Microscopic investigation of the emission efficiency of nanostructures

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List of publications

- (Chapter 2) B. van Dam, B. Bruhn, I. Kondapaneni, Y. Mudde, A. Wilkie, J. Krivanek, J. Valenta, P. Schall, K. Dohnalova. Critical artifact present in standard quantum yield methodology. - **Under review**
- (Chapter 2) B. van Dam, B. Bruhn, K. Dohnalova. Limits of emission quantum yield determination. Preprint at https://arxiv.org/abs/1711.06200 - **Under review**
- (Chapter 3) B. van Dam, C.I. Osorio, M.A. Hink, R. Muller, A.F. Koenderink, K. Dohnalova. High internal emission efficiency of silicon nanoparticles emitting in the visible range. ACS Photonics, 2018, doi:10.1021/acsphotonics.7b01624
- (Chapter 3 and 6) B. van Dam, C.-C. Huang, M. Demmenie, K. Dohnalova. Linearly polarized emission from organically passivated Si-QDs (working title) - **In preparation**
- (Chapter 4) B. van Dam, B. Bruhn, D. Cöl, K. Dohnalova. PL Blinking of organically passivated Si-QDs (working title) - **In preparation**
- (Chapter 5) B. van Dam, H. Nie, B. Ju, E. Marino, J. M. J. Paulusse, P. Schall, M. Li, and K. Dohnalova. *Excitation-dependent photoluminescence from single-carbon dots*, Small, 2017, 13(48), 1702098
- A. Sciortino, E. Marino, B. van Dam, P. Schall, M. Cannas, and F. Messina. *Solvatochromism unravels the emission mechanism of carbon nanodots.* The Journal of Physical Chemistry Letters, 2017, 7(17), 3419-3423

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.

Samenvatting

Door het absorberen en uitzenden van licht kunnen nanodeeltjes, zoals moleculen, eiwitten en halfgeleider *quantum dots* (QDs) gebruikt worden om licht te manipuleren. Het uitgezonden licht hangt sterk af van de atomische samenstelling, vorm, structuur en grootte van de nanodeeltjes, interessant voor een breed scala aan toepassingen. Bijvoorbeeld voor het gebruik in beeldschermen en LEDs, maar ook voor biologische toepassingen zoals voor *bio-imaging*, als (bio-)sensoren en voor superresolutie microscopie. Voor al deze doeleinden is de emissie-efficiëntie, het rendement waarmee geabsorbeerde energie kan worden omgezet in licht, een cruciale eigenschap. In dit proefschrift wordt de emissie-efficiëntie in detail bestudeerd, beginnende met de emissie-efficiëntie van een verzameling van lichtgevende deeltjes, naar de emissie-efficiëntie van individuele deeltjes. Dit wordt hier onderzocht aan de hand van silicium quantum dots (Si-QDs). Si-QDs hebben over het algemeen veelbelovende eigenschappen - silicium is niet giftig, is veelvoorkomend op aarde en er zijn vele mogelijkheden om de oppervlakte van de Si-QDs te functionaliseren - maar worden niet overwogen voor toepassingen door hun lage emissie-efficiëntie.

De emissie-efficiëntie van een verzameling van deeltjes kan het best gekwantificeerd worden aan de hand van de *quantum yield* (QY), gedefinieerd als de verhouding tussen het aantal uitgezonden en geabsorbeerde fotonen. Het juist bepalen van de QY is cruciaal voor de ontwikkeling van nanodeeltjes en daarom wordt in hoofdstuk 2 de betrouwbaarheid van een methode die vaak gebruikt wordt voor het bepalen van de QY, getest. Zowel experimenteel als theoretisch wordt er aangetoond dat de methode gevoelig is voor een artefact, die als resultaat heeft dat de QY onderschat wordt als de absorptie van het bestudeerde materiaal laag is. Het artefact wordt met behulp van gedetailleerde theoretische simulaties geïdentificeerd en er wordt een oplossing voorgesteld. Vervolgens wordt deze aangepaste methode gebruikt om de QY van verschillende soorten Si-QDs te bepalen.

In hoofdstuk 3 wordt de *internal quantum efficiency* (IQE) bestudeerd, die de emissie-efficiëntie van de meest heldere deeltjes in de verzameling geeft. De IQE geeft daarmee de hoogst haalbare emissie-efficiëntie van het materiaal, in het geval niet-radiatieve vervalmechanismen niet verder onderdrukt kunnen worden. De IQE kan bepaald worden uit de vervalsnelheid van de fotoluminescentie, door controle over de *local density of optical states* (LDOS) uit te oefenen. Hiervoor wordt een Drexhage-methode toegepast, die gebruik maakt van een ronde spiegel, om voor het eerst de radiative vervalsnelheid

en de IQE van een type Si-QDs bedekt met organische moleculen (C:Si-QDs) te bepalen. Deze C:Si-QDs zenden licht uit in het zichtbare deel van het spectrum, met golflengtes onder de 600 nm, een gebied dat niet toegankelijk is voor de meeste soorten Si-QDs. Er wordt aangetoond dat ondanks de lage QY die meestal wordt gevonden voor Si-QDs die licht uitzenden in het zichtbare gebied, C:Si-QDs een hoge radiatieve vervalsnelheid hebben, die leidt tot een hoge IQE van ongeveer 50%. Dit toont aan dat Si-QDs in principe een goede kandidaat zijn als lichtgevend materiaal voor verlichtingstoepassingen en voor *bio-imaging*. Daarbij wordt er aangetoond dat C:Si-QDs een statisch emissie overgangsmoment hebben, wat duidt op een gelokaliseerde toestand die betrokken is bij het radiatieve verval.
Om de oorzaak van het verschil tussen de QY en IQE te herleiden wordt in hoofdstuk 4 de emissie-efficiëntie van individuele QDs onderzocht. Op deze schaal wordt de emissie-efficiëntie bepaald door fotoluminiscentie *blinking* (knipperen), wat zich uit als het periodiek schakelen tussen een toestand waarin het deeltje licht geeft en een toestand waarin het deeltje donker is. Met behulp van *single-QD* microscopie worden de *blinking* eigenschappen van C:Si-QDs onderzocht. De C:Si-QDs staan meestal uit en worden gekenmerkt door enkele korte heldere periodes met een aan-uit verhouding van minder dan 4%. Deze resultaten tonen aan dat het proces dat *blinking* veroorzaakt een belangrijke beperking is voor de QY van een verzameling van C:Si-QDs. Waarschijnlijk kan *blinking* onderdrukt worden door de oppervlakte van de QDs beter te passiveren, omdat de oppervlakte van de QD een belangrijke rol speelt in het *blinking*-proces. Daarentegen zouden de korte maar heldere lichtgevende periodes de C:Si-QDs geschikt kunnen maken voor superresolutie microscopietechnieken.
Naast Si-QDs wordt ook een alternatief groep-IV nanomateriaal onderzocht, koolstof deeltjes (CDs), in hoofdstuk 5. Met behulp van *single-dot* spectroscopie wordt de microscopische verdeling van de verschillende emissiemechanismen in deze complexe materialen bestudeerd. Onder verschillende excitatiegolflengtes vertonen de individuele CDs, emissiespectra met verschillende piekpositie, breedte en vorm, wat er op wijst dat er verschillende emissiemechanismen in het materiaal voorkomen. Excitatieafhankelijke metingen aan enkele CDs leveren bewijs dat individuele CDs deze verschillende emissie spectra al tonen, wat suggereert dat deze emissiemechanismen ook binnen één enkele CD aanwezig kunnen zijn. Deze resultaten doen vermoeden dat een eenvoudige synthese kan leiden tot het verengingen van meerdere afzonderlijke emissiemechanismen in dit veelzijdige materiaal.
De inzichten verkregen doormiddel van de verschillende emissie-efficiëntie metingen worden in hoofdstuk 6 voor de C:Si-QDs samengevoegd. *Blinking* wordt geindentificeerd als de voornaamste beperking van de emissie-efficiëntie. Dit betekent echter dat zonder enige optimalisatie, C:Si-QDs een geschikte kandidaat zijn voor superresolutie microscopie, waar korte maar heldere lichtgevende periodes juist wenselijk zijn.

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