ODMR in CdS nanocrystals

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Introduction

In this report I'll present the main aspects of the ODMR experiments I conducted during my internship in the Photonic Nanomaterials Group headed by Dr Jason Smith in the Department of Materials. This may help to continue the work I started and it's addressed to someone that is working in the PNG lab and that will use the same instrumentation because I won't give information about it.

In the ODMR experiments the aim is to study the optical properties of an ensemble of semiconductor nanocrystals. If a high-energy photon hits a NC this will create an exciton (bound state of an electron and a hole). Once the electron is in the excited state may be trapped in a defect with a lower energy somewhere in the NC. Here usually the electron decays in a non-radiative way but there are some NCs, with a certain composition, where the trapped electron recombines radiatively and the analysis of the optical properties of the trap emission is possible.
In an ODMR experiments a constant magnetic field causes an energy levels splitting (Zeeman effect) in the QDs because of the orientation of the magnetic dipole of the electrons in those levels. At the same time a microwaves source hits the NCs and if its frequency is the right one it excites a resonance condition between two energy levels. An unpaired electron can move between the two energy levels by either absorbing or emitting electromagnetic radiation and this phenomenon is detectable by a spectral analysis.

CPW Preparation

To generate the microwaves source is used a CPW that creates a magnetic field of the same frequency of the signal that is passing through it. To create a pattern on a metal surface in a very precise way a possibility is the electron beam lithography. There are 2 types:

I. Negative lithography
II. Positive lithography (lift off)

I. Negative lithography procedure:
   - Metal coating of the sample
   - PMMA spin coating on the top
   - Etching of the PMMA where you want to remove the metal
   - Removal of the PMMA from the etched area
   - Removal of the metal

II. Positive lithography procedure
   - Sample uncoated
   - PMMA spin coating on the top
   - Etching of the PMMA where you want to deposit the metal
   - Removal of the PMMA from the etched area
   - Deposition of the metal
   - Lift off of the PMMA

If you want to remove the metal from a small area, the negative procedure is the best choice.

Negative Lithography

i) Metal Coating

The person I contacted is Richard Makin (r.makin1@physics.ox.ac.uk).
To obtain a better result, clean carefully the substrate with acetone and methanol.
Richard will stick the sample with an adhesive to hold it in the right position, so one or two corners won't be coated. You may lose 2 mm.
The thickness I deposited was 10 nm of Cr plus 200 nm of Au.

ii) Electron beam lithography

You may want to contact Alex Robertson (alex.robertson2@materials) or Volker Lang (volker.lang@materials).

Things you need:

- Metal-coated sample. There are two spare spectrosil 2000 substrates in the lab that have the right dimension (20x20x0.5 mm) to fit in the electron beam microscope holder. If you want to use another substrate, there is the restriction on the thickness; it has to be less then 1 mm. (There are more holders with different dimensions).
- Pattern Drawing. The ebl software accepts files with .dxf(2007) extension. Save it in this extension with autocad. It's always worth to have also the .dwg file just in case you need to make some changes in the ebl lab.

Find attached the CPW pattern drawing. The electron beam software accepts only drawings made with close figures (rectangles, squares).

iii) Metal Etching

At this point the metal needs to be removed. Radka knows which chemical is better, but it's important to expose the metal to the chemical enough because there is the possibility that after the etching a thin metal layer creates a short-circuit in between the contacts. It's not enough to check the goodness of the etching just putting it against the light; it's better to use a tester. Use a soft metal like indium or the tin lead alloy to not scratch the surface.

If after the etching the metal layer is still there slip gently a lens tissue on the surface until there metal is removed. The optical microscope in the lab it's useful to check the state of the scratching.

NCs and capping

Materials

In ODMR experiments a variation of the intensity of the trap emission is expected. It's important to have a strong and stable photoluminescence in that region of the spectra. We achieved that using CdS NCs with TOPO as capping.
Different types of NCs and capping have been tested.

NCs:

1) CdS
2) CdS/ZnSe
3) CdS/ZnS

Capping:

1) HDA
2) TOPO
3) Oleic Acid

We analysed different NCs with HDA and all of them showed a good trap emission when in solution, but only the band emission when spin coated on the CPW. Probably an interaction with air or moisture changes the properties of the NCs. In fact as Figure 1 points out, when the PMMA is added on the solution that is going to be spin coated there is a slight increase of the trap emission, even though it's much weaker that the one from the NCs in solution.

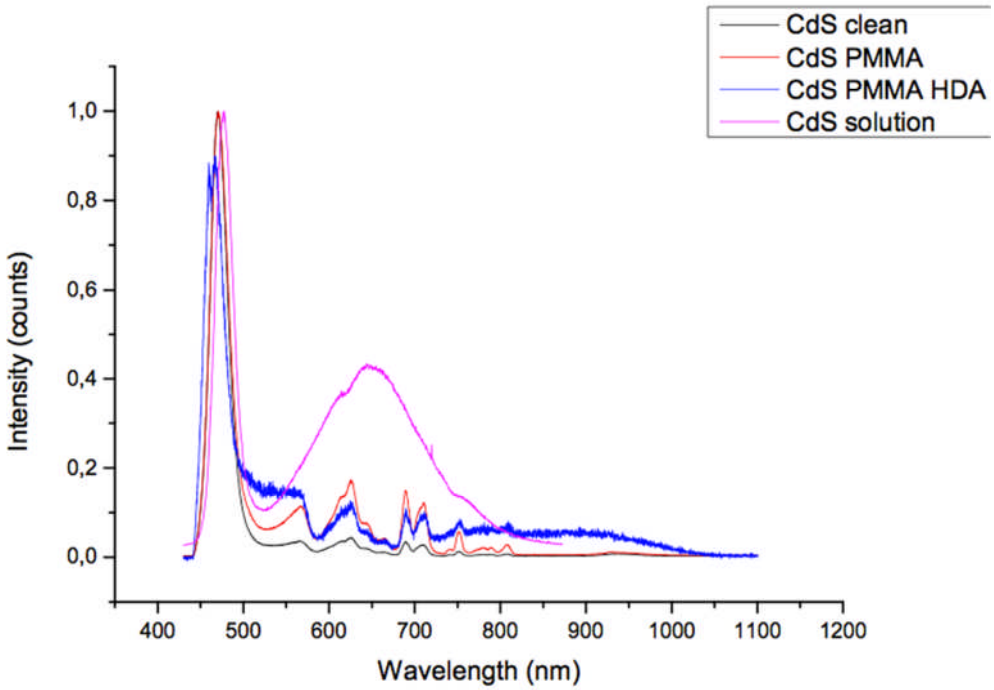

Figure 1. Comparison of CdS PL in solution (pink) or spin coated without any addition (black), with PMMA (red) and with PMMA and HDA (blue).

Both the TOPO and the OA give a better response. We found that CdS with TOPO has different quantum yields and different stabilities than with OA. The CdS capped with OA has a higher quantum yield, as you can see in Figure 2, where the same laser excitation power is maintained.

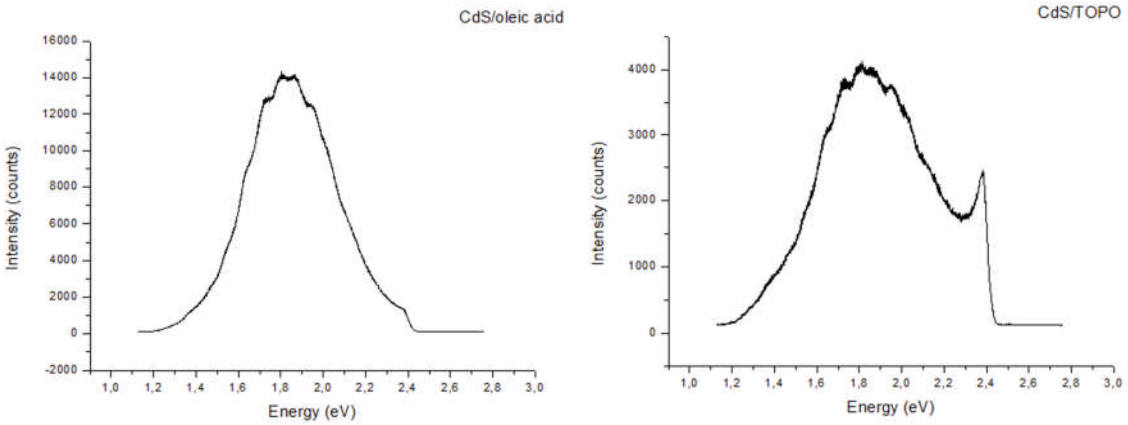

Figure 2. CdS spectra excited with a 473nm laser (10uW of power, 1 second integration time). In the left graph the capping is oleic acid and in the right one is TOPO.

On the other hand the TOPO gives a higher stability to the CdS PL. When the intensity of the trap emission is monitored without delivering microwaves, it's more constant than when AO is used. This behaviour is shown in the following figures, where the X-axis is the time, the Y-axis is the wavelength of the emitted radiation and the Z-axis is its intensity. In a 300 seconds experiment when we used OA a variation of intensity appears without any apparent reason.

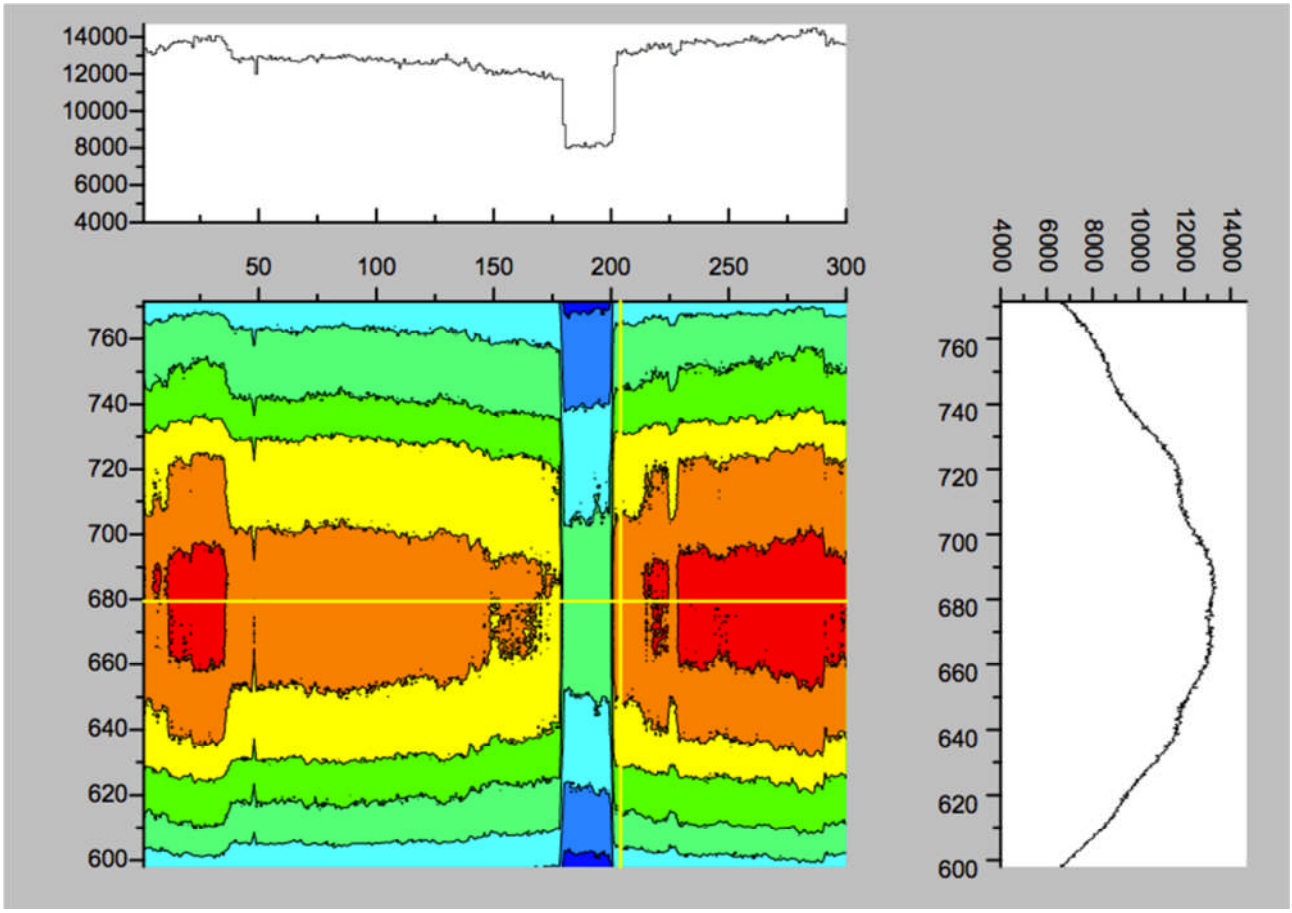

Figure 3. Spectral Video of CdS PL capped with OA. The X-axis is the time (300 seconds), the Y-axis is the wavelength of the emitted radiation and the Z-axis is the intensity if the emitted radiation.

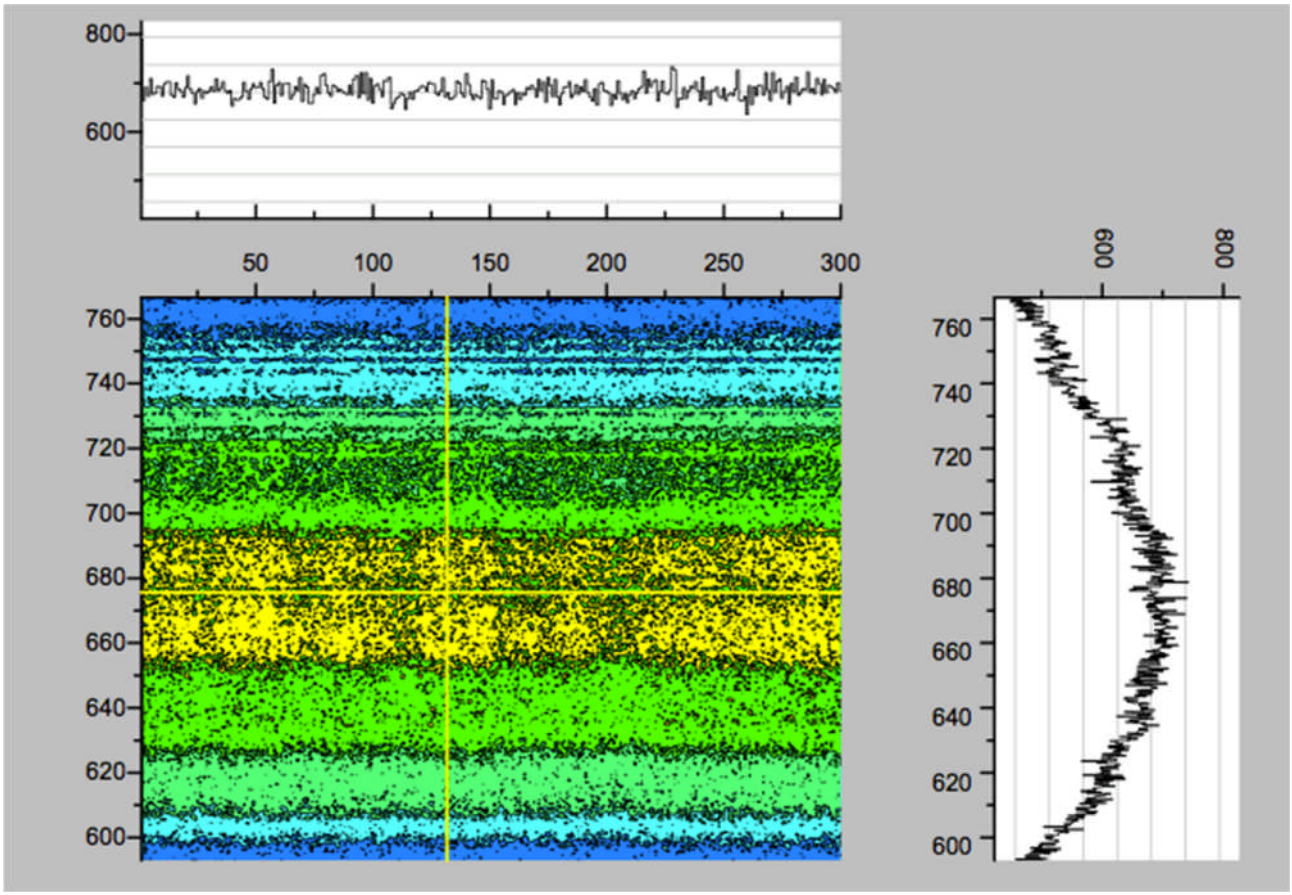

Figure 4. Spectral Video of CdS PL capped with TOPO. The X-axis is the time (300 seconds), the Y-axis is the wavelength of the emitted radiation and the Z-axis is the intensity if the emitted radiation.

CdS/ZnSe and CdS/ZnS haven't been tested with OA and TOPO.

Concentration

The solution I used was very concentrated. I dropped NCs directly from the bottle Simon prepared for me in Begbroke; I didn't add any solvent to dilute.

Sample preparation

The main steps I've followed to make the sample (CPW/NCs) are:

- Take the black round plate (I left a couple of samples where I used this plate, the diameter is 3 cm more or less). I used this plate because I could screw it in a tube; in this way I could easily hold the sample under the microscope and at the same time I had space under the sample/inside the tube to place the magnet.
- Cut 2 contacts that will connect the signal analyser and the 50-ohm resistance. Each contact has two pins. You may find a strip of pins in the lab in the box where the electric wires are.
- Solder a copper wire (the reddish one, I suppose they're half a millimetre thick) in every pin contact, you've to scratch the red insulation layer of the copper

wire first. I found easier to use the Indium alloy to solder, not the tin lead one, it's more malleable. At this point you should have 2 contacts, every one with 2 pins (you need one pin for the signal and one for the ground) and everyone with a copper wire soldered.

- Glue the contacts on the plate with the araldite glue and leave it 24 hours resting. It's important the length of the wires and the distance you are going to glue the 2 contacts, you have to be sure that all the 4 ends of the wires will be exactly above the CPW contacts. The set up I used was with the CPW in the middle and one contact on the left and one on the right.
- Put the CPW in the right place and glue it, I used the silver paint in this case.
- Solder the 4 contacts on the CPW. Also in this case I suggest using the indium. Prepare the wires in the exact place you want them to be, that is nearly in contact with the gold film of the CPW and use a small amount of indium on the tip of the welder.
- Put one drop of nanocrystal solution on the CPW, the solvent will evaporate and the sample it's ready.

Magnetic field

To create the magnetic field I used the 1x4 cm cylindrical magnet. I placed it vertically under the epifluorescence spectroscope inside the cylindrical tube where the plate with the CPW is screwed. I used a screw, placed in a hole of the table, to adjust the height of the magnet to modify the strength of the field. I put the sample on top of the magnet at the distance I calculated (1.3 cm) and then I fixed it to the x-y positioner so it couldn't move.
The last thing to do is to connect the microwave generator in one contact and the BNC terminator with 50-ohm resistance in the other end.
I may suggest finding another solution to place the magnet in a way that could be moved without removing sample.

Microwaves Generator

Frequency and Intensity

The range of frequency I used in the microwave generator depended on the distance between the magnet and the sample. I calculated the range of energy where there could be an ODMR signal from the results shown in Lifshitz's paper [1].
A visible change in the intensity is visible sweeping the frequency from 0,25 GHz to 0,85 GHz with an intensity of -5dB. In all the experiments I used the amplifier (with the knob placed at 0) that increase the intensity from -5dB to 5dB more or less; I measured it with the John Morton's group signal analyser.

Synchronization

The synchronization between the signal generator and the spectrometer software may help the data analysis. Setting up the same value in the integration time of the spectral video and the sweeping time between two steps in the signal generator will be easy to calculate the frequency delivered during each step.

Spectrometer

Laser and filters

The aim of the experiment is to analyse only the intensity variation of the trap emission. The band emission of our CdS is 476 nm, and the trap emission starts from 540 nm, so the 510 nm filter cuts the part of the spectrum unnecessary.
The 473 nm laser excites the NCs. The decision to use this laser instead of the 400 nm one has been taken in order to leave the same alignment of others experiments were conducted at the same time on the epifluorescence microscope. Even if the absorption in a situation where the excitation is so close to the band emission isn't optimal, it was enough to see a trap emission.

Software limit

The maximum number of spectra that the spectral video can save is 300.

Sample Positioning

The area of the CPW where the NCs are involved in the excitation by the microwave radiation is the two gaps between the signal and the ground (10micrometer wide). It's important to be able to place the CPW in a way that one of the two gaps is exactly under the microscope. The best position it's the one where the gap is vertical in the image mode of the spectrometer software. In this case you'll be able to close the shutters and to excite only the NCs that are in the gap.

- Place the magnet in the right position.
- Place the CPW under the lens by eye and fasten it; it may help leaving the laser on to monitor the laser spot position to find the right position.
- Use the webcam to find the focus. Use the "narrow" illumination that is without the broad illumination lens.
- Open the spectrometer software in image mode and move the x-y position to find the gap.
- Once found it, rotate the sample to place it vertically in the monitor.
- Close the shutters to excite only the gap area.

Results

When the microwave radiation is conveyed to the NCs the trap emission intensity varies as in Figure 5.

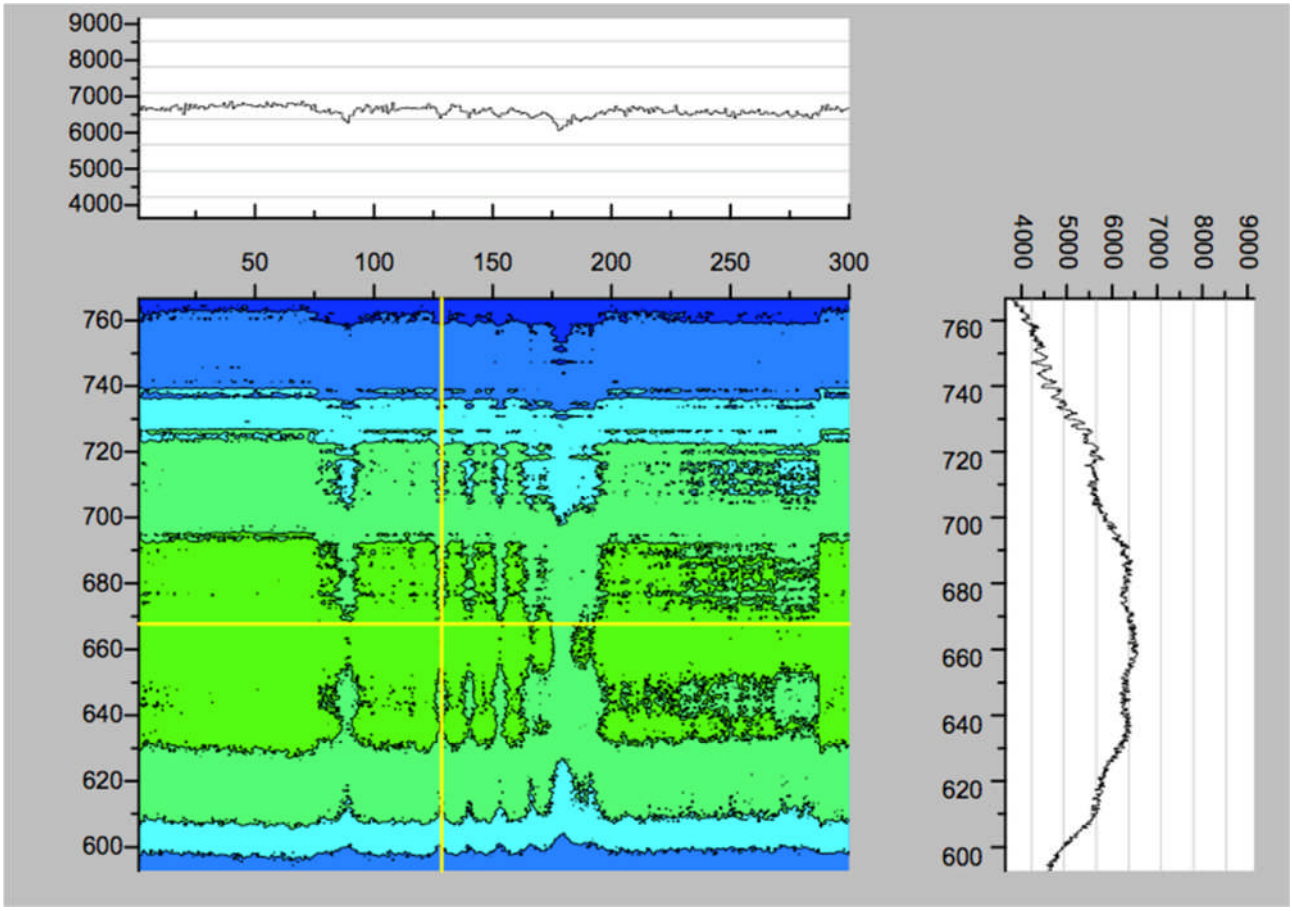

Figure 5. Spectral Video of CdS PL capped with TOPO under microwave excitation. The X-axis is the time (300 seconds), the Y-axis is the wavelength of the emitted radiation and the Z-axis is the intensity if the emitted radiation.

To evaluate better the ODMR effect we grouped together the intensity of the emission of the NCs in every instant, and we plotted it as a function of the frequency of the microwave radiation (see Code in the Supplemental Documentation). The results (Figure 6) show a decrease of the Photoluminescence Intensity when the microwaves sweep from 0.25 GHz to 0.85 GHz. This behaviour is reliable in fact three different experiments conducted at the same conditions have the same feature at the same frequencies.
The green line seems to increase during the experiment and the violet one seems to decrease but probably this is a laser related effect or it might depend on the organic part of the solution.
These results are in contrast with the ones that Lifshitz and colleagues showed in their work [1] where they achieve an increase of the intensity. It's worth to say that probably it's hard to compare our work with the Lifshitz's one because of the different materials and temperature used; we worked with a core of CdS at room temperature instead of a core shell system of CdSe/CdS at helium temperature.

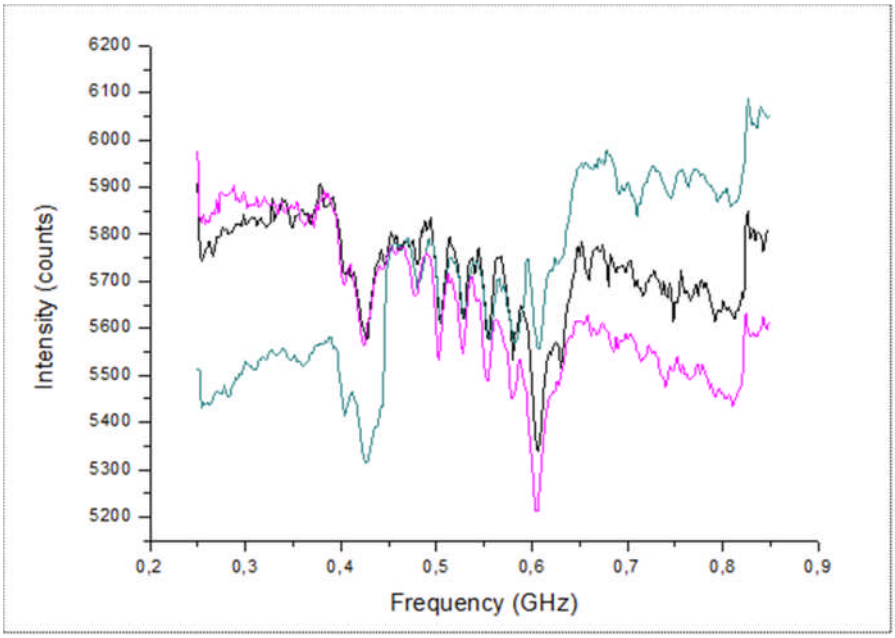

Figure 6 ODMR effect at room temperature of CdS NCs capped with TOPO.

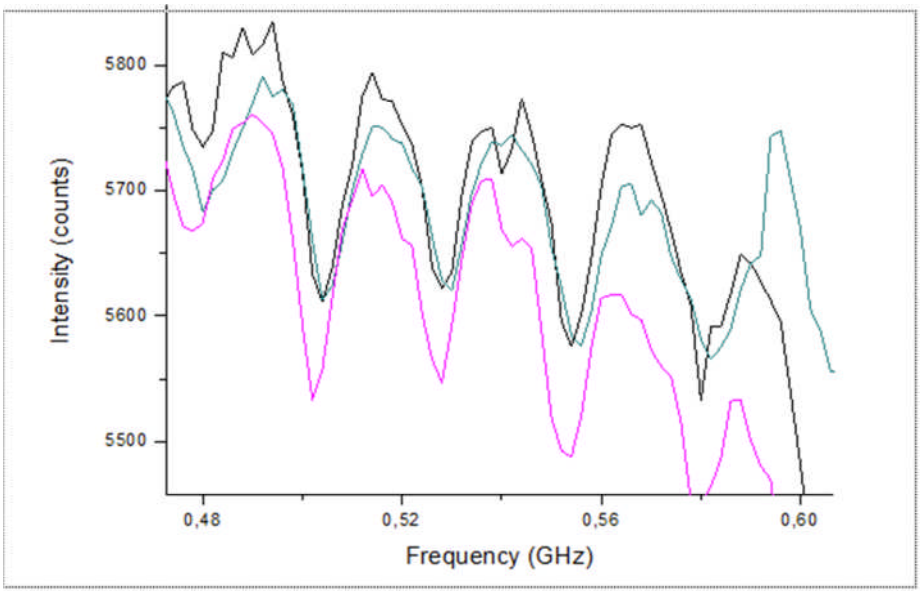

Figure 7 Feature of the ODMR effect.

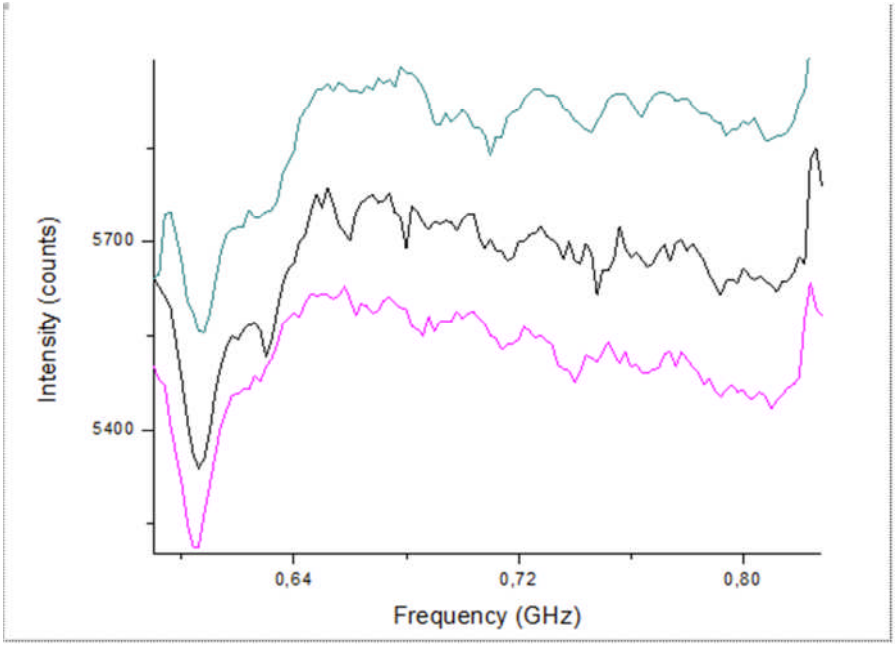

Figure 8 Feature of the ODMR effect.

Supplemental documentation

1) CPW Electron beam Facility user manual
2) CPW AutoCAD files
3) CPW writing time for the Electron beam Facility
4) Code. Once the spectral video data are recorded, it's possible to group together the intensities of the emission of the NCs in every instant if it's not important the radiation wavelength. This code accepts the txt file created by the microscope software after the ASCII conversion of the spectral video.
   First install the Fortran compiler. Modify the name of the file inside the program in line 23 with the name of your file, including the extension. Put the file in the same folder of the program. Using the computer terminal go to that folder. Copy the instruction from line 3 to compile and then write ./stef to run.
5) Magnetic field vs. distance
6) Short bibliography

Bibliography

[1] (E. Lifshitz, A. Glozman, I. D. Litvin, and H. Porteanu, Optically Detected Magnetic Resonance Studies of the Surface/Interface Properties of II-VI Semiconductor Quantum Dots, *J. Phys. Chem. B* **2000,** *104*, 10449-10461).