Microscopic investigation of the emission efficiency of nanostructures
van Dam, B.

Citation for published version (APA):
Chapter 1

Introduction

1.1 Emission efficiency of nanomaterials

Fluorescent nanomaterials, such as proteins and molecules, but also semiconductor quantum dots (QDs) enable the manipulation of the wavelength of light through the absorption and re-emission of photons. The emission color is determined by the electronic energy levels of the material, which result in general from the material’s atomic composition and structure (symmetry). However, in contrast to dyes and rare earth ions, the emission of QDs also strongly depends on the size and shape of the particles. This results from the confinement of the electron and hole wavefunctions within the nanometer-sized particle, giving rise to an increase in the bandgap energy compared to the bulk value. This broadens the range of emission colors that can be achieved with a single material. For materials such as silicon (Si) and germanium (Ge) this range even spans from the ultra-violet (UV) to near-infrared (IR) spectral region [1, 2]. The emission properties arising from the QD core can be further modified via surface engineering. For II-VI class semiconductor QDs significant progress has been made by adding a shell of a different compound around the core, which allows further control over the emission properties and, moreover, can significantly improve the surface quality of the QD, through passivation of surface defects [3]. For Si based QDs, the type of surface passivation was shown not only to influence the emission wavelength [2, 4], but also the emission rate [2, 5–7], enabling to partially overcome the indirect bandgap nature of silicon.

The versatility of nanomaterials makes them of great interest for many lighting applications: As phosphors for light emitting diodes (LEDs), as the active material in solid state lasers, as a solar shaper for photovoltaics and for bio-medical applications, such as bio-imaging and drug delivery. For such applications, the most crucial characteristic is the emission efficiency of the emitter, i.e. the efficiency with which excitation energy can be converted into emission photons. In this thesis, we discuss important factors that determine the emission efficiency of fluorescent nanomaterials. This we do by quantifying the emission efficiency on different levels, starting from the efficiency on a macroscopic
scale, i.e. from a collection of nanoparticles, to the emission efficiency on a microscopic scale, from individual nanoparticles. While the methods described here are generally applicable to any type of emitter, here we use them to investigate carbon and silicon based nanoparticles. These materials exhibit in general advantageous properties, such as bio-compatibility, resource abundance, covalent functionalization options etc, but for which application is blocked by their limited emission efficiency. For Si-QDs this especially concerns emission in the visible spectral range as shown in Figure 1.1, where the ensemble emission efficiency is typically below 20%.

Figure 1.1: Emission efficiency of Si-QDs. Overview of the quantum yield (QY) (filled symbols) and internal quantum efficiency (IQE) (open symbols) of values found in literature for different types of Si-QDs (black symbols). IQEs from Miura et al. [8] and Walters et al. [9] and QYs from Dohnalova et al. [2], Jurbergs et al. [10], Kusova et al. [11], Mastronardi et al. [12], Sangghaleh et al. [13] and Tu et al. [14]. The shaded area indicates the emission wavelength range for which high QYs and IQE have been reported.

1.2 Microscopic origin of the emission efficiency

1.2.1 Quantum yield

The efficiency with which an emitter converts excitation photons into emission photons, can be quantified by the photoluminescence (PL) quantum yield (QY), given by the ratio of the number of emitted ($N_{em}$) and absorbed photons ($N_{abs}$):

$$QY = \frac{N_{em}}{N_{abs}}.$$ 

The QY determines the fraction of light that is converted into photons that can be harvested and hence is for practical purposes an important parameter. It is commonly used to characterize ensembles of emitters, in which case the QY gives the average efficiency of the individual emitters and impurities that form the ensemble. This depends on the their internal quantum efficiency (IQE) and duty cycle ($\delta$) and on the out-coupling
1.2. Microscopic origin of the emission efficiency

Efficiency ($\eta$) of emission into the far-field [13]:

$$QY = \frac{1}{N} \sum_{i=1}^{N} QY_i = F_{br} \left[ \frac{1}{N_{br}} \sum_{i=1}^{N_{br}} IQE_i \delta_i \eta_{i}^{det} \right],$$

where $N_{br}$ and $F_{br}$ are the number of bright emitters and the fraction of bright emitters in the sample and $N$ the total number of emitters. The QY considers all losses within the ensemble, including those arising from non-emissive but absorbing (‘dark’) emitters with an IQE close to zero, and due to inefficient coupling of the emission towards the detector. Therefore the QY gives the lowest estimate of the emission efficiency, which could still be considerably improved by e.g. filtering the sample from impurities or via improved surface passivation.

1.2.2 Internal emission efficiency

The internal quantum efficiency (IQE) is determined by the competition between radiative and non-radiative recombination pathways available to the photo-excited electron-hole pair. The probability of both processes is given by their recombination rates $\gamma_r$ and $\gamma_{nr}$, respectively, from which the IQE is defined:

$$IQE = \frac{\gamma_r}{\gamma_r + \gamma_{nr}},$$

i.e. the ratio between the radiative recombination rate $\gamma_r$ and the total decay PL decay rate $\gamma_{PL} = \gamma_r + \gamma_{nr}$. Unlike the QY, which quantifies the emission efficiency via comparison of the number of emitted and absorbed photons by the sample, the IQE is determined solely from the PL of the studied material. This is typically done in time-resolved PL measurements, in which the rate ($\gamma_{PL}$) is probed at which carriers relax from the excited state back to the ground state. Since only bright emitters contribute to the PL signal, the IQE gives the average emission quantum efficiency of the bright subset of the ensemble of emitters only. As such, it provides insight into the most efficient emitters and gives the upper bound for the emission efficiency, provided that the non-radiative rate cannot be further improved (e.g. by removing trap states through surface passivation). Ultimately, in the absence of non-radiative channels, the IQE reaches 100%.

1.2.3 Duty cycle

For almost all quantum emitters it is generally observed that they do not emit continuously [15], but switch between ON periods during which the emitter is optically active, and dark OFF periods where the brightness is significantly reduced and close to zero. This so called PL intermittency or ‘blinking’ is observed over a broad range of time scales ranging from microseconds to minutes and results from different states of the emitter, which are characterized by a different IQE. The OFF-state occurs either due to change in the radiative probability, e.g. due to inter-system crossing of the emitter from a singlet to a triplet state, from which radiative recombination is inhibited, or
from the activation of a non-radiative channel. For QDs, blinking is most commonly interpreted in terms of charging of the QD [16, 17], e.g. as a result of the trapping of the photo-excited electron or hole on the QD surface. This leaves the core charged so that subsequent excitation will be efficiently quenched by Auger recombination. In most cases, the quenched OFF state of the emitter is optically inactive and considered dark (IQE_{OFF} \sim 0). In that case, the efficiency of the blinking process can be quantified by its duty cycle:

$$\delta = \frac{T_{ON}}{T_{ON} + T_{OFF}},$$

i.e. the fraction of time during which the QD is emissive. However, even in the OFF state radiative recombination can be sufficiently efficient to compete with the non-radiative recombination, resulting in a ‘gray’ state [18, 19] for which the IQE > 0.

### 1.2.4 Dark QDs

In addition to temporary switched off emitters, the ensemble might also contain permanently dark species [20, 21] or impurities. These species absorb excitation light but do not emit, as energy is dissipated via non-radiative channels. In contrast to the OFF state resulting from blinking, the non-emissive state is permanent and dark QDs are generally thought to be responsible for the low QY in poly-disperse ensembles of QDs [8, 20, 21]. For QDs, these dark species are expected to arise from poor surface passivation, which results in dangling bonds at the surface of the nanoparticles. The missing bonds break the crystal symmetry and contribute energy levels within the bandgap of the material, which constitute efficient non-radiative channels. Already a single dangling bond results in the full quenching of the emission of Si-QDs in an oxide matrix [22], demonstrating the importance of surface passivation.

For Si-QDs, the highest surface coverage can be obtained with hydrogen, which, however, is not stable in ambient conditions and makes the surface prone to oxidation. Alternatives are passivation by SiO_2, potentially followed by a hydrogen post-treatment to further decrease the amount of dangling bonds [23]. Passivation using organic ligands is also explored, although with the decreasing QD-size it becomes increasingly difficult to achieve full surface coverage due to steric hindrance.

### 1.2.5 Out-coupling efficiency

The QY concerns the efficiency with which excitation can be converted into harvested photons, which for most applications concerns photons ending up in the far-field. In addition to the excitation that is lost via non-radiative channels, however, not all radiative recombination transitions result in photons that couple to the far field: Photons can be trapped in the embedding medium via internal reflection, or can couple to surface plasmon polaritons (SPPs) or lossy surface waves in nearby metal interfaces [24, 25]. Moreover, the photonic environment also affects the directionality of the emission, which can be strongly anisotropic for emitters in an anisotropic environment. As a result, the observed brightness (and QY) is reduced. This was demonstrated for Si-QDs above a
Benign luminescent nanoparticles

1.3 Silicon quantum dots

Silicon has become the cornerstone of CMOS technologies, implemented in microelectronics, photovoltaics and photodetector technologies. However, as an active emitter in lighting or photonic applications, silicon is hindered by its indirect bandgap. The indirect bandgap is characterized by an inefficient band-edge absorption and low radiative rates, which result in impractically low photon fluxes and emission efficiencies in the presence of non-radiative channels. The limitations of the indirect bandgap can be partly overcome with silicon QDs (Si-QDs) via quantum confinement [1, 5, 27]. Si-QDs show room temperature size-tunable luminescence and have many advantages when compared to typically used phosphors, such as direct bandgap QDs, organic dyes or rare earth ions: Si-QDs are photo-chemically robust and stable due to covalent bonding of ligands [28, 29], they offer spectrally broad PL, tunable from the infrared (IR) to the ultraviolet (UV) [1, 5, 30], are non-toxic (bio-compatible and bio-degradable [31, 32]) and can be (bio-)functionalized by a large diversity of covalently bonded ligands [33, 34].

While the emission efficiency of Si-QDs remains comparatively low with respect to direct band gap materials and dyes, it has been significantly improved since their discovery [27]. E.g. for Si-QDs emitting in the near-IR spectral region, QYs exceeding 60% [10, 35, 36] have been reported, which could see even further improvement as the IQE has been reported to reach unity [8, 13, 36]. This shows that bright subsets within the ensemble of QDs exist for which non-radiative channels are already completely suppressed and suggests a promising future for the application of Si-QDs.

For emission in the visible spectral region the situation is very different. The QY of intrinsic PL is only sparsely reported on and have not exceeded 20% [5]. This is typically argued to be the consequence of the non-radiative contribution due to the increased number of surface defects for smaller Si-QDs [5, 12, 37, 38]. Furthermore, tunability of the PL by the size of the Si-QD through the visible spectral range seems inaccessible for Si-QDs in the presence of oxygen defect states [4], rendering the most commonly studied oxide passivated Si-QDs (O:Si-QDs) unsuitable for this spectral range. Potentially, these limitations can be overcome with a class of Si-QDs capped with organic molecules (C:Si-QDs), which extend emission into the visible spectral region [1, 2, 5, 11, 39, 40]. The emission rates in C:Si-QDs have been shown to approach those of direct bandgap materials [2, 6, 7, 11, 39, 40], suggesting significant enhancement of the radiative recombination rates by 2-3 orders of magnitude compared to hydrogen or oxide passivated Si-QDs [2, 5–7, 11]. Unfortunately, despite the greatly enhanced radiative rates in C:Si-QDs, the QY remains comparatively low in the visible range (<20%) [5, 11, 39], with the most probable cause being the low degree of surface passivation by organic
1.3.2 Carbon dots

Carbon dots (CDs) are a promising class of carbon-based fluorescent nanoparticles that consist of a mixture of sp$^2$ and sp$^3$ hybridized carbon atoms [41]. Since their discovery in 2004 [42], CDs have drawn much attention due to their facile synthesis [43], bio-compatibility [44–47] and the large natural abundance of carbon. Even more interestingly, some synthetic routes yield CDs with excitation-dependent PL that spans the entire visible spectral region. This broad PL allows for flexible ‘tuning’ of the light emission from blue to red via changes in excitation wavelength [48–51], offering new opportunities for emission color engineering with a single material. Owing to the great application potential, many studies have been devoted to unraveling the mechanism behind the PL of CDs, providing evidence for emission controlled by the CD core size [49], emission from functional groups on the CD surface [52] and a combination of both [50, 53, 54]. The emission tunability has been most prominently ascribed to selective excitation of subsets of CDs within the CD ensemble [55–57]. Indeed, multiple studies have shown that it is possible to tune the emission by using different types of CDs that are themselves excitation-independent [58–60]. On the other hand, Pan et al. [51] and Fu et al. [61] have suggested that different emission sites within individual CDs are responsible for the excitation-dependent emission. Establishing a generic model for the excitation-dependent PL of CDs has proven to be challenging [62], due to the great variety of chemical and structural compositions resulting from the different synthetic routes [63] and even observed within one and the same CD ensemble. Until now, the majority of studies is focused on ensemble spectroscopy techniques that provide only limited insight into the microscopic distribution of different emission mechanisms within CD ensembles and within a single CD. Spectroscopic investigations of the single CDs provide significant insight, but these are scarce [64, 65], while the improved understanding of the origin of the PL is a prerequisite for the understanding and optimization of the emission efficiency. Hence, there is an active debate regarding the microscopic origin of the PL, motivated by the possibility of excitation-dependent single CD emission.

1.4 Synergy of this thesis

In this thesis, different factors that critically affect and determine the emission efficiency of fluorescent nanomaterials are investigated. This is demonstrated in great detail in Part I on C:Si-QDs, for which the limited emission efficiency is the major limitation of this otherwise promising material. This is divided into three chapters, starting with the ensemble emission efficiency in Chapter 2, which is quantified by the QY. Here, the reliability of the methodology most commonly used to measure the QY is assessed and shown to yield underestimated values for low-absorbing materials. By comparison with theoretical simulations, a corrected QY method is proposed and applied to evaluate the QY of different types of C:Si-QDs. In Chapter 3, the emission efficiency limit of Si-QDs
1.4. Synergy of this thesis

emitting in the visible range is investigated, by measurement of the IQE through a Drexhage-type setup. This gives the emission efficiency of the emissive subset of QDs and therefore the maximum QY that could potentially be achieved with this material. Finally, in Chapter 4 the emission efficiency of individual C:Si-QDs is studied, by employing single-dot microscopy. In addition to Si-QDs, an alternative group-IV nanomaterial is explored in Chapter 5: carbon based nanoparticles. Using single-dot spectroscopy, the microscopic organization of different emission mechanisms within these complex materials is investigated. This shows that CDs have versatile PL properties, as additional emissive channels can be introduced via nitrogen and oxygen containing surface groups. The thesis is concluded in Chapter 6 were the insights obtained through the emission efficiency measurements are combined. The factors that limit the efficient emission of C:Si-QDs are identified and the potential of C:Si-QDs and CDs for lighting applications is discussed.