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Surface Phonon Coupling within Boron Nitride Nanotubes Resolved by a Novel Near-Field Infrared Pump-Probe Imaging Technique.

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Surface phonon-polariton (SPhP) modes exist under optical excitation of polar materials, and are accessible using scattering type near-field optical microscopy (s-SNOM). Hexagonal boron nitride (h-BN) and boron nitride nanotubes (BNNTs) can exhibit such modes under IR excitation, in spectral regions where the permittivity is negative. Herein we present pump-probe continuous wave (CW) s-SNOM - a novel two color pump-probe infrared technique that uses two cw tunable light sources and is based on s-SNOM, see Figure 1. [1] The technique for the first time enables the nanometer spatial resolution of couplings between surface phonons longitudinal optical and surface phonon polaritons.

The central spectroscopic approach is to control a constant phase (out-of-phase/in-phase) of a Mickelson interferometer including the nanoscale scattering process governed by the separation between a metal coated AFM tip and the sample. Thereby we obtain the optical signal which is directly related to the absorption/reflection of the material under a scanned probe tip.

Hexagonal boron nitride (h-BN) is isoelectronic with graphene but is polar and much less studied. For detection s-SNOM provides spatial resolution of ~10nm, several hundred fold smaller that the far field diffraction limit. This sub-diffraction opportunity has inspired us to improve our apparatus to examine energy transfer between different surface or between bulk and surface modes. Apparently, it is not necessary for the modes to be polaritons.

For BNNTs, couplings between the longitudinal optical and surface phonon polariton modes of boron nitride nanotubes were measured. Figure 2 presents an experimental illustration of the couplings, where the pump laser was tuned to 1532cm^{-1} and the probe field was varied over the range from the TO mode resonance to 1440cm^{-1}. Our analysis of the energy mismatch and the dependence on sample features leads us to conclude that a low frequency mode enables the coupling, and the mode frequency is likely related to the spatial separation between the multiple, concentric sheets of BNNT.

Finally, this work suggests useful pump-probe experimental studies comparing BNNTs with h-BN crystals. [2]

References:

[1] L Gilburd *et al*, G *J. Phys. Chem. C 7 (2016)* 289.
[2] We gratefully acknowledge support from NSERC and Bruker Nano.

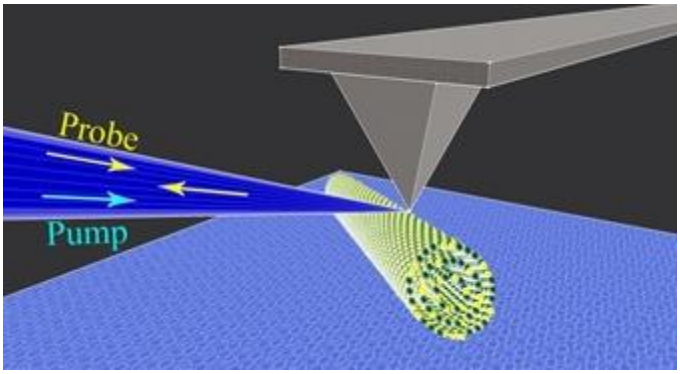

Figure 1. A novel near-field infrared pump-probe imaging technique.

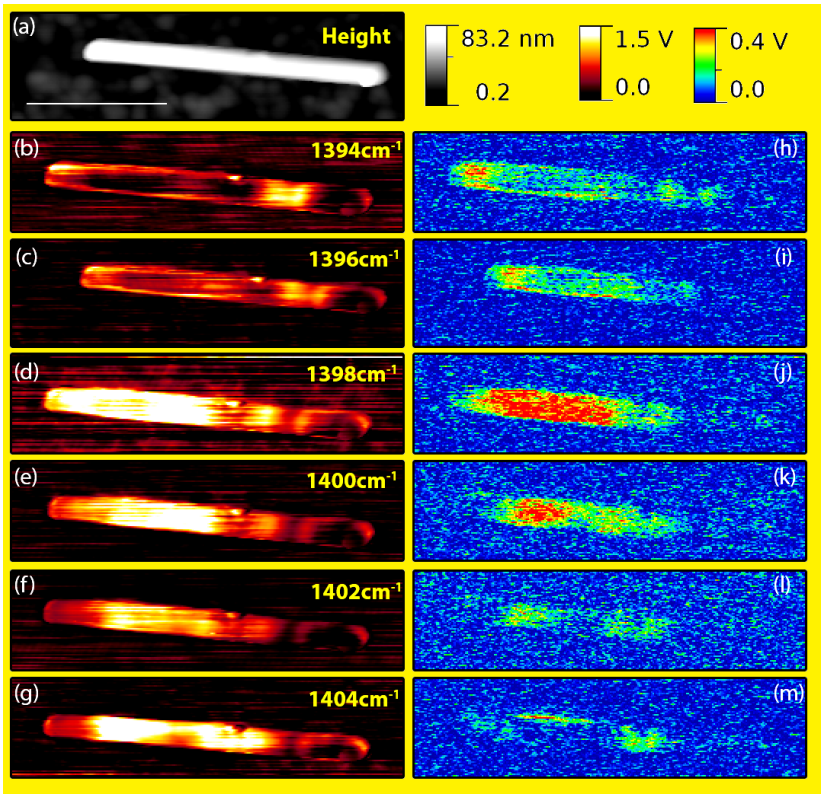

Figure 2: Topography and near field IR mages of a BNNT. (a) AFM topography image. Near-field images at 1394(b), 1396(c), 1398(d), 1400(e), 1402(f) and 1404(g) cm^{-1} probe frequencies (obtained absent a pump field). (h-m) are $1532cm^{-1}$ pump-induced / 1394(h), 1396(i), 1398(j), 1400(k), 1402(l) and 1404(m) cm^{-1} probe images. No pump-induced response was observed at wavenumbers less than ~$1388cm^{-1}$. The scale bar in the topography image is 200 nm.

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