AFM-Raman and tip enhanced Raman studies of carbon nanostructures

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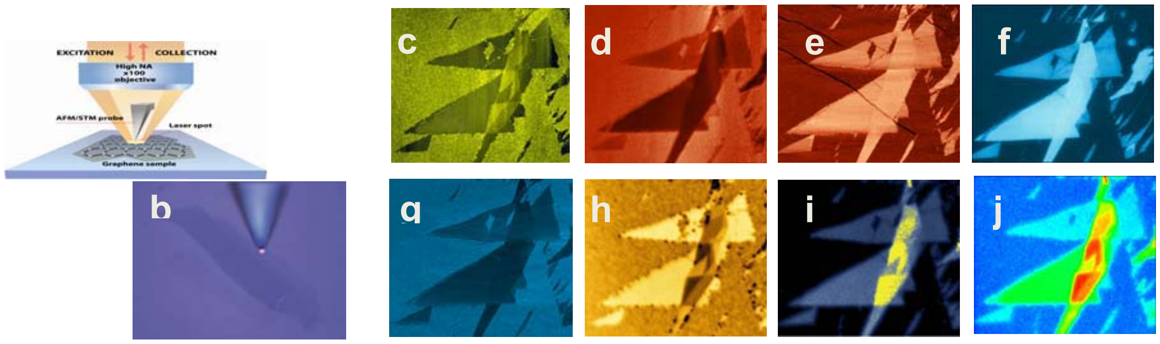
We demonstrate capabilities of Atomic Force Microscopy integrated with Confocal Raman/Fluorescence/Rayleigh microscopy when applied to carbon nanomaterials. Results on various carbon nanostructures are demonstrated: graphene, carbon nanotubes, detonation nanodiamonds etc.

Graphene on gold is investigated by different 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. Studies are performed both in ambient air conditions and in controlled atmosphere and humidity.

We present results of Tip Enhanced Raman Spectroscopy (TERS) or “nano-Raman” mapping realized using integrated AFM-Raman system. Measurements are realized in two different excitation configurations: Inverted (for transparent samples) and Upright (reflected light configuration, for opaque samples, with side illumination option). In both geometries 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. Carbon nanotubes and graphene are studied by TERS technique. 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 layers of the sample etc. Finally, the ultimate performance of TERS is demonstrated by measuring Raman 2D maps with *subwavelength lateral resolution (down to 14 nm)* – determined not by the wavelength of light, but by the localization area of the surface plasmon electromagnetic field.



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).