

Supplementary Materials:
Tunable optical excitations in twisted bilayer graphene form strongly bound excitons

Hiral Patel1, Robin W. Havener2,3, Lola Brown2,3, Yufeng Liang4, Li Yang4, Jiwoong Park2,3, and Matt W. Graham1
1. Department of Physics, Oregon State University, Corvallis, OR USA
2. Department of Chemistry and Chemical Biology, Cornell University, Ithaca, NY USA
3. Kavli Institute at Cornell for Nanoscale Science, Ithaca, NY USA and
4. Department of Physics, Washington University in St. Louis, St. Louis, MO USA

S.1: Fabrication & characterization of twisted bilayer graphene

Figure S1: Areas containing low-angle tBLG were first identified using TA microscopy, they were then verified using hyperspectral linear absorption spectroscopy technique, and dark field TEM (DF-TEM).

Characterization: Transient absorption (TA) microscopy on tBLG requires (i) identification of large-area tBLG regions (ii) diffraction limited probe-beam resolution TA. First identification of tBLG domains was done using diffraction-limited scanning confocal TA microscopy. tBLG regions were detected by exciting above resonance and probing well-below resonance (typically at 0.8 eV), as shown in Figure S1. tBLG regions show a markedly enhanced TA when the resonance lies between the pump and probe beam energies, owing to the strong electronic relaxation bottleneck effect in the interlayer tBLG states. Once the regions with anomalous electronic dynamics are identified, the precise absorption resonances were measured using hyperspectral absorption imaging. 2 By collecting the full-frames absorption movies (such as those in section S.10), specific absorption spectra can be acquired by integrating over a defined region, and plotting as a function of absorbing wavelength.

Figure S2: Hyperspectral Microscopy Characterization 2 (a) off-resonant linear absorption maps reveals large areas of bilayer absorption, (b) hyperspectral absorption map shows two dominant absorption resonances corresponding to tBLG regions that are ~6.5° and ~8° oriented, (c) the plot of how the twist angle absorption scales with stacking angle as determined by darkfield TEM.
The correspondence between absorption resonance and twist angle has been previously established. Once all optical measurements were complete, darkfield transmission electron microscopy (TEM) was used to determine precise angle assignments (see Fig. S1), and a composite image is constructed such as the one shown in Fig. S2. Similar results were obtained for rBLG on silicon, silicon nitride and fused silica substrates.

**S.2: Transient absorption (TA) microscopy**

**Figure S3** - (a) Optical setup for transient absorption (TA) microscopy. Sub-diffraction limited pump, and probe pulses are raster scanned, and the sample can be imaged against the laser noise floor by employing a lock-in amplifier detection synched to an acousto-optical (AO) modulator (1 MHz), (b) Stacked TA images for a movie of the localized electronic decay.

To combine the unmatched spatial resolution of TEM with ultrafast temporal resolution, we can interface darkfield TEM with ultrafast transient absorption (TA) microscopy. In Fig. S1 and S3, we show bilayer CVD graphene locally excited with a modulated (1 MHz) 140 fs pump pulse at 980 nm. We then probe graphene at 1650 nm using a second collinear probe pulse at some time-delay, $t$. By collecting the change in reflectance ($\Delta R(t)$) of the probe pulse we plot the dynamics of graphene in both space and time. By stacking the frames as shown in Fig. S3, we can reconstruct a ‘movie’ of photoexcited hot electrons relaxing. This electron-relaxation ‘movie’ is also a novel fast imaging technique for nanomaterials, and requires only seconds to acquire each frame.
S.3: Transient Optical Conductivity

**S.3.1: the intralayer transient optical conductivity (i.e. single-layer graphene TA)**

In transient absorption microscopy, we measure the change in the amplitude of the reflected probe-beam at a probe energy $E_o$, in the absence $(R_2)$ and presence $(R_1)$ of a pump beam. Under optical excitation conditions, transient reflectivity is related to the optical conductivity by\(^4,7\):

$$\frac{\Delta R(t, E_o)}{R} = \frac{R_2 - R_1}{R_1} = \frac{4 \pi}{\hbar^2 - 1} \sum_i \text{Re} \left[ \sigma_i(E_o, T_e(t)) - \sigma_i(E_o, T_i) \right]$$

Both interband and intraband processes contribute to the total optical conductivity, $\sigma_{\text{TOT}} = \sigma_{\text{inter}} + \sigma_{\text{intra}}$.

When the Fermi populations are evaluated (to first order) it has been shown that\(^3,7\):

$$\Delta \sigma_{\text{intra}} = \frac{2 k_b T_f}{(E_o^+ - E_p^+)^2 + \Gamma^2}$$

$$\Delta \sigma_{\text{inter}} = \frac{2 k_b T_i}{(E_o^+ - E_p^+)^2 + \Gamma^2}$$

The absolute sign of the intraband and interband transient signals are opposite, permitting experimental separation.\(^7\)

We attribute the bleach to the transient interband optical conductivity, and the excited state absorption (ESA) to intraband transitions.

As observed in previous works (e.g. ref 7), we observed that intraband contribution is best determined by its absolute sign (under the specific sample and carrier densities used in our manuscript). For probe energies <1.3 eV, we have shown in Fig. S4 the relative intraband kinetic contribution is weak, and can be approximately ignored. When probe energies are >1.3 eV, we can approximately remove this contribution for the TA kinetics by plotting, $\Delta \sigma_{\text{BLG}}(t)$, approximately leaving just the transient optical conductivity of the interlayer electrons. A similar approach ($\sigma_{\text{BLG}} - \sigma_{\text{BLG}}$) has been recently used to analyze the properties of linear absorption microscopy.\(^2\)

**S.3.2: the interlayer transient optical conductivity**

Currently, there exists no closed-form expression for the transient optical conductivity near the $\text{BLG}$ optical absorption resonance. In the limit that the two layers of graphene are electronically decoupled, the transient optical conductivity, $\Delta \sigma(t)$ is obtained by evaluating the Fermi-Dirac electronic population at the desired energy (see S.3.1). In the opposite regime, the layers of $\text{BLG}$ could be strongly coupled and form bound exciton states. These resultant strongly correlated electron-hole pairs are predicted to be initially decoupled from the exciton states below, and have a well-defined, common exciton ground state.

Generally, the relative magnitude of a pump-probe or transient absorption (TA) response is given by $\Delta \sigma(t, E_{pr}) \propto n(t) \left[ \sigma_{\text{ESA}}(E_{pr}) - \sigma_{\text{SE}}(E_{pr}) - \sigma_{\text{o}}(E_{pr}) \right]$, where $n(t)$ is the electronic carrier population occupying the probed state energy ($E_{pr}$), $\sigma_{\text{ESA}}$, $\sigma_{\text{SE}}$, $\sigma_{\text{o}}$, are the absorption cross-sections of the excited state absorption (ESA), stimulated emission (SE) and the ground state spectral bleach at an incident probe energy, $E_{pr}$. The ESAs (e.g. intraband absorption in graphene) gives the opposite (negative) $\Delta \sigma(t)$ sign, while the “ground state bleach” response is positive signed, arising from interband Pauli blocking effects.

In the free carrier model, Pauli blocking is referred to the photo excited holes or electrons lying at the same energy of the probe beam, leading to decreased absorption (positive signal by our convention). In the bound exciton
model, Pauli blocking chiefly refers to decreased probe beam absorption from a depleted ground exciton band. Excitons tend to inherently have very narrow electronic distribution in their center of mass momentum space, $K_{cm} = (k_e + k_h)/2$, enabling us to approximately treat the ground and excited states as a discrete energy broadened by static and dynamic environmental interactions. In such a bound-exciton model, from the carrier density in the above equation can be found that $\Delta \sigma(t)$ decays approximately exponentially in time, according to the rate equation:

$$\frac{dn}{dt} = P\delta(t) - \frac{n}{\tau}$$

where, $P$ is the incident photon flux, $\delta(t)$ approximates our 140 fs excitation pulses, and $\tau$ is the exciton relaxation lifetime of the X_A state. If there are multiple states (e.g. X_A and X_s) or multiple relaxation pathways there will be multiple lifetimes $\tau_1$ and $\tau_2$ in the rate law.

S.4 - Resonant vs. off-resonant tBLG electronic dynamics

S.4.1: Bernal stacked graphene vs. off-resonant tBLG electronic dynamics

The manuscript concerns the interlayer electronic properties of resonantly excited tBLG. However at most twist angles, light will photoexcite electrons below the tBLG resonance. The data in Fig. S5 give interband transient bleach signals, which was acquired at a 1.25 eV pump and 0.95 eV probe. In Fig. S5c, we compare against single layer graphene (black), and show that, the tBLG amplitude (green) is twice as large and the electronic dynamics are virtually indistinguishable. Consequently, we conclude that presence of high energy resonance states, do not appreciably change the electronic dynamics of low lying states; as expected.

Interesting, we find the Bernal stacked graphene has systematically longer dynamics than single layer graphene in other two configuration presented. This suggests that subtle band bending associated with bBLG, may serve to (marginally) slow the overall relaxation rate of the Fermi-Dirac distribution. Previous bilayer graphene TA studies did not have access to twist angle information, so precise comparison of the dynamic response under identical excitation condition were not possible. This manuscript focuses on the electronic bottleneck behavior of resonantly excited tBLG electronic carriers, and the subtle below resonance excitation behaviors are not discussed in depth here.

S.4.2: Resonant vs. non-resonant TA maps

Figure S6 shows scanning TA microscopy maps of graphene for resonant (a), and non-resonant excitation (b, and c). Enhanced TA Pauli blocking response (positive signed) is observed from ~ 6° tBLG domain (a) green arrow) for resonant pump (1.33 eV), and probe (1.23 eV) excitation, however, the surrounding graphene gives opposite signed, intraband response. On the other hand, when the electron population is probed above (Figure S6 (b)), or below (Figure S6 (c)) the resonance, the relative electron population localized to the ~ 6° tBLG domain decreases, which is consistent with the TA relaxation
dynamics discussed in the manuscript (Figure 5). These observations suggest that when interlayer electrons are excited at resonance \( (E_\Theta) \), the tBLG carriers are decoupled from the lower lying continuum states, creating stable exciton states, suggesting that the resonant excitation conditions may be necessary for the bound exciton state formation as discussed in the manuscript.

Figure S6 – Resonant vs. non-resonant TA microscopy map:
Scanning TA map of graphene (a) resonant excitation, (b), and (c) non-resonant excitation

S.5: Lattice Temperature Dependence

TA can also contain transient behavior that results from thermal induced shifts to absorption peaks. In tBLG however, these temperature induced absorption shifts appear to be very weak compared to the strong electronic response observed. In Fig. S7, we measured the linear absorption of tBLG at 295 and 5K and show that there is no detectable shift within our noise limit.

Likewise, in Fig. S8 we show transient absorption measurement at 295 K (pink) and 5 K (navy) and find that the interlayer relaxation dynamics are also roughly lattice temperature insensitive. Specifically, since the 5 K (navy curve) experienced a much larger laser induced lattice temperature change, we would expect a much larger amplitude contribution at low temperatures, if the long component was thermally induced. However we instead observe that the interlayer dynamics are identical to the 295 K case. We conclude that since thermal induced
absorption shifts cannot be observed over a ~300K lattice temperature ramp, the tBLG TA absorption components we report in the manuscript is likely not thermal in nature. The dynamics are also roughly insensitive to photon flux, as further discussed in section S.8, and no TA sign-flips were observed when the blue tBLG spectral edge is probed instead of the red edge.

**S.6: Substrate dependence**

We measured the linear, and TA response of tBLG on silicon, silicon, nitride, and fused silica substrate, and both the linear, and TA response was similar. Figure S9 shows one-photon scanning TA movie frames of tBLG domains on a fused silica. The strong, enhanced interband (Pauli blocking) TA signal is localized to the 6.3°, and 6.6° tBLG domains (yellow arrows).

![Figure S9 – One-photon on-resonance TA movie frames on a fused silica substrate:](image)

For resonant pump, and probe combination (E_pump=\(E_{probe}=E_0\)), positive signed, TA Pauli blocking response (ground state depletion) is enhanced for the 6.3°, and 6.6° tBLG domains (yellow arrows).

The excited carriers in 6.3°, and 6.6° tBLG domains stay excited even at 6 ps after the initial excitation, whereas the excited carriers in the surrounding graphene decay away. Figure S10 shows one-photon long-lived, TA relaxation kinetics of 6.3° tBLG domain (red), and opposite signed, short- lived, TA relaxation kinetics of bBLG on a fused silica. The relaxation kinetics, and the decay lifetime are similar to that of the tBLG, and bBLG domains on SiN substrate reported in the manuscript (Figure 2c), confirming that the interlayer electronic response is invariant to the substrate, and it is electronic in nature.

![Figure S10 – One photon TA relaxation kinetics:](image)

The electron relaxation dynamics of 6.3° tBLG domain (red), and bBLG (green) labeled on a fused silica substrate.
S.7: One-photon dynamics for various tBLG domains

Figure S11 shows normalized relaxation kinetics of 7.5°, 6.8°, 8°, and 5.1° tBLG domains for resonant excitation. Both one-, and two- photon on, and off resonance TA were performed on various tBLG domains with angles ranging from 5° to 10°. The long-lived components were consistently present for both one-, and two-photon resonant excitations. The measured long-lived, strong, positive signed, Pauli blocking response of various tBLG domains suggests that the resonant excited interlayer electrons experience electronic relaxation bottleneck as discussed in the manuscript (Figure 2c), in contrast to short lived, weak, negative signed, intraband response form bBLG.

Figure S11 - Transient absorption signal vs. photon flux, f. i. Graphene, showing Fermi-Dirac and quadratic fits, ii. tBLG TA, showing square root function and linear fits for 1-photon, and 2-photon excitation respectively.

S.8: One and two-photon flux dependence

Figure S12 suggests that Auger annihilation contributes strongly to the TA power dependence of tBLG. Auger exciton annihilation effects are commonly including the electron dynamics of strongly-bound excitonic systems such as (s-SWCNTs), with the following characteristic kinetics:

$$\frac{dn}{dt} = P\delta(t) - \frac{n}{\tau} - \frac{n^2}{2}\gamma$$

Here, $P$ is the incident photon flux, $\delta(t)$ approximates our 140 fs excitation pulses, $\tau$ is the exciton relaxation lifetime of the $X_A$ state, and $\gamma$ the exciton annihilation rate constant. In the short-time limit, when exciton density is high annihilation is the dominant term, the above equation may be approximated by,

$$n_o = \sqrt{\frac{2P}{\gamma}}$$

This suggest, that if the tBLG TA signal comes for bound exciton states, the TA amplitude may scale with the square root of photon flux for a one-photon excitation, and linearly for two-photon excitation. Accordingly, for tBLG, we observe in Fig. S12ii a characteristic square root amplitude dependence that is seen in analogous systems like the SWCNTs. Consistent with dominant exciton annihilation, we find the two-photon tBLG response grows only linearly with photon flux.

As a control, we also show in Fig. 12i, the graphene interband TA power dependence fit to graphene's characteristic Fermi-Dirac electronic filling function. Conversely, the two-photon TA fits to a quadratic function for delay times near $t=0$, as required. We conclude that underlying square root behaviors observed suggest Auger
annihilation processes in tBLG. This is further in agreement with a bound excitonic model, and suggests further parallels between tBLG and s-SWCNTs, motivating future investigations.

S.9: Two-photon transient absorption maps

Figure S13 shows relative electron population in 6.5°, and 8° tBLG domains for fixed probe energy of 1.40 eV, and two-photon pump energy 1.04 eV (blue), 1.16 eV (black), and 1.31 eV (green) labeled. The strong two-photon positive signed signal from 8° tBLG domains corresponds to the TA Pauli blocking response (electronic bleach), and the weak, two-photon negative signed signal from 6.5° tBLG domains corresponds to the intra-band response as discussed in the manuscript. The amplitude of the TA Pauli blocking response from 8° tBLG domains is relatively weak as we tune the two-photon pump energy slightly below ((a) 1.04 eV, blue), or above ((c) 1.31 eV, green) the two-photon resonance ((a), 1.6 eV, black). This observation is consistent with the electron kinetics reported in the Figure 5 of the manuscript. Our observations suggest that the electron population stay excited for longer if excited at two-photon resonance, which again suggests that the resonant excitations may be important for formation of stable, bound exciton state.

Figure S13-Two-photon transient absorption maps for a fixed probe energy (1.40 eV), and pump energy (a) 1.04 eV, (b) 1.16 eV, and (c) 1.31 eV. 8° tBLG domains give strong two-photon TA Pauli blocking response, whereas, the surrounding gives weak, intra-band response.

S.10: Supplementary Movies of tBLG

Movie 1: tBLG vs. excitation wavelength using hyperspectral absorption microscopy. Different graphene domains appear darker at certain wavelength showing resonant absorption of incident light upon scanning the wavelength from 400 nm to 700 nm. Similar such movies have been previously reported.2,3

Movie 2: Transient absorption microscopy of graphene vs. time for fixed pump, and probe energies. The relative population of electrons in graphene is decaying as a function of time (in femtoseconds).

Movie 3: TA microscopy of a tBLG domain vs. time in picoseconds. Long-lived electronic dynamics are localized to the twisted bilayer region. Specific frames of this movie are shown in Fig. 2b in the manuscript.
S.11: References