Optical Studies of Single Molecules and of Single Gold Nanoparticles

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Compared to electron or scanning probe microscopies, optical studies of single objects in far field is non-invasive, reaches beyond surfaces, and opens many time-resolved and frequency-resolved techniques. I shall give examples of informations these methods provide about single nano-objects and their surroundings [1].

i) We study single gold nanoparticles by photothermal and pump-probe microscopy. We detect their acoustic oscillations launched by a pump pulse [2]. These experiments can be done in an optical trap, where a single nanorod orients along the polarization of the trapping laser. We could thus clarify the origin of the damping of mechanical vibrations in gold nanoparticles.

ii) Photothermal microscopy opens the study of non-fluorescent absorbers, down to single-molecule sensitivity [3]. Combining photothermal contrast with photoluminescence, we can measure the luminescence quantum yield on a single-particle basis and gain insight into the complex relaxation phenomena leading to emission by metal particles. Moreover, the high signal-to-noise ratio of this contrast mechanism opens up uses of individual gold nanoparticles for local plasmonic and chemical probing. Binding and unbinding events of single protein molecules can be detected in this way [4].

iii) Gold nanorods generate strong field enhancements near their tips. By matching the rods' aspect ratio to a dye's fluorescence and excitation spectra, we observe enhancements in excess of thousand-fold for the fluorescence of single Crystal Violet molecules [5].

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Manipulation and assembly of functional organic molecules - the role of the surface

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The manipulation of single functional molecules on crystal surfaces is of great interest for a detailed understanding of physical and chemical processes at the single molecule level and consequently for their use in future molecular nanotechnology. Important aspects are on the one hand the influence of the molecular adsorption and configuration on the function and on the other hand the controlled linking of molecules to larger functional networks. In this presentation, the manipulation of single molecules and polymers with various molecular functions by scanning tunneling microscopy (STM) will be presented. As substrates, metal single crystal surfaces are used as well as ultrathin crystalline films. Particular emphasis will be given on the role of the surface for the molecular function and polymerization properties.

A prototype of a functional molecule is a molecular switch that can exist in various stable states with different optical/electronic properties. Single molecules can be switched on a surface by different stimuli and it turns out that the atomic-scale environment plays a fundamental role for the activity of the optical switching function, leading to surface-defined periodic switching. In order to create functional polymers that act as “molecular wires”, the controlled covalent assembly of molecules by “on-surface-synthesis” is used, allowing the bottom-up construction of stable molecular networks with pre-defined topology and shape. This is done on the one hand on various metal surfaces that allow a pre-defined orientation and on the other hand in the presence of ultrathin NaCl films on a surface, leading to very particular adsorption geometries.