Supporting Information for

Atmospheric Pressure Chemical Vapor Deposition Growth of Millimeter-Scale Single-Crystalline Graphene on the Copper Surface with a Native Oxide Layer

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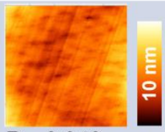
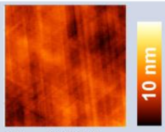
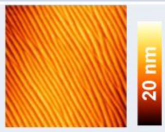
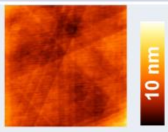
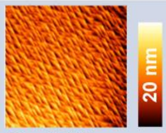
	As-received	30-min Annealing	120-min Annealing
JX in H_2	 R_q=8.77 nm	 R_q=0.949 nm	 R_q=0.338 nm
JX in Ar		 R_q=2.39 nm	 R_q=0.335 nm
Alfa in Ar	 R_q=77.6 nm	 R_q=4.26 nm	 R_q=1.77 nm

Table S1. Morphology and roughness of commercial Cu foils treated with Ar and Ar/H_2 annealing under atmospheric pressure. The scan scale is 5 μm X 5 μm.

As one of the conventional CVD substrates, Alfa foils (No. 13382, 99.8% purity, 25 μm, Alfa Aeser) are used to present the comparison with JX foils. The annealing temperature is 1075°C. And the flow rates for Ar and H_2 are 1000 sccm (Ar-only and H_2 mixture condition), and 35 sccm (H_2 mixture condition), respectively. The morphology images of JX foils annealed in Ar, which has been shown in the manuscript (Fig. 2), are also listed. It is clear that the roughness of JX foils is strongly suppressed by the annealing treatment, and the foil annealed in H_2 shows smoother surface, which is consistent with previous results.[1, 2] Moreover, with the same Ar-only annealing treatment, JX foils always show more flat surface than Alfa foils, whose surface contains terrace- and trench-like structure with 2 hour annealing. It suggests that the thermal treatment induced morphology change is highly dependent on the intrinsic properties of commercial Cu foils. For the industrial production, the refining technique is supposed to modify the surface properties of metal foils, such as type and concentration of impurities.[3]

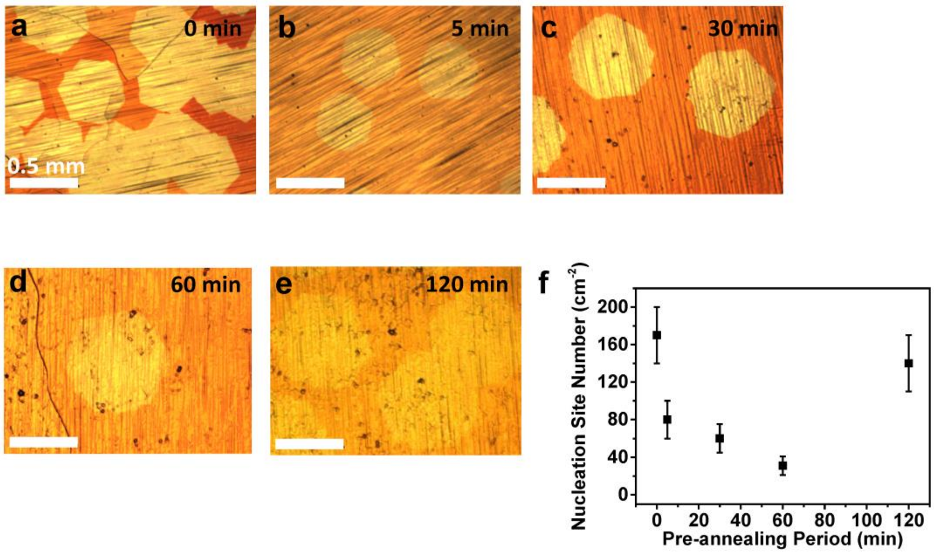


Figure S1. (a-e) Optical images of graphene domains grown on the Alfa Cu foils treated with different pre-annealing periods of (a) 0, (b) 5, (c) 30, (d) 60, and (e) 120 min. The growth time was 60 min. (f) Evolution of the nucleation density graphene domains with different pre-annealing periods.

In agreement with JX foils shown in the manuscript (Figure 2), graphene grown on Alfa foils also exhibits the nonmonotonic dependence of the nucleation density on the annealing duration, suggesting competitive contribution between surface morphology and oxide layer coverage on the nucleation kinetics of CVD graphene.

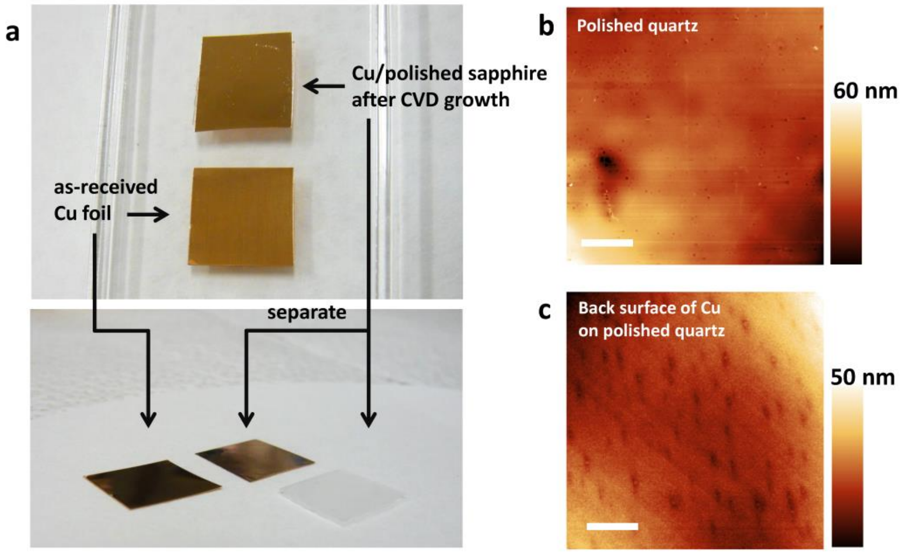


Figure S2. (a) Optical images of Cu/polished sapphire after CVD process and as-received Cu foil. (b-c) Morphology images of polished quartz and back surface of Cu foil attached on the polished quartz. The related R_q values are 3.8 and 5.2 nm, respectively. The scale bar is 2 μm. The CVD process includes 30 min Ar-annealing and 120 min growth.

As shown in Figure S2 (a), the Cu foil (JX) used in the experiment is flat without obvious waviness in the wafer scale. It can be easily separated from the sapphire support after the whole CVD process, excluding the possibility of melting-induced adhesion between Cu and support during the growth step. However, at the elevated temperature (1075 ^{o}C) close to the melting point of Cu, the foil still tends to sag and approach to the support, [4] and eventually form a confined geometric space on the back surface of Cu foil. If we presume that the attachment of support is uniform on the whole Cu surface, the dimension of this confinement space, *d*, can be estimated in a simplified way: the sum of the roughnesses of support and Cu. In the case of Cu on polished quartz, the dimension of confined space is ~ 9 nm.

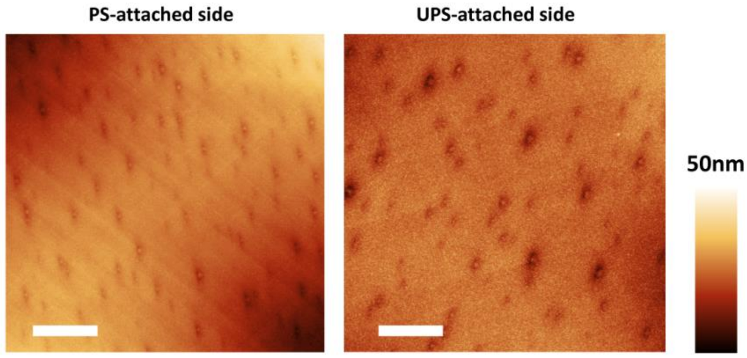


Figure S3. Morphology images of Cu foil attached to polished (PS) and unpolished sapphire (UPS). The scale bar is 2 μm. The R_q values of the Cu foil on the PS and UPS are 4.4 and 4.9 nm, respectively.

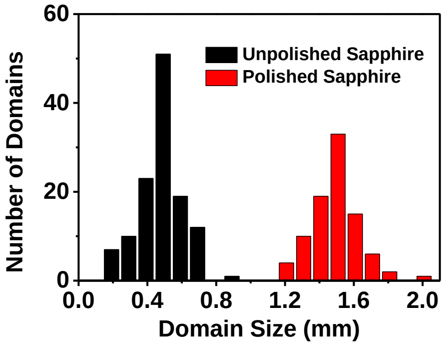


Figure S4. Statistic data of graphene grown on Cu surface attached by polished and unpolished sapphire with 60 min growth. This data contains 3 batches of samples: 7 chips of polished sapphire and 6 chips of unpolished sapphire.

References

[1] Wang, H.; Wang, G.; Bao, P.; Yang, S.; Zhu, W.; Xie, X.; Zhang, W.-J. Controllable Synthesis of Submillimeter Single-Crystal Monolayer Graphene Domains on Copper Foils by Suppressing Nucleation. *J. Am. Chem. Soc.* **2011**, *134*, 3627-3630.

[2] Gan, L.; Luo, Z. Turning off Hydrogen to Realize Seeded Growth Subcentimeter Single-Crystal Graphene Grains on Copper. *ACS Nano* **2013**, *7*, 9480-9488.

[3] Davis J. R. Copper and copper alloy. *ASM International* **2011**.

[4] Chen, C.; Kuo, C.; Liao, C.; Chang, C.; Tseng, C.; Liu, C.; Chen, Y. Growth of Large-Area Graphene Single Crystals in Confined Reaction Space with Diffusion-Driven Chemical Vapor Deposition. *Chem. Mater.* **2015**, *27*, 6249-6258.