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1 **One-Step Hydrothermal Synthesis of**
2 **Photoluminescent Carbon Nitride Dots Derived from**
3 **Ionic Liquid**

4
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18

19 **Abstract**

20 We present an economical and facile hydrothermal approach to synthesize
21 fluorescent carbon nitride dots (CNDs) derived from ionic liquids. It
22 suggests these CNDs thus obtained are well water-soluble and exhibit
23 strong fluorescence. The one-step preparation process is simple and
24 effective, neither a strong acid solvent nor surface modification reagent is
25 needed, which makes this approach very suitable for industrial
26 production.

27

28 **Keywords:** fluorescent, carbon nitride dots, ionic liquids, hydrothermal
29 approach

30 **Introduction**

31 Since the Fluorescent semiconductor quantum dots (QDs) have some
32 unique optical and biochemical properties and several magnificent
33 applications in optoelectronic devices, biological labelling, etc,^[1-6] they
34 are considered to be a top subject in academic researches and various
35 industrial areas. However, heavy metals which are essential elements in
36 these conventional semiconductors, are of restrictive use for concerns
37 about their toxicity, stability and environmental hazard.^[7-9] Therefore, it is
38 a critical issue to search for benign nanomaterials with similar optical
39 properties.

40 Recently a new type of visible emitters has been reported exclusively
41 based on carbon dots (CDs) which have shown great impact in health and
42 environmental applications. Also they have been proved to be a kind of
43 promising building blocks for future nanodevices due to their fascinating
44 photoluminescence and potential as nontoxic replacements for traditional
45 heavy-metals-based quantum dots.^[10-13] On the other hand, carbon nitride
46 dots(CNDs) have got attention from materials researchers because of their
47 unique characteristics and wide performances in catalysis, sensors,
48 corrosion protection, etc.^[14,15] Several methods to prepare CDs or CNDs
49 have been reported, such as chemical oxidation of arc-discharge
50 single-walled carbon nanotubes,^[16] electrochemical oxidation of graphite
51 and multiwalled carbon nanotubes,^[17,18] laser ablation of graphite,^[10]

52 separation of combusted carbon soot,^[19,20] and carbonizing polymerized
53 resols on silica spheres.^[21] However, most of these synthesis methods
54 involve intricate processes, surface modification, expensive starting
55 materials or great energy-consuming devices, consequently leading to
56 limited yield quantities of CDs or CNDs. Therefore, it is still a critical
57 issue to build an economical, facile, effective and green synthetic route to
58 produce strong fluorescent CDs or CNDs on a large scale for practical
59 application.

60 Nowadays, ionic liquids (ILs) have been gaining great exposure for
61 potential use in chemical synthesis because of their “green”
62 characteristics such as negligible volatility and nonflammability under
63 ambient conditions, large liquid range, high thermal and chemical
64 stability, strong solubility power and a number of possible variations in
65 cation and anion features which allow fine-tuning of the ILs
66 properties^[22-25]. However, to the best of our knowledge, one-step
67 preparation of CNDs derived from ionic liquids through hydrothermal
68 approach has not been reported so far. In the last decade, the
69 hydrothermal technique has offered several advantages, such as
70 decomposition of hazardous and/or refractory chemical substances,
71 homogeneous precipitation using metal chelates under hydrothermal
72 conditions, and a host of other chemical engineering and environmental
73 engineering issues dealing with recycling of rubbers and plastics, and so

74 on. Recently Zhao *et al.* have reported the hydrothermal carbonization of
75 chitosan under mild aqueous conditions for the production of N-doped
76 carbonaceous materials[26] and Tian *et al.* have exploited a hydrothermal
77 synthesis route for enhanced photoluminescence of carbon
78 nanoparticles.[27]

79 In this work, we report an economical and facile hydrothermal
80 approach to synthesize CNDs derived from ionic liquids. It is found that
81 the CNDs formed through heat-treatment-based strategy are well
82 water-soluble and exhibit strong fluorescence. The one-step preparation
83 process is simple and effective, neither a strong acid solvent nor surface
84 modification reagent is needed, which makes this approach very suitable
85 for industrial production.

86

87 **Experimental**

88 **Reagents**

89 1-butyl-3-methylimidazolium tetrafluoroborate ([Bmim]BF₄),

90 1-butylpyridinium tetrafluoroborate ([BPy]BF₄),

91 1-hexyl-3-methylimidazolium tetrafluoroborate ([Hmim]BF₄)

92 1-dodecyl-3-methylimidazolium tetrafluoroborate ([C₁₂mim]BF₄)

93 1-hexadecyl-3-methylimidazolium bromide ([C₁₆mim]Br) were

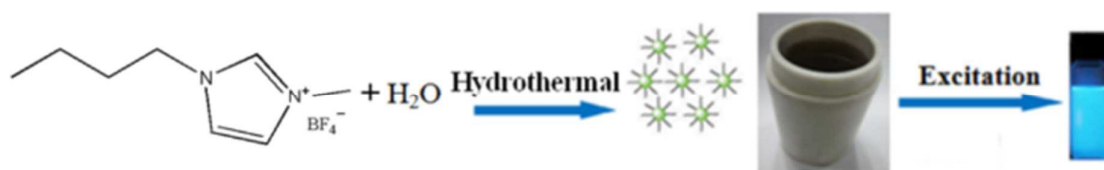
94 purchased from Lanzhou Greenchem ILS, LICP. CAS. China. All the

95 chemicals were used as received without further purification.

96 Apparatus
97 UV-vis absorption was characterized by UV1800 UV-Vis
98 spectrophotometer (Shimadzu Corporation, Japan). Photoluminescence
99 (PL) emission measurements were performed using a RF-5301PC
100 fluorescence spectrophotometer (Shimadzu Corporation, Japan). The
101 morphology of the as-synthesized nanoparticles was studied using a FEI
102 Tecnai G2 F20 transmission electron microscope (TEM) and a IX71
103 inverted research microscope (Olympus, Japan). The surface groups on
104 CNDs were measured with a 8400s FTIR spectrometer (Shimadzu
105 Corporation, Japan). X-ray photoelectron spectroscopy (XPS) analysis
106 was measured on an ESCALAB MK-II X-ray photoelectron spectrometer.
107 Raman spectra were recorded using a DXR Raman Microscope (Thermo
108 Fisher Scientific, America).

109

110 Synthesis of CNDs



112

Scheme 1 Hydrothermal approach to CNDs.

113 As shown in Scheme 1, the photoluminescent CNDs were prepared by
114 polymerization of ionic liquid and distilled water. In a typical procedure,
115 0.5g of 1-butyl-3-methylimidazolium tetrafluoraborate ([Bmim]BF₄) was

116 added to 20 mL of distilled water, which was then transferred to a
117 Teflon-lined stainless-steel autoclave and sealed to heat at 200 °C. After
118 reaction for 12 h, a dark brown solution was obtained, which implied the
119 formation of the CNDs.

120 Quantum yield

121 The quantum yield (Φ) of CNDs was measured by comparing the
122 integrated photoluminescence intensities and the absorbency values with
123 the reference quinine sulfate (QS). The quinine sulfate (literature $\Phi = 0.54$)
124 was dissolved in 0.1M H₂SO₄ (refractive index (η) of 1.33) and the CNDs
125 was dissolved in distilled water ($\eta = 1.33$).

$$126 \quad \Phi = \Phi_R \times \frac{I}{I_R} \times \frac{A_R}{A} \times \frac{\eta^2}{\eta_R^2}$$

127 Where Φ is the quantum yield, I is the measured integrated emission
128 intensity, η is the refractive index, and A is the optical density. The
129 subscript R refers to the reference fluorophore of known quantum yield.

130

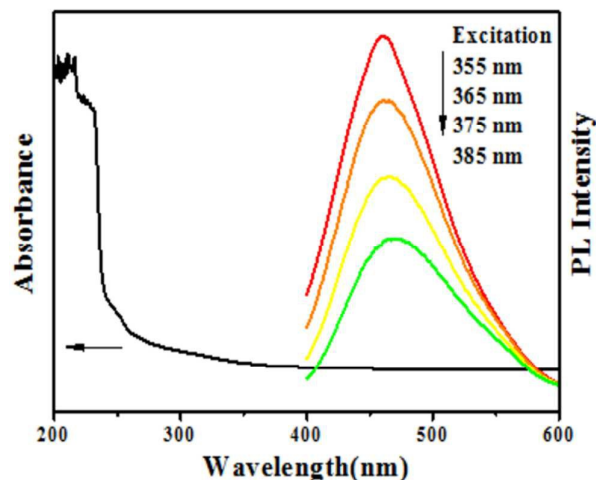
131 **Results and discussion**

132 Optimization of preparation

133 In order to acquire high quantum yield, the synthesis conditions of CNDs,
134 including the amount of ion liquid, the volume of water, reaction
135 temperature and time, were optimized. As shown in Table S1, the optimal
136 result (No. 9) demonstrated that high quantum yield needed higher
137 temperature, longer time, higher gas pressure and appropriate proportion

138 of reactants.

139 Characterization of CNDs



140

141 **Fig. 1** UV-vis absorption spectra and PL spectra for CNDs.

142 Fig. 1 depicts the UV-vis absorption and photoluminescence (PL) spectra

143 for the sample. The first absorption band at 240 nm was observed for both

144 samples. When it was excited at 355 nm, the PL spectra showed a peak

145 position at 458 nm. A 218 nm red shift from the first absorption peak was

146 observed. In addition, the fluorescent intensity gradually decreases with

147 increasing excitation wavelength. Such observation is similar to other

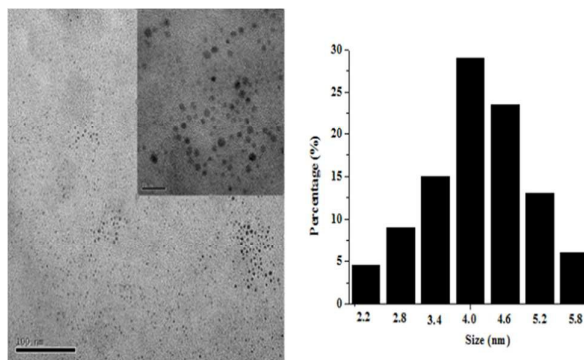
148 carbon nitride dots²⁴, which may be attributed to the optical selection of

149 differently sized nanoparticles (quantum effect) or different emissive

150 traps on the CNDs surface or another mechanism altogether. The

151 fluorescence quantum yield of CNDs is about 8.34% with quinine sulfate

152 as a standard reference (Table S2).

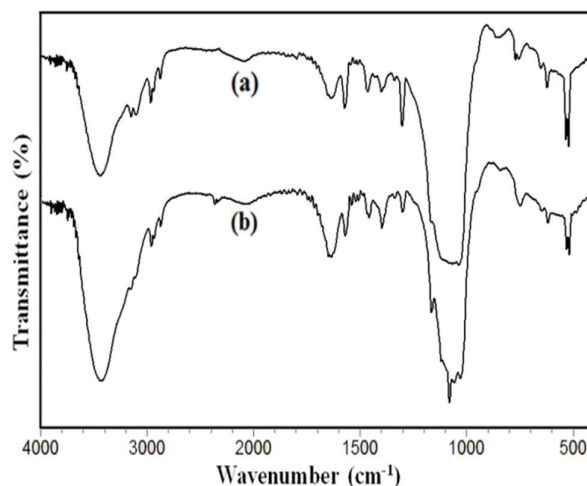


153

154 **Fig. 2** TEM images and their size distributions for CNDs. The inset scale
155 bar is 20 nm.

156 The transmission electron microscopic (TEM) image (Fig.2) and FL
157 images of CNDs (Fig. S1) showed that the nanoparticles were uniform
158 with spherical shape, and the as-prepared CNDs were well dispersed in
159 narrow distributions of 4.15 ± 1.95 nm diameter. The chemical
160 composition of these nanoparticles was further determined by collecting
161 the corresponding energy-dispersed spectroscopy (EDS) results, as shown
162 in Fig. S2. The peaks of C, N and O elements are observed, indicating
163 these nanoparticles are formed by [Bmim]BF₄ and H₂O. Furthermore, the
164 peaks of F, S, Si and Cu elements are also observed, which are originated
165 from [Bmim]BF₄ adsorbed on the surface of CNDs and glass substrate
166 used for EDS analysis. The elemental analysis indicated that the
167 composition of the CNDs was C 48.97 wt%, N 8.56 wt% and H 5.72 wt%
168 (Table S3). It was found that after hydrothermal carbonization the carbon
169 content of the CNDs obviously increased, which was mainly due to the
170 loss of nitrogen and hydrogen in the hydrothermal process. The surface

171 composition and elemental analysis for the overall composition of the
172 resultant nanoparticles were characterized by XPS techniques. The XPS
173 spectrum of the nanoparticles shown in Fig. S3-S6 exhibits three peaks at
174 285, 401 and 532 eV, which are attributed to C1s, N1s, and O1s,
175 respectively. Another two peaks at 193 and 685 eV associated with B_{1s}
176 and F_{1s} are also observed, which may come from [Bmim]BF₄ and
177 adsorbed on the surface of particles. All these results indicate that
178 nanoparticles thus obtained are mainly composed of C, N, O, H and
179 limited amounts of B and F elements.



180

181 **Fig. 3** FT-IR spectrum of (a) [Bmim]BF₄ and (b) CNDs.

182 As shown in Fig. 3, Fourier Transform Infrared (FT-IR) measurements
183 of CNDs showed that the peaks at 3446 cm⁻¹ and 1635 cm⁻¹ were
184 attributed to the stretching vibrations and in-plane bending vibration of
185 -OH, respectively. The peaks at 2964 cm⁻¹, 2874 cm⁻¹ and 1302 cm⁻¹
186 corresponded to the asymmetric and symmetric stretching vibrations of

187 C–H bonds. There were typical peaks around 1060cm^{-1} , which were
188 ascribed to stretching vibrations of B-F. The characteristic absorption
189 bands of aromatic C–N heterocycles at 1465 cm^{-1} and 1572 cm^{-1} were
190 observed, revealing that the local structure of nanoparticles thus obtained
191 is composed of CN units.[28,29] Compared to [Bmim]BF₄, the CNDs
192 showed a decrease in adsorption of C–H unsaturated stretching vibrations
193 at 3095 cm^{-1} and 3156 cm^{-1} , which can be interpreted as the
194 decomposition of the imidazole ring through the hydrothermal process.

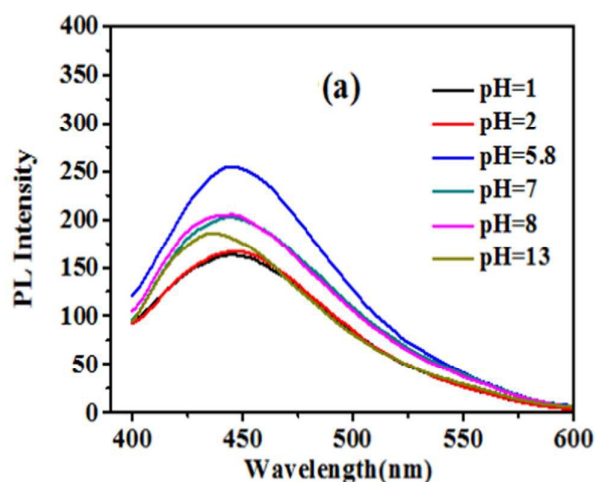
195 Influence of pH and ionic strengths.

196 Typical Raman spectra in Fig. S7 shows a strong D band at 1100 cm^{-1} ,
197 a very weak G band at 1419 cm^{-1} and a peak at 2436 cm^{-1} , ascribed to
198 disordered carbon and sp^2 clusters, indicating an amorphous nature^[30].

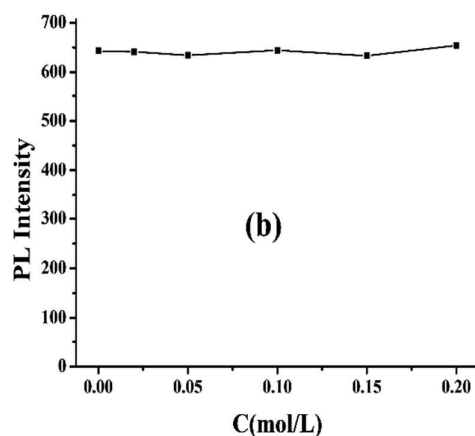
199 As shown in Fig. S8, the CNDs showed excellent photostability as the
200 fluorescence intensity did not change obviously, even after continuous
201 excitation under a 150 W Xe lamp for 11 hours.

202 The impact of pH and ionic strengths on the fluorescence intensity of
203 CNDs was investigated (Fig. 4). The results indicated that even in
204 aqueous solution with a high ionic strength the fluorescence intensity of
205 the CNDs were stable. However, the fluorescence intensity of the CNDs
206 increases when the solution pH varied from 1.0 to 5.8. On the contrary,
207 the fluorescence intensity decreased significantly when the pH value
208 varied from 5.8 to 13. These phenomena show the potential of the

209 fluorescent CNDs as good candidates for biological applications and pH
210 sensors. It is found that such observations are similar to those of carbon
211 nanoparticles modified passivated by the N-containing polymer, which
212 are attributed to the presence of N-containing groups on the surface,²⁴ but
213 our one-step “green” process is absolutely more economical and facile,
214 which does not require strong acid treatment or surface modification.



215

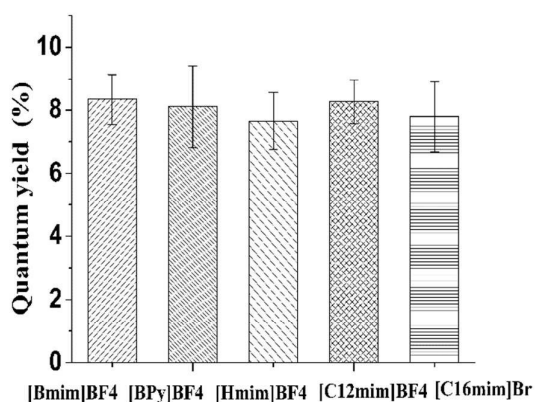


216

217 **Fig. 4** The influence of pH and ionic strengths on the fluorescence
218 intensity for CNDs

219 Method practicability

220 In addition, it was also found that other ionic liquids may serve as the
221 carbon precursor for synthesizing fluorescent CNDs. Different types of
222 nitrogenous ionic liquids ([Bmim]BF₄, [BPy]BF₄, [Hmim]BF₄,
223 [C₁₂mim]BF₄, [C₁₆mim]Br) had been applied to test the possibility of
224 producing fluorescent CNDs. As shown in Fig. 5, The quantum yield of
225 carbon nitride dots derived from different types of ionic liquid ranged
226 from 7.65% to 8.34%, suggesting that this simple method can be widely
227 applied in synthesizing different CNDs towards specific demands
228 originated from ionic liquids.



229

230 **Fig. 5** Quantum yield of carbon nitride dots derived from different types
231 of ionic liquid

232

233 Comparison with other method

234 Table 1 compared the present method with other methods for the
235 synthesis of CNDs. As can be seen, the present method exhibited higher
236 quantum yield than most of previous reported methods [31-33,29].

237 What's more, this method bears several unique merits, such as clean,
 238 cheap, convenient and potential advancement for large-scale
 239 industrialization.

240 Table 1. Comparison of fluorescent carbon nanoparticles with different
 241 methods

| Method | Source | Color of Products | Excitation and emission wavelength | Composition | Quantum yield | Reference |
|------------------------|------------------------------------------|-------------------|------------------------------------|-------------|---------------|-------------|
| Hydrothermal treatment | L-ascorbic acid | Dark brown | 340 nm, 420 nm | -- | 6.79 % | [26] |
| Microwave | poly(ethylene glycol) and saccharide | Dark brown | 330 nm, 425 nm | C, O | 6.3% | [27] |
| Hydrothermal treatment | Pomelo peel | -- | 365 nm, 444 nm | C, N, O | 6.9% | [28] |
| Reflux or microwave | CCl ₄ and 1,2-ethylenediamine | -- | 360 nm, 440 nm | C, N, O | 11% | [29] |
| Hydrothermal treatment | Ionic liquids | Dark brown | 355 nm, 458 nm | C, N, O, H | 8.34 % | This method |

242

243

244 4. Conclusions

245 In conclusion, fluorescent carbon nitride dots have been prepared by
 246 hydrothermal reaction derived from ionic liquids. The synthesized carbon
 247 nitride dots showed some benign properties such as higher
 248 photoluminescence efficiencies (8.34%), monodispersity and small

249 diameter (4.15 ± 1.95 nm). In comparison with the previous methods, this
250 method bears several unique merits, such as clean, cheap, convenient and
251 potential advancement for large-scale industrialization. This one-step
252 “green” process is no need for strong acid treatment or surface
253 modification. In particular, the as-prepared carbon nitride dots exhibit
254 excellent stability in biological media, and their luminescence intensity is
255 also stable with the ionic strength or pH in the physiological and
256 pathological range of pH 4.5–8.8. The strong fluorescence and excellent
257 water dispersion is attribute to the abundant surface traps and functional
258 groups. We believe that the as-prepared carbon nitride dots can be one of
259 the most promising candidates for a new type fluorescence marker,
260 biomedical imaging, bio-sensors, and drug delivery for applications in
261 bioscience and nano-biotechnology.

262

263 **Acknowledgement**

264

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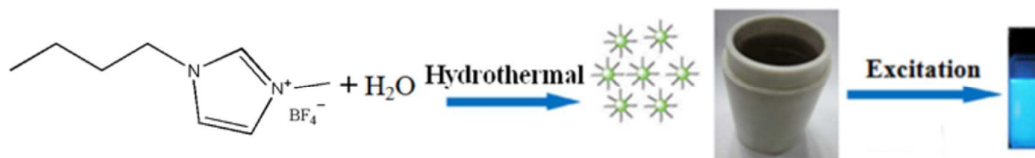
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332

Graphical abstract



A novel hydrothermal approach to synthesize fluorescent carbon nitride dots derived from ionic liquids has been reported. In comparison with the previous methods, this method bears several unique merits, such as clean, cheap, convenient and potential advancement for large-scale industrialization.