

Supporting Information

Decoupling of CVD Graphene by controlled Oxidation of Recrystallized Cu

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S1: Molecular Dynamics Simulations

MD simulations were carried out using the Lammmps MD package.¹ The C-C interaction, C-Cu interaction, and Cu-Cu interactions were described by AIREBO,² Lennard-Jones,³ and EAM⁴ potentials, respectively. The system was monolayered graphene on thick (or bulk) Cu(111) or Cu(001). The work of adhesion was computed through the formula $\Gamma = E_{\text{graphene}} + E_{\text{Cu}} - E_{\text{graphene+Cu}}$, where $E_{\text{graphene+Cu}}$, E_{graphene} and E_{Cu} are the potential energies of Cu surface covered with graphene, stand-alone graphene and stand-alone Cu surface, respectively.

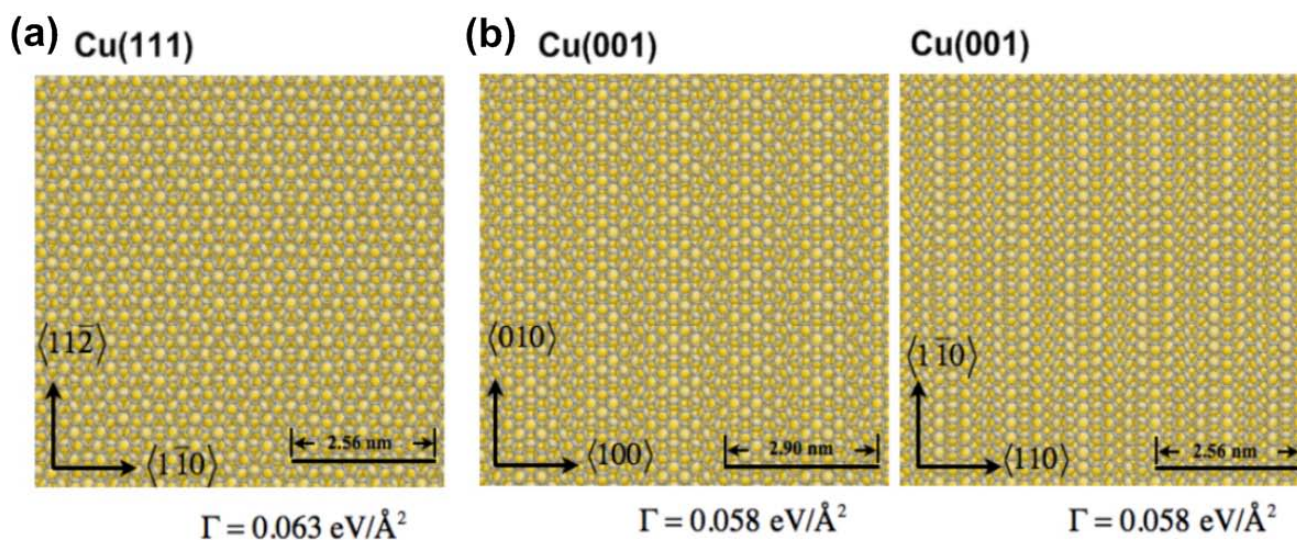


Figure S1

Figure S1a and S1b display the top view of the monolayer graphene on bulk Cu(111) and Cu(001) from molecular dynamics (MD) simulations. The work of adhesion Γ of each interface from MD simulations is shown at the bottom of each figure. We conclude that graphene on Cu(111) is thermodynamically more stable due to a larger Γ compared with the graphene on Cu(001). Thus, Cu(111) is a preferred orientation in slow cooling process, as discussed in text. The observation of Cu(001) indicates that the Cu(001) resulted from fast cooling process is kinetically determined. We suspect that the presence of graphene may provide easy heterogeneous nucleation sites for Cu(001).

S2: Cu coating on inner surface of quartz tube



Figure S2

At process temperatures of CVD ~ 1000 °C, the inner surface of quartz tube near low-temperature zone of the furnace is coated by a thin Cu film after processing. This phenomenon corroborates that Cu is vaporized at this temperature, and implies that graphene growth occurs at a semi-molten state of the Cu substrate.

S3: EBSD result of CVD-grown graphene/Cu sample with slow-cooling process using high-purity Cu foil as substrate

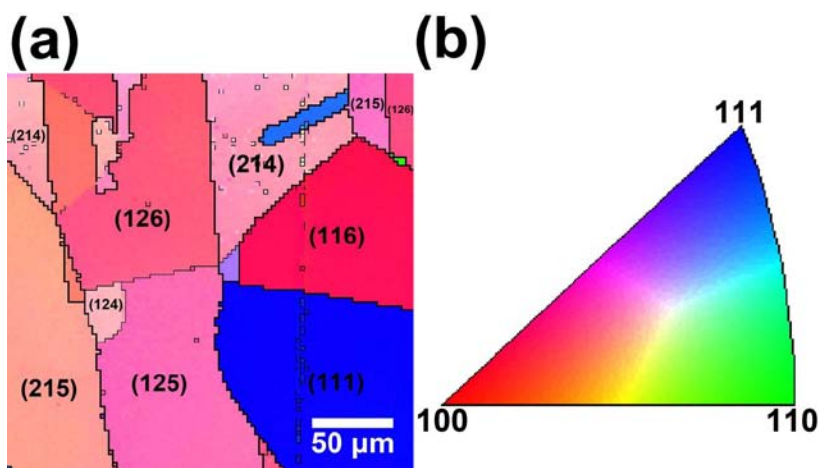


Figure S3

As discussed in the main text, high purity Cu has a higher melting point than Cu foils which suggest that process temperatures ~ 1000 °C its crystal structure remains unchanged therefore recrystallization does not occur under cooling.

S4: EBSD/Raman mapping of slow-cooled sample

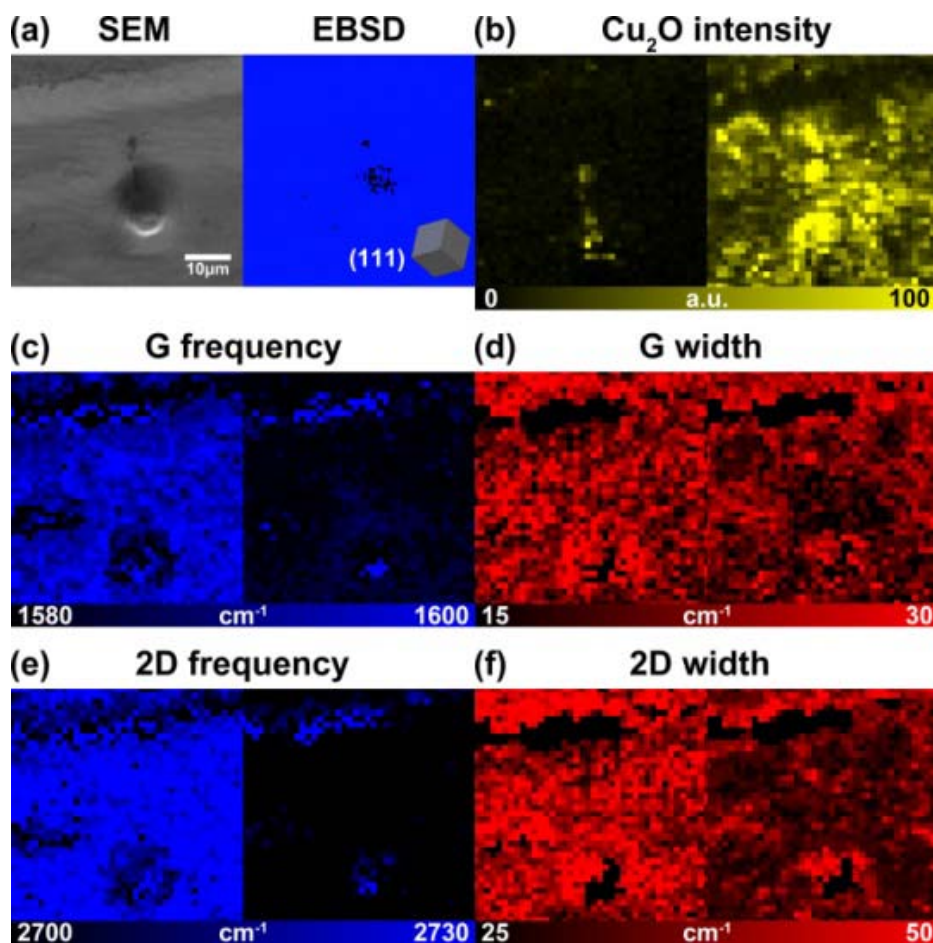


Figure S4

S5: Reported Raman data for identifying decoupled, on SiO₂ and suspended SLG.

Table S1. A review of Raman features of micromechanically exfoliated SLG

Exfoliation SLG				
Laser energy (eV)	Substrate for Raman measurement	I _{2D} /I _G	FWHM of 2D (cm ⁻¹)	Ref.
2.33 eV	Suspended SiO ₂	6.21 2.16	24.8 – 30.5 27.7 – 37.1	5
1.96 eV	SiO ₂	2 – 4.62	22.4 – 28.9	6
2.41 eV	Suspended	4	32	7
2.41 eV	SiO ₂	2 – 2.75	28	8
2.41 eV	SiO ₂	na	28	9
2.33 eV	SiO ₂	3.4 – 4.5	30	10
2.41 eV	SiO ₂	2.9 – 3.1	27 – 29	11

Table S2. A review of Raman features of CVD-grown SLG

CVD-grown SLG				
Laser energy (eV)	Substrate for Raman measurement	I _{2D} /I _G	FWHM of 2D (cm ⁻¹)	Ref.
1.96 eV	SiO ₂	2.92	32.2	6
2.33 eV	Suspended	3.52	35	12
2.33 eV	SiO ₂	2	33	13
2.33 eV	SiO ₂	3.77 – 3.8	32	14
2.41 eV	SiO ₂	2	37 – 38	15
2.41 eV	SiO ₂	4	30	16
1.96 eV	SiO ₂	2.6	35	17
2.33 eV	Suspended	2.8 – 4.2	25 – 35	18
2.33 eV	Ni SiO ₂	0.5 – 1 5.6	30 – 40 35	19
2.33 eV	SiO ₂	2 – 5	35	20
na	na	2.9	44	21

Based on the results in Table S1 and Table S2, we can set a convenient criterion for identification of SLG, that is, $I_{2D}/I_G \geq 2$ and FWHM of 2D = 25 – 35 cm⁻¹. In the case of $I_{2D}/I_G < 2$ and FWHM of 2D > 35 cm⁻¹ in ref. 15 and ref. 17, most probably the number n of graphene layers is ≥ 2 . Another possibility is that external factors influence the Raman features of SLG making it “look like” $n \geq 2$ with FWHM of 2D > 35 cm⁻¹, for example, in the case of strong interacting CVD graphene on metal substrates.

In the case of CVD-grown graphene, regardless the surface precipitation (on Ni) or growth mechanism (on Cu), one has no reason to believe that the interaction between metal substrates and as-grown graphene could be neglected. Thus another criterion for identification of as-grown SLG on metal

surface is needed.

From the Raman spectra of as-grown graphene in Figure 3, a suggested criterion for coupled SLG on Cu could be that FWHM of 2D = 40 - 50 cm^{-1} and $I_{2D}/I_G = 1 - 2$. Since the lattice orientation of Cu could be probed locally by EBSD in our study, the criterion for as-grown SLG on different Cu lattices such Cu(111) and Cu(100) could be realized in detail as shown in Table 1. Note that the band-shifts of G and 2D are not shown in Table 1 as the position of these features does not influence the identification of SLG.

S6: Raman results from Cu/SiO₂ substrate and cold-walled CVD system

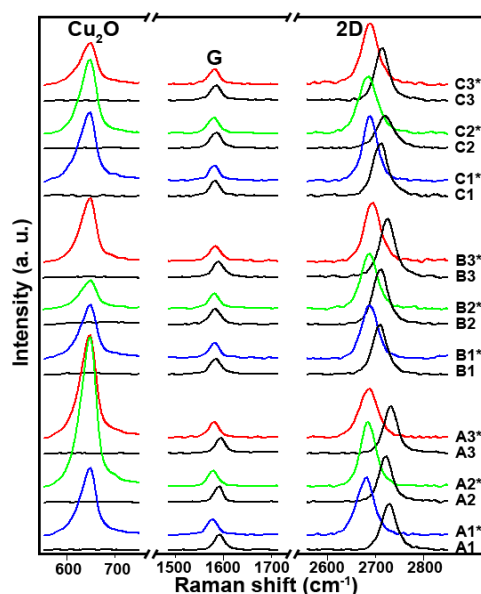


Figure S5

We also use the Cu thin film (300 nm) coated SiO₂/Si substrate and another cold-walled CVD system (Black Magic II, AIXTRON) to reconfirm the decoupling effect. The results are similar to that reported by Ismach, et al.¹⁴ We took Raman spectra of 9 different positions (A1-3, B1-3 and C1-3) from 3 as-grown graphene samples (sample A, B and C). After 7 days exposure in air with controlled moisture for oxidation, another 9 Raman spectra were taken at the same positions as shown as spectra in Figure S5 with *. The result clearly reveals the decoupling effect is universal, and has nothing to do with types of Cu (thin film or foil) and CVD (cold-walled or hot-walled).

S7: Thickness control of Cu₂O intercalation layer

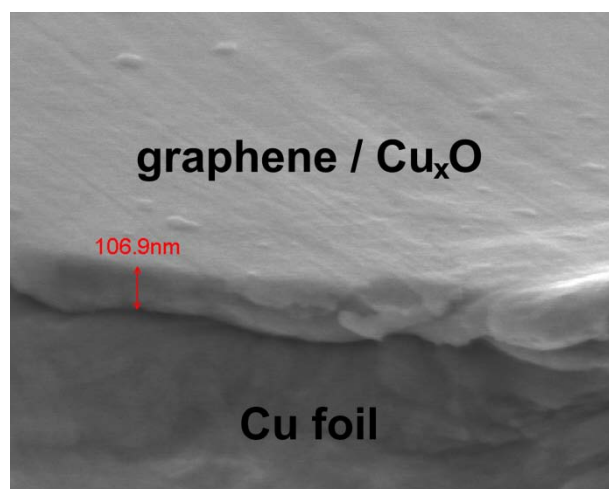


Figure S6

The thickness of Cu₂O could be controlled by two parameters, i.e. temperature and humidity. In the case in main text, the temperature and humidity were kept at room-temperature and ~ 50 % respectively, and result in a thickness of Cu₂O around 10nm. For thicker Cu₂O as shown in Figure S6, the sample was putted into a thermostatic oven at 150 °C for 8 hours. Another way is that putting sample into a glass jar with a water-contained petri dish at room-temperature. After that, the jar was sealed for few days. The water-contained petri dish provides a considerable and stable humidity for helping the oxidation of Cu. By these strategies, the thickness of Cu₂O intercalation layer could be controlled ranging from tens to hundreds nm.

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