Absorption, luminescence and scattering of single nano-objects

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Summary

The optical properties of nano-objects depend on their structure and composition. Therefore, it is essential to characterize the optical properties of nano-objects to explore their use in scientific or technological applications. In this thesis, we study the absorption, luminescence, and scattering of individual nano-objects including single molecules, organic dye nanoparticles and gold nanoparticles. We combine photothermal (absorption), luminescence, and scattering signals on a single-particle basis to gain fundamental insight into the radiative and nonradiative properties of the nano-objects.

In chapter 1, we present a brief overview of a variety of nano-objects, discussing their properties and giving some examples of their fundamental and technological applications. We also shortly introduce the optical methods to detect these nano-objects, discussing their advantages and disadvantages.

In chapter 2, we describe the technique of photothermal microscopy by which we can detect single nano-objects by their absorption at room temperature. The nano-objects produce heat upon their excitation with an intensity-modulated laser light within their absorption band and a time-dependent thermal lens is created around the nano-object. The corresponding refractive-index profile, a nanolens, is detected with a second laser that is tuned outside the absorption band of the nano-object. We utilize different ways (e.g. index matching, using a liquid with high photothermal strength, careful compensation of chromatic aberrations, etc.) to optimize the detection sensitivity of this photothermal microscopy technique. We use single gold nanospheres as a reference to estimate the absolute absorption cross sections. These gold nanoparticles provide good photostability and do not show saturation effects. Using this method, we first show that our detection limit lies at 3 nW dissipated power (in an integration time of 10 ms), which is of the order of the power dissipated by a single molecule at saturation. Secondly, we demon-

strate the detection of individual nonfluorescent molecules by their absorption at room temperature. Our study over 30 individual chromophores yields an average absorption cross-section of 4 $Å^2$ per molecule. This value is in satisfactory agreement with the isotropic value, 2.1 $Å^2$, deduced from the absorption spectrum of the dye in glycerol. The room-temperature detection of a single molecule by its absorption has been a challenge since the first observation of a single molecule by its fluorescence.

Combining photothermal contrast with measurements by fluorescence microscopy allows us to gain insight into the luminescence properties of nanoparticles, i.e., we are able to calculate the absolute quantum yield of single nano-objects. In chapter 3, we study the luminescence properties of spherically shaped organic dye nanoparticles which are prepared by reprecipitation of a triarylamine dye solution in acetone in vigorously stirred water. These nanoparticles exhibit a complex excitation-power-dependent luminescence quantum yield due to singlet-singlet or singlet-triplet annihilation, and their luminescence quantum yield can be as high as 10^{-2}. We also count the number of molecules in a single dye nanoparticle using luminescence and absorption signals. We find that there are $10^4 - 10^5$ molecules in a dye nanoparticle with a diameter of about 60 nm. The results of correlated optical and scanning probe measurements (AFM) are in good agreement with each other showing the potential use of correlated measurement for study and characterization of complex systems. Another interesting property of these dye nanoparticles is that they can form net-shaped and labyrinth-shaped patterns which are probably induced by dewetting of the dye nanoparticle suspension on the substrate during sample preparation. The patterns fromed from nanoparticles can find applications, for instance, in organic thin film transistor or solar cells.

We studied the one-photon luminescence properties of gold nanoparticles in chapter 4 (spheres) and 5 (rods). In contrast to organic dye nanoparticles, gold nanoparticles yield very stable optical signals providing good photoluminescence contrast. In chapter 4, we studied the effect of the particle volume on their luminescence quantum yield. We present simultaneous detection of luminescence and photothermal (absorption) signals of individual gold nanospheres with diameters ranging from 5 to 80 nm. We also correlate the size of the same individual nanospheres measured independently by AFM with their optical signals. Our results confirm that absorption and lumi-

nescence signals scale with the volume of the nanosphere. Their photoluminescence quantum yield is nearly independent of size and is about 3×10^{-7}. Because the gold nanospheres can be imaged by conventional fluorescence microscopy with good signal-to-noise ratios, they can be applied to studies that require stable optical signals.

In chapter 5, we investigate the effect of the aspect ratio of single gold nanorods on their luminescence quantum yield. We find that the quantum yield of single gold nanorods can be as high as $\sim 10^{-5}$. Compared to single gold nanospheres, we observe an increase of quantum yield by about an order of magnitude for particles with a plasmon resonance wavelenghts longer than 650 nm. In order to gain insight into the mechanism of luminescence from gold nanoparticles, we correlated scattering and luminescence spectra of individual nanorods with different plasmon resonances and we performed polarization sensitive measurements. We find that there are two components which contribute to the luminescence spectrum, one around 500 nm and one coinciding with the longitudinal plasmon band. Our study contributes to the understanding of luminescence from gold nanorods for their applications in biological and soft matter studies.

The study of chapter 6 concerns novel optical methods to study contact mechanics at interfaces of materials over a large area (several 10 μm^2). In detail, we exploit the sensitivity of the plasmon resonance of a gold nanoparticle to the nearby presence of a dielectric. We study the effect of the substrate-nanorod distance on the plasmon resonance of a gold nanorod. We built a setup that allows bringing two substrates closer to each other in steps of a few nanometers. For distances less than 400 nm, we observe a significant redshift of the plasmon resonance wavelength of the nanorod while decreasing the distance between the nanorod and the substrate; the observed changes are reversible. Although preliminary, these results point the way towards applying single gold nanorods as a tool to measure distances between dielectric interfaces on a nanometer scale with good control and high resolution.