

# Microwave-assisted one-step green synthesis of amino-functionalized fluorescent carbon nitride dots from chitosan

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**ABSTRACT:** We present an economical, facile and effective microwave pyrolysis approach to synthesize highly amino-functionalized fluorescent carbon nitride dots (CNDs). The formation and the functionalization of CNDs was accomplished simultaneously through the dehydration of chitosan. It is suggested that these CNDs have good water solubility and exhibit strong fluorescence. Copyright © 2013 John Wiley & Sons, Ltd.

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**Keywords:** microwave; green synthesis; fluorescent carbon nitride dots; chitosan

## Introduction

In recent years, fluorescent semiconductor quantum dots (QDs) have been a common subject of academic research because of their unique optical and biochemical features (1–6). However, the use of heavy metals, which are essential elements in these conventional semiconductors, is restricted because of concerns about their toxicity, stability and environmental impact (8,7). Therefore, the fabrication of benign nanomaterials with similar optical properties is an interesting challenge inspiring intensive research. In recent years, a new type of visible emitter has been reported, based exclusively on carbon dots (CDs) (9–12) or carbon nitride dots (CNDs) (13,14). CDs and CNDs seem to be a promising alternative to traditional toxic metal-based semiconductor QDs in many fields of applications due to their stable photoluminescence (PL), strong fluorescence, broad excitation spectra, tunable emission spectra, low cytotoxicity and excellent biocompatibility.

Approaches to synthesizing eco-friendly fluorescent CDs or CNDs can be generally classified into two main groups: top-down and bottom-up (15). Top-down methods are used to etch a larger carbon structure into individual nanoparticles, such as arc-discharge single-walled carbon nanotubes (16), laser ablation of graphite (9), electrochemical oxidation of graphite and multi-walled carbon nanotubes (17,18), carbonizing polymerized resols on silica spheres (19), chemical oxidation soots of candles, natural gas, commercially activated carbon and lampblack (20–22) and chemical oxidation of oxide graphene (23). By contrast, bottom-up methods are used to form nanoparticles from molecular precursors, such as chemical and thermal oxidation or in the microwave pyrolysis of carbonaceous compounds (14,24–28). However, most of these synthesis methods involve expensive starting materials, devices that consume a great deal of energy, intricate processes, and the as-synthesized CDs or CNDs are typically oxidized by strong acid and further surface-passivated by a diamine-terminated organic molecule to improve the water solubility of the CNDs and modify the PL properties. Therefore, building an economical, facile, effective and green synthetic route

to produce strong fluorescent CDs or CNDs on a large scale for practical application remains critical.

Herein, we present an economical, facile and effective microwave pyrolysis approach for the synthesis of highly amino-functionalized fluorescent CNDs. A characteristic feature of this one-step approach is that the formation and the functionalization of CNDs was accomplished simultaneously through the dehydration of chitosan; neither a strong acid solvent nor surface modification reagent is needed. The synthetic process occurs in a domestic microwave oven using inexpensive chitosan as the carbon source and has the advantage of being inexpensive and completely 'green'.

## Experimental

### Preparation of fluorescent CNDs

In a typical procedure, amino-functionalized fluorescent CNDs were synthesized as follows: 0.5 g chitosan was dissolved in 10 mL water to form a homogeneous solution, which was then put into a domestic microwave oven (700 W) and heated for 9.5 min. The color-changed solution was centrifuged at 13,000 rpm for 30 min to remove the less-fluorescent deposit, and dialyzed against pure water through a dialysis membrane for 4 days to remove residual chitosan. Finally, amino-functionalized fluorescent CNDs were dried in a vacuum at 65 °C overnight.

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### Characterization methods

UV-vis absorption was characterized using a UV1800 UV-vis spectrophotometer (Shimadzu Corporation, Japan). PL emission measurements were performed using a RF-5301PC fluorescence spectrophotometer (Shimadzu Corporation). The morphology of the as-synthesized nanoparticles was studied using a FEI Tecnai G2F20 transmission electron microscope (TEM). Elemental analysis was carried out using an Elementar Vario ELIII. The surface groups on CNs were measured with a 8400s FT-IR spectrometer (Shimadzu Corporation). X-Ray photoelectron spectroscopy (XPS) analysis was measured on an ESCALAB MK-II X-ray photoelectron spectrometer.

### Quantum yield measurements

The quantum yield ( $\Phi$ ) of CNs was measured by comparing the integrated PL intensities and the absorbency values against the reference quinine sulfate (QS). QS (literature  $\Phi=0.54$ ) was dissolved in 0.1 M  $H_2SO_4$  (refractive index,  $\eta_r$ , of 1.33) and the CNs were dissolved in distilled water ( $\eta=1.33$ ).

$$\Phi = \Phi_R \times \frac{I}{I_R} \times \frac{A_R}{A} \times \frac{\eta^2}{\eta_R^2}$$

where  $\Phi$  is the quantum yield,  $I$  is the measured integrated emission intensity,  $\eta$  is the refractive index and  $A$  is the optical density. The subscript R refers to the reference fluorophore of known quantum yield.

### Results and discussion

As shown in Scheme 1, in a typical procedure, amino-functionalized fluorescent CNs were synthesized as follows: an appropriate amount of chitosan was dissolved in water to form a homogeneous solution, which was then put into a domestic microwave oven (700 W) and heated for different lengths of time. The color-changed solution was centrifuged and dialyzed to remove less-fluorescent deposit and residual chitosan. Finally, a clear yellow-brown aqueous solution containing CNs was obtained. The yield of fluorescent CNs is ~6.4% and the sample shows good water solubility. Experiments revealed that the solubility of the CNs

reached 60 mg/mL in water and there was no precipitation for months. Our preparation method presents a facile approach to producing highly amino-functionalized fluorescent CNs on a large scale. The functional groups on its surface improve its water solubility and reduce its potential biotoxicity, which is essential for biologically motivated work.

Figure 1 depicts the UV-vis absorption and PL spectra for CNs. The first absorption band was observed at 282 nm. When it was excited at 338 nm, the PL spectra showed a peak position at 440 nm, a 158 nm red shift from the first absorption peak. In addition, the fluorescent intensity gradually decreased with increasing excitation wavelength. Such an observation is similar to that of carbon dots, which may be attributed to the optical selectivity of differently sized nanoparticles (quantum effect) or different emissive traps on the CN surface or another mechanism altogether. In addition, abundant functional groups, such as carboxyl acids and amines, which are introduced simultaneously during the microwave pyrolysis, may introduce different defects onto the surface of CNs, acting as excitation energy traps and leading to different PL properties.

The fluorescence quantum yield of CNs is ~6.4% when the microwave pyrolysis time is 9.5 min with QS as a standard reference (Table S1). These values are comparable with previous

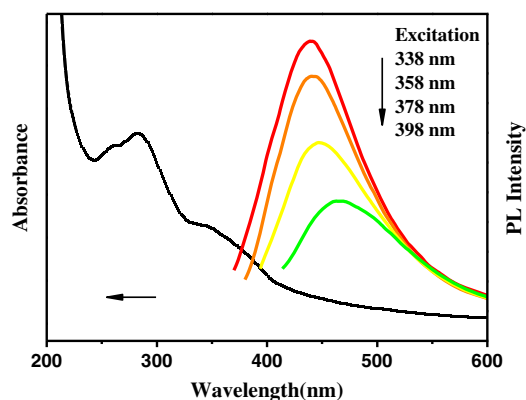
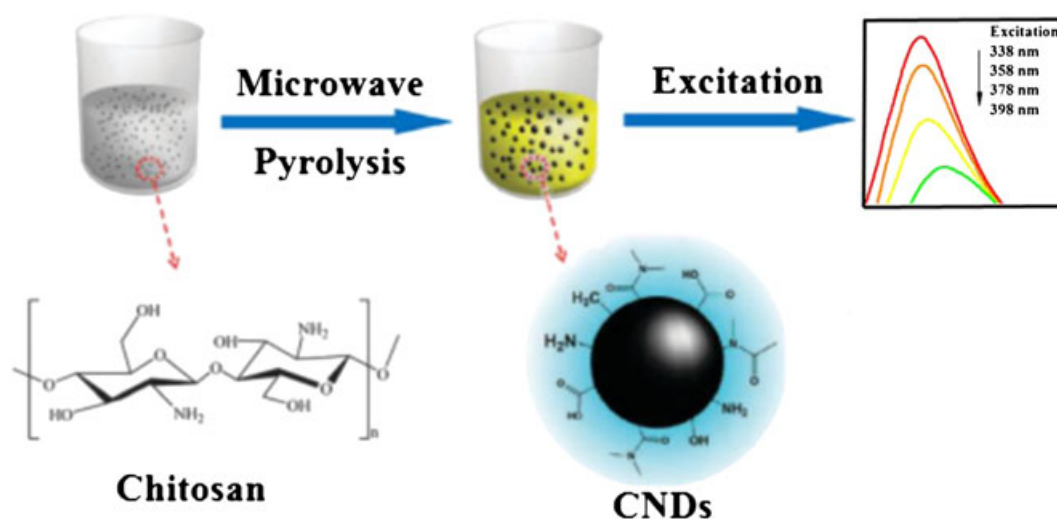


Figure 1. UV-vis absorption spectra and PL spectra for CNs.



Scheme 1. A schematic illustration of the preparation procedure of CNs by microwave pyrolysis of chitosan.

reports (13,29). Table S2 shows the PL quantum yield of CNDs for various microwave pyrolysis times. It can be seen that the PL quantum yield increased sharply when microwave pyrolysis time varied from 3.5 to 9.5 min, which indicated that the formation of CNDs is very fast and facile.

The TEM image (Fig. 2) showed that the nanoparticles were monodispersed and uniform with a spherical shape. The as-prepared CNDs were well dispersed in narrow distributions of  $4.6 \pm 1.9$  nm diameter with a microwave pyrolysis time of 9.5 min. As the time increased to 11.5 min, the diameter of the CNDs increased slightly and an aggregate phenomenon was observed. Thus, a microwave pyrolysis time of 9.5 min was chosen in the subsequent study. The chemical composition of these nanoparticles was further determined by collecting the corresponding energy-dispersed spectroscopy (EDS) results, as shown in Fig. S1. Peaks of C, N and O are observed, indicating that these nanoparticles are formed by chitosan and H<sub>2</sub>O. Furthermore, peaks of F, S, Si and Cu are also observed, which originate from the glass substrate used for EDS analysis. Elemental analysis indicated that the composition of the CNDs was: C, 34.93 wt%; N, 6.43 wt%; H, 6.97 wt% and O, 51.67 wt%. It was found that after microwave carbonization the carbon and nitrogen content of the CNDs increased, which was mainly due to the loss of oxygen and hydrogen during dehydration of the chitosan (Table S3). The surface composition and elemental analysis for the overall composition of the resultant nanoparticles were characterized using XPS techniques. The XPS spectrum of the nanoparticles shown in Figs S2–S5 exhibited three peaks at 285, 401 and 532 eV, which were attributed to C1s, N1s and O1s, respectively. All these results indicated that the nanoparticles thus obtained were mainly composed of C, N, O and H.

As shown in Fig. 3, Fourier transform infrared (FT-IR) measurements of pure chitosan powder showed that the peaks at  $3447\text{ cm}^{-1}$  were attributed to O–H and N–H stretching vibrations of amine groups. The peaks at  $1644\text{ cm}^{-1}$  and  $1593\text{ cm}^{-1}$  corresponded to N–H bending vibrations. For the CNDs, the result showed an increase in absorption of the amino group at  $1634\text{ cm}^{-1}$  compared with chitosan. C–H vibrations at  $1130\text{--}1064\text{ cm}^{-1}$  associated with the pyranose were almost lost. These distinctions may be caused by degradation of the chitosan chain and decomposition of the pyranose ring through dehydration. Similar results are also reported in the literature

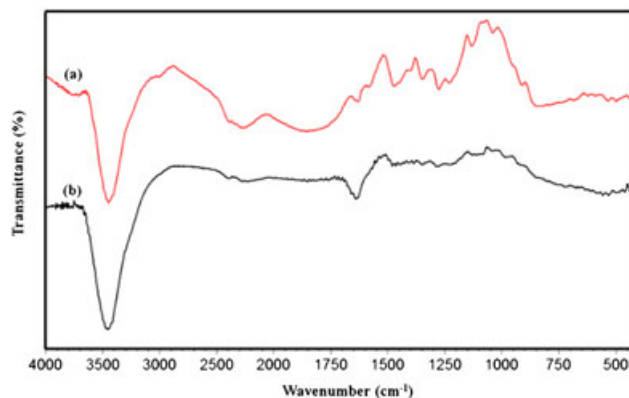


Figure 3. FT-IR spectrum of (a) pure chitosan, (b) fluorescent CNDs.

(27). The zeta-potential measurements showed that the surface of the CNDs has the amine groups because it is positive when the pH was  $< 6.6$ , suggesting that microwave pyrolysis of chitosan was an effective way to obtain amino-functionalized fluorescent CNDs.

Moreover, the impact of pH and ionic strength on the fluorescence intensity of CNDs was investigated (Fig. S6). The results indicated that the fluorescence intensity of CNDs changed slightly when the solution pH varied from 5.3 to 7.7, and even in an aqueous solution with a high ionic strength the fluorescence intensity of the CNDs was stable. These phenomena show the potential of the fluorescent CNDs to be good candidates for biological applications.

## Conclusions

In conclusion, fluorescent CNDs were prepared by microwave pyrolysis derived from chitosan. The synthesized CNDs showed some benign properties such as higher PL efficiencies (6.4%), monodispersity and small diameter ( $4.6 \pm 1.9$  nm). In comparison with previous methods, this one-step 'green' process has no need for strong acid treatment or surface modification. In particular, the as-prepared CNDs exhibit excellent stability in biological media, and their luminescence intensity is also stable within the

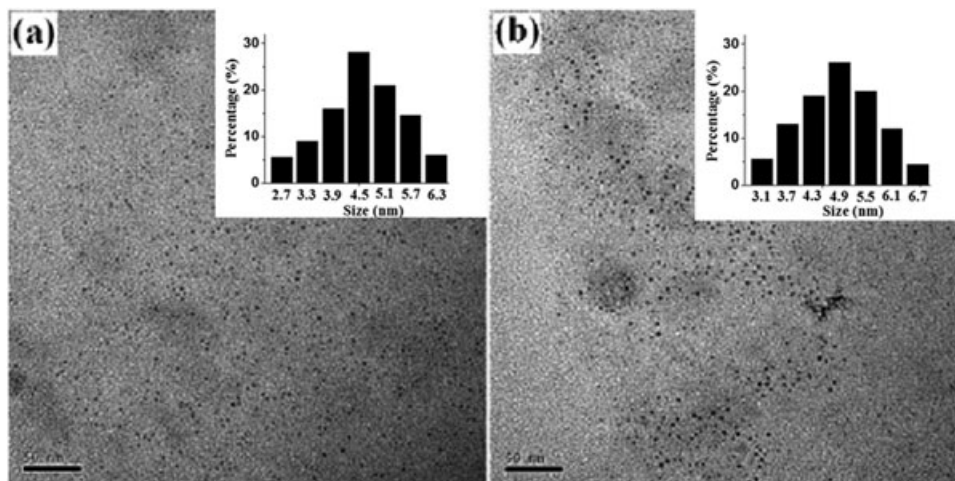


Figure 2. TEM images and their size distributions for CNDs with different microwave pyrolysis time of (a) 9.5 min and (b) 11.5 min; scale bars: 50 nm.

physiological and pathological ranges for ionic strength or pH. The strong fluorescence and excellent water dispersion can be attributed to the abundant surface traps and functional groups. Combining their low cytotoxicity, low cost, green method of synthesis, ease of labeling and favorable optical properties, CNDs provide promising applications in biological labeling and biosensors.

## SUPPORTING INFORMATION

Supporting information may be found in the online version of this article.

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