Electronic Supplementary Material (ESI) for Nanoscale.

Electronic Supplementary Information for

Exciton and phonon dynamics in highly aligned 7-atom wide armchair graphene nanoribbons as seen by time-resolved spontaneous Raman scattering

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1. Resonance Raman spectra of 7-AGNRs aligned on silica/silicon surface at different wavelength of laser pulse

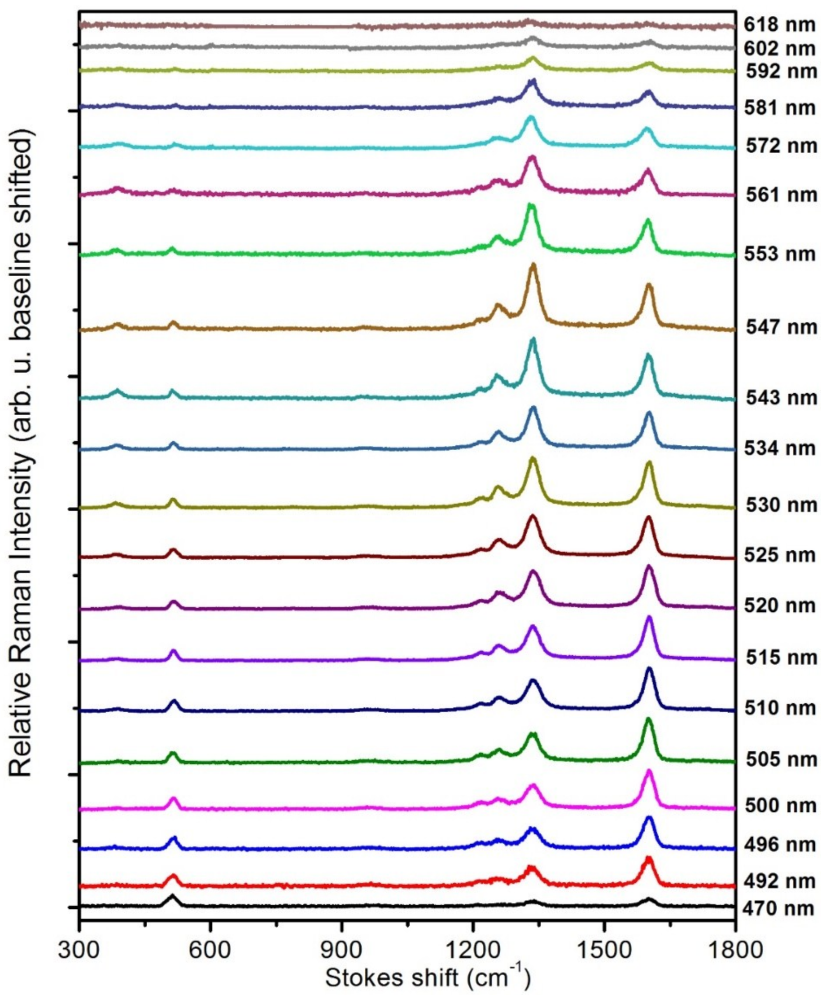

Fig. S1. Wavelength dependent Raman scattering spectra of 7-AGNRs, recorded with ps laser pulses.

2. Time dependent Raman spectra of 7-AGNRs with excitation at 2.5eV

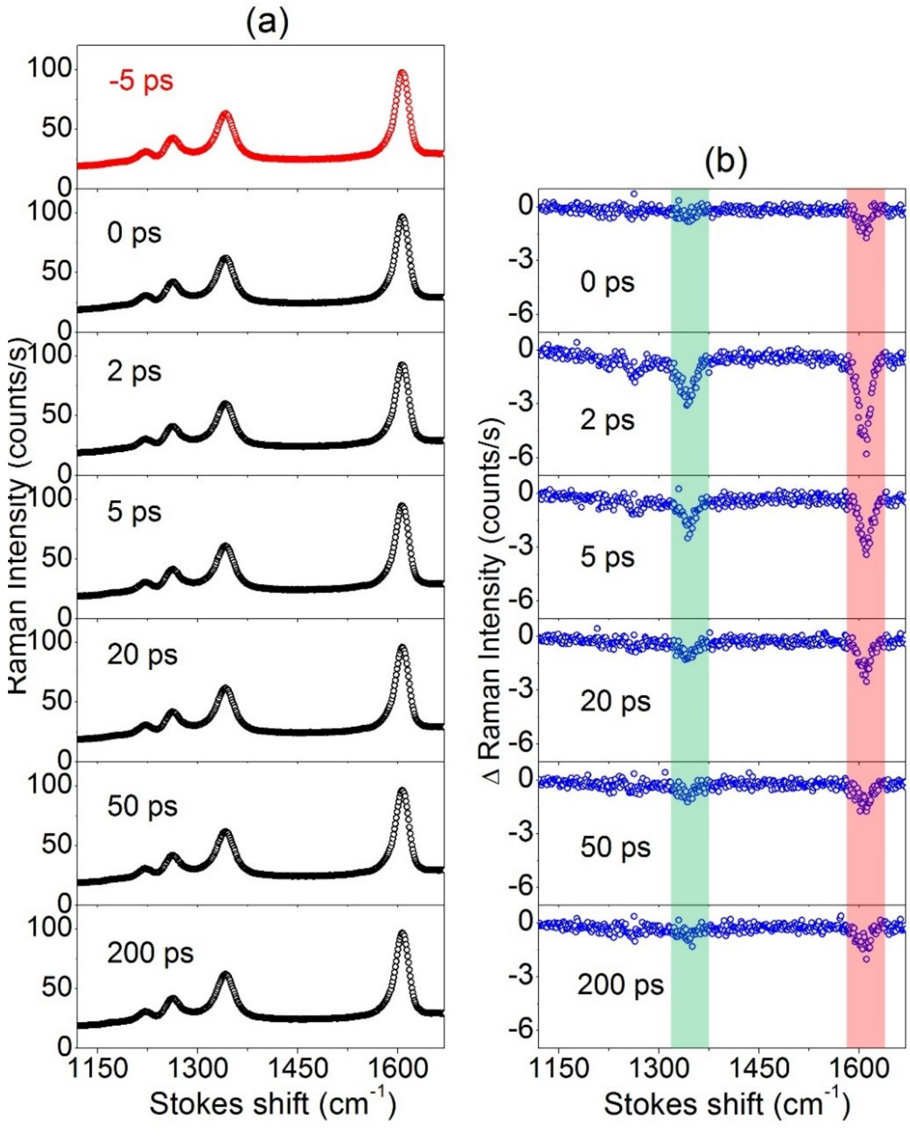

Fig. S2. Time-resolved spontaneous Raman scattering spectra of the 7-AGNRs recorded on Stokes side, with excitation energy at 2.5 eV and Raman probe energy at 2.4 eV. Both the pump and probe polarizations are parallel to the long axis of the 7-AGNRs. (a) Raman

scattering intensity spectra at different delay times after optical excitation. (b) Difference spectra obtained by subtraction the spectrum at -5 ps from each spectrum in (a) at different corresponding delay time.

3. Phonon temperature estimation

We write down the Raman scattering signals from anti-Stokes side[1] as:

$I_{as} = C_{as}\, \chi_{as}^2\, n_p\, (\omega+\Omega)^4$ ……………………………………………………..(1)

where C_{aS} is a factor including optical constants, geometry factors, laser intensity, detector sensitivity and other instrumental aspects, χ is the Raman tensor, n_p is the phonon population number, and ω and Ω are the laser frequency and phonon frequency, respectively.

In quasi-equilibrium assumption, the phonon population can be calculated according to Bose-Einstein statistics, *i.e.,*

$$n_p = \frac{1}{1 - exp(\frac{\hbar\Omega}{kT})}$$ ………………………………………………………….... (2)

From formula (2) the phonon temperature can be calculated, if we know n_p , which can be estimated from formula (1). In order to determine the prefactor $C_{as}\, \chi_{as}^2$ in (1), we further make the assumption that, before time zero, the temperature is close to the room temperature (300 K).

4. Phonon population and Raman tensor changes vs carrier population

Without loss of generality, we write down the electronic susceptibility[2] tensor χ_{ij} of a two-energy level system as:

$$\chi_{ij} \propto N(\rho_{00} - \rho_{11})\left(\frac{\langle\psi_0|r_i|\psi_1\rangle\langle\psi_1|r_j|\psi_0\rangle}{\omega_{01} - \omega - i\Gamma} + \frac{\langle\psi_0|r_j|\psi_1\rangle\langle\psi_1|r_i|\psi_0\rangle}{\omega_{01} + \omega + i\Gamma}\right), \quad \text{……………… (3)}$$

where N represents atom or molecule density of the system, and ρ_{00} and ρ_{11} are the diagonal density matrix elements referring to the ground state ψ_0 and excited state ψ_1, ω is the laser excitation frequency, and Γ is the damping constant. The Raman susceptibility tensor associated with a general vibration model Q can be written as:

$$\frac{\partial\chi_{ij}}{\partial Q}|_{Q_0} \propto N(\rho_{00} - \rho_{11})\frac{\partial}{\partial Q}\left(\frac{\langle\psi_0|r_i|\psi_1\rangle\langle\psi_1|r_j|\psi_0\rangle}{\omega_{01} - \omega - i\Gamma} + \frac{\langle\psi_0|r_j|\psi_1\rangle\langle\psi_1|r_i|\psi_0\rangle}{\omega_{01} + \omega + i\Gamma}\right)|_{Q_0} \quad \text{…… (4)}$$

Thus, Raman tensor is proportional to the population difference $N(\rho_{00} - \rho_{11})$, *i.e.*

$$\frac{\partial\chi_{ij}}{\partial Q}|_{Q_0} \propto N(\rho_{00} - \rho_{11}) \quad \text{……………………………………………………. (5)}$$

With

$$\rho_{00} + \rho_{11} = 1 \quad \text{……………………………………………………………….. (6)}$$

(5) becomes:

$$|\frac{\partial\chi_{ij}}{\partial Q}|_{Q_0}{}^2 \propto N\left(1 - 4\rho_{11} + 4{\rho_{11}}^2\right) \quad \text{…………………………..……………… (7)}$$

Since $\rho_{11} \ll 1$, the term ${\rho_{11}}^2$, can be dropped such that,

$$|\frac{\partial \chi_{ij}}{\partial Q}|_{Q_0}{}^2 \propto N(1-4\rho_{11}) \quad \ldots\ldots\ldots (8)$$

Finally,

$$\Delta|\frac{\partial \chi_{ij}}{\partial Q}|_{Q_0}{}^2 \propto -4N\rho_{11} \quad \ldots\ldots\ldots (9)$$

I.e., the reduction of the squared Raman susceptibility tensor $|\frac{\partial \chi_{ij}}{\partial Q}|_{Q_0}{}^2$ is linearly proportional to 4 times the excited state population Nρ_{11}.

5. References:

1. R. Loudon, *Adv Phys*, 1964, **13**, 423-482.
2. R. W. Boyd, Nonlinear optics, Elsevier, third eddition, *in page 163, chapter 3, Quantum-Mechanical Theory of the Nonlinear Optical Susceptibility*, ISBN: 978-0-12-369470-6 , 2008.