Preparation of Carbon Dots by Pyrolyzing Carboxylate Ammonium Salt and its Application in Probing Ferric Ions

Chen Nie¹, Hao Zhang¹, Ruifang Guan¹,²,* and Duxia Cao¹,*

¹School of Materials Science and Engineering, University of Jinan, Jinan, Shandong, 250022 China
²Shandong Engineering Centre for Fluorinated Materials, University of Jinan, Jinan, Shandong, 250022 China.
Email: mse_guanrf@ujn.edu.cn; duxiacao@ujn.edu.cn.

Abstract. In this paper, we have reported a novel and facile synthesis approach of fluorescent carbon dots (C-Dots) through a one-step pyrolytic route of carboxylate ammonium salt (formed between citric acid (CA) and N-(β-aminoeethyl-γ-aminopropyl) methyl dimethoxysilane (AEAPMS)) without further passivation. The as-synthesized C-Dots possess excitation dependent fluorescence behaviors, strong blue photoluminescence (PL) emission with a quantum yield of 20.5% and pH stability. The morphology and structure of prepared C-Dots have been characterized by transmission electron microscope (TEM), X-ray diffraction (XRD) and Fourier transformed infrared spectroscopy (FTIR). TEM spectra reveal that the C-Dots are spherical nanoparticles with the size about 6.5 nm; FTIR indicate that there are lots of hydrophilic functional groups on C-Dots’ surface, which contribute to good water dispersibility. In addition, the obtained C-Dots exhibit a highly sensitive and selective fluorescence quenching effect toward Fe³⁺ ions in aqueous solution with a linear range of 0.05-0.20 mM and a detection limit of 19.3 nM, which has great potential in environmental applications for Fe³⁺ detection.

1. Introduction
Carbon dots (C-Dots) define a new type of visible emitters that have recently drawn tremendous attention thanks to their attractive optical properties [1], good biocompatibility [2], low toxicity [3], robust chemical inertness and environmental-friendly compared with traditional semiconductor quantum dots (QDs). In recent years, the promising applications of C-Dots in bioimaging, sensing, catalysis, and light emitting devices have been widely investigated especially for sensor application. For example, they can act as fluorescent sensing probes for metal ion detection such as Fe³⁺, which plays a crucial role in environment as well as in the biological systems [4].

Though a broad series of methods have been demonstrated for the advanced synthesis of C-Dots including laser ablation, chemical or electrochemical oxidization, microwave-assisted methods, hydrothermal carbonization and pyrolysis, the synthesis by pyrolyzing molecular organic salts in a single precursor without further passivation is a charming route. Bourlinos reported the preparation of luminescent C-Dots using citric acid salt as precursor and then subsequent surface passivation with organic ammonium salt under high temperature with a quantum yield (QY) of 3%[5]. Solid phase pyrolysis is a new tool in nanoscience to overcome bottlenecks in the characterization of nanomaterials. However, in most cases, the QY of the solid-phase synthesized C-Dots is less than 10%, and poor dispersibility of C-Dots in water limits their applications. Therefore, it is still a great challenge to establish a facile and high-output method to prepare fluorescent C-Dots with good optical properties for their wide applications.
In this paper, the ammonium salt of the carboxylic acid is used as the precursor, and the QY of resulting C-Dots is up to 20.5%. The obtained C-Dots particles are uniform and small, exhibiting good solubility and stability in water. Moreover, the obtained C-Dots can be used as an effective fluorescence probe for Fe$^{3+}$ in aqueous solution for the quenching effect.

2. Experiments

2.1. Chemicals and devices

Citric acid (CA), N-(β-aminoethyl-γ-aminopropyl) methyl dimethoxysilane (AEAPMS), Ethylenediamine (EDA) and ethylene diamine tetraacetic acid (EDTA) were all purchased from Aladdin Industrial Corporation (China). Alcohol and light petroleum were purchased from Tianjin Fuyu Fine Chemical Co., Ltd. All reagents are of analytical reagent grade and used as received. The solution of different ions ($10^{-2}$ mol L$^{-1}$) were prepared in deionized water from the respective salts of NiCl$_2$·6H$_2$O, NaCl, HgCl$_2$, FeCl$_3$·6H$_2$O, CuCl$_2$·2H$_2$O, CoCl$_2$·6H$_2$O, ZnCl$_2$ and CaCl$_2$. Precursors were heated on a tube furnace (SG-GL1200K), which was purchased from Shanghai Jujing Precision instrument Co., Ltd.

2.2 Characterization

Ultraviolet-Visible and Photoluminescence spectra were recorded by a Shimadzu UV2550 spectrophotometer and a Fluoromax-4 spectrophotometer (Horiba JY, France). Transmission electron microscope (TEM) image of C-dots was carried out using a JEOL TEM-3010 instrument, operating at an acceleration voltage of 200 kV. Fourier transformed infrared spectroscopy (FTIR) spectra were carried out on a Nicolet 380 FTIR (Thermo Nicolet). X-ray diffraction (XRD) analysis was recorded on a D8-ADVANCE diffractometer using CuKa radiation (Germany).

2.3 Synthesis

The whole synthesis routes of C-Dots are shown in figure 1, and the detailed prepared processes are described followed.

![Figure 1. The synthesis routes of C$_{SCN}$-Dots](image)

2.3.1 Synthesis of carboxylate ammonium salt.

A 50 ml round flask is placed in an ice-bath with 1g (5mmol) citric acid dissolved in 10 ml water. Next, 1.60g (7.5mmol) AEAPMS was slowly added with stirring. The mixture was kept stirring for 12 hours and the precipitate formed was filtered, washed with light petroleum and dried by rotatory evaporator. The resulting white solids are CA-AEAPMS salt (SCN).

2.3.2 Synthesis of C-Dots.

The carboxylate ammonium salt (SCN) was calcined in a tube furnace at 250°C for 1 h at a heating rate of 5°C min$^{-1}$ in a Argon atmosphere. Then the resultant dark brown mixture was ground to a uniform powder and dissolved with 10 mL of water. The supernatant was collected by removing the large dots through centrifugation at 12000 rpm for 10 min and then dialyzing against deionized water through a dialysis membrane (molecular weight cut off = 3.5 kDa) for 24 h. Finally, the blue fluorescent C$_{SCN}$-Dots were collected and stored in the refrigerator for further research.
3. Results and discussion

3.1. Characterizations of C-Dots

![Figure 2](image1.png)

Figure 2. (a) TEM of C\textsubscript{SCN}-Dots. Inset: size distribution of C\textsubscript{SCN}-Dots; (b) XRD pattern of C\textsubscript{SCN}-Dots

The size and morphology of C\textsubscript{SCN}-Dots were characterized by TEM. As shown in figure 2(a), C\textsubscript{SCN}-Dots are mostly uniform nanoparticles around 6.5 nm and with good dispersion. XRD pattern (figure 2(b)) of C\textsubscript{SCN}-Dots shows a broad diffraction peak at about 21.303° (2θ), which indicates that the structure of C\textsubscript{SCN}-Dots is amorphous carbon ordered in a considerably random fashion [6]. These results proved that the pyrolysis of ammonium carboxylate is efficient method for the fabrication of C-Dots.

![Figure 3](image2.png)

Figure 3. FTIR spectra of C\textsubscript{SCN}-Dots

The functional groups of C\textsubscript{SCN}-Dots were detected by FTIR spectra. As shown in figure 3, there are stretching vibration absorption peaks of N-H and O-H groups from 3713 cm\textsuperscript{-1} to 3226 cm\textsuperscript{-1}. C-H stretching vibration absorption peaks from 3064 cm\textsuperscript{-1} to 2921 cm\textsuperscript{-1}, C-H bending vibration absorption peaks between 1421 cm\textsuperscript{-1} and 1365 cm\textsuperscript{-1} and the bending vibration absorption peak of C-N at 1266 cm\textsuperscript{-1}. Especially, C\textsubscript{SCN}-Dots exist COO\textsuperscript{-} at 1300 cm\textsuperscript{-1} to 1420cm\textsuperscript{-1} and a stretching vibration absorption peak of Si-O-C at 1093 cm\textsuperscript{-1}. Those absorption bands indicate that there exist lots of amino-containing functional groups and hydroxyl groups on the surface of C-Dots, which result in good hydrophilic properties of the C-Dots [7].
Figure 4. (a) UV-vis absorption spectrum (red line), PL excitation (black line, λem=437 nm), and emission spectra (blue line, λex=349 nm) of C\textsubscript{SCN}-Dots dispersed in water. The inset shows the photograph (left) and PL of C\textsubscript{SCN}-Dots solution under UV light of 365 nm (right); (b) PL emission spectra of C\textsubscript{SCN}-Dots at different excitation wavelengths.

Subsequently, the optical properties including UV-vis absorption, PL emission, excitation, QY of the C\textsubscript{SCN}-Dots were fully examined. As shown in figure 4(a), the C\textsubscript{SCN}-Dots show a typical absorption peak at 347 nm, which is consistent with the excitation wavelength. When excited at 349 nm, the C\textsubscript{SCN}-Dots show strong PL with the maximum located at around 437 nm. In right inset of figure 4(a), we can see that C-Dots aqueous solution emits strong blue light under UV irradiation of 365 nm.

Furthermore, the C\textsubscript{SCN}-Dots exhibit excitation wavelength-dependent PL properties (figure 4(b)) and the QY of C\textsubscript{SCN}-Dots was thus calculated to be 20.5\% using quinine sulfate (0.1M, \(\lambda_{ex}=360\) nm) as a reference. What’s more, we also prepared other C-Dots from different carboxylate ammonium salts by choosing different carboxylic acid (EDTA) and organic amine (EDA) and their PL properties are showed in table 1, which prove that pyrolyzing carboxylate ammonium salts is an effective and simple method for the preparation of C-Dots.

Table 1. The QY, absorbance peak, \(\lambda_{ex}\), \(\lambda_{em}\) and detection limit of other different C-Dots.

| C-Dots precursor | Absorbance peak (nm) | \(\lambda_{ex}\) (nm) | \(\lambda_{em}\) (nm) | QY (%) | Detection limit (nM) |
|-----------------|----------------------|----------------------|----------------------|--------|----------------------|
| CA-EDA salt     | 348                  | 346                  | 450                  | 18.0   | 93.3                 |
| EDTA-EDA salt   | 351                  | 350                  | 416                  | 22.4   | 57.9                 |
3.2. Sensing properties of C-Dots

![Comparison of PL intensity with and without Fe³⁺](image1.png)

**Figure 5.** (a) Effect of metal ions (1 mM) on the PL intensity of C\(_{\text{SCN}}\)-Dots solution at 450 nm. The inset shows the emission spectra recorded with different metal ions respectively; (b) PL response of C\(_{\text{SCN}}\)-Dots to various metal ions without/with Fe\(^{3+}\)(1mM) at 450nm.

Next, we studied the sensing ability of C\(_{\text{SCN}}\)-Dots. Figure 5(a) shows PL intensity of aqueous C\(_{\text{SCN}}\)-Dots solution (50 μg·mL\(^{-1}\)) toward different metal ions including Ni\(^{2+}\), Na\(^{+}\), Hg\(^{2+}\), Fe\(^{3+}\), Cu\(^{2+}\), Co\(^{3+}\), Zn\(^{2+}\), Ca\(^{2+}\). Compared with other metal ions, the addition of Fe\(^{3+}\) in C\(_{\text{SCN}}\)-Dots aqueous solution resulted in remarkably PL decrease by complexation between Fe\(^{3+}\) and abundant surface carboxyl, amine, and hydroxyl groups [8]. Moreover, the competitive experiments were also conducted by observing the change in PL intensity at 450 nm with other ions added to the detection experiments for Fe\(^{3+}\) respectively. Actually, all the metal species have no effect or only a slight effect on the PL detection of Fe\(^{3+}\) (figure 5(b)), which indicates that C\(_{\text{SCN}}\)-Dots possess excellent selectivity to Fe\(^{3+}\).

![PL titrations of C\(_{\text{SCN}}\)-Dots and quenching efficiency](image2.png)

**Figure 6.** (a) PL titrations of C\(_{\text{SCN}}\)-Dots at 450 nm with the concentration of Fe\(^{3+}\) from 0 mM to 1 mM. The inset shows the photographs of C\(_{\text{SCN}}\)-Dots solution in the absence and presence of 0.5 mM Fe\(^{3+}\) under UV light (365 nm); (b) Quenching efficiency of C\(_{\text{SCN}}\)-Dots with different concentrations of Fe\(^{3+}\). The inset shows the dependence of the changes of PL intensity on the concentration of Fe\(^{3+}\) (from 0.05 to 0.20 mM).

In addition to the high selectivity of C\(_{\text{SCN}}\)-Dots towards Fe\(^{3+}\), their sensitivity was investigated. Figure 6(a) shows the PL intensity of the C\(_{\text{SCN}}\)-Dots solution was gradually quenched with the concentration of Fe\(^{3+}\) from 0 mM to 1mM. And figure 6(b) presents the relationship of the changes of PL intensity with the concentration of Fe\(^{3+}\) and there is a good linear relationship from 0.05 to 0.20
mM (figure 6(b) inset). The detection limit (DL) of 19.3 nM was calculated according to the IUPAC 3σ criterion (DL=3SD/S, where SD is the standard error of the intercept and S is the slope of the calibration curve). What’s more, the DL of other two C-Dots prepared by different precursors are shown in table 1, which obviously reveal that the C-Dots’ sensitivity towards Fe$^{3+}$ ions improved with the QY increasing. These results clearly demonstrate that the C$_{SCN}$-Dots fluorescent sensor is highly selective and sensitive toward Fe$^{3+}$ ions over the other metal ions, which may be useful for Fe$^{3+}$ detection with aqueous environments [9].

4. Conclusion
In conclusion, we have developed a novel route to highly efficient blue fluorescent C$_{SCN}$-Dots with high QY by pyrolysis of carboxylate ammonium salts. The C$_{SCN}$-Dots exhibit good water solubility, excitation dependent PL behaviors and stable PL property against variation of pH. More notably, the C$_{SCN}$-Dots can be utilized as a PL probe for detection of Fe$^{3+}$ in aqueous solution, which promise to broaden the range of applications as environmental sensor systems.

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6. References
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