## AFM-Raman and Tip Enhanced Raman studies of graphene

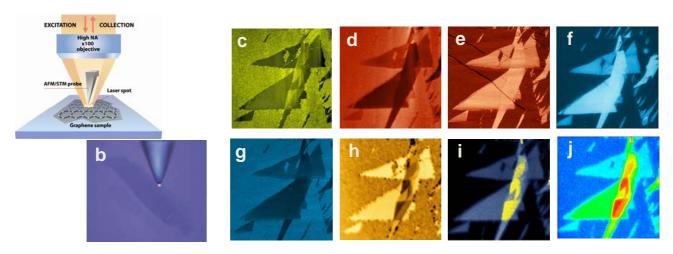
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We demonstrate design and applications in graphene research of an Atomic Force Microscope integrated with Confocal Raman/Fluorescence/Rayleigh microscopy and Tip Enhanced Raman Scattering microscopy.

Different graphene samples are investigated by different types of AFM and spectroscopy techniques providing comprehensive information about the sample. We study in details how the thickness (number of monolayers) in graphene affects its physical properties: surface potential (work function), local friction, elastic modulus, capacitance, conductivity, charge distribution, Raman and Rayleigh light scattering etc. Results for graphene flakes are qualitatively compared to those for carbon nanotubes of different diameters. We show how electrostatic charging of graphene flakes can be effectively measured and modified by AFM cantilever. Raman C-peak of graphene is studied by using high transmission volume bragg grating filters.

Studies are performed both in ambient air conditions and in controlled atmosphere and humidity.



- a), b). AFM Raman configuration: schematics (a) and white light image (b); Raman laser is tightly (400 nm spot diameter) focused onto the very end of a "nose"- shaped AFM cantilever using 100x objective; Graphene layer is positioned below the cantilever and under the laser spot; while scanning the sample, AFM and Raman data is obtained simultaneously.
- c) g). Various AFM images characterizing different physical properties of the sample Topography (c), Electrostatic Force (d), Force Modulation (elastic properties) (e), Kelvin Probe (f), Lateral Force (g).
  - $h)-j). \ Confocal \ optical \ images-Rayleigh \ light \ (h), \ Raman \ 2D \ band \ mass \ center \ (i), \ Raman \ G \ band \ intensity \ (j).$

The ultimate goal of integrating AFM with Raman/fluorescence spectroscopy is to break diffraction limit and to bring spatial resolution of optical methods down to resolution of AFM (a few nm). We also present results of Tip Enhanced Raman Spectroscopy (TERS) or "nano-Raman" mapping of graphene on Si substrate. We demonstrate near field Raman enhancement effect due to resonant interaction of light with localized surface plasmon at the apex of a metal AFM probe. Actual plasmonic and near field nature of the Raman enhancement is proven by a number of ways: dependence of the enhancement on the excitation wavelength and polarization, enhancement versus tip-sample distance curves, observation of selective enhancement of Raman signal from thin surface layer etc. Finally, the ultimate performance of TERS is demonstrated by measuring Raman 2D maps with subwavelength lateral resolution – determined not by the wavelength of light, but by the localization area of the surface plasmon electromagnetic field.