Supporting Information for

# **Building Large-Domain Twisted Bilayer Graphene With van**

# **Hove Singularity**

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# Growth of building blocks

Chemical vapor deposited (CVD) single crystal graphene with square shape were grown on copper foil (99.8% purity, 25  $\mu$ m thick, Alfa Aesar) in a low pressure chemical vapor deposition system consisting of a horizontal tube furnace (Lindberg Blue M TF55035KC-1) equipped with a 1-inch-diameter quartz tube. Polished copper foils were loaded in the hot center of the furnace. After the copper foils were annealed at 1035 without gas pumped into (~1 Pa) for 60 min, 200 sccm H<sub>2</sub> (~320 Pa) and 1 sccm CH<sub>4</sub> (~12 Pa) were introduced for 4 min to grow single crystal graphene domains. Finally, the sample was pulled out from the high-temperature zone to room-temperature with a magnet without changing the gas flow.



**Figure S1.** (a) The procedure for square graphene growth in low pressure CVD. (b) The optical image for graphene on copper after heating in air. (c) The SEM image for as-grown square graphene on copper.

# Transmission electron microscope (TEM) characterization of building blocks

After being transferred from the copper foil onto a TEM grid with location marks, the square domains could be found under SEM upper mode (Figure S2a). Afterwards, the marked position could be sought under TEM low-magnification (Figure S2 b-d). Selected area electron diffraction (SAED) patterns at single domain indicated the consistent lattice orientation, which confirmed the single crystal nature of the building blocks.



**Figure S2.** (a) The SEM image for square graphene domain on TEM substrate at location D1. (b)(c)(d) Low-magnification TEM image of the same location in (a). (e)(f)(g)(h) SAED patterns at the red loops in Figure S2d.

The orientation of different domains was characterized within a small area range (about 500  $\mu$ m) and four adjacent domains were investigated (Figure S3a). SAED patterns indicated the consistent lattice orientation of different building blocks as shown in Figure S3b.



**Figure S3.** (a) TEM low-magnification image (under magnification: 35000×) for different domains of square graphene. (b) SAED patterns at red points of image (a).

## Oxygen etching of the square graphene domain

After the growth of graphene,  $H_2$  and  $CH_4$  were shut off and the as-obtained graphene is annealing with no gas at high temperature for 1 min. The well-aligned as-etched hexagon holes in the domain reflect the

consistent lattice orientation and hint the terminal edge type of the square domain (Figure S4a and S4b).<sup>1</sup> Illustrated in Figure S4c, the terminal edge is zigzag type when the angle between the hexagonal lattice diagonal (red dashed line) and the edge is 30°, and it is armchair type when the angle is 60°. Thus, the etched hexagon holes (representing the consistent lattice orientation) in Figure S4b hint the bottom edge of the square graphene domain is armchair type and the right edge is zigzag type.



**Figure S4.** (a) The SEM image of a square graphene domain after etching. Scale bar: 100  $\mu$ m. (b) The enlarged image of the area marked in Figure S4a. Scale bar: 50  $\mu$ m. (c) The schematic diagram of the armchair and zigzag terminal edges.

#### Building method for tBLG domains

The building process for tBLG using the as-grown monolayer graphene domains included (shown in Figure S5):

1. The grown graphene samples with suitable shape and size were selected under SEM. The selected graphene/copper was cut into two

pieces. (Size of each piece:  $\sim 1 \text{ cm} \times 1 \text{ cm}$ )

- 2. PMMA (966K 4% ethyl lactate) was spun on one piece of Graphene/Copper (3500 r/s). Graphene on the back was removed by oxygen plasma and a thin plastic box was affixed to support the PMMA. Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (1 mol/L) solution was used to etch the Cu. The "dry transfer" procedure<sup>2</sup> was used to avoid the p-type doping caused by the adsorbed H<sub>2</sub>O and O<sub>2</sub>. The graphene/PMMA film detached from the copper foil was cleaned by deionized (DI) water, isopropanol and then dried in air for 6 h before it was placed onto another piece of Graphene/Copper.
- 3. Another piece of Graphene/Copper was stacked with the as-prepared PMMA/Graphene (in step ii) together, and the two edges were aligned by certain rotation angle under optical microscope (Figure S6). The as-prepared PMMA/tBLG/Copper sample was kept under the infrared lamp for 1-2 hours, and then etched by Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub> solution again. After washing in DI water, isopropanol, the PMMA/tBLG was transferred onto a substrate such as SiO<sub>2</sub>/Silicon. The as-fabricated sample was kept on super clean bench, and then placed on heating plate under 150°C for 2 h.
- 4. Finally, the PMMA was removed using hot acetone vapor, and isopropanol was used to dissolve the acetone.



Figure S5. Schematic process of the fabrication for stacked tBLG.



**Figure S6.** (a) The PMMA/Graphene stacked onto another piece of Graphene/Copper. (b) Zoom in Figure S6a. (c) The contrast of Graphene on PMMA. (d) The contrast of Graphene on copper after heating slightly. Page S6

# Micro-ARPES experiments

The ARPES sample preparation process is as below. Monolayer Graphene domains (~20  $\mu$ m) were direct grown on single crystal Cu (100), as shown in Figure S7a. Then, square graphene domains (100  $\mu$ m) on copper were direct transferred onto the single crystal Cu using poly-dimethylsiloxane (PDMS), as shown in Figure S7b. The stacked tBLG/single crystal Cu structure (Figure S7c) was prepared for Micro-ARPES test.



**Figure S7.** (a) The SEM image of graphene domains grown on single crystal Cu. (b) SEM low-magnification image of square graphene domains on single crystal Cu. (c) The SEM image for tBLG on single crystal Cu.

For AB stacked bilayer graphene,  $\Delta k$  from over- and underlayer equals zero, which is clearly shown in Figure S8a. From the formula,  $\theta = \Delta k/K = 0$ , this means the most stable stacked structure, due to the case without rotation where the AB configuration is energetically favored.

For tBLG built by our method, the fine structure in figure S8b & figure 2, originates from the interlayer electronic interaction, which leads to the formation of VHSs in the DOS. Both the twist angle and energy interval can be measured from the ARPES data.



**Figure S8.** (a) Band structure of AB stacking bilayer graphene. (b)  $E_{VHS}$  of our data shown in Figure 2, was around 1.7 eV.

The  $E_{VHS}$  in our data, showing in Figure S8b, was measured to be ~1.7 eV. Therefore, the extracted energy interval should be ~ 3.4 eV. Note that energy positions of the two Dirac points are slightly different. This is due to separation-dependent charge transfer process between the copper substrate and graphene layers (as a result, the upper layer will get fewer electrons from the substrate, and the binding energy position will be closer to the Fermi level than the lower layer)<sup>3</sup>. Here we adopt the Dirac point of the upper layer (which is the Dirac cone appearing on the right) to calculate the energy interval (Figure S8b).

Micro-ARPES (Angle Resolved Photo Emission Spectroscopy) experiments were performed at the Spectro Microscopy beamline (3.2L) at ELETTRA Synchrotron, Trieste, Italy. Photon energy 74 eV was used with energy and angle resolution of 50 meV and 0.2°, respectively. By using Schwarzschild optics, the diameter of beam spot was limited to 600 nm, which makes the submicron scanning of the sample possible. During the experiment, sample stage was maintained in ultrahigh vacuum system under a base pressure better than  $5 \times 10^{-10}$  millibar, with a low temperature of 100K. After loading samples into vacuum system, a 20 minutes annealing at 340 °C was carried out in the interface chamber, to remove

absorbed water and also to clean the surface of graphene samples.

## Fabrication of devices

The two-terminal devices of tBLG for photocurrent measurement were fabricated by following steps: (see in Figure S9)

- 1. Samples of devices were selected under optical microscope. Clean and G-band enhanced area was selected for constructing devices.
- 2. The channel was cut open through electron beam lithography (EBL) and oxygen plasma etching.
- 3. The electrode (6/40 nm Cr/Au) was fabricated through the second EBL and subsequent thermal evaporation. The device was lifted-off by acetone and washed with isopropanol. Finally, it was blow dried with nitrogen gas.
- 4. Au wire was bonded with Cr/Au pad for photocurrent measurement.



**Figure S9.** (a) Optical image for selecting samples with strong interlayer coupling. (b) Optical image after the first electron beam lithography. (c) Optical image for the tBLG devices. (d) The devices after wire bonding.

## Photoelectrical measurements of devices

For 13° (Figure S10a) and 10° (Figure S10b) tBLG, the Raman G-band

was resonant enhanced with 532 nm and 633 nm incident laser, respectively, as shown in Figure S10d and 9e (blue spectrum line for 532 nm laser excitation and red line for 633 nm laser excitation). Correspondingly, under the irradiation of 532 nm and 633 nm incident laser respectively, photocurrent generated at bilayer area enhances by 5-6 fold compared to that at monolayer area (Figure S10g and 9h). Changing the twist angle (Figure S10c), for the device without G-band enhancement (Figure S10f), photocurrent generated at bilayer area enhanced at bilayer area enhanced at bilayer area (Figure S10f). All incident laser power was: 200  $\mu$ W. All scale bars in Figure S10: 4  $\mu$ m.

This enhancement is resulted from VHSs. When the incident photon energy matches the energy interval between two VHSs in band structure, it gives rise to the enhanced photocurrent generation.



**Figure S10.** (a) Optical image of 13° tBLG device. The channel comprises of mono-/bi-layer area. (b) Optical image of 10° tBLG device. (c) Optical image of G-band non-enhanced tBLG device. (d) Raman spectra at bi-layer area in Figure S10a with 532 nm laser (blue line) and 633 nm laser (red line), respectively. (Inset: Raman mapping of the device in Figure S10a with 532 nm incident laser.) (e) Raman spectra at

bi-layer area in Figure S10b with 532 nm laser (blue line) and 633 nm laser (red line), respectively. (Inset: Raman mapping of the device in Figure S10b with 633 nm incident laser.) (f) Raman spectra at bi-layer area in Figure S10c with 532 nm laser (blue line) and 633 nm laser (red line), respectively. Black line is the Raman spectrum at mono-layer area of the device. (g) Photocurrent mapping for one of the electrodes in Figure S10a with 532 nm incident laser (under zero bias voltage). (h) Photocurrent mapping for one of the electrodes in Figure S10b with 633 nm incident laser (under zero bias voltage). (i) Photocurrent mapping for one of the electrodes in Figure S10b with 633 nm incident laser (under zero bias voltage). (ii) Photocurrent mapping for one of the electrodes in Figure S10b with 633 nm incident laser (under zero bias voltage). (ii) Photocurrent mapping for one of the electrodes in Figure S10b with 633 nm incident laser (under zero bias voltage). (ii) Photocurrent mapping for one of the electrodes in Figure S10b with 633 nm incident laser (under zero bias voltage). (ii) Photocurrent mapping for one of the electrodes in Figure S10b with 633 nm incident laser (under zero bias voltage). (ii) Photocurrent mapping for one of the electrodes in Figure S10c (identical results for 532 nm and 633 nm laser).

#### References

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