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# Identifying the stacking order of multilayer graphene grown by chemical vapor deposition via Raman spectroscopy

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Large-area monolayer (1LG) and multilayer graphene (MLG) grown by chemical vapor deposition (CVD) have been of great technological importance for the graphene electronics and photonics. Such CVD-grown MLG (CVD-MLG) flakes consist of multiple single crystal domains, whose stacking orders can be diverse due to the various choices of layer number, stacking sequence, and twist angle. Here, we demonstrated a way to identify the stacking order of CVD-MLG via Raman spectroscopy. The CVD-grown 1LG can be identified by comparing its optical contrast or G mode intensity with those of the corresponding mechanically exfoliated 1LG on the same substrate. Once the CVD-grown 1LG is distinguished, all the layer numbers of CVD-MLG flakes can be ascertained by the peak positions of their layer-breathing modes. The stacking sequence of a CVD-MLG flake can be determined by the shear modes, and the twist angles of twisted interfaces in the CVD-MLG flake are accessible by the so-called R modes. In this way, one can determine whether an MLG sample exhibit a fully nonstacked arrangement or if 2 or 3 of these layers are stacked in the AB stacking, including the order where the stacked layers would appear with respect to the nonstacked layers. This reliable way to identify the stacking orders advances an important step for the characterization of CVD-MLGs, shedding light on tailoring the properties of CVD-MLGs with specific stacking order on demand. Copyright © 2017 John Wiley & Sons, Ltd.

Keywords: layer-breathing mode; shear mode; stacking order; twisted multilayer graphene

#### Introduction

Monolayer graphene (1LG) and multilayer graphene (MLG) are the two-dimensional crystals and have attracted a plethora of attentions because of their remarkable physical, mechanical, and optical properties,<sup>[1,2]</sup> promising the ideal materials for post-silicon electronics and optoelectronics.<sup>[3–5]</sup> The bilayer graphene (2LG) prepared by mechanical exfoliation (ex-2LG) exhibits a stable crystallographic configuration of AB stacking. However, 2LG grown by chemical vapor deposition (CVD) tends to produce twisted 2LG (t2LG), in which one graphene monolayer sheet rotates by a certain angle  $(\theta_t)$  relative to the other.<sup>[6,7]</sup> t2LG exhibits with a series of fancy physical properties, e.g. lower Fermi velocity than 1LG<sup>[8]</sup> and  $\theta_t$ -dependent optical absorption,<sup>[9,10]</sup> and thus can be employed as photoelectric detector<sup>[11]</sup> and pressure sensors.<sup>[12,13]</sup> Similarly, N-layer graphene (NLG; N > 2) can exhibit AB stacking (AB-NLG) or twisted stacking (tNLG). By assembling m-layer (AB-mLG if m > 1) and *n*-layer (AB-nLG if n > 1) flakes with a  $\theta_t$ between them, a twisted (m+n)LG system can be formed, which is denoted as t(m+n)LG, a kind of twisted MLG (tMLG). In general, for a given total layer number N (with N = n + m + ...), t(n+m+...)LG is assumed to denote NLG stacked by each nLG, mLG, ... (AB-stacked constituents if n > 1, m > 1, ...) with twist angles  $(\theta_t)$  between them. The remarkable properties and underlying applications of 1LG, AB-stacked MLG (AB-MLG) and tMLG have motivated the development of their large-scale and synthetic growth methods,<sup>[14,15]</sup> such as graphitization of SiC surfaces<sup>[16]</sup> and CVD on various metal substrates.<sup>[3,17,19]</sup> The CVD method is scalable because of its simplicity and effectiveness.<sup>[18,19]</sup> It was revealed

MLG (CVD-MLG) that the CVD-grown flakes are polycrystalline,<sup>[9,20]</sup> consisting many single crystal domains separated by grain boundaries. Each domain can exhibit AB stacking<sup>[21,22]</sup> or twisted stacking with at least one twisted interface.<sup>[23-25]</sup> In a CVD-grown graphene flakes, approximately five to ten graphene layers can be grown at the central region of each single crystal domain while they gradually decrease the layer number toward 1LG at the edges of the domain.<sup>[26,27]</sup> Interestingly, in the same crystal domain, monolayer or multilayer hexagons show decreased lateral sizes and share almost the same hexagonal center, implying that they nucleated from the same active sites.<sup>[9,28,29]</sup> The stacking configuration of the nuclear center can be determined by the low-energy electron diffraction, low-

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energy electron microscopy, and isotopic labeling. It directly showed that the second graphene layer grows under the first layer on Ir(111), Ru(0001), and Cu substrate.<sup>[24,30–32]</sup> The  $\theta_t$  of t2LG can widely spread<sup>[9,28]</sup> from 0° to 30°, and phonon dispersion curve can be evenly deduced from Raman spectra of t2LG with different  $\theta_t$ .<sup>[7]</sup> This is also true for tMLG. There can exist up to *N*-1 twisted interface with different specific  $\theta_t$  in t*N*LG. The larger *N* of CVD-grown *N*LG (CVD-*N*LG, *N* > 1) is, the more complex its stacking order is. How can the novel properties of CVD-MLG be tailored by controlling its stacking order such as the layer number, stacking sequence, and  $\theta_t$  of each twisted interface is essential to the commercial applications of graphene flakes. Before addressing this strategic question, a convenient and reliable way to identify the stacking order of CVD-MLG is highly desired.

Raman spectroscopy is one of the most used and nondestructive characterization techniques in graphene-based systems. The Raman spectrum of AB-MLG consists of two sets of Raman peaks. The D, G and 2D modes are attributed to the in plane vibrations and are also present in 1LG,<sup>[33]</sup> and the so-called shear (C) and layer-breathing (LB) modes are ascribed to the relative motions of the adjacent layers.<sup>[34–37]</sup> Traditionally, the layer number and stacking order (e.g. AB or ABC stacking) of MLG can be distinguished by the profile of the 2D mode, the interference effect on the G mode intensity, and so on.<sup>[35,38-48]</sup> However, such method cannot be applied to CVD-NLG because of the existence of more complicated stacking orders. The stacking orders of CVD-2LG have been characterized in combination of Raman spectroscopy and transmission electron microscopy and the selected area electron diffraction patterns.<sup>[25]</sup> Selected area electron diffraction is a time-consuming technique and can only measure small region (around 0.1-1 µm). It cannot provide with a clear signature for the stacking sequences of CVD-NLG (N > 2) because the images become really complicated with increasing N. Our previous work<sup>[29]</sup> reported one kind of CVD-MLG with only one type twisted structure of t(1+n)LG. A complete method to distinguish all the stacking orders in CVD-MLG flakes with different layer numbers is still critically required.

In this letter, all the stacking sequences of two to four layer CVD-MLG are summarized, and the CVD-tMLG flakes are found to exhibit various stacking orders. We developed a method to figure out the layer number and stacking sequence of CVD-tMLG by optical contrast (OC) and Raman spectroscopy. CVD-grown 1LG (CVD-1LG) can be identified by comparing OC or Raman intensity of the G mode with those of exfoliated 1LG (ex-1LG). It is found that the OC of CVD-tMLG tends to raise an absorption peak with the position related to the presence of saddle-point excitons because of novel electronic structure in tMLG.<sup>[49]</sup> Under the excitation wavelengths associated with the absorption peak, a series of C and LB modes can be detected. By analyzing the C and LB modes of CVD-tMLG with arbitrary layer number, the layer number and stacking sequence can be easily figured out. Finally, the  $\theta_t$  of the twisted interface in CVDtMLG can also be identified by the so-called R modes, which originates from double resonance Raman inter-valley processes mediated by static potentials in rotationally stacked N-layers graphene.<sup>[50]</sup>

## Experimental

## Sample preparations

Multilayer graphene samples were grown by the low-pressure CVD in a tube furnace (inner diameter of 50 mm; Thermo Scientific Lindberg/Blue M) with the copper substrates (Alfa Aesar 46365, purity of 99.8%, and thickness of 25  $\mu$ m). Firstly, the system was

evacuated to 0.5 Pa, and then the Cu substrate was annealed at 1060 °C for 100 min under 50 sccm H<sub>2</sub> with a pressure of about 50 Pa. One additional step was also adopted by flowing 0.3 sccm O<sub>2</sub> for 10 min to reduce the nucleation density.<sup>[51,52]</sup> With the slight incorporation of the oxygen on the Cu surface, the MLG flakes grow under the typical condition of 50 sccm H<sub>2</sub> and 0.4 sccm CH<sub>4</sub>. After one-hour growth, the system was cooled down to room temperature with the gas flowing. Finally, CVD-MLG flakes were transferred onto the Si substrate with 90 nm SiO<sub>2</sub> thickness under the assist of poly(methyl methacrylate) (Aldrich). In addition, the exfoliated 1LG and MLGs (ex-MLGs) used in this work was mechanically exfoliated from a highly oriented pyrolytic graphite onto a 90 nm SiO<sub>2</sub>/Si substrate.

### Characterizations

The OC and Raman spectroscopy were performed under backscattering configuration at room temperature<sup>[53]</sup> using the Jobin-Yvon HR800 system equipped with a liquid nitrogen cooled chargecoupled device, a 100× objective (NA = 0.9) and a 50× objective (NA = 0.45) and two gratings (100 and 1800 lines/mm). Tungsten halogen lamp was used as a light source for OC measurements. The excitation wavelengths are 488 nm from an Ar<sup>+</sup> laser, 530 nm from a Kr<sup>+</sup> laser, and 633 nm from a He-Ne laser. The 1800 lines/mm grating enables us to have a resolution of 0.35 cm<sup>-1</sup> per chargecoupled device pixel at 633 nm as estimated from full width at half maximum of the Rayleigh peak. The plasma lines are removed from the laser signals using BragGrate Bandpass filters (OptiGrate Corp.). The measurements down to 5  $cm^{-1}$  for each excitation are accessible by three BragGrate notch filters with optical density 3 and a full width at half maximum of  $\sim$ 5–10 cm<sup>-1</sup>.<sup>[34]</sup> The typical laser power is ~0.5 mW to avoid samples heating.

## **Results and discussions**

Besides the AB stacking, MLG can exhibit other stacking configurations, i.e. ABC stacking and twist stacking. Fig. 1(a) show the atomic schematic of AB-2LG with the top (red) and bottom (blue) layers. t(1+1)LG can be formed if the bottom layer of the AB-2LG adjacent to the substrate exhibit a random  $\theta_t$  relative to the top layer, as shown in Fig. 1(b) with  $\theta_t = 21.8^\circ$ . The atoms in the two layers of t(1+1)LG give rise to a periodic superlattice, whose unit cell is defined by the lattice vector  $L_1$  and  $L_2$  in Fig. 1(b). This superlattice forms the so-called Moiré patterns. Similar Moiré patterns can also represent at each twisted interface of tMLG with the twist vector (p,q). The twist vector (p,q) is defined as the lattice vector of a unit cell of two adjacent twisted layers having p, q coordinates with respect to the basic vectors ( $\mathbf{a_1}$  and  $\mathbf{a_2}$ ) in Fig. 1(a) of 1LG<sup>[54]</sup> The twist angle can be derived from the twist vector as  $\cos \theta_t = (q^2 + 4qp)$  $(p^{2})/2(q^{2}+qp+p^{2})$ .<sup>[54,55]</sup> Thus, the t(1+1)LG with  $\theta_{t} = 21.8^{\circ}$  can be also depicted using the twist vector (1,2), as shown in Fig. 1(b) in purple arrows. Under this definition,  $\theta_t$  of 0° and 60° corresponds to AB-2LG and AA-2LG, respectively. AA stacking is not considered for CVD-MLG here because it is unstable.<sup>[56]</sup> We can also only restrict our analysis for  $0 \leq \theta_t \leq 30^\circ$  because of the hexagonal symmetry. For  $\theta_t$  ranging from 30° to 60°, its partner can be found with equivalent lattice constant, whose twist angle is  $60^{\circ}-\theta_{t}$ . The periodic superlattice structure in the real space always results in the corresponding periodic structure in the reciprocal space, and the twist wavevector can be defined by the relative rotation of the basic vectors in reciprocal lattice for each layer,<sup>[50]</sup> whose



**Figure 1.** Atomic structure schematics of AB-2LG (a) and t(1+1)LG with twist angle  $\theta_t = 21.8^{\circ}$  (b). The pink arrows ( $a_1$  and  $a_2$ ) in (a) represent the basic vectors of 1LG while the blue arrows ( $L_1$  and  $L_2$ ) in (b) are the lattice vectors in a twist supercell. t(1+1)LG can also be depicted with twist vector (1,2), which defined as the lattice vector having (1, 2) coordinates with respect to the basic vectors. (c) The summarization of the stacking sequences in CVD-*N*LG (N = 2,3,4).

absolute value is estimated as  $q(\theta_t) = 8\pi \sin(\theta_t/2)/\sqrt{3}$  a, where a = 2.46 Å is the lattice constant of 1LG.

In principle, there may exist up to *N*-1 twisted interfaces in t*N*LG (*N* > 1). Therefore, the stacking sequence of *N*LG becomes more and more complicated with increasing *N*. Once an additional layer is incorporated to an *N*LG, AB-stacked or twisted interface can be formed relative to its adjacent layer. Following this tendency, the number of stacking sequences for *N*LG (*N* > 1) can be easily pointed out as  $2^{N-1}$ . Fig. 1(c) summarizes all the stacking sequences for 2-4LG, taking all the AB-stacked and twisted interface into considerations. In Fig. 1(c), the layers represented with the same color are in AB stacking whereas a twisted interface rises between the adjacent layers with different colors. Two branches of stacking sequences can be separately derived from 2LG and t(1+1)LG; 1, 2, and 3 twisted interfaces can be found in t(1+1) LG, t(1+1+1)LG, and t(1+1+1+1)LG, respectively.

It should be noted that the AB-MLG is the most stable structure in the natural graphite, and the ratio of ABC-stacked one (ABC-MLG) is much smaller. Therefore, most of ex-MLG are AB-MLG. During exfoliation, *m*LG flakes can be unintentionally folded onto *n*LG flakes to form t(*m*+*n*)LG flakes.<sup>[36,37]</sup> A *m*LG flake from one substrate can also be transferred onto an *n*LG flake on another substrate to form a t(*m*+*n*)LG.<sup>[36,37]</sup> In fact, micrometer-sized MLG can be grown by CVD.<sup>[22,25]</sup> The transition temperature from ABC-MLG to AB-MLG is about ~1000 °C. The growth temperature of CVD-MLG in this work is about 1060 °C; therefore, ABC-MLG is expected to be a very small component in CVD-MLG grown at high temperature, and hereafter, we did not take ABC stacking into considerations.

Chemical vapor deposition-grown *NLG* is usually polycrystalline, consisting of several single crystal graphene domains with multiple layer numbers. Because CVD-*NLG* flakes cannot be strictly stacked layer by layer and the thinnest flake may be not 1LG, the determination of the layer number of each CVD-*NLG* in the flakes, in particular, the identification of CVD-1LG, is the crucial step to ascertain stacking sequence of the CVD-MLG flakes. To address this goal,

the CVD-NLG and ex-NLG flakes are first transferred or exfoliated on SiO<sub>2</sub>/Si substrates with the same thickness of SiO<sub>2</sub> layer. One typical optical image of polycrystalline CVD-NLG flakes can be shown in Fig. 2(a). One can easily distinguish that NLG flakes with different layer numbers coexist in a single crystal domain according to their discriminating OCs. Furthermore, all the graphene layers shared the same nuclei center and the lateral size decreases as N increases, which is in good agreement with the previous reports.<sup>[26,27,57]</sup> From the Fig. 2(a), we can deduced that there should be several different kinds of MLG in this grain. Accordingly, the optical image of ex-NLGs (N = 1, 2, 3, 4) is also shown in Fig. 2(b), whose layer number is identified by their distinguishable spectral features of the 2D modes<sup>[45,53]</sup> and OC profile.<sup>[53,58,59]</sup> The OC profile can be estimated by a formula of OC ( $\lambda$ ) = 1-R<sub>MLG+sub</sub>( $\lambda$ )/R<sub>sub</sub>( $\lambda$ ), where  $\lambda$  is the illumination wavelength and  $R_{MLG+sub}(\lambda)$  and  $R_{sub}(\lambda)$  are the reflected light intensity from the samples deposited on the SiO<sub>2</sub>/Si substrate and that from the SiO<sub>2</sub>/Si substrate. The measured OC( $\lambda$ ) for ex-1LG and ex-2LG as well as the four outmost layers in CVD-NLG flakes is depicted in Fig. 2(c). In the wavelength ranging from 600 to 800 nm, OC( $\lambda$ ) of the two outmost layers in CVD-NLG flakes is in good accordance with that of ex-1LG and ex-2LG, respectively. Thus, the outmost layer in the CVD-NLG flake can be recognized as CVD-1LG, and the inner layer area is CVD-2LG. In addition, a peak at ~488 nm raise in the OC( $\lambda$ ) of CVD-2LG indicates that the CVD-2LG is t(1+1)LG and the peak results from the fancy electronic structure of t(1+1)LG because of the presence of saddle-point excitons.<sup>[49]</sup> Similarly, there are two absorption peaks in OC( $\lambda$ ) of CVD-3LG, which indicates the existence of two twisted interfaces in this CVD-3LG. However, with the layer number increasing, the absorption peaks may overlap with each other, so sometimes it is not easy to distinguish the number of the twisted interfaces and the twist angles for each interface, like that of CVD-4LG in Fig. 2(c).

It is reported that the energy can be fitted with  $E_s = E_0 \sin(3\theta_t)$ , where  $E_0 = 3.9$  eV obtained experimentally.<sup>[49,60]</sup> The G mode intensity (I(G)) will be largely enhanced under the excitation energy close



**Figure 2.** The optical images of CVD-*N*LG (a) and ex-*N*LG (b) flakes for N = 1-4. The scale bars are shown. (c) The OC profiles of the CVD-1LG, CVD-2LG, CVD-3LG, CVD-4LG, ex-1LG, and ex-2LG in (a,b), which are offset for clarity. The two vertical lines correspond to the wavelengths of 488 nm (blue) and 633 nm (dark red), respectively. (d) The Raman spectra of CVD-1LG, CVD-2LG, and ex-1LG, ex-2LG in the G spectral region excited by 633 and 488 nm (only for CVD-2LG). The R modes of CVD-2LG are indicated by the purple arrows. The spectra are scaled and offset for clarity, and the scaling factors are shown for each spectrum.

to  $E_{c}^{[9,28,39,49,60]}$  We further performed the Raman studies on these four graphene flakes with the excitation wavelengths of 633 nm (off-resonance) and 488 nm (in-resonance). All the spectra are normalized by I(G) of ex-1LG. For the Raman spectra under the off-resonance condition, the peak positions of G mode (Pos(G)) for ex-1LG and ex-2LG remain the same (at  $\sim$ 1582 cm<sup>-1</sup>), whereas I(G) of ex-2LG is around two times as that of ex-1LG.<sup>[44,48]</sup> In addition, there is no peak in the D-mode region indicates that the ex-1LG and ex-2LG are in good quality. Pos(G) of CVD-1LG and CVD-2LG exhibit an obvious blueshift compared with those of the corresponding ex-1LG and ex-2LG, which may be attributed to the introduction of chemical doping<sup>[61]</sup> in the CVD growth. Further, the asymmetric profile of the G mode in CVD-2LG can also confirms this hypothesis, which usually results from the inhomogeneous doping and the breaking of the inversion symmetry induced by the doping.<sup>[62–64]</sup> I(G) of CVD-1LG and ex-1LG is approximately equal to each other. I(G) of 1LG is mainly determined by multiple reflections at the interfaces and optical interference within the medium.<sup>[48,53]</sup> If the substrate of CVD-1LG and ex-1LG is the same, I(G) should be approximately the same. Thus, by comparing I(G) and OC( $\lambda$ ) of CVD-1LG with those of ex-1LG on the same substrate, CVD-1LG can be easily identified. Under the off-resonance condition, I(G) of CVD-2LG is ~1.5-2 times as much as that of CVD-1LG, similar to the case of I(G) between ex-2LG and ex-1LG. As for the Raman spectrum of CVD-2LG, we observed a significant enhancement (~20 times larger than that under 633 nm excitation) of I(G) under 488 nm excitation. Such enhancement is in line with the previous reports.<sup>[36,60,65,66]</sup> In addition, in the region of G mode under both 488 and 633 nm excitation, a so-called R mode at ~1480  $\text{cm}^{-1}$  is observed. In tMLG, not only the phonons in the

center of BZ (denotes as  $\Gamma$ ) in the 1LG but also the phonons away from the center, which are selected by the twist wavevector q ( $\theta_t$ ), can be observed in the Raman spectra.<sup>[7,50,60]</sup> From Pos(R), we can deduce  $\theta_t$  of 15.2°. In principle, if two or more twisted interfaces exist in a specific tMLG, the number of twisted interfaces can be derived from the observed R modes. However, just based on the R modes, it is hard to figure out the stacking sequences in CVD-MLG, especially when the R modes are not so obvious or there are two twist angles remain almost the same.

Besides the G, 2D, and R modes, the C and LB modes in AB-MLG and tMLG have been investigated in details.<sup>[34,36,37]</sup> The C and LB modes in tMLG can just be observed in a small resonant window, which can be roughly defined by the absorption peak in the OC. Now we try to correlate the stacking sequences of CVD-MLG with the observed C and LB modes. There are *N*-1 C and LB modes in AB-NLG with layer number *N*. They can be denoted as  $C_{NN-i}$  and LB<sub>NN-i</sub> (i = 1, 2, ..., *N*-1), respectively, in which  $C_{N1}$  and LB<sub>N1</sub> represent the C and LB modes with the highest wavenumber. Pos(C) and Pos(LB) can be calculated by the linear chain model where just the nearest-neighbor interlayer interactions are concerned for the C mode<sup>[34,36]</sup> and additional weak next-nearest-neighbor interlayer interactions are necessary for the LB mode.<sup>[37]</sup> If only the nearestneighbor interlayer interactions are considered, Pos( $C_{NN-i}$ ) and Pos(LB<sub>NN-i</sub>) can be estimated as

$$P_{OS}(C_{NN-i}) = \frac{1}{\pi c} \sqrt{\frac{a^{\parallel}}{\mu}} \sin(\frac{i\pi}{2N})$$
(1)

and

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$$P_{OS}(LB_{NN-i}) = \frac{1}{\pi c} \sqrt{\frac{a^{\perp}}{\mu}} \sin(\frac{i\pi}{2N})$$
(2)

respectively, in which  $c = 3.0 \times 10^{10}$  cm/s is the speed of light and  $\mu = 7.6 \times 10^{-27} \text{kg}\text{\AA}^{-2}$  is the monolayer mass per unit area.  $a^{||}$ and  $\alpha^{\perp}$  are the interlayer force coupling per unit area parallel or perpendicular to the graphene plane. In the case of graphite, the C and LB modes are Pos(C<sub>bulk</sub>) =  $\frac{1}{\pi c} \sqrt{\frac{\alpha^{||}}{\mu}}$ =43.5 cm<sup>-1</sup> and Pos(LB<sub>bulk</sub>)=  $\frac{1}{\pi c} \sqrt{\frac{\alpha^{\perp}}{\mu}}$ =128 cm<sup>-1</sup> when N approaching to  $\infty$ , which are  $\sqrt{2}$ Pos(C<sub>21</sub>) and  $\sqrt{2}$ Pos(LB<sub>21</sub>), respectively. Only the C<sub>N1</sub> modes in AB-MLG can be directly detected at room temperature<sup>[34]</sup> and the LB modes should be observed though the combination Raman modes<sup>[35,47]</sup> due to the different symmetry and weak electron-phonon interactions (EPC). Pos(C) in tNLG with layer number N (N = m + n + ...) follow those of AB-stacked multilayer constituents, such as mLG, nLG,... (m > 1, n > 1).<sup>[36]</sup> However, Pos(LB) follow those of AB-NLG, that is, Pos(LB) is determined by total layer number N of tNLG. Pos(C) and Pos(LB) are not clearly dependent on  $\theta_t$ . Therefore, more C and LB modes can be observed in tMLG than AB-MLG due to the reduced lattice symmetry in tMLG.<sup>[36,37]</sup> This suggests that the C and LB modes are good signatures to determine stacking sequences of tMLG. The total layer number of tMLG can be accessible by Pos(LB), and the layer number of the AB-stacked constitutes can be ascertained by Pos(C).

Figure 3(a),(b) show two typical optical images of single crystal domains of CVD-*N*LG flakes (denoted as region Z1 and Z2, respectively). At first, it is necessary to identify whether the outer graphene flakes near the edge is 1LG. Indeed, 1LG flakes denoted in Fig. 3(a),(b) have been verified by OC( $\lambda$ ) (as shown in Fig. S1) and I(G) in the way stated above. It is clear that both the CVD-*N*LG flakes shown in Fig. 3(a),(b) consist of several single crystalline domains and contain layer number ranging from one to four. It should be noted the lateral size should be large enough to measure the Raman spectroscopy (~1 µm). Considering that the

lateral size becomes smaller and smaller when it approaching the center, some other techniques can be utilized to distinguish the stacking information. Furthermore, the stacking order of center is still difficult to be distinguished because various crystal domains share the same nucleation center. Figure 3(c),(d) shows the Raman spectra of CVD-NLG (N = 1, 2, 3, 4) in the C and LB region  $(0-150 \text{ cm}^{-1})$ , which are excited by the resonant wavelength of 488 nm determined by their OC( $\lambda$ ). The LB modes are observed in CVD-NLG (N = 2, 3, 4), and N of each CVD-NLG has been confirmed by the corresponding Pos(LB). However, no C modes are observed in each CVD-2LG and CVD-3LG, indicating a fully non-stacked arrangement. Because the number of the observed C modes depend on the layer number of the AB-stacked constitutes, we can conclude that only 1LG constitute exists in the CVD-2LG and CVD-3LG. Thus, the CVD-2LG and CVD-3LG in both Z1 and Z2 correspond to t(1+1)LG and t(1+1+1)LG, respectively. However, different Raman signatures can be observed in CVD-4LG in Z1 and Z2. The absence of the C mode in CVD-4LG of Z1 implies that it should be t(1+1+1+1)LG. An additional peak at ~31 cm<sup>-1</sup> in CVD-4LG of Z2 is the C<sub>21</sub> of its 2LG constituent, suggesting that the fourth layer and the third layer in Z2 are in AB stacking. Thus, the stacking sequence of CVD-4LG in Z2 should be t(1+1+2)LG, as showed in the right panel of Fig. 3(d). Hence, by performing the Raman spectra in the C and LB region on CVD-MLG flakes layer by layer, the stacking sequence of CVD-MLG in a single crystalline domain can be identified although there is no significant difference between their optical images.

To explore the possibility to figuring out all the stacking sequences of CVD-*N*LG, we performed the investigations on another two CVD-*N*LG flakes, whose optical images are depicted in Fig. 4(a),(b). The Raman spectra depicted in Fig. 4(c),(d) for the samples show diverse features compared with those depicted in Fig. 3(c),(d). CVD-*N*LG (N = 2, 3, 4) in Z3 and Z4 show similar LB modes to the corresponding CVD-*N*LG in Z1 and Z2, which is a powerful tool to ascertain the layer number *N*. In particular, there are peaks at ~91 cm<sup>-1</sup> in the upper spectra of both Fig. 4(c) and (d), which can be assigned as LB<sub>42</sub> according to linear chain



Figure 3. Two typical optical images of CVD-*N*LG flakes whose *N* ranges from one to four. The scale bars are shown. The corresponding Raman spectra in the C and LB spectral regions excited by 488 nm and schematic diagrams of stacking sequences for each CVD-*N*LG in Z1 (c) and Z2 (d). The spectra are scaled and offset for clarity.

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**Figure 4.** Another two typical optical images of CVD-NLG flakes whose *N* ranges from one to four. The scale bars are shown. Raman spectra of CVD-NLG in Z3 (c) and Z4 (d) in the C and LB spectral regions, which are excited by 488 and 530 nm, respectively. The spectra are scaled and offset for clarity. Schematic diagrams of stacking sequences for each CVD-NLG are also shown in (c) and (d).

model.<sup>[37]</sup> This further confirms the layer number of the corresponding flakes in Z3 and Z4. However, various Raman features arise in the C spectral region. For both CVD-2LGs, no observable C mode suggests that both of them are t(1+1)LG. When we grow one more layer to reach CVD-3LG, CVD-3LG from Z3 and Z4 flakes unambiguously show one additional peak at ~31 cm<sup>-1</sup> labeled as C<sub>21</sub>. This implies that an AB-2LG constitute exists in the CVD-3LG of Z3 and Z4, so the CVD-3LG is t(1+2)LG. With increasing *N* to 4, the CVD-4LG of Z3 and Z4 exhibits different Raman features from each other. C<sub>31</sub> and C<sub>32</sub> are observed in CVD-4LG in Z3 at~36 and ~21 cm<sup>-1</sup>, respectively, which are close to those observed in AB-3LG (~38 and ~22 cm<sup>-1</sup>). This suggests that all the layers below the top layer in Z3 are in AB stacking, as shown in the right panel of

Fig. 4(c). However, there is still one peak at 30 cm<sup>-1</sup> for CVD-4LG in Z4, whose wavenumber is the same as that in adjacent CVD-3LG and can be assigned as  $C_{21}$ . This indicates that the fourth layer displaces with another twist angle relative to the third layer, resulting that the CVD-4LG is t(1+2+1)LG. Therefore, on the base of identifying CVD-1LG, by probing the C and LB modes of CVD-MLG flakes in the same single crystal domain from outer CVD-1LG to the nuclei center layer by layer, we can distinguish stacking sequences of CVD-MLG.

In order to well obtain the stacking orders of CVD-MLG,  $\theta_t$  of twisted interface in CVD-MLG needs to be determined. We further show the Raman spectra of CVD-MLG in Z1–Z4 in the region close to the G mode, as depicted in Fig. 5. The presence of R modes



**Figure 5.** Raman spectra in the R spectral region for CVD-NLGs (*N* = 1, 2, 3, 4) in Z1 (a), Z2 (b), Z3 (c), and Z4 (d). Several R peaks (denoted as R1, R2, and R3 if necessary) are observed. The spectra are scaled and offset for clarity.

confirms that there exist twisted interfaces in all the CVD-MLG flakes. The interface number and corresponding  $\theta_t$  can be identified by Pos(R) in the vicinity of the G mode. For the t(1+1)LG in Z1, Pos(R) is observed at ~1475  $\text{cm}^{-1}$  denoted as R1, which gives  $\theta_t = 15.2^\circ$ . One more R peak (R2) is observed in t(1+1+1)LG in Z1 and  $\theta_t$  between the second and third layer can be determined as 24°. Furthermore, one should expect three R peaks in t(1+1+1+1)LG. Indeed, additional R peak (R3) are observable at 1451 cm<sup>-1</sup>, which corresponds to  $\theta_t$  of 18°. However, the R2 mode corresponding to the interface between the second and third layer is absent in t(1+1+1+1)LG. This may result from the off-resonance condition because the addition of the fourth layer may bring the change of electronic structure. Similarly, the two twist angles in Z2 can be estimated as 13.2° and 16.2° according to the R1 (~1495 cm<sup>-1</sup>) and R2 (~1466 cm<sup>-1</sup>) peaks. For t(1+1) LG, t(1+2)LG, and t(1+3)LG in Z3, there is only one twisted interface for all CVD-MLG flakes and the R peak at ~1472 cm<sup>-1</sup> indicates  $\theta_t$  of 15.5°. The R peak in t(1+3)LG is a little blueshifted. This may result from a little change of interlayer coupling when an additional layer in CVD growth is inserted between t(1+2)LG and substrate. As for the CVD-MLG in Z4, the twist angle in t(1+1)LG and t(1+2)LG can be defined as 14.7° based on the R1 peak at ~1479 cm<sup>-1</sup>. However, only one peak at ~1481 cm<sup>-1</sup> is observed in t(1+2+1)LG, indicating that the second  $\theta_t$  is almost the same as the first one. Based on the experience in Z3, the t(1+2+1)LG may be incorrectly assigned as the t(1+3)LG if the C and LB modes are not assisted for this assignment as shown in Fig. 4(d). Besides the R mode, the so-called R' modes<sup>[7,36,37,50,60]</sup> can also be utilized to define  $\theta_t$ . The R' mode is originating from the LO phonon selected by the twist wavevector  $\mathbf{q}(\theta_t)$ .<sup>[7]</sup> However, most R' modes of the samples in Z1, Z2, Z3, and Z4 may be submerged in the broad profile of the G modes because the twist angles (13°-18°) give Pos(R') approaching to Pos(G) (1570-1600 cm<sup>-1</sup>). This demonstrates that the R (R') mode can be used to identify  $\theta_t$  of the twisted interface once it is detected; however, it is difficult to identify  $\theta_t$  if the R mode cannot be observed or the two interfaces have almost the same  $\theta_t$ . This further declares the importance of the C and LB modes in the characterization of stacking orders. In general, Pos(C) and Pos(LB) of AB-MLG are above 10 cm<sup>-1</sup> for N < 7 owing to weak interlayer coupling and the small mass of carbon atoms. Therefore, some special longpass edge filters can also applied to detect the C and LB modes in common CVD-MLG.[67]

The above results show that CVD-grown 2-4LG can exhibit different stacking sequences and  $\theta_t$ . It is expected that more combinations of the stacking sequences should be considered with increasing the layer number. Our measurements on CVD-grown graphene flakes indicate that the second layer of most CVD-MLG tends to rotate by a certain  $\theta_t$  relative to the top layer, leading to most of the CVD-MLGs exhibit as twisted structures under the synthesis conditions in this work. Therefore, the second branch of stacking sequences in Fig. 1(c) derived from t(1+1)LG, i.e. t(1+ ...)LG, is observed, and the first branch derived from AB-2LG, i.e. t(2+ ...)LG, is not observed under the synthesis conditions in this work. Considering that AB-2LG had been found under specific synthesis conditions,<sup>[21-23]</sup> the branch derived from AB-2LG could be synthesized under the proper conditions. In this case, it is expected to distinguish the corresponding stacking orders of CVD-MLGs in this branch by the C and LB modes as described above. For the sake of this approach to be applied by graphene community, we summarize the expected Pos(C) and Pos(LB) for NLG (N = 2, 3, 4) with various stacking sequences in Table 1. Please note that in the table,

Table 1.	Expected peak positions (cm <sup>-1</sup> ) of the C and LB modes in NLG			
(N=2,3,4) with different stacking sequences				

NLG	Stacking sequences	Pos(C)/cm <sup>-1</sup>	Pos(LB)/cm <sup>-1</sup>
2LG	AB-2LG	C <sub>21</sub> : ~31	LB <sub>21</sub> : ~91
	t(1+1)LG	_	LB <sub>21</sub> : ~91
3LG	AB-3LG	C <sub>31</sub> : ~38	LB <sub>31</sub> : ~111
		C <sub>32</sub> : ~22	LB <sub>32</sub> : ~70
	t(2+1)LG	C <sub>21</sub> : ~31	LB <sub>31</sub> : ~111
	t(1+2)LG		LB <sub>32</sub> : ~70
	t(1+1+1)LG	—	LB <sub>31</sub> : ~111
			LB <sub>32</sub> : ~70
4LG	AB-4LG	C <sub>41</sub> : ~40	LB <sub>41</sub> : ~119
		C <sub>42</sub> : ~31	LB <sub>42</sub> : ~95
		C <sub>43</sub> : ~17	LB <sub>43</sub> : ~54
	t(3+1)LG	C <sub>31</sub> : ~38	LB <sub>41</sub> : ~119
	t(1+3)LG	C <sub>32</sub> : ~22	LB <sub>42</sub> : ~95
			LB <sub>43</sub> : ~54
	t(2+1+1)LG	C <sub>21</sub> : ~31	LB <sub>41</sub> : ~119
	t(1+2+1)LG		LB <sub>42</sub> : ~95
	t(1+1+2)LG		LB <sub>43</sub> : ~54
	t(1+1+1+1)LG	—	LB <sub>41</sub> : ~119
			LB <sub>42</sub> : ~95
			LB <sub>43</sub> : ~54

Please note that the change of constitute order in the stacking sequence does not obviously modify Pos(C) and Pos(LB) of tMLG; e.g. t(1+3)LG and t(3+1)LG share the same groups of Pos(C) and Pos(LB).

the change of constitute order in the stacking sequence does not obviously modify Pos(C) and Pos(LB) of tMLG; e.g. Pos(C<sub>21</sub>) of ~31 cm<sup>-1</sup> can be observed in all of t(2+1+1)LG, t(1+2+1)LG, and t(1+1+2)LG. Therefore, for any *N*LG (N = 2-4), by following the above approach and referring to Table 1, its stacking order can be fully determined.

## Conclusion

To conclude, CVD-MLGs are usually polycrystalline, consisting of randomly orientated single crystal domains with different layers and twisted interfaces between two adjacent constituents. On the base of identifying 1LG, we developed a rapid way to distinguish stacking orders of CVD-MLG by Raman spectroscopy. The LB modes are helpful to identify the total layer number of CVD-MLG, while the C modes provide us a convenient method to determine the stacking sequence of the constituents in CVD-MLG. Furthermore, the twist angles of the twisted interfaces in CVD-MLG can also be ascertained by the wavenumber of R modes. This work paves the way to characterize the stacking orders of CVD-MLG for fundamental research and for optimizing experimental conditions to grow CVD-MLG with specific stacking order.

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## **Supporting information**

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