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Synthesis of Nitrogen Doped Carbon Quantum Dots (NCQDs) from *Dieffenbachia seguine* Leaves for Fluorescent pH Sensing

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Synthesis with the goal of developing new fluorophores and characterizing them to find suitability for various applications is of great importance in energy transfer in optoelectronics and biomedicine, detection of metal ions, *etc*. In this study, a hydrothermal method was employed to synthesize nitrogen doped carbon quantum dots (NCQDs) as pH sensor materials using *Dieffenbachia seguine* leaves as a carbon source. A detailed characterization of the NCQDs revealed an absorption spectrum from 200 to 800 nm with multiple peaks and an energy-band gap of 3.58 eV. Carbon was found to have the highest weight percentage, followed by nearly equal amounts of N and O and minor amounts of the other elements. The analysis revealed the presence and crystal morphology of functional groups such as OH, C=C and C–H. Variation of fluorescence intensity with pH was found in the pH range considered from 1 to 10 with a correlation of 0.92. The results of these parameters support the utility of synthetic NCQDs as fluorescent pH sensors.

Keywords: Carbon quantum dots, Hydrothermal method, Nitrogen-doped, pH sensor, Energy band gap.

INTRODUCTION

Carbon dot (CD) synthesis using renewable materials has gained attention worldwide due to their potential in a wide range of disciplines [1-4]. Natural resources containing carbohydrates are used for the same purposes. Almost all parts of the plant act as reducing and stabilizing agents and are used to obtain nanoparticles [5]. The advantages of extracting plant products are affordability, accessibility and above all, no harm to the environment [6]. Quantum dots (CDs, > 10 nm in size) consist of several polar hydrophilic carboxyl and hydroxyl groups, which leads to the significant differences in the properties and behaviour of the synthesized CDs [7]. The physico-chemical characteristics of the synthesized CDs differ enormously because of the large variety of synthetic methods and precursors used in their formation. Bottom-up and top-down synthesis are the two main approaches to synthesize quantum particles. Top-down methods require harsh chemical reactions, expensive equipment and materials and long reaction times [8], as this involves electrochemical oxidation through the method arc discharge [9]. Carbonization between small compounds is essential for the bottom-up approach to function. The use of plasma, thermal deposition, hydrothermal and reactive heat techniques are all included [9]. These are simple, inexpensive, environmental friendly and highly effective methods. This approach has the advantage of aggregating CDs with specific properties. To synthesize CDs using a bottom-up approach, citric acid, glucose and urea are the most common precursors and have been used in many applications [10-12]. In comparison to pyrolysis and other methods, the hydrothermal carbonization approach is claimed to be a green synthetic technique for producing CQDs [13].

Doped CDs have excellent surface passivation properties and tunable fluorescence capabilities. It has been demonstrated that adding heteroatoms to CQDs improves their optical characteristics [14] and the most often used methods for improving the optical characteristics of CQDs synthesized from biomass involve adding heteroatoms like nitrogen, phosphorous and sulphur [15,16]. Nitrogen-doped carbon dots (NCQDs) have various benefits, including electrocatalytic and photocatalytic applications. Additionally, the same is useful for light-emitting diode and bioimaging applications [17,18].

Biomedical nanoparticles are typically smaller than their target biological entities, giving them the special ability to interact with biomolecules both on the surface of cells and within the cytoplasm and organelles of the cells. This makes nanoparticles a promising class of nano-vehicles for targeting and diagnosing illnesses in their earlier stages. The activity of many organelles is typically adjusted by pH values and the misbalance of the same may cause several diseases [19]. Therefore, it is important to measure the intra-cellular pH value precisely. A few of the materials that have been developed to date for pH monitoring are CDs [20], encoded red fluorescent protein sensors [21], polymer dots by the use of semiconductors [22] and probes of CQDs [23]. In present study, *Dieffenbachia seguine* leaves were used to synthesize nitrogen-doped carbon dots (NCQDs). The excitation-dependent photoluminescence characteristics and applicability as a pH sensor were investigated using the hydrothermal process.

EXPERIMENTAL

Fresh *Dieffenbachia seguine* leaves were collected from the local region, near the campus of Uttaranchal University, Dehradun, India. Double distilled water was used throughout the experimental work. All the chemicals and solvents were of highest analytical grade and procured form various reputed commerical sources.

Synthesis of nitrogen-doped carbon dots (NCQDs): A systemic diagram of the process of synthesis of NCQDs by the hydrothermal method. Fresh leaves of *Dieffenbachia seguine* were washed throughly with distilled water and then dried at room temperature. After adding 5 g of dried leaves and 60 mL of water to an autoclave, the mixture was heat ed at 200 ºC for 2 h in the furnace. Then, 1.5 mL of ethylenediamine was added to 15 mL of CQDs solution and placed in the refrigerator at 200 ºC for 3 h and then then allowed to cool at room temperature. The resulting solution was centrifuged and filtered to to remove the large particles. After drying at 75 ºC, a solid particle was obtained [23].

RESULTS AND DISCUSSION

The resulting nitrogen-doped carbon dots (NCQDs) may have useful information about their potential performance in a specific application based on their properties [24]. Several characterization techniques were employed in this investigation and their findings are presented here.

Optical studies: Absorption spectra of the synthesized NCQDs was observed in the range from 200 to 800 nm, with absorption peak positions respectively at 236, 422 and 464 nm (Fig. 1). The energy band gap was evaluated by using Tauc equation [25]. For this purpose, the photon energy was plotted against the photon energy and found to be 3.58 eV.

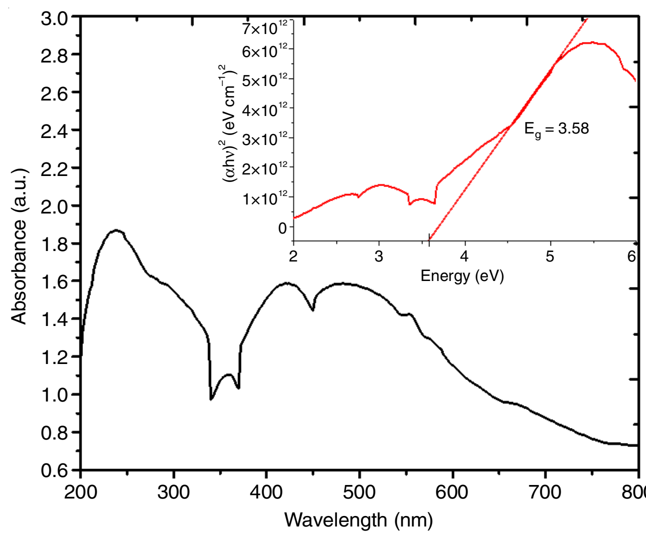

Fig. 1. Plot of absorbance *versus* wavelength and $(\alpha h\nu)^2$ *versus* energy

SEM and EDX studies: The SEM was used to examine the surface shape and porous structure of nitrogen-doped carbon dots (NCQDs). The SEM images shows some agglomeration and a flow-shaped particle (Fig. 2a), which might be formed during the synthesis processing. Fig. 2b predicts the EDX spectrum of NCQDs. The weight percentage of C and N was high due to the decomposition of plant material and the addition of ethylenediamine, respectively. The presence of other elements in NCQDs was confirmed as a result of the non-washing process used [26]. The mapping of the elements present in the synthe-

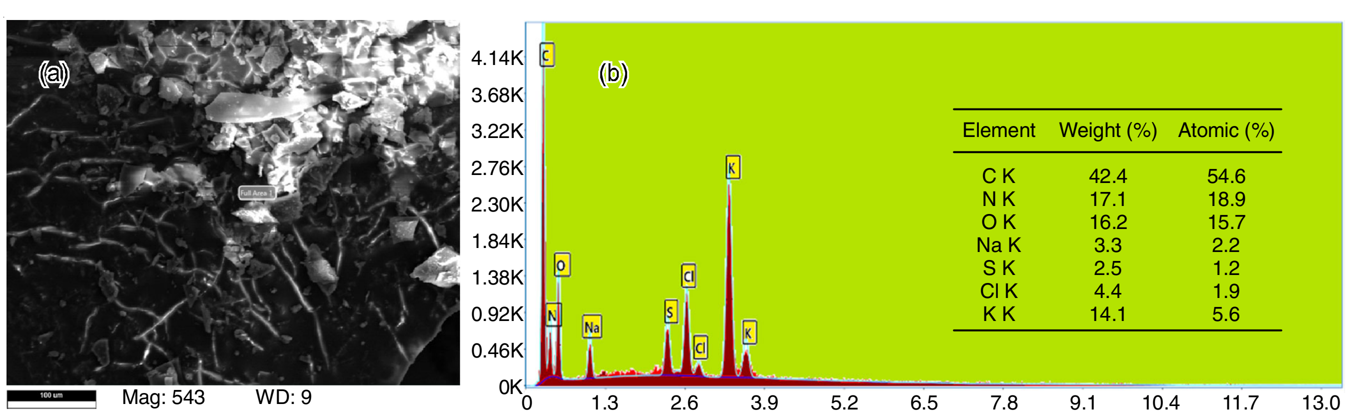

Fig. 2. SEM image (a) and EDX spectrum (b) of green synthesized nitrogen doped carbon quantum dots (NCQDs)

sized NCQDs is shown in Fig. 3. This confirms the even distribution of the elements.

Crystallographic studies: The XRD pattern of NCQDs is shown in Fig. 4 and indicates the crystallinity of the material.

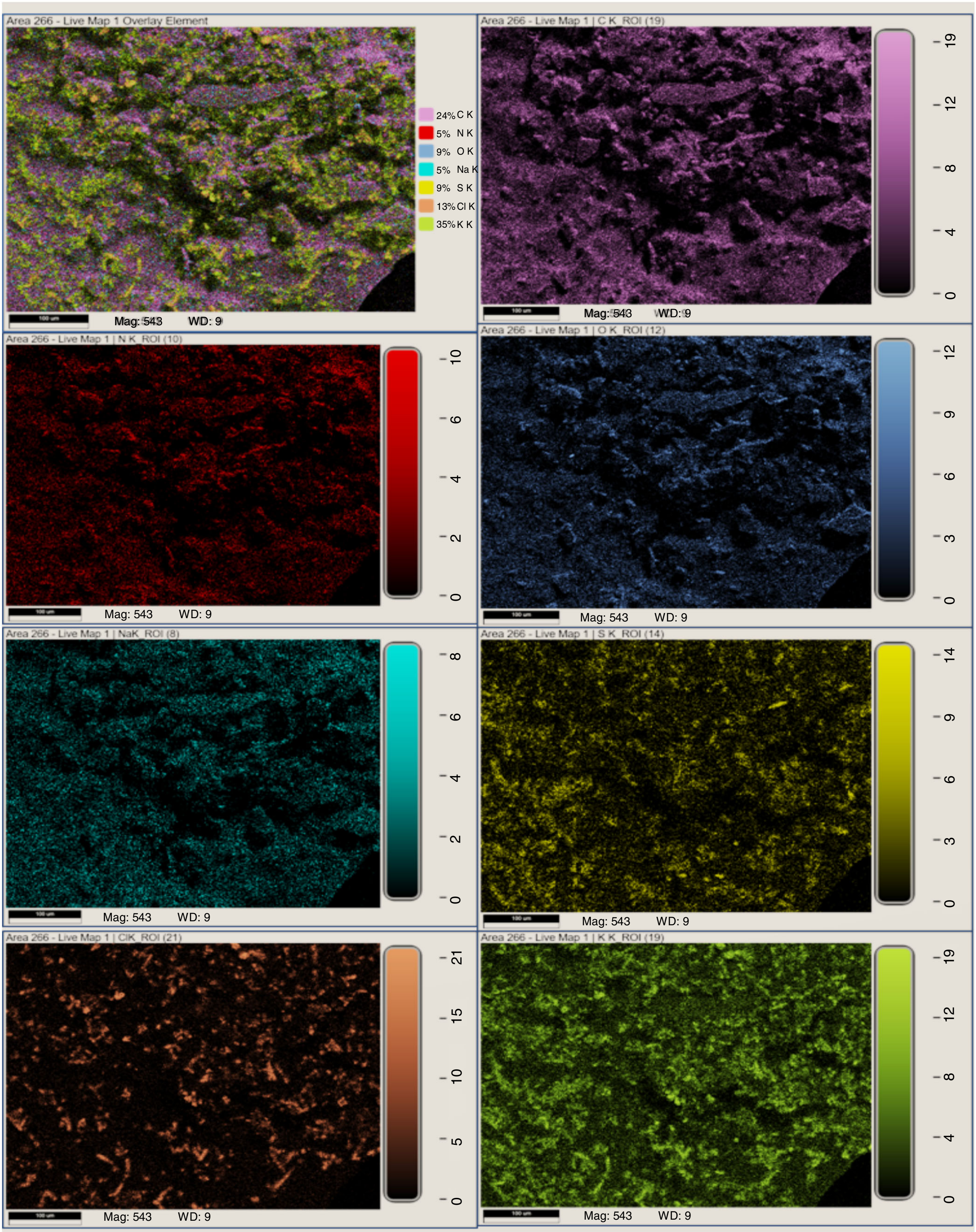

Fig. 3. Mapping of elements present in the green synthesized nitrogen doped carbon quantum dots (NCQDs)

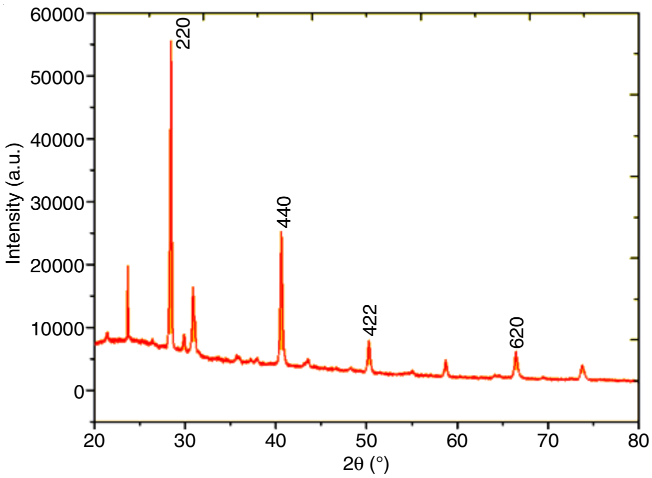

Fig. 4. Intensity *versus* 2θ in XRD pattern of NCQDs

Further, the multiple peaks at 2θ = 28.42º, 30.99º, 40.60º, 50.27º and 66.49º and *hkl* values of 220, 400, 422-620 were compared with the standard JCPDS card No. 00-042-0667. The sharp peak corresponding to 28.42º is stronger than the other planes, indicating that (220) has the dominant orientation and the peak clearly indicates the crystallinity of the NCQDs. The sharpness of the peaks and the absence of unidentified peaks confirmed the crystallinity and high purity of the NCQDs. The *d*-spacing values were measured and found to be 3.06, 2.82, 2.17, 1.77 and 1.37, respectively. Further, particle size was investigated 57 nm of the synthesized particles. Debye Scherrer's equation was used to evaluate the particle size and found to be 57 nm [27].

FT-IR studies: Functionalization is a necessary strategy that gives rise to the unique properties of CDs, which can be achieved by incorporating various metallic and non-metallic elements onto the surface of CDs. Most abundantly used non-metallic dopants include sulphur, nitrogen and phosphorous, which provide unique catalytic and colorimetric properties and high performance [28,29]. The spectrum (Fig. 5) shows that these particles have hydrophilic groups such as N-H (3453 cm^{-1}) on their surface, confirming the good water solubility.

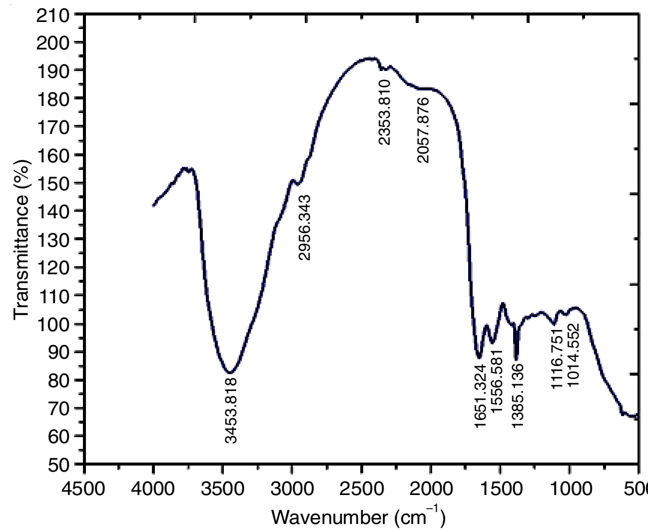

Fig. 5. FT-IR spectra of NCQDs

In addition, the C-H (2956 cm^{-1}), C=O (1651 cm^{-1}) and C-N (1556 cm^{-1}) vibrations also appeared. A trough observed at 1550 cm^{-1} was due to N-H bending and the peaks at 1385 and 1080 cm^{-1} were due to –C≡N stretching. These findings confirmed that nitrogen was effectively incorporated into the CQDs' structure.

Effect of pH effects on fluorescence emission: The solution of NCQDs was adjusted to a suitable pH range of 2-10 using either HCl or NaOH solution. Fig. 6a depicts the effect of pH on the intensity and showed that the fluorescence intensity of these particles are pH dependent. Fluorescence becomes stronger with increasing pH. The excitation wavelength of the sample was adjusted to 350 nm. This result is consistent with previous research demonstrating that carbon dots emit a significant amount of blue light that decreases in the red region, which is frequently characterized by excitation wavelength dependence [30]. Fluorescence properties often depend on the CD-specific surface properties and other factors [31]. Further, the plot of intensity with pH shows the relationship among them with the linear correlation coefficient of 0.92 (Fig. 6b). This predicted

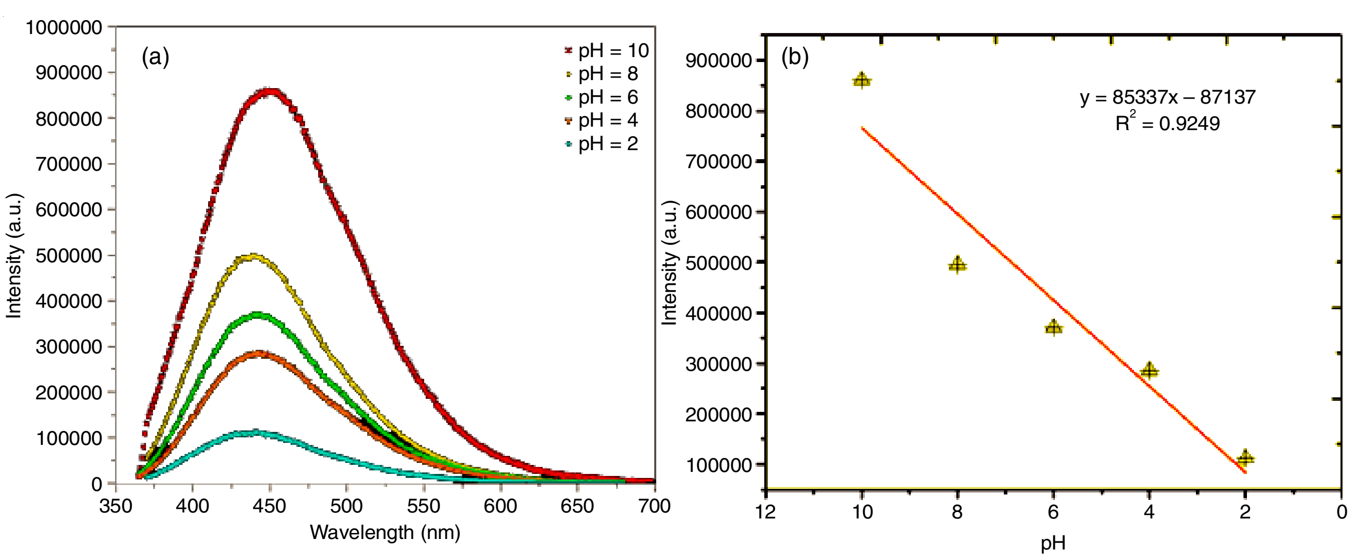

Fig. 6. Fluorescence intensity *versus* wavelength (a) and fluorescence intensity *versus* pH values (b)

phenomenon claims the potential of the synthesized NCQDs as a pH sensor material.

Photoluminescence studies: The photoluminescence spectrum of the synthesized NCQDs was measured at two excitation wavelengths. The PL emission clearly demonstrates the excitation dependent photoluminescence (Fig. 7), which has benefits for a variety of applications including biosensors, bioimaging and LED devices [32,33].

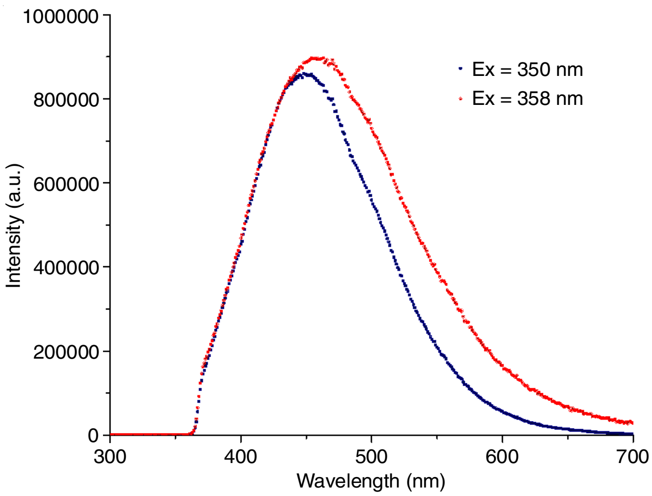

Fig. 7. Fluorescence intensity *versus* wavelength at different excitation

Conclusion

In this work, a water-soluble nitrogen doped carbon quantum dots (NCQDs) was synthesized using *Dieffenbachia seguine* leaves using hydrothermal method. The NCQDs exhibited a consistent morphology, strong fluorescence characteristics, fluorescence stability, low toxicity and high biocompatibility. According to preliminary results, the NCQDs have a good ability to respond to fluorescence as sensing pH material.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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