Supplementary Information

Excitation Energy Dependent Raman Signatures of ABA- and ABC-stacked Few-layer Graphene

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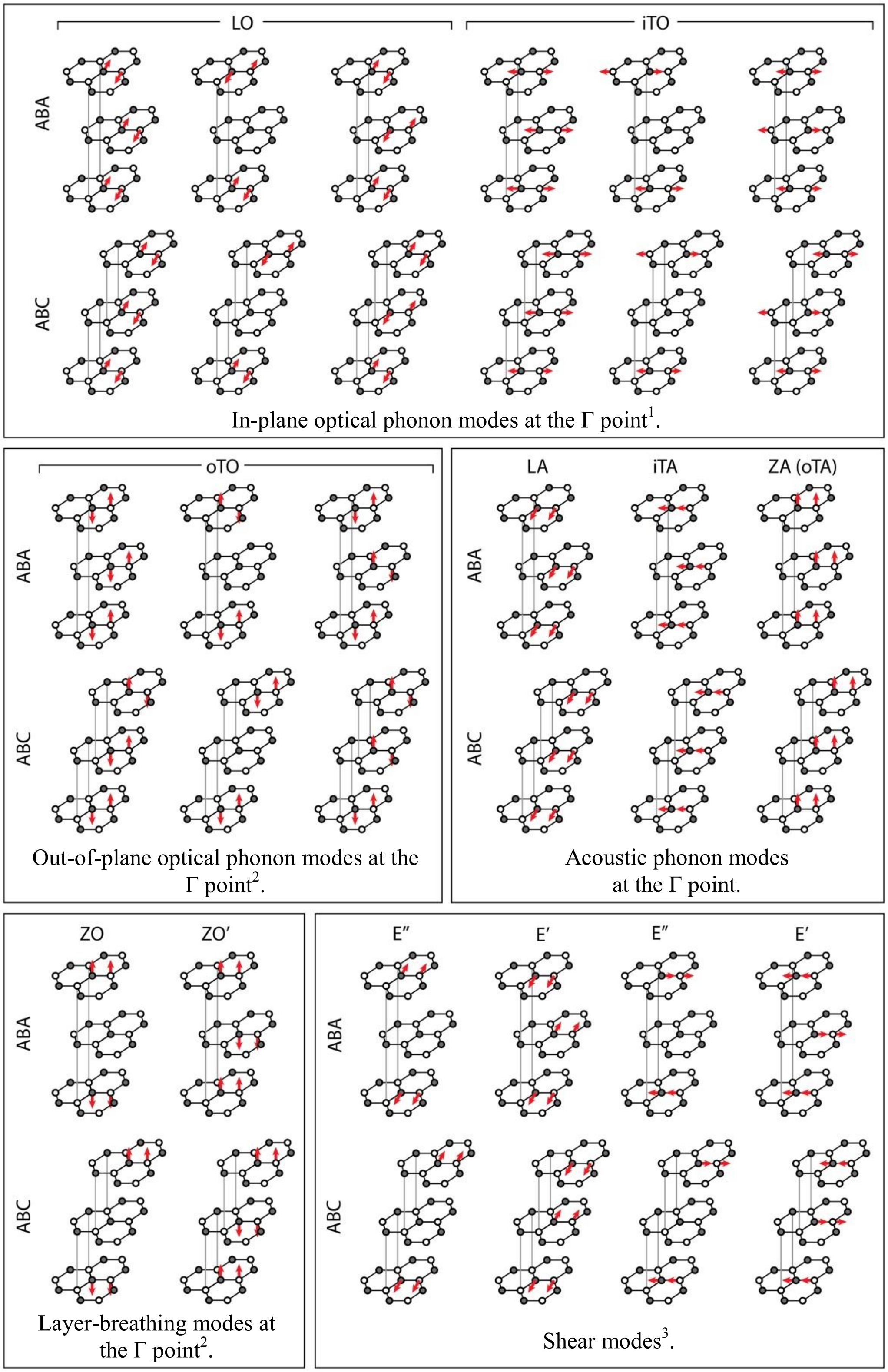
1. Schematics of vibration modes in 3LG



In-plane optical phonon modes at the Γ point[1].

Out-of-plane optical phonon modes at the Γ point[2].

Acoustic phonon modes at the Γ point.

Layer-breathing modes at the Γ point[2].

Shear modes[3].

Figure S1. Schematics of vibration modes in 3LG.

2. Visualizing areas with different stacking orders by using Raman imaging technique

Since Bernal (ABA) and rhombohedral (ABC) stacked few-layer graphene (FLG) have distinct Raman 2D line shapes, we can exploit this feature to visualize areas of FLG samples which have different stacking orders[4]. Compared to ABA-stacked FLG, the Raman 2D band in ABC-stacked FLG has a more asymmetric shape and an enhanced peak and a shoulder. As a consequence, by fitting the 2D band into a single Lorentzian peak, one can expect the widths and peak positions of the fitted peaks to be different between these 2 stacking orders. A study by Lui *et al.* and our results agreed that the *single*-Lorentzian fitted 2D bands in ABA-stacked FLG samples have narrower peak 'widths' and blueshifted peak positions compared to samples which are ABC-stacked [Fig. S2(a)][4]. By imaging such 'width' and 'position', one can visualize domains with different stacking orders. Figures S2(b) and (c) show an optical image of a graphene sample and its image of 2D-peak 'width' as determined by the *single*-Lorentzian fitting. The optical image shows regions in uniform colors, indicating the same thicknesses. However, the Raman image shows domains with different stacking orders in one sample.

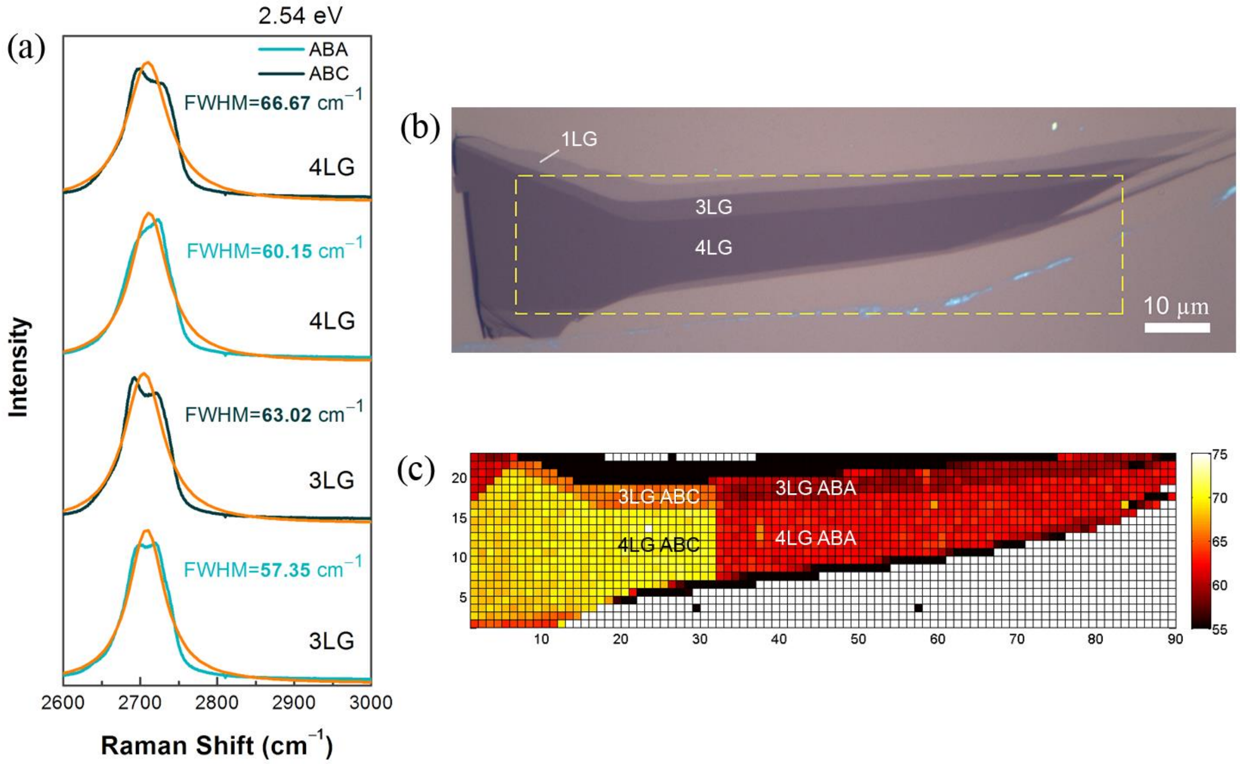


Figure S2. (a) Raman 2D bands of 3LG and 4LG with 2 different stacking orders (cyan and dark blue spectra) and their *single*-Lorentzian-fitted peaks (orange lines). (b) Optical image of a graphene sample. (c) Image of the 2D-peak ‘width’ of the same sample in (b). The yellow domain on the left-hand side is 4LG with the ABC-stacking order, and the red domain is 4LG with the ABA-stacking order. Near the top of this sample, there are narrow areas of ABA- (orange) and ABC-stacked 3LG (dark red).

3. Distinguishing stacked multilayer graphene and twisted/folded graphene.

During our investigation on ABA- and ABC-stacked graphene, we also encountered several incommensurate FLG samples. The misorientation or twist between two or more layers can modify the electronic structure[5-8]. The Raman spectra of such twisted FLG show some distinctive features, such as enhanced G and 2D band intensities or appearance of a small extra peak on the lower side of the G peak[9-12].

We compared the Raman 2D bands between folded FLG and stacked FLG. Figure S3(a) shows an optical image of a graphene sample in which an area of AB-stacked 2LG folds on domains of 2LG and 1LG. Figure S3(b) shows another folded graphene sample, in which a region of 3LG with the ABA stacking order folds onto itself. The Raman spectra of these folded graphene and stacked graphene [Figure S3(c), (d)] were measured under the same condition. We observed that under the same measurement conditions, the intensities of the 2D peaks in folded graphene are always several times larger than in FLG which has a stacking order. Additionally, the 2D line shapes of folded FLG do not resemble the line shapes of stacked FLG despite their same thicknesses. For example, Fig. S3(d) shows that the Raman 2D band of folded 3LG (3LG on 3LG) does not share similarity with the 2D band of ABA-stacked 6LG, in terms of intensity and line shapes.

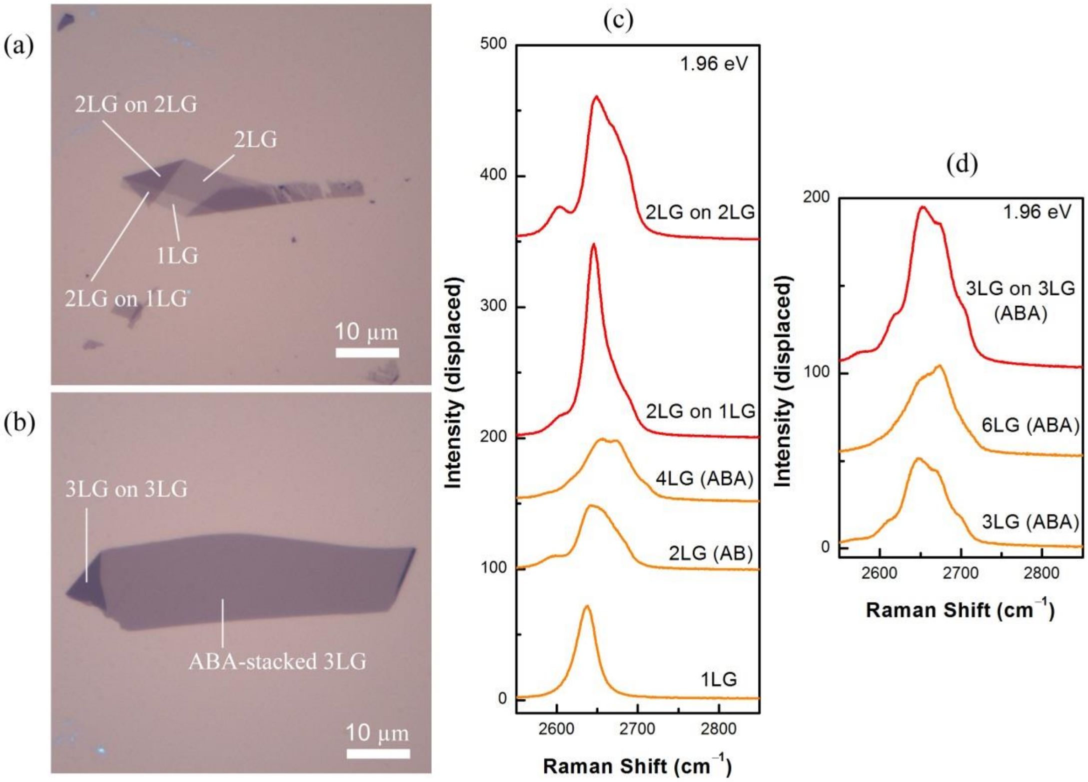


Figure S3. (a, b) Optical images of folded graphene samples on SiO_2/Si substrates. (c, d) Raman 2D bands of ABA-stacked FLG (orange lines) and folded FLG (red lines) were measured in the same condition with the excitation energy of 1.96 eV. The intensities of the folded-graphene samples are much larger than those of ABA-stacked FLG.

Beside the 2D band, we measured the Raman combination modes in the range from 1700 to 2250 cm^{-1} of folded FLG. We observed no blueshift of the LOLA-mode peak (Figure S4). As explained in the main report, the blueshift of the LOLA-mode peak occurs in ABC-stacked FLG but not in ABA-stacked FLG. If the excitation energy is 2.41 eV, the Raman spectra of ABC-stacked FLG will show a LOLA-mode peak at 2057 cm^{-1}. There is no sharp peak at 2057 cm^{-1} in the spectra of folded FLG as we have seen in the cases of ABC-stacked FLG. This means that the twisting or mismatching between graphene layers does not cause the blueshift of the LOLA-mode peak.

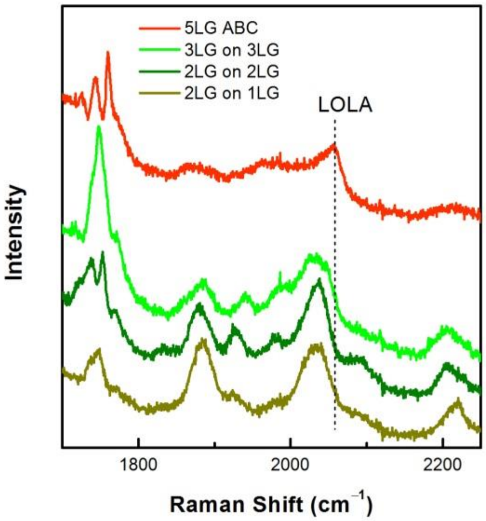


Figure S4. Combination Raman modes in the range between 1700 and 2250 cm^{-1} of folded graphene (green spectra) and ABC-stacked 5LG (red spectrum) for the excitation energy of 2.41 eV. The blueshifted LOLA-mode peak appears in ABC-stacked FLG only.

4. Excitation Energy Dependence of the Raman 2D band of FLG

The line shapes of the Raman 2D bands in ABA- and ABC-stacked FLG for different excitation energies are summarized in Fig. S5. These are the same data as those presented in Fig. 1 of the main paper but arranged differently to allow easy comparison between different excitation energies.

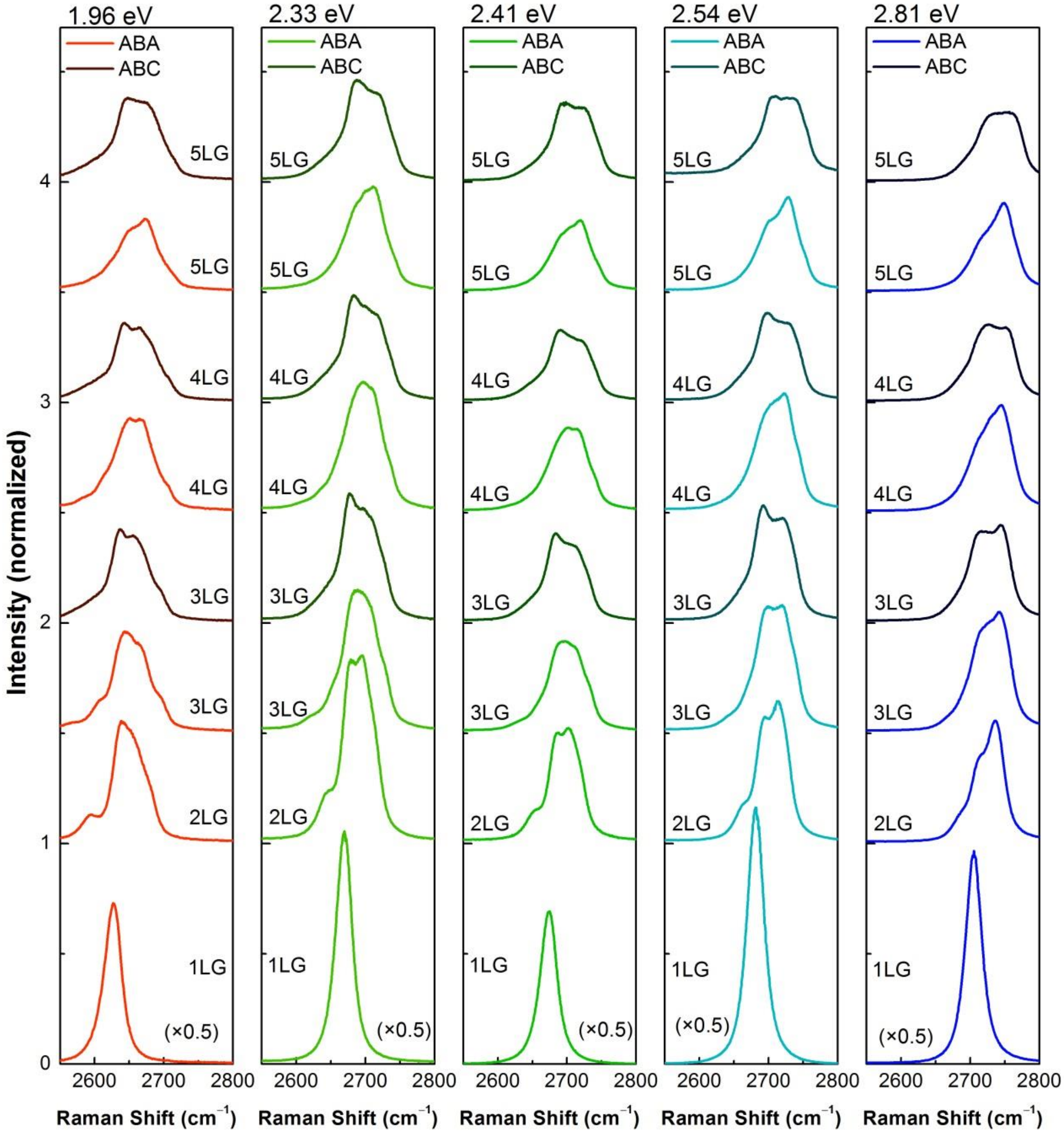


Figure S5. Raman 2D bands in ABA- and ABC-stacked FLG. The 2D peak intensity is normalized to the G peak intensity for each spectrum.

5. Raman spectra of combination modes from 1450 to 2250 cm^{-1}

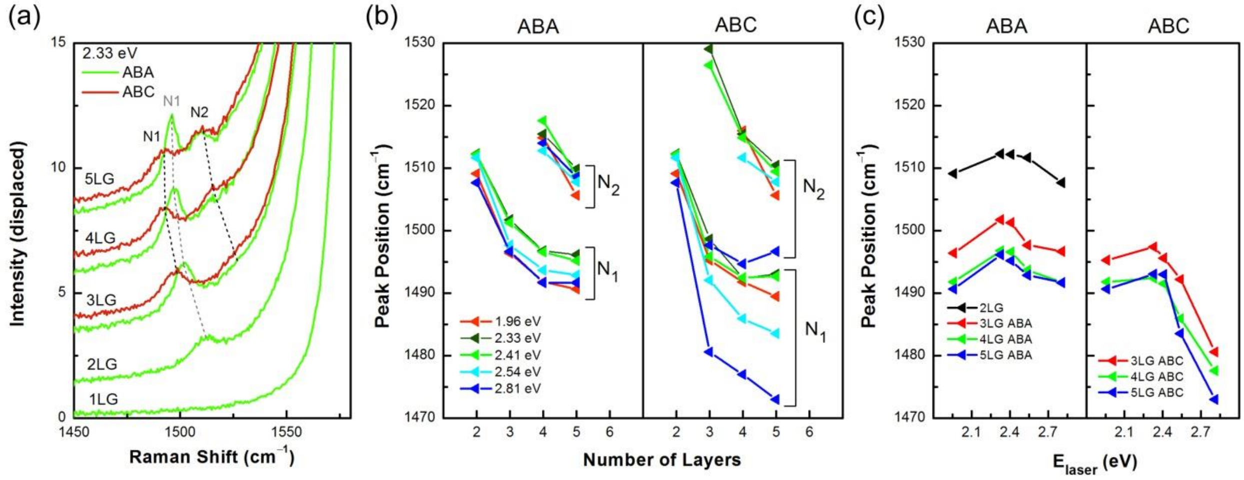


Figure S6. (a) Raman N-mode in FLG for an excitation energies of 2.33 eV. Green spectra are from monolayer and ABA-stacked FLG. Red spectra are for ABC-stacked FLG. Spectra from other excitation energies are shown in Fig. 7 of the main paper. (b) Dependence of the N-mode peak positions on the number of layers and the stacking order. (c) Excitation energy dependence of N_1 peak position in ABA- and ABC-stacked FLG.

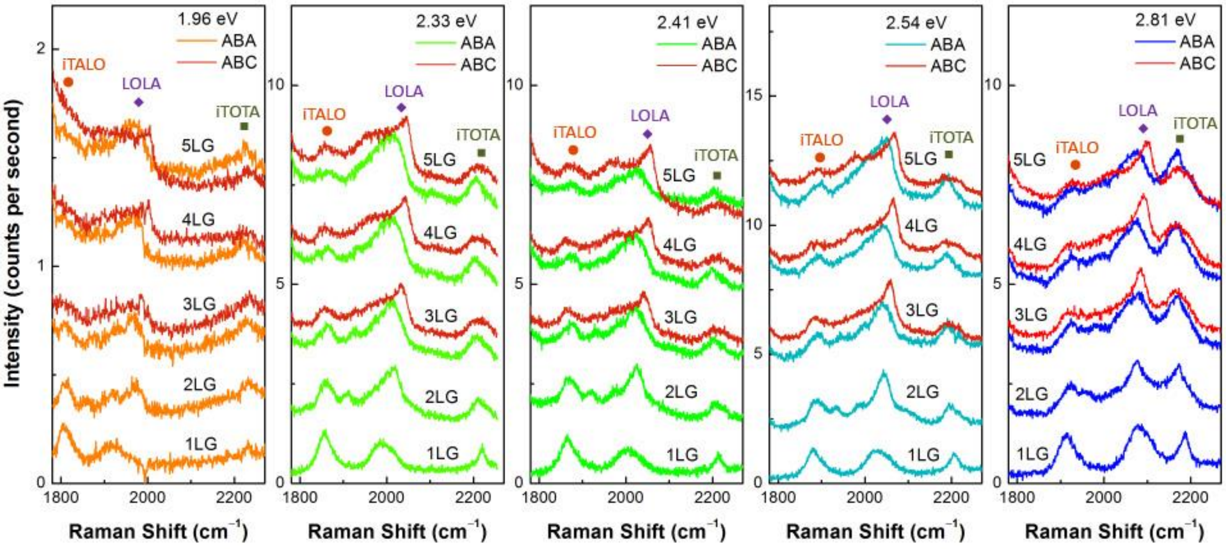


Figure S7. Combination Raman modes from 1780 to 2270 cm^{-1} in FLG, measured with 5 different excitation energies. Most of the peaks are similar between ABA- and ABC-stacking orders, except the LOLA peak. The LOLA peak in ABC-stacked FLG is sharper and stays at higher frequency side compare to that in ABA-stacked FLG.

REFERENCES

1. Yan, J.-A., Ruan, W. Y. & Chou, M. Y., Phonon dispersions and vibrational properties of monolayer, bilayer, and trilayer graphene: Density-functional perturbation theory. *Phys. Rev. B* **77**, 125401 (2008).
2. Cong, C. *et al.*, Raman Characterization of ABA- and ABC-Stacked Trilayer Graphene. *ACS Nano* **5** (11), 8760–8768 (2011).
3. Tan, P. H. *et al.*, The shear mode of multilayer graphene. *Nature Materials* **11**, 294-300 (2012).
4. Lui, C. H. *et al.*, Imaging Stacking Order in Few-Layer Graphene. *Nano Lett.* **11**, 164-169 (2011).
5. Novoselov, K. S. *et al.*, Two-dimensional gas of massless Dirac fermions in graphene. *Nature* **438** (10), 197-200 (2005).
6. Santos, J. M. B. L. d., Peres, N. M. R. & Neto, A. H. C., Graphene Bilayer with a Twist: Electronic Structure. *Phys. Rev. Lett.* **99**, 256802 (2007).
7. Laissardière, G. T. d., Mayou, D. & Magaud, L., Localization of Dirac Electrons in Rotated Graphene Bilayers. *Nano Lett.* **10**, 804-808 (2010).
8. Shallcross, S., Sharma, S., Kandelaki, E. & Pankratov, O. A., Electronic structure of turbostratic graphene. *Phys. Rev. B* **81**, 165105-165120 (2010).
9. Yoon, D., Cheong, H., Choi, J. S. & Park, B. H., Enhancement of the Raman scattering intensity in folded bilayer graphene. *J. Korean Phys. Soc.* **60** (8), 1278-1281 (2013).
10. Kim, K. *et al.*, Raman Spectroscopy Study of Rotated Double-Layer Graphene: Misorientation-Angle Dependence of Electronic Structure. *Phys. Rev. Lett.* **108** (24), 246103 (2012).
11. Podila, R., Rao, R., Tsuchikawa, R., Ishigami, M. & Rao, A. M., Raman Spectroscopy of Folded and Scrolled Graphene. *ACS Nano* **6**, 5784-5790 (2012).
12. Havener, R. W., Zhuang, H., Brown, L., Hennig, R. G. & Park, J., Angle-Resolved Raman Imaging of Interlayer Rotations and Interactions in Twisted Bilayer Graphene. *Nano Lett.* **12** (6), 3162-3167 (2012).