Supporting Information

Sequential Growth and Twisted Stacking of Chemical-Vapor-Deposited Graphene

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Surface aryl functionalization of graphene stacks

The selective surface aryl functionalization of graphene stacks was conducted by immersing the graphene-on-SiO_2/Si sample into a mixed aqueous solution of 20 mM 4-nitrophenyldiazonium tetrafluoroborate (NO_2–$C_6H_4N_2^+BF_4^-$) and 1% w/v sodium dodecyl sulfate (SDS) for 5 hours.[1, 2] The functionalized sample was cleaned in deionized (DI) water overnight to remove the excess ions and dried by a N_2 gun. Only the topmost layer will be modified by the nitrophenyl groups to generate defect sites and the position of the D peak from these defect sites is indicative of the isotope type for the topmost layer (~1335 cm^{-1} for ^{12}C graphene D peak and ~1290 cm^{-1} for ^{13}C graphene D peak).

We functionalized the $^{12/13}C$ AB-BLG and $^{12/13}C$ *t*-BLG samples derived from the sequential growth modes and list their typical Raman spectra in Figure S2. The spectra of functionalized ^{12}C MLG and ^{13}C MLG samples are also shown as comparison. All the Raman spectra were measured from transferred graphene onto SiO_2/Si substrates, and the stacking order of graphene and adlayers is not influenced by the PMMA-assisted transfer process. The highlighted window of the Raman spectra that contains additional peaks induced by aryl groups is zoomed in Figure S2c. The center positions of the D and G peaks from isotopic graphene are marked as well (denoted as D^{12} and G^{12} for ^{12}C graphene, D^{13} and G^{13} for ^{13}C graphene, respectively), and the peaks located at 1285, 1321, 1392, 1443 and 1591 cm^{-1} (grey subpeaks in Figure S2c) detectable in all functionalized graphene samples are from the vibrations of aryl groups. Although with multiple peaks, the distinct lineshapes around the D^{13}/D^{12} region (~1250–1350 cm^{-1}) for ^{13}C and ^{12}C graphene still demonstrate the efficiency of functionalizing graphene surface. For functionalized $^{12/13}C$ AB-BLG and *t*-BLG samples, both of their lineshapes within 1250–1350 cm^{-1} are the same as that for ^{12}C MLG, but significantly different from that for ^{13}C MLG, suggesting that in these two BLG samples only D^{12} peaks are generated by the aryl groups and the topmost layer is formed by ^{12}C atoms. Considering that in both $^{12/13}C$ BLG the ^{12}C layer grows first and the adlayers are sequentially formed by ^{13}C atoms only, these surface functionalization and Raman experiments clearly demonstrate that the graphene adlayers by sequential growth mode are also grown underneath the dominant layer, the same as in other cases of growing multilayer graphene using CH_4.

Supporting figures

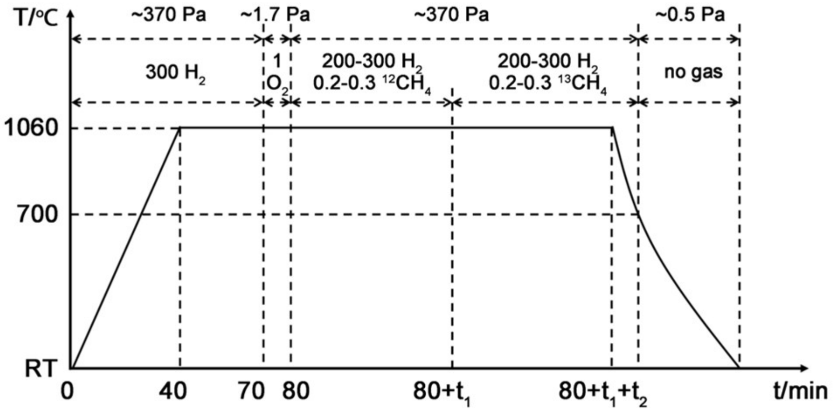

Figure S1. The temperature and flow program of the CVD process. Graphene was grown by a mixed gas of $^{12}CH_4$ and then $^{13}CH_4$. A recommendation of time and corresponding mass flow is 0.3 sccm $^{12}CH_4$ for 90 min and another 90 min for $^{13}CH_4$ with 300 sccm H_2 during the whole growth.

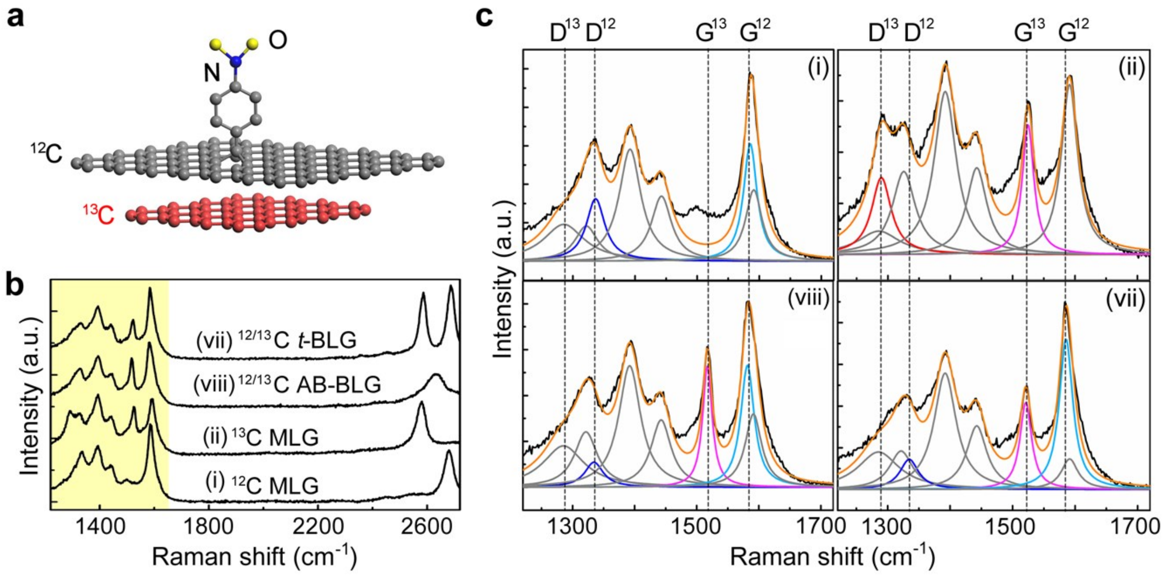

Figure S2. (a) Schematic of aryl group functionalization on isotopically labelled graphene. Only the topmost layer of the stack can be modified. (b) Typical Raman spectra of functionalized graphene samples. (c) Enlarged D-band spectrum windows from the highlighted areas in (b). The positions of the D and G peaks for ^{12}C and ^{13}C graphene are marked in the figure and the grey subpeaks indicate the peaks from the aryl groups.

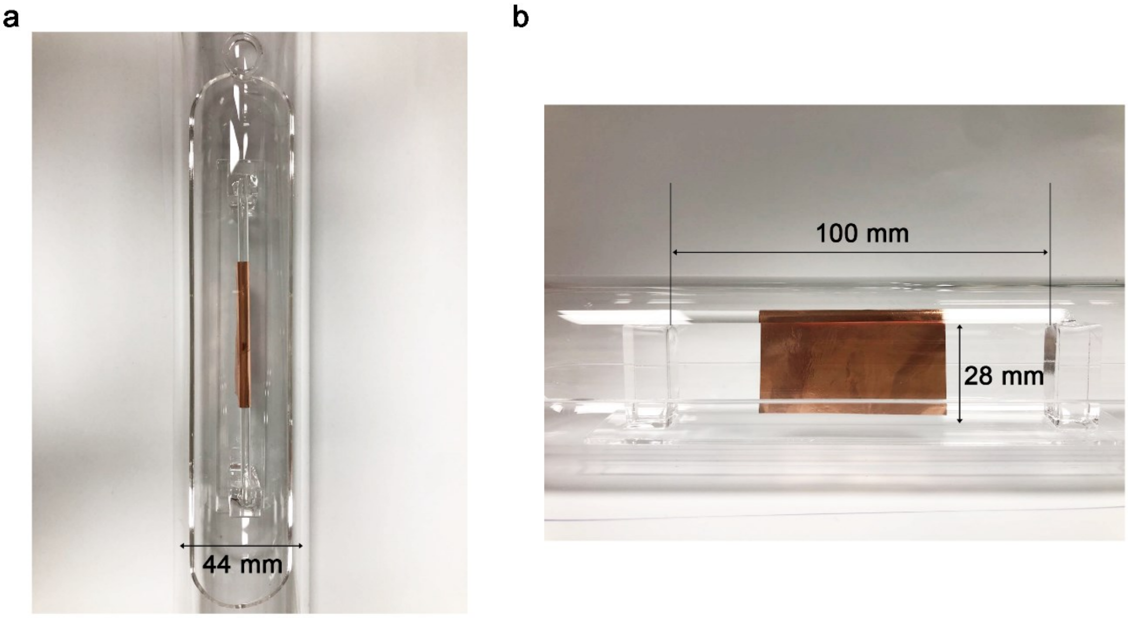

Figure S3. The top view (a) and front view (b) of Cu foil hanging on the quartz holder in the tube.

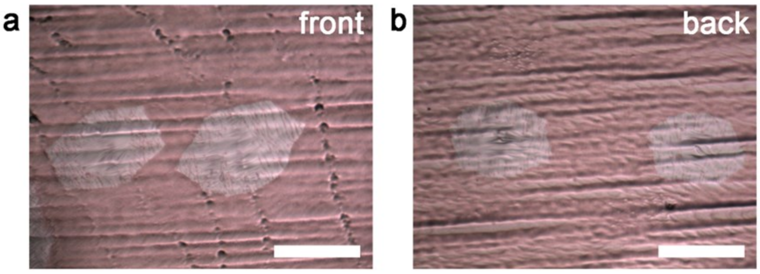

Figure S4. OM images of CVD grown graphene on (a) front and (b) back sides of the Cu foil after oxidation in air at 180 °C. Scale bars: 200 μm.

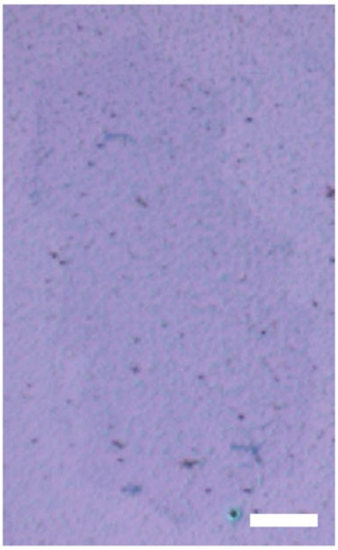

Figure S5. The OM image of the transferred bilayer graphene domains (Figure 3) on a SiO_2/Si substrate. The scale bar is 50 μm.

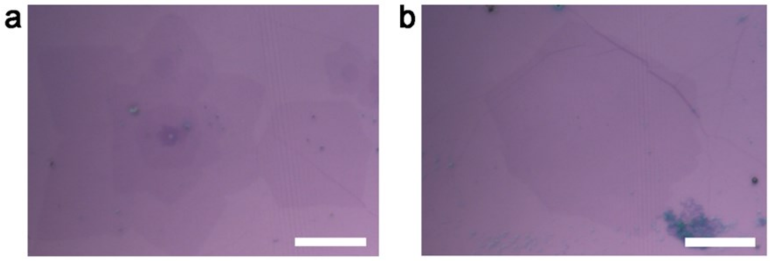

Figure S6. The OM images of the transferred graphene adlayers (Figure 4a and c) on a SiO_2/Si substrate. The scale bar is 25 μm.

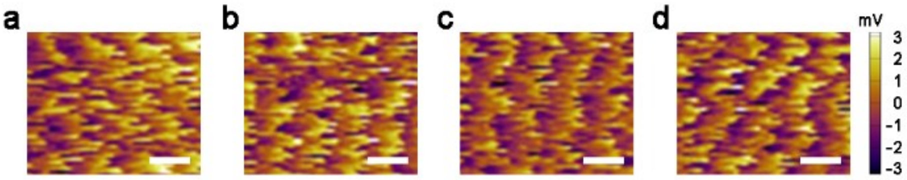

Figure S7. The original AFM images corresponding to the 1, 2 and 3 areas (a) and 4, 5 and 6 areas (b) in Figure 4a, and that correspond to the 7 and 8 areas (c) and 9 and 10 areas (d) in Figure 4b. The scale bars is 0.25 nm.

Table 1. Information on the fitting peaks of isotope labeled BLG for Fig.1(e).[3]

No. of subpeaks	^{12}C AB-BLG (cm^{-1})		$^{12/13}$C AB-BLG (cm^{-1})	
	Peak position	FWHM	Peak position	FWHM
1	2712.6	36.3	2721.7	36.1
2	2693.8	36.3	2700.6	36.1
3	2672.7	36.3	2679.0	36.1
4	2644.6	36.3	2651.7	36.1
5	–	–	2632.8	36.1
6	–	–	2613.3	36.1
7	–	–	2589.2	36.1
8	–	–	2561.9	36.1

[1] Bekyarova, E.; Itkis, M. E.; Ramesh, P.; Berger, C.; Sprinkle, M.; de Heer, W. A.; Haddon, R. C. Chemical modification of epitaxial graphene: spontaneous grafting of aryl groups. *J. Am. Chem. Soc.* **2009,** 131, 1336-1337.

[2] Zhao, P.; Kim, S.; Chen, X.; Einarsson, E.; Wang, M.; Song, Y.; Wang, H.; Chiashi, S.; Xiang, R.; Maruyama, S. Equilibrium chemical vapor deposition growth of Bernal-stacked bilayer graphene. *ACS Nano* **2014,** 8, 11631-11638.

[3] Fang, W.; Hsu, A. L.; Caudillo, R.; Song, Y.; Birdwell, A. G.; Zakar, E.; Kalbac, M.; Dubey, M.; Palacios, T.; Dresselhaus, M. S.; Araujo, P. T.; Kong, J. Rapid identification of stacking orientation in isotopically labeled chemical-vapor grown bilayer graphene by Raman spectroscopy. *Nano Lett.* **2013,** 13, 1541-1548.