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High-Precision Twist-Controlled Bilayer and Trilayer Graphene

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Twisted bilayer graphene (tBLG), a prototypical bilayer system with van der Waals interlayer coupling, exhibits novel physical properties and a tunable electronic structure,[1-7] such as renormalization of the Fermi velocity,^[1,2] θ -dependent van Hove singularities (vHSs),^[3,4] optical conductivity,^[5,6] and electronic localization.^[2,7] Because of the relative orientation and interlayer coupling, tBLG is expected to display characteristics that are distinct from monolayer and AB-stacked few-layer graphene.^[8,9] Currently, tBLG can be obtained by (i) chemical vapor deposition (CVD) on metal catalysts,^[10,11] (ii) folding graphene,^[6,12–14] or (iii) stacking graphene layers on top of each other.^[15,16] However, the relative twist angle of BLG is random when fabricated by these existing methods, and numerous samples must be fabricated to select one with the designated angle (Discussion S1 and Table S1, Supporting Information). Because a distribution of small twists with sizes as small as $\approx 0.1^{\circ}$ is sufficient to generate a completely new electronic spectrum,^[17] the lack of the capability to control the twist angle seriously limits the general applications of these materials.

In addition, current research focuses on tBLG; however, further study of graphene superlattices with more than two twisted layers, such as double twisted trilayer graphene (DTTG), is required. For DTTG, the first and second layers as well as the second and third layers are twisted (**Figure 1**a). However, the existing methods for tBLG are not suitable for the fabrication of DTTG because the uncontrolled twist angles make it nearly impossible to select a DTTG with two designated twist angles. Further breakthroughs are required to fabricate twisted

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few-layer graphene to promote experimental studies and potential applications.

Based on femtosecond laser micromachining and a specific transfer technique, we developed a new method that can be used to fabricate tBLG and DTTG with the designated twist angles, as illustrated in Figure 1 and Figure S1 (Supporting Information). Femtosecond laser is widely used in the micromachining, since its machining precision is much higher than long pulse lasers (Discussion S3, Supporting Information). A single-crystal graphene is cut into two pieces by femtosecond laser, with a pair of straight and parallel edges. And these parallel "cutting lines" play a key role for the control of the twist angles. As shown in Figure S3a,b (Supporting Information), while the two divided graphene flakes are relatively rotated with angle θ , the relative angles between the two crystal orientations and between the two cutting lines both equal θ . Thus the control of the twist angles can be achieved by tuning the relative angle between the two cutting lines. A poly(methyl methacrylate) (PMMA) layer was coated on Si/SiO₂ substrate and then divided into two pieces along the cutting lines of graphene. After the separation of the PMMA/graphene films from the Si/SiO₂ substrate, one of the graphene was transferred to a new Si/SiO₂ substrate, and another was flipped over and adhered to a suspended polymer layer on a glass slide with a hole (Discussion S6, Supporting Information).^[18] Then, the two flakes were precisely stacked with a relative rotation angle θ . After the polymer/PMMA dissolving and thermal annealing processes, tBLG with a twist angle θ was successfully fabricated. Details can be seen in Experimental Section and Discussion S2-S6 (Supporting Information). Thermal annealing is an important step to obtain a clean surface and provide good contact between the two graphene flakes (Discussion S7, Supporting Information).^[18,19] Figure 1b,c presents a tBLG with twist angle of 13° and a DTTG with twist angles of 13° and 7° fabricated by this cutting-rotation-stacking (CRS) method. Electrical devices always have regular shapes, such as the hall-bar structure, which will benefit the measurement. This method also has the capability to fabricate twisted bilayer graphene with specific patterns. Graphene flakes are firstly cut into required patterns by femtosecond laser, and then the CRS procedure is performed. Figure S1c-e (Supporting Information) shows the tBLG samples fabricated with precutting graphene flakes.

In order to demonstrate the accuracy of the twist angle fabricated by the CRS method, we fabricated a serious of bilayer graphene samples with twist angles from 6° to 30°, and determined their twist angles by selected area electron diffraction (SAED). **Figure 2**a shows the SAED results of these bilayer graphene samples, and the results demonstrate that the deviations of the





Figure 1. a) Schematic of the CRS technique used to fabricate tBLG and DTTG. b) Fabrication process of tBLG with twist angle $\theta = 13^{\circ}$. c) DTTG with twist angles $\theta_1 = 13^{\circ}$ and $\theta_2 = 7^{\circ}$. The scale bars in (b) and (c) are 50 µm. d–f) HR-TEM images of tBLG with twist angles of d) 7°, e) 10°, and f) 13°. The insets in (d–f) are the SAED images of the samples.

determined angles from the designated twist angles are less than 0.1°, which are rarely achieved by using other methods. A comparison of the twist angles determined by measuring the relative rotation angle of the cutting lines and by SAED is shown in Table S2 (Supporting Information). From the comparison, we can conclude that the direct measurement of the relative rotation angles also provides high accuracy in verifying the twist angles (Discussion S8, Supporting Information). This method is convenient and does not damage the samples.

To demonstrate the quality of the tBLG fabricated by CRS, Raman spectra of tBLG with twist angles from 6° to 30° were measured, with monolayer and Bernal stacking bilayer graphene as reference (Figure 2b). The evolution of the Raman signature with twist angle is consistent with previous reports (Discussion S9, Supporting Information),^[10–15,20] demonstrating that tBLG fabricated by CRS has the same electronic and phonon structures as the samples fabricated by other methods. After the Raman spectra measurements, the samples were transferred to copper grids for high-resolution transmission electron microscopy (HR-TEM) observation (Discussion S10, Supporting Information). The HR-TEM images of tBLG samples with twist angles of 7°, 10°, and 13° are shown in Figure 1d–f. The Moiré patterns are produced by the interaction of the two neighboring graphene layers. While the two graphene layers are separated by a thin PMMA film, the periodic patterns will be disturbed by the disordered PMMA structure, and the amorphous PMMA layer will greatly mask the observation of the bottom-layer graphene.^[21,22] Thus, the unambiguous and periodic Moiré patterns can be used as a definitive evidence of the effective remove of the PMMA and the intimate contact of the two graphene layers (Discussion S7, Supporting Information).^[11,15]

The interlayer interaction and intimate contact are required for the application of tBLG. At the end of tBLG fabrication,

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Figure 2. a) SAED images of bilayer graphene with twist angles from 6° to 30°. b) Raman spectra of the twisted bilayer graphene with angles from 6° to 30°, with monolayer and Bernal stacking bilayer graphene as reference.

the Raman spectra and HR-TEM images demonstrated the high quality of tBLG prepared by the CRS method on a small scale. To demonstrate the large-area uniformity, we scanned the Raman intensity and optical absorption of the tBLG sample, as shown in Figure 3. In the Raman spectrum, the appreciable enhancement of the G-band intensity (Figure 3a) indicates that the twist angle is close to the critical rotation angle θ_{c} , which is 13° for the 514 nm laser excitation.^[15] SAED was used to determine the twist angle from the diffraction spots (inset in Figure 3a). The relative angle of the two sets of hexagonal patterns suggests that the BLG is rotated by 13.0°. The SAED and Raman spectrum of the tBLG demonstrate the accuracy of the twist angle. A Raman G-band intensity map was measured in the region marked in Figure 1b. As shown in Figure 3b,c, the relatively narrow distribution and high intensity of the G-band indicate that tBLG exhibits good uniformity. The absorption scanning images in Figure 3e also shows the good uniformity with the same absorption enhancement, indicating the strong and uniform interaction between layers (Discussion S11, Supporting Information).

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Because of the strong interlayer interaction, when two graphene layers are stacked with a twist angle θ , the electronic band structure becomes more complicated in a θ -dependent manner.^[5,6,23] New θ -dependent vHSs are generated in the density of states (DOS).^[3,15] The optical conductivity of graphene is proportional to the joint DOS, which can be deduced form its DOS.^[6,24] Therefore, the vHSs in the visible light range will induce a new θ -dependent peak in the absorption spectrum.^[5] When determined by the laser with energy around the peak, tBLG will have an absorption enhancement. While increasing twist angle θ , the peak position will have a blueshift,^[5] and larger laser energy is required to achieve the absorption enhancement. Thus the twist angle and excitation laser energy have a one-to-one correspondence. For a given twist angle θ , there is only one laser energy that can achieve the absorption enhancement. Previous studies have demonstrated that the peak structure in the optical absorption spectrum nearly continuously evolves with the twist angle.^[25] Thus, the absorption enhancement at an arbitrary wavelength will be achieved by fabricating tBLG with the corresponding twist angle.

The successful fabrication of twist BLG with designated twist angles by CRS provides a method to develop tunable optical devices by freely tuning the twist angles. In this study, we used a total internal reflection (TIR) method based on the polarization-sensitive absorption effect of graphene to image the absorption of the sample (Figure 3d).^[26] The fabrication and measurement of the devices are discussed in Discussion S11 (Supporting Information). Compared with the direct absorption measurement, the TIR method is convenient to operate and is substantially more sensitive and accurate. To demonstrate the one-to-one correspondence of the twist angle and laser energy, the absorption difference ΔA mapping images of tBLG with twist angles of 5°, 10°, 13°, 20°, and 30° were determined by 1.96 and 2.41 eV laser energies, respectively. As shown in Figure 3e,f and Figure S11 (Supporting Information), the absorption of tBLG with twist angle of 13° is only enhanced under 2.41 eV laser excitation, while 1.96 eV laser can excite the absorption of tBLG with twist angle of 10°. For tBLG twist angles of 5°, 20°, and 30°, neither of the two lasers could enhance the absorption (Figure S11, Supporting Information).

To get a more direct comparison of the absorption enhancement, four different graphene films (monolayer, Bernal stacking bilayer, and bilayers with twist angles of 10° and 13°) were transferred onto the same quartz (Figure 4a) and determined their absorption by 1.96 and 2.41 eV laser energies. Figure 4b presents the line scanning results of the sample by different lasers. The signal is enhanced \approx 35% at the domain with a twist angle corresponding to the excitation laser. Absorption mapping was performed to identify the different graphene areas. As shown in Figure 4c,d, the monolayer, Bernal stacking bilayer, and tBLG are distinguished successfully.

The photoelectric responses of tBLG were also investigated under TIR. As discussed in Discussion 11 (Supporting Information), the absorption of graphene for s-polarized light is substantially larger than that for p-polarized light under TIR.^[26] Thus the photocurrent of graphene changes with the polarization of the incident light in a sine curve (Figure 4e). In addition, the photocurrent exhibits a linear dependence on the incident laser intensity under TIR (inset in Figure 4e).^[27] To



Figure 3. a) Raman spectra of tBLG with twist angle $\theta = 13^{\circ}$ and the graphene monolayer. The inset is an SAED image of tBLG. b) Raman G-band image of tBLG with twist angle $\theta = 13^{\circ}$. c) The histogram of the G-band intensities in (b). d) Schematic of the TIR method to measure the absorption of graphene. e,f) The optical absorption images obtained by using the TIR method with laser energies of e) 2.41 eV and f) 1.96 eV.

investigate the enhancement of the photocurrent caused by the twist angles, devices based on monolayer and tBLG with twist angles of 10° and 13° were fabricated, and their photocurrent was detected by s- and p-polarized lights with a wavelength of 514 and 633 nm, respectively. The results demonstrate that the photocurrent of tBLG could be significantly enhanced by both s- and p-polarized lights with corresponding wavelength (Figure 4f and Figure S12a–f, Supporting Information). The photocurrent results are consistent with the absorption enhancement of the bilayer graphene (Figure 4b). Thus, the optical absorption and photocurrent enhancement can be achieved by tuning the twist angles of tBLG.

The characterizations in microscale, such as the Raman and absorption mapping in Figure 3, demonstrate the intimate contact of the two layers. However, the complete remove of the PMMA residues is difficult.^[21] Atomic force microscope (AFM) was used to identify the distribution of the residual nanoparticles on the graphene after the fabrication (Figure S7, Supporting Information). The average density of the nanoparticles is 113 μ m⁻², indicating the average spacing of the particles is about 100 nm. As previously discussed, these residual PMMA particles have little effect on the optical and photoelectric properties of tBLG fabricated by the CRS methods. However, twolayer graphene will become two single-layer graphene at the location of the particles, causing the potential fluctuation, carrier scattering and dephasing. Thus the PMMA particles will reduce the performance of the tBLG fabricated by the CRS method in the study of transport physics and other applications requiring lone mean free path or phase coherent of carriers. To satisfy the requirements to the samples in these areas, new transfer techniques are necessary to get a clean surface.

Compared with the widely investigated tBLG, DTTG is poorly studied,^[25] especially on experiment. The lack of a sample

fabrication technique limits experimental studies on DTTG, because the twist angles cannot be controlled by the common fabrication methods. The CRS technique provides a reliable method to fabricate DTTG with any designated angles. To investigate the interaction of the coupled layers for DTTG, numerous samples were fabricated by the CRS method (Discussion S13, Supporting Information). The samples were simply named according to their stacking layers and twist angles, for example, trilayer ($13^{\circ}-7^{\circ}$), denotes three layers that are stacked with the twist angles between the top and the middle layer and between the middle and the bottom layer of 13° and 7° , respectively.

Raman spectroscopy was used to study the electronic properties of DTTG. First, the interaction between neighboring graphene layers was investigated. The sample trilayer (13°-7°) was designed and fabricated (left part of Figure 5e), because the Raman signatures of the twist angles of 7° and 13° are easily distinguished. Figure 5a,b presents the Raman spectra of the trilayer domain and the corresponding bilayer domains with twist angles of 13° and 7°. For the trilayer domain, the enhancement of the G-band is observed, along with the appearance of the R- and R'-bands. Compared with the corresponding bilayer Raman spectra (Figure 5b), we observed that the Raman spectrum of DTTG resembles the superposition of the two independent bilayer Raman spectra, without new features appearing. As observed in Figure 5c, the Raman spectra of the superposition and trilayer are matched well at the R, G, and R' band regions, where x and y are the factors for the contribution of tBLG (7°) and tBLG (13°), respectively. For trilayer (13°-7°), x = 0.8795 and y = 0.5045. For another trilayer (7°–13°) sample, a similar superposition was performed, and the proportions were x = 0.9731 and y = 0.4220, as shown in Figure 5d.

The 2D band is the most sensitive peak to electronic and phonon band-structure changes in graphene,^[15] exhibiting



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Figure 4. a) Optical image of the graphene array with four different graphene films. b) The line scanning results of the sample for 1.96 and 2.41 eV laser energies. The scanning route is marked in (a). c,d) Absorption mapping images obtained by the TIR method with laser energies of c) 2.41 eV and d) 1.96 eV. e) The relationship between the photocurrent and incident light polarization. The upper inset shows the photocurrent detected by different powers. The sample has a twist angle of 10° , and an S-polarized 633 nm laser is used. The measurement position is marked in the lower inset. f) The photocurrent of the samples with different twist angles, detected by S- and P-polarized lights with wavelengths of 514 and 633 nm, respectively. The scale bars in (c) and (e) are 50 μ m.

more complex twist angle dependence. A slight difference between the 2Dband of the trilayer and the superposition spectra is observed in Figure 5c,d. We fit the 2D peaks with a single Lorentzian peak for simplicity. Compared with the superposition spectra, the trilayer graphene 2Dband has a slightly larger peak width $(1-3 \text{ cm}^{-1})$, and the center location exhibits slight blueshift (4–6 cm⁻¹).

Finally, we investigated the interaction between the top and bottom layers, which are separated by the middle layer. A double-twisted sample trilayer (6.5°–6.5°) was designed and fabricated (right part of Figure 5e), because the relative rotation angle between the top and the bottom layers equaled the critical angle θ_c for a 514 nm laser. The resulting Raman spectra of the trilayer domain and the neighboring bilayer domains are similar (left part of Figure 5f). In addition, the enhancement of the G-band is observed only at the domain where the top and bottom layers are in direct contact without the separation of the middle layer (right part of Figure 5f). Because of the







Figure 5. a) Raman spectrum of the sample trilayer (13°-7°). b) Raman spectra measured at corresponding bilayer domains with twist angles of 13° and 7°. c,d) Raman spectra comparisons between trilayer and the superposition of two corresponding bilayers for c) trilayer (13°-7°) and d) trilayer (7°-13°) samples. Magnifications in the G and 2D band regions are shown on the right. e) Optical images and corresponding SAED patterns of trilayer (13°-7°) and trilayer (6.5°-6.5°) samples. The red and blue lines represent the cutting lines fabricated during the CRS process. All of the scale bars are 50 μm. f) Raman spectra of the sample trilayer (6.5°-6.5°) sample measured in the trilayer domain and corresponding bilayer domains. The Raman spectra in (a and f) were measured at the position marked in (e) with corresponding colors.

separation of the middle layer in the trilayer domain, the interaction between the top and bottom layers is weak, leading to the absence of the G-band enhancement.

Our experimental results can be explained by the electronic band structure of the twisted trilayer graphene (TLG). Previous calculations have demonstrated that for DTTG, the electronic band structure, $^{\left[28\right]}$ DOS, and optical absorption spectrum are similar to those expected from a superposition of two uncoupled twisted bilayer structures.^[25] Thus, DTTG can be considered as the superposition of two twisted BLG flakes with corresponding twist angles (Discussion S14, Supporting Information).

In conclusion, the CRS technique provides a method to investigate the θ -dependent electrical and optical properties of twisted multilayer graphene. The twist-control capability of this

technique is important for the heterostructures because their physical properties strongly depend on the relative orientation of the component layers. The resonant tunneling in graphene/ hexagonal boron nitride/graphene heterostructures has been investigated by some groups, and their results show that twist angles between graphene layers are important for the resonant tunneling.^[29,30] The more important contribution of the CRS technique is that DTTG with arbitrary twist angles can be successfully fabricated by this method, which is an important breakthrough in the experimental research of twisted TLG. Compared with a bilayer, an unprecedented degree of control of the electronic and optical properties is available for this DTTG. The rapid development of CVD-grown graphene provides an alternative choice for the fabrication of large-area



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tBLG (Discussion S2, Supporting Information). Several CVD methods have been developed to grown single-crystalline monolayer graphene with the grain size up to several millimeters.^[31–34] Recently, a 1.5 in. single-crystalline monolayer graphene was synthesized on Cu-Ni alloys.^[35] The fabrication of the twisted multilayer graphene with larger area and more stacking layers will benefit from these individual, single-crystalline and large-area monolayer CVD graphene flakes. Furthermore, this method is also compatible with other 2D materials, such as boron nitride and molybdenum disulfide, for the fabrication of twisted samples. This method will be very useful for advanced physical studies of van der Waals heterostructures with controlled twist angles.

Experimental Section

Fabrication of tBLG: One monolayer graphene prepared by mechanical exfoliation was cut into two pieces by a femtosecond laser (100 fs, 20 mW). A 1 μ m thick film of PMMA (M_w = 996 000; Sigma-Aldrich) was spincoated as a support layer during the fabrication. This PMMA layer was also divided into two pieces along the cutting line of the graphene by the femtosecond laser (100 fs, 40 mW). The sample was immersed in buffered oxide etch solution for 1 h to separate the PMMA/graphene membranes from the original substrate. One of the PMMA/graphene membranes was transferred to a new Si/SiO2 substrate, and the PMMA was then dissolved with acetone. Thermal annealing was then performed in flowing H_2/Ar gas at 340 °C for 3.5 h to remove residual PMMA. One 2 μm thick polymer layer (poly(bisphenol A carbonate) (PC):PMMA = 4:1) was adhered to a glass slide with a 9 mm hole to form a suspension layer and the other PMMA/graphene membrane was flipped over and adhered to this suspended polymer layer, forming a polymer/PMMA/graphene structure. Utilizing the two cutting lines as a reference, the two graphene flakes were rotated with a relative rotation angle θ , which equaled the designated twist angle, and was then precisely stacked together on Si/ SiO2. During the stacking process, the target substrate was heated to 110 °C to drive off any water absorbed on the graphene surface and to promote good adhesion of the PMMA to the target substrate. The polymer and PMMA were dissolved in acetone, and a thermal annealing was performed under the same conditions to obtain a clean surface and to provide good contact between the two graphene flakes.

Fabrication of Double-Twisted TLG: For trilayer $(7^{\circ}-13^{\circ})$ and trilayer $(6.5^{\circ}-6.5^{\circ})$ samples, one graphene monolayer was first divided into two pieces to fabricate tBLG with a twist angle of 7° (or 6.5°). This process was then repeated to fabricate the other twist angle 13° (or 6.5°). For the trilayer $(13^{\circ}-7^{\circ})$ sample, one graphene monolayer was divided into three pieces, and similar to the fabrication process for tBLG, one graphene flake was transferred to the target substrate, and the other two PMMA/ graphene membranes were flipped over and adhered to the suspended polymer layers. These two graphene flakes were sequentially stacked on top of the first flake with twist angles of 7° and 20°. It is important to emphasize that a thermal annealing treatment is required after every PMMA dissolving operation.

Polarization-Sensitive Absorption Measurement: The graphene-based optical device on quartz was attached to a right angle prism (BK7 glass) by using index matching fluid. The prism was mounted on a 3-axis stage with piezo drives (PI). Circularly polarized light (514 or 633 nm, 1 mW) was focused by using a 50× objective lens. The focused light entered the prism with normal incidence and was reflected by TIR at the quartz/ graphene/air interface. The light was separated into transverse electric (TE) and transverse magnetic (TM) modes by a polarization beam splitter. The difference in the TE and TM was compared and recorded by using a balanced photodetector (THORLABS PDB210A).

Characterization: A Micro Raman spectrometer (RENISHAW RM2000) equipped with a motorized sample stage was used to acquire the Raman

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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