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Gold Nanorod Photoluminescence

Applications to Imaging and Temperature Sensing

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Voor mijn ouders en mijn zus

Preface

Behind every thesis lies a story that involves much more people than the mere author whose name is on the cover. This book is the conclusion of four years of work in the MoNOS group at the physics institute in Leiden, where I have focused on the study of single gold nanorod luminescence and its possible applications.

The project was framed within a larger collaboration with three more groups from biophysics, biology and chemistry. The aim of the project was utilizing single gold nanorods as labels in the nucleus of cells, focusing into the study of the glucocorticoid receptor. My part in the collaboration was the understanding of the mechanisms that give rise to the luminescence of single gold nanorods, crucial for the imaging and tracking in living cells. Even if my work was not biophysical, I always kept an eye into the biological applications of my research.

A Friday afternoon idea, triggered by postdoc Saumyakhanti Khatua evolved into what now is chapter 2 of this booklet. He asked me if it was possible to monitor the etching process of gold by cyanide ions in single gold nanoparticles. The first trial showed already something interesting: single particles on glass were behaving completely different than in bulk suspension. More importantly, to answer the question it was clear that we needed better software to control the setup.

Ferry Kruidenberg, a bachelor student at the time, joined the group to help develop the software even further. He designed the core layout of the program and the first graphical user interface. Together we learned about version control, instrumentation and programming patterns. Simultaneously, a master student, Irina Komen, joined the group to start working on an optical tweezer. Together we managed to obtain photothermal signals from single nanoparticles that were trapped in water and glycerol. However, the final objective was to study the fluorescence enhancement of a dye in the vicinity of the rod while away from any other surface, thus preventing sticking of the molecules to the coverslip.

Even if the results on the optical tweezer didn't fit into this thesis, while characterizing the emission from different nanoparticles an interesting phenomenon appeared: emission at higher energies than the excitation energy, the anti-Stokes emission. This emission proved to be reasonably efficient, sometimes even comparable to the Stokes-shifted counterpart. The detection of anti-Stokes luminescence was consistent between different samples and under different conditions.

Anti-Stokes luminescence opened the door to two different approaches. Firstly it was possible to exploit the emission at shorter wavelengths to suppress the background when imaging under biological conditions. Cells are known to fluoresce under laser irradiation and therefore dim emitters such as small nanoparticles are hard to distinguish from the background. After discussing with Veer Keizer, a PhD candidate in biology belonging to the same project, we embarked into the exploitation of the anti-Stokes emission for imaging. These ideas led to Chapter 3 and its publication in the Biophysical Journal. It was very well received by the reviewers, one of them qualified the findings as a "very important breakthrough".

However, there was more in the anti-Stokes emission than solely the application to imaging. If the emission depends on temperature, it can be used as a nano-thermometer. Photothermal therapy is a fertile subject that relies on locally increasing the temperature to kill specific cells. This is achieved by shining a laser onto gold nanoparticles inside or in the vicinity of those cells. However there are so far no ways of controlling the temperature of the particles. Studying the anti-Stokes emission can be a solution to a long standing problem in the medical and biological sciences.

To prove the usefulness of the method, the measurements were performed in a temperature variable flow cell. An air spaced objective was needed to avoid altering the temperature of the observed area, which in turn lowered the collection efficiency. At higher temperatures (around 60 ^{o}C) the setup drifts several micrometers and therefore an accurate control of temperature and a proper tracking of the particles was needed.

Chapter 4 shows that it is indeed possible to determine the absolute temperature of single nanoparticles just by measuring their anti-Stokes spectrum. The method does not require any form of *ad-hoc* calibration and can be easily implemented in any confocal microscope coupled with a spectrometer. These findings can have a major impact on photothermal therapy and in material sciences, where the question of the temperature reached by the particles has been open for more than 20 years. Testing the method in real situations is the next logical step but was outside the time frame of the thesis.

With the experience built on the anti-Stokes luminescence, characterizing the scattering of single gold nanoparticles at different temperatures did not prove to be particularly challenging. Since the first inception of the computer software until the last version, that allowed to acquire all the data in Chapter 5, almost 4 years had passed.

This work summarizes a lot of effort by a lot of people. It neglects all the failed experiments and frustrations. It is important to remind that failure is only a relative measure; while we learn something either of nature or of ourselves, we are being successful.

Aquiles Carattino
Leiden, March 2017

Contents