

Hot Phonon Dynamics in Graphene

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Supporting Information

Detailed description of the experimental setup and measurement

Figure S1 shows the experimental setup consisting of three main parts: laser system, optical microscope and detection system. The laser system consisted of a femtosecond Ti:Sapphire oscillator (~150 fs, 76 MHz, Mira F, Coherent) and a synchronously-pumped optical parametric oscillator (~200 fs, 76 MHz, Mira OPO, Coherent). While a large fraction of the Ti:Sapphire oscillator power was used to synchronously pump the OPO, some of the power at 830 nm was used as the pump beam to excite carriers in graphene samples and generate hot optical phonons due to strong carrier-phonon coupling. A time-delayed weaker probe beam at 565 nm from the OPO was used to probe the population of hot zone-center optical phonons via anti-Stokes Raman scattering. The temporal overlap of the pump and probe beams can be easily found with the aid of a BiB_3O_6 nonlinear crystal by monitoring their sum frequency generation signal. The exact zero time delay between the pump and probe beams was defined by finding the maximum four-wave mixing signal emitted from Si substrate of the samples mounted on the optical microscope. The pump and probe beams were sent collinearly and focused on the sample through the microscope objective ($\times 100$, NA = 0.95, Nikon) for dynamic studies. The microscope was a modified sample-scanning inverted optical microscope (Nikon TE2000-U). The sample can be raster scanned by a piezo-actuated three-dimensional nanopositioning stage (Nano-PDQ375, Madcity). At each pixel, the back-scattered optical signal was collected through the same objective, and passed through a beamsplitter (50/50 NIR,

Chroma) and 2 short-pass filters (SP01-532RU-25, Semrock), which completely filtered out the pump and probe beams. After passing through a confocal pinhole, the optical signal was recorded either by a SPAD (SPCM-AQR-15, Perkin-Elmer) or by a spectragraph (SP-2356, Acton) equipped with a CCD detector (Spec-10:400BR/LN, Princeton Instruments). With this configuration, the setup allowed us to pinpoint an area of interest on graphene samples and conduct time-resolved anti-Stokes Raman spectroscopy.

In addition to the time-resolved anti-Stokes Raman spectroscopy, the setup enabled us to image and characterize the samples with both nonlinear photoluminescence¹ and spontaneous Raman spectroscopy.^{2,3} Raman spectroscopy is used to identify the number of layers in graphene samples and characterize the quality of samples as widely described in the literature (for example, Ref. 2 and 3). It is conducted by using the continuous wave lasers (532 nm and 633nm) as the excitation source in the setup (Fig. S1) and choosing appropriate beam splitter and optical filters. The nonlinear photoluminescence refers to an observation that we reported in our previous publication in Ref. 1. The broad upconverted luminescence background in Fig. 1(b) and (c) is a result of this phenomenon. It arises from radiative recombination of a broad distribution of nonequilibrium electrons and holes, generated by rapid scattering between photoexcited carriers within tens of femtoseconds after femtosecond laser irradiation. The nonlinear photoluminescence can be used to image the graphene samples. For example, Figure S2 shows the nonlinear photoluminescence image of the same sample as in Fig. 2(a). Therefore, one can study

different layers or different locations on a same sample while excluding area of defects or suspicious areas. Furthermore, we also combined in-situ transport measurement for graphene field effect devices in our experimental setup, which allowed us to control the Fermi level in gate-dependent lifetime measurements.

Besides the hardware setup, an important feature of our experimental apparatus is the software integration of all related hardwares by Labview programming. For the time-resolved anti-Stokes Raman spectroscopy on graphene reported in this paper, we could automate the experiments by controlling the stepping motor for time delay between the pump and the probe, spectrometer for anti-Stokes Raman spectroscopy, and sourcemeters and lockin amplifier for transport measurement. A big benefit of this integration is that we could take as many measurements as necessary for data averaging in a timely manner. To have a sense of the measurement, the 2D plot of anti-Stokes Raman spectra as a function of the time delay between pump and probe beams shown in Fig. 1(b) is an average of 6 sets of data. Each set of data consisted of anti-Stokes Raman spectra with 60 seconds accumulation at 46 different time delays. Therefore, it took about 5 hours to obtain one phonon dynamic curve such as in Fig. 1(e). Of course, we could also present each set of data individually without averaging. Figure S3 shows 9 separate phonon dynamic measurements on a monolayer graphene sample. Some of the curves were measured on different locations of the sample by utilizing the microscopic imaging capability of our setup. They all yielded a lifetime of 1.5 ± 0.1 ps for the hot *G* mode phonons in the supported monolayer graphene. Combined with other measurements on different samples, we concluded that the

values of lifetime reported in the paper are all reproduced within an error of 0.1 ps by using different clean samples and choosing different area of samples.

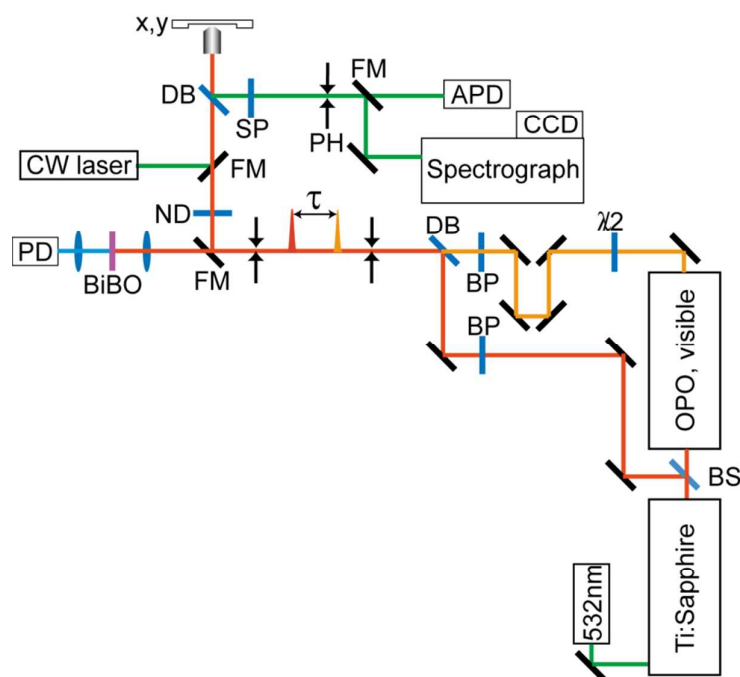


Figure S1. Sketch of the experimental setup. BS: beam splitter; FM: flip mirror; BP: band pass filter; DB: dichroic beamsplitter; ND: neutral density filter; SP: short pass filter; PH: pin hole; APD: avalanche photodiode; PD: photodiode; BiBO: BiB_3O_6 nonlinear crystal.

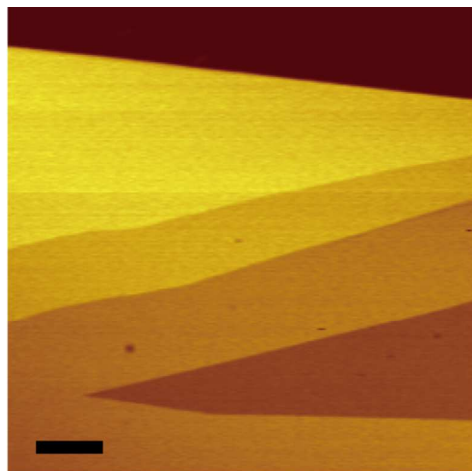


Figure S2. Nonlinear photoluminescence image of the same sample as in Figure 2(a).

The nonlinear photoluminescence was excited by 830 nm femtosecond pulses as described in our previous publication.¹ The scale bar is 10 μm .

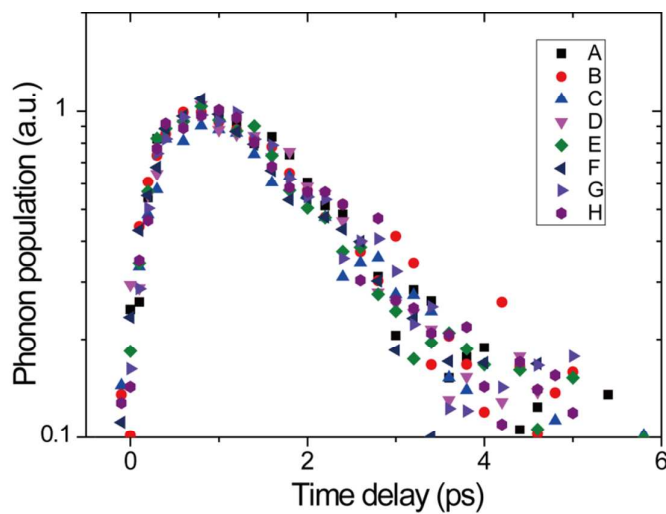


Figure S3. Separate phonon dynamic measurements on a monolayer graphene sample.

Some of the curves were measured on different locations of the sample.

References

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