

# Emerging Tunable Fluorescence in Nitrogen Doped Carbon Quantum Dot

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**Abstract**—Optically active carbon-based materials have attracted much attention and have been widely applied in different scientific fields, because of their superior advantages such as aqueous solubility, low toxicity, facile functionalization and good biocompatibility. These unique properties make carbon based materials promising alternatives to common metal-based quantum dots (QDs) for numerous exciting applications such as imaging, sensing, drug delivery, and optoelectronic devices. Though a number of fluorescent carbon-based materials, including C<sub>60</sub>, CNT and carbon nanoparticles have been reported earlier, carbon dots (C-dots) have attracted tremendous research interest because of their strong fluorescence with tuning properties, as well as facile synthetic routes with abundant and cheap raw materials. To enhance the potential applications, the doping of other elements into carbon nanostructures is one of the efficient ways to tune the electronic as well as band structures. N is a general dopant within the carbon materials, which can inject electrons into carbon-based materials, thus changing the electronic and transport properties. Based on the benefits of N-doping in carbon nanostructures, in the present work, fluorescent Nitrogen doped carbon dots (N-CQDs) have been produced by a bottom-up wet-chemical method employing citric acid as a precursor. The as-synthesized N-CQDs exhibit strong and stable blue emission when excited at uv region and the emission is excitation dependent. The measured fluorescence lifetime of N-CQDs indicates about multiple decay pathways. The obtained N-CQDs could be used for specific applications in different research fields such as sensors, solar cells, biomedicine and catalysis.

## 1. INTRODUCTION

In the past several decades, semiconductor quantum dots (QDs) have been examined closely in terms of strong and tunable fluorescence emission properties, which enable their applications in sensing and imaging. However, semiconductor quantum dots possess certain limitations such as high toxicity due to the use of heavy metals in their production. It is known that heavy metals are highly toxic even at relatively low levels, which may prove prohibitive to any clinical studies. This encouraged the creation of CQDs to replace semiconductor quantum dots. Fluorescent carbon quantum dots (CQDs) are a new class of carbon nanomaterials that have emerged recently and have garnered much interest as potential competitors to conventional semiconductor quantum dots. In addition to their comparable optical properties, CQDs have the

desired advantages of low toxicity, environmental friendliness low cost and simple synthetic routes. Moreover, surface passivation and functionalization of CQDs allow for the control of their physicochemical properties. Since their discovery, CQDs have found many applications in the fields of chemical sensing, biosensing, bioimaging, nanomedicine, photocatalysis and electrocatalysis [1-6].

To enhance the potential applications, the doping of other elements into carbon nanostructures is one of the efficient ways to tune the electronic as well as band structures. N is a general dopant within the carbon materials, which can inject electrons into carbon-based materials, thus changing the electronic and transport properties. Based on the benefits of N-doping in carbon nanostructures, in the present manuscript, we report a simple, economical, and one-pot method to synthesize highly fluorescent N-CQDs through hydrothermal method using citric acid and ammonia. The as-synthesized N-CQDs exhibit strong and stable blue emission when excited at uv region and the emission is excitation dependent. PL intensity varies with pH variation. Photoluminescence life time measurement that gives an insight about the excitonic dynamics, indicate to the two different decay pathways of fluorescent N-CQDs. We hope that the obtained N-CQDs could be used for specific applications in different research fields such as sensors, solar cells, biomedicine and catalysis.

## 2. EXPERIMENTAL PROCESS

### 2.1 Synthesis

50 mg citric acid was dissolved into 40 ml water and 1 ml NH<sub>3</sub> (30%) was added drop wise with stirring to obtain a clear solution of pH ~8. Then the solution was transferred into a 50 ml Teflon stainless autoclave. The sealed autoclave was heated to 180°C in a vacuum oven and kept for 9 hours. The final product was collected after three time centrifuging at 6000 rpm for 5 min. The synthesis scheme is shown in Scheme 1.



Fig. 1: Synthesis of N-CQDs

### 3. CHARACTERIZATION

To characterize the final product, FTIR spectroscopic measurements are carried out using a Shimadzu IR Affinity-1 spectrometer system. For the TEM study, we used a JEOL-2011 high resolution transmission electron microscope. PL spectra are collected using Shimadzu RF-5301PC Spectrofluorophotometer. For the time-correlated single-photon counting (TCSPC) measurement, QD solution is excited at 340 nm (by picosecond Nano LED) in Edinburgh luminescence spectrometer (Model No. FLSP-980). Average fluorescence lifetimes ( $\tau$ ) for exponential fitting are calculated from the decay times ( $\tau_i$ ) and the relative amplitudes ( $a_i$ ), using the following relation

$$\langle \tau \rangle = \frac{\sum_i a_i \tau_i^2}{\sum_i a_i \tau_i}$$

### 4. RESULT AND DISCUSSION

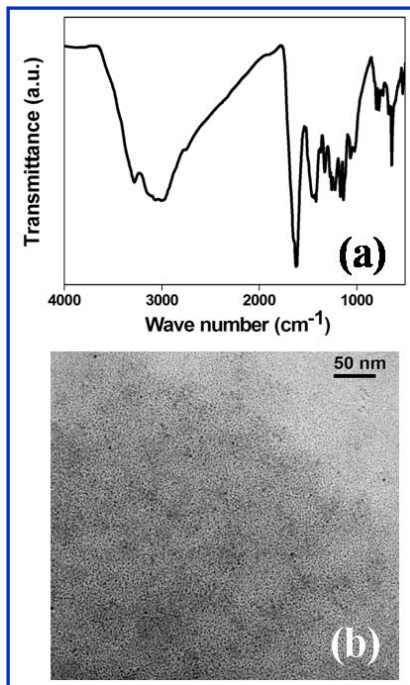


Fig. 2: (a) FTIR and (b) TEM images of N-CQDs

The functionalities present in N-CQDs are further confirmed by the FTIR analysis. Fig. 1a shows the FTIR spectra for N-CQDs. The FTIR analysis revealed the presence of  $-\text{OH}$ ,  $-\text{COOH}$ ,  $\text{NH}_2$  groups in the surface of the CDs, with the fact: the broad peak in the region  $3600\text{--}1800\text{ cm}^{-1}$  is due to the presence of the OH,  $\text{NH}_2$  groups. Asymmetric and symmetric stretching vibration peaks of COO bond at 1624 and 1420  $\text{cm}^{-1}$  and the peaks  $\sim 1100\text{--}1260\text{ cm}^{-1}$  are due to OH deformation and C-N stretching vibrations.

Transmission electron microscopy (TEM) is used to investigate the morphology of prepared N-CQDs. From Fig. 1b it can be seen that the N-CQDs have a uniform dispersion without any apparent aggregation and the average size of  $\sim 3\text{--}7\text{ nm}$ .

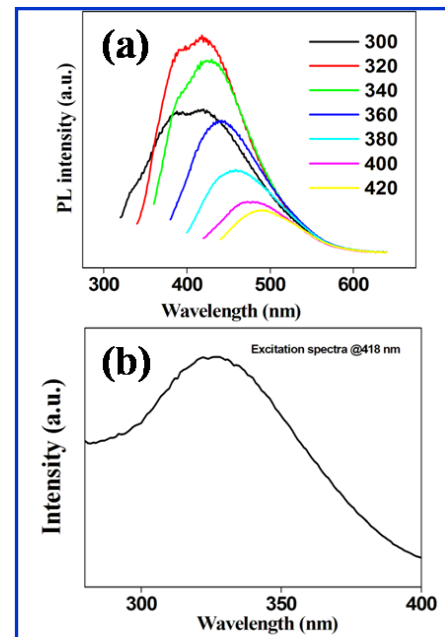


Fig. 2: (a) PL and (b) PLE of N-CQDs

Fig. 2a shows the PL spectra of N-CQDs. The as-synthesized N-CQDs exhibit excitation-dependent emission behavior. When the N-CQDs are excited at wavelengths from 300 to 420 nm, the corresponding emission peaks are tuned from  $\sim 417\text{--}490\text{ nm}$ . The strongest PL maximum with PL quantum yield of  $\sim 5.32\%$  appears at 418 nm upon 320 nm excitation. This is in accordance with the photoluminescence excitation (PLE) spectrum with a strong excitation peak at  $\sim 324\text{ nm}$  (Figure. 2b). Moreover, the PL intensity of N-CQDs enhanced with the increase in pH. These observations indicate that the changes of pH mainly influence the surface of N-CQDs. The protonation and deprotonation of the  $-\text{OH}$ ,  $-\text{NH}_2$  and  $-\text{COOH}$  groups due to the changes in pH may cause electrostatic doping/charging to the C-QDs, thereby shifting the Fermi level. With decrease in pH i.e., increase in  $[\text{H}^+]$  concentration the  $-\text{OH}$ ,  $-\text{NH}_2$ ,  $\text{COOH}$  groups are get protonated which destabilizes  $n\text{-}\pi^*$  state, thus reducing the energy gap between

the states and which in turn, decreases the vibronic interaction resulting a decrease in radiation less decay which explains the bright fluorescence intensity of the N-CQDs with decrease in pH. Fig. 3b shows the CIE 1931 chromaticity diagram for N-CQDs. The CIE chromaticity coordinate calculated from the PL spectrum is (0.14637, 0.11483).

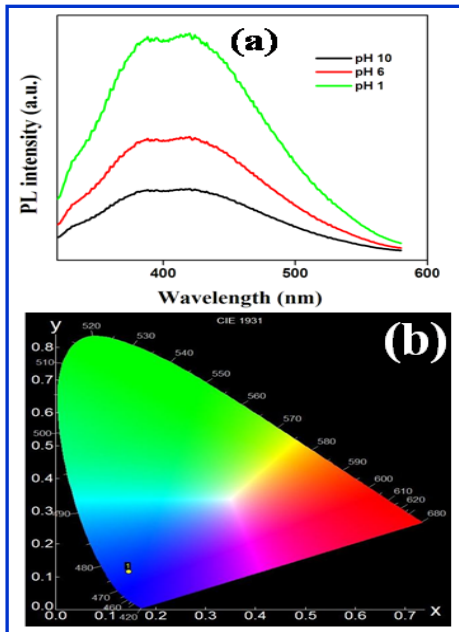


Fig. 3: a) PL with pH variation and (b) CIE index of N-CQDs

To obtain insight into the excitonic dynamics, we have measured the fluorescence lifetimes of N-CQDs. The average lifetime together with the component decay times obtained from the fitted decay curves (Fig. 3), are summarized in Table 1.

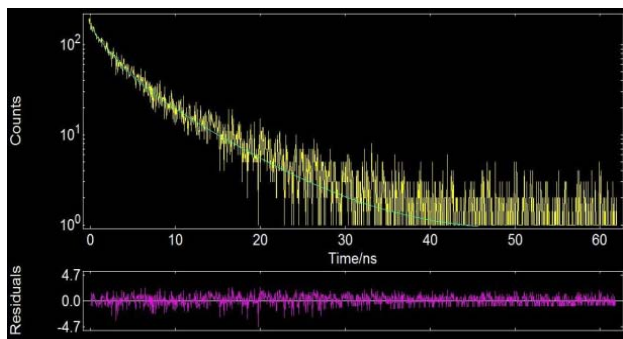


Fig. 4: Decay curves of N-CQDs

Average fluorescence lifetime  $\langle\tau\rangle$  for exponential fitting is calculated from the decay times  $\tau_i$  and the relative amplitudes  $a_i$  using the following relation:

$$\langle\tau\rangle = \frac{\sum_i^n a_i \tau_i^2}{\sum_i^n a_i \tau_i}$$

Table 1: Table example

$\tau_1$ (ns)	$a_1$	$\tau_2$ (ns)	$a_2$	$\langle\tau\rangle$ (ns)	$\tau_1$ (ns)
N-CQDs	<b>2.23</b>	<b>29.38</b>	<b>7.57</b>	<b>70.62</b>	<b>6.987</b>

Due to the presence of different functional groups (OH, COOH, NH<sub>2</sub>) in the N-CQDs surface which facilitates the nonradiative recombination of the ions to the nearby holes, the radiative recombination of excitons with the holes decreases and the excitons decay through two different path.

## 5. CONCLUSION

In summary, this work describes a convenient approach for the preparation N-CQD from citric acid and ammonia using simple hydrothermal technique. As synthesized N-CQDs show excellent excitation dependent bright blue PL spectra. PL intensity is also changed with pH. We believe this study will expand the applications of N-CQDs in optoelectronic devices.

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