Effects of Dopants (N & P) and Synthesis Conditions on the Size and Quantum Yield of Carbon Quantum Dots

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Abstract

Quantum dots (QD) have numerous applications across various fields including biomedical, optics, electronics, replacements for dyes, and energy sources. This project investigated the synthesis and optical properties of carbon quantum dots (CQDs), a new addition to the QD family, since limited quantitative research has been published in this specific area. In the first part of this study, synthesis conditions of CQDs have been varied to see the effect on fluorescence wavelength and to optimize the fluorescence intensity. In the second part, the CQDs are prepared by doping with nitrogen and phosphorous to observe the variation in fluorescence wavelength. Due to instrumental limitations, a constant excitation wavelength of 405 nm is used for all trials. Results showed that the synthesis conditions significantly affect the fluorescence quantum yield and the type of dopants affect both the quantum yield and the fluorescence wavelength.

Introduction

Quantum confinement refers to decreasing the particle size of a material to typically less than 10 nanometers which causes a change in its electronic and optical properties.[1] Named as such, quantum dots (QD) are semiconducting nanocrystals that are typically 2-10 nm in size, which have quantized energy levels like atoms do. When QDs are exposed to light, their electrons in the valence band become excited and move to the conduction band leaving a positive hole behind. Smaller nanoparticles have a larger energy band gap, which requires more energy to excite their electrons from the valence band to the conduction band (see figure 1). This phenomenon can be explained by the exciton Bohr radius—the distance between electron-hole pairs.[2] As the electrons relax back to the valence band, fluorescence occurs. The emission color is tunable due to the variable band gaps based on QD size. Manipulation of the size of the QDs causes the change in fluorescence color and the band gap size, which are both dependent on synthesis conditions and doping. Doping allows for attachment of other elemental atoms to the surface of QDs as impurities during the growth process of the quantum dots. The impurities either inhibit or increase the growth of the QDs, which in turn change the band gap size and by extension, the wavelength of fluorescence.

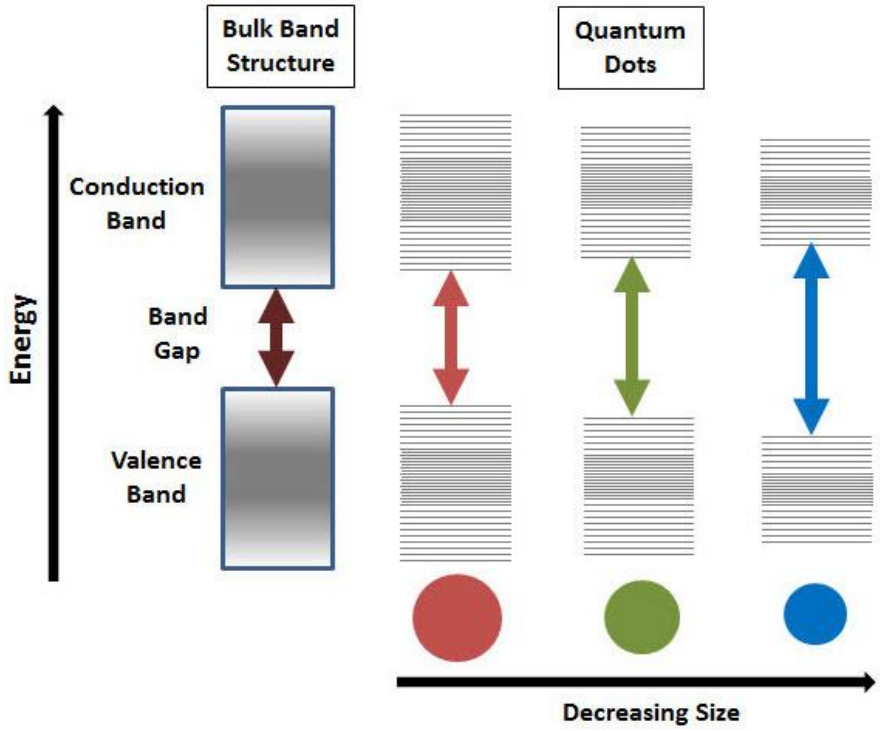

Figure 1: Band gap energy levels due to quantum confinement[3]

Since their properties can easily be manipulated, QDs have numerous applications across various fields including biomedical, optics, electronics, replacements for dyes, and energy sources.[2] Similar to QDs are carbon quantum dots (CQD). The only difference between the two is QDs are made with heavy metal combinations—such as CdSe, PbSe, PbS, and InAs—whereas CDs are made solely of carbon. CDs are more efficient, have a considerably lower toxicity, and cost less than their heavy metal counterparts. Additionally, they have a high quantum yield and are good electron donors and acceptors.[4]

In this study, the synthesis conditions of CQDs are optimized for the highest possible fluorescence, quantum yield, and the effect of two different dopants on CQDs fluorescence wavelength and quantum yield were investigated.

Experimental Method

The CQDs are synthesized by Maillard reaction. A Maillard reaction occurs between a monosaccharide and amino acid in alkaline conditions at a high temperature. L-cysteine and D-(+)-galactose react in a 1.0 M NaOH solution, forming Maillard reaction products (MRPs). The MRPs are then dehydrated to furan-like molecules, which condense and polymerize to form soluble polymeric fragments. The fragments then undergo aromatization and carbonization resulting in aromatic clusters, in which the nuclei in the clusters burst and isotropically grow into CQDs (see Figure 2).

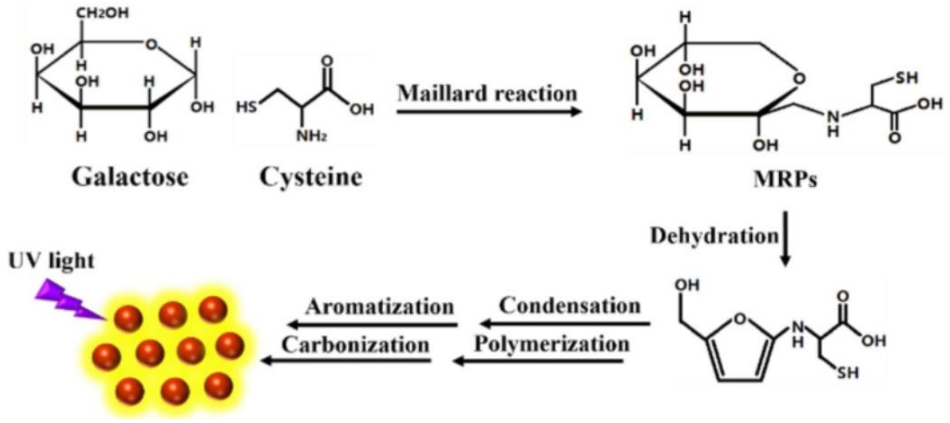

Figure 2: Formation of CQDs[5]

Optimization of Synthesis Conditions

0.29 g of L-cysteine (Sigma Aldrich) and 0.036 g of D-(+)-galactose (Carolina) were dissolved in 2.0 mL 1.0 M NaOH (39.997 g Fisher pellets) and 18.0 mL of DI water. Reflux was the original method of synthesis. The CQD solution was heated at approximately 80°C and 100°C for 12 and 24 hours. The solutions heated for 24 hours were too dark to produce fluorescence. Additionally, the solution heated for 12 hours did not fluoresce.

Synthesis via autoclaving (Harvey) proved to be the better method of synthesis. CQD solutions were heated at 100°C, 110°C, 118°C, and 136°C for 3.5 and 7.5 hours.

N-doped CQDs synthesis

4.803 g of Citric Acid (CA-Sigma Aldrich) and diethylenetriamine (DETA-Sigma Aldrich) were dissolved in 30.0 mL of DI water, then added to the CQD solutions. The ratio of the doping solution to the CQD solution was varied between 1 and 4. Autoclave heating time was kept the same (3.5 hours) at 110 and 118°C.

P-doped CQDs synthesis

The test solutions were prepared with 18.0 mL of o-Phosphoric Acid (o-PA-Fisher) and were added to the CQD solution. The ratio of the doping solution to the CQD solution varied from 0.3 to 1.5 Autoclave heating time was kept the same (3.5 hours) at 110 and 118°C.

Initially, P-doping solution was prepared with CA and DETA, and less than a milliliter of o-PA. A decrease in the fluorescence wavelength compared to the N-doped CQDs yielded the decision to increase the amount of o-PA to 6.0 mL. The fluorescence wavelength was still lower than that of the N-doped CQDs. DETA and CA were removed and eventually the amount of o-PA was increased.

Measurement of Absorbance and Fluorescence

Vernier Go Direct SpectroVis Plus was used to measure absorbance and fluorescence. It uses an incandescent LED bulb to scan a wavelength range of 380-950 nm, and has two fluorescence excitation sources of 405 and 500 nm. The wavelength accuracy is ±4.0 nm, with a photometric accuracy of ±0.1 AU.[6] (Figure 3)

Figure 3: Vernier Go Direct SpectroVis Plus

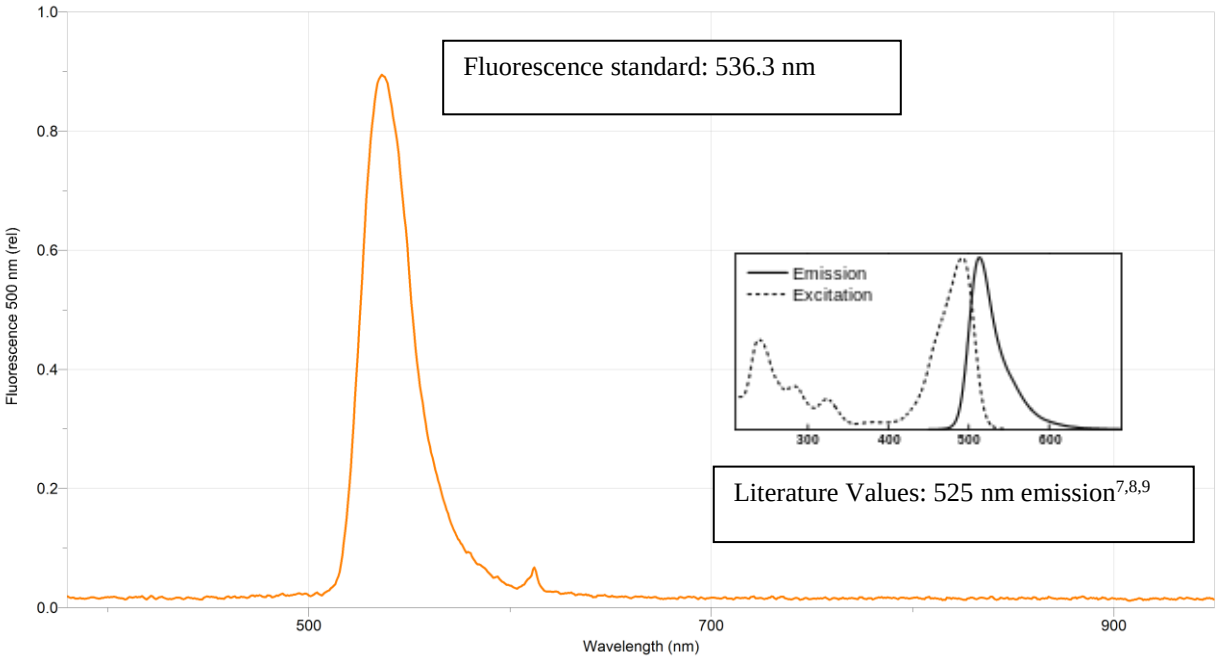

Figure 4: Calibration of instrumental accuracy (5.0 mM fluorescein isothiocyanate, pH 4.83)

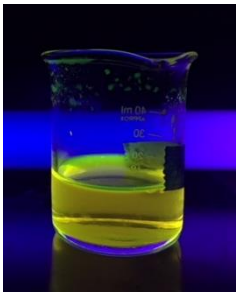

Figure 5: Fluorescein isothiocyanate fluorescence

Measurement of Refractive Indexes

A refractometer was used to measure the refractive indexes of each solution.

Figure 6: Refractometer (ABBE Mark III)

Quantum yields were calculated using Equation 1.

$$QY_s = QY_r \frac{(I_s A_r n_s^2)}{(I_r A_s n_r^2)} \qquad \text{(Equation 1)}$$

Where QY_r, A_r, I_r, n_r^2 is the quantum yield, absorbance, fluorescence intensity, and refractive index, respectively, of the reference fluorescein isothiocyanate.[10]

Data and Results

Table 1: CQD temperature and duration of autoclave time optimization

Temp (°C)	Heating time (hr)	Absorbance λ wavelength (nm)	intensity (rel)	Fluorescence-405 nm excitation wavelength (nm)	intensity (rel)
100	3.5	385.1	0.431	499.7	0.356
110	3.5	385.8	0.750	494.3-495.1	0.471
110	3.5	388.1	1.090	495.8-496.6	0.293
118	3.5	390.5-931.2	1.557	499.7-500.5	0.340
118	uncovered 3.5	385.1	0.695	492.8	0.112
136	3.5	404.3-408.1	1.491	495.1	0.189
136	7.5	398.1	1.951	499.7	0.157

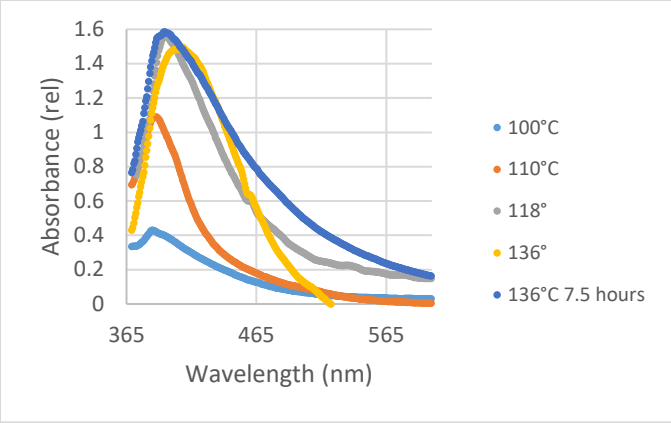

Figure 7: CQD absorbance curves

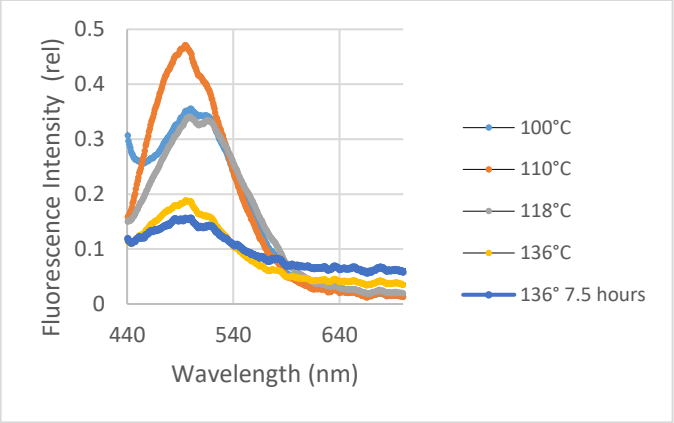

Figure 8: CQD fluorescence curves

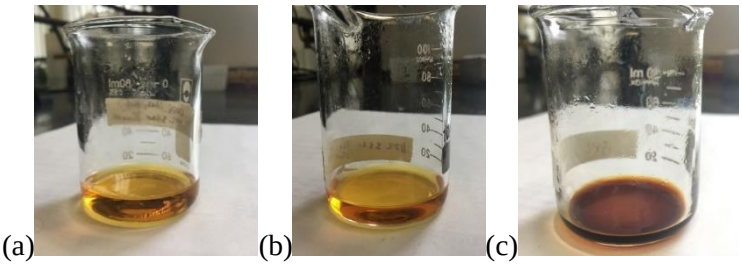

Figure 9: (a) 110°C CQD solution, (b) 118°C CQD solution, (c) 136°C CQD solution after being autoclaved

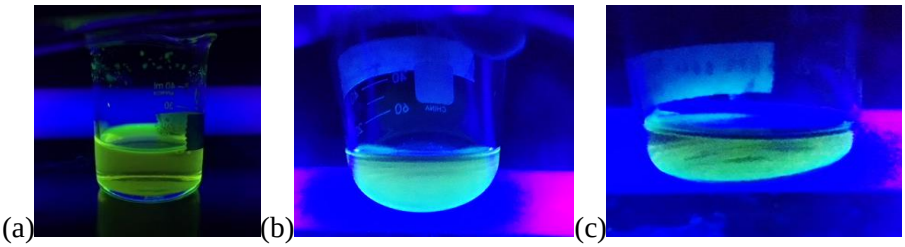

Figure 10: CQD fluorescence (a) 110°C, (b) 118°C, (c) 136°C

After comparing data, it was decided synthesis for 3.5 hours at 110°C and 118°C were the optimal conditions, considering their fluorescence had a standard deviation of 0.149.

Table 2: Nitrogen doped CQD excitation and emission wavelengths

Doping Ratio & Temp (°C)	Absorbance λ wavelength (nm)	intensity (rel)	Fluorescence-405 nm excitation wavelength (nm)	intensity (rel)
110				
1:1	397.4	1.852	354.1 & 554.4-555.1	0.295 & 0.382
1:1	390.5	1.557	458.4-458.9	0.955
2:1	391.2	1.664	461.2	0.962
2:1	398.7	1.007	439.7-440.4	0.972
3:1	386.6	0.863	439.7-440.5	0.968
4:1	385.8	0.881	438.9-439.7	0.967
118				
1:1	393.5	1.714	459.8-461.2	0.800
1:1	390.5	1.503	446.6	0.923
2:1	396.6-398.1	1.821	458.9	0.816
2:1	386.6	0.955	439.7-441.2	0.730
3:1	385.1-385.8	0.773	440.4-442.0	0.964
3:1	385.1	0.695	440.4-442.8	0.964
4:1	385.1	0.780	441.2-442.0	0.947

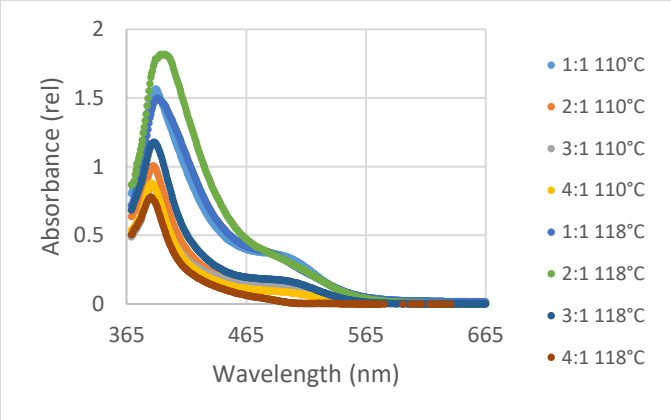

Figure 11: Nitrogen doped absorbance curves

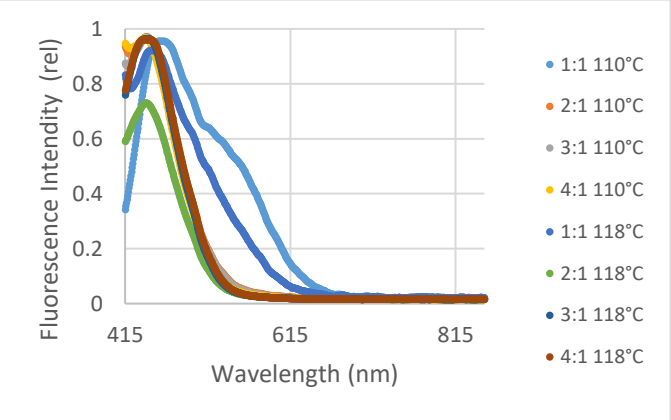

Figure 12: Nitrogen doped CQDs fluorescence curves

Figure 13: N-doped CQD solution after being autoclaved

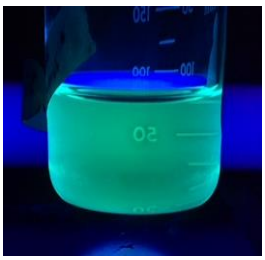

Figure 14: Fluorescence of 3:1 Nitrogen doped CQD

Table 3: Phosphorus doped CQD excitation and emission wavelengths

Doping Ratio & Temp (°C)	Absorbance λ wavelength (nm)	intensity (rel)	Fluorescence-405 nm excitation wavelength (nm)	intensity (rel)
110				
no CA-0.3:1	394.7	0.151	471.2-472.8	0.322
0.6:1	396.6-397.4	0.545	495.1	0.283
0.9:1	387.4-388.9	0.693	495.8-497.4	0.419
0.9:1	388.1	0.67	495.8-496.6	0.458
1:1	388.1	0.841	495.8-496.7	0.445
1.5:1	390.5-392.0	0.599	494.3-496.6	0.343
118				
0.9:1	395.1	1.38	497.4	0.535
0.9:1	392.8-394.3	1.263	495.8-498.1	0.407
0.9:1	393.0-395.1	1.291	495.8-497.4	0.524

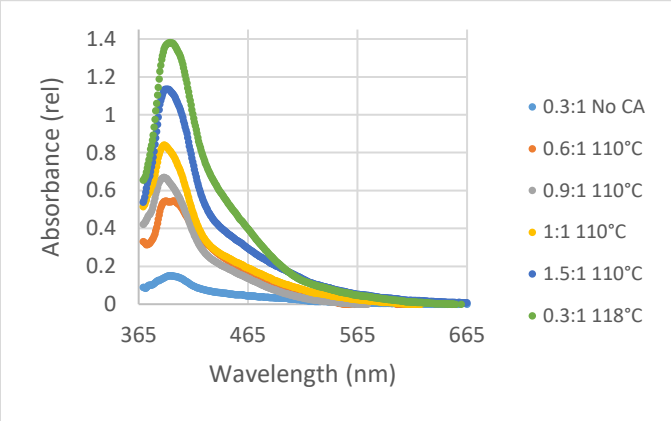

Figure 15: Phosphorous doped CQDs absorbance curves

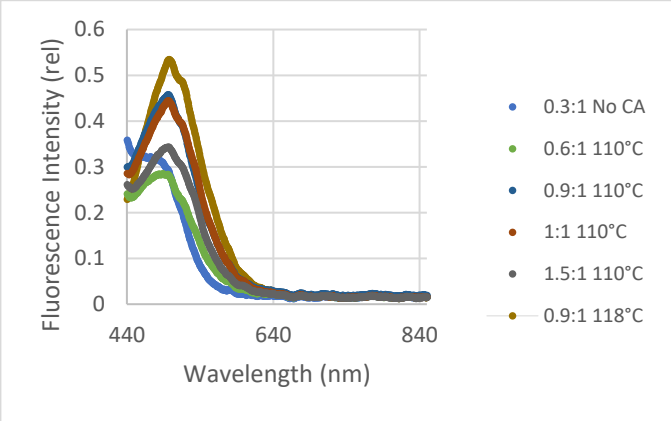

Figure 16: Phosphorous doped CQD fluorescence curves

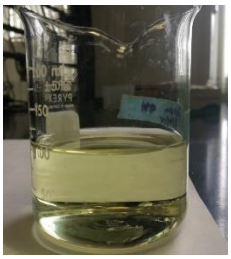

Figure 17: P-doped CQD solution after being autoclaved

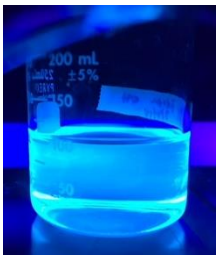

Figure 18: Fluorescence of 0.9:1 Phosphorous CQDs

Table 4: Refractive indexes

Solution	Refractive Indexes
FITC	1.6984
110°C	1.6987
118°C	1.6971
136°C	1.701
N-doped 3:1 110°C	1.7012
N-doped 3:1 118°C	1.7017
P-doped 0.9:1 110°C	1.6951
P-doped 0.9:1 118°C	1.6947

Table 5: Quantum yields of CQDs and doped CQDs

Solutions	Quantum Yields (%)
FITC	93
110°C	35.5
118°C	12
136°C	7.2
N-doped 3:1 110°C	63.6
N-doped 3:1 118°C	70.8
P-doped 0.9:1 110°C	38.5
P-doped 0.9:1 118°C	108

Discussion and Conclusion

Synthesis Conditions

As autoclave heating time and temperature increased, the size of the CQDs increased as well. This caused the solution to darken considerably. With an increase in size, it would be expected for the fluorescence to shift to longer wavelengths. Unfortunately, due to instrumental limitations, an excitation wavelength was not available to confirm this assumption. At the available excitation wavelengths of 405 and 500 nm, the 136°C solution that was heated for 3.5 hours would not fluoresce. This can be attributed to collisional deactivation and potentially carbonization not occurring after polymerization during synthesis. After testing several different temperatures and heating times, it was determined synthesis at 110°C and 118°C for 3.5 hours would be optimal, as they produced fluorescence that deviated by ±0.148—too small of a deviation to pick only one.

Effects of Nitrogen Doping

Compared to the undoped dots with fluorescence emission slightly above 500 nm, N-doped dots fluorescence emission was generally in the 450 nm range. The shift in the emission wavelengths is attributed to the decrease in size of the CQDs. N-doping slowed the growth of the CQDs, as the dots fluoresced at a lower wavelength, signaling an increase in band gap size. Additionally, the fluorescence intensity increased in the nitrogen-doped dots in comparison to the undoped CQDs.

Effects of Phosphorous Doping

The emission wavelength of P-doped dots was generally in the 495 nm range. The shift in the wavelength is attributed to the decrease in size of the CQDs. Similar to N-doped CQDs, P-doping slowed the growth of the CQDs. This was signaled by the fluorescence at lower wavelengths compared to the undoped CQDs.

Interpretation of Quantum Yields

Due to fluorescein isothiocyanate giving a 93% quantum yield at a pH of 8.0, the quantum yield calculations had to be corrected since the pH of the standard solution used was 4.83 to match with the

CQD sample solutions. After corrections, the quantum yields of the doped solutions were significantly higher in comparison to the undoped dots. The 108% yield in 0.9:1 P-doped 118°C CQDs is considered to be due to the uncertainty involved in the corrections.

References

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