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Structured doping of upconversion nanosystems for biological applications

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Summary

Rare earth ions doped upconversion nanoparticles (UCNPs) have attracted much attention in recent years because of their unique spectroscopic properties such as low photobleaching rates, multicolor labeling, and deep penetration of (near-IR) excitation light into human tissues. Different from most upconversion processes for which high peak powers are usually required, these materials allow for the conversion of CW NIR light into UV/Vis light at relatively low excitation power. As a result, there is a large potential in various fields, especially in biology/biomedicine where there is an increasing need for more sensitivity in applications such as detection, imaging, and therapy. Despite many efforts the upconversion efficiency is so far often the major bottleneck in (bio-)medical applications, especially when *in vivo* tests are concerned for which excitation power density is restricted. This thesis describes spectroscopic research of rare earth ions (co-)doped NaYF₄ UCNPs with the aim of exploiting possible routes to improve the upconversion efficiency.

Chapter 1 provides an overview of the recent advances in the research on the fundamental properties of lanthanide ions doped UCNPs, including the techniques used to prepare nanoparticles, the surface chemistry of nanoparticles, and the history of UCNPs with respect to their use in different (bio-)medical fields. **Chapter 2** describes the research that has been done on the characterization of the upconversion photoluminescence properties of NaYF₄:Yb³⁺,Er³⁺ and NaYF₄:Yb³⁺,Er³⁺@NaYF₄ core/shell structures. The core/shell structure has been regarded as an efficient approach to enhance efficiently the emission intensity and increase the decay lifetime. However, in **Chapter 2** we show that the upconversion emission intensity of the core can be stronger than that of core/shell nanoparticles when the excitation power density is high enough. We show that the explanation for this behavior lies in a photon-induced “annealing” process. From a study of the luminescence dynamics it becomes clear that the green emission from the core is more sensitive to quenching.

Nanoscale materials differ in two important aspects from bulk materials. Firstly, quantum confinement starts to play a critical role. This has become evident, for example, in quantum dots. However, for rare earth ions the De Broglie wavelength is on the order of 0.1 nm and thus the effects of quantum confinement are less important. Secondly, the

surface to volume ratio is dramatically increased on the nanoscale. Surface effects thus are the main factor determining the spectroscopic properties of discrete luminescence centers in nanoscale materials. For biological/biomedical applications, the surface of the nanoparticles has to be modified which inevitably affects the photophysical properties of the nanopatform. Such effects are studied in **Chapter 3** where we focus on the influence of the surface-related organic vibrational modes on the spectroscopic properties of rare earth ions doped NaYF₄ nanoparticles. In these experiments we investigate spectroscopically the role of the surface quenching centers, the surface related luminescent centers, the surface related organic high-frequency vibrational modes, as well as the role of shell properties, excitation power density, and ligand exchange. Our results demonstrate that the surface related high frequency vibrational modes play an important role in the upconversion process as well as in possible laser annealing processes. We show that the surface-related high-frequency vibrational modes can be critical to the spectral properties of the nanosystems once the surface is not well separated from the discrete luminescent centers.

Aiming at improving the upconversion luminescence of UCNPs, we have discovered a novel mechanism to increase the doping level of the activators. **Chapter 4** presents a strategy of spatially separating the doping area by a sandwich-like core/shell architecture. This structure serves two purposes. On the one hand, the shell, doped only with sensitizing Yb³⁺ ions, protects the luminescent ions from the influence of the surroundings and transfers the absorbed NIR photon energy to the activators on both sides of this shell. On the other hand and more importantly, it also minimizes the energy transfer between the activators inside and outside, which leads to a significant improvement of the concentration quenching threshold. It is demonstrated that such a structured doping strategy doubles the activator doping level as far as Er³⁺ is concerned. The results of these studies open new pathways to improve rationally the upconversion emission, facilitate the realization of biological applications of lanthanide ions doped nano-platforms, and enable new opportunities in energy harvesting and energy conversion.

Photodynamic therapy (PDT) has come into the clinic in the 1980s as a medical technology for treating premalignant pathology and cancer. It is based on the effective localization of photosensitizers (PSs) into tumor tissues and the selective destruction of these tissues after irradiation with light. In **Chapter 5** application of upconversion nanoconjugates in PDT is explored. A model, which may be used as a dual-functional probe for live-cell target imaging and PDT, is established. We have designed and constructed covalently bound UCNPs-PSs that emit two main bands at 540 and 650 nm

under excitation of a CW NIR light source. The 540 nm band is employed to excite PSs for PDT treatment, while the 650 nm emission band is simultaneously used for cell imaging.

Application of a core/shell structure in UCNPs-PSs conjugates for PDT is not trivial because the efficiency of the platform, constructed from UCNPs-PSs conjugates and targeting vectors, does not only depend on the upconversion intensity. The shell layer can significantly improve the upconversion luminescence by protecting the emitters from nonradiative decay caused by surface defects and high-energy vibrational modes outside the UCNPs. On the other hand, the shell also increases the distance between the donor and acceptor and thus impedes excitation of the PS via a FRET process. In **Chapter 6** NaYF₄:Yb³⁺,Er³⁺@NaYF₄ core/shell UCNPs are used to form UCNPs-PSs conjugates. Our results indicate that as far as the singlet oxygen generation is concerned an optimal shell thickness exists that can be considered as a trade-off between the opposing effects the shell thickness has on luminescence enhancement and FRET enhancement.