Supporting Information

Self-regulating homogenous growth of high-quality graphene on Co-Cu composite substrate

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Characteristics of graphene films growth on the Co-Cu substrates

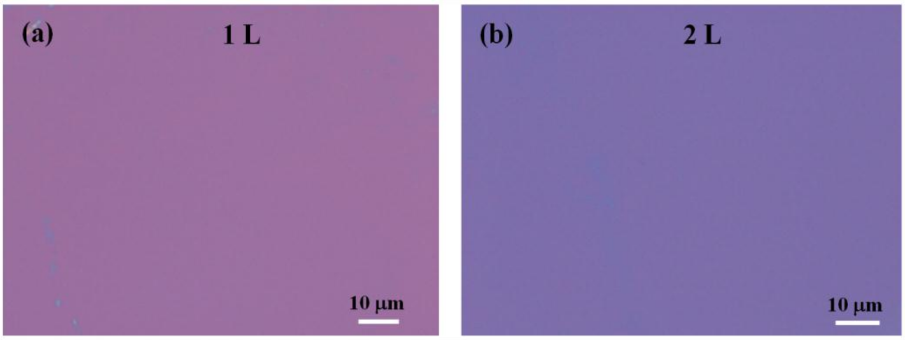

Figure S1. The optical microscope images of the single-layer (1L) and bilayer (2L) graphene films transferred on ~300 nm SiO_2/Si surface.

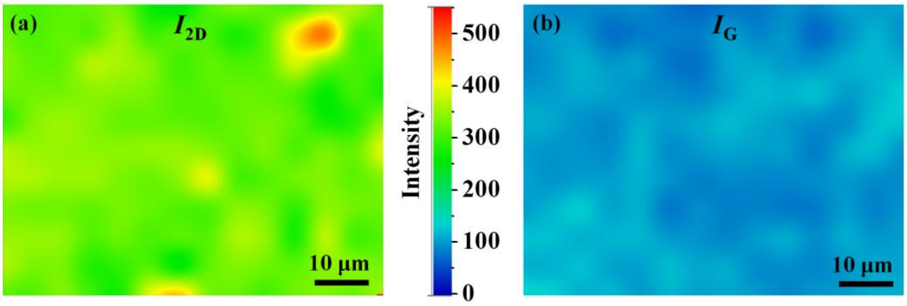

Figure S2. Raman mapping images of 2D/G band intensity ratio (a) and D/G band intensity ratio (b) of the single-layer graphene film over a 70×55 μm^2 area.

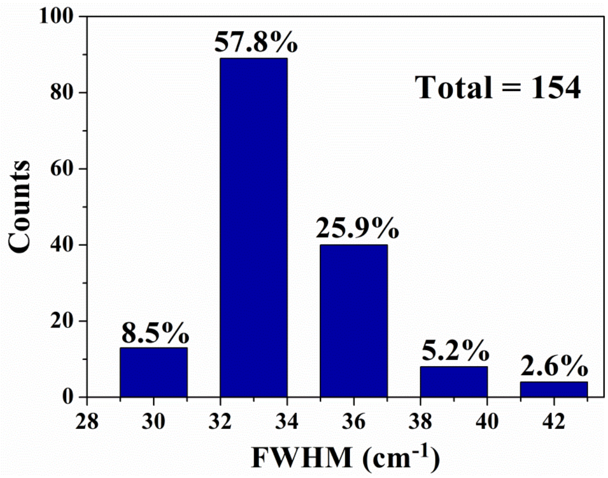

Figure S3. Histogram of the FWHM of Raman 2D peak of transferred graphene film growth on 80 nm Co-Cu substrate. The FWHM of 150 samples among all 154 counted samples lies between 29 cm^{-1} and 40 cm^{-1}, indicating ~98% single-layer coverage.

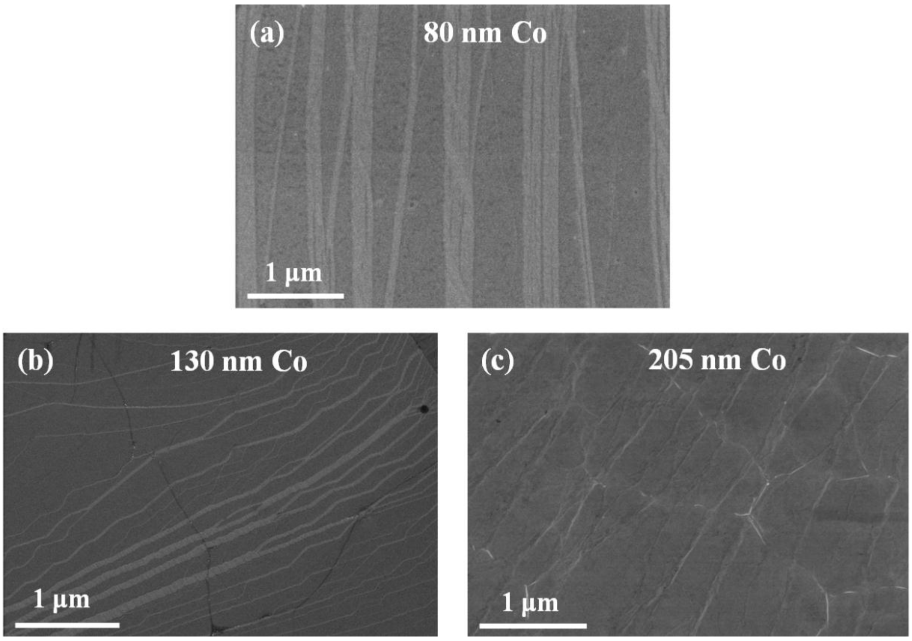

Figure S4. SEM images of graphene films growth on Co-Cu substrates with different Co thickness.

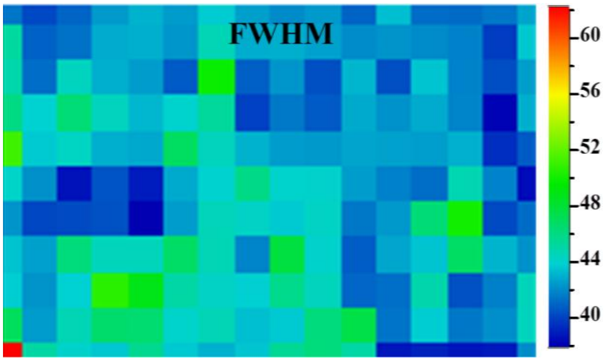

Figure S5. Raman mapping images of full-width at half-height maximum (FWHM) of the transferred graphene film growth on 130nm-Co-Cu substrate.

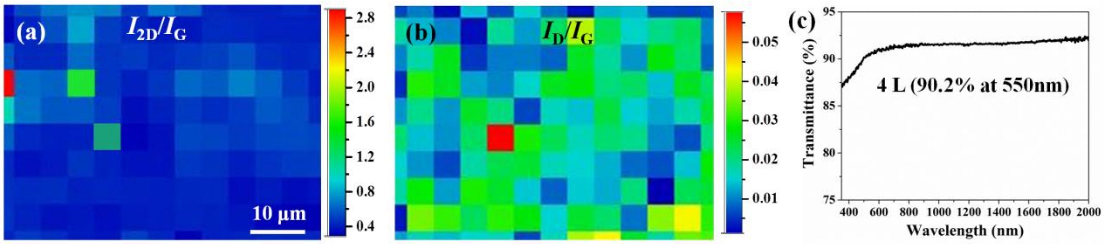

Figure S6. Raman mapping images of 2D band and G band intensity ratio $I_{2D/G}$ (c) and D/G band intensity ratio (b) of a transferred graphene film growth on 260nm-Co-Cu substrate. The color gradient bar to the right of each map represents the 2D/G band ratio (c) or D/G band ratio (d).

Measurements of Electrical Properties.

The electrical conductivities and mobility of our graphene films were measured by a standardized van der Pauw method in order to eliminate contact resistance, and each sample was measured three times to obtain an average value. Van der Pauw developed a method for measuring the sheet resistance of an arbitrary shaped thin film sample with four very small ohmic contacts along the sample boundary. A schematic of a van der Pauw configuration is shown in Figure R3. Here, typical probe spacing *l* is ~1 mm.

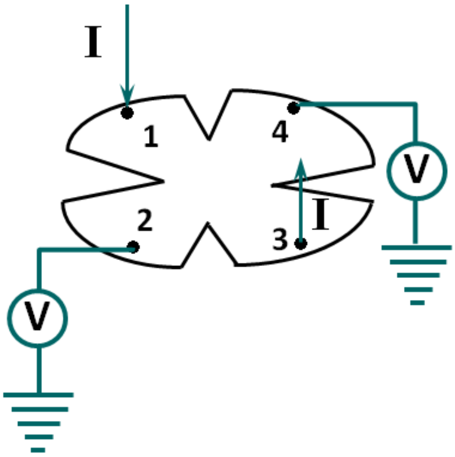

Figure S7. Schematic of a Van der Pauw configuration used in the determination of the sheet resistances.

In this case, the sheet resistivity (R_{sq}) of a homogeneous layer is calculated using the formula:

$$R_{sq} = \frac{\pi}{2\ln 2} \cdot \frac{V_{43} + V_{32}}{I} f$$

where f is a factor that is a function only of the ratio of R_{43}/R_{32}. Here the resistances are calculated by $R_{43} = V_{43}/I$ and $R_{32} = V_{32}/I$.

The first step in determining carrier mobility is to measure the Hall voltage (V_H) by forcing both a magnetic field perpendicular to the sample and a current through the sample. The combination of the current flow (I) and the magnetic field (B) causes a transverse current. The resistivity can be determined using van der Pauw measurement technique. With just these five parameters (B, I, V_H, and R_{sq}), the Hall mobility (μ_H) can be calculated using this formula:

$$\mu_H = \frac{V_H}{BIR_{sq}}$$

Explanation for tolerance of Co-Cu substrate to variations in the temperature range from 850 to 1050 °C.

Our Co-Cu CVD approach was immune to temperature variations from 850 to 1050 °C confirmed by Raman spectroscopy shown in Figure S8, which was consistent with previous studies on Ni-Mo alloy CVD.[S1] We envision two diffusion processes occurring in the top layer of the substrate. (a) Prior to and during CVD, Cu/Co interdiffusion lowers the C solubility with a kinetics controlled by D_{Cu}. (b) During CVD, adsorbed C invades the substrate with a kinetics controlled by D_C. Therefore, the C incorporation and its spatial spread in the top layer are promoted by (b) but limited by (a), meaning that they should scale with D_C/D_{Cu}.

Massaro and Petersen[S2,3] concluded that above 700 °C the activation energy for the bulk diffusion of C in Co (Q_C) was only about 20 kcal/mol while Fisher and Rudman[S4,5] found that the Q_{Cu} was about 58 kcal/mol in the temperature range 850°C to 1050 °C. Therefore, the ratio D_C/D_{Cu} $\frac{D_C}{D_{Cu}} = D_0 \exp\left(\frac{Q_{Cu} - Q_C}{RT}\right)$ is plotted versus temperature (T) shown in Figure S9. The ratio D_C/D_{Cu} shows little change in the temperature range 850°C (1123 K) to 1050 °C (1323 K). There is similar kinetics at the temperature range. This explains the widening of processing window, which extends from 850 to 1050 °C.

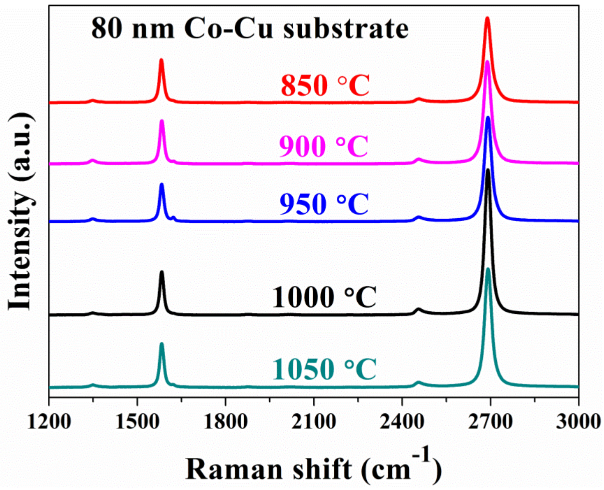

Figure S8. Raman spectra of the transferred graphene films grown on 80 nm Co-Cu substrates at different temperature.

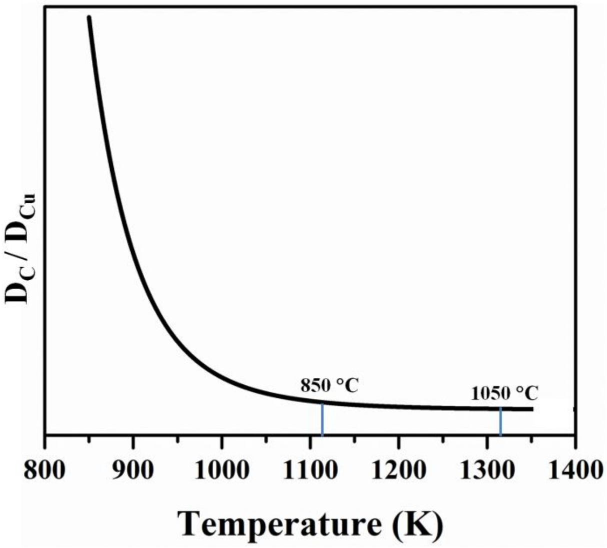

Figure S9. The ratio D_C/D_{Cu} is plotted versus temperature.

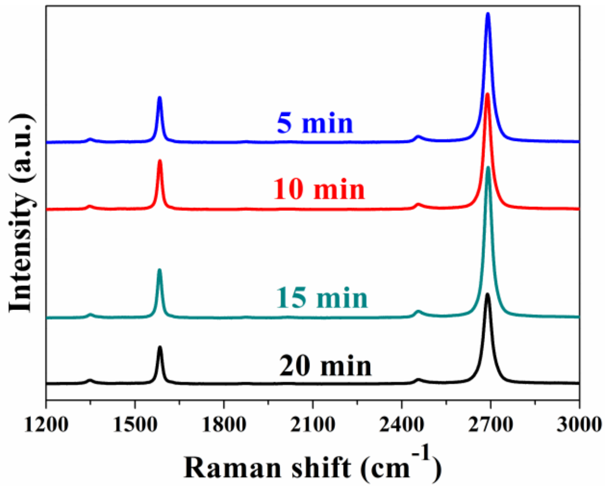

Figure S10. Raman spectra of the transferred graphene films grown on 80 nm Co-Cu substrates for different growth time.

XPS profiles of the Co-Cu substrate after pre-annealing for 5 min.

In this process, the Co-coated Cu foil was initially cleaned at 1000 °C under a 50 sccm H_2 flow for 5 min before the carbon exposure. For 80nm Co-coated Cu substrate, the alloying didn’t occur within ~70 nm region during this period, which was confirmed using XPS aided by depth profiling. Figure S9 exhibits the XPS depth profiles of the substrate after the annealing treatment at 1000 °C for 5 min. The Cu signals were not detected in a wide range down into the bulk metal until near the interface of the 80nm-Co-coated Cu substrate (~70 nm). After that the alloying was initiated. The substrate also shows shallow distribution of carbon as well as oxygen on surface vicinity, attributable to the adsorbed residues.

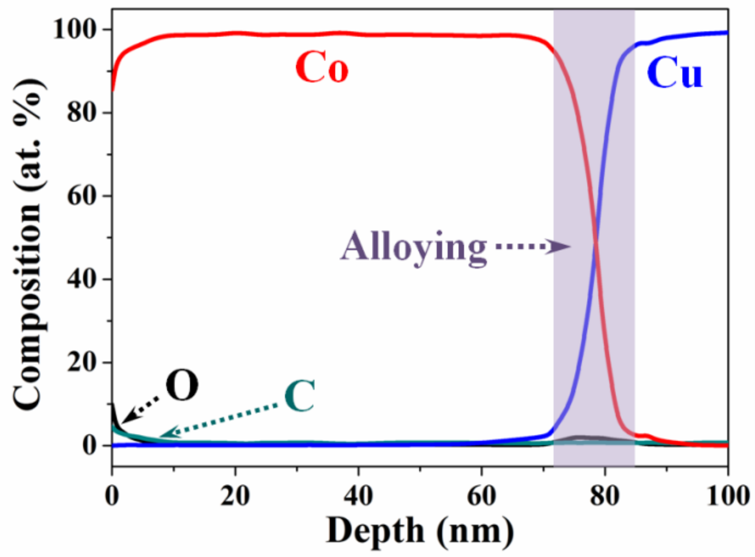

Figure S10. XPS composition depth profiles of elements on the 80nm Co-Cu substrate after heat treatment at 1000 °C under a 50 sccm H_2 flow for 5 min before the carbon exposure.

Minimum thickness of Co layer on Cu foil that can be achieved by dissolution and segregation mechanism.

The minimum mass of a single layer graphene is:

$$m_{1L} = N_C / N_A \times 12.01 \tag{1}$$

Where the N_C is the number of carbon atoms, N_A is Avogadro's constant 6.022×10^{23} and the relative atomic mass of carbon is 12.01.

Each hexagon of the honeycomb contains two carbon atoms in the hexagonal lattice. Therefore, the number of carbon atoms N_C need to form a 1L graphene is

$$N_C = 2\times S_{Co} / S_H \tag{2}$$

Consider one hexagon in graphene lattice and the distance between two carbon atoms a = 1.42 Å. The area of one hexagon of graphene is:

$$S_H = \frac{3\sqrt{3}}{2}a^2 \tag{3}$$

We can assume all carbon atoms dissolution into Co layer were to precipitate to form graphene. Therefore, here the the lower limit carbon mass m_C is equal to m_{1L}:

$$m_C = m_{1L} \tag{4}$$

Since the solubility of C in Co layer is about 0.2 wt.% (1.0 at.%) at 1000 °C, and the mass of dissolution carbon is:

$$m_C = 0.2\% \times m_{Co} \tag{5}$$

As the bulk density of Co $\rho = 8.90$ g/cm^3, the mass of the Co layer is:

$$m_{Co} = \rho V = \rho \times S_{Co} \times t \tag{6}$$

From the formula (1)–(6), the minimum Co layer t_{min} is calculated to be:

$$t_{\min} = \frac{m_{Co}}{\rho \times S_{Co}} = \frac{m_C / 0.2\%}{\rho \times S_{Co}} = \frac{(N_C / N_A \times 12.01) / 0.2\%}{\rho \times S_{Co}} = \frac{(\frac{2S_{Co} / S_H}{N_A} \times 12.01) / 0.2\%}{\rho \times S_{Co}} = \frac{(\frac{2S_{Co} / (3\sqrt{3}a^2 / 2)}{N_A} \times 12.01) / 0.2\%}{\rho \times S_{Co}}$$

The minimum thickness t_{min} of Co layer is calculated to be 43 nm.

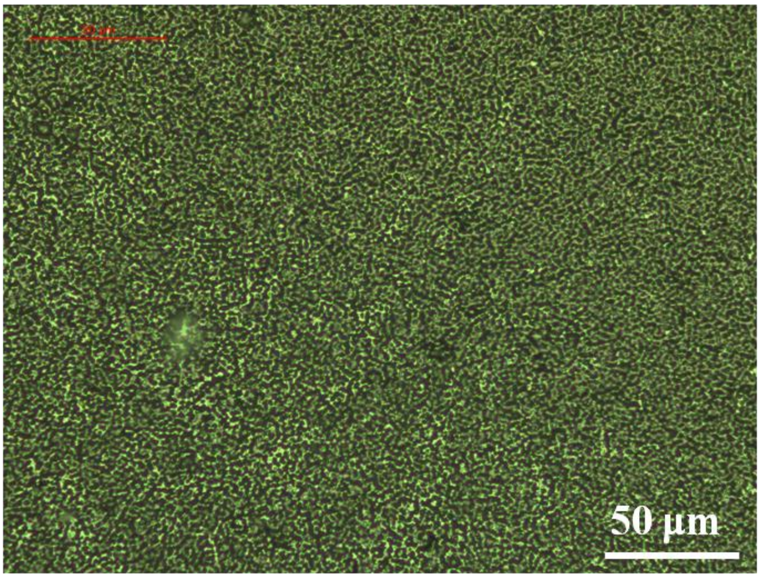

Figure S11. Optical image of graphene growth on Co film having thickness ~60 nm at the lowest growth temperature (850 ºC), showing agglomeration of the Co film.

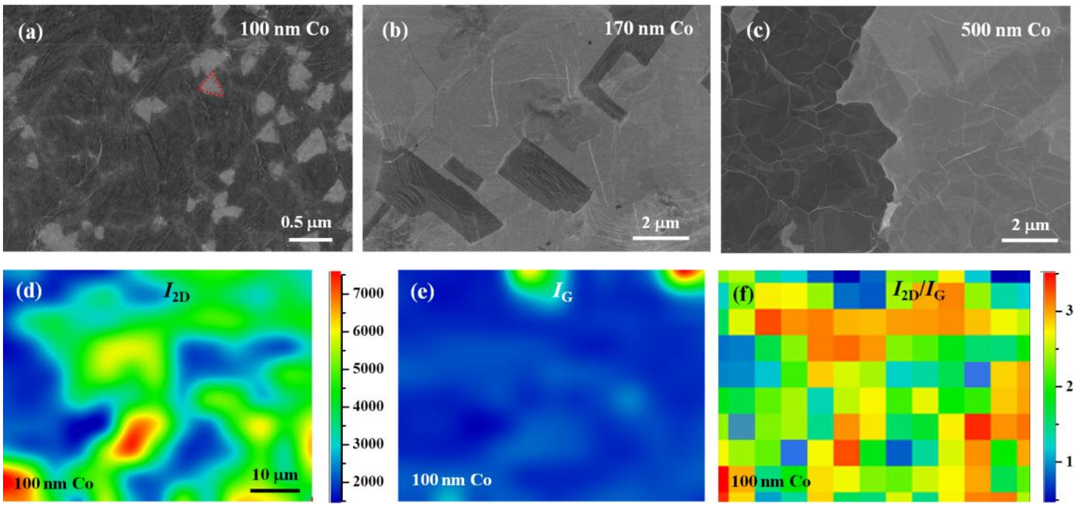

Figure S12. SEM images of graphene growth on Co-Cu substrate with different Co layer thickness: (a) 100 nm Co layer, (b) 170 nm Co layer, and (c) 500 nm Co layer. (d) Raman mapping images of 2D band intensity (a), G band intensity (b), corresponding 2D/G band ratio (c) of the graphene growth on 100nm-Co-Cu substrate. The color gradient bar to the right of each map represents the 2D/G band ratio (c).

References

S1 B. Dai, L. Fu, Z. Zou, M. Wang, H. Xu, S. Wang and Z. Liu, *Nat. Commun.* 2011, 2, 522.

S2 B. S. Berry, *J. Appl. Phys.* 1973, 44, 3792.

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S4 Bertina Fisher, P. S. Rudman. *J. Appl. Phys.* 1961, 32, 1604.

S5 G. O. Trønsdal, H. Sørum. *Physica Status Solidi.* 1964, 4, 493.