EPJ Web of Conferences **190**, 02002 (2018) https://doi.org/10.1051/epjconf/201819002002
HBSM-2018

Imaging and force transduction in correlative scanning force and confocal fluorescence microscopy

Thomas Basché[*]

Institute of Physical Chemistry, Johannes Gutenberg-University, Mainz, Germany

Abstract. Correlative scanning force and confocal fluorescence microscopy has been used to study individual molecules, nanoparticles and nanoparticle oligomers. By applying a compressive force via the AFM cantilever, spectral blue and red shifts in the range of several meV/GPa have been observed for single dye molecules and semiconductor quantum dots. Moreover, individual Au nanoparticle dimers linked by a chlorophyll binding protein have been imaged in both modes and plasmonic fluorescence enhancement of the chlorophyll emission of up to a factor of 15 has been found.

Correlative microscopies are gaining increasing attention, since they allow for correlating structure or morphology of individual nano-sized objects from a potentially heterogeneous population with their electronic or photo-physical properties. An early example have been measurements of the emission spectra and polarization of single semiconductor nanocrystal quantum dots as well as their crystallographic structure by a combination of confocal fluorescence microscopy and transmission electron microscopy [1]. Recently, relying on the same approach it has been shown that the fraction of "on"-times of single CdSe/CdS nanocrystals decreased when stacking faults were present [2]. Besides transmission electron microscopy, single molecule spectroscopy has also been combined with scanning electron microcopy or scanning probe techniques [3].

We have used confocal fluorescence and scanning force (AFM) microscopy of single molecules and nanoparticles for two purposes: i) To correlate structural information with photo-physical properties, and ii) To apply compressive stress and track the effects of the impact on the electronic states by fluorescence spectroscopy.

In a first set of experiments we applied compressive forces via the AFM cantilever to single terrylenediimide molecules decorated with large side-groups and deposited on a mica surface. Reversible blue and red-shifts as well as irreversible shifts were observed and attributed to different conformations of the terrylene core induced by the compressive force [4]. Similar experiments were conducted with CdSe/CdS/ZnS nanocrystals and again blue and red shifts were registered under the directional force [5]. These experiments clearly have shown that a given particle either shifts to the red or blue under pressure (see Fig.1), resolving a controversial issue remaining from bulk studies of semiconductor quantum dots

[*] Corresponding author: thomas.basche@uni-mainz.de

in diamond anvil cells. The direction of the spectral shifts largely depends on the crystallographic axis of the quantum dot onto which the non-hydrostatic pressure is applied. However, the orientation of the approximately spherical core-shell particles typically is not known. This obstacle can be mediated by the use of nanocrystal platelets which can be deposited in a well-defined way and therefore expose a known crystallographic face.

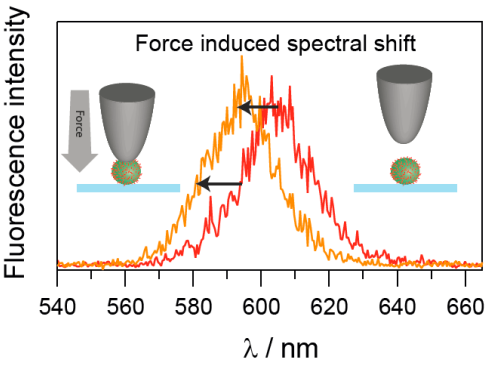

Fig. 1. Scheme how to apply force to a single nanoparticle with the tip of an AFM-cantilever. (after Ref. 5) For the case shown the emission spectrum of a single CdSe/CdS/ZnS-nanocrystal was shifted to the blue with increasing force. After force was released, the spectrum shifted back to its original position.

Correlative atomic force and confocal microscopy has also been employed to study the properties of Au nanoparticle oligomers, linked by the water-soluble chlorophyll binding protein (WSCP). For individual dimers - as identified by AFM - fluorescence enhancements of up to a factor of 15 with a clear dependence on the excitation polarization were observed and attributed to mainly plasmonic enhancement of the *Chl* excitation rate. Promising features of this protein-directed assembly of a plasmonic nanoantenna are the simple transfer of the construct into different environments and the structure-driven positioning of the pigments in the plasmonic hotspot.

References

1. F. Koberling, U. Kolb, G. Philipp, I. Potapova, Th. Basché, A. Mews, J. Phys. Chem. B **107**, 7463 (2003)
2. N.J. Orfield, J.R. McBride, J.D. Keene, L.M. Davis, S.J. Rosenthal, ACS Nano **9**, 831 (2015)
3. M. Vacha, D. Sharma, S. Hirata, J. Photochem. Photobiol. C **34**, 121 (2018)
4. S. Stöttinger, G. Hinze, G. Diezemann, I. Oesterling, K. Müllen, Th. Basché, Nature Nanotechnology **9**, 182 (2014)
5. T. Fischer, S. Stöttinger, G. Hinze, A. Bottin, N. Hu, Th. Basché, Nano Lett. **17**, 1559 (2017)