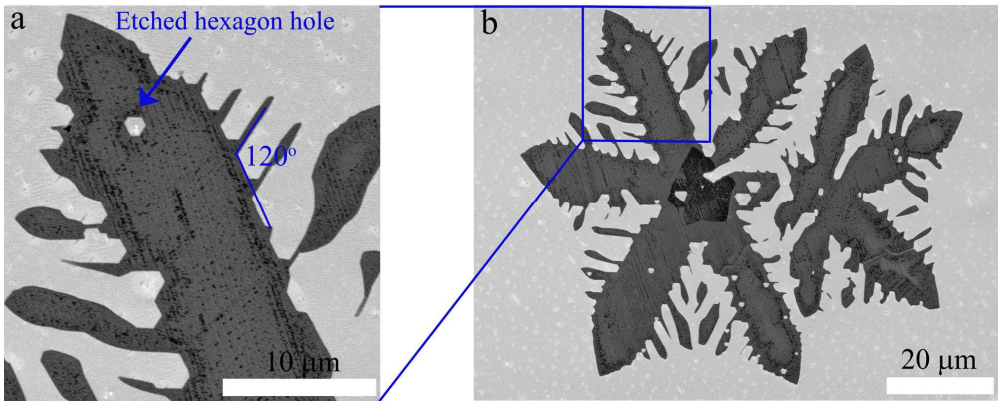

Figure S1. (a) Magnified SEM image taken from a lobe of (b) graphene with etching-controlled growth using a mixture of 0.5 sccm CH_4 and 30 sccm H_2 by low pressure CVD.

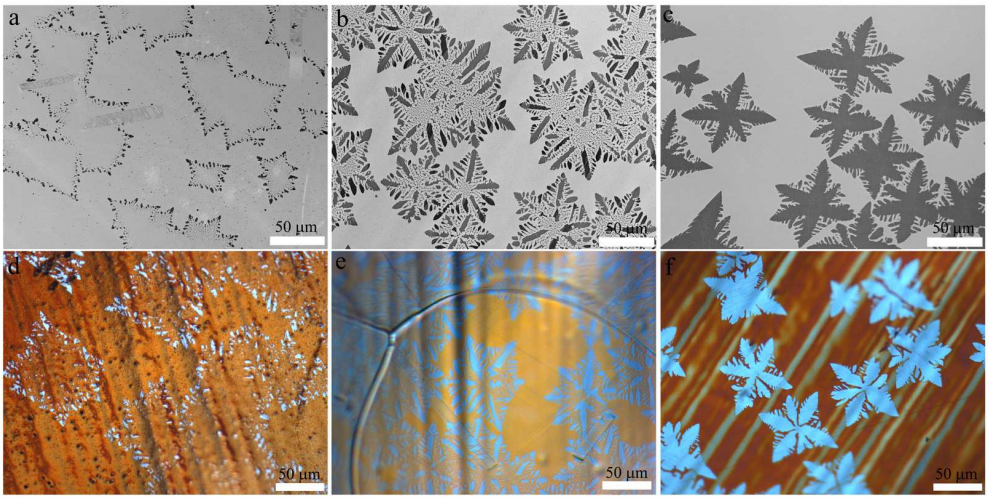

Figure S2. (a-c) SEM images and corresponding (d-f) optical images of graphene with etching-controlled growth using different H_2 flow rate (15, 25, 30 sccm) and 0.5 sccm CH_4.

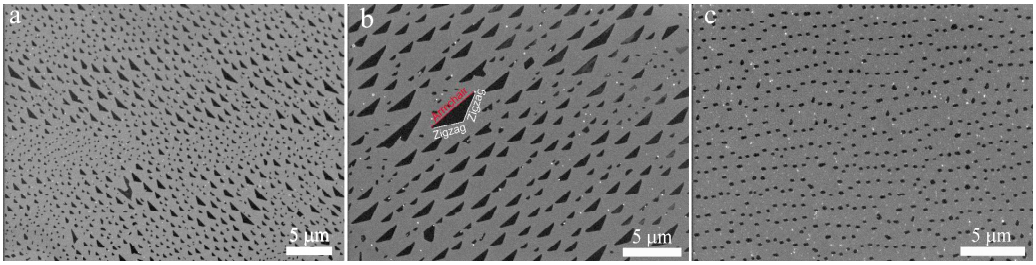

Figure S3. SEM images of graphene debris formed during the etching-controlled growth of graphene using a mixture of 0.5 sccm CH_4 and 20 sccm H_2 by low pressure CVD.

4 Details of phase-field theory and the simulations

In phase-field models [1-3], one order parameter is introduced to characterize the phase of material, which varies smoothly between multiple phases with a diffused interface of finite width. In our simulations to simulate the growth and etching patterns of graphene, the phase-field model consists of an order parameter ψ and a concentration field u for the carbon species. The order parameter ψ equals -1 for the graphene-absent substrate and 1 for the graphene layer. In addition, it is generally agreed that the CVD growth process of graphene on copper follows nucleation-growth model, which begins with an influx of precursors onto the copper surface. This leads to a local supersaturation of active carbon species and triggers the nucleation of graphene domains. The growth of these budding nuclei depletes the carbon concentration within their vicinity, leading further expansion growth of graphene. So, based on this view, the dynamics of the growth process are highly influenced by the flux rate of precursors (F) onto the Cu surface and further the concentration of the carbon species (u). Here our phase-field simulation also includes these two critical parameters. With carbon species deposited onto the substrate with flux F, the concentration field is $u(x, y)$, and the equilibrium concentration of the carbon species on the surface is u_{eq}.

The relation between u and u_{eq} determines whether the growth and etching process is dominating. The free energy functional $G(\psi, u)$ is constructed based on that given by Karma and Plapp [1,3], which can be expressed as

$$G = \int \frac{1}{2}\varepsilon^2 |\nabla\psi|^2 + \frac{1}{\pi}\cos[\pi(\psi-\psi_0)] - \varphi(u-u_{eq})\{\psi + \frac{1}{\pi}\sin[\pi(\psi-\psi_0)]\} \quad (1)$$

The growth equations for ψ and u can be written as,

$$\begin{aligned}\tau_\psi \frac{\partial\psi}{\partial t} &= -\frac{\partial G}{\partial\psi} \\ &= -\frac{\partial}{\partial x}(\varepsilon\varepsilon'\frac{\partial\psi}{\partial y}) + \frac{\partial}{\partial y}(\varepsilon\varepsilon'\frac{\partial\psi}{\partial x}) + \varepsilon^2\nabla^2\psi + \nabla(\varepsilon^2).\nabla\psi \\ &\quad + \sin[\pi(\psi-\psi_0)] + \varphi(u-u_{eq})\{1+\cos[\pi(\psi-\psi_0)]\}\end{aligned} \quad (2)$$

$$\tau_\psi \frac{\partial u}{\partial t} = D\nabla^2 u + \frac{(1-\psi)}{2}(F - \frac{u}{\tau_s}) - \frac{1}{2}\frac{\partial\psi}{\partial t} \quad (3)$$

Here ε is a small parameter which determines the thickness of the interface. The anisotropy of the graphene edge energy is included in terms $\varepsilon = \varepsilon_0[1+\delta\cos(n\theta)]$ and $\varepsilon' = -\varepsilon_0\delta n\sin(n\theta)$, where ε_0 is the mean value of ε, δ is the strength of the anisotropy and n corresponds to the symmetry (n = 6 for six-fold anisotropy in this work). The characteristic time of attachment of the carbon species is τ_ψ, the mean life time of the species on the surface is τ_s with $\tau_\psi << \tau_s$. F is the flux of the carbon species arriving at the surface, φ is a dimensionless coupling constant and D is the diffusion coefficient of the carbon species. The minima of the free energy G is at $\psi - \psi_0 = 2m+1$, where m is an integer that is independent of u. The growth morphology of graphene is controlled by the competition among a few parameters, such as the flux F, equilibrium concentration of the carbon species u_{eq}, and the diffusion coefficient D (D

is a constant in this work), but its symmetry is controlled by the graphene edge energy, that is, six-fold anisotropy.

The equations are discretized in both space and time, with a 512×512 spatial mesh, and solved using the finite difference method (in the nine-point finite difference scheme) with periodic boundary conditions applied in the two in-plane directions. We start with a circular nucleus of radius 10 and initial concentration $3u_{eq}$. Simulations are carried at different values of F and u_{eq}, and the results are shown as Figure 6 and S4.The parameters used to generate the results here are $D = 60$, $\delta = 0.04$, $\tau_{\psi} = 1.0$. It should be noted that, further consider the etching process starting from the nucleation point for growth, we initialized a hole in the center of grown graphene pattern and adjust u_{eq} to let u-u_{eq} in **Eq. 2** be negative (Figure. 6a), which reflects the fact that the catalyst there could lower the reaction barrier and facilitate the etching process from inside out.

Reference

[1] Karma A., M. Plapp, M. *Phys. Rev. Lett.* **1998**, *81*, 4444-.

[2] Hao *Y., Science* **342**, 720 (2013).

[3] Kobayashi, R., Physica D: *Nonlinear Phenomena* **1993**, *63*, 410.

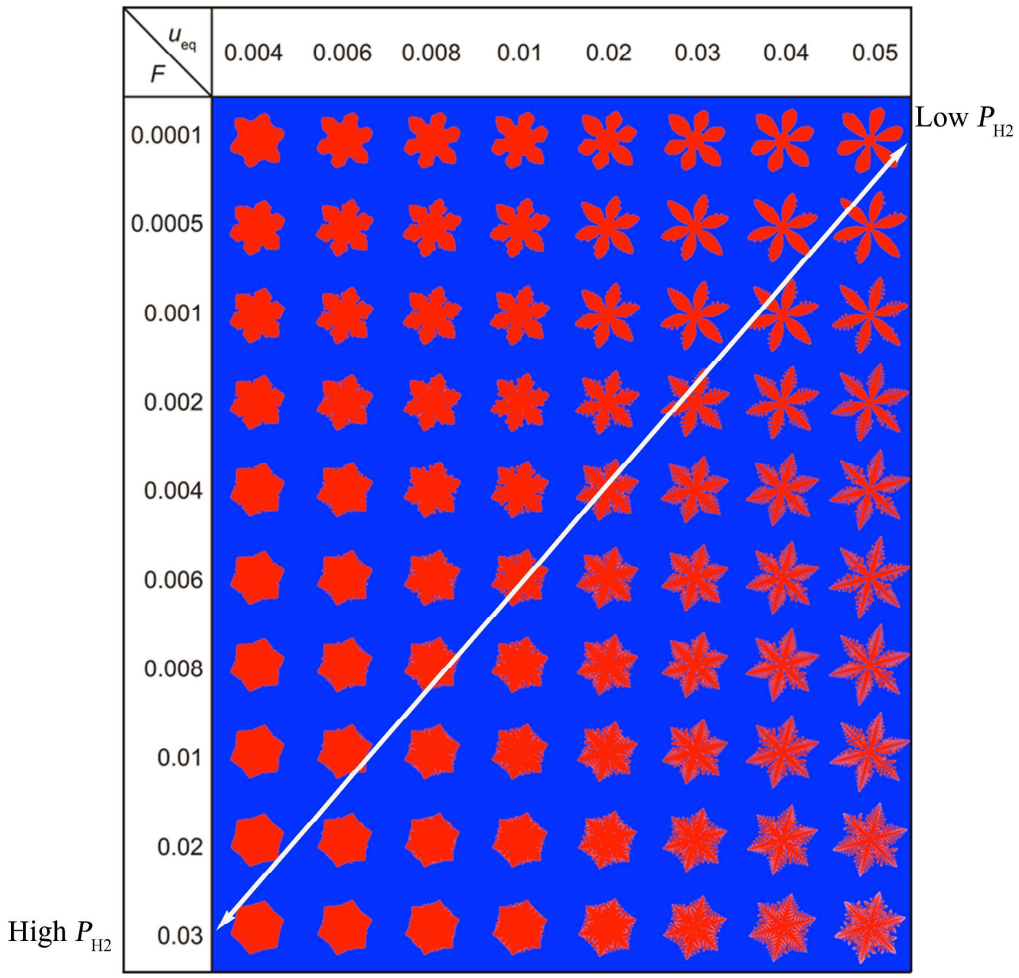

Figure S4. Phase field simulation results for the growth patterns at different values of F and u_{eq}.

5 Growth of conventional graphene

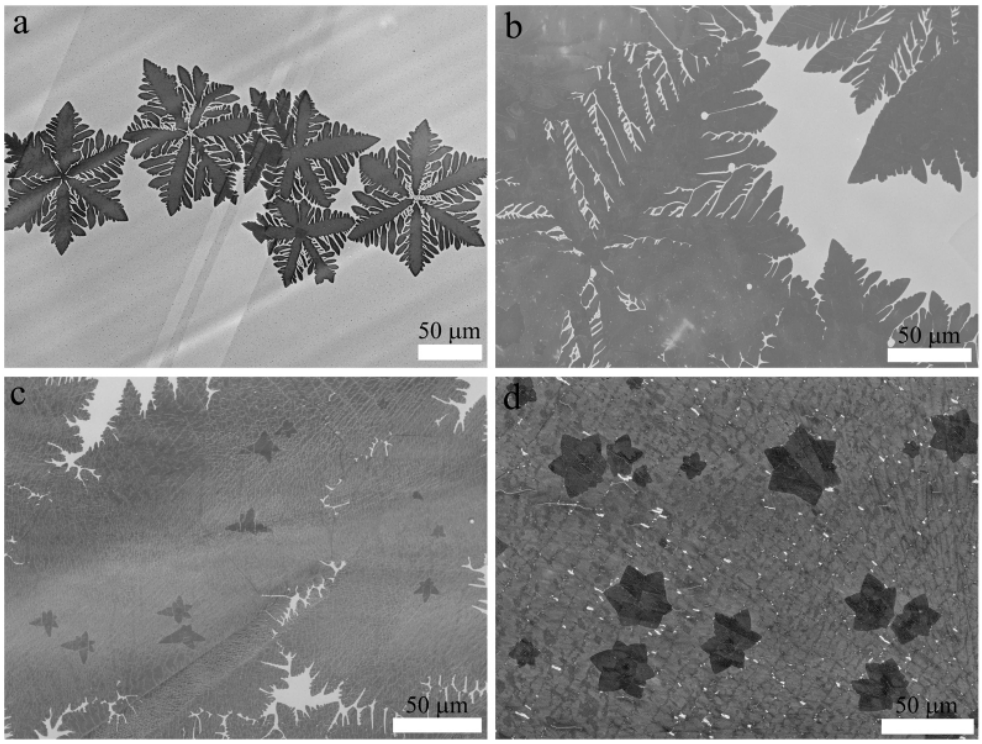

Figure S5. (a-c) Evolution of etching-controlled growth of graphene recorded as a function of CH_4 flow rate from 0.5, 1.5, 3, to 5 sccm under the fixed H_2 flow rate of 25 sccm at 1020 ℃.