Supporting Information

Gas Flow-Driven Aligned Growth of Graphene on Liquid Copper

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Experimental section

Graphene preparation: The growth of aligned graphene was carried out in an atmospheric pressure chemical vapor deposition (APCVD) system with methane (CH$_4$, 99.9 % purity) as carbon precursor, hydrogen (H$_2$, produced by hydrogen generator) as reduction reagent and argon (Ar, 99.999 % purity) or nitrogen (N$_2$, 99.999 % purity) as carrier gas. Before growth, Cu and W foils were conducted through a thorough clean procedure by ultrasonication in dilute hydrochloric acid, deionized water, ethanol and acetone successively to remove any impurity and metal oxide on surface. The growth process could be described briefly as follows. Firstly, placing the Cu foil (100 μm thick, 99.8% purity) on W foil (100 μm thick, 99.95% purity) and locating them into quartz tube at the heating zone of furnace (Lindberg/Blue M, TF55035A). The W foil was used to enable liquid Cu spreading on it, unless the liquid Cu would change to spheres.$^{1,2}$ Before heating, 1,000 sccm (standard cubic centimeters per minute) Ar was flushed into the quartz tube to clear air trapped in the system. Secondly, the system was heated from room temperature to target temperature in about 45 min and annealed for 30 min with 100 sccm H$_2$ as reduction gas. When the temperature was set below the melting point of Cu (1083 °C) or above the critical point (1140 °C) in our system, graphene samples with random orientation were obtained. However, when the temperature was set between 1083 and 1400 °C, graphene domains with perfectly identical tropism can be yielded. Thirdly, certain of flow rate of CH$_4$ gas was introduced into the system to induce graphene growth, with Ar and H$_2$ gas were set at 500 sccm and 80 sccm, respectively. And after the growth step finish, CH$_4$ gas was switched and the system rapidly cooled down to room temperature by directly opening the furnace (from growth temperature to 1000 °C in about 40 s).

Characterizations: The as-grown graphene samples were systematically characterized by optical microscopy (Olympus BX51), SEM (Hitachi S-4800; operating at 15 kV), Raman spectroscopy
Transfer of graphene: The transfer of graphene from Cu/W substrate to target substrate was performed by the electrochemical delamination method. Briefly speaking, the obtained graphene samples were protected by a solidified PMMA (polymethyl methacrylate) layer and then electrochemically separated by H$_2$ bubbling as a cathode in a 1 M NaOH aqueous solution. After the total detachment of PMMA/graphene from Cu/W substrate, graphene was transferred onto TEM grids or 300 nm thick SiO$_2$/Si followed by dissolving PMMA in warm acetone for further characterization.

Simulation method in details: To simulate the dynamic motion of graphene domains on liquid copper substrate, we employed the empirical COMB3 potential (the third generation of charge optimized many-body potential) with previous parameterizations for C, Cu in all our MD (molecular dynamics) simulations by using MD software LAMMPS. The COMB3 potential has already been successfully used to study hydrocarbons on Cu surfaces, and graphene sheets on Cu, which is able to describe the dynamic bond breaking and formation by bond-order calculation and to determine the dynamic atomic charge by a self-consistent charge equilibration approach. Cu bulk melting temperature was studied through the coexistence method, which demonstrated the melting temperature in the COMB3 model lied between 1140 and 1145 K. For simulating the melting liquid copper in CVD experiments, we firstly attained the amorphous structure by melting the Cu (100) substrate containing 8295 Cu atoms. Then, the atoms in the bottom of the Cu substrate were held fixed. Hexagonal-shaped graphene flake with a side length of 1.72 nm and with zigzag edge (whose energy was higher than that of the armchair edge) was placed on top of amorphous Cu surface to simulate the graphene domain in the CVD growth system. Then, 560 nitrogen gas molecules with a density of 1.3 g/L were introduced to simulate the gas flow during the CVD process. The size of simulation box was 72.3 Å × 72.3 Å × 46 Å (the MD model was shown in Figure 4a). A Langevin thermostat was applied to the 6 Å-thick layer of Cu above the fixed layer to control the temperature in MD simulations. The total simulation time was 2.1 ns including 100 ps for system relaxation and 2 ns for simulating nitrogen gas flowing on liquid copper surface. Here the mobility of the nitrogen gas molecules was given by using Poiseuille flow with an additional force of 0.16 nN, and an upper wall was used to constrain the molecular movement in the Z direction. The velocity is much larger than that used experimentally, in order to save the computational costs. The time step in MD simulations was 0.2 fs.
## Supporting Tables

### Table S1. Contrast among the three methods for producing large single crystal graphene.

| Methods                      | Only one graphene nucleus on substrate | Aligned graphene islands “seamlessly stitch” on single crystal metals | Aligned graphene islands “seamlessly stitch” on liquid Cu |
|------------------------------|----------------------------------------|----------------------------------------------------------------------|---------------------------------------------------------|
| Substrate                    | Polycrystalline Cu                      | Solid Cu and Ge single crystals                                      | Liquid Cu                                               |
| Growth time                  | 2.5 h-12 h                              | 20 min-1 h                                                           | Less than 30 min                                        |
| Largest size                 | 1.5-inch                                | (5 × 50) cm²                                                         | Only limited to the size of substrate (2 cm × 2 cm in this work) |
| Advantages                   | (1) no need of single crystal metals;   | (1) very short growth time; (2) suitable for industrial-level applications | (1) very short growth time; (2) no need of single crystal metals; (3) suitable for industrial-level applications |
|                             | (2) very large single crystal graphene with perfect hexagonal shape |                                                                      |                                                         |
| Disadvantages                | (1) typically low growth rate; (2) sensitive to the growth condition (small growth window) | (1) high price of the single crystal substrate; (2) long time treatment of the single crystal substrate; (3) defects even very few remain in the single crystal graphene | (1) high growth temperature compared to solid metal; (2) very few defects even remain in the single crystal graphene |
| Ref.                         | Nat. Commun. 2013, 4, 2096; Science 2013, 342, 720-723; Nat. Mater. 2016, 15, 43-47; Nat. Nano. 2016, 11, 930-935 | Science 2014, 344, 286-289; Adv. Mater. 2015, 27, 1376-1382; Sci. Bull. 2017, 62, 1074-1080; Adv. Mater. 2016, 28, 8177-8183 | This work                                               |
Supporting Figures

Figure S1. AFM image and corresponding height profile taken at the aligned graphene domains. The height profile confirms their monolayer nature.

Figure S2. Atomic-resolution AFM characterization of as-grown aligned graphene. (a) Lateral force trace image of aligned graphene sample on Cu. (b-d) Raw atomically resolved lateral force images for islands I, II, and III marked by the white dots in a, respectively.
Figure S3. Atomic-resolution AFM characterization at the connected region of two graphene grains indicated by blue dotted lines. (a-c) Lateral force trace image of as-grown connecting graphene, in which b is the enlarged photo of the green dashed box in a, and c is the enlarged photo of the green dashed box in b. (d-f) Atomic-resolution friction images of region I, II, and III in c, respectively.
Figure S4. High-resolution TEM (HRTEM) characterizations at the junction of graphene domains. (a) SEM image of graphene transferred onto TEM copper grid, in which two adjacent graphene grains are merging with same orientation. (b) Bright-field TEM image of an edge at the junction of two graphene grains indicated by white dotted lines. (c-d) HRTEM images of regions in b, marked by (c) blue and (d) green box respectively, showing no grain boundary in the merged area.

Figure S5. Raman mapping of as-grown graphene after transfer onto SiO$_2$/Si substrate. (a) Raman mapping of the intensity ratio of 2D/G band in a random region of graphene sample, indicating its uniform single-layer feature. (b) Raman mapping of the intensity ratio of D band/substrate in the same region with a. (c) Raman mapping of the intensity ratio of 2D/G band in another region of graphene sample, also indicating its uniform single-layer feature. (d) Raman mapping of the intensity ratio of D band/substrate in the same region with c.
Figure S6. SEM images of graphene grown under different flow rates of CH$_4$ and hydrogen gas. (a-c) Increasing the flow rate of CH$_4$ from 0.6 to 1.2 sccm. The flow rates of Ar and H$_2$ gas were set at 500 and 80 sccm, respectively. (d-f) Increasing the flow rates of the H$_2$ and CH$_4$. The flow rates of H$_2$/CH$_4$ in d was 80 sccm/0.8 sccm, in e was 160 sccm/1.6 sccm, and in f was 200 sccm/2.0 sccm. The flow rate of the Ar gas was set at 500 sccm.

Figure S7. SEM images of graphene grown under different flow rate of Ar. (a-b) CVD graphene growth without Ar gas and under 250 sccm Ar gas. Growth conditions: 2 sccm CH$_4$ and 50 sccm H$_2$ for 20 min at 1100 °C in a and 0.8 sccm CH$_4$ and 100 sccm H$_2$ for 20 min at 1100 °C in b. (c-f) CVD growth by increasing the flow rate of Ar from 600 to 1500 sccm. Growth conditions: 0.8 sccm CH$_4$ and 100 sccm H$_2$ for 8 min at 1100 °C.
Figure S8. SEM images of graphene samples obtained at different annealing times of the Cu/W substrate.

Figure S9. SEM images of graphene samples obtained at different growth temperatures. (a-c) Below the critical value (1140 °C), graphene domains grown on liquid Cu aligned in the same orientation. (d-f) Above the critical value, graphene domains grown on liquid Cu were observed to be in different tropism. Growth conditions: 500 sccm Ar, 80 sccm H₂ and 0.8 sccm CH₄ for 5-12 min at different temperature, respectively.
Figure S10. Distribution of rotation angles of graphene domains obtained at growth temperature of 1150 °C (a), 1160 °C (b), 1170 °C (c), and 1180 °C (d), respectively. Once the growth temperature was above the critical value of 1140 °C, graphene nucleated according to a random rule. Growth conditions match the samples grown at the same temperature in Figure 10.

Figure S11. SEM images of graphene samples obtained at different growth temperatures with N$_2$ as the carrier gas. (a-c) Graphene growth below the critical value (1140 °C). (d) Graphene growth above the critical value. Growth conditions: 500 sccm N$_2$, 100 sccm H$_2$ and 0.8 sccm CH$_4$ for 12 min at 1100 °C (a), 1120 °C (b), 1140 °C (c) and 1160 °C in (d), respectively.
Figure S12. SEM images of graphene domains with different layer number. (a) Single-layer graphene domains aligned in same orientation in the liquid Cu-catalyzed graphene growth process. (b) The multilayer graphene sample aligned in same orientation.

Figure S13. Illustration of the definition of $\theta$ angle in simulation. $\theta$ was defined as the angle between X axis and centrally vertical line of the specified side. The C* atom was in the central of the graphene edge. If the side of graphene domain is vertical to the gas flow, the graphene domain will rotate and the value of $\theta$ angle will change.
Figure S14. Nitrogen flow drives graphene domains to rotate and form ordered orientation on melted Cu at 1200 K when the gas flow direction is perpendicular to one side of this hexagonal graphene. (a) After full relaxation for 100 ps, graphene domain stays in original place with initial $\theta = 59.47^\circ$ in the absence of nitrogen flow. (b) With introducing nitrogen flow in X direction, the graphene domain moves forward and rotate until its two sides are parallel to the flow direction of nitrogen. (c) Mean square displacement for the Cu atoms as a function of simulation time. (d) Velocity variation of surface (Sub4) and bottom (Sub1) Cu atoms.
Figure S15. Nitrogen flow drives graphene domains to rotate and form ordered orientation on melted Cu at 1200 K when the gas flow direction is parallel to one side of this hexagonal graphene. (a) Snapshot of top view of graphene after full relaxation. Graphene domain stays in original place in the absence of nitrogen flow. (b) Snapshot of top view of graphene with orientation attained after nitrogen flow driving graphene domain for 1680 ps. (c) Mean square displacement for the Cu atoms as a function of simulation time. (d) Velocity variation of surface (Sub4) and bottom (Sub1) Cu atoms.
Figure S16. XRD characterization of Cu/W substrates after aligned graphene growth. (a-f) XRD spectra for six Cu/W samples on which graphene growth all developed aligned behaviour. In order to maintain the crystal structure of Cu substrate in liquid phase as far as possible, all samples were conducted rapid cooling after growth procedure finishing (40 s from 1140 °C to 1000 °C). The peak at about 58° was assigned to the exposed W substrate. Their XRD characterizations with different crystal orientations indicate that the facet of Cu takes no effect on the orientation of graphene domains in our preparation method.
Figure S17. Effects of temperature on the migration of graphene domain and Cu substrate at temperature of 300 K and 1400 K, respectively. (a) Mean square displacement of the Cu atoms as a function of simulation time. (b) Flow velocity variation of surface (Sub1) Cu atoms. (c-d) Movement and rotation of graphene domain driven by gas flow at different temperature.
Reference

(1) Wu, Y. A.; Fan, Y.; Speller, S.; Creeth, G. L.; Sadowski, J. T.; He, K.; Robertson, A. W.; Allen, C. S.; Warner, J. H. Large Single Crystals of Graphene on Melted Copper Using Chemical Vapor Deposition. *ACS Nano* 2012, 6, 5010-5017.

(2) Geng, D.; Wu, B.; Guo, Y.; Huang, L.; Xue, Y.; Chen, J.; Yu, G.; Jiang, L.; Hu, W.; Liu, Y. Uniform hexagonal graphene flakes and films grown on liquid copper surface. *Proc. Natl. Acad. Sci. U. S. A.* 2012, 109, 7992-7996.

(3) Wang, Y.; Zheng, Y.; Xu, X.; Dubuisson, E.; Bao, Q.; Lu, J.; Loh, K. P. Electrochemical Delamination of CVD-Grown Graphene Film: Toward the Recyclable Use of Copper Catalyst. *ACS Nano* 2011, 5, 9927-9933.

(4) Gao, L.; Ren, W.; Xu, H.; Jin, L.; Wang, Z.; Ma, T.; Ma, L.-P.; Zhang, Z.; Fu, Q.; Peng, L.-M.; Bao, X.; Cheng, H.-M. Repeated growth and bubbling transfer of graphene with millimetre-size single-crystal grains using platinum. *Nat. Commun.* 2012, 3, 699.

(5) Klaver, T. P. C.; Zhu, S.-E.; Sluiter, M. H. F.; Janssen, G. C. A. M. Molecular dynamics simulation of graphene on Cu (100) and (111) surfaces. *Carbon* 2015, 82, 538-547.

(6) Plimpton, S. Fast Parallel Algorithms For Short-Range Molecular-Dynamics. *J. Comput. Phys.* 1995, 117, 1-19.

(7) Liang, T.; Devine, B.; Phillpot, S. R.; Sinnott, S. B. Variable Charge Reactive Potential for Hydrocarbons to Simulate Organic-Copper Interactions. *J. Phys. Chem. A* 2012, 116, 7976-7991.

(8) Parr, R. G.; Donnelly, R. A.; Levy, M.; Palke, W. E. Electronegativity-Density Functional Viewpoint. *J. Chem. Phys.* 1978, 68, 3801-3807.

(9) Sanderson, R. T. Electronegativity and Bond-Energy. *J. Am. Chem. Soc.* 1983, 105, 2259-2261.

(10) Gan, C. K.; Srolovitz, D. J. First-principles study of graphene edge properties and flake shapes. *Phys. Rev. B* 2010, 81, 125445.

(11) Koplik, J.; Banavar, J. R.; Willemsen, J. F. Molecular-Dynamics of Poiseuille Flow and Moving Contact Lines. *Phys. Rev. Lett.* 1988, 60, 1282-1285.