Realization of an in-situ Fluorescence & Raman Spectroscopy Setup for studying Quantum Dot Films

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ABSTRACT

A new experimental setup for studying charge transfer in Quantum Dot (QD) films has been designed, built and tested. The setup combines three spectroscopic methods; Raman, Fluorescence and Absorption Spectroscopy. First data on a Cadmium Selenide (CdSe) films reveals that radiative emission quenches while charging, attributed to Auger-decay. When fully discharged, the emission remains partly quenched, indicating that not all electrons are removed. Since charge transfer is a fundamental process in solar cells, the setup could be essential for designing and optimizing cost efficient future QD based solar cells.

Keywords

Quantum Dots, Fluorescence Spectroscopy, Raman Spectroscopy, Electrochemistry, Charge Transfer

INTRODUCTION

The future impact of nanotechnology on society has been recognized all over the world. Due to their wide range of applications (solar cells, detectors, LEDs, etc), semiconductor QD films are of special interest. The group of dr. Houtepen is specifically interested in charge transfer within these films. [3, 9, 10] For this purpose, QD films are fabricated on an Indium Tin Oxide (ITO) covered quartz substrate. For implementation in solar cell devices, the injected charges should ideally remain localized in the films over a long period of time. However, the injected charges leak out over the course of hours. Currently, the transfer of charges in and out of the films are monitored with in-situ absorption spectrometry (AS) only. This method reveals important but still insufficient information. Trap states within the bandgap for example, which are electronical states which ‘‘trap’’ electrons within the quantum dots, are not apparent in absorption spectroscopy. Yet knowledge is essential in order to properly study e.g. charge transport. By combining AS with Photoluminescence Spectroscopy (PLS) and Raman Spectroscopy (RS), new insights into the dynamics of the electronic and crystal structure of the QD films are expected. The research objective within this bachelor project is to design, build and test a fiber optic based set-up for both PLS and RS, and to combine the data with AS, and also interpreting the first results.

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A fiber-optic based set-up was preferred due its flexibility, since only then, the measurements can be conducted in a N2 purged glovebox, thus preventing oxidization of the QDs.

THEORY

The amount of atoms in a single QD crystal lies between 100-1000 atoms. Therefore, its behavior is expected to deviate from both bulk material as well as single molecule behavior. The energy levels of QD crystal can indeed be understood as an intermediate level scheme (figure 1 A, B and C) The electronic energy structure of a single molecule shows an energy gap between its Highest Occupied Molecular Orbital (HOMO) and its Lowest Unoccupied Molecular Orbital (LUMO) (Figure 1C), well understood from quantum mechanics [2, 3, 5, 7]. This energy gap (band gap) remains present even for bulk material (figure 1A), representing the core of its semiconducting behavior. An important difference, however, is that the discrete energy levels have now turned into an energy continuum, also known as a band structure. In the bulk material the LUMO levels have turned into the standard Valence Band (VB), and the HOMO levels have now turned into the standard Conduction Band (CB).

In a quantum dot the VB and CB are also present, yet they still contain (single molecule like) discrete energy levels (near the band edge) (figure 1 B). Another interesting property of QDs is that the bandgap depends on its size (which is tunable [1, 6]). Since the bandgap mainly dictates the optical properties, these can be tailored with high precision. This is one of the reasons why QDs are so interesting for various innovative devices [3, 7]. It is possible for an electron to jump from the VB) into the CB usually by absorbing a photon. After this, the excited electron may fall back to the VB while emitting a photon (fluorescence). As mentioned in the introduction, for studying the possibility for usage of QDs in solar cells, it is important to study the behavior of charged QD films. The injected electrons will occupy states within the CB, since all states in the VB are already occupied. Absorption and Fluorescence spectroscopy are therefore very interesting techniques to learn more about the changes of the electronic structure while charging QD crystals. These techniques however, do not reveal any information on the crystal structure. Recent research however, suggests that the crystal structure may also change due to charging [4]. Unique fingerprints for the crystal structure are the vibrational modes of the crystal [8]. Raman Spectroscopy is capable of measuring these vibrational modes, therefore revealing information about the crystal structure [8].

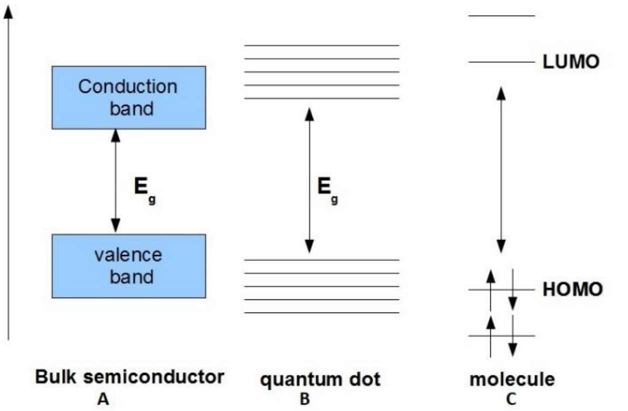

Figure 1; A. Standard electronic band structure of bulk semi-conductor, B. Electronic structure of semiconductor QD, C. Electronic structure representing single molecule.

EXPERIMENTAL SETUP

This section will cover the process of charging quantum dot films, next, the designed fluorescence-spectroscopy setup will be explained. As stated before, quantum dot films are fabricated; resulting in a glass substrate with a conductive layer of Indium Tin Oxide (ITO) coated on the glass. On top is the quantum dot coating, which is around 100 nm thick. Shown in figure 2A is the setup used to electrochemically charge the quantum dot film. The electrochemical setup uses a cell which consists of an Ag wire pseudo-reference electrode, Pt sheet counter electrode and one working electrode (the quantum dot film). Now, by applying voltage between the reference electrode and film, the Fermi level of the working electrode will raise. Eventually the Fermi level will raise beyond the CB of the quantum dot film, and since systems in nature always strive for the lowest energy, the electrons will be injected in the CB of the quantum dot film, shown in figure 2B. Simultaneously the charge will be compensated by the cations within the electrolyte. The injected electrons will be drawn from the counter electrode, therefore one can measure the charging current by monitoring the counter electrode since it acts like an ammeter.

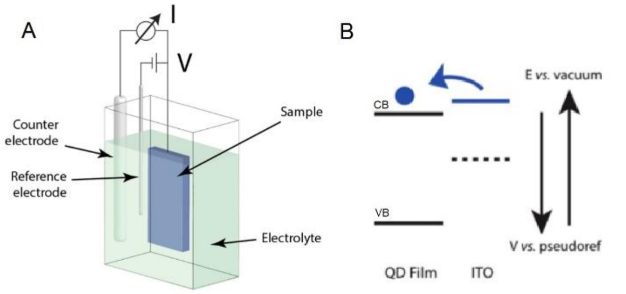

Figure 2; (a); Schematic of the electrochemical set-up, with the QD film as working electrode, the Ag wire as reference electrode and the Pt sheet as counter electrode, which acts as current sink. (b); Schematic of the electron injection process, the injected electron in the CB may cause bleaching. Meaning decreased absorption since less electrons form the VB excite to the CB [3].

As stated before, an absorption spectroscopy setup able to determine the differential absorbance while charging the film is already established. However to gain information about traps within the bandgap, a Fluorescence spectroscopy setup needs to be designed and build. For the ideal setup various aspects were taken into consideration; excitation laser (power and wavelength), ideal coupling of the light into the fiber and a lens-system which collects as much fluorescence emission as possible. For the latter the lens alignment, coating, focal length and curvature were chosen carefully by modeling and experimental tests. The final designed and built setup is shown in figure 3.

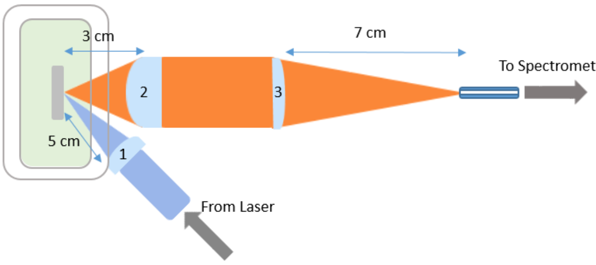

Figure 3; Schematic top-view of the used set-up used for in-situ fluorescence spectrometry. With the focal length of lens 1, 2 and 3 respectively 5 cm, 3 cm, 7 cm.

In short, the lens indicated as 1 will focus the collimated laser beam to its focal point, where the sample is located. This causes the sample to emit fluorescence in a uniform radiation pattern. The light is collected using lens 2, which has a relatively large aperture to maximize the light collected from the sample. Lens 2 will collimate the collected light and it will be focused onto the fiber using lens 3, which has a lower aperture than the optical fiber, hence no light will be discarded. The optical fiber will guide the light towards a fiber based spectrometer which analyzes the light and sends it to the PC for data analysis.

RESULTS

First, the absorbance of an uncharged CdSe QD film will be analyzed to have a first indication of the electronic structure of the film, the result is shown in figure 4.

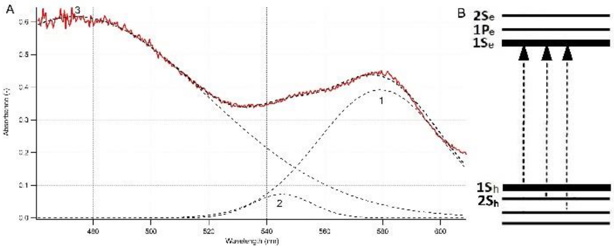

Figure 4; (a); Absorption spectrum of the CdSe film (red solid line) which can be fitted by multiple Gaussians (black dashed lines) (peak-fitting function IGOR) which can be ascribed to the possible transitions. (b); Schematic representation of these transitions.

Next, the already established absorption spectroscopy-setup will be used to determine the effect of electrochemically injecting electrons in the CB of the quantum dot film, the result is shown in figure 5.

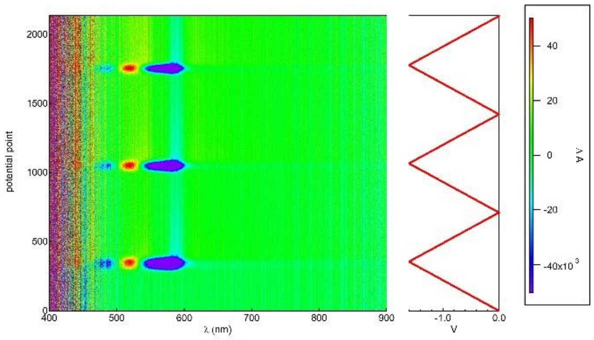

Figure 5; Differential absorbance as function of applied potential, scanned from 0 Volt to -1.6 Volt.

Figure 5 shows negative change in the film's absorbance upon scanning to -1.6 Volts (which is therefore the voltage needed to raise the Fermi level of the ITO beyond the CB of the film as described in the experimental setup) compared to the absorption at open circuit. The most distinct bleach is attributed to transitions from the highest energy band within the VB to the lowest energy band within the CB the $1S_e$ band. A less distinct bleach occurs at 480 nm, attributed to the transitions to the lowest but one energy level within the VB ($2S_h$) to the $1S_e$ band. These bleaches of the absorption indicate that the transition to the $1S_e$ level is blocked, due to the injection of electrons into this electronic level at -1.6 Volts. When cycling back to zero Volts, the bleach vanishes, indicating that the electrons are diffusing out of the QD film. This is expected due to the fact that upon scanning to zero Volts, the Fermi level of the working electrode is back to its original position.

Now the results will be presented regarding in situ fluorescence spectroscopy with the setup as described earlier, the result is shown in figure 6.

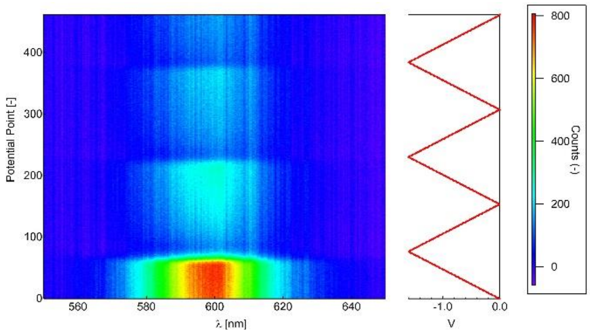

Figure 6; In-situ fluorescence results regarding the CdSe QD film, the Figure shows the amount of counts for a wavelength range of 540-640 nm as function of applied potential.

One can observe that when applying -1.6 Volts, the signal caused by the photoluminescence of the film quenches. A hypothesis to understand this event is due to the fact that in-situ absorption measurements results imply that at this point, the 1Se band of the QDs are filled with excess electrons. Due to these electrons the creation of an exciton by laser excitation will promote the injected electrons to higher energy states (within the CB), which will cool again to the 1Se level, without release of a photon, hence quenching the photoluminescence, this process is known as Auger decay.

When scanning back to 0 Volts, hence removing the previously injected electrons according to the in-situ absorption measurements, the signal does not return to its initial strength. The PL signal returned to initial value after 15 minutes from the end of the electrochemical experiment. The formed hypothesis to explain the decreased emission is that the injected electrons fill trap states within the electronic structure of the quantum dots. As stated before; these trap states have no effect on the absorption properties, therefore one might think that the process of electron injection is very reversible and behaves perfectly when the electrons are taken out again. Yet the PL-setup clearly reveals more processes; possible trap states which largely influence the PL. This clearly shows the importance of the setup.

Now, with the fluorescence setup designed, built and the first results analyzed; the possibility to conduct in-situ Raman-spectroscopy will be determined. First, the Raman signal of a Copper Sulfide (CuS)- QD film will be analyzed using a dedicated bench-top microscopic based InVia Raman spectrophotometer (Renishaw).

This spectrophotometer has a 50x objective, which will result in a focused spot of 1 µm, the same order of magnitude as the thickness of the sample. The sample will be positioned on a XYZ micrometer stage, by using this stage one can visually put the CuS particles in the focus of the objective. The results are shown in figure 7.

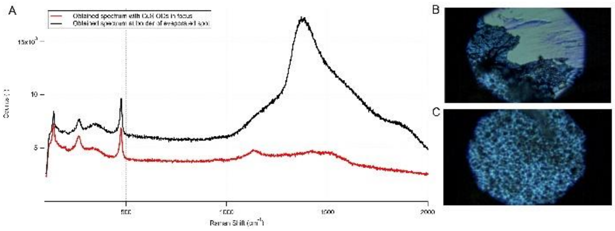

Figure 7; (a); Red: spectrum acquired while image C was in focus. Black: spectrum acquired while image B was in focus, showing a significant higher amount of fluorescence by the glass substrate, implying that a part of the CuS particles shown in the image are in fact evaporated.

The distinct peak at 474 cm^{-1} is in agreement with the main vibrational mode of CuS, however one can determine that when image B was in focus, which is half CuS particles and half bare glass substrate, the fluorescence of the glass substrate becomes more dominant (1500 cm^{-1}). The smallest excitation spot size one could achieve with a fiber based Raman-spectroscopy setup (which is needed to conduct in-situ measurements) is 50 µm. Therefore measurements with the fiber based Raman-setup will be overwhelmed by fluorescence caused by the glass substrate since the glass substrate will be within the focused spot whenever one intends to focus on the QD film.

CONCLUSION

The main aim of this study was to determine the possibility, and if so, the realization of fiber optic based set-ups for two different kinds of spectroscopic techniques within a set-up used for the electrochemical charging of QD films. The first spectroscopic technique is PL-spectroscopy, since with this technique one could determine the change of the PL properties of (dis-)charged QDs. Second one being Raman spectroscopy to determine whether the injected electrons cause the crystal structure of the QDs to change. With these two techniques and the already established absorption spectroscopy, one can thoroughly study various processes within quantum dot films. And since that is a fundamental process in solar cells, the setup could be essential for designing and optimizing cost efficient future QD based solar cells.

An in-situ fluorescence spectroscopy set-up is designed and build. During the process of designing the set-up the physics behind e.g. the lens-system, excitation laser, light collection and data acquisition was studied to eventually end up with the ideal setup. The setup is tested during charging experiments with CdSe QD films and first results were interpreted. It has been determined what happens with the photoluminescence properties of charged CdSe QDs; it decreases significantly. In-situ absorption spectrometry results have shown that these excess electrons occupy states in the CB of the film. Hence the hypothesis is formed that these electrons quench the emitted power by photoluminescence due to Auger-decay. When discharged, absorption-spectrometry shows total removal of electrons from the CB of the film. However, the PL remains quenched, therefore the hypothesis is formed that trap states are still filled within the film. This hypothesis could be tested by using ultrafast spectroscopy techniques, since the time scale of Auger decay is significantly lower than PL.
Examination of Raman-measurements conducted with the high end microscopic based Raman setup have shown that the acquired Raman spectrum of a CuS QD film is overwhelmed by the fluorescent glass substrate underneath. This happens if one does not focus the 1 µm laser spot accurately on the 1 µm film. Since a fiber-based Raman setup is only capable of a minimum laser spot of ~50 µm, it is concluded one cannot use a fiber based setup to acquire the Raman signal of the CuS film without any amplification or additional techniques.

ROLE OF THE STUDENT

Written by Jurgen Dijkema (Student)

Jurgen was a Bachelor student from THUAS working under supervision of Lodewijk Arntzen (THUAS) and Ward van der Stam (TU Delft) in the research group of Arjan Houtepen (TU Delft). The research group desired a setup for in-situ Fluorescence and Raman spectroscopy, therefore the topic was proposed by the research group. The design of the setup (including the necessary literature study) and the realization and testing of the setup were done by the student. The data processing data regarding the conducted experiments with the designed setup and the QD films were done by the student. The stated conclusions and hypotheses were are result of several discussions with the student and the supervisors.

Written by Lodewijk Arnzten (Supervisor THUAS)

It was always a great pleasure to guide and teach Jurgen during his Bachelor period (Applied Physics at THUAS). Already at the start of his studies, it became clear that Jurgen is indeed a skillful student. Jurgen has always been extremely keen on learning Physics, this accounts for both the theoretical aspects as well as laboratory skills. Anything new was absorbed with the same great intensity. It became clear to me that a special internship had to be found for him. The group of dr. Houtepen brought exactly this. In this research group Jurgen could show that he is really capable of introducing state of the art experimental methods in a complex new field of application. He has proven to learn new lab skills quickly, and has proven to be able to work very independently in an interdisciplinary context. Jurgen also always joined the scientific debates, and contributed to these discussions at a very high level. Considering all this, Jurgen has proven to be an extraordinary student. A bright mind with a bright future.

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