SPECTROMETRIC EVALUATION OF CARBON QUANTUM DOT SIZE DISTRIBUTION

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Abstract: The discovery of graphene affected a large amount of scientific fields, as the material under correct circumstances can have amazing properties applicable in numerous disciplines. Because of graphene's interaction with light and carrier physics it also makes a good material for the construction of quantum dots. It is important to be able to measure the size of the quantum dot after fabrication, because many of the properties vary with its radius. Photoluminescence is an effect dependant on the radius of the dots, and coupled with proper calculation it can provide a quick and straightforward way to analyze the spread of the dot sizes in the sample.

Keywords: Quantum dots, graphene, photoluminescence

1 INTRODUCTION

With the increase of interest in usage of nano-scale parts and components and the improvement of our ability to fabricate them the focus of today's research is being shifted more towards their implementation in modern science. Even when there is still a lot of ground to cover, the first products of quantum mechanic engineering are being slowly integrated into existing technologies and we can only expect their rise to prominence. One such product is the creation of quantum dots. Objects in nanometer scale, usually created from a semiconductor material, have different optical, electric and magnetic properties then they would have in a normal scale. Because of quantum entrapment [1] they can absorb and then release photons of discrete energy depending on the size of the dots. This effect called photoluminescence can also be used to identify the dots by their size, since the amount of energy stored and released directly depends on the radius of the illuminated dot [2]. Dots created from graphene, a single layer of sp^2 bonded carbon in honeycomb lattice [3] can also be used to create the desired quantum dot effect. Even though the graphene itself is not a semiconductor, dots manufactured from it also function as quantum traps, absorbing and then releasing the photons. Their properties slightly differ because of the crystallographic composition and the material itself [4], but the photoluminescence is still quite well observable. In the process of fabrication of quantum dots it is virtually impossible to ensure a uniform size for all of the dots created [5] and therefore it is important to be able to quickly and easily identify their size distribution before further use.

2 MEASUREMENT SETUP AND CALCULATION

Measurement of the samples was performed by an Avantes AvaSpec 2048 spectrometer. The measured sample was placed in a chamber with a diode, working at 12V and 15 mA with a maximum output at 405 nm. The measurement fiber was placed perpendicularly to the diode – the source of the illumination, to limit the influence of the excitation light on the resulting signal. Another measurement fiber was installed directly opposite the diode for a potential measurement of the transmitted light. This remained unused during the acquisition of the output signal in our case.

The coverable measurement chamber with the fibers for signal and power wires for the diode can be seen in the figure 1.
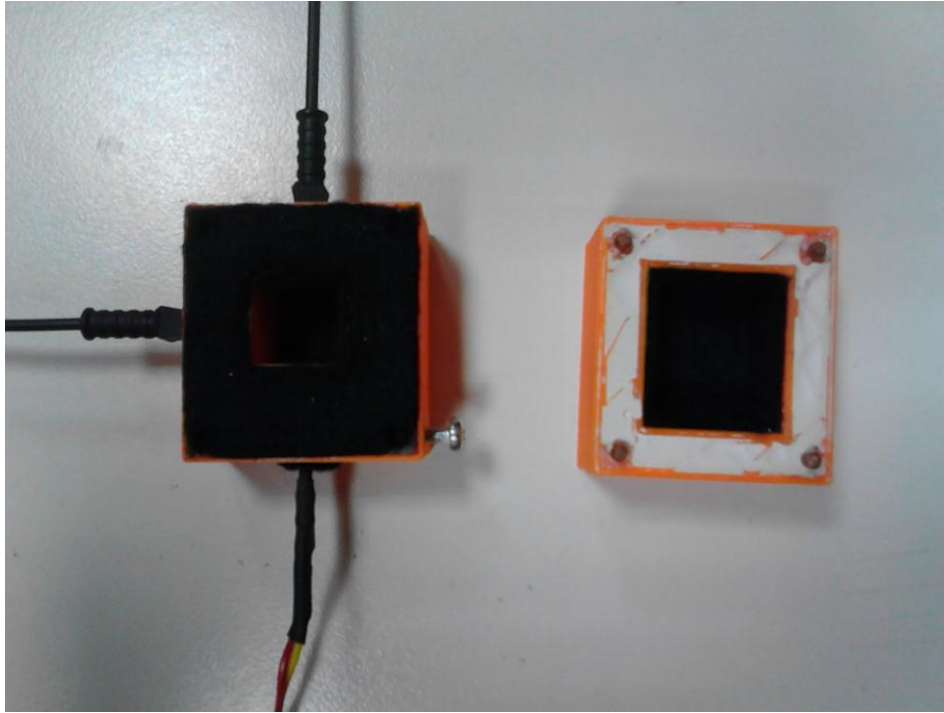

Figure 1: Measurement chamber with cover.

Because no detector has the same sensitivity in the whole detection range it is capable of, a correction of the measured signal has to be performed. The two main possibilities are either acquiring the sensitivity curve from the manufacturer of the device or measuring the background and then subtracting it from the main signal itself. Because a carbon quantum dot photoluminescence measurement is plagued by a number of factors affecting the intensity of the signal at different wavelengths [6] the background method was selected for this endeavor. Because the quantum dots are immersed in water, a signal for background with only water was acquired. Afterwards the acquisition of the quantum dot photoluminescence signal was carried out and both signals were processed in MATLAB. Even though the setup should limit any influence of the excitation signal on the detector, its peak is clearly visible in figure 2 with peak on 405 nm, as is expected from the light source used. Since it is present in both background and main signal measurement, it can be subtracted without it remaining a problem. It is necessary to normalize the values, because the integration time was changed for every measurement to provide the cleanest signal possible. On the purified curve the maximum was located and the relevant range of wavelengths was chosen as being greater than 25% of the maximum value. Anything below was judged to be irrelevant either because of the light pollution from the source or because of the detector imprecision. The smoothness of the signal is dependant not only on the quality of the detection device and the measurement chamber but also on the approximative signal processing procedures applied after the acquisition of the signal. For the best informational value of the result and the limitation of possible artifacts and distortions caused by post processing no smoothing or approximation was used. Additional measurements of the effects of lighting levels outside of the measurement chamber were performed and the level of intensity was three orders of magnitude below the values measured from the signal itself, making them irrelevant to the resulting data.
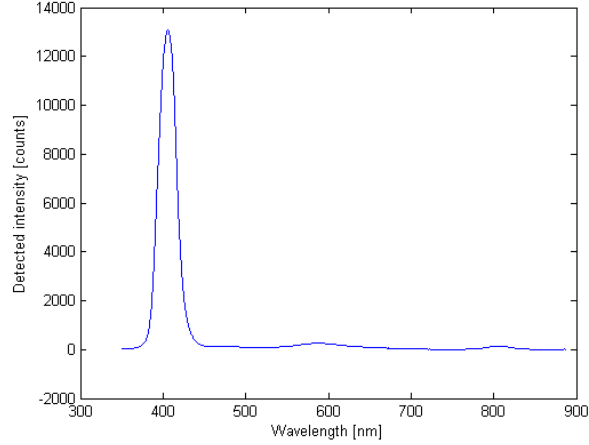
Figure 2: Background signal with visible excitation signal.

2.1 SIZE CALCULATION

As per the theory of quantum confinement in quantum dots [7] the size of the dot affects the wavelengths of the released photon because of photoluminescence. The wavelength distribution therefore also carries the information about the quantum dot size distribution. The equation for the average radius R of the quantum dot calculation is as follows:

$$R = \sqrt{\frac{\hbar^2 \pi^2 \left(\dfrac{1}{m_e} + \dfrac{1}{m_h} \right)}{2 \left(E_g^{QD} - E_g^{bulk} \right)}} \ , \tag{1}$$

where $\hbar$ is the reduced Planck constant, m_e is the effective mass of electrons for layered graphene, m_h is the effective mass of holes, the E_g^{bulk} is the bandgap value of layered graphene and E_g^{QD} is the effective bandgap of the quantum dot, which can be calculated from Planck constant h, speed of light c and wavelength λ by the equation:

$$E_g^{QD} = \frac{hc}{\lambda} \ . \tag{2}$$

2.2 ISSUES WITH CARBON QUANTUM DOTS

While the aforementioned equations and procedures would be enough to calculate the exact quantity of semiconductor quantum dots, there are some factors present in carbon that affect our ability to do so. One of the most important factors is the shape and edge effect [8]. Graphene sheet can be cut along different crystallographic directions, which results in different types of edges, like armchair and zigzag edges. This together with the shape of the quantum dot, as not every dot has to be spherical, affects the optical, electronic and magnetic properties greatly. These different modifications can result in different energy of the photoluminescent spectrum which limits our ability to assign specific values of energy to all of the quantum dots, as the present dots are usually a mix of different shapes and edges. If the dots were specially manufactured to be all of one specific form, a more precise quantification would be possible. When the dots are mixed, as they usually are when not adhering to a precise form of fabrication, it prevents us from determining the absolute numbers of the dots. The relative numbers, that is what size of dots is the most common in the measured sample, are still calculable.

3 RESULTS

After taking the anomalies and issues of the carbon quantum dot behavior into account, it was decided that the best approach would be the background subtraction. With the current equipment it is virtually impossible to quantify the number of the quantum dots from the intensity of the signal, but the size distribution is still measurable. If we focus on the relative amount rather than the absolute one, we can omit the sensitivity function of the detector and use background measurement, in this case water since the quantum dots are immersed in water as well. After measuring both background signal and the signal with quantum dots present, the difference was not clearly quantifiable by eye, but the prepared algorithm was able to purify the result and provide us with quantum dot photoluminescence signal. After acquisition of the clean signal the calculation was performed and the signal width was matched to the distribution on the calculated curve. The matched wavelength distribution can be seen in figure 3, while the matched wavelength size dependency can be seen in figure 4. The resulting spread of sizes proved to be constant throughout several measurements on quantum dots from the same source with only minor deviations in the detected signal shape.
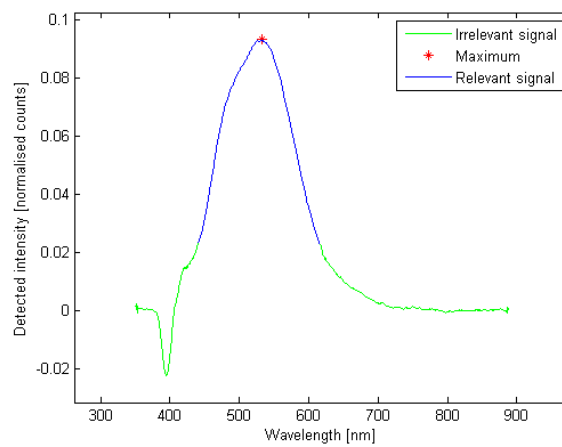

Figure 3: Wavelength distribution of the measured and clean quantum dot signal with matched intensities.
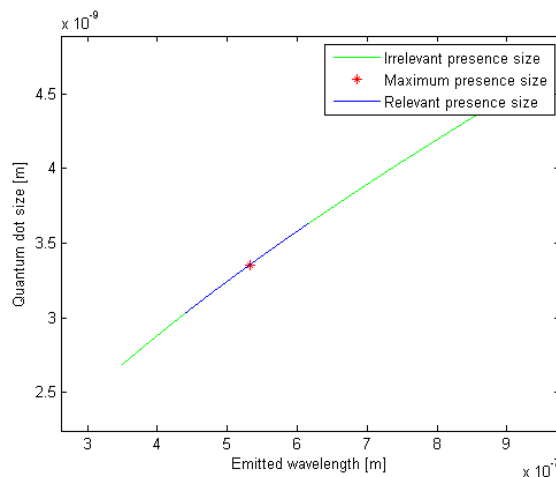

Figure 4: Calculation of the wavelength size dependency for graphene quantum dots with matched measured distribution.

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4 CONCLUSION

The proposed method of size distribution analysis of the carbon quantum dots via photoluminescence signal detection provides us with quick and cheap way of measurement. The downside of the method, the inability to quantify the absolute number of the quantum dots present in the sample, could be rectified by the usage of a better spectrometer with available detector sensitivity curve and a minor adjustment to the computational algorithm.

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