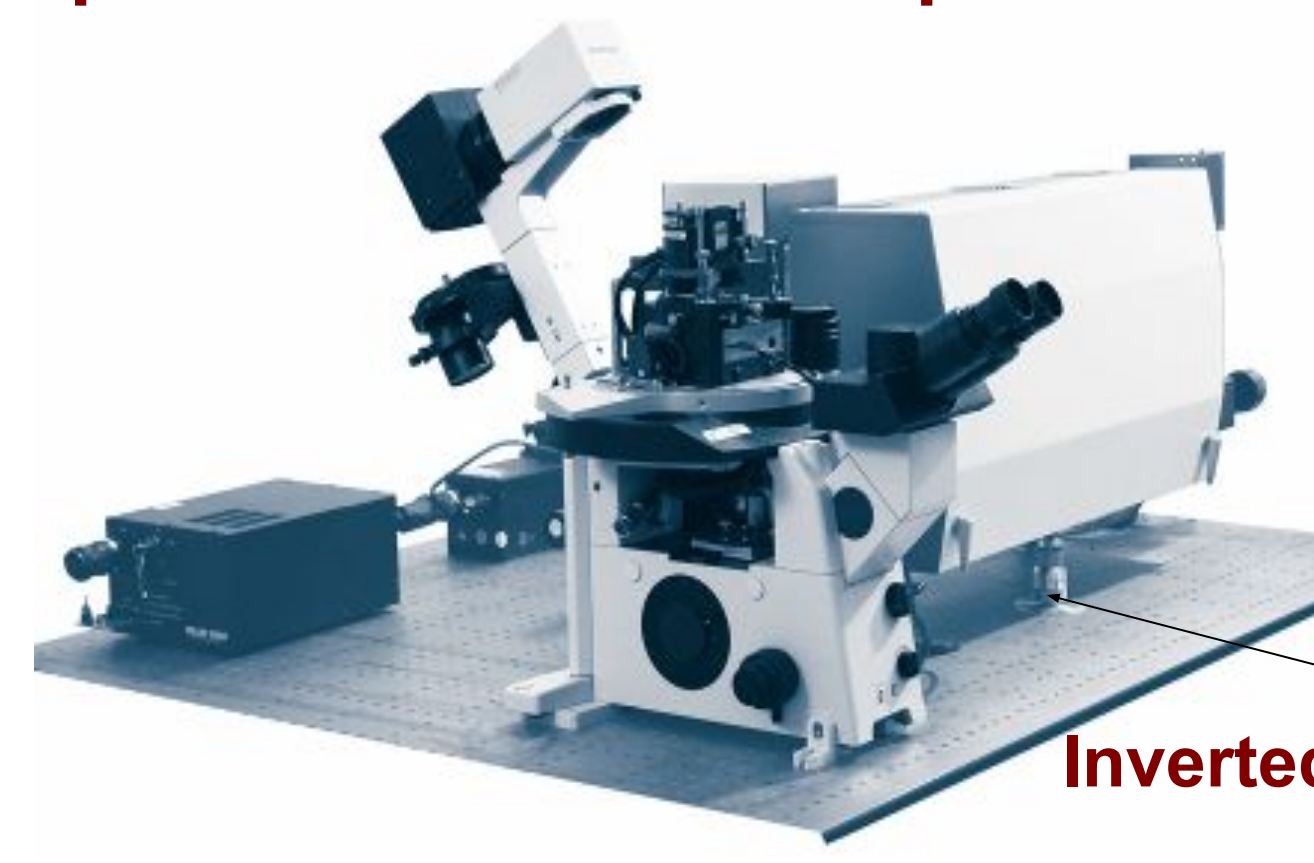
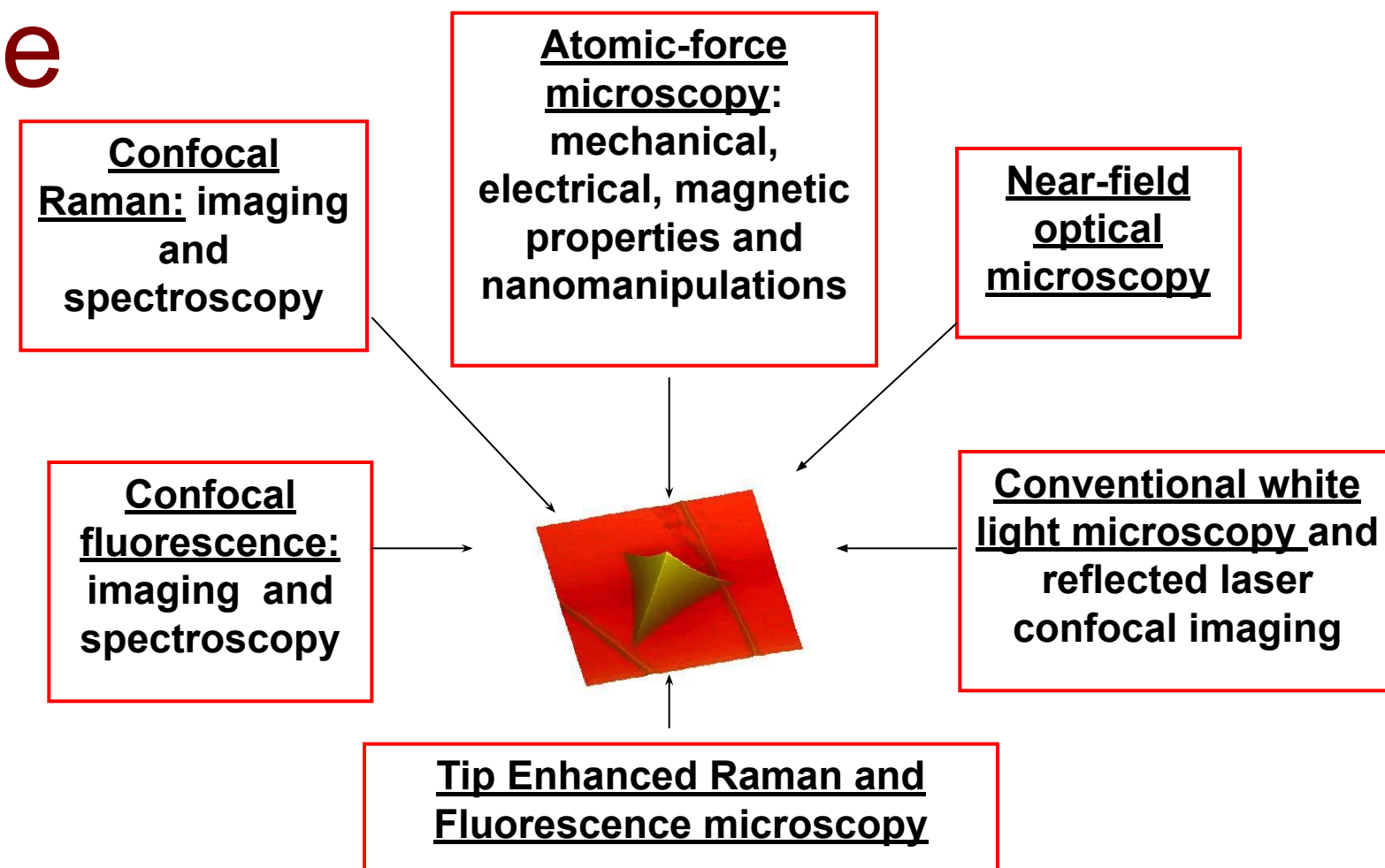


# AFM-Raman and Tip Enhanced Raman studies of modern nanostructures

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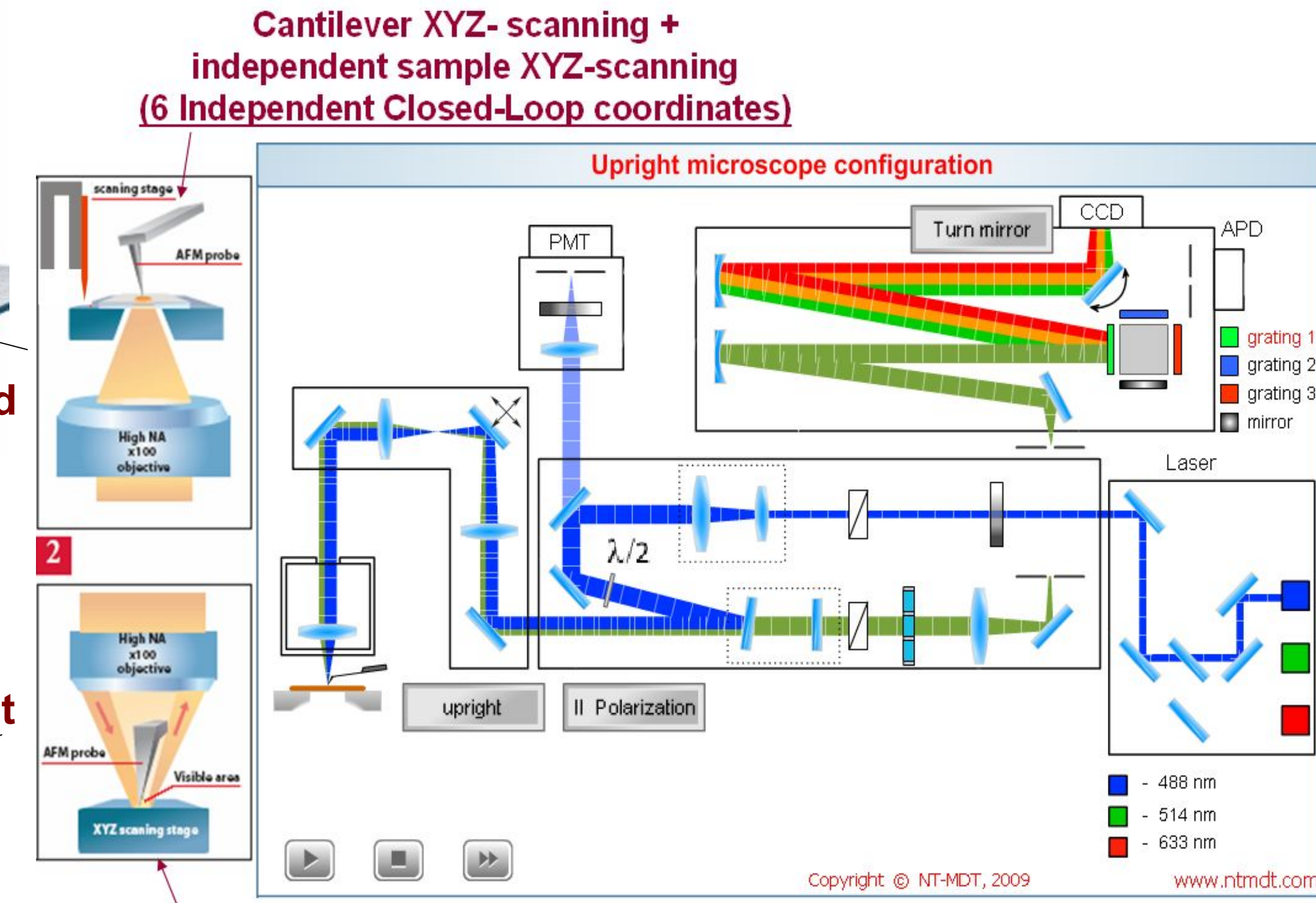
## 1. Experimental setup – integrated AFM, optical microscope and confocal Raman/Fluorescence microscope



Inverted



Upright



Laser spot XYZ - scanning + independent sample XYZ-scanning (6 Independent Closed-Loop coordinates)

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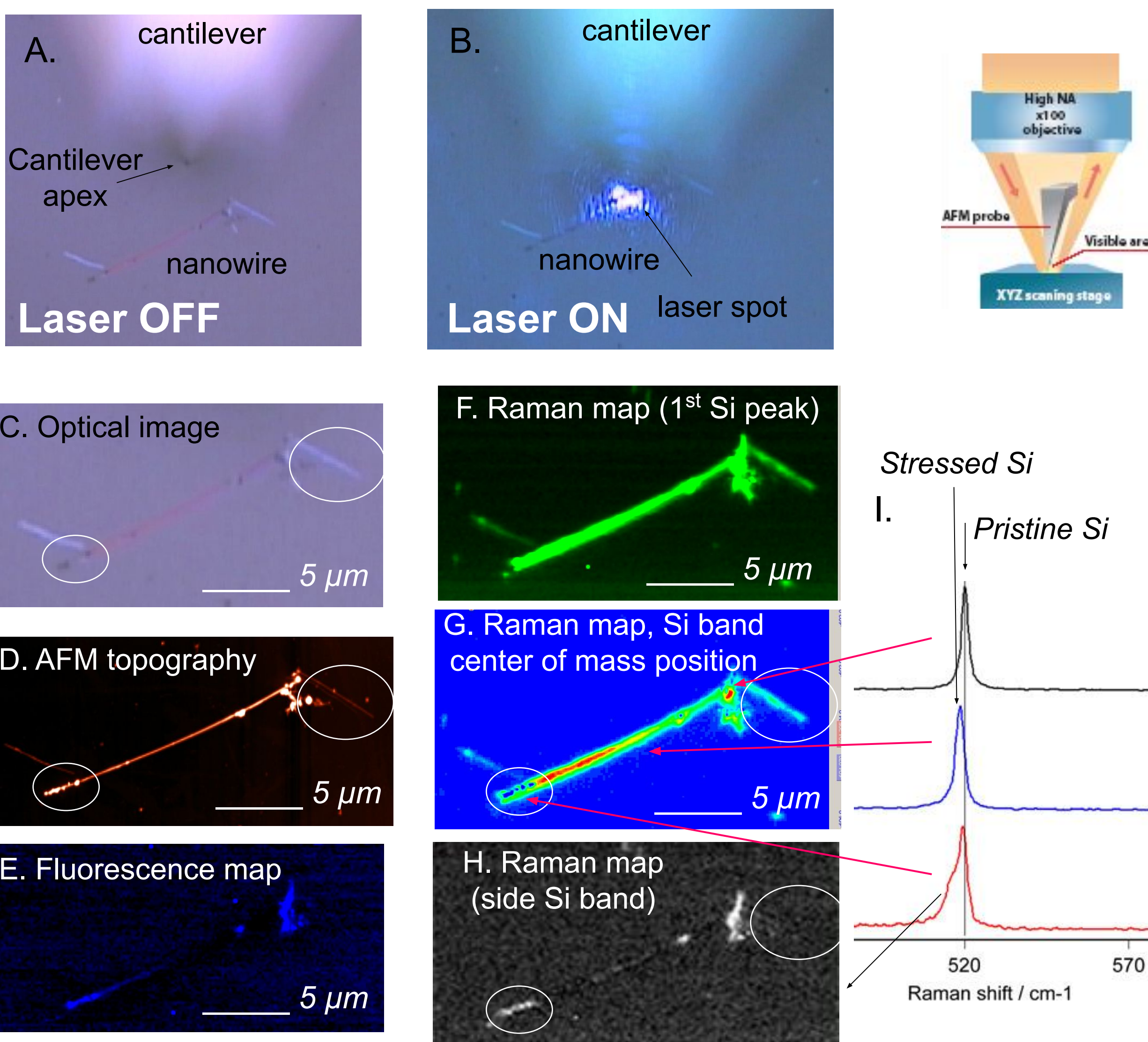
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NT-MDT combines Atomic Force Microscope, Scanning Near Field Optical Microscope and Confocal Raman/Fluorescence Microscope in one experimental platform run by a single software.

Individual nanoscale object can be studied *simultaneously* by many different techniques: AFM (up to 40 different measuring modes possible) and confocal Raman/fluorescence or SNOM. AFM maps provide information about topography and physical properties of the surface – mechanical electrical, magnetic, elastic etc. Raman imaging gives insight into the sample chemistry. When they are combined, extensive sample characterization becomes possible.

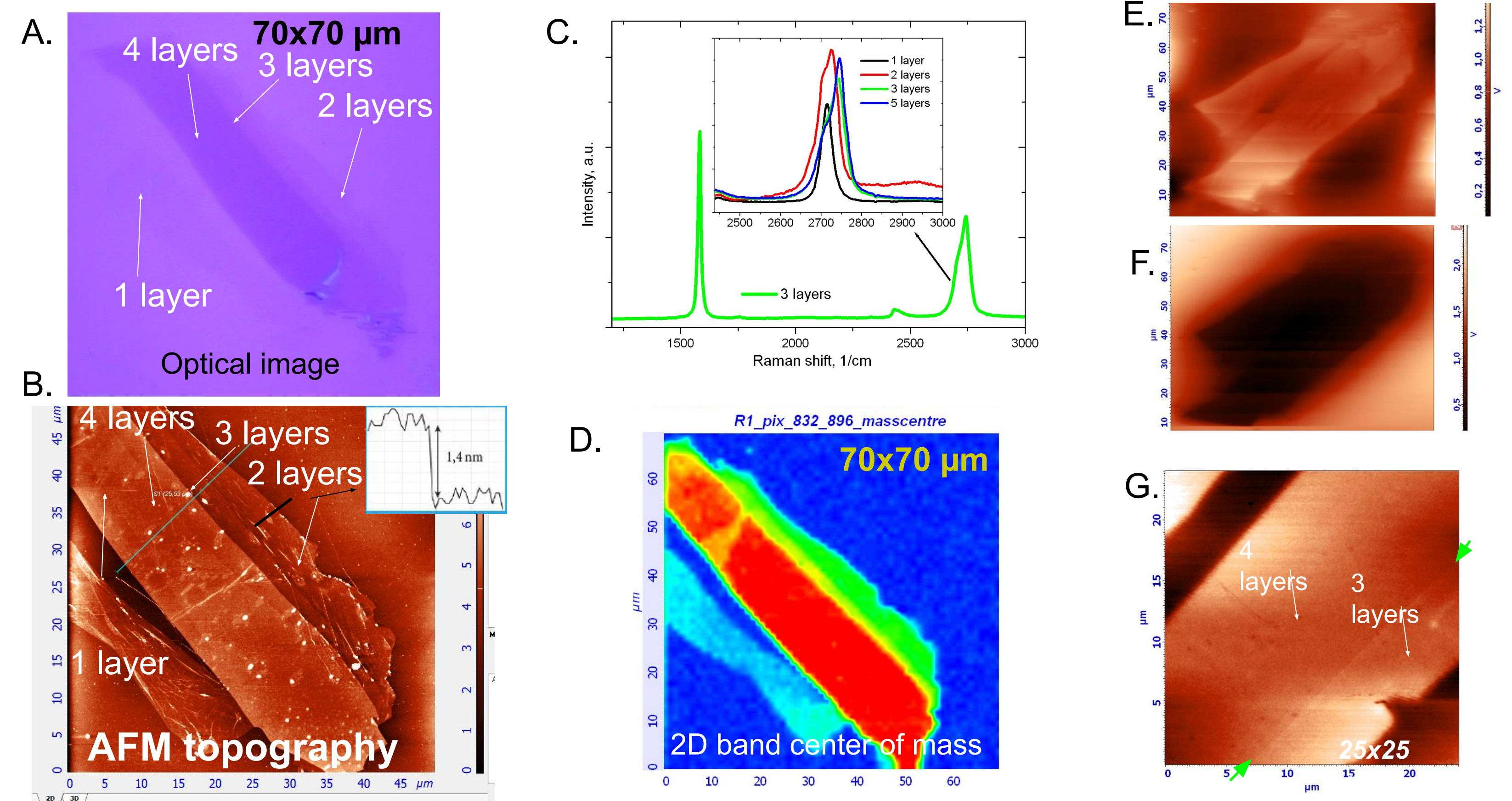
AFM is integrated with optics in two different configurations: Inverted (based on commercial IOM) – for transparent samples and samples on microscope glass; Upright – for opaque samples. Dual scanning is realized: “Scan by sample + scan by tip” or “Scan by sample + scan by laser spot”.

## 2. AFM-Raman mapping of nanostructures (Si nanowires, Graphene)



**Simultaneous AFM-Raman-Fluorescence measurements of individual Si nanowire.**

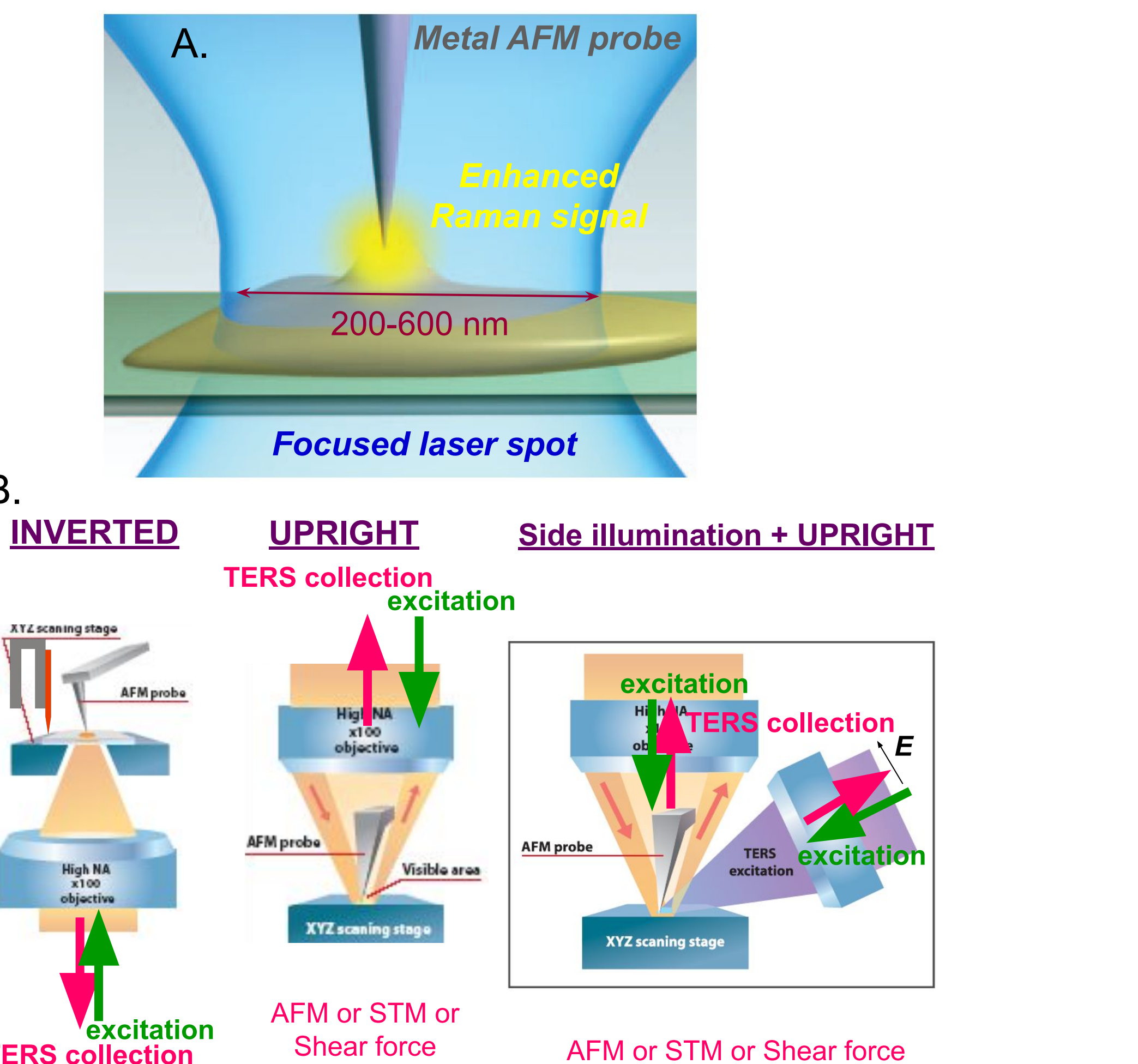
(A),(B),(C) Optical bright field images of the sample and AFM cantilever. AFM tip is positioned directly under 100x, 0.7 NA objective – with 400 nm resolving power. End of the AFM tip can be clearly seen. Laser is switched on and focused into 500 nm spot onto the tip apex. (D) AFM topography of the nanowire. Some (Si) nanoparticles attached to the high quality nanowire can be seen. (E) Mapping fluorescence from impurities. Fluorescence can only be seen in the regions where nanoparticles are present. (F) Intensity of the 1<sup>st</sup> order Si Raman band. (G) Center of mass position of Si band. Band shift is directly proportional to internal stress in the nanowire crystal lattice. (H) Mapping intensity of low energy side Raman band, corresponding to Si nanoparticles.



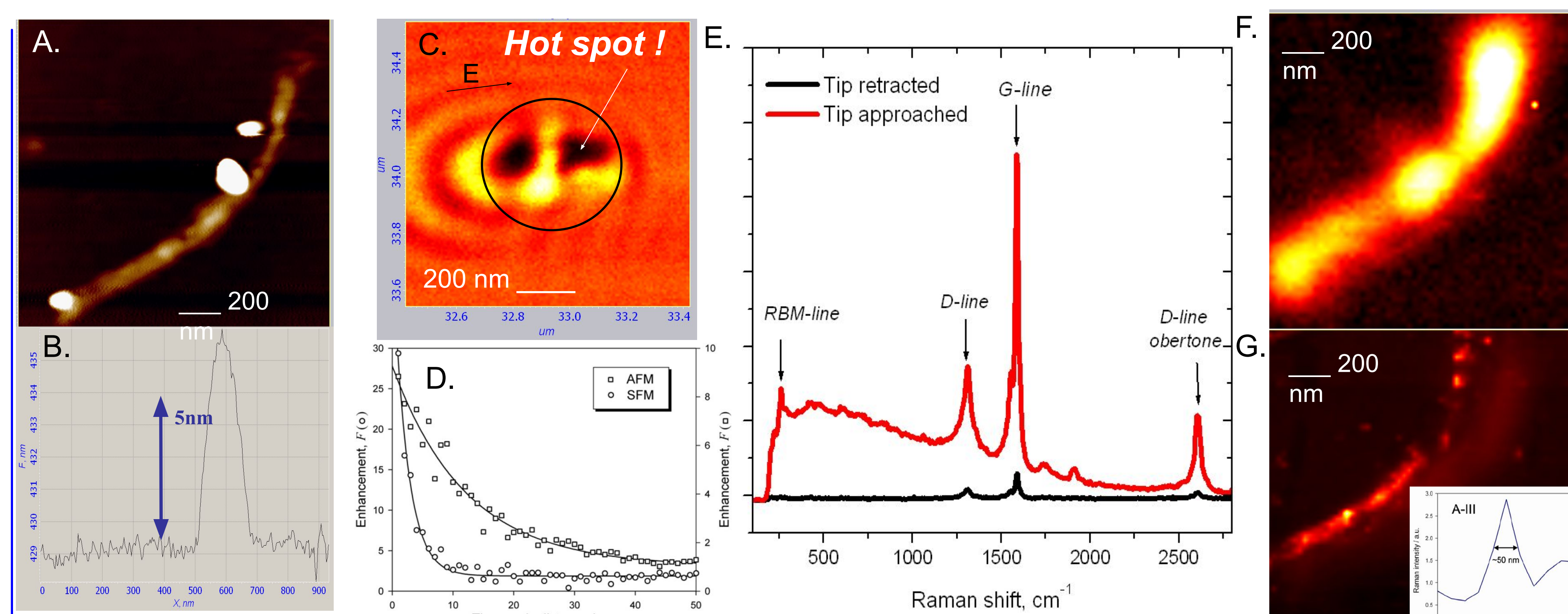
**Simultaneous AFM-Raman measurements of Graphene flakes.**

(A) White light image of multi-layer graphene sample obtained with high resolution 100x, 0.7 NA objective. 1-, 2-, 3-, and 4- layered flakes are observed. (B) High resolution AFM topography of the same sample with corresponding line profile. (C) Raman spectra of graphene flakes. 2D (G') Raman peak changes in shape width and position for an increasing number of layers reflecting a change in electron band structure. (D) Confocal Raman map (2D band center of mass position). 1-, 2-, 3-, and 4- layered flakes can be easily distinguished when using a color palette scale. (E), (F) Electrostatic force microscopy image of positively and negatively charged flakes. The flakes were charged by applying +/-3V with conductive cantilever to several points. Resulting charge is uniformly distributed across the flakes. (G)

## 3. Tip Enhanced Raman Scattering – Raman maps with subwavelength lateral resolution



(A) In Tip Enhanced Raman Scattering (TERS), metallized AFM probe is used to enhance light locally around the tip apex. Power density of the focused laser light can be increased by a few orders of magnitude in the vicinity (~10 nm) of the tip if the light frequency is in resonance with localized surface plasmon at the tip apex. Effectively, tip acts as a “nano-source” of light. If the sample is now scanned below the tip, lateral resolution of resulting Raman/fluorescence maps is defined by the localization volume of the surface plasmon field rather than by light wavelength. (B) NT-MDT provides commercial solution for all possible excitation/collection geometries for TERS experiments with all possible TERS probes (AFM, STM, Shear force). Different geometries / probes are advantageous depending on type of sample and tip used. Experiments can be done in air, in liquid, in controlled atmosphere.



**Tip Enhanced Raman Scattering (TERS) on single-walled carbon nanotube (CNT) bundle**

(A),(B) AFM topography and line profile of the CNT bundle studied. Real height of the bundle is 5 nm. Observed width of the bundle is convolution of tip size. Some catalysis nanoparticles are attached to the bundle. (C) Searching for Hot Spot. Tip is scanned across the laser spot and Rayleigh (elastically scattered) light is recorded. Two “hot” spots where Rayleigh scattering reflection is maximum correspond to maximum interaction of light with localized surface plasmon at the end of the tip (this takes place in regions with maximum Z-polarization of electromagnetic field). TERS tip is then precisely positioned into one of the hot spots. Precision and temporal stability of tip positioning must be very high: 10-20 nm. After that, sample is scanned to get TERS map (thanks to the Dual scan mode where both tip and sample can be scanned independently). (D) Intensity of Raman signal from CNT bundle as a function of tip-sample distance for two types of probes: gold coated AFM cantilever in tapping mode and etched Au wire with Shear Force (SFM) feedback. In Shear-force regime, Raman signal starts to increase when tip is only <10 nm away from the sample – proving real *near-field* Raman regime. In AFM mode, approach curve is less steep due to vertical oscillations of cantilever in tapping mode. (E) Corresponding Raman spectra with and without the TERS tip. About 30 times signal increase is observed. (F) Conventional micro-Raman map of the CNT bundle. Width of the bundle on the map is ~250 nm – resolution is diffraction limited (laser – 633 nm, objective 1.3 NA). (G) Raman map taken with TERS tip approached. Measured width of the bundle is now about 50 nm – the resolution of the TERS map is 4-5 times higher than diffraction limit. In this experiment, resolution is mostly determined by the size of the TERS tip.

