Budak E, Ünlü C. JOTCSA. 2021; 8(3): 969-976. **RESEARCH ARTICLE**

Effect of Nitrogen Precursor on Optical Properties of Hexagonal Boron Nitride Quantum Dots

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Abstract: Boron nitride quantum dots (BNQDs) are of high interest with their excellent photophysical and structural characteristics. BNQDs can be synthesized through hydrothermal synthesis methods with different nitrogen precursors; however, until now, the optical properties of BNQDS synthesized with different nitrogen precursors have not been compared in details yet. In this study, BNQDS were synthesized through hydrothermal synthesis methods by using urea, melamine, and thiourea as nitrogen precursors and optical properties of BNQDS were compared by comparing emission and excitation characteristics of each BNQD synthesized by different nitrogen precursor. Structural properties of BNQDs were compared through infrared spectrum of each BNQDs. Our results revealed that the change in nitrogen precursor causes significant differences in photophysical and structural properties of BNQDs.

Keywords: Quantum dots, boron nitride, fluorescence.

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INTRODUCTION

Quantum dots made of 2-dimensional materials, in other words graphene like materials, are called 2D quantum dots and have become the center of attention with their excellent photophysical and structural properties (1–4). 2D quantum dots have a lateral size in the range of 2 – 6 nm with thickness less than 1 nm and display graphene-like geometry (1–4). These nanomaterials are simply nanometer-sized blocks of well-known 2D materials such as graphene, graphitic carbon nitride, hexagonal boron nitride, molybdenum sulfide, molybdenum selenide, tungsten sulfide, etc (1–4). 2D quantum dots have been considered as versatile materials since their discovery and have been used in many different application and research areas such as optoelectronics, supercapacitors, batteries, cell imaging, and sensors (1–7).

Amongst all, BNQDs have been studied widely with their unique features such as low toxicity and high biocompatibility (1–4). BNQDs were discovered in 2014 by Lin et al. and firstly synthesized through reducing the size of bulk hexagonal boron nitride (top-down approach) (8). After their discovery, BNQDs have been synthesized through top-down synthesis methods (8–16) and bottom-up synthesis methods (15,17–19) in many different studies. In most of studies in which bottom-up synthesis methods were used, boric acid was used as the boron precursor; however, the nitrogen precursor was different (15,17–19). The most common used nitrogen precursors were ammonia, urea, and melamine (15,17–19). Each study claimed the final product that they obtained were BNQDs, and also the spectral outcomes were pointing out the quantum dots were indeed similar in structure, however, no detailed comparison on optical properties of BNQDs synthesized with different nitrogen precursor was conducted until now.

In this study, we synthesized BNQDs through hydrothermal bottom-up synthetic methods by using boric acid as the boron precursor and 3 different nitrogen precursors; urea, melamine, and thiourea. The photophysical properties of BNQDs were analyzed in details by collecting emission and excitation spectrum of each quantum dot type. Detailed structural analysis was conducted by using Fourier transform infrared spectroscopy. Our results showed that each BNQD type had its unique optical and structural properties and therefore they should be considered as different quantum dot type.

MATERIALS AND METHODS

All chemicals that were used in this work were of the highest purity and were purchased from Sigma-Aldrich Co. They were used without further purification.

Synthesis of Boron Nitride Quantum Dots

Boron nitride (BN) quantum dots were synthesized through a modified hydrothermal synthesis method (17). To synthesize BN quantum dots, boric acid was used as a boron precursor and three different nitrogen precursors (urea, thiourea, and melamine) were selected to accompany boric acid. Firstly, 300 mg of boric acid and 100 mg of nitrogen precursor were completely dissolved in 5 mL of distilled water. Then, the clear solution was transferred into a Teflon-lined stainless steel reaction chamber, sealed, and placed in a furnace oven (brand: Isolab). The reaction chamber was heated until 200 °C and kept at that temperature for 24 hours. After 24 hours, the reaction chamber was taken out and cooled down to room temperature. A colorless clear solution was obtained as the crude product, which was purified by filtering with 0.22 micrometer syringe and centrifuging at 14,000 rpm for 30 minutes. The purified solution was kept at 4 °C for further use.

Optical and Structural Characterization of C-BN and BCN QDs

Optical properties of BN QDs were characterized by Scinco Neosys-2000 single - beam ultraviolet–visible (UV–Vis) spectrophotometer and Varian Cary Eclipse fluorescence spectrofluorimeter. Each sample was dissolved in 10 mL of ultrapure water after purification and diluted until optical density was under 0.1 in order to prevent errors resulting from self-absorption, then the absorption spectrum of each sample was collected by a UV-Vis spectrophotometer. The further optical properties were determined through aqueous solutions of quantum dots. Emission spectrum of each sample was collected by using different excitation wavelengths (λ_{exc}) in the range of 250 - 400 nm. The emission color of each sample was observed under 366 nm UV-light. Photoluminescent excitation (PLE) spectrum of each sample was collected at 440 nm. Quantum yields of the BN QDs were measured by using coumarin 102 in ethanol as a standard (the reference quantum yield was 0.93) (20,21).

Structural analysis of BN quantum dots was performed through Fourier transform infrared spectroscopy (FTIR) and Transmission electron microscopy (TEM). Bonding characteristics of BN quantum dots were determined by attenuated total reflectance FTIR spectroscopy. FTIR spectrum of each quantum dot was carried out in the range of 3750–800 cm^{-1} by using a Perkin Elmer Spectrum One ATR-FTIR spectrometer.

The shape and size of quantum dots were determined by using TEM. TEM measurements were conducted with JEOL JEM 1220 at an acceleration voltage of 100 kV.

RESULTS AND DISCUSSION

Synthesis of BN quantum dots

Bottom-up synthesis of BN QDs are generally carried out by using various boron and nitrogen precursors (15,17–19). In most of the studies, even though the precursors for boron and nitrogen differ, the synthesis conditions are similar to synthesize BN quantum dots (15,17–19). In this study, boric acid was chosen to be the sole boron precursor (Figure 1). As nitrogen precursor, melamine, urea, or thiourea were used with boric acid separately to synthesize BN QDs in order to check the effect of nitrogen precursor on structural and optical properties of BN QDs. The duration for synthesis and synthesis temperature were chosen to be 24 hours and 200 °C, respectively, as these conditions were frequently used to synthesize BN QDs (Figure 1) (15,17–19).

As the molecular structure of nitrogen precursors were compared, it was seen that in fact all these precursors can also act as precursor of additional elements, such as sulfur, oxygen, and carbon (Figure 2). Urea and melamine are frequently used in synthesis of BN QDs, however, thiourea has not been preferred widely (15,17–19). In the literature, it was suggested that BN QDs can be synthesized through using either melamine or urea, however, it should be considered that different molecular structures of urea and melamine most likely cause a distinct difference in the structure of QDs, therefore in the optical properties of QDs.

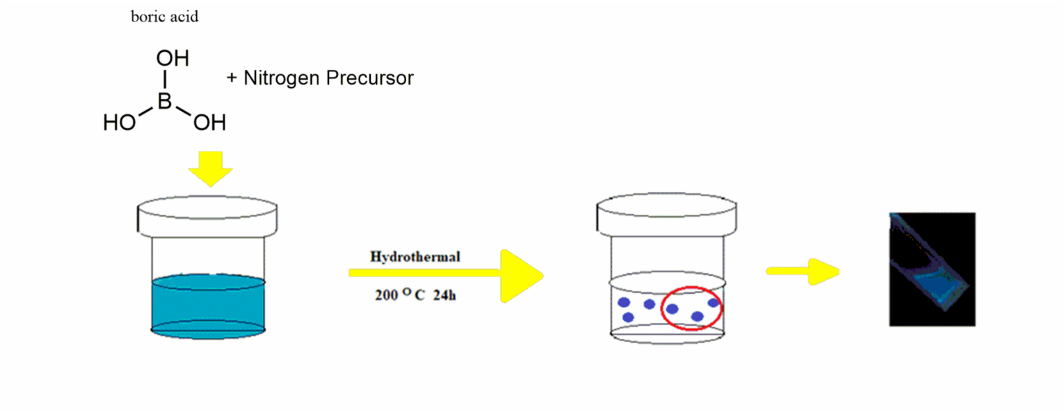

Figure 1. Schematic representation of synthesis of Boron Nitride quantum dots.

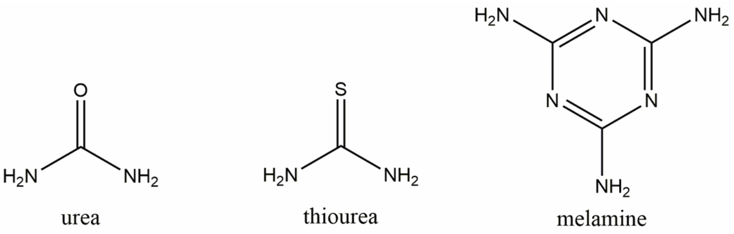

Figure 2. Structures of nitrogen precursors.

Structural characterization of BN QDs

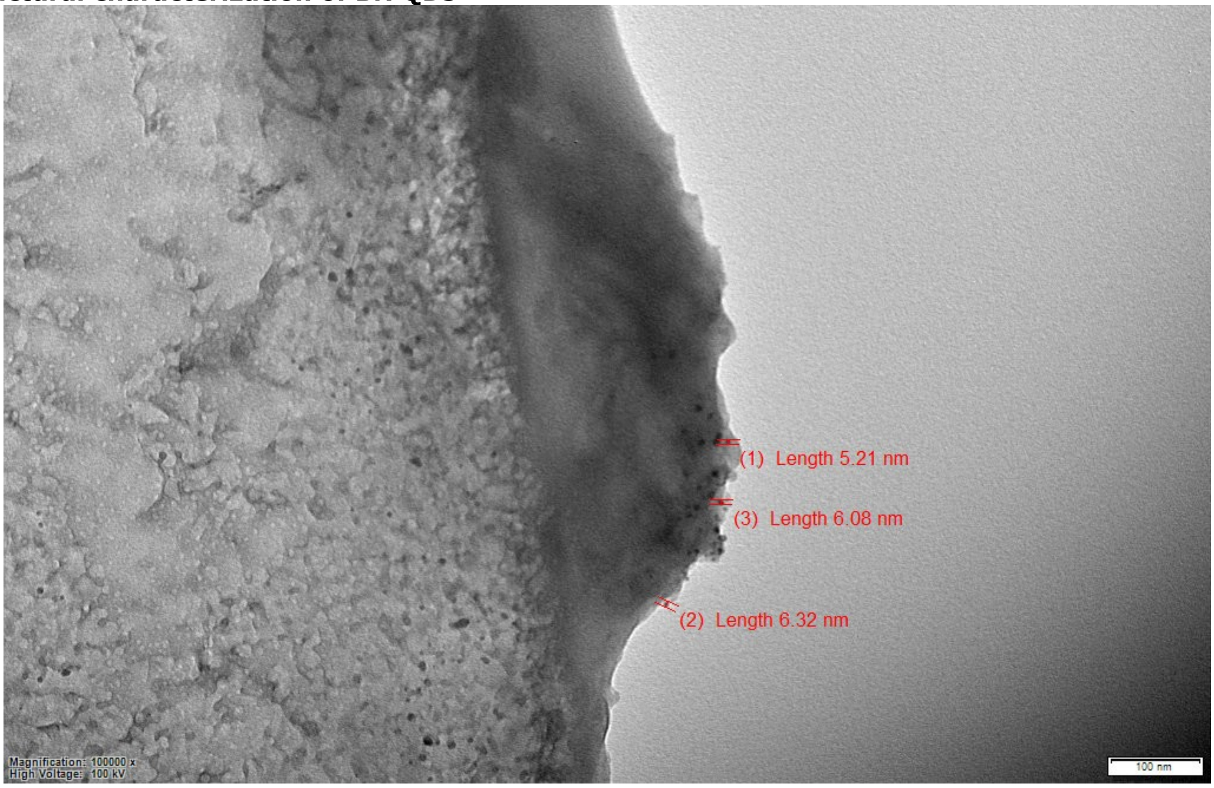

Figure 3. TEM image of BNQDs.

The size characterization was performed on U-BNQDs by TEM and it was found out that BN QDs had a size around 2 – 5 nm, which is the typical size range for BNQDs (Figure 3). The structural differences in BN QDs synthesized by different nitrogen precursors displayed themselves in FTIR spectrum of each QD (Figure 4). The most observable difference was explained as follows; BN QDs derived from thiourea (T-BNQDs) had a very sharp and intense peak at 2550 cm^{-1} which corresponded to S-H bonding where neither BN QDs derived from urea (U-BNQDs) nor BN QDs derived from melamine (M-BNQDs) had (Figure 4) (15,17–19). This peak showed that S=C double bond in thiourea was broken during synthesis of BN QDs and thiol groups were formed in the structure of T-BNQDs. FTIR spectrum of U-BNQDs and M-BNQDs had typical -BOH bonding peaks around 1180 cm^{-1}, however, this peak shifted to 1210 cm^{-1} in FTIR spectrum of T-BNQDs due to existence of –SH groups on the surface of T-BNQDs (Figure 4) (15,17–19). Each BN QD had typical B-N bonding peak around 780 – 800 cm^{-1} and 1380 – 1420 cm^{-1} (Figure 4). As the structures of U-BNQDs and M-BNQDs were compared, the main difference between the FTIR spectra of U-BNQDs and M-BNQDs was the peak around 920 cm^{-1}, the –N-B-O edge peak, which was the clear evidence of structural difference between U-BNQDs and M-BNQDs (Figure 4). Adjacent to the peak at 880 cm^{-1}, attributed to stretching vibration bands of C–O, the U-BNQDs possessed a peak at 920 cm^{-1} which showed that U-BNQDs had N-B-O groups on the surface (Figure 4). These clear differences showed that depending on nature of nitrogen precursor, BN QDs had different structural characteristics.

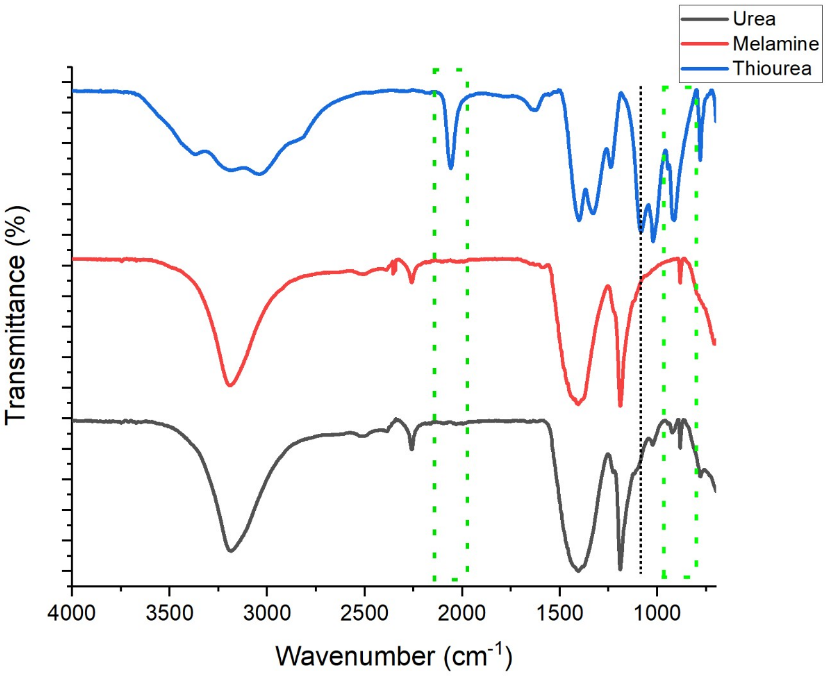

Figure 4. FTIR spectra of BNQDS synthesized with urea (black), melamine (red) and thiourea (blue).

Optical characterization of BN QDs

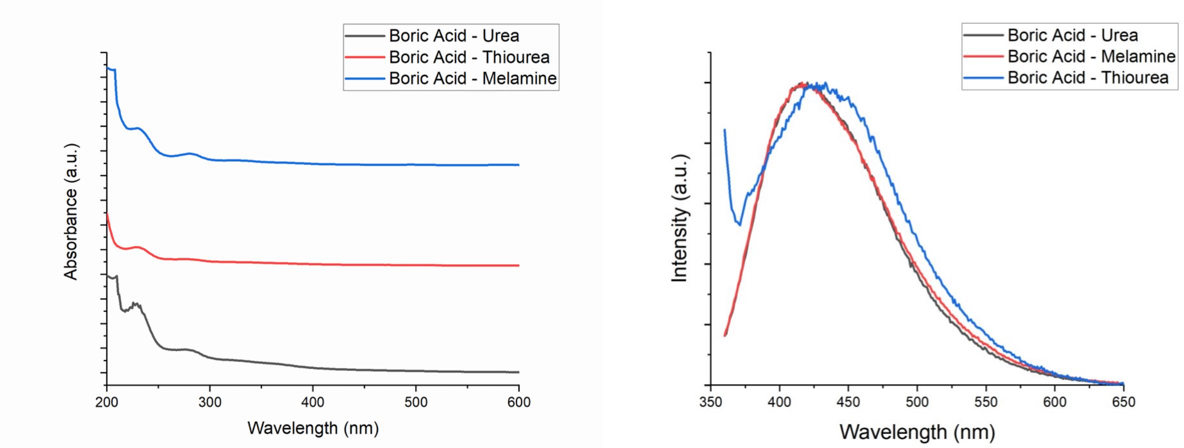

Figure 5. Absorption (left) and Fluorescent spectrum (right) of BNQDS synthesized with urea (black), melamine (blue), and thiourea (red). For fluorescent spectrum, each BNQDs were excited by 350 nm light.

Absorption spectrum and emission (PL) spectrum of a quantum dot are the two main indicators that let us characterize optical properties of all types of quantum dots (15,17–19). The comparison of absorbance spectrum of each BN QDs revealed that the absorption characteristics of M-BNQDs and U-BNQDs were similar, where absorbance spectrum of T-BNQDs was different from those of U-BNQDs and

M-BNQDs (Figure 5). Absorbance spectra of U-BNQDs and M-BNQDs possessed an intense peak around 230 nm, due to C=C peak in the structure of BN QDs and a relatively mild peak around 280 nm, due to band-edge transition in BN QDs (Figure 5) (15,17–19). Both of these peaks also appeared in T-BNQDs, but with a dramatically low intensity, which showed that the structure of T-BNQDs was considerably different from structure of M-BNQDs and U-BNQDs, as was also indicated through FTIR spectrum of each BN QDs. The emission spectrum of each BN QDs revealed the same story; emission spectrum of M-BNQDs upon λ_{exc}= 350 nm and emission spectrum of U-BNQDs upon λ_{exc}= 350 nm were almost identical, a single peak around 416 nm, where the emission peak of T-BNQDs red-shifted almost 15 nm, a single peak around 432 nm (Figure 5). The incorporation of S into BN QD structure caused a considerable red-shift in emission peak of BN QDs, and also caused a significant decrease in quantum yield of BN QDs; the U-BNQDs and M-BNQDs had quantum yield of 24% and 21%, respectively, where T-BNQDs had quantum yield of 6%. Although the FTIR spectrum of M-BNQDs and U-BNQDs were different, the absorption and emission spectrum were quite similar. Yet, the further analysis on optical properties of BN QDs showed that M-BNQDs and U-BNQDs had different excitation properties (Figures 6, 7, and 8).

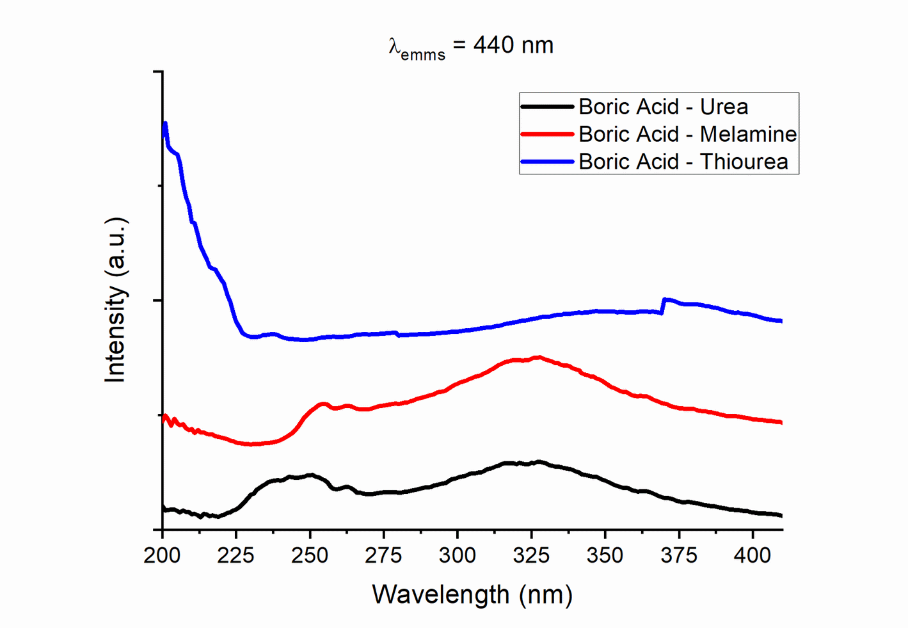

Figure 6. PLE spectrum of BNQDS synthesized with urea (black), melamine (red), and thiourea (blue).

U-BNQD and M-BNQD had similar photoluminescence excitation (PLE) spectra; however, there was one significant difference that U-BNQD had broadened the excitation peak in 225 – 250 nm region while M-BNQD did not (Figure 6). T-BNQD had an entirely different PLE spectrum with an intense peak between 200 - 225 nm (Figure 6). The difference in the PLE spectrum of U-BNQD and M-BNQD resulted in an observable difference in emission spectrum of these quantum dots with λ_{exc} = 250 nm.

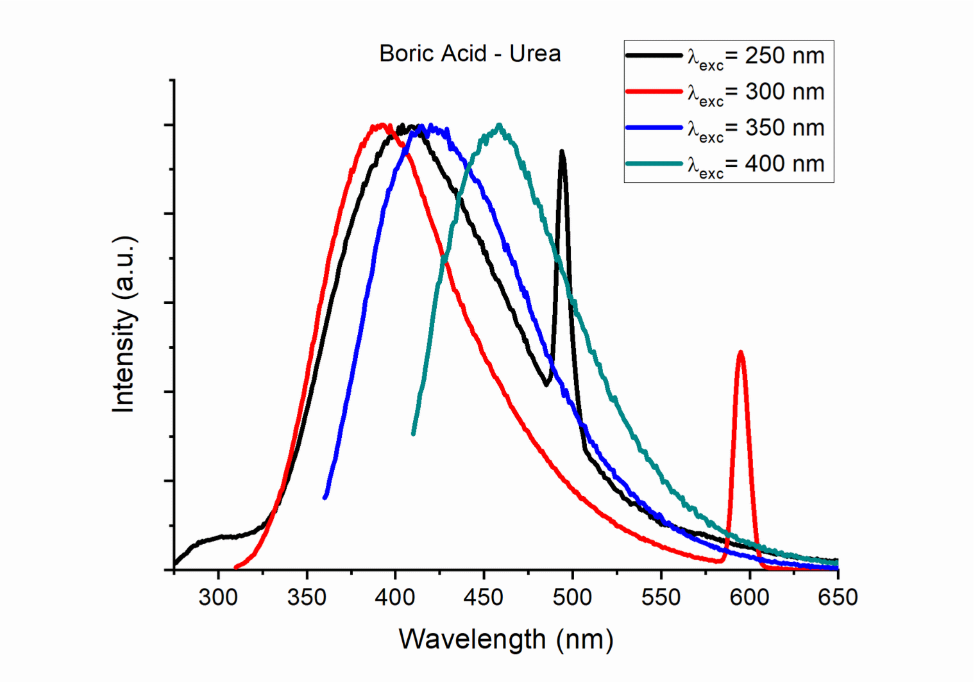

Figure 7. Fluorescent spectra of BNQDS synthesized with melamine with different excitation wavelengths.

The emission spectrum of M-BNQD had a single peak at 415 nm with λ_{exc} = 250 nm (Figure 7) where the emission spectrum of U-BNQD had a single peak at 395 nm with λ_{exc} = 250 nm (Figure 8). This difference is most likely due to existence of different groups on the surface of M-BNQD and U-BNQD, the existence N-B-O groups on the surface of U-BNQDs. It should be noted that U-BNQD and M-BNQD had very similar emissive properties with λ_{exc} = 300 nm, λ_{exc} = 350 nm and λ_{exc} = 400 nm (Figures 7 and 8).

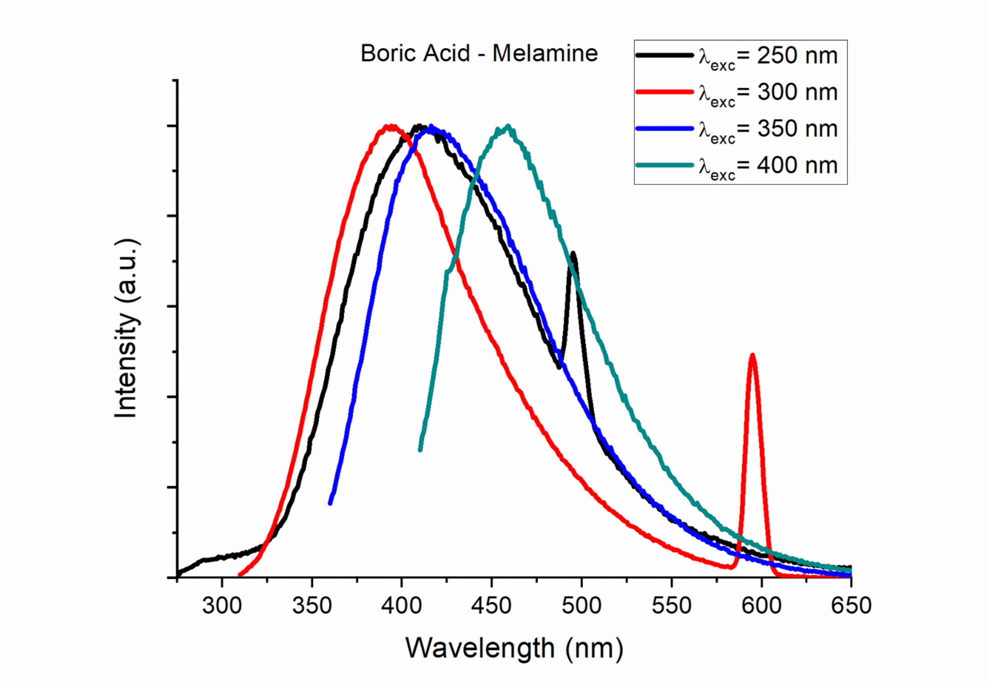

Figure 8. Fluorescent spectrum of BNQDS synthesized with urea with different excitation wavelengths.

These observations showed that, despite the differences on the surface of U-BNQD and M-BNQD, these quantum dots had similar inner crystal structure and the crystal structure can be excited through lower energy possessing light (300 – 400 nm), where surface of BN QDs could be excited through higher energy possessing light (250 nm).

CONCLUSION

Boron nitride quantum dots are generally synthesized through hydrothermal methods by using boric acid as a boron precursor and various chemicals such as urea, melamine, and thiourea as nitrogen precursors. The BN quantum dots synthesized with different nitrogen groups had significant optical and structural differences. When thiourea was used as nitrogen precursor, it was observed that sulfur was incorporated with crystal structure and incorporation of sulfur to nanocrystal structure caused significant changes in optical properties of quantum dots, such as decrease in quantum yield and shift in emission peak wavelength. The BN quantum dots synthesized by using urea and melamine as nitrogen precursors had similar emission properties upon excitation through 300, 350, and 400 nm light, however, the U-BNQD had a broadened PLE spectrum compared to M-BNQD and had different emission properties upon excitation through 250 nm, which was a consequence of existence of N-B-O bonding on the surface of U-BNQD that was observed in FTIR spectrum of U-BNQD.

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