One-Step Synthesis of Acidophilic Highly-Photoluminescent Carbon Dots Modified by Ionic Liquid from Polyethylene Glycol

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ABSTRACT: Acidophilic highly-photoluminescent ionic liquid (IL)-modified carbon dots (CDs) were fabricated directly from polyethylene glycol-2000 (PEG_{2000N}) by a simple one-step hydrothermal method in a system containing an IL (1-butyl-3-methylimidazolium bromide [C4mim]Br) and hydrochloric acid (HCl). In this process, PEG_{2000N} works as the carbon source, [C4mim]Br as the modifier, and HCl as the accelerator. CDs with low photoluminescence (PL) intensity and quantum yields (QYs) were generated in the system without H+, but CDs with high PL intensity and QYs could be prepared after H+ was introduced. Moreover, with the increase of H+ concentration, the QYs of the prepared CDs increase subsequently, and the highest QY reaches up to 43%. The formation mechanism was explored, and the results showed that H+ changes the surface groups of the CDs generated without H+ into those that exist on the CDs generated with H+, which further improves the PL performance of the CDs. Different from most CDs reported in the literature, the as-prepared CDs can still exhibit high PL intensity even under strong acidic condition.

INTRODUCTION

In recent years, carbon dots (CDs), one novel type of “zero-dimensional” nanomaterials, have received much attention owing to their low cost, superior chemical stability, alluring optical properties, and high biocompatibility.1,2 Owing to these attractive merits, CDs have recently been regarded as one of the most promising nanomaterials for bioimaging, fluorescence sensors, drug delivery, optoelectronic devices, and so forth.3−8 During the last decades, many methods have been proposed to prepare CDs, and they can be generally classified into two approaches including “top-down” and “bottom-up”. The former involves cleaving or breaking down of carbonaceous materials via chemical, electrochemical, or physical approaches. The latter is realized by pyrolysis/carbonization of small organic molecules or by a stepwise chemical fusion of small aromatic molecules.9 However, the CDs obtained from the above methods still required further surface passivation or oxidation to improve their fluorescence properties. Therefore, it is urgent to develop a simple method for the synthesis of self-passivated CDs.

During the formation process of CDs, acids usually work as the oxidation reagent or the catalytic reagent,10,11 and the concentration of acids has been demonstrated to be a decisive factor in governing the photoluminescence (PL) properties of the obtained CDs.12,13 However, the effect and function of acids added to the reaction systems have rarely been investigated.

Polyethylene glycol (PEG) is a hydrophilic linear polymer and the most popular surface-passivating material. Moreover, PEG has been widely used to functionalize CDs for improving their PL performance.14,15 However, the research on the CDs made from PEG as the carbon source has been rarely reported, and the obtained CDs usually suffer from low quantum yield (QY) and are easily quenched under strong acidic condition. For example, Fan et al.16 used PEG with different molar weights (PEG_{400N}, PEG_{1000N}, and PEG_{6000N}) as the carbon source to prepare CDs by a simple hydrothermal method, and their QYs were lower than 4%. Chen et al.17 synthesized different CDs directly from PEG_{400N} by a one-pot thermal treatment under different conditions, and the QYs were lower than 4%. Li et al.18 reported an electrolytic method to synthesize three CDs from different PEGs with different molecular weights (PEG_{200N}, PEG_{600N}, and PEG_{800N}), and their QYs were in the range of 30−38%. However, the PL intensity of all of these CDs would be quenched under strong acidic condition. Thus, it is a very challenging goal to improve the QYs of the prepared CDs using PEG as the carbon source and to maintain their PL stability under strong acidic condition.

Ionic liquids (ILs) are organic salts consisting of entire ionic species, and they have been gaining great attention because of their unique characteristics.19−22 ILs have some obvious...
advantages in the synthesis of nanomaterials. For example, they can increase the nucleation rate because of their low interfacial tension. Consequently, particles with small sizes can be easily generated in them. In addition, ILs have the capacity to stabilize the particles because of their low interface energy and designable structures, which can prevent aggregation among nanoparticles effectively. Besides, ILs can also be adopted as doping agents to synthesize high PL CDs without additional doping agents or processes because of their heteroatom-containing structures.

Herein, we report a facile and low-cost route to prepare highly fluorescent CDs by a one-pot hydrothermal treatment. In this process, PEG2000N plays a role as the carbon source, 1-butyl-3-methylimidazolium bromide ([C4mim]Br) as the modifier, and H+ as the accelerator. The obtained CDs not only emitted bright blue fluorescence in water but also showed green fluorescence in common organic solvents. Compared with other CDs synthesized from PEG, the obtained CDs have the highest QY (43%) to our knowledge and could exhibit high PL intensity under strong acidic condition.

■ EXPERIMENTAL SECTION

Materials and Reagents. [C4mim]Br (≥99.0%) and 1-butyl-3-methylimidazolium chloride ([C4mim]Cl, ≥99.0%) were purchased from Lanzhou Institute of Physical Chemistry, China. PEG-2000 (PEG2000N) was obtained from Tokyo Chemical Industry Co., Ltd., Japan. H2SO4 (95.0–98.0%), HCl (36.0–38.0%), HBr (40.0%), K2HPO4·3H2O (≥99.0%), KH2PO4 (≥99.0%), and H3PO4 (85.0%) were obtained from Luoyang Haohua Reagent Co., Ltd., China. NaOH (96.0%) and NaCl (99.5%) were purchased from Aladdin Industrial Corporation, China, and Nanjing Reagent Co., Ltd., China, respectively. All chemicals were used as received without further purification.

Apparatus. Ultraviolet–visible (UV–vis) absorption spectra and fluorescence spectra were recorded on a TU-1900 UV–vis spectrophotometer (Purkinje, Beijing) and an FP-6500 fluorescence spectrophotometer (JASCO, Japan), respectively. Fourier transform infrared (FTIR) spectra were carried out on a spectrum 400F spectrophotometer (PerkinElmer Instrument Co., Ltd, America). The X-ray diffraction (XRD) patterns were recorded on a Bruker D8 XRD diffractometer with Cu Kα as the incident radiation (Bruker, Germany). The morphology and size dimension of the CDs were analyzed by transmission electron microscopy (TEM) images using a JEM-2100 electron microscope (JEOL, Japan). The X-ray photoelectron (XPS) spectra were performed on an ESCALAB 250Xi spectrometer using Al Kα as the X-ray excitation source (Thermo Fisher Scientific, America).

Synthesis. A series of CDs were synthesized through a one-step hydrothermal method. In brief, 0.3 g [C4mim]Br and 0.9 g PEG2000N were mixed, respectively, with 0/20/40/60/80/120/140/160/180/200 μL of concentrated HCl (12 mol/L), and then the solution volumes were fixed at 2 mL with deionized water. Each mixture obtained was sealed into a 15 mL Teflon stainless steel autoclave and subjected to heat at 200 °C for 12 hours. The obtained CDs were centrifuged and washed with deionized water and ethanol for several times and dried in a vacuum.

Table 1. QYs of the CDs Prepared with Various HCl Concentrations

| cHCl (mol L⁻¹) | 0.12 | 0.24 | 0.36 | 0.48 | 0.60 | 0.72 | 0.84 | 0.96 | 1.08 | 1.20 |
|---------------|------|------|------|------|------|------|------|------|------|------|
| QYs (%)       | 2.0  | 3.8  | 3.8  | 2.0  | 20.5 | 40.5 | 43.1 | 42.2 | 41.6 |      |

Figure 1. (a) TEM image, (b) HRTEM image, and (c) XRD pattern of CDs-0.96. Inset of (a) is the size distribution of the CDs.
h. The resultant orange liquids were neutralized by NaOH and HCl solution, and then they were dialyzed against water using dialysis membranes (retained molecular weight: 3500 Da) for 48 h to remove impurities. Finally, dry brown CDs were obtained by heating the dialysate, and the CDs prepared with different concentrations of HCl were denoted as CDs-0, CDs-0.12, CDs-0.24, ..., and CDs-1.20, respectively.

QY Measurements. The QYs of the CDs were determined by comparing the integrated PL intensity of the CDs (excited by 410 nm) with the absorbance values (at 410 nm) of the samples using quinine sulfate as the standard. The QYs were obtained by the following equation\textsuperscript{24,25}

\[ \Phi = \frac{\Phi_{ST}}{\left(\frac{m_S}{m_{ST}}\right)\left(\frac{\eta_S^2}{\eta_{ST}^2}\right)} \]

where \( \Phi \) is the QY, \( m \) is the slope of integrated fluorescence intensity versus absorbance, and \( \eta \) is the refractive index of the solvent. The subscripts ST and S refer to the standard and the sample, respectively.

\section*{RESULTS AND DISCUSSION}

Optimization of the Experimental Conditions. The digital images of different CD suspensions under sunlight are shown in Figure S1a, and the corresponding digital images taken under UV light are displayed in Figure S1b. It can be seen from Figure S1a that the solution color hardly changed under sunlight. All CD suspensions exhibited blue fluorescence when exposed to an ultraviolet lamp unit at 365 nm (Figure S1b). The PL intensity first increases with the increase of HCl concentration and then remains unchanged. The QYs of all of the CDs are listed in Table 1. It can be seen that the QYs increase obviously with the increase of HCl concentration up to 0.96 mol/L, and the highest QY is 43%, which is higher than the QYs of most CDs prepared from PEG (Table S1).\textsuperscript{16,17,26} On the basis of the QYs, other reaction conditions were optimized, and the selected optimal conductions were as follows: 0.3 g [C\textsubscript{4}mim]Br, 0.9 g PEG\textsubscript{2000}N, and 0.96 mol/L HCl were heated at 200 °C for 12 h.

Structures. CDs-0.96 with the highest QY were selected for further investigation. The size and morphology of CDs-0.96 were investigated by TEM. The TEM image (Figure 1a) shows that CDs-0.96 have quasi-spherical morphology with relatively uniform sizes distributed within 1.0−5.4 nm, and their average diameter is 2.5 nm. High-resolution TEM (HRTEM) image (Figure 1b) shows that CDs-0.96 have complicated structures. Most of the CDs-0.96 are amorphous carbon particles without any lattices, whereas rare CDs possess well-resolved lattice fringes. The carbon structure of CDs-0.96 can be confirmed by the XRD pattern (Figure 1c). Figure 1c displays two diffraction peaks centered at around 11.8° (0.75 nm) and 19.7° (0.44 nm), which are ascribed to highly disordered carbon atoms.\textsuperscript{27} The elemental compositions of CDs-0.96 were determined by XPS. The XPS spectrum (Figure 2a) indicates that CDs-0.96 are composed of carbon (C\textsubscript{1s}, 284.3 eV), nitrogen (N\textsubscript{1s}, 401.3 eV), oxygen (O\textsubscript{1s}, 531.7 eV), and bromine (Br\textsubscript{3d}, 67.3 eV), with atomic percentages of 90.66, 1.50, 7.38, and 0.45%, respectively. The high-resolution scan of the C\textsubscript{1s} region (Figure 2b) exhibits three main peaks at 284.1, 284.7, and 287.4 eV, corresponding to C=−C, C=−OH, and C=−N/C=O, respectively. Two peaks at 401.1 and 401.5 eV in the N\textsubscript{1s} spectra (Figure 2c) are attributed to N−H and C=N groups, respectively. The O\textsubscript{1s}
spectra in Figure 2d exhibit two peaks at 531.4 and 532.4 eV, which are assigned to C==O and C−OH/C−O−C species, respectively.30

FTIR spectrum was used to get more information about the functional groups present in CDs-0.96 (Figure 3). The peaks at 3366 and 1696 cm⁻¹ are ascribed to the stretching vibration of −OH and C==O.31 Three characteristic peaks at 2960, 2930, and 2872 cm⁻¹ are attributed to the stretching bands of C−H.32,33 whereas the peak at 1384 cm⁻¹ belongs to the symmetric carboxylate stretch, confirming the existence of rich −OH and −COOH groups.34 The asymmetric and symmetric stretching vibrations of C−O−C35 appear at 1086 and 1040 cm⁻¹. The peaks at 1572, 3146, and 3088 cm⁻¹ are assigned to the stretching vibrations of N−H.36 and the peaks at 1640, 1454, and 1167 cm⁻¹ represent the absorptions of C==N,37 C−N, and −COOR,36 respectively. For comparison, the FTIR spectra of CDs-0.96, PEG2000N, and [C4mim]Br are also shown in Figure 4. Apparently, in the spectrum of CDs-0.96, most of the peaks from PEG2000N have disappeared, whereas those from ILs remained, indicating that PEG2000N decomposed while [C4mim]Br survived and worked as the surface modifier linked to CDs-0.96 during the pyrolytic process.

**Optical Properties.** Figure 5a shows the UV−vis and PL absorption spectra for CDs-0.96 dispersed in water. In the UV−vis absorption spectrum, a peak at around 205 nm is attributed to the π−π* transition of aromatic sp² domains. Meanwhile, the maximum excitation/emission wavelengths are located at 410/455 nm, respectively. From the fluorescent emission spectra of CDs-0.96, down-conversion fluorescence properties have been observed. The maximum emission peaks red-shift from about 465 to 540 nm with the increasing excitation wavelengths from 415 to 495 nm (Figure 5b). This common phenomenon may be attributed to the complicacy of surface-excited states and allows for multiple colors to be emitted under different excitation wavelengths.37 Meanwhile, the up-conversion PL behaviors are also exhibited in CDs-0.96 suspension, which red-shift from 410 to 435 nm with decreasing excitation wavelengths from 750 to 680 nm (Figure 5c). The up-conversion PL is a well-known nonlinear optical process of converting low-energy incident radiation into higher-energy output radiation, which shows considerable promise for applications in areas of 3D luminescent displays, optical storage disks, optically written displays, and photovoltaic cells.38

Subsequently, we investigate the effects of pH, ionic strength, irradiation times under a UV lamp, and solvent species on the PL properties of CDs-0.96. As shown in Figure 6a, the PL intensity of CDs-0.96 remains high even at low pH values and decreases sharply at pH = 9. The PL intensity of CDs-0.96 remains invariant when exposed to UV laser for 150 min, showing that the CDs are highly resistant to photobleaching (Figure 6b). In addition, CDs-0.96 show excellent stability when exposed to environments with high concentrations of NaCl (Figure 6c). Interestingly, the as-synthesized CDs exhibit more favorable solubility in organic solvents (such as ethanol, ethyl acetate, acetone, methanol, and dichloromethane) than in water, which may be due to their small sizes and multitudinous functional groups on their surfaces.29 Different from being dispersed in water, CDs-0.96 have an optimal excitation/emission wavelength at 479/550 nm when dispersed in all organic solvents (Figure 6d). This strong red shifting is attributed to the solvation occurring in the organic solvents. The dipoles of the organic solvents could rotate to align with the excited fluorophore, which reduces their interaction energy and thus lowers the energy of the excited fluorophore. Therefore, the results of the solvent relaxations cause the red shifting of fluorescence.39

**Influence of H⁺ on Structures and Properties of the CDs.** Four CDs (CDs-0.48, CDs-0.72, CDs-0.96, and CDs-1.20) were chosen to further explore the influence of H⁺ concentration on their structures and properties of the prepared CDs. The FTIR spectra of these four CDs are collected and shown in Figure 7a. Obviously, they have almost the same functional groups on their surfaces. More information about the surface functional groups was further provided by XPS analysis (Figure 7b). The results show that all of these CDs have the same elemental compositions. However, the contents of each element in different CDs are different (Table S2). As shown in Table S2, CDs-0.96 and CDs-1.20 have higher N content and QYs. Accordingly, the doped nitrogen enhances the emission of the CDs through introducing a new kind of surface state which could induce an upward shift of the Fermi level and electrons in the conduction band.40 Moreover, the nitrogen bonding to carbon disorders the carbon hexagonal rings and creates emission energy traps for the CDs through the radiative recombination induced by electron−hole pairs.41−44

The optical properties of other three CDs in Figure S2 (CDs-0.48, CDs-0.72, and CDs-1.20) are similar to those of CDs-0.96: (1) the optimal excitation/emission wavelengths of these three CDs are nearly identical to that of CDs-0.96; (2) all four CDs have similar UV−vis absorption at about 205 nm; (3) just as CDs-0.96, the three CDs also exhibit down-conversion and up-conversion PL behaviors during the same wavelength

**Figure 3.** FTIR spectrum of CDs-0.96.

**Figure 4.** FTIR spectra of CDs-0.96, [C4mim]Br, and PEG2000N.
Figure 5. (a) UV−vis absorption and optimal excitation/emission spectra, (b) down-conversion PL properties, and (c) up-conversion PL properties of CDs-0.96. Insets of (a) are images of the CDs under sunlight and UV irradiation.

Figure 6. Effects of (a) pH, (b) irradiation times under a UV lamp, (c) ionic strength, and (d) solvent species on the PL intensity of CDs-0.96.
regions (Figure S3). These results clearly indicate that these four CDs should have the same PL origin.45

From the above results, it can be found that the concentration of H⁺ just slightly influenced the surface states of the prepared CDs but did not change their PL origin.

**Formation Mechanism of the CDs.** It is very challenging to study the formation mechanism of CDs from the bottom-up method because of their complicated reaction progresses. Here, we try to propose a formation mechanism of the CDs based on the available characterization data of the prepared CDs. Initially, a large number of polymer nanoparticles form because of the aggregation among PEG2000N during heating. Then, the polymer nanoparticles shrink because of continuous intramolecular dehydration.46 A number of −COOH/−OH groups form at this stage, and simultaneously aromatic clusters are produced inside the polymer nanoparticles.36 When the concentration of the aromatic clusters in some local areas in the polymer nanoparticles reaches the critical supersaturation point, the nucleation of the CDs takes place.47 The nuclei grow up with the enhancement of aromatization degree of the polymer nanoparticles to form the original CDs. Finally, the imidazole rings are linked to the surface of the CDs through dehydration between H atoms of imidazole rings and −COOH/−OH groups, which makes the CDs to be functionalized.

**Figure 7.** (a) FTIR spectra and (b) XPS spectra of CDs-0.48, CDs-0.72, CDs-0.96, and CDs-1.20.

**Figure 8.** UV–vis absorption and fluorescence excitation/emission spectra of the CDs prepared without and with (a) HCl, (b) PEG2000N, and (c) [C₄mim]Br.
To further confirm the formation mechanism, we constructed four control experiments:

(1) A system (0.9 g of PEG2000N and 0.3 g of [C₄mim]Br) free of H⁺ was heated at 200 °C for 12 h and then cooled to room temperature; the system showed an extremely weak fluorescence. Subsequently, we introduced HCl into this system (0.96 mol/L HCl) and continued to heat it at 200 °C for 12 h; strong blue fluorescence in this system was observed, and the QY increased to 26%. Obvious changes resulting from the addition of HCl were also observed from the PL and UV–vis absorption spectra: the optimal excitation/emission wavelengths exhibited a large red shift after H⁺ was introduced into the system; no UV–vis absorption was observed before HCl was introduced, but a peak located at 199 nm appeared after HCl was added into the system (Figure 8a). The UV–vis absorption and excitation/emission wavelengths of the CDs obtained after the introduction of H⁺ were approximate to those of CDs-0.96. These results indicate that the CDs generated without HCl have surface states different from that with CDs-0.96, but those prepared after the introduction of HCl have surface groups similar to that with CDs-0.96. It implies that the presence of HCl changes the surface groups, emitting weak PL into those generating strong PL. On the basis of the experimental phenomenon, we can deduce that HCl accelerates the formation of −COOH/−OH groups which can react with [C₄mim]Br and thus enhances the degree of functionalization.

(2) A system (0.3 g of [C₄mim]Br and 0.96 mol/L HCl) free of PEG2000N was heated at 200 °C for 12 h and then cooled to room temperature. Subsequently, 0.9 g of PEG2000N was added into the system, and the system was continually heated at 200 °C for 12 h. The results showed that before PEG2000N was introduced into the system, very weak fluorescence was observed, whereas strong blue fluorescence was generated and the QYs increased to 28% after PEG2000N was introduced into the system. Figure 8b shows that the UV–vis absorption blue-shifted from 203.0 to 198.5 nm, and the optimal excitation/emission wavelengths remained unchanged before and after PEG2000N was introduced into the system. Also, the UV–vis absorption and excitation/emission wavelengths of the obtained CDs before and after PEG2000N was added were similar to those of CDs-0.96. These results indicate that the CDs generated without and with PEG2000N have surface states similar to that with CDs-0.96, implying that [C₄mim]Br just works as a modifier during the formation process.

(3) Similar to the above two control experiments, a system (0.9 g of PEG2000N + 0.96 mol/L HCl) was treated before and after [C₄mim]Br was introduced into the system, and their performances were also measured. Similar to the first control experiment, the optimal excitation/emission wavelengths of the CDs prepared before and after [C₄mim]Br was added into the system remain nearly unchanged, and their UV–vis absorption blue-shifted from 229 to 198.5 nm (Figure 8c). Their QYs increased from 32 to 37%. The UV–vis absorption of the CDs obtained before [C₄mim]Br was added was different from that of CDs-0.96. These results indicate that PEG2000N works as the carbon source during the formation process of the CDs.

(4) Another IL ([C₄mim]Cl) was adopted as the modifier, and two inorganic acids (HBr and H₂SO₄) were adopted as the accelerator to prepare CDs through the one-step method. The experimental results showed that only very weak fluorescence of the CDs without acids (H₂SO₄/HBr) could be observed, but strong blue emission could be generated with H₂SO₄/HBr similar to that with HCl; when [C₄mim]Cl was used instead of [C₄mim]Br, the CDs with strong PL could also be obtained (Figure S4). On the other hand, all CDs prepared with acids have optimal excitation/emission wavelengths (Figure S4) and QYs (Table S2) similar to CDs-0.96. Consequently, we can conclude that the H⁺ cation works as the accelerator instead of the anions of acids (Cl⁻, SO₄²⁻, and Br⁻) and that [C₄mim]⁺ cations of ILs work as the modifier instead of anions (Cl⁻/Br⁻).

In summary, the above results show that during the formation process of CDs, PEG2000N works as the carbon source, H⁺ as the accelerator, and [C₄mim]⁺ as the modifier, which is consistent with the formation mechanism deduced by the FTIR spectra in Figure 4. H⁺ accelerates the formation of −COOH/−OH groups on the original CDs and then enhances their functionalization degree, which improves subsequently the PL performance of the CDs.

### CONCLUSIONS

Herein, we have successfully synthesized novel CDs using PEG2000N as the carbon source, [C₄mim]Br as the modifier, and HCl as the accelerator. The as-prepared CDs exhibit down-conversion and up-conversion fluorescence properties and could disperse in both water and organic solvents, which could enlarge their application fields. Meanwhile, the prepared CDs also had the highest QY compared with other CDs prepared from PEG as the carbon source, and they can also exhibit strong PL under strong acidic condition. Some control experiments confirmed that the H⁺ cation in acids works as the accelerator to enhance the PL performance of the as-prepared CDs. This work provides a novel method for effectively improving the performance of CDs.

### ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.7b01014.

Images of CD suspension, PL and UV–vis absorption spectra, up-conversion PL spectra and down-conversion PL properties, optimal excitation/emission PL spectra of CDs, QYs of different CDs, and element content data (PDF).

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