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The Synthesis of Near-Infrared Carbon Dots Based On Polyethyleneimine-Methylene Blue

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***Abstract*—Fluorescent carbon dots have shown significant potential for biomedical applications such as bioimaging, sensing, and theranostics, owing to their remarkable properties, including superior optical characteristics, good biocompatibility, low toxicity, and facile preparation. In this report, near-infrared fluorescent carbon dots, termed PM-CDs, were synthesized by a simple hydrothermal method using branched polyethyleneimine (bPEI) and methylene blue (MB) as raw materials. The optimal reaction conditions for the carbon dots were determined by measuring their UV-visible absorption spectrum, fluorescence emission spectrum, and absolute quantum yield. The best preparation conditions were found to be a weight ratio of bPEI to MB of 1:10 in an alkaline NaOH medium, a reaction temperature of 210°C, and a reaction time of 9 hours. Additionally, the synthesized carbon dots were characterized using Fourier-transform infrared spectroscopy (FTIR) and X-ray diffraction (XRD). This study provides an efficient method for synthesizing near-infrared carbon dots**

***Index Terms*—Abo Carbon dots, Near-infrared fluorescence, Polyethyleneimine, Methylene blue.**

I. Introduction

As a new kind of zero-dimensional (0D) material, carbon dots (CDs) have attracted increasing attention. CDs inherit the advantages of small molecules and traditional semiconductors, exhibiting unexpected benefits in fluorescence imaging and sensing, such as photostability, biocompatibility, and low toxicity [1-5]. However, most reported CDs only emit short-wavelength (blue and green) light, making them unsuitable for in vivo applications due to shallow tissue penetration, strong tissue absorption, and high interference from the biological system's autofluorescence or severe photodamage [6,7]. Therefore, it is highly significant to achieve efficient red-light emissive CDs, which are more suitable alternatives to photobleaching-prone organic dyes and toxic semiconductor quantum dots.

Generally, there are two common strategies for CD synthesis: top-down and bottom-up methods [8]. Compared with other physical and chemical approaches, the bottom-up approach, involving hydrothermal synthesis from small molecules, is more convenient, feasible, and compatible with various carbon sources [9-11]. Fortunately, similar to genetic processes, certain characteristics of the original carbon source are transferred to the downstream CDs [12]. It has been reported that using organic dyes as precursors to prepare CDs is a promising strategy to improve the fluorescence properties of CDs, such as high quantum yield and long-wavelength emission [12-14]. For example, Tong et al. fabricated functional carbon dots with a 90% fluorescence quantum yield for long-term lysosome imaging by preparing CDs with high quantum yield using rose bengal (RB) dye and branched polyethyleneimine (bPEI) [13]. Xu et al. prepared carbon dots using methylene blue (MB) as the carbon source. These CDs not only inherit the photodynamic therapy (PDT) capabilities of MB but also demonstrate good biocompatibility and low toxicity [12]. Chen et al. synthesized functional carbon dots with long-wavelength emission for gene delivery and bio-imaging using low molecular weight PEI and rhodamine dye as precursors [14].

Inspired by these results, we demonstrate that it is possible to produce CDs with the desired properties by employing the fluorescent dye methylene blue (MB) and nitrogen-rich branched polyethyleneimine (bPEI) via one-step hydrothermal treatment. The optimal reaction conditions for carbon dots were screened, and the fabricated P-M CDs exhibit near-infrared (NIR) fluorescent emission.

II. Experimental

A. Materials

Branched polyethylenediamine (bPEI, MW=10000 Da) and methylene blue were purchased from Innochem. NaOH, H_2SO_4, *N*,*N*-dimethylformamide (DMF), anhydrous ethanol were purchased from Energy Chemical. All chemical reagents were used as received without further purification. Deionized (DI) water was used throughout this study.

B. Characterization

UV–vis spectra and fluorescence emission spectra were recorded on a Dual-FL spectrophotometer (HORIBA, USA). The Fourier transform infrared (FT-IR) spectrum was obtained on a IR200 spectrometer (Thermo). X-ray diffraction (XRD) was performed on a XD-6 (Beijing Puxi).

C. Synthesis of carbon dots

Typically, bPEI and methylene blue were dissolved in 20 mL solvent. The as-prepared solution was then transferred to a Teflon-lined autoclave chamber (50 mL), which was then sealed, heated at an appropriate temperature for a few hours, and then cooled down to room temperature naturally. The obtained solution was centrifuged at 12 000 rpm for 20 min and filtered through 0.22 μm membrane filter to remove large or agglomerated particles. Then, the supernatant was collected and subjected to dialysis (MWCO: 3500 Da) for 24 h. Finally, the CDs can be obtained as a black powder by freeze-drying.

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III. Results and Discussion

A. *Synthesis of carbon dots*

Near-infrared fluorescent carbon dots were synthesized by a simple hydrothermal method using bPEI and MB as raw materials. The optimal reaction conditions including weight ratio of raw materials (bPEI to MB), reaction medium, reaction time, reaction temperature was screened by measuring the UV-visible absorption spectrum, fluorescence emission spectrum and absolute quantum yield of carbon dots.

B. *Influence of weight ratio of raw materials*

To investigate the influence of weight ratio of raw materials, the carbon dots were prepared with five different weight ratios (1:4, 1:5, 1:6, 1:8, and 1:10, respectively) of bPEI to MB at 90 ℃ for 9 hours by using H_2O as solvent. The collected photophysical data, including maximal emission (λem max), maximal fluorescent intensity (Fmax) and absolute quantum yield (AQY) were recorded in **Fig. 1** and **Table 1**. The result indicated emission intensities and the AQY of the carbon dots increased gradually along with the weight ratio value of the raw materials from 1:4 to 1:10 and reached the maximum at weight ratio of 1:10. Therefore, the optimal weight ratio of bPEI to MB is 1:10.

Table 1 Spectral properties of PM-CDs with different ratios of raw materials

Entries	raw material	Weight ratio	λ^{em}_{max}	AQY	F_{max}
1	bPEI/MB	1:4	670	2.31%	9382
2	bPEI/MB	1:5	670	2.81%	12882
3	bPEI/MB	1:6	670	2.75%	10278
4	bPEI/MB	1:8	670	3.08%	12466
5	bPEI/MB	1:10	659	3.19%	12529

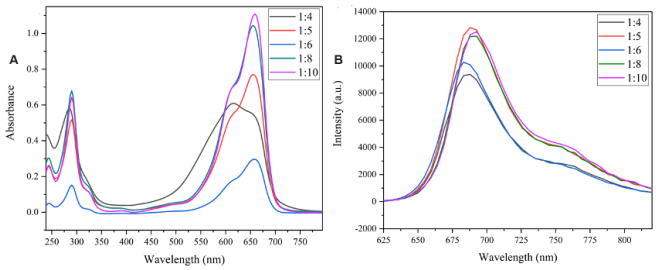

Fig. 1 (A) UV-Vis absorption spectra, and (B) fluorescence emission spectra of PM-CDs with different ratios of raw materials

C. *Influence of reaction medium*

To study the influence of reaction mediums, the carbon dots were prepared with five different reaction mediums, including H2O, EtOH, DMF, H2SO4 (1 M), NaOH (1M) at 90 0C for 9 hours with constant weight ratio of raw materials of 1:10. The reaction yield and collected photophysical data, including maximal emission (λem max), maximal fluorescent intensity (Fmax) and absolute quantum yield (AQY) were recorded in **Fig. 2** and **Table 2**. The result showed reaction medium with negative effect on AQY and Fmax of the CDs. On the contrary, it has significant influence on the reaction yield of the CDs. The reaction yield of 20.17% was obtained at alkaline NaOH medium. Therefore, the optimal reaction medium is NaOH.

Table 2 Reaction yield and spectral properties of PM-CDs with different reaction medium

Entries	Reaction medium	Yield	λ^{em}_{max} (nm)	AQY	F_{max}
1	H_2O	8.23%	659	3.19%	12529
2	EtOH	3.72%	665	3.60%	10879
3	DMF	9.37%	665	2.74%	10082
4	H_2SO_4	11.68%	680	3.11%	10540
5	NaOH	20.17%	680	3.31%	10908

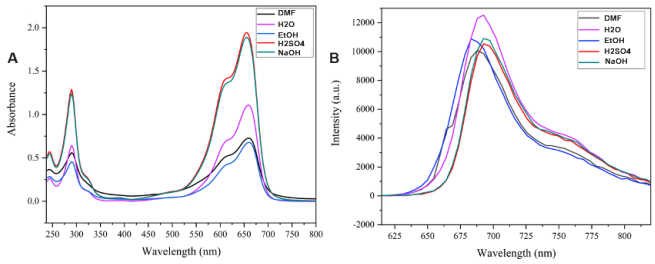

Fig. 2 (A) UV-Vis absorption spectra, and (B) fluorescence emission spectra of PM-CDs with different reaction medium

D. *Influence of reaction temperatures*

To investigate the influence of reaction temperatures, the carbon dots were prepared with six different reaction temperatures (90 ℃, 60 ℃, 120 ℃, 150 ℃, 180 ℃, and 210 ℃, respectively) with constant weight ratio of raw materials of 1:10 in NaOH medium for 9 hours. The collected photophysical data, including maximal emission (λem max), maximal fluorescent intensity (Fmax) and absolute quantum yield (AQY) were recorded in **Fig. 3** and **Table 3**. The result indicated reaction temperatures has significant influence on the reaction AQY and Fmax intensity. The Fmax of 11472 was obtained at the temperature of 210 ℃. Therefore, the optimal reaction temperature is 210 ℃.

Table 3 Spectral properties of PM-CDs at different reaction temperatures

Entries	Temperature	λ^{em}_{max} (nm)	AQY	F_{max}
1	60 ℃	670	2.56%	5185
2	90 ℃	680	3.31%	10908
3	120 ℃	660	1.87%	2455
4	150 ℃	670	2.09%	2412
5	180 ℃	660	1.94%	2281
6	210 ℃	665	2.74%	11472

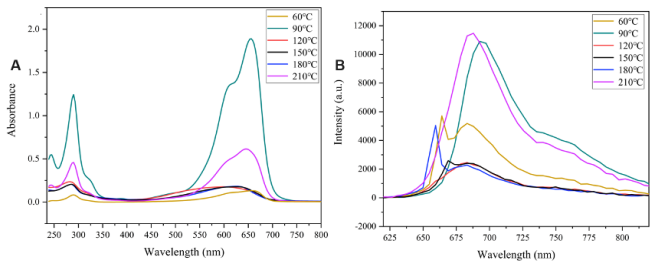

Fig.3 (A) UV-Vis absorption spectra, and (B) fluorescence emission spectra of PM-CDs at different reaction temperatures

E. Influence of reaction time

To investigate the influence of reaction time, the carbon dots were prepared with five different reaction time (9 h, 3 h, 6 h, 12 h and 15 h, respectively) with constant weight ratio of raw materials of 1:10 in NaOH medium at 210 ℃. The collected photophysical data, including maximal emission (λem max), maximal fluorescent intensity (Fmax) and absolute quantum yield (AQY) were recorded in **Fig. 4** and **Table 4**. The result indicated reaction time has significant influence on the reaction AQY and Fmax intensity. The AQY of 2.74 % and Fmax of 11472 was obtained at the reaction time of 9 h. Therefore, the optimal reaction time is 9 h.

Table 4 Spectral properties of PM-CDs at different reaction times

Entries	Reaction time	λ^{em}_{max} (nm)	AQY	F_{max}
1	3 h	650	1.4%	2249
2	9 h	665	2.74%	11472
3	6 h	630	1.17%	2103
4	12 h	640	1.7%	2756
5	15 h	660	2%	2249

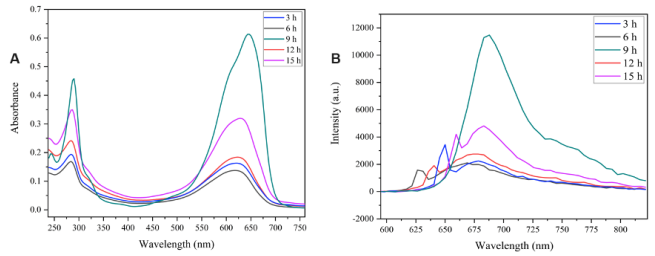

Fig. 4 (A) UV-Vis absorption spectra, and (B) fluorescence emission spectra of PM-CDs at different reaction times

F. Characterization of NIR-CDs

To explore the functional groups on the surface of the PM CDs, FTIR was used to investigate and compare functional groups of bPEI, MB and the PM CDs. The chemical groups of the PM CDs were displayed in the inset of Fig. 5A. The results showed that the PM CDs can inherit the typical characteristics of bPEI and MB. The center of the broad peak at ~3400 cm−1 was attributed to the stretching vibrations of C–H and N–H, which originated from C-H of MB and amines of PEI. The absorption band at 1605 cm-1 is assigned to the stretching vibration of C=C/C=N and bending vibration of N-H. Furthermore, XRD is also used to characterize the crystal structure of the CDs. As shown in **Fig. 5B**, a broad peak centered at ~23° indicated the amorphous structure of the CDs.

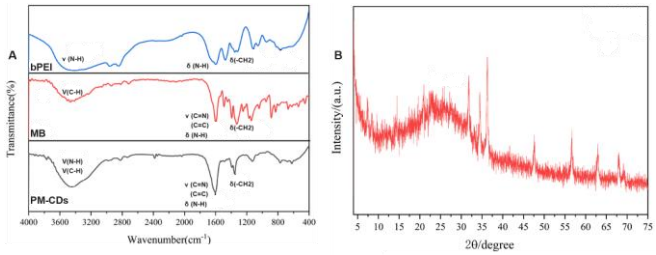

Fig. 5 (A) FTIR spectrum, and (B) XRD spectrum of PM CDs

IV. Conclusion

In summary, near-infrared fluorescent carbon dots were prepared using a simple hydrothermal method with bPEI and MB as raw materials. The optimal reaction conditions, including the weight ratio of raw materials, reaction medium, reaction temperature, and reaction time, were determined. The synthesized carbon dots were characterized using UV-visible absorption, fluorescence spectroscopy, FTIR, and XRD. The results showed that the carbon dots inherited the typical characteristics of bPEI and MB, displaying an amorphous structure and near-infrared fluorescent emission (> 675 nm). Further studies to investigate the bio-applications of these carbon dots are in progress.

V. Conclusion

In summary, near-infrared fluorescent carbon dots were prepared using a simple hydrothermal method with bPEI and MB as raw materials. The optimal reaction conditions, including the weight ratio of raw materials, reaction medium, reaction temperature, and reaction time, were determined. The synthesized carbon dots were characterized using UV-visible absorption, fluorescence spectroscopy, FTIR, and XRD. The results showed that the carbon dots inherited the typical characteristics of bPEI and MB, displaying an amorphous structure and near-infrared fluorescent emission (> 675 nm). Further studies to investigate the bio-applications of these carbon dots are in progress.

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