Electronic supplementary information

The Edge Termination Controlled Kinetics in Graphene Chemical Vapor Deposition Growth

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Atomic structures of freestanding, metal-passivated, and H-terminated graphene nanoribbons



Fig. S1 Side and top views of the atomic structures for (a) freestanding GNR, (b) metal-supported GNR, and (c) H-passivated GNR, respectively. Small green, medium black and large orange balls represent H, C, and metal atoms.

Energy convergence of graphene nanoribbons on Cu(111) surface with respect to the *k*-point mesh and the thickness of vacuum layer



Fig. S2 The total energies of (a) zigzag graphene nanoribbon with a width of \sim 7.4 Å and (b) armchair graphene nanoribbon with a width of \sim 5.1 Å on Cu(111) surface with respect to the *k*-point meshes. The red circles denote the used *k*-point mesh setting in the present study.



Fig. S3 The total energy of armchair graphene nanoribbon with a width of ~ 5.1 Å on Cu(111) surface as a function of the thickness of vacuum layer. The red circle denotes the used thickness of vacuum layer in the present study.

The computational models for calculating formation energies of graphene edges on metal surfaces



Fig. S4 Side and top views of the atomic models used to calculate the edge formation energies of (a) armchair and (b) zigzag edges on metal surface. Small black and large orange balls represent C and metal atoms. The solid rectangles in all panels represent the calculated unit cells. The width of armchair (w_A) and zigzag (w_Z) nanoribbons is ~4.9 Å and ~7.1 Å, respectively. The length of unit cell along the armchair direction (L_A) is 8.65 Å, 4.43 Å, 4.32 Å, and 4.34 Å on Au(111), Cu(111), Ni(111), and Co(0001), respectively. The length of unit cell along the zigzag direction (L_Z) is 4.99 Å, 2.56 Å, 2.49 Å, and 2.51 Å on Au(111), Cu(111), Ni(111), and Co(0001), respectively.

Computational details for thermodynamic phase diagram of graphene edges

The thermodynamic phase diagram of graphene edges on TM surfaces by comparing the difference of edge free energy ΔG between the G-M and the G-H structures as follows¹

$$\Delta G = \Delta E_{\rm f} + \Delta F_{\rm vib} - N_{\rm H} \mu_{\rm H} \tag{1}$$

where ΔE_f is the difference of formation energy between H-passivated and metalpassivated graphene edges, ΔF_{vib} is the vibrational entropy of H at the graphene edge contribution to the free energy, N_H is the number of H atoms at the graphene edges, and μ_H is the H chemical potential that is the functions of H₂ pressure *p* and temperature *T*. The vibrational entropy contribution to Gibbs free energy ΔF_{vib} is calculated as follows²

$$\Delta F_{\nu i b} = -kT \left[\frac{\beta h \omega}{e^{\beta h \omega} - 1} - \ln(1 - e^{-\beta h \omega})\right]$$
(2)

where $\beta = 1/kT$ and ω is the vibrational frequency of H at a graphene edge. Fig. S5

shows the ΔF_{vib} of H at (a) AC and (b) ZZ graphene edges as a function of temperature T on Cu(111) and Ni(111) surfaces, respectively. At both AC and ZZ edges, the ΔF_{vib} values on Cu(111) are almost same to that on Ni(111) surface. The result suggests that the ΔF_{vib} of H at the graphene edges does not sensitive to the type of metal substrate. Therefore, on Au(111) and Co(0001) surfaces, we use the temperature dependence of ΔF_{vib} on Ni(111) surface. The chemical potential of hydrogen as the functions of T and *p* can be written as¹

$$2\mu_{H} = E_{H_{2}} - kT \ln(\frac{kT}{p} \times g \times \zeta_{trans} \times \zeta_{rot} \times \zeta_{vib})$$
(3)

where E_{H2} is the energy of a H₂ molecule at the T = 0 K, g is the degree of degeneracy of the electron energy level. ζ_{trans} , ζ_{rot} , and ζ_{vib} are the partition functions for translational, rotational, and vibration motions, respectively. Details of these partition functions are expressed elsewhere^{3,4}. The dependence of μ_{H} temperature *T* and pressure *p* is shown in Fig. S6.



Fig. S5 The vibration entropies of hydrogen at (a) graphene armchair edges and (b) zigzag edges on Cu and Ni surfaces contribute to the Gibbs free energy as a function of temperature.



Fig. S6 The dependence of H chemical potential difference on temperature T and H₂ pressure p.

The experimental parameters and the corresponding growing graphene morphology.

Catalysts	Total pressure (Torr)	Temperature (°C)	Granhene	References
Catalysis	Total pressure (Toll)		Graphene	References
Cu	19	1000	Regular hexagon edges	[6]
Cu	0.09	920-1030	Irregular edges	[7]
Cu	~100	1050	Regular hexagon edges	[8]
Cu	~100	1000	Regular hexagon edges	[9]
Cu	0.05	1035	Irregular edges	[10]
Cu	~100	1120	Regular hexagon edges	[11]
Cu	0.15-0.3	1000	Irregular edges	[12]
Cu	atmospheric pressure	1000-1075	Regular hexagon edges	[13]
Pt	Ambient pressure	1040	Regular hexagon edges	[14]
Со	Low pressure	~800	Irregular edges	[15]
Со	0.003	800-1000	Irregular edges	[16]
Ni	~100	1000	Single and bilayer	[17]
Au	~100	975	Single and few layers	[18]

Table S1. Experimental growth parameters and the corresponding growing graphene morphology.

Computational details for formation energies and phase diagrams of graphene edges on Ni and Co substrates with surface carbide

The surface carbide models were constructed by using Ni₂C (or Co₂C) phase in the substrate subsurface (Ni(111) and Co(0001)). The similar model was also used in previous study.⁵ To investigate the interactions between graphene edges and the metal substrates with surface carbide, graphene nanoribbons were put on the substrate surfaces for the further optimization (see Fig. S7). In the calculations, the *k*-point meshes are $6 \times 2 \times 1$ for metal-supported armchair edges and $2 \times 6 \times 1$ for metal-supported zigzag edges, respectively. The formation energies of graphene edges on carbide surfaces of Ni and Co were calculated by Eq. (3) in main text and the calculated results have been listed in Table S1. For the comparison, the formation energies of graphene edges on clean Ni(111) and Co(111) surface have also been listed in Table S1. The phase diagram of graphene edges on Ni₂C and Co₂C surfaces was calculated by Eq. (4) in the main text and the calculated result was listed in Fig. S8.



Fig. S7 Top and side views of the atomic models used to calculate formation energies of armchair and zigzag edges on (a) Ni(111) and (b) Co(0001) surface with the carbide phase in the subsurface. Black and orange balls represent C atoms in graphene nanoribbons (GNRs) and the subsurface of metal substrates, respectively. w and L denote the width of GNRs and the length of unit cell along the periodic direction.

	Armchair edge		Zigzag edge	
	Ni ₂ C	Ni(111)	Co ₂ C	Co(0001)
Ni	5.62	5.38	4.21	3.61
Со	5.66	5.26	4.37	3.98

Table S1. Formation energies of armchair and zigzag graphene edges (in eV/nm) on clean and carbide Ni and Co surfaces.



Fig. S8 Phase diagrams of armchair (solid lines) and zigzag (dash lines) graphene edges on Ni_2C , Co_2C , Ni, and Co surfaces as functions of temperature and H_2 pressure. The patterned area denotes the typical experimental temperature range of graphene CVD growth.

Kinetic Wulff construction



Fig. S9 The schematic growth process of graphene edges based on the kinetic Wulff construction that the fast growing edges will disappear and the slow growing edges will be reserved.

Computational details of threshold energies for the incorporation of C atoms at H-passivated graphene edges.

We use larger surface slabs with the unit cell of 8.85 Å × 15.34 Å for AC edge and the unit cell of 17.71 Å × 10.22 Å for ZZ edge to calculate threshold energies for the carbon addition at H-passivated armchair (AC) and zigzag (ZZ) edges on Cu(111) surface, respectively. For the C addition at the H-passivated AC edge, the incorporation of each two carbon atoms into the graphene edge will induce a new hexagon and the addition process is shown in Figure 4a. While there needs the incorporation of three C atoms onto the ZZ edge in sequence to form a new hexagon ring, as shown in Figure 4b. The threshold energy is defined as the formation energy of the highest structure relative to the ground-state structure without the C addition. Owing to the large supercells, the *k*-point meshes for the calculations of incorporation of C atoms at AC and ZZ edges are $2 \times 1 \times 1$ and $1 \times 2 \times 1$, respectively.

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