Electronic Supplementary Information

Self-assembly and continuous growth of hexagonal graphene flakes on liquid Cu

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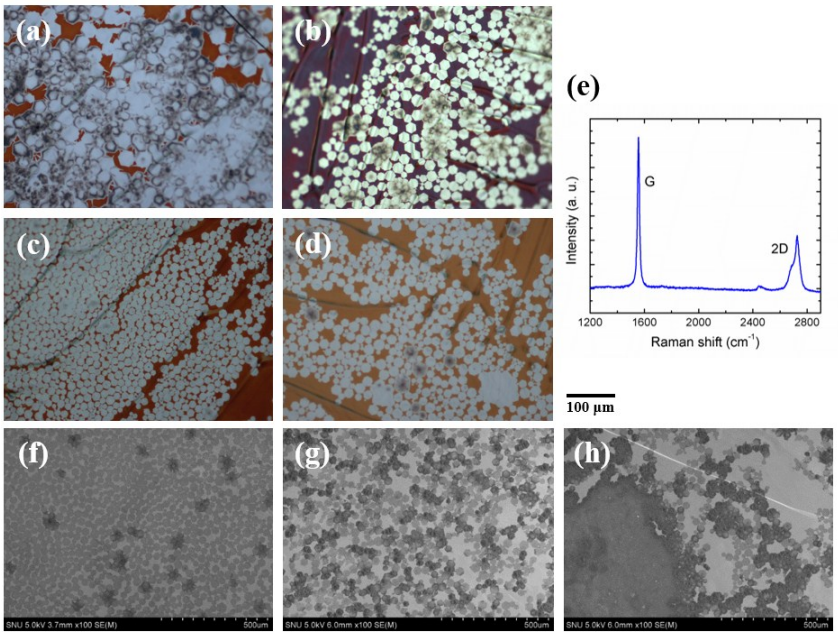

Fig. S1. Optical microscope images of graphene grown on liquid Cu varying CH_4 flux with H_2 at 500 sccm. (a) CH_4 flux is 4 sccm at 10 minutes, (multilayers were observed) (b) 3.8 sccm at 10 minutes, (c) 3.5 sccm at 40 minutes, and (d) 3.3 sccm at 50 minutes. Under 3.0 sccm of CH_4 flux, no graphene growth was observed meaning that supersaturation ratio cannot build up, (scale bar indicates 100 μm in (a) to (d)) and (e) Raman spectrum of multilayer graphene on liquid Cu achieved from dark contrast region in (a). (f) to (h) SEM image of graphene growth on liquid Cu varying CH_4 flux. (f) 3.5 sccm for 30 minutes, (g) 4.0 sccm for 10 minutes, and (h) 7 sccm for 5 minutes.

For structural study of graphene grown on liquid Cu, we transferred graphene grown on liquid Cu to Quantifoil TEM grid for observation of diffraction patterns. Fig. S2 (a) shows SEM image of carbon square mesh area in Quantifoil grid where misaligned graphene islands are visible by secondary electron contrast. The same area was found in TEM since graphene islands are not easy to observe in TEM bright field mode. (Same method was used in Fig. S3) Two grains are aligned in the same direction which are indicated by alphabetical letters A, B, C and D, and Arabic number 1, 2, and to 6 as shown in Fig S2. (b). With respect to two grains, grain located upper area of TEM image is rotated 11 ^{o} degree. Selected area diffraction patterns were achieved at each position and all the grains were single crystal. Two neighboring grains show the same orientations of diffraction patterns at all the position, but other grain shows 11 ^{o} rotated diffraction patterns as shown in Fig. S2 (c). For a comparison of well alignment sample, bright field TEM image of well-aligned graphene grains are shown in Fig. S3. (a), all the grains are touched each other (edges of grain are indicated by dotted line) and aligned in the same axis according to diffraction patterns. Diffraction patterns were achieved at various positions marked by numbers and alphabetical letters show the same directions as shown in Fig. S3 (b).

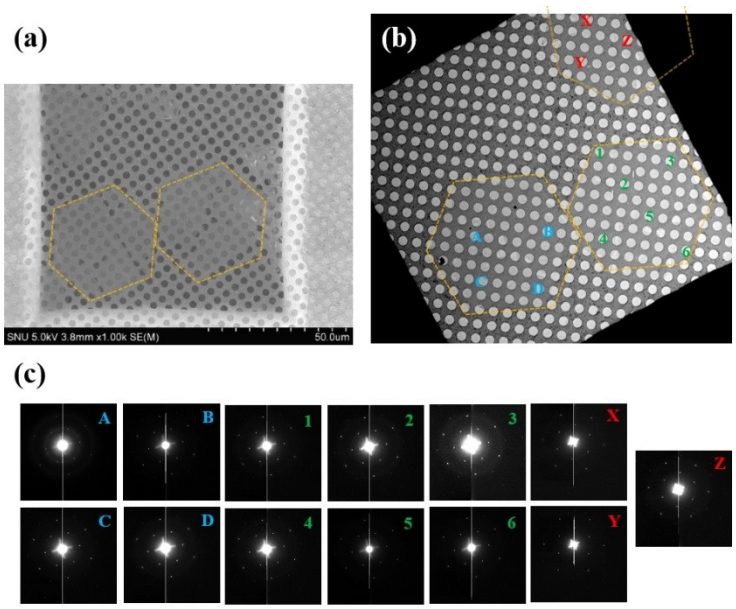

Fig. S2. Grain boundaries revealed in single-step grown graphene by hydrogen etching and NaCl-assisted oxidation. SEM images of graphene islands (a) after 2 h of growth time (as-grown) and (b) the corresponding sample after the hydrogen etching for 5 min. Optical microscopy images of (c) graphene after 2 h of growth time and (d) the corresponding sample after the NaCl-assisted oxidation for 24 h. Scale bar indicates 30 μm.

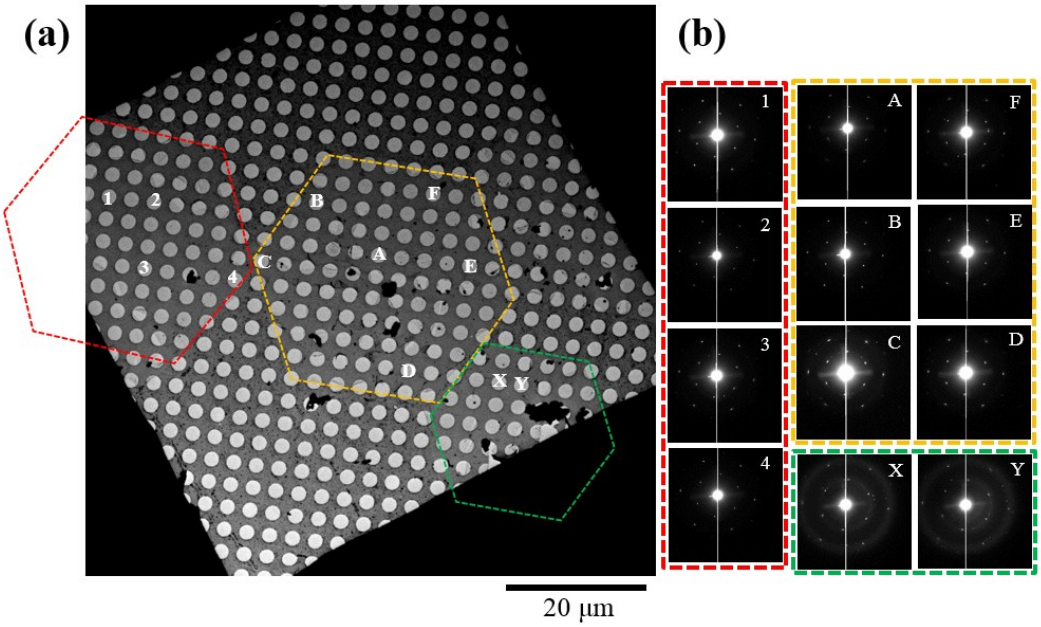

Fig. S3. TEM analysis of three adjacent graphene grains on liquid Cu after transfer to TEM grid, (a) bright field image of grains (indicated by dotted line), and (b) diffraction patterns of each position marked in (a) by numbers and letters and diffraction patterns show all the same orientations.

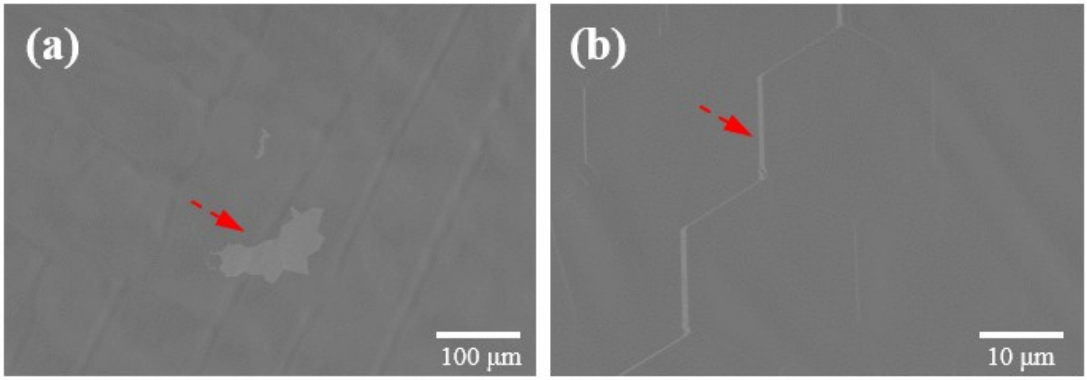

Fig. S4. SEM images of graphene after 4 hours of growth time showing (a) voids and (b) gap between the graphene islands (indicated by arrows).

NaCl assisted oxidation method was applied in order to prove continuity of two-step grown samples. Contrary to single step grown graphene on liquid Cu where grain boundaries are revealed through oxidation in NaCl solution, two-step grown samples were relatively safer to severe oxidation environment.

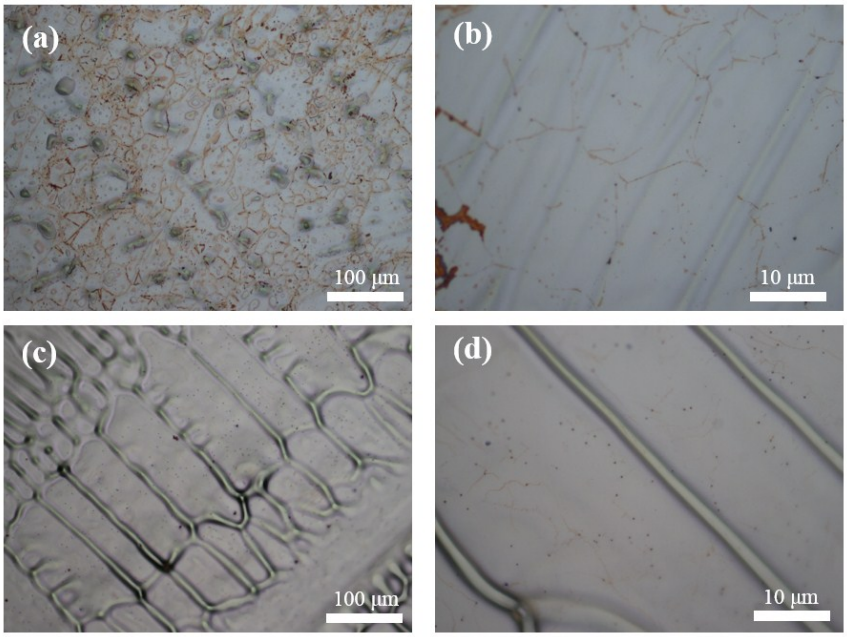

Fig. S5. NaCl-assisted oxidation method for visualization of graphene grain boundaries. (a) Optical microscope image of graphene grown by single-step growth after oxidizing in NaCl 6 wt. % solution, (b) magnified image of (a), (c) optical microscope image of graphene grown by two-step growth after oxidation, and (d) magnified image of (c). Ceullar structure was genrateted by cooling of liquid Cu.[1]

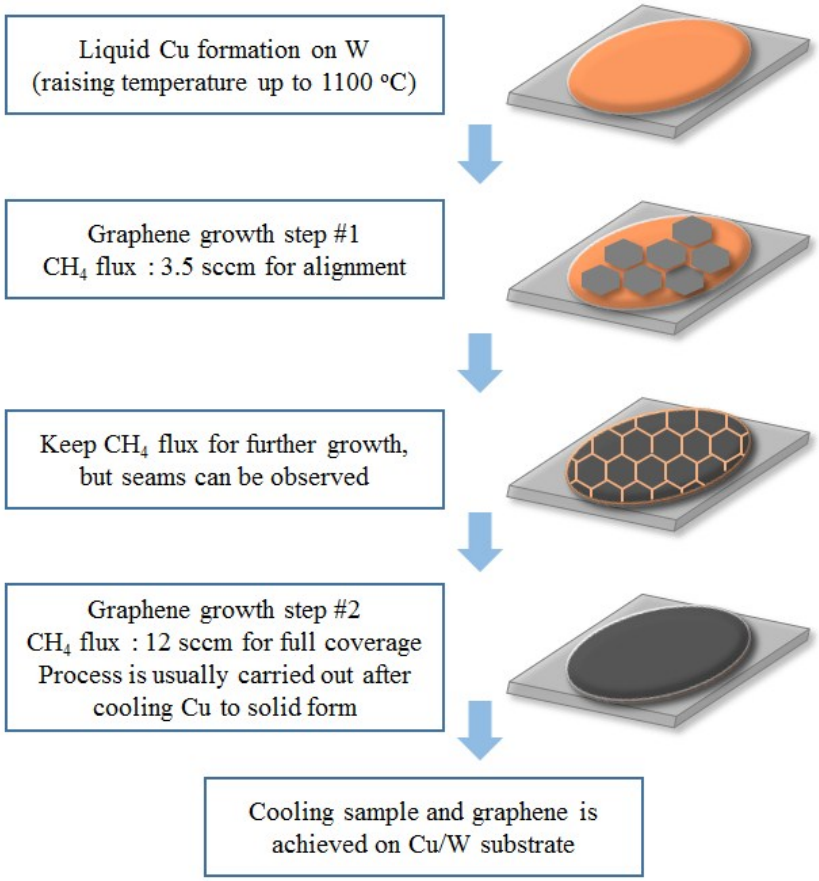

Fig. S6. Reaction scheme for two-step growth in this experiment.

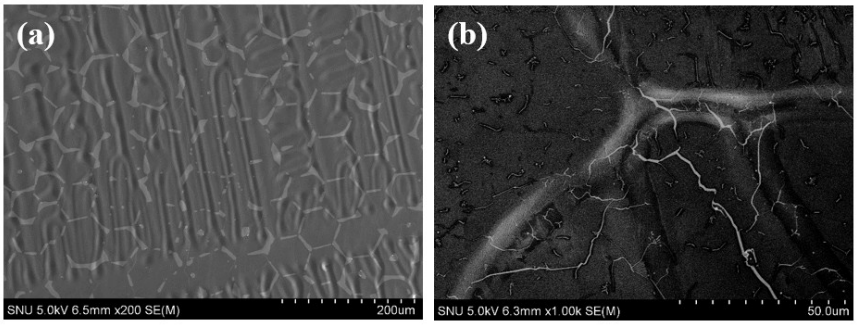

Fig. S7. SEM images of thermal crack and tearing of graphene on liquid Cu during cooling to solid. (a) SEM image of graphene sample just before coalescence of each graphene island, (b) SEM image of full coverage graphene after rapid cooling.

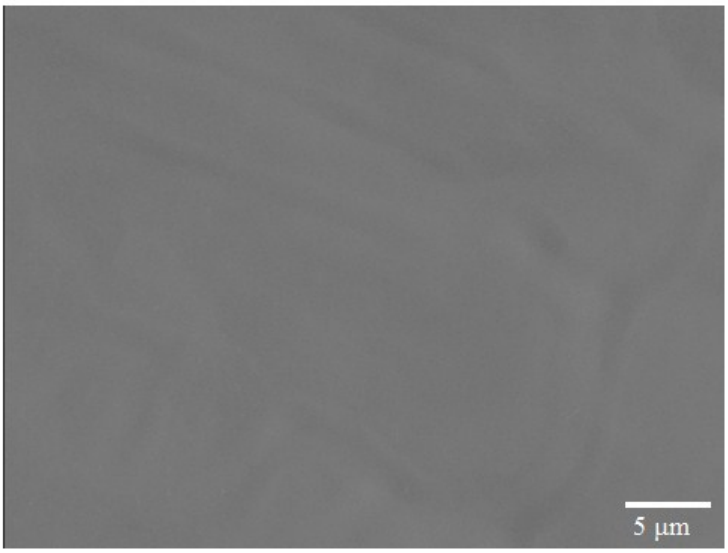

Fig. S8. High magnification SEM image of Fig. 2 (a) showing no gap or voids between graphene islands after two-step growth.

On top-side of SiO_2/Si wafer, notch was formed by partial cutting (just half of the wafer thickness, 200-300 μm). Then, graphene layers was transferred to substrate and electrode was deposited via shadow metal mask and e-beam evaporation. The thickness of Ti and Au was 5 and 80 nm, respectively. After deposition of electrode, chip was finally cut into 8 by 8 mm size based on pre partial-cutting line.

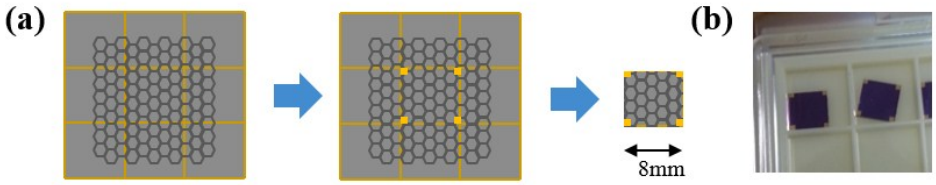

Fig. S9. (a) Schematic picture showing Van der Pauw pattern formation by partial-cut SiO_2/Si substrate, and (b) photograph of VDP devices after electrode deposition and cutting.

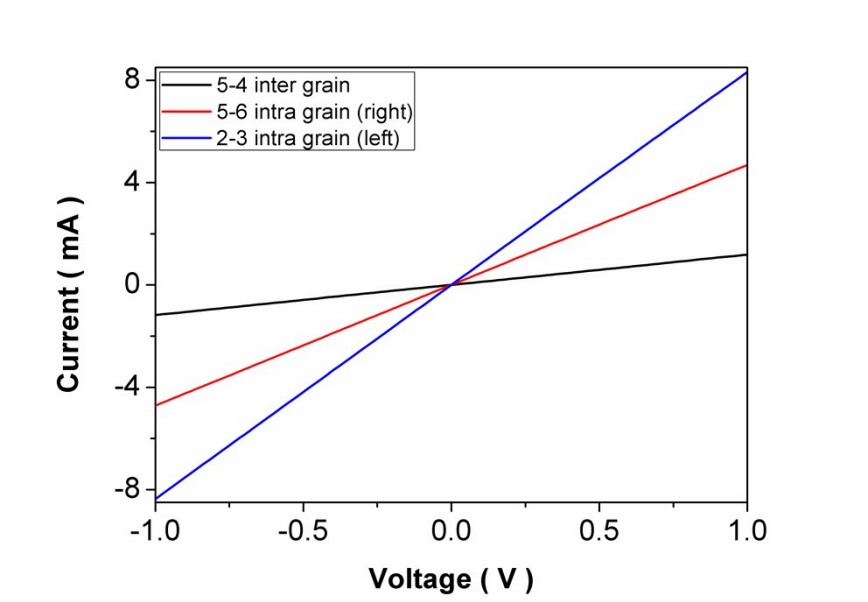

Fig. S10. (a) Current-Voltage curve of two adjacent graphene grains in Fig 5 (c).

References

[1] J. J. Hoyt, M. Asta, A. Karma, Materials Science and Engineering: R: Reports 2003**,** 41, 121.