Supporting Information

Layer-by-Layer AB-Stacked Bilayer Graphene Growth Through an Asymmetric Oxygen Gateway

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Methods

(1) Growing SLG films on both Cu sides (SLG-Cu-SLG)

First, 25-μm-thick Cu foils (99.8%, Alfa Caesar, 13382, cut into 2 cm × 5 cm pieces) were electrochemically polished in a polishing solution (H_3PO_4 : H_2O = 3:1) under 2.5 A, 5.0 V for 1 min, then rinsed for several times with deionized water and dried in a N_2 blow. Then the pre-treated Cu foils were placed into a quartz boat and loaded into a 1-inch quartz tube of a home-built CVD system. The CVD system was pumped down to a vacuum of 10-20 mTorr and heated to 1,060 °C. Then the quartz boat was moved into the heating center of furnace (Thermofisher, Lindberg/Blue M) with a magnetic rod without introducing any gas. The residual O_2 in quartz tube with a partial pressure of ~ 3.0 mTorr was used to oxide the Cu foils for 2-5 min. After oxidization, 500 sccm H_2 and 100 sccm 1% CH_4

(diluted in Argon) were introduced into the CVD system to start the SLG growth for 1-1.5 h under the pressure of ~ 3,000-3,500 Pa. After growth, the quartz boat was moved out of the heating zone and cooled down to room temperature under H_2 and CH_4.

(2) Etching SLG film on one Cu side and oxidizing the exposed Cu surface (SLG-Cu-Cu_2O)

One side of SLG film on Cu was protected by PET film while the other side of SLG film on Cu was exposed and etched with plasma. In our PECVD system, the plasma of residual O_2 in the background vacuum of 60-100 mTorr was employed to etch the exposed SLG film and oxide the Cu surface under it to form Cu_2O layer. The plasma power was kept at 40-120 W for 1-2 h.

(3) Growing the second graphene layer of AB-BLG underneath the existing SLG template

The temperature of furnace was firstly increased to 1,000 °C and the CVD reactor was pumped down to ~ 10-20 mTorr. Then 0.5-1.0 sccm CH_4 and 500 sccm H_2 were introduced with a total pressure of ~ 300 Pa. After that, the SLG-Cu-Cu_2O substrate was moved into the hot zone in furnace to grow the second layer for several hours, with SLG protected by CH_4 and H_2. The cooling process was the same as that of Step (1).

(4) Fabricating dual-gate FET devices on AB-BLG samples

Firstly, BLG film grown on Cu was transferred onto SiO_2/Si substrate (300 nm SiO_2) via a PMMA-assisted method, and then spin-coated with a uniform layer of photoresist on the surface of AB-BLG. Secondly, the pattern of source/drain (S/D) electrodes were exposed by Micro-Writer and the photoresist on exposed regions were washed away in a developer solution. Thirdly, a 35 nm-thick Au layer was deposited on the top by electron beam evaporation. The photoresist and the Au on it, except those on S/D regions, were removed to form S/D Au electrodes on the surface of AB-BLG. Fourthly, AB-BLG channels with a width of 5 μm between S/D Au electrodes were made and other unwanted BLG regions were removed by reactive ion etching of O_2 plasma. Fifthly, the samples were annealed in oxidative atmosphere at 200 °C for 2 hours to get rid of the adsorbed chemicals. Sixthly, 2 nm-thick SiO_2 layer was deposited above by electron beam evaporation and then 35 nm-thick HfO_2 layer was deposited on the top by atomic layer deposition, which works as top-gate dielectric. Lastly,

the top-gate Au electrodes were fabricated following the same process of S/D Au electrodes fabrication. The electrical test is carried out in a shielded platform equipped with four probes connected Keysight-b1500.

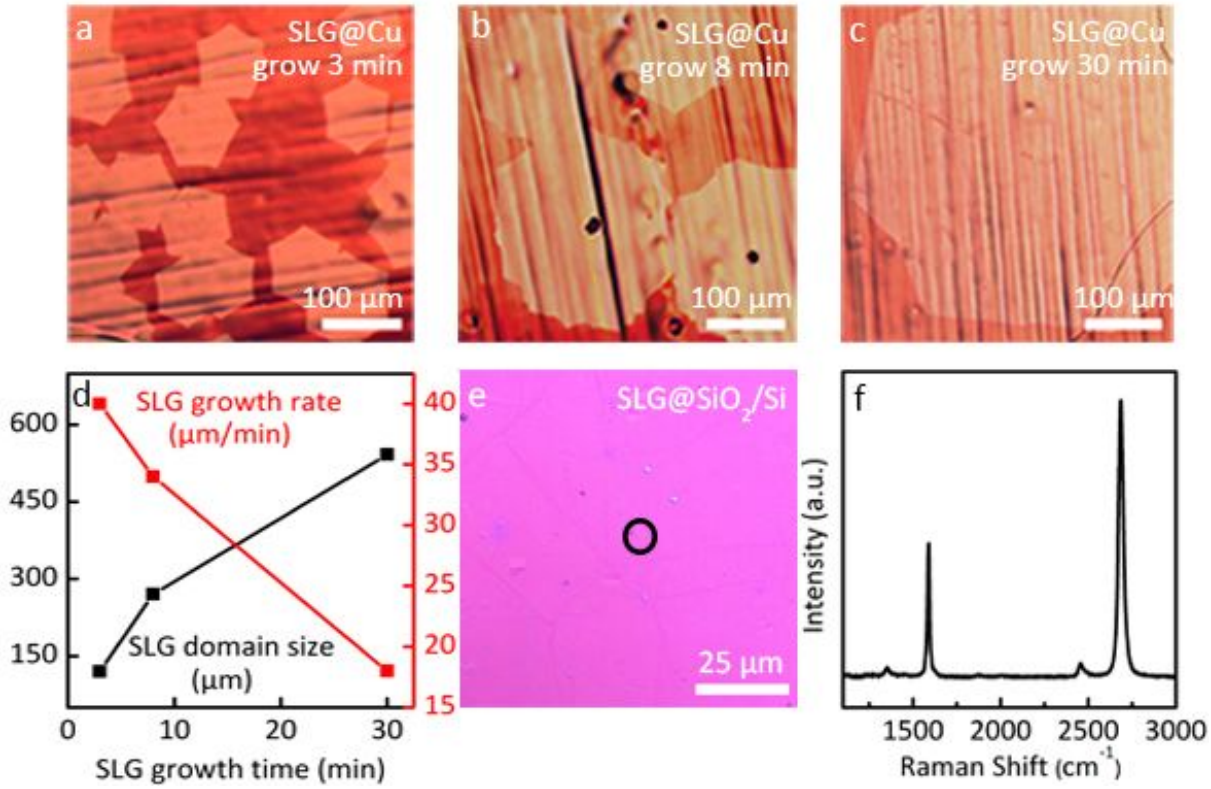

Figure S1. Growth of large domain-sized SLG template. (a-c) Optical images of SLG domains on Cu substrates with growth time of 3 min, 8 min and 30 min, respectively. (d) The growth rate and domain size of SLG vs growth time. (e) Optical images of SLG transferred onto 300 nm SiO_2/Si substrate. (f) Raman spectrum of SLG from black-circled region in (e). As growth proceeds, the domain sizes of SLG increase rapidly and will gradually coalesce with neighboring domains to form continuous SLG film, which will work as templates for the next growth of the second layer of BLG.

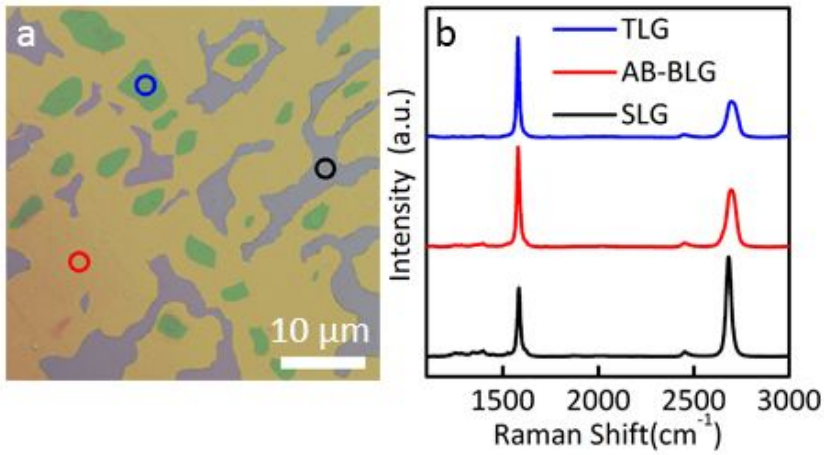

Figure S2. Independent study on Raman spectra of graphene with layer numbers of 1, 2 and 3. (a) False-colored optical images of graphene after transferring onto 300 nm SiO_2/Si substrate showing different color contrasts of SLG, AB-BLG and TLG (tri-layered graphene). The black, red and blue-circled regions are SLG, AB-BLG and TLG, respectively. (b) Raman spectra of graphene chosen from the three representative regions in (a). We used Raman spectroscopy with 514 nm laser to characterize graphene samples in this work. The intensity ratio of I_{2D} to I_G is more than ~ 1.7 for SLG, ~ 0.6 for AB-BLG and less than ~ 0.3 for TLG. PMMA doping in the process of graphene transfer may lead to the decrease of peak 2D intensity. The values of the FWHM of 2D peak are ~ 35 cm^{-1} for SLG, ~ 55 cm^{-1} for AB-BLG and ~ 65 cm^{-1} for TLG.

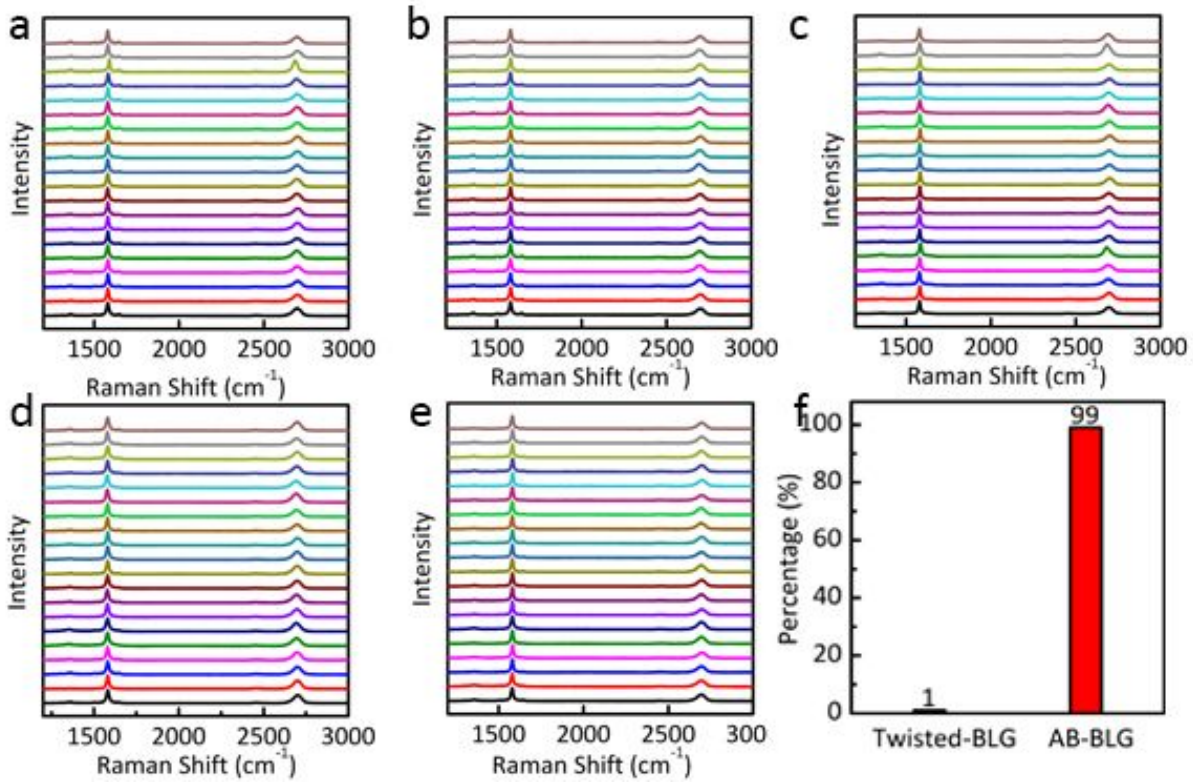

Figure S3. The study on AB-stacking percentage of BLG films. (a-e) The Raman spectra of 100 chosen points in BLG regions randomly across the whole sample area of 1 cmx1 cm. (f) Histogram of the percentage distributions of AB-stacked or twisted BLG. The FWHM of 2D peak between 50 and 60 refers to AB-stacking mode and the FWHM of 2D peak less than 40 cm^{-1} refers to twisted mode. Only one point in (**a**) gives a FWHM of 2D peak less than 40 cm^{-1}. Therefore, the AB-stacking percentage of BLG films is ~ 99%.

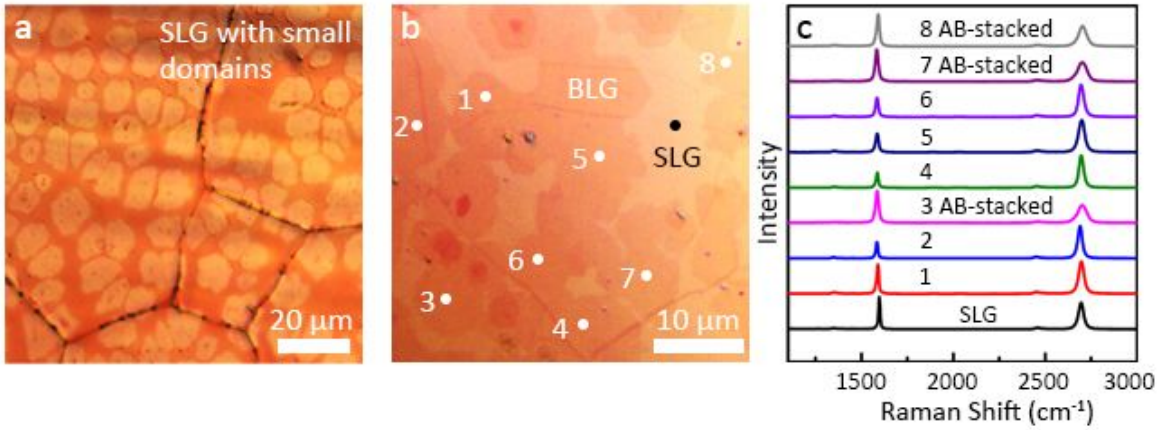

Figure S4. Effects of SLG domain size on AB stacking proportion of BLG. (a) Optical image of small domain sized SLG grown on Cu. These small domains would grow for additional time to

coalesce into a continuous SLG film for the next second layer growth. (b) Optical image of as-grown BLG transferred on 300 nm SiO_2/Si substrate. (c) Raman spectra taken from different spots labeled from (b).

It illustrates that when the domain size of SLG template is smaller (less than 20 μm in Fig. S4a), the corresponding AB-stacking proportion is much lower. Only 3 out 8 BLG's spectra in Fig. S4c exhibit a typical AB-BLG Raman feature. The corresponding AB-stacking proportion is calculated to be ~ 37.5%. In comparison, when the domain size is ~ 800 μm in Fig. 1a, the AB-stacking proportion can reach up to 99%. We ascribe this high AB-stacking preference to the template effect from a large domain sized SLG template[12, 21]. AB-stacking order in BLG is energy-favorable when the growth of second layer do not trespass different SLG domains[12, 21]. We can also expect that the BLG could be 100% AB-stacked if the SLG template is single-crystalline.

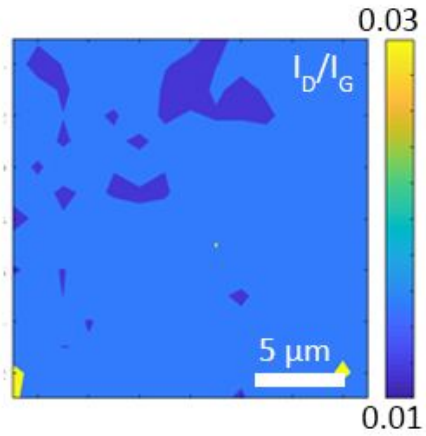

Figure S5. Raman mapping of the intensity ratio of peak D to peak G (I_D/I_G). ~ 99% area shows that I_D/I_G is less than 0.02, indicating few defects and high quality of our AB-BLG films.

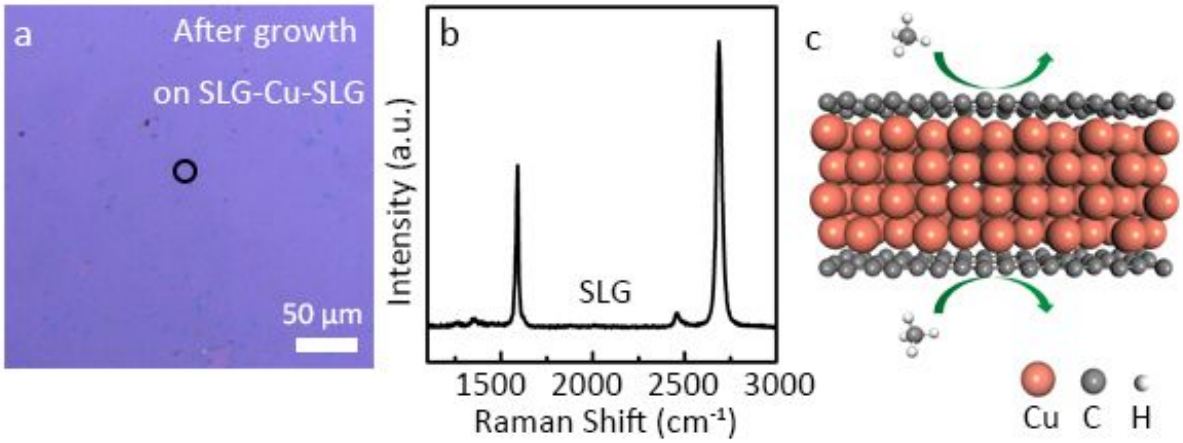

Figure S6. Control experiment showing the self-terminating growth on a symmetric SLG-Cu-SLG substrate. (a) Optical image of BLG growth results on symmetric SLG-Cu-SLG substrate. (b) Raman spectrum taken from the black circle region in (a). (c) Illustration of impossible BLG growth on SLG-Cu-SLG substrate. When SLG films fully cover the entire catalytic Cu surface, the growth of graphene would be shut down because carbon diffusion is blocked. To verify this, we grow BLG on SLG-Cu-SLG substrate for 5 h. However, we found no BLG regions after transferring it onto SiO_2/Si substrate as shown in (a). Raman spectra in (b) shows that the film is still SLG.

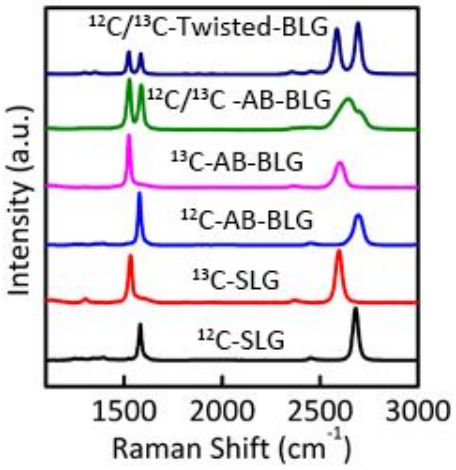

Figure S7. Independent study on Raman spectra of different graphene structures. It displays the differences of G and 2D peak position among different graphene. The peaks of ^{12}C-SLG and ^{13}C-SLG are similar except their shifted positions. The peaks of ^{12}C-AB-LG and ^{13}C-AB-BLG are also similar except the shifted positions. The ^{12}C/^{13}C-AB-BLG with a ^{12}C-layer and ^{13}C-layer shows a much wider 2D peak, whose FWHM is ~ 100 cm^{-1}, about twice that of ^{12}C-AB-LG and ^{13}C-AB-BLG of ~ 50 cm^{-}

[1]. As for the $^{12}C/^{13}C$-twisted-BLG, there are two distinct 2D peaks and two distinct D peaks.

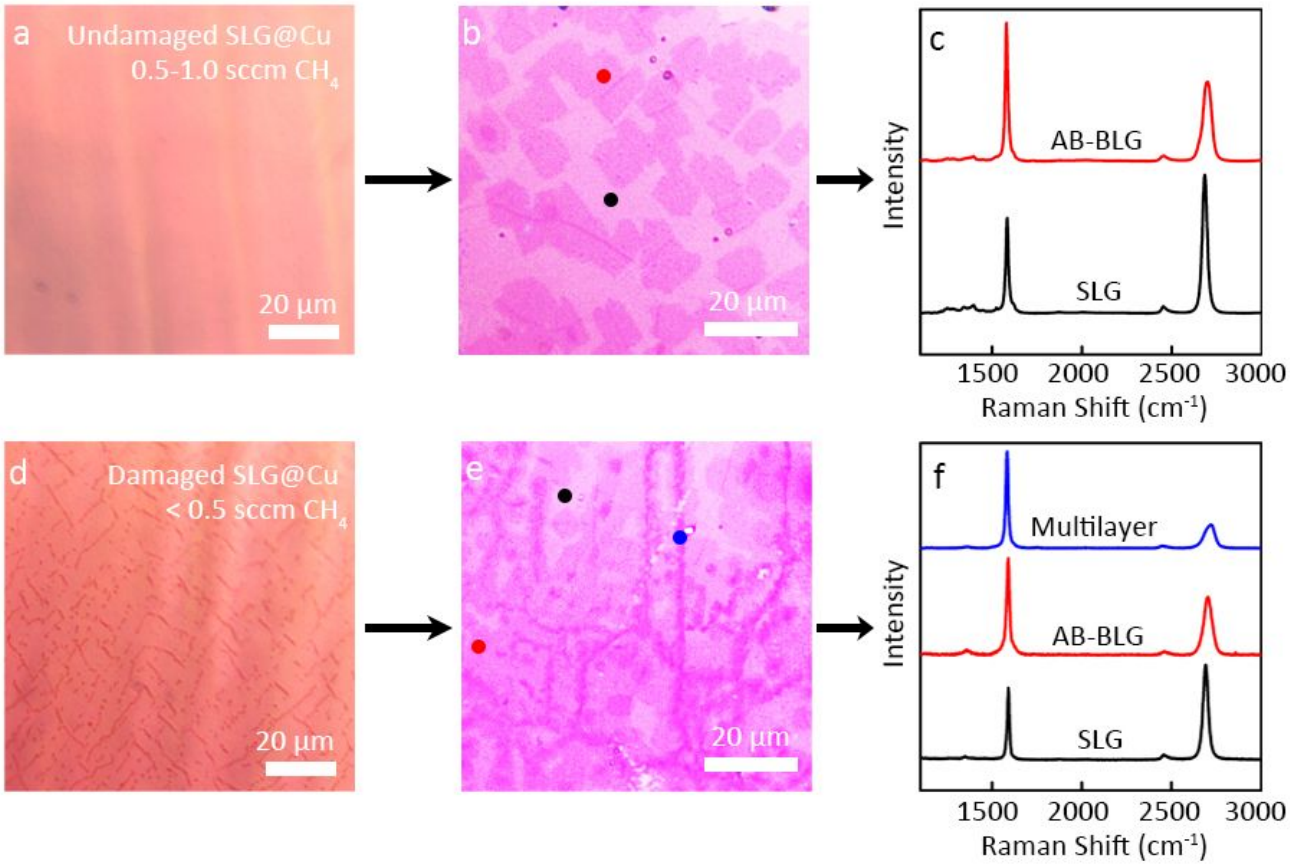

Figure S8. The effect of SLG's integrity on the growth of second layer. (a, d) Optical images of undamaged/damaged SLG on Cu, respectively. (b, e) Optical images of BLG after growth the second layer underneath undamaged/damaged SLG, respectively. (c, f) Raman spectra taken from the marked regions in (b, e), respectively.

As the existing SLG film works as a template for the growth of second layer, its integrity during the growth should be strictly preserved. In our optimized growth conditions (See Methods of Supporting Information), the SLG template can keep intact, displaying no obvious etching on the front side under microscope (Fig. S8a). Underneath such undamaged SLG template, isolated BLG domains can form after the growth of second layer (Fig. S8b and Fig. 2a). Raman spectra in Fig. S8c confirms these isolated domains are AB-BLG. In a different growth scenario, when the flow rate of CH_4 is lower than

0.5 sccm during growth, many etched stripes appear on SLG (Fig. S8d), which could be ascribed to the etching from background O_2 in CVD reactor or the released O_2 from Cu_2O. After the second growth, many few-layer domains (labeled with the blue spot) can form along these etched stripes (Fig. S8e), next to some BLG domains (red spot), showing different shapes from those in Fig. S8b. Raman spectra in Fig. S8f clearly shows these domains along stripes are multilayer graphene, whose value of I_{2D}/I_G is prominently less than 0.3, compared with that of SLG (>1) and AB-BLG (~ 0.7).

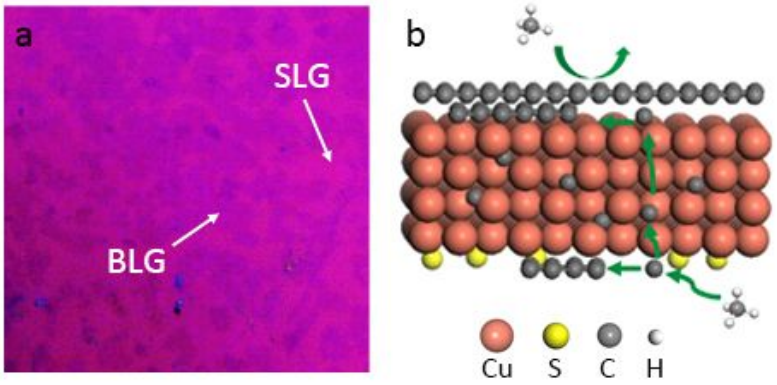

Figure S9. AB-BLG growth on a SLG-Cu-S substrate. (a) Optical image of BLG transferred on SiO_2/Si substrate. (b) Illustration of BLG growth process on SLG-Cu-S substrate. We employed air plasma, followed by H_2 plasma, to remove the SLG film on one Cu surface and then deposited a layer of S onto the plasma-treated Cu surface, forming a SLG-Cu-S substrate. Then we conducted BLG growth process to mimic BLG growth on SLG-Cu-Cu_2O substrate. Growth result in (a) shows that many irregular-shaped BLG domains are grown. It seems S can play the similar role with Cu_2O, as a channel for carbon diffusion to grow the second layer as shown in (b).

Table S1. The summary of different methods to grow AB-BLG

Method	Cu Substrate	Coverage of BLG	AB-stacking proportion	Single crystal (SC) or film	Controlling factors	References
Co-nucleation	Flat	~ 100%	~ 85%	Film	Partial pressure	Ref 11
	Flat	Low density	~ 100%	SC	Partial pressure	Ref 12
Layer-by-layer (above)	Flat	~ 67%	~ 100%	SC	Cu catalyst	Ref 18
Layer-by-layer (under)	Pocket	~ 100%	–	Film	Confined diffusion	Ref 19
	Pocket	~ 78%	~ 83%	SC	Confined diffusion	Ref 20
	Pocket	Low density	–	SC	Confined diffusion	Ref 21
	Flat	~ 96%	~ 99%	Film	Asymmetric diffusion	This work