



# Effects of chemical bonds between nitrogen and its neighbor carbon atoms on fluorescence properties of carbon quantum dots

Y. Liang, Y.F. Shen, C.L. Liu, X.Y. Ren\*

School of Materials Science and Engineering, Southwest University of Science and Technology, Mianyang 621010, China

## ARTICLE INFO

### Keywords:

Carbon quantum dots  
Pyridine N  
Fluorescence  
Nitrogen atoms

## ABSTRACT

The nitrogen atoms have been attracting enormous attention in improving the fluorescent properties of carbon quantum dots (CQDs), but the contribution varies widely. In this work, the effects of chemical bonds between nitrogen and its neighbor carbon atoms as well as the nitrogen/carbon molar ratio (N/C) on fluorescence properties of CQDs were investigated. Importantly, the former was disclosed based on two kinds of well-designed nitrogen doped CQDs (N-CQDs-1 and N-CQDs-2) that show differences in chemical bonds of doped nitrogen atoms but contain the same N/C ratio and are common in the content of  $sp^2$  hybridized carbon atoms and particle size. We concluded that pyridine N rather than pyrrole N is beneficial to increasing the emission intensity of CQDs, probably caused by the enhancement of electron exchange of complex luminescent centers, and the formation and introduction of electron traps. And the emission intensity does increase with the amount of doped nitrogen atoms. Therefore, the N-CQDs-1 containing the most amount of N atoms as forms of pyridine and pyrrole shows amazing fluorescent properties and highly quantum yield (QY) up to 34.23%.

## 1. Introduction

As a rising star in carbon nanomaterial family, luminescent CQDs have attracted ever increasing attention in recent years because of their excellent biocompatibility [1], low toxicity [2], facile synthesis [3,4], as well as fascinating optical properties [2,5]. CQDs have gained great interest in promising applications over these years [6], such as disease diagnosis, targeted tracer and luminescent probes for the detection of proteins, metal ions, enzymes, and other small molecules [7–12]. Therefore, efforts to enhance the fluorescent performances of CQDs are made continually, for example, surface passivation and doping with heteroatom. Heteroatoms such as nitrogen [13–15], phosphorus [16], boron [17], fluorine [18] and sulfur [19,20] have been widely employed to strengthen the emission properties of CQDs.

Among the heteroatoms, the nitrogen (N) atom is the first and the most one that has been reported and has shown its responsibility. It has been demonstrated that N atom can increase the electron density of its neighbor carbon atoms and provide new radiation recombination pathway, and thus increase the fluorescence efficiency. For example, Zhang et al. prepared NCDs with QY approximately 22% using  $CCl_4$  and  $NaNH_2$  as starting materials [21]; Dong et al. facilely synthesized CDs with PL QY up to 42.5% via carbonization of branched polyethylenimine and citric acid (CA) [22]. However, the reported CQDs doped with N atoms (N-CQDs) show significant differences in PL

intensity and emission color. N-CQDs extracted from different carbonized precursor and nitrogen sources possess quantum yield sitting in a wide range of 6–80% [14,21–28].

The fundamental reason for such significant differences stems from the insufficient understanding of the tailor behavior of N atom, including how does the doping amount and doping bonds influence the PL performances. There are kinds of conclusions as follows. Pyrrole N alone can participate in the protonation process and result in fluorescence enhancement [28]; Pyridine N leading to an increase of cyclic imines can enhance the conjugated system and improve the PL intensity [14]; Graphitic N can effectively tailor the electronic energy level which corresponds with optical transitions [29].

It is clear that the reported conclusion varies widely, which is probably due to the fact that most of them were concluded without taking other factors into consideration, such as the extent of carbonization, particles size and content of doped N atoms. For example, a series of N-CQDs have been prepared with amine-based compounds as precursors leading to a conclusion that pyrrole N enhances the fluorescence of N-CDs while pyridine N inhibits it [30]. However, the conclusion was drawn ignoring the effect of the concentration of isolated  $sp^2$  carbon atoms on the fluorescence. Different compounds show their character in thermal stability though their structure is similar, so those amine-based compounds pyrolyzed under the same temperature of 200 °C probably show different carbonization degrees and thus give

\* Corresponding author.

E-mail addresses: [liangyingswust@163.com](mailto:liangyingswust@163.com) (Y. Liang), [18381660278@163.com](mailto:18381660278@163.com) (Y.F. Shen), [liucailin@swust.edu.cn](mailto:liucailin@swust.edu.cn) (C.L. Liu), [renxianyan@swust.edu.cn](mailto:renxianyan@swust.edu.cn) (X.Y. Ren).

birth to N-CQDs containing different concentration of  $sp^2$  carbon atoms.

In the paper, not only is the effect of the Nitrogen/Carbon molar ratio (N/C) on the PL intensity of CQDs investigated, but also the chemical bonds between nitrogen and its neighbor carbon atoms on the PL intensity of CQDs will be studied. The former will be uncovered focusing on a series of N-CQDs prepared by the thermal-treatment of precursor composed of glucose (GLU, C source) and different amount of metformin hydrochloride (MH, N source); The latter will be lighted focusing on two kinds of N-CQDs that doped by N atom possessing different chemical states but the same N/C ratio and are common in the content of  $sp^2$  hybridized carbon atoms and particle size. Here, the chemical states of N atoms in N-CQDs are controlled by the structure of N source, and the diethylenetriaminepentaacetic acid (DTPA) is employed as another N source.

## 2. Experimental section

### 2.1. Preparation of the N-CQDs

The N-CQDs were synthesized by carbonization of the precursor composed of Glucose anhydrous (GLU) and diethylenetriaminepentaacetic acid (DTPA) or Metformin hydrochloride (MH) through a hydrothermal method. In a typical experimental procedure, 0.050 g GLU and appropriate amount of MH (from 0.05 g to 5.0 g) was dissolved in 50 mL deionized water. Then, the clear and homogeneous solution was transferred into the Teflon-lined autoclave chamber and heated at 240 °C for 2 h (the heating rate at temperature-rise period is about 10 °C/min). After being cooled down to room temperature, the sediment was removed by 11,000 rpm centrifugation for 15 min. The supernatant was passed through a membrane filter (pore size 0.22  $\mu$ m) then dialyzed by molecular weight cut-off (MWCO) of 5000 against fresh DDI water for 24 h to remove impurities and dried under vacuum. N-CQDs were stored for further characterization and use.

### 2.2. Characterization

In order to preliminarily determine the temperature for the pyrolysis of the precursor, thermogravimetric analysis (TGA) was performed at heating rate of 10 °C/min by TG209C thermogravimetric analyzer (NETZSCH). The chemical environment of N and C atoms was confirmed by X-ray photoelectron spectroscopy (XPS, K-Alpha, Thermo Scientific Company). The structures of N-CQDs were analyzed by an infrared spectrometer (IR, Bruker TENSOR 27), X-ray diffractometer (XRD, X Pert pro) and an ultraviolet-visible spectrophotometer (UV-vis, Hitachi U2001). The doping content of N atoms was determined by an elemental analyzer (Elementar, Germany). The particle size of N-CQDs was studied with JEOL JEM-2100 high resolution transmission electron microscopy (HRTEM, 200 kV).

### 2.3. Photoluminescence properties

The excitation and emission spectra ( $\lambda_{\text{excitation}} = 365$  nm) of N-CQDs were collected with a LS55 fluorescence spectrometer (Perkin Elmer, America). The QY was determined by comparing the integrated PL emission spectral intensity ( $\lambda_{\text{excitation}} = 365$  nm) and the absorption value (at  $\lambda = 365$  nm) of N-CQDs using quinine sulfate ( $QY_R = 0.55$ ) in 0.1 M  $H_2SO_4$  ( $\eta = 1.33$ ) [31] as a reference. The QY was calculated according to Eq. (1): [32]

$$QY = QY_R \frac{I_{AR}}{I_R} \frac{A_R}{A} \frac{\eta^2}{\eta_R^2} \quad (1)$$

Where A is the absorbance at the excitation wavelength,  $\eta$  is the refractive index of the solvent (for present case  $\eta/\eta_R = 1$ ), and I is the integrated emission intensity calculated from the area under the emission peak on the same wavelength scale.

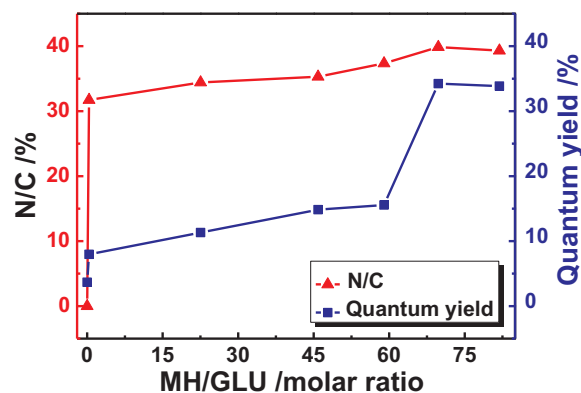


Fig. 1. N/C (molar ratio) in N-CQDs-1 synthesized by different amount of MH and the corresponding QY.

## 3. Results and discussion

### 3.1. The effect of the Nitrogen/Carbon molar ratio (N/C) on the PL intensity of CQDs

It is facile to prepare N-CQDs-1 containing an unprecedented amount of N atoms by employing MH as nitrogen source which contains a great number of nitrogen atoms. The N/C molar ratio in the N-CQDs-1 reaches to 39.9% (Fig. 1), which is higher than most of reported ones (about 2–10%) [25,33].

In addition, the results further confirm the general positive effects of nitrogen atoms on the QY of CQDs, which may originate from protonation of nitrogen atoms in N-CQDs or polyaromatic structures composed of a N atom and its neighbor C atoms [28]. As shown in Fig. 1, the QY of CQDs made by only GLU as a precursor was 3.67% which increased to 7.97% as soon as the N atoms was introduced to a N/C ratio of 31.3%, and sharply increased to 34.23% along with the N/C ratio increasing to 39.8%. We could get the optical properties of N-CQDs-1 more intuitively from Fig. S1.

### 3.2. The effects of chemical bonds between nitrogen and carbon atoms on fluorescence properties of carbon quantum dots

After the contribution of N atoms to PL intensity of CQDs has been confirmed, effects of different chemical bonds of N atoms on the optical properties of CQDs attract our main attention. We focus on the effect employing two kinds of N-CQDs (named as N-CQDs-1 and N-CQDs-2, separately) that doped with N atoms at the same N/C ratio, containing the same  $sp^2$  hybrid carbon atoms, and showing similar particle size. The N-CQDs-2 is extracted from a partial carbonized mixture composed of a carbon source GLU and a N source DTPA instead of MH. Through continuous adjustment and testing, we finally got N-CQDs-1 and N-CQDs-2 meet the above requirements from 0.05 g GLU as carbon source, 0.276 g MH and 0.35 g DTPA as nitrogen source, respectively. Importantly, the doping structures of N atoms in N-CQDs are designed based on the inherent difference of the chemical bond that between N atoms and its neighbor C atoms in DTPA and MH (Scheme 1).

It's worth mentioning two kinds of N-CQDs were prepared successfully and agree with our design. The two kinds of N-CQDs are identical in N/C ratio, particle size and containing similar concentration of  $sp^2$  hybrid carbon atoms, but showing distinct differences in the doping bond of the N atoms. As shown in Fig. 2, the monodispersed spherical N-CQDs-1 with an average size of 3.95 nm can be seen clearly. Similarly, the N-CQDs-2 shows a mean particle size of about 3.58 nm. The resemblances regard to N/C ratio (30.8% and 31.3%, respectively) and  $sp^2$  domains (confirmed by UV-vis and XPS) are demonstrated in detail and shown in the Supporting Information (Fig. S2-S3).

It can be seen from the IR spectra (Fig. 3a) that the N-CQDs-1

Download English Version:

<https://daneshyari.com/en/article/7840253>

Download Persian Version:

<https://daneshyari.com/article/7840253>

[Daneshyari.com](https://daneshyari.com)