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Microscopic Investigation of the Emission Efficiency of Nanostructures

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Summary

Fluorescent nanoparticles, such as molecules, proteins and semiconductor quantum dots (QDs) enable the control over light via the absorption and emission of photons. The strong dependence of the emission properties on the atomic composition, shape, structure and size of the particles makes these materials in general very interesting for a wide range of lighting applications. E.g for displays, light-emitting diodes but also for biological applications, such as bio-imaging, (bio-)sensing and super resolution microscopy. The most crucial property is the emission efficiency, i.e. the efficiency with which energy can be converted into emitted photons. In this thesis the emission efficiency of nanoparticles is studied in detail, starting with the efficiency of an ensemble of emitters, to the efficiency of individual particles. This is demonstrated on silicon quantum dots (Si-QDs). Si-QDs have in general many advantageous properties, such as bio-compatibility, resource abundance, surface functionalization options etc, but are not considered for applications due to their limited emission efficiency.

The ensemble emission efficiency is best quantified by the quantum yield (QY), given by the ratio of the number of emitted and absorbed photons. The correct evaluation of the QY is crucial for the development of emitters and therefore, in Chapter 2, the validity of the method that is commonly used to measure the QY is critically examined. Both experimentally and theoretically, it is demonstrated that the QY methodology suffers from an artifact, resulting in the underestimation of the QY when the absorption of the sample is low. By detailed theoretical simulations the artifact is identified and a remedy is proposed. The corrected methodology is then applied to determine the QY of different types of Si-QDs.

In Chapter 3 the internal quantum efficiency (IQE) is investigated, which gives the emission efficiency of the brightest emitters in an ensemble. The IQE therefore gives the upper limit of the material's emission efficiency in case non-radiative recombination pathways cannot further be suppressed. The IQE is extracted from the photoluminescence (PL) recombination rate, through control of the local density of optical states (LDOS). For this, a Drexhage-type method that employs a spherical mirror is employed to study, for the first time, the radiative rate and IQE of a class of organically passivated Si-QDs (C:Si-QDs). This class of C:Si-QDs shows emission in the visible spectral range below 600 nm, which is inaccessible for most types of Si-QDs. It is shown that despite the low QY that is typically found for Si-QDs emitting in the visible spectral range, C:Si-QDs

have high direct bandgap-like radiative rates, which enable a high IQE of ∼50%. This shows that in principle Si-QDs can be a competitive candidate for a phosphor in lighting applications and for medical imaging. Moreover, it is demonstrated that these C:Si-QDs have a static emission transition dipole moment, characteristic for a localized state involved in the radiative recombination.

To resolve the origin of the discrepancy between ensemble QY and IQE, in Chapter 4 the emission efficiency of individual QDs is studied. On this level, the emission efficiency is determined by PL blinking, which shows as the periodic switching between an emissive and a non-emissive state. Using single-QD microscopy the PL blinking of C:Si-QDs is studied. C:Si-QDs appear mostly OFF and are characterized by short bright ON periods with a duty cycle below 4%. These results demonstrate that blinking poses a critical limitation to the ensemble QY of C:Si-QDs. Most likely, blinking can be suppressed through improved surface passivisation strategies, since the QD surface assumes a major role in the blinking process. Alternatively the short, but high-intensity ON events could make C:Si-QDs interesting for super-resolution microscopy techniques.

In addition to Si-QDs, an alternative group-IV nanomaterial, carbon dots (CDs), is explored in Chapter 5. Using single-dot spectroscopy, the microscopic organization of different emission mechanisms within these complex materials is investigated. Under different excitation wavelengths the single CDs show different spectra with distinct peaks that vary in peak position, spectral width and shape, indicating the presence of distinct emission sites in the ensemble. Excitation-dependent single-CD measurements provide evidence that also individual CDs can exhibit multiple of such emission spectra, suggesting that the emission sites can be present already within the same single CD. These results indicate that a facile synthesis route can lead to the integration of multiple emission sites within this versatile material.

The insights obtained through the different emission efficiency measurements are combined for C:Si-QDs in Chapter 6. Blinking is identified as the major limitation of the emission efficiency. This means, however, that without any optimization of the blinking dynamics, C:Si-QDs could be promising for super-resolution microscopy, in which low duty cycles are required.