

RISE Worldwide Internship Report

Topic: Agro-based Synthesis of Carbon Quantum Dots for Thermal Sensing and WLED

Institution: National Institute of Technology Kurukshetra

Sponsor: German Academic Exchange Service (DAAD)

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Duration: 15. June – 31. August 2022 (10 weeks)

1 Travel Arrangement

The visa was not required for me because I had a Nepalese passport. I booked a direct flight from Frankfurt via Air India. The fare was comparatively cheaper among other airlines. It is also important to note that it is mandatory for everyone to fill up a form called „Air Subidha“ and provide the proof of vaccination against COVID-19 prior to the travel.

After arrival at Indira Gandhi International Airport in Delhi, there are few means to go to Kurukshetra.

1. The easy, cheap, and fast means is the train, but one needs to book the ticket at least few days prior to the travel. You can get to the train station in New Delhi or Old Delhi via metro (recommended) or bus. You can easily find trains boarding to Kurukshetra from either train station. Get off at the Kurukshetra Junction and take an auto-rickshaw to Kurukshetra University second gate. NIT Kurukshetra can be reached on foot from the gate
2. Bus from the Interstate Bus Terminal (ISBT), which can be reached from a bus available at Airport Bus Terminal 18. You need to get off at New Bus Stand in Kurukshetra, and take an auto-rickshaw to Kurukshetra University second gate. NIT Kurukshetra is few minutes walk from the gate.

It is necessary to have offline maps saved in your smartphone for easy navigation. One cannot use any public Wi-Fi networks without verification using Indian SIM-Card. Thus, either to save offline copy of the maps or get a local SIM Card. The mobile data plan is very cheap in India. It costs about €4.88 per month for daily renewable 2.5 GB data plan.

2 Accommodation and Daily Life

NIT Kurukshetra is a campus university, and students reside in student dormitories inside the area of NIT. Like other guests, I was also provided accommodation in a guest room, adjoined with a student dormitory. The 3-course meals were provided. You can always try to go to shops and canteens inside NIT or Kurukshetra University for snack options.

The NIT Market has everything for you to offer. From pharmacy, hairdresser, everyday grocery to fruits stall. Essentially, you never have to leave the campus for everyday needs. You can either visit banks or foreign exchange office to exchange euros to INR. This option might be quite expensive. I suggest one to transfer money to someone's account through „Sofort Klarna“ and ask to withdraw. This will save few euros in exchange.

Kurukshetra is a holy place for Hindus, and you can often see temples and prayer houses inside the city. Most of the people are vegetarian here . Apart from religious point of view, Kurukshetra also hosts exceptional historical importance of Indian culture. Places like „Dharohar“ are center point for understanding local tradition that was common in the past. I highly recommend anyone to visit „Dharohar“. Other tourist places are Kurukshetra Panorama, Krishna Museum, Bramhasharobar. Chandigarh is nearby large city. Rose garden and rock garden are famous tourist places.

3 Research Project

The primary focus of my research project was to synthesize carbon quantum dots from agro-based source for production of White Light Emitting Diode (WLED) and thermal sensors. The quantum dots are realized as fluorescent nano-particles, and they are very well known for this optoelectric property. They are often used in television display and cell imaging techniques [9]. The generic source of the quantum dots is heavy metals that have certain level of toxicity to human health [4]. Carbon quantum dots (CQDs) prepared from agro-based sources would have minimum toxicity and can also help to solve the environmental challenges of waste management. Many agro-based sources that are rich in citric acid can be considered as good sources of CQDs [3]. We took lemon peel as our source for the CQDs. We performed few characterization techniques such as Fourier Transform Infrared Spectroscopy (FTIR), X-Ray Diffraction (XRD), and photoluminescence (PL) to understand the properties of the synthesized CQDs. The final part of the project was to look for applications of the agro-based CQDs. Thermal sensing and White LED were our primary focus on the application domain.

4 Technical Background and Working Method

Quantum dots are semiconductor nanoparticles with the property to emit photons of specific wavelength upon excitation. The emission wavelength depends on the particle size, correspondingly the band gap. The frequency of the emitted light increases as the particle size decreases. The theory of quantum dots can be explained with Brus equation, which describes the energy gap of three-dimensional nano particles.

$$\Delta E(r) = E_{gap} + \frac{h^2}{8r^2} (1/m_e^* + 1/m_h^*)$$

where $\Delta E(r)$, E_{gap} , h , r , m_e^* , m_h^* are emission energy, band gap, Planck's constant, radius of the quantum dot, effective mass of electron, and effective mass of holes respectively [2].

Carbon quantum dots are not different from other quantum dots, apart from their source as a carbon. In general, citric fruits like lemon or mango are used for synthesis. Other items like onions, bread can also be used [3, 1]. The common synthesis processes used today is shown in the Figure 1.

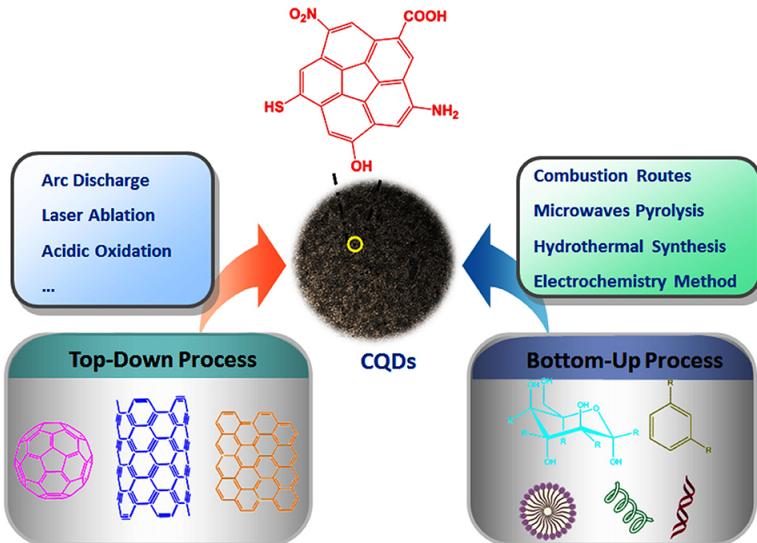


Figure 1: Synthesis Process for Carbon Quantum Dots. [8]

We followed the microwave heating and hydrothermal process for our experiment. Initially, peel from one lemon was taken and cut into small pieces of size less than 5mm. The experimental details for both microwave and the hydrothermal methods are outlined below.

4.1 Synthesis Methods

4.1.1 Microwave Heating Method

The cut lemon peel along with 20 ml of deionized (DI) water was heated in a microwave with settings 800 W for a period of 2-3 minutes or until they turn brownish. The result was mixed with 5ml ethanol. For preliminary test, we used a laser of wavelength 405 nm to excite the carbon quantum dots and observed the emission in the green region. For characterization of the prepared quantum dots, we did the photoluminescence measurement.



Figure 2: Photographs of CQDs prepared through microwave heating method in (a) normal condition and (b) exciting with blue laser.

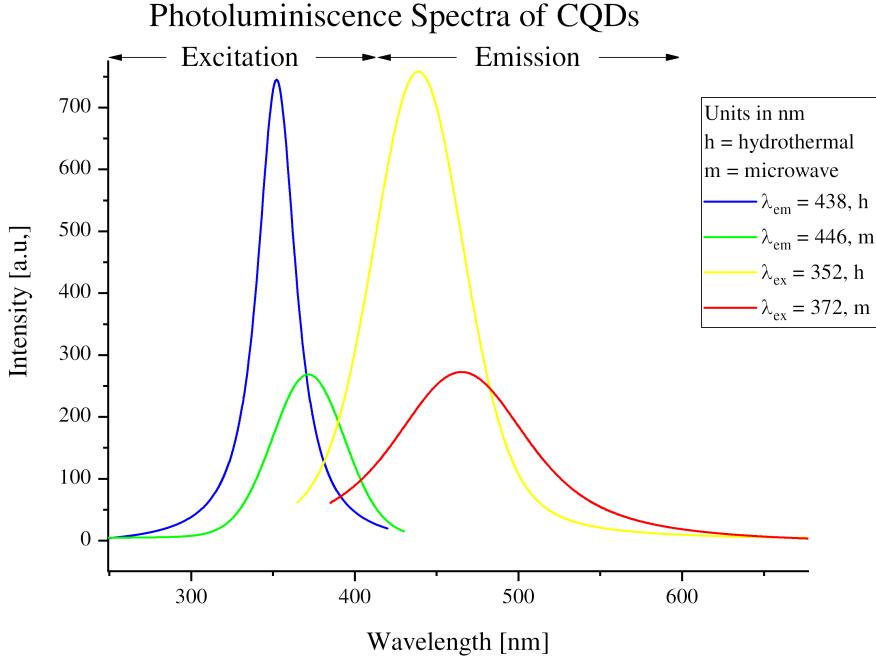


Figure 3: Photoluminescence Characteristics of CQDs from Microwave Heating and Hydrothermal methods

The emission wavelength is peaked at around 460 nm when the excitation was set to 372 nm. Similarly, the excitation wavelength is peaked at around 370 nm, when the emission wavelength was set to 446 nm. In the Figure 2 (b), when the CQDs from microwave was excited with the blue laser, the emission showed the red-shifting, i.e. in the green region. Thus, we can easily tune the wavelength of the emitted light in between the far-blue and near-green region by shifting the wavelength of the excitation source.

The observed UV spectrum is graphed below. It shows $n - \pi^*$ and $\pi - \pi^*$ transition at 297 nm due to the presence of carbonyl group, as demonstrated in [7].

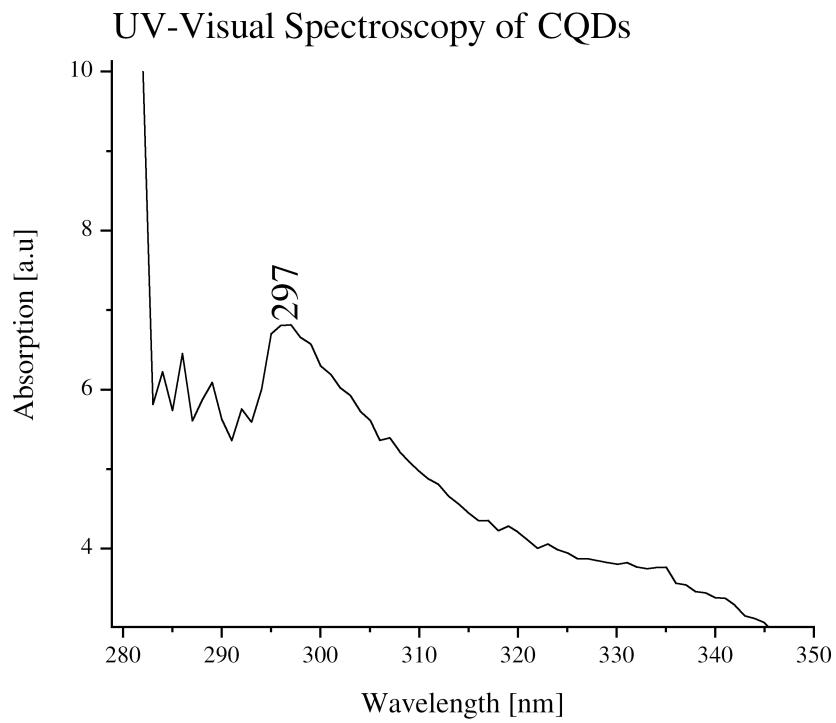


Figure 4: UV Spectrum of CQDs.

4.1.2 Hydrothermal Method

About 50ml of DI water was added to the small pieces of lemon peel. The mixture was placed inside an autoclave. The autoclave was placed inside a furnace at 200 degrees centigrade for 12 hours. The result was solid black. The mixture was crushed into powder form with the help of mortar and pestle. The powdered form was suitable to carry out FTIR spectroscopy and XRD measurements.



Figure 5: Photographs of CQDs prepared through hydrothermal method in (a) normal condition and (b) exciting with blue laser.

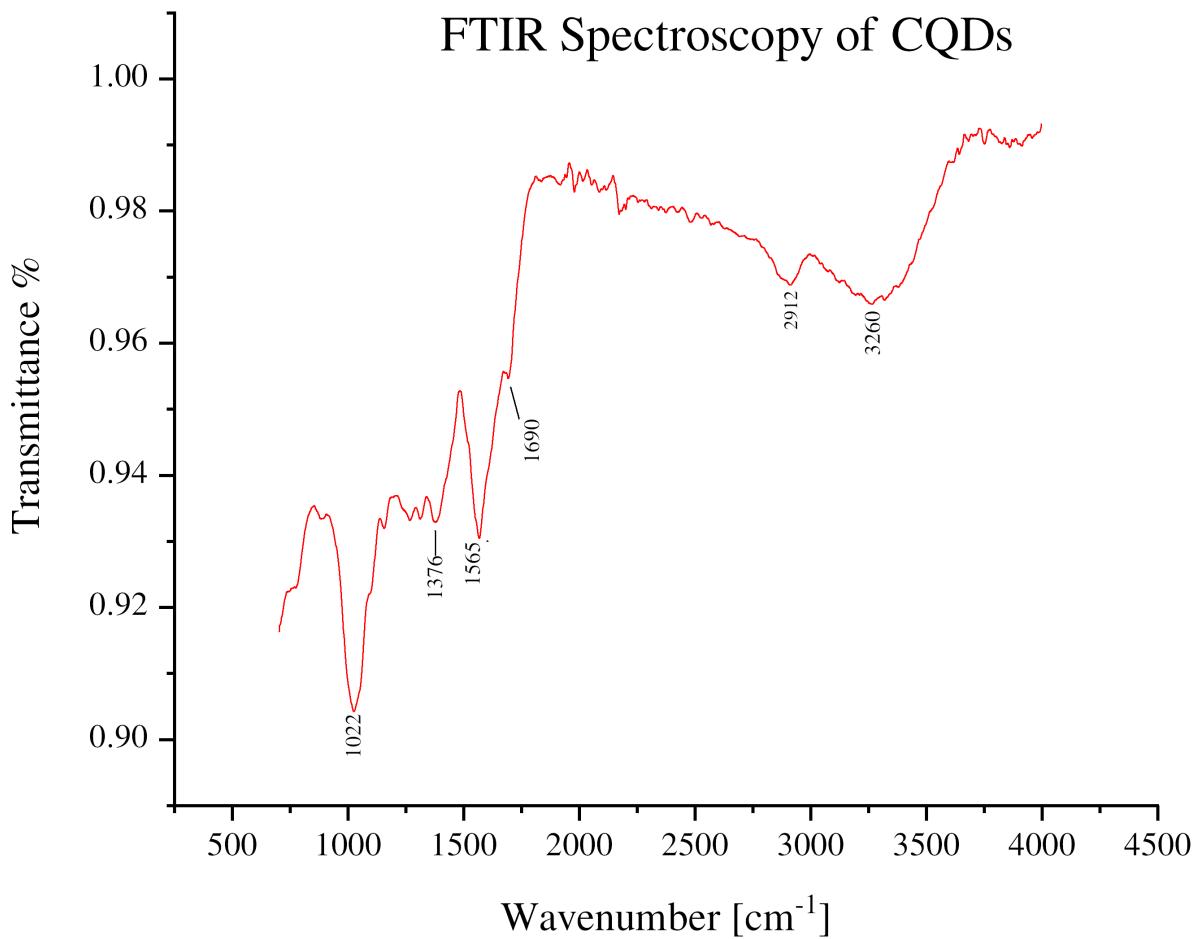


Figure 6: FTIR Spectroscopy results of CQDs prepared through hydrothermal method

The FTIR measurement is crucial to determine the presence or absence of the functional groups in the material. It shows the presence of -OH group due to broadening of the peak at 3260 cm^{-1} . Similarly, the peak at 1690 cm^{-1} is due to the existence of C=O. The peaks at 1565 cm^{-1} and 1376 cm^{-1} are due to the presence of -COO^- . Peak at 2912 shows the C-H vibration, which shows the excellent solubility nature of the CQDs. The results are comparable to [7].

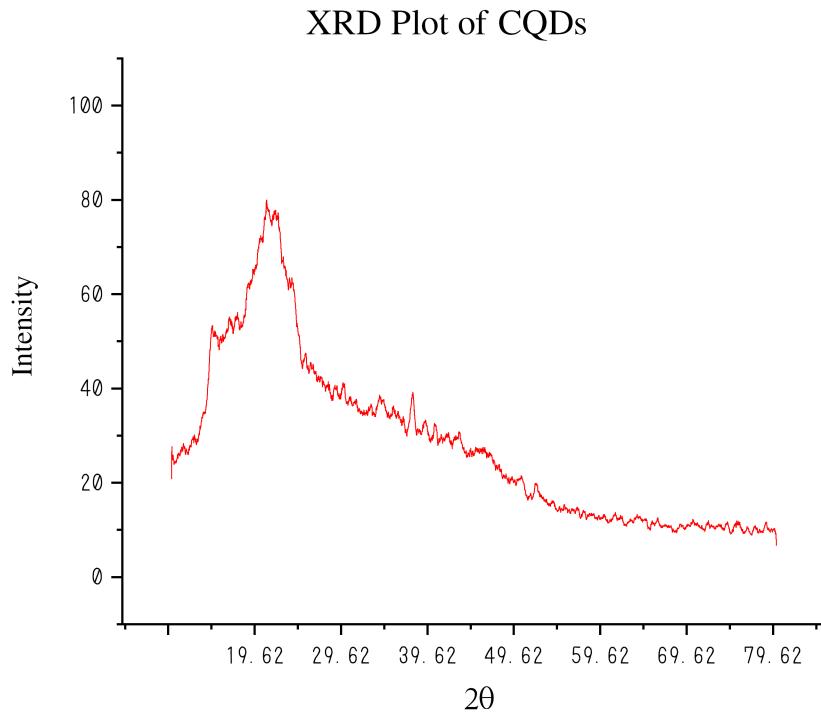


Figure 7: X-Ray Diffraction Graph of CQDs prepared through hydrothermal method

From XRD result, the broadening of the peak at around 20° suggests the larger interlayer spacing and the presence of the oxygen-containing group in CQDs. [5]

The powdered form of CQDs was then mixed with DI water. The result was centrifuged at 6000 rpm for 20 minutes. The resulting solution was then used for photoluminescence measurement. From the Figure 3, the emission peak is observed at around 440 nm, when excited at 352 nm. Similarly, the excitation peak is at around 350 nm, when emission wavelength was set to 438 nm.

The synthesized quantum dots from microwave heating and hydrothermal methods were primarily used a proof-of-concept for the following two main applications.

4.2 Applications

4.2.1 White Light Emitting Diode

The primary goal of the research was to always make use of bio-products that go waste. Prepared carbon quantum dots were emitting in blue and green region, and to make a white light source, a red light emitting source was needed. Carbon quantum dots can also be doped with Nitrogen rich compounds like urea to red-shift the emission. However, green leaves that are rich in chlorophyll are natural candidate to complete the mission of our project. Chlorophyll was extracted from green leaves by forming a green paste of leaves and dissolving it into 15 ml of ethanol for 15 minutes, followed by filtration. The photoluminescence characterization was carried out for the extracted chlorophyll solution.



Figure 8: Photographs of mixture of chlorophyll with ethanol in (a) normal condition and (b) exciting with blue laser.

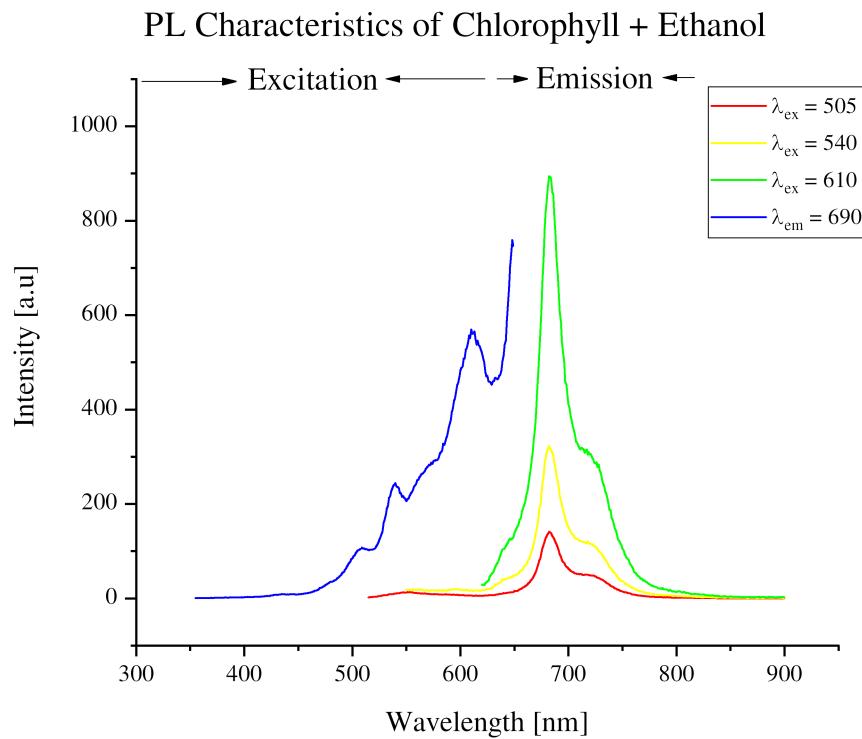


Figure 9: Photoluminescence characterization of chlorophyll mixed with ethanol

The emission wavelength was found to be at 690 nm and is maximum when the excitation wavelength is 610 nm. The emission intensity being tunable while keeping the fixed emission wavelength is good news for us to produce white light. 1 ml of Chlorophyll solution was mixed with 5 ml of CQDs prepared through microwave heating method. The PL characterization graph is presented in the next page.



Figure 10: Photographs of carbon quantum dots mixed with the solution of chlorophyll (a) normal condition and (b) exciting with blue laser.

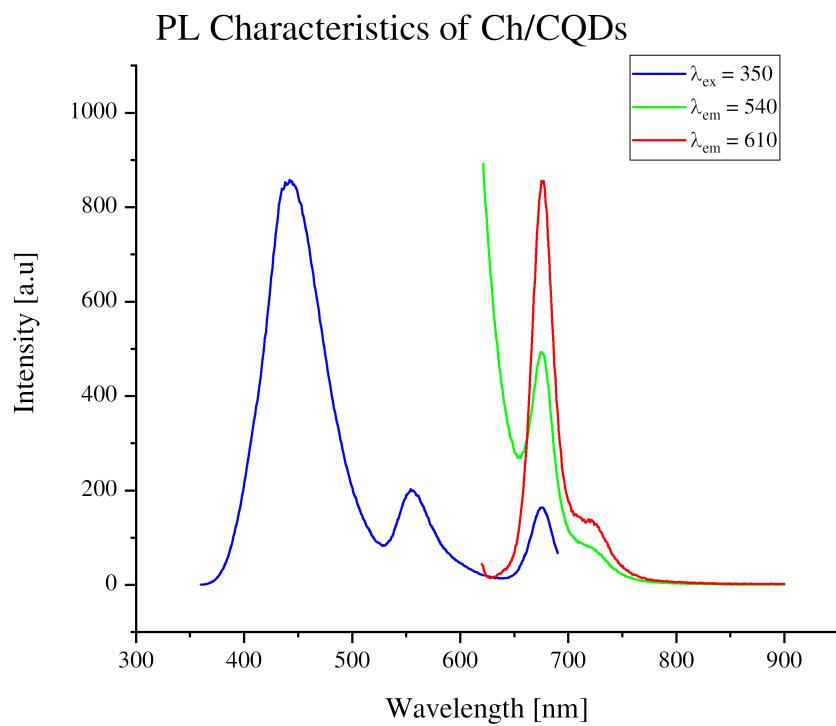


Figure 11: Photoluminescence characterization of Chlorophyll mixed with CQDs prepared through microwave method

The broadening of the emission wavelength and emission in all red, green, and blue region verifies the production of white light using only agro-based products. The second picture, where the mixture of chlorophyll and CQDs, when excited with blue pen laser, seems to emit a reddish-white color, or at least our eyes perceive it as a reddish-white color.

We also made a comparison to the light produced by mixing red dye (10^{-4} wt. %) with the prepared quantum dots.



Figure 12: Photographs of carbon quantum dots mixed with red dye solution (a) normal condition and (b) exciting with blue laser.

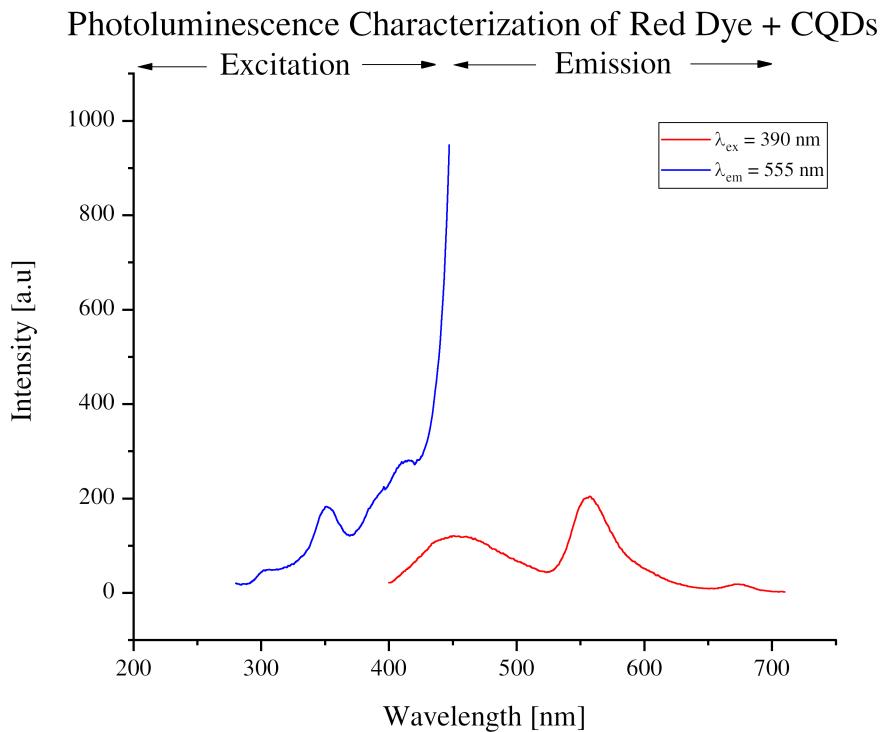


Figure 13: Photoluminescence Characterization of mixture of red dye with carbon quantum dots prepared through microwave method

The emission spectrum is spread from 400 to 700 nm, indicating that the mixture behaves like a white light, but more as greenish-white.

4.2.2 Temperature Sensor

The next goal of the project was to develop a temperature sensor using the synthesized CQDs. For this, the carbon quantum dots prepared through microwave method (0.5 ml) was mixed with the Polyvinyl Alcohol solution (1 ml, 7 wt.%), and dried for more than 2 hours on a glass slid as shown in the figure 14.

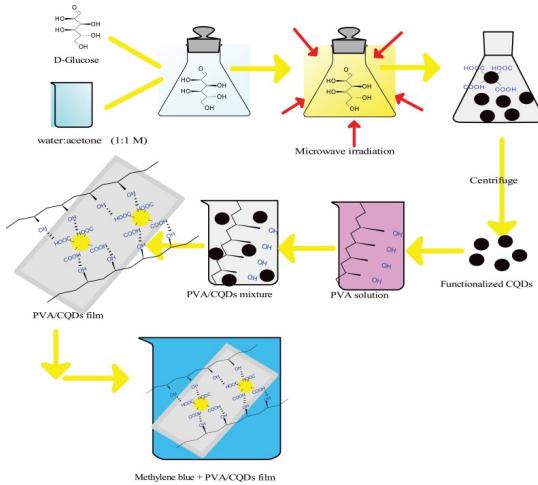


Figure 14: Illustration of the fabrication of PVA/CQDs nanocomposite [6]

The film was gradually heated from 35°C to 80°C while exciting with 405 nm laser, and the corresponding photon counts were measured using CCD camera. The photon counts in dependent of temperature is graphed below.

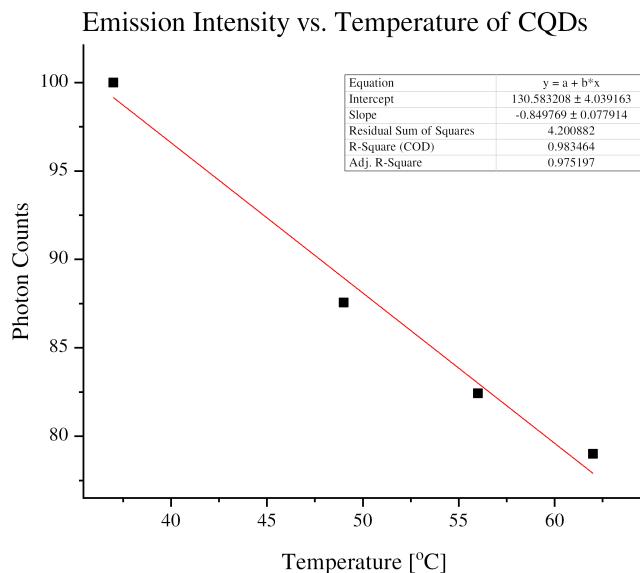


Figure 15: Temperature dependent of photon counts emitted by PVA/CQDs nanocomposite when excited with 405 nm laser.

The linear relationship shows that such PVA/CQDs composition can be easily used as a

temperature monitoring device for temperatures in between 35°C and 65°C. Beyond 65°, the values get saturated and is unsuitable for higher temperature measurement.

5 Conclusion

The overall experience of doing short-term research project abroad was truly new and exciting experience in my life. I thank German Academic Exchange Service (DAAD) for providing me such an opportunity. Through RISE Worldwide research program, one can learn and exchange cultures and language apart from sharing knowledge of the domain, and I am thankful to be a part of it.

References

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