PL Lab Report (SK2901)

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1. Introduction

Photoluminescence is a phenomenon of light emission by matter, after it absorbs photons. One of the materials which exhibit such a property is a quantum dot (QD). When a QD is illuminated by UV light, electrons get excited, and transit from valence band to conduction band, leaving behind holes. If an electron returns to the valence band, it releases energy in the form of light.

QDs are semiconducting nanoparticles, which due to their size, function according to quantum confinement, and exhibit unique electronic and optical properties, which are different from the properties of bigger, dependent on classical mechanics, particles.

QDs appear in different sizes and shapes, which leads to their different properties. One of them is the size of a band gap - the smaller the size of a QD, the bigger the band gap. Moreover, the colour of the emitted by a QD light depends on the size of a band gap.

Quantum dots have gained much popularity in the last years and are still heavily researched. So far, they have been widely applied in electronics, e.g. in displays, LEDs, solar cells as well as in medicine and biology, e.g. for medical imaging. [1]

2. Experimental

During the laboratory, four experiments were conducted. In the experiments, a spectrometer with a blue-LED probe was used.

In Task N1, four different light sources were examined with the spectrometer, and their photoluminescence spectra were analysed. The light sources used were: LED, White LED Flash (torch), Incandescent Lamp and Mercury Discharge Lamp.

In Task N2, photoluminescence spectra of five different QD solutions with CdSe nanocrystals of various sizes were obtained and examined. The sizes of nanocrystals are presented in Table 1.

Table 1. Sizes of CdSe nanocrystals in QD solutions used for examination

Label	Number of CdSe QD	AB	EM
QD1	ED-C11-TOL-0490	478 nm	493 nm
QD2	ED-C11-TOL-0520	497 nm	511 nm
QD3	ED-C11-TOL-0540	523 nm	542 nm
QD4	ED-C11-TOL-0560	537 nm	552 nm
QD5	ED-C11-TOL-0600	585 nm	600 nm

In Task N3, QD2 was chosen to be investigated how its photoluminescence spectra change after QD2 exposure to oxygen and ambient conditions. Two drops of QD2 were pipetted onto a substrate, which was then placed in a box without any light source, except the light from the probe put in the hole of the box at an angle (so that reflection peaks could be avoided). Then a few measurements were taken in time intervals of a few minutes for ~25 minutes.

In Task N4, photoluminescence spectra of porous Si particles (powder) was obtained and compared with the spectra of QD2.
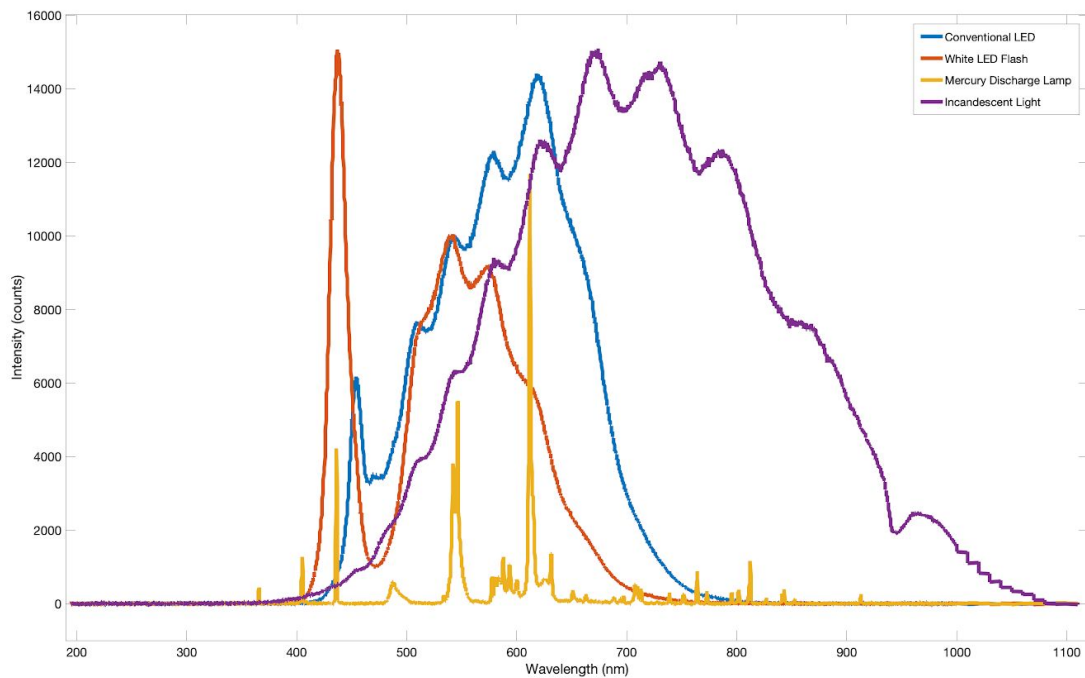
3. Results and discussion

Fig. 1. PL spectra of examined light sources.

In Fig. 1, there have been shown photoluminescence spectra of the aforementioned light sources, obtained in Task N1 of the laboratory session. One can observe from Fig. 1 that sources such as Conventional/White LED Flash and Mercury Discharge Lamp have discrete peaks which correspond to discrete energy level transitions occurring in these sources, hence the final spectra appear white in colour due to a mixture of all the discrete transition spectra. The Incandescent Light spectra resembles that of a black body radiation (wide spectral range), due to its radiative emission of electron collision energies in the Tungsten filament.

Task 1. Calculation and plotting of confinement energy as a function of CdSe nanocrystal diameter.

Calculation of confinement energies for the five examined samples of CdSe QDs has been done with the following formula:
$$E = \frac{hc}{\lambda} = \frac{1238}{\lambda} \, [eV] \,,$$
where h is the Planck's constant, c is the speed of light and λ is the emission wavelength.
The emission wavelengths have been read from the photoluminescence spectra obtained for the different samples, which have been shown in Fig. 3 and 4. The values have been read for the spectra of intensity normalised w.r.t the background noise.

The calculated values of confinement energies are presented in Table 2.

Table 2. Confinement energies calculated for different CdSe QD samples

Label	$\lambda\ [nm]$	$E\ [eV]$
QD1	501	2.471
QD2	515	2.404
QD3	542	2.284
QD4	557	2.223
QD5	587	2.110

In order to plot confinement energy as a function of CdSe nanocrystal diameter, the following formula in the strong confinement limit has been used:

$$E_{1s1s}\ =\ E_g\ +\ \Pi^2 \cdot \left(\frac{a_B}{\frac{d_0}{2}}\right)^2 \cdot Ry^* - 1.786 \cdot \frac{a_B}{\frac{d_0}{2}} \cdot Ry^* - 0.248 \cdot Ry^*\ ,$$

where $E_g\ (CdSe)\ =1.84\ eV$, $a_B\ (CdSe) = 4.9\ nm$, $Ry^*\ (CdSe) = 16\ meV$.

Therefore,

$$E_{1s1s}\ =\ 1.84\ eV\ +\ \Pi^2 \cdot \left(\frac{2 \cdot 4.9\ nm}{d_0}\right)^2 \cdot 16\ meV - 1.786 \cdot \frac{2 \cdot 4.9\ nm}{d_0} \cdot 16\ meV - 0.248 \cdot 16\ meV\ . \quad (1)$$

The plot of confinement energy as a function of CdSe nanocrystal diameter has been shown in Fig. 2. The axes have been deliberately adjusted to the logarithmic axes of Fig. 3 of the Laboratory Guide Notes.
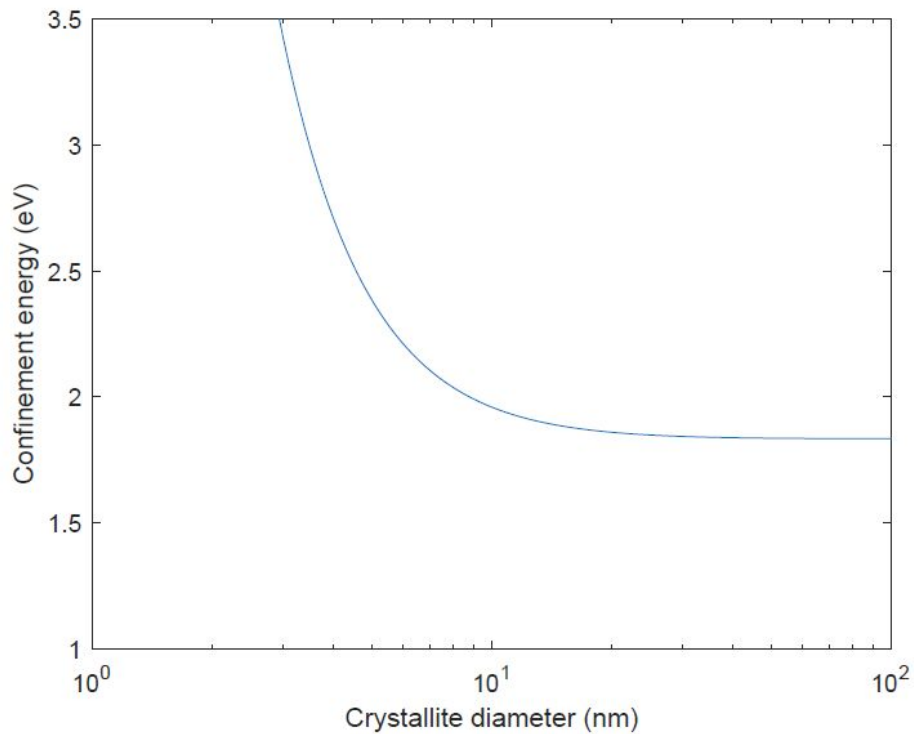

Fig. 2. Confinement energy as a function of CdSe crystallite diameter.

Task 2. Deduction of diameters of nanocrystals in the examined QD samples.

The crystallite diameters d_0 have been calculated for each QD sample from formula (1), using the values of confinement energy E calculated in **Task 1**. The obtained values have been shown in Table 3.

Table 3. Crystallite diameters calculated for different CdSe QD samples

Label	$E \ [eV]$	$d_0 \ [nm]$
QD1	2.471	4.672
QD2	2.404	4.928
QD3	2.284	5.514
QD4	2.223	5.909
QD5	2.110	6.947

The PL spectra for all CdSe QD samples have been plotted with reduction of background in Fig. 3 as well as have been noise-filtered with 'robust locally weighted quadratic regression (rloess)' in Fig. 4.
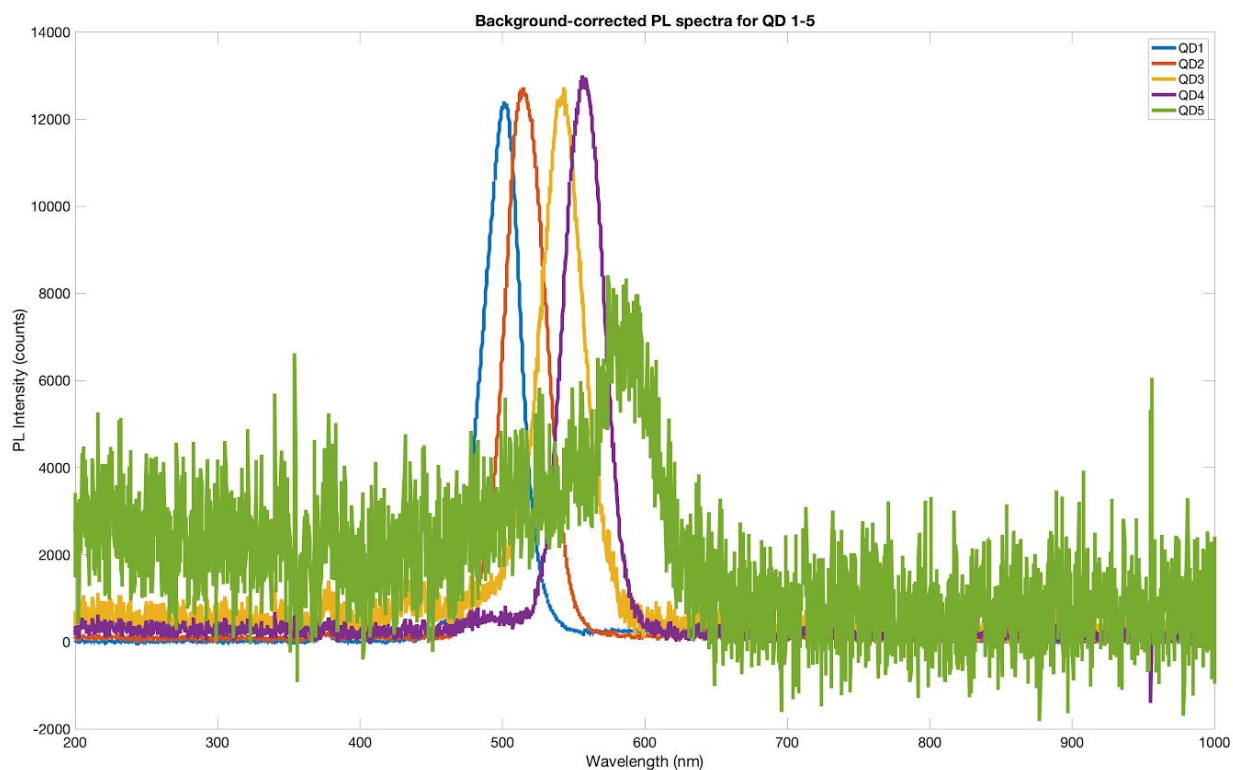

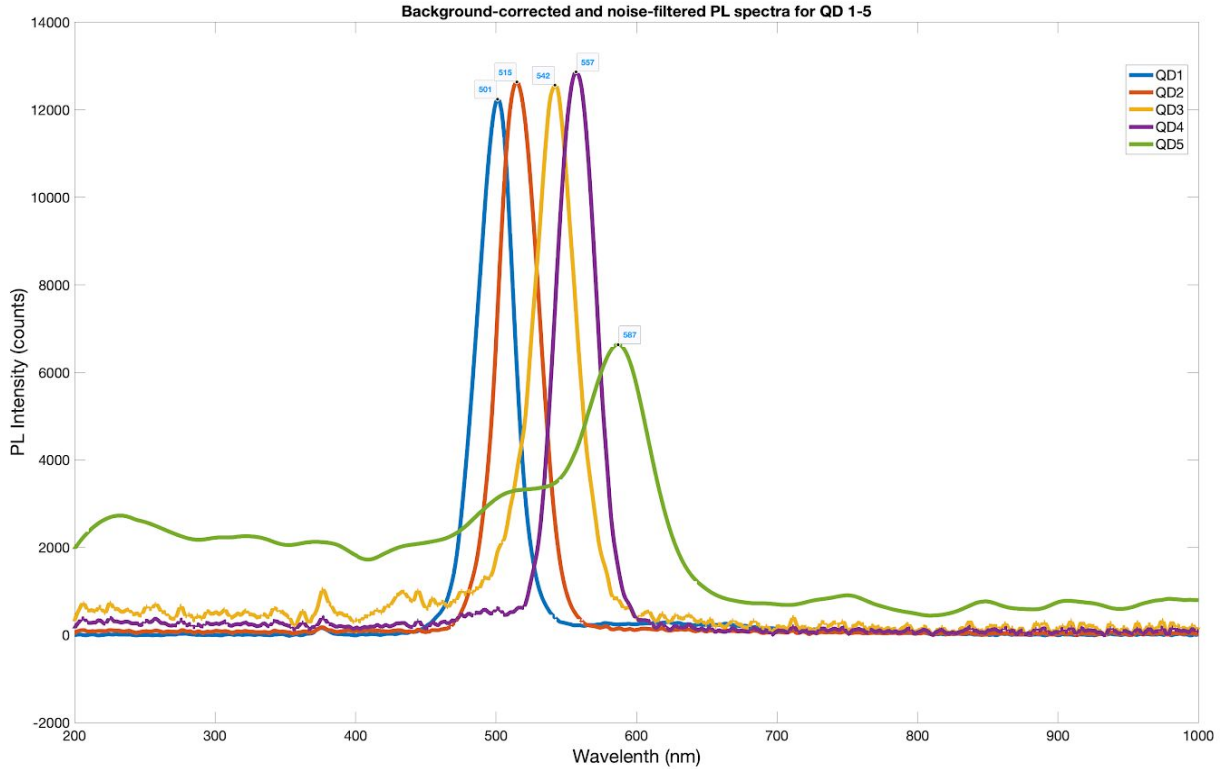Fig. 3. PL spectra of CdSe QDs with background correction.

Fig. 4. PL spectra of CdSe QDs (as in Fig. 3) when noise-filtered with 'rloess'.

As it can be seen from Table 3, higher crystallite diameters yield lower confinement energies. From Fig. 3 and 4 one can see that for the higher crystallite size, the absorption wavelength increases.

Task 3. Calculation of the QD1 nanocrystal size variation.

In this task, we chose the QD1 sample for calculation, as it had the highest signal-to-noise ratio. The QD1 nanocrystal size variation was found in a few steps.

3a. First, the emission wavelengths at half maximum of the QD1 peak were found and the FWHM was calculated (Fig. 5):

$$\Gamma_{exp} = |\lambda_1 \, [nm] - \lambda_2 \, [nm]| = |484 \, nm - 515 \, nm| = 31 \, nm \,.$$

3b. Then, the obtained value of FWHM was converted from nm to eV:

$$\Gamma_{exp} = \frac{1238}{\lambda_1} - \frac{1238}{\lambda_2} \, [eV] = 0.154 \, eV \,.$$

3c. The inhomogeneous linewidth (linewidth broadening due to size variations) was obtained:

$$\Gamma_{in \, hom} = \sqrt{\Gamma^2_{exp} \, [eV] - \Gamma^2_{spec} \, [eV] - \Gamma^2_{hom} \, [eV]} = \sqrt{0.154^2 - 0.01^2 - 0.045^2} \, eV = 0.147 \, eV \,,$$

where spectrometer resolution: Γ_{spec} = 0.01 eV and homogeneous linewidth: Γ_{hom} = 0.045 eV.
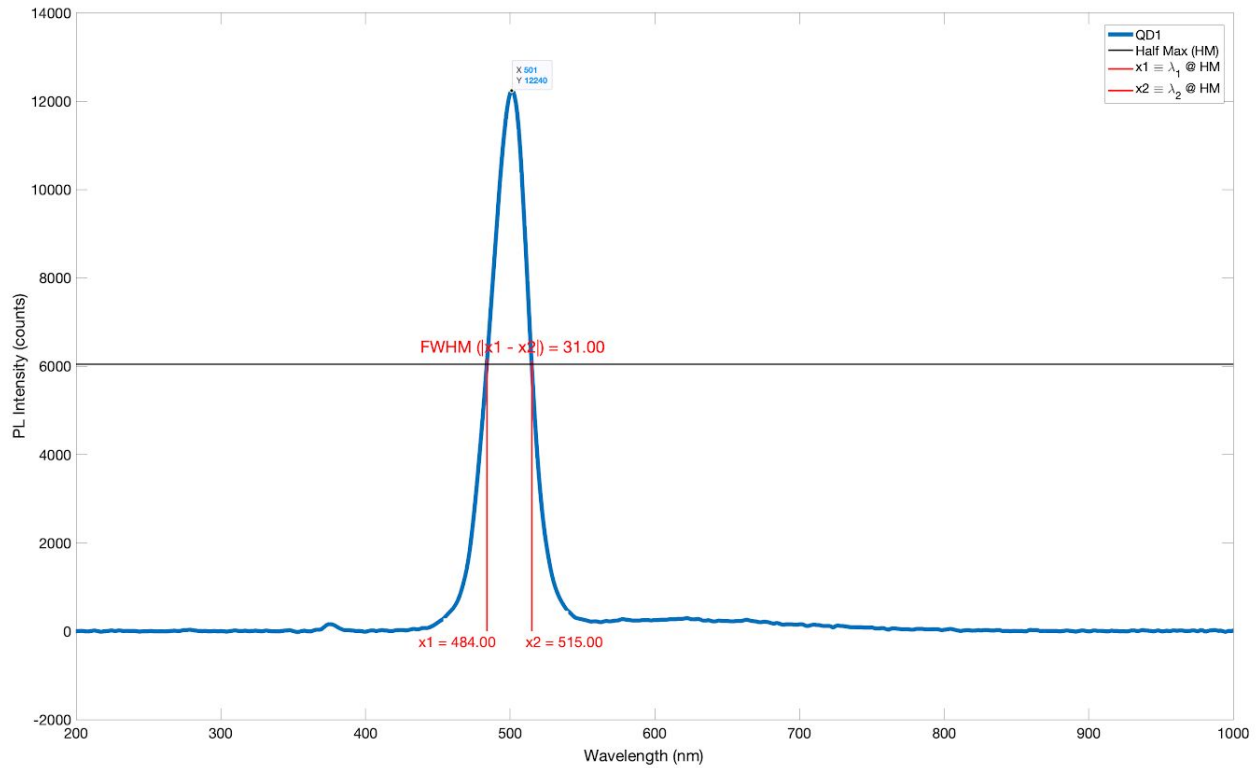
Fig. 5. Finding FWHM in PL spectra of CdSe QD1 (selected from Fig. 4).

3e. Then, the CdSe size-distribution was estimated using induced positions $\lambda_{1\ in\ hom}\ [nm]$ and $\lambda_{2\ in\ hom}\ [nm]$:

$$\lambda_{1\ in\ hom} = 1238/[\ \frac{1238}{\lambda_0} - \frac{\Gamma_{in\ hom}}{2}\ ] = 1238/[\frac{1238}{501} - \frac{0.147}{2}] = 516.359\ nm$$
$$\lambda_{2\ in\ hom} = 1238/[\ \frac{1238}{\lambda_0} + \frac{\Gamma_{in\ hom}}{2}\ ] = 1238/[\frac{1238}{501} + \frac{0.147}{2}] = 486.528\ nm\ .$$

3f. The nanocrystal size values $d_1\ [nm]$ and $d_2\ [nm]$ corresponding to $\lambda_{1\ in\ hom}\ [nm]$ and $\lambda_{2\ in\ hom}\ [nm]$ from the plot in Fig. 2, **Task 1** (and hence from formula (1)), were obtained:

$$E_1\ [eV] = \frac{1238}{\lambda_{1\ in\ hom}} = 2.398\ eV = 1.84\ eV + \Pi^2 \cdot (\frac{2 \cdot 4.9\ [nm]}{d_1\ [nm]})^2 \cdot 16\ meV - 1.786 \cdot \frac{2 \cdot 4.9\ [nm]}{d_1\ [nm]} \cdot 16\ meV - 0.248 \cdot 16\ meV$$
$$\therefore d_1 = 4.952\ nm$$

$$E_2\ [eV] = \frac{1238}{\lambda_{2\ in\ hom}} = 2.545\ eV = 1.84\ eV + \Pi^2 \cdot (\frac{2 \cdot 4.9\ [nm]}{d_2\ [nm]})^2 \cdot 16\ meV - 1.786 \cdot \frac{2 \cdot 4.9\ [nm]}{d_2\ [nm]} \cdot 16\ meV - 0.248 \cdot 16\ meV$$
$$\therefore d_2 = 4.432\ nm\ .$$

3g. The size variation $\Delta d\ [nm] = |d_2 - d_1|$ expressed in percentage to the mean size d_0 [nm], obtained (as d_0 = 4.672 nm for CdSe, QD1) in **Task 2,** is as follows:

i.e. $\gamma = \Delta d/d_0 = \frac{|4.432 - 4.952|}{4.672} \times 100\% = 11.13\ \%$.
$\because \gamma > 5\%$ (manufacturer-claimed size tolerance), $\therefore$ we cannot trust the manufacturer's claim.

This disagreement on size tolerance with the manufacturer's claim may be due to the agglomeration of CdSe QDs dispersed in their respective solution, with time. A quick re-dispersion of these QD solutions in a vibrational centrifuge may help in breaking these QD agglomerates, and in getting back the uniform

size distribution (and hence the claimed size tolerances) similar to when the QDs were freshly prepared by the manufacturer.

Task 4. Examination of effect of the air exposure to luminescence properties of nanocrystals.
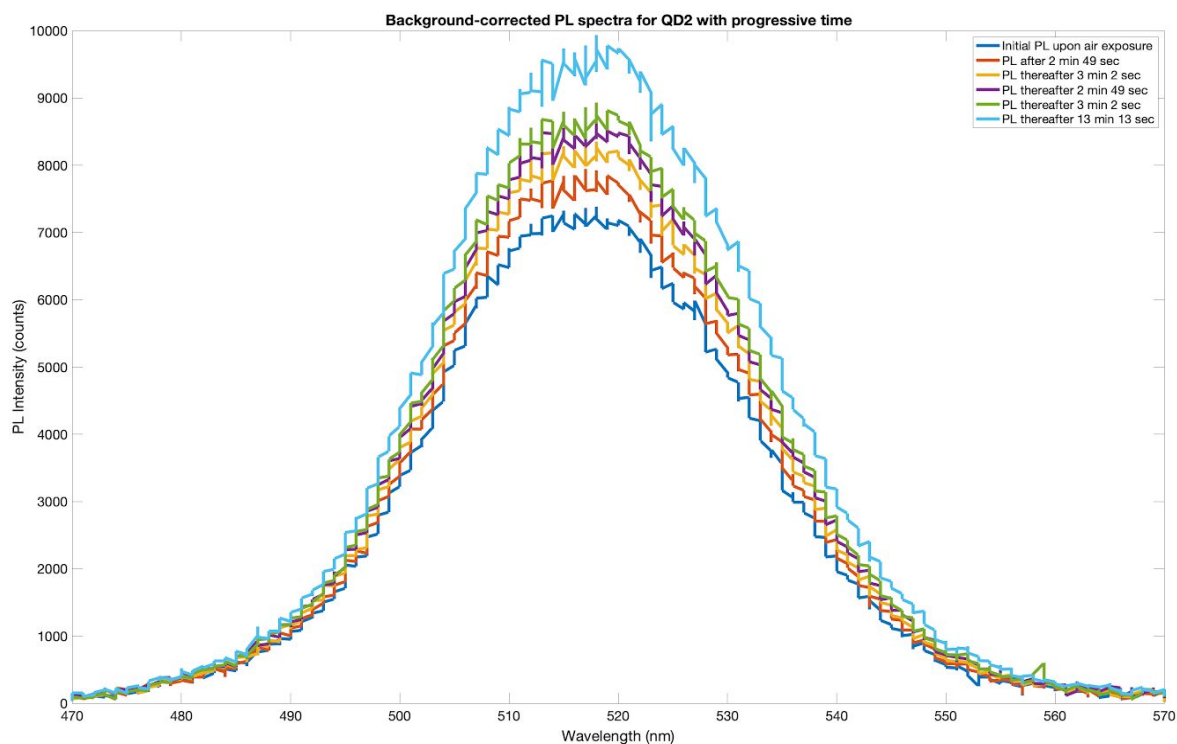

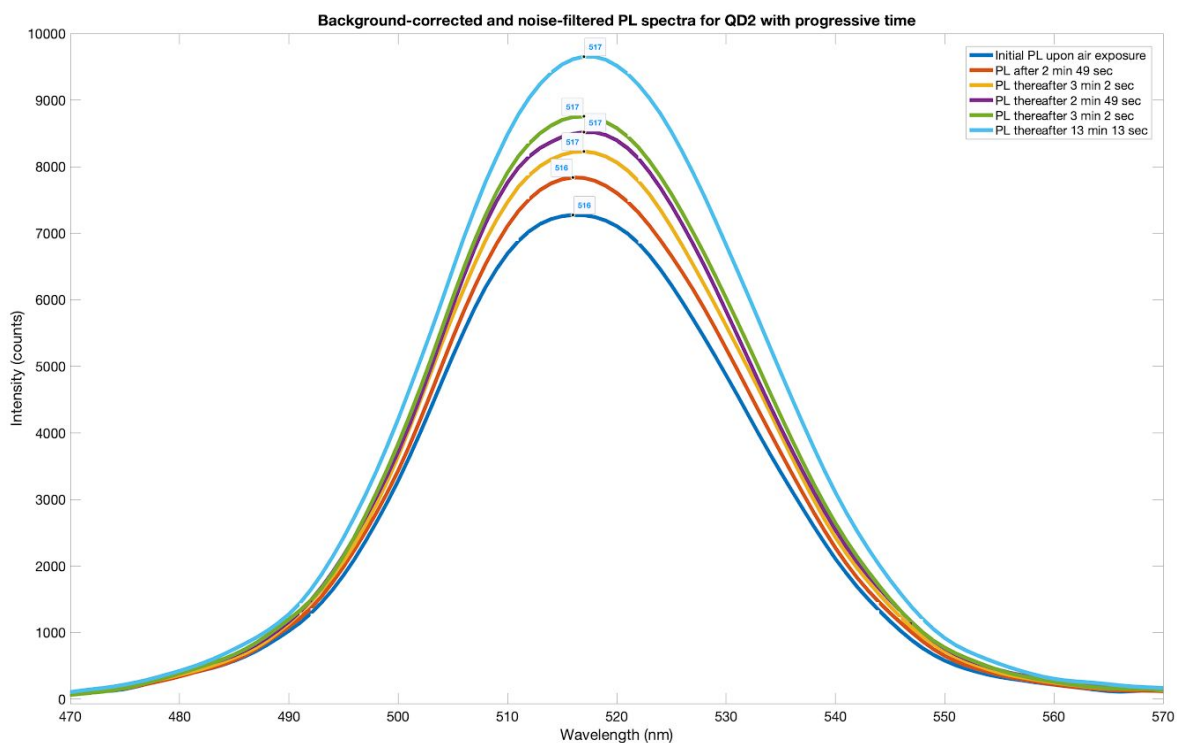Fig. 6. PL spectra of QD2 exposed to ambient, over time, with background correction.

Fig. 7. PL spectra of QD2 exposed to ambient, over time (as in Fig. 3), when noise-filtered with 'rloess'.
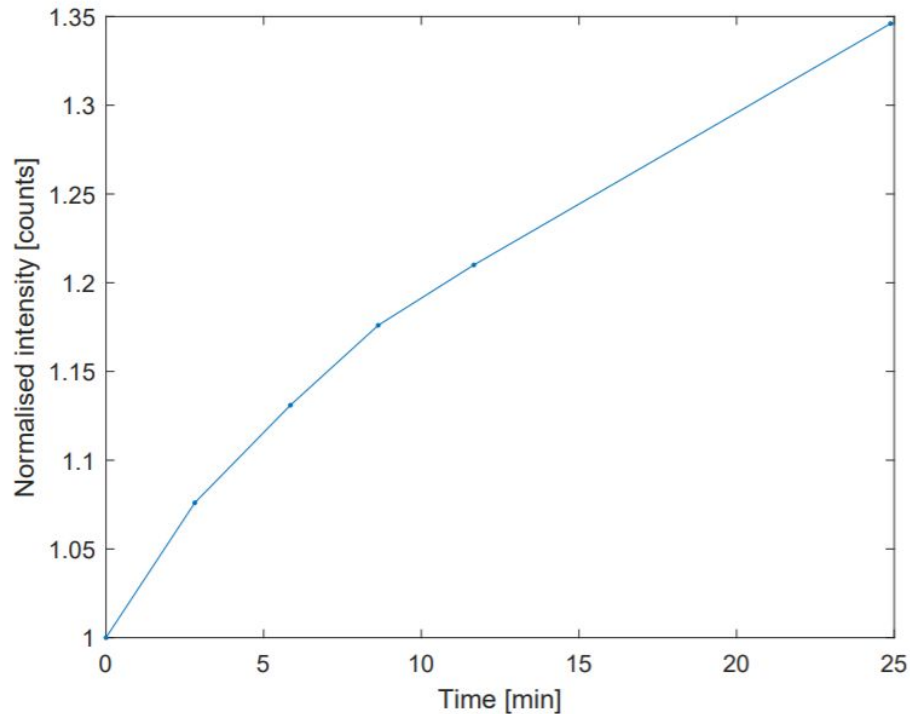
Fig. 8. Normalised intensity of QD2 PL with background correction, over time.

Fig. 6 and 7 show PL spectra (with background and background-noise reduction, respectively) of QD2 exposed to ambient, over a period of ~25 min, while a few measurements were taken. In Fig. 8 there has been shown a plot of the normalised intensity of photoluminescence of QD2, with reduction of background, versus time. The normalised intensity values have been obtained as ratios of the intensities measured after specific periods of time, to the initial photoluminescence intensity (at t = 0).

As it can be seen in Figure 6, 7 and 8,

- PL peak red-shifts with time. The reason behind that may be the ZnS shell oxidation and decomposition in air, exposing CdSe core. Now, due to weak confinement of core excitons in this shallow spherical well, carriers may start to escape out leading to little or eventually no possible electron transitions to occur when optically excited, with progressive time.
- There is an increase of the peak intensity of the ambient exposed QD2, over time. Similar thing has been reported by Talapin et. al, where they suggested that dislocations and grain boundaries present in a ZnS shell of CdSe/ZnS QDs promote diffusion of oxygen to the CdSe core. [2] Hence, these oxygen defect states in the core may contribute to an increase in PL intensity with time.
- Peak linewidth also increases with time, and this may be indicative of increasing degree of inhomogeneous QD size distribution upon oxidation and/or decomposition in air with time.

Task 5. Comparison of PL of CdSe and porous Si nanocrystals samples.

PL spectra of CdSe QD5 (Fig. 11) have been chosen to compare its peak characteristics with that of Si nanocrystals (Fig. 9 and 10). This is because of its widest linewidth, highest peak position and lowest intensity among other CdSe QDs (worst-case scenario of QD1-5), hence when PL spectra of Si nanocrystals is compared with that of QD5 it is imperative that the results would apply same to all other CdSe QDs.
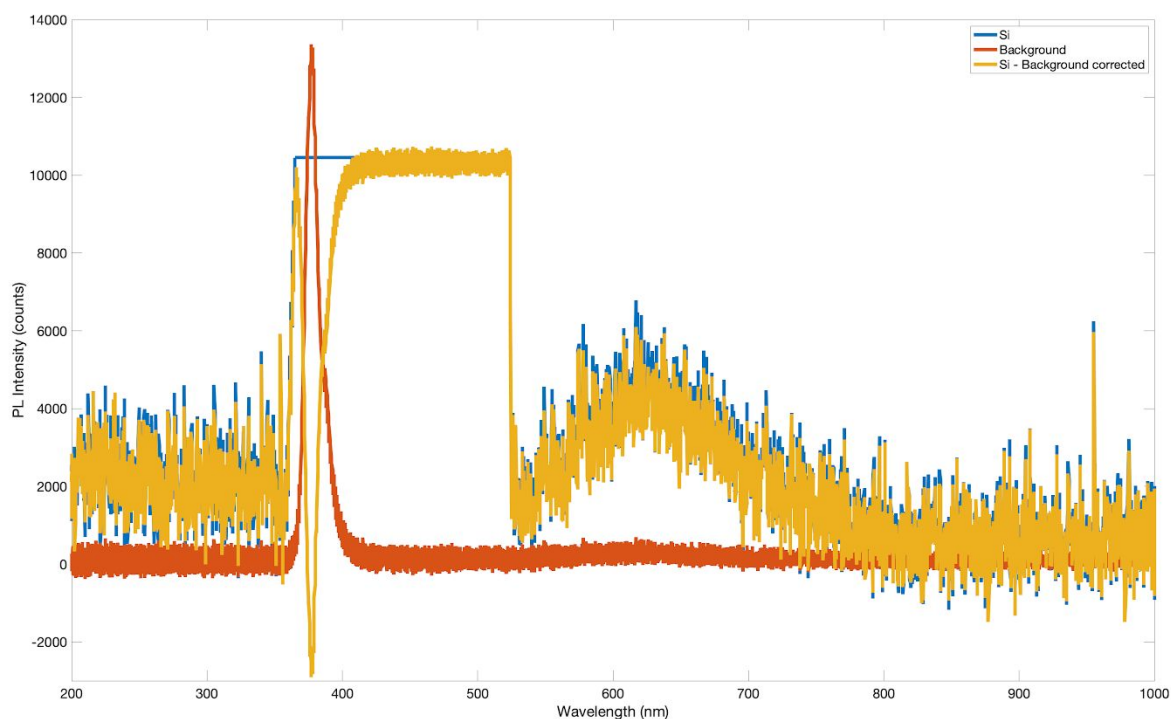
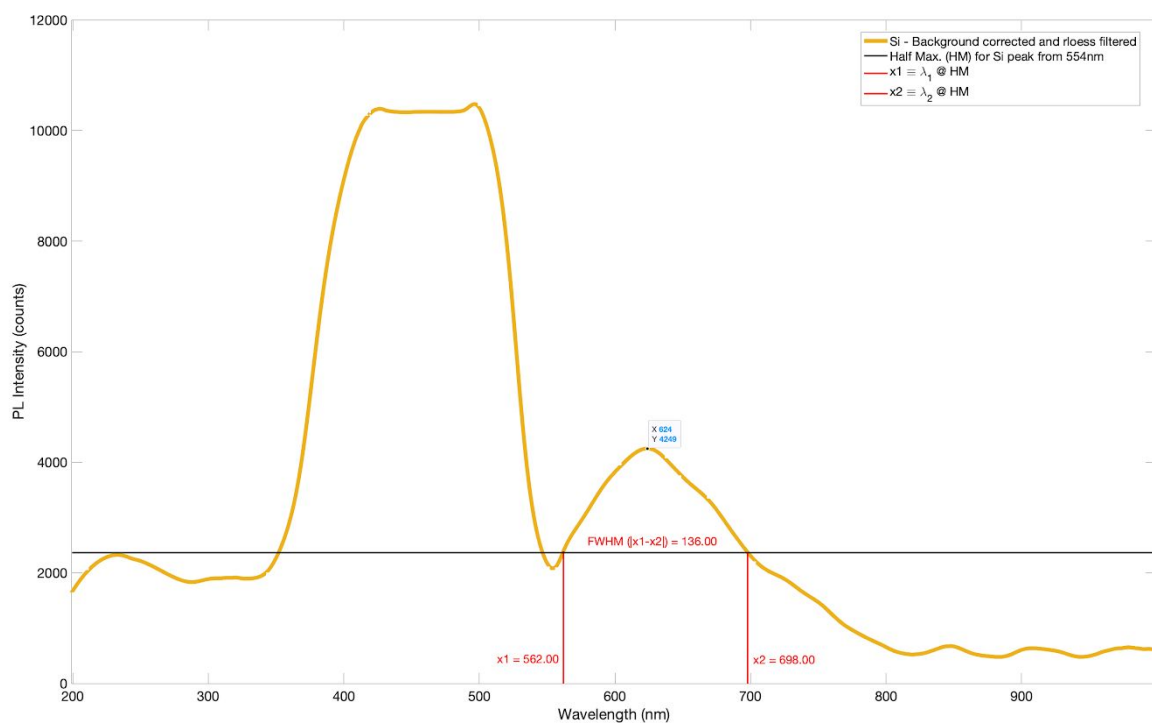Fig. 9. PL spectra of Si nanocrystals with background correction.

Fig. 10. PL spectra of Si nanocrystals with background correction when noise-filtered with 'rloess'. Note that spectra only from 554 nm is considered for FWHM analysis, and spectra between 360 - 554 nm is attributed to external noise.
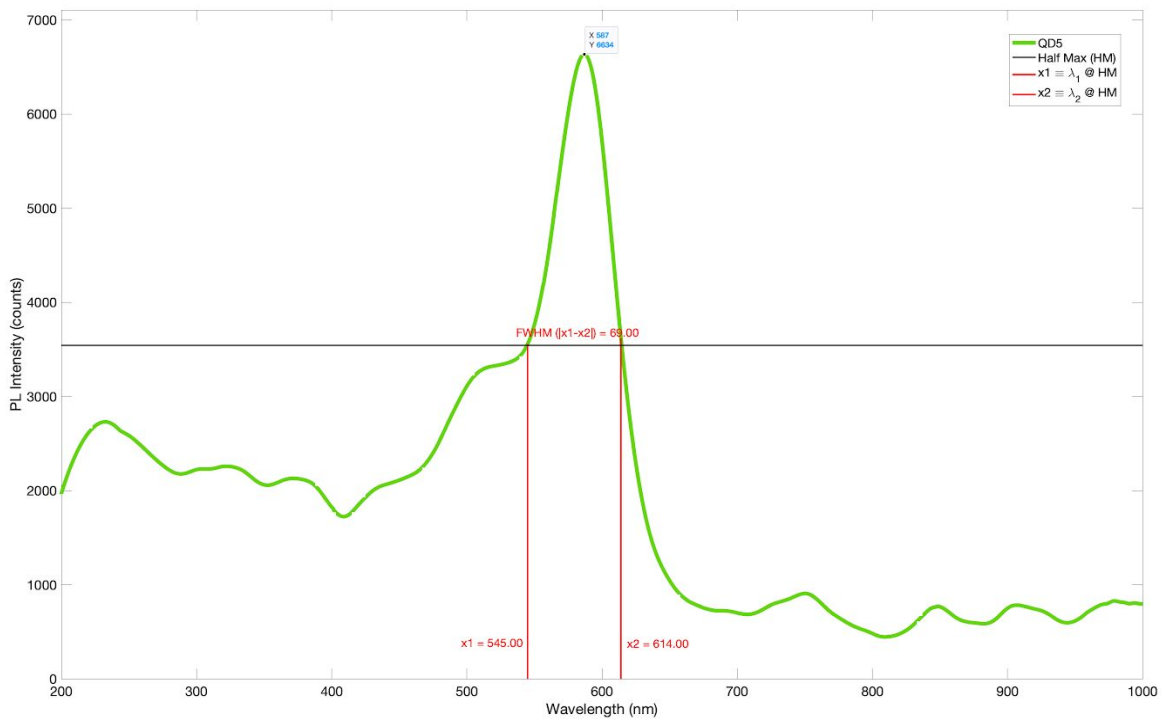
Fig. 11. Finding FWHM from PL spectra of CdSe QD5 (widest linewidth of QD1-5, from Fig. 4).

Based on the aforementioned comparison, the following conclusions have been made -

- Si peak is broader (FWHM = 136 nm) when compared to the peak of CdSe QD5 (FWHM = 69 nm), and this is due to a greater degree of inhomogeneous size distribution of the porous Si nanocrystals.
- Si peak position is lower in energy (624 nm) than CdSe QD5 (587 nm) due to its lower bandgap than CdSe QD5 first confinement energy.
- Si peak intensity is lower (4249 counts) than that of CdSe QD5 (6634 counts), and this may occur due to a lower number (amount) of Si nanocrystals than CdSe QD5s dispersed in respective solutions. However, since the integration time used for examination of QD5 was higher than Si (QD5: 23 sec, Si: 16 sec), the value of higher measured intensity could have been then enhanced also by the higher integration time.

4. Conclusion

Main properties of PL of QDs have been examined. Quantum dot dependence of confinement energy on the crystallite diameter has been shown as well as the effect of a QD air exposure has been analysed and discussed. The PL of QDs has been compared with the PL of a powder sample.

5. References

1. Chon, Chan H., and Li, Dongqing. "Quantum Dot". In: Encyclopedia of Microfluidics and Nanofluidics. New York, NY: Springer New York (2015), pp. 2905–2907.

2. Talapin, Dmitri V., Mekis, Ivo, Götzinger, Stephan, Kornowski, Andreas, Benson, Oliver, and Weller, Horst. "CdSe/CdS/ZnS and CdSe/ZnSe/ZnS Core−Shell−Shell Nanocrystals". In: The Journal of Physical Chemistry B 108.49 (Dec. 2004), pp. 18826–18831.