Green Synthesis of Blue Fluorescent P-doped Carbon Dots for the Selective Determination of Picric Acid in an Aqueous Medium

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A fluorescence method for the determination of picric acid (PA) using phosphorus-doped carbon dots (P-CDs), synthesized from β-cyclodextrin and sodium pyrophosphate, is described. The P-CDs are very uniform and monodisperse with a diameter of about 2.8 nm. Under an excitation of 350 nm, the P-CDs emit bright blue fluorescence with an emission peak at 440 nm. The as-synthesized P-CDs serve as a sensitive, selective, and label-free fluorescent probe for the detection of PA. Based on an inner filter effect between PA and P-CDs, a linear response is obtained for PA from 0.1 to 10 μM with a detection limit of 82 nM. Finally, this sensing system has been demonstrated to have practicability for PA detection in the environmental water samples.

Keywords Probe, fluorescence, β-cyclodextrin, picric acid detection

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Introduction

Nitroaromatic explosive is a kind of hazardous material with an explosive property, which can induce health hazards, environmental problems, and a homeland security threat.1,2 Hence, developing reliable and effective nitroaromatic explosive detection methods is a significant research topic. As a representative nitroaromatic explosive, picric acid (PA) has been used for military explosives because of its strong explosion property.3,4 In addition, PA has been applied to fireworks, dyes, and the medicine industry.5,6 Meanwhile, PA can cause serious environmental pollution, which widely exists in the ground water of nearby industrial facilities. If living organisms inhale or touch PA carelessly, they may suffer from cyanosis, aplastic anemia or skin irritation,7,8 especially human beings. Therefore, it is distinctly important to find efficient methods for detecting PA.

So far, many techniques, like high-pressure liquid chromatography, electrochemical method, and surface enhanced Raman spectrometry, have been used for testing nitroaromatic explosives.9,10 Nevertheless, these techniques always have some restrictions, such as environmental pollution, less sensitivity, high cost, and low selectivity, which greatly limit their actual applications. Nowadays, a fluorescence-based method for detecting PA has attracted enormous attention due to its high sensitivity, short response time, good selectivity, and simple detection by using semiconductor quantum dots (QDs), metal-organic frameworks, small organic molecules, and other nanomaterials.11–14 However, the strategies mentioned above have some insufficiencies, such as a complex synthesis process and low photostability. Furthermore, severe environmental and health problems can be caused by using some heavy-metal-based QDs. Hence, it is highly attentive to research advanced fluorescent sensing materials that can overcome the above problems.

As a kind of nanomaterial, fluorescent carbon dots (CDs) are highly popular due to their numerous advantages, including good biocompatibility, eco-friendliness, and great optical properties.15 In the meantime, the CDs-based fluorescent sensing platform is applied to chemical analysis. Functionalized CDs are used to detect biomolecules, such as dopamine16 and glucose.17 Metal ions can be sensed, including Hg2+, Fe3+, Cu2+, and Ag+, which can result in the fluorescence quenching of CDs.18,19 But, the research of CDs also has some limitations. The most previous studies focus on that the surface dispose of CDs is obtained by oxidation with organic molecules to obtain a high photoluminescence performance.20 However, some modification may be not environmentally friendly, and the synthesized CDs are always mixtures due to some indispensable post-processing.

Generally, carbon dots doped with heteroatom can change their entitative property.21 A previous report indicated that nitrogen and boron co-doped CDs have a high fluorescence quantum yield and strong fluorescence emission.22 Phosphorous atom can form a substitutional defect in diamond sp3 thin film, and hence it can improve the optical property as an n-type donator.23 Because of the edge effects and quantum-confinement of carbon dots, P-doped C-dots (P-CDs) can change their electronic properties and provide many active sites, thus exhibiting new properties.

In this work, we synthesized blue-emitting P-CDs by a one-step hydrothermal method. Since β-cyclodextrin is rich in hydroxyl groups and carbon, and sodium pyrophosphate has abundant phosphorus, they can serve as carbon and phosphorous sources to prepare P-CDs. Considering that both of them are cheap materials and easy to be obtained, the synthesis of P-CDs is cost-effective by using β-cyclodextrin and sodium pyrophosphate. As shown in Scheme 1, β-cyclodextrin and sodium pyrophosphate were carbonized to form the blue-emitting
P-CDs at 180°C for 10 h; based on an inner filter effect between picric acid (PA) and P-CDs, the fluorescence of P-CDs was quenched by PA. Hence, the as-prepared P-CDs can be used as a fluorescent probe for a selective, sensitive, and reliable determination of PA.

**Experimental**

**Reagents**

\(\beta\)-Cyclodextrin, sodium pyrophosphate (Na\(_2\)P\(_2\)O\(_7\)·10H\(_2\)O), NaOH, \(\alpha\)-dihydroxybenzene (\(\alpha\)-DHB), 2,4-dinitrophenol (2,4-DNP), 2,4,6-trinitrophenol (PA), \(p\)-nitrotoleune (\(p\)-NT), \(\alpha\)-nitrophenol (\(\alpha\)-NP), aniline (AN), phenol (PHE), \(p\)-dihydroxybenzene (\(p\)-DHB), 2,4-dinitrobenzene (2,4-DNT), methylbenzene (MB), 2,4,6-trinitrotoluene (TNT), benzoic acid (BA), nitrobenzene (NB), and \(m\)-dinitrobenzene (\(m\)-DNB) were purchased from Aladdin Reagent Co., Ltd. (Shanghai, China). Aqueous solutions of Fe\(^2+\), Ag\(^+\), Hg\(^2+\), Zn\(^2+\), Na\(^+\), Mg\(^2+\), Fe\(^3+\), Cu\(^2+\), and Cr\(^3+\) were prepared, respectively. The chemical reagents used were of analytical reagent grade. Tris–HCl buffer (20 mM) (Aladdin Reagent Co., Ltd., Shanghai, China) was prepared. Ultrapure water (18 M\(\Omega\) cm) was used in experiments.

**Apparatus**

The structure of P-CDs was analyzed by high-resolution transmission electron microscope (HRTEM) (JEM-2100, JEOL Ltd., Japan). The UV-vis absorption spectrum was recorded using a UV-vis 2450 spectrophotometer (Suzhou Shimadzu Instrument Co., Ltd., China). The fluorescence spectrum was recorded with an F-2700 fluorescence spectrophotometer (Hitachi Ltd., Japan). The Fourier-transform infrared (FTIR) spectrum shows a specific absorption band at about 283 nm. Moreover, the maximum emission wavelength of the P-CDs is 440 nm with 350 nm excitation (Fig. 2A). The inset of Fig. 2A shows that the P-CDs solution emits a strong blue fluorescence at 440 nm with 350 nm excitation (Fig. 2A). The inset of Fig. 2A shows that the P-CDs solution emits a strong blue fluorescence at 440 nm with 350 nm excitation (Fig. 2A).

**Synthesis of P-doped C-dots**

The P-CDs were synthesized by a green hydrothermal process. Briefly, \(\beta\)-cyclodextrin (30 mM, 4.0 mL) and sodium pyrophosphate (30 mM, 1.0 mL) were treated in a tetrfluoroethylene autoclave at 180°C for 10 h. Then, the deep-yellow product was centrifuged at 12000 rpm for 10 min. The yellow solution was dialyzed using a dialysis bag (molecular weight cut off = 1.0 kDa) in ultrapure water for 1 day. Finally, the product was gathered for further use.

**Fluorescence quantum yield measurement**

The quantum yield (QY) of P-CDs was determined using a high-resolution transmission electron microscope (HRTEM) (JEM-2100, JEOL Ltd., Japan). The UV-vis absorption spectrum was recorded using a UV-vis 2450 spectrophotometer (Suzhou Shimadzu Instrument Co., Ltd., China). The fluorescence spectrum was recorded with an F-2700 fluorescence spectrophotometer (Hitachi Ltd., Japan). The Fourier-transform infrared (FTIR) spectrum was obtained using a Bruker IFS 113v spectrometer (Bruker, Germany).

The QY of P-CDs was calculated by

\[
\varphi = \varphi_s (\text{Grad}_x/\text{Grad}_s)(\eta/\eta_s)^2, \tag{1}
\]

where \(\varphi\) is the QY, and \(\text{Grad}\) is the slope of curves, and \(\eta\) is the refractive index. The subscripts ‘st’ and ‘x’ denote the standard and P-CDs samples, respectively. The refractive indexes of quinine sulfate and P-CDs solutions are 1.33, \(\eta/\eta_s = 1\).

**Detection of picric acid**

A portion of 50.0 \(\mu\)L of P-CDs (16.7% v/v) was diluted with 440.0 \(\mu\)L of Tris–HCl buffer (20 mM, pH 7.0). Subsequently, 10.0 \(\mu\)L of PA with different concentrations was added. After 13 min, the fluorescence spectra were recorded under excitation at 350 nm.

**Results and Discussion**

**Characterization of P-doped C-dots**

The P-CDs were monodispersed, homogeneous, and spherical (Fig. 1A). Figure 1B displays that the as-synthesized P-CDs have the main distribution in the range of 2.0 – 3.5 nm with an average size of 2.8 nm. The lattice fringes are high-resolution with very small interplanar spacing (inset of Fig. 1A). The crystallinity and monodisperse performance of the P-CDs were ascribed to the continuous, synchronous, uniform calefaction of \(\beta\)-cyclodextrin, sodium pyrophosphate, and solvent (H\(_2\)O), which afforded homogeneous nucleation and growth for the formation of P-CDs.

Figure 2A exhibits the UV-vis absorption spectrum of the P-CDs. On account of the electron transition of the P-CDs, the fluorescence of P-CDs was quenched by PA. Hence, the as-prepared P-CDs can be used as a fluorescent probe for a selective, sensitive, and reliable determination of PA.

The functional groups of the as-prepared P-CDs were explored by FTIR spectroscopy. Figure 2B shows an obvious absorption peak at 3397 cm\(^{-1}\), which might represent O–H stretching vibration. The stretching vibration of C–H is situated at 2931 cm\(^{-1}\). The peaks at 1522 and 1669 cm\(^{-1}\) represent C=C and C=O stretching vibrations, respectively. The peak at 1023 cm–1 ascribed to the continuous, synchronous, uniform calefaction of \(\beta\)-cyclodextrin, \(p\)-nitrophenol (\(p\)-NP), aniline (AN), phenol (PHE), \(p\)-dihydroxybenzene (\(p\)-DHB), 2,4-dinitrophenol (2,4-DNT), \(p\)-nitrophenol (\(p\)-NP), aniline (AN), phenol (PHE), \(p\)-dihydroxybenzene (\(p\)-DHB), 2,4-dinitrophenol (2,4-DNT), methylbenzene (MB), 2,4,6-trinitrotoluene (TNT), benzoic acid (BA), nitrobenzene (NB), and \(m\)-dinitrobenzene (\(m\)-DNB) were purchased from Aladdin Reagent Co., Ltd. (Shanghai, China). Aqueous solutions of Fe\(^2+\), Ag\(^+\), Hg\(^2+\), Zn\(^2+\), Na\(^+\), Mg\(^2+\), Fe\(^3+\), Cu\(^2+\), and Cr\(^3+\) were prepared, respectively. The chemical reagents used were of analytical reagent grade. Tris–HCl buffer (20 mM) (Aladdin Reagent Co., Ltd., Shanghai, China) was prepared. Ultrapure water (18 M\(\Omega\) cm) was used in experiments.

The structure of P-CDs was analyzed by high-resolution transmission electron microscope (HRTEM) (JEM-2100, JEOL Ltd., Japan). The UV-vis absorption spectrum was recorded using a UV-vis 2450 spectrophotometer (Suzhou Shimadzu Instrument Co., Ltd., China). The fluorescence spectrum was recorded with an F-2700 fluorescence spectrophotometer (Hitachi Ltd., Japan). The Fourier-transform infrared (FTIR) spectrum was obtained using a Bruker IFS 113v spectrometer (Bruker, Germany).

The QY of P-CDs was calculated by

\[
\varphi = \varphi_s (\text{Grad}_x/\text{Grad}_s)(\eta/\eta_s)^2, \tag{1}
\]
groups, and these groups can enhance the hydrophilicity and stability of the P-CDs in aqueous solutions as well as take a significant part in PA detection with the as-prepared P-CDs as a representative fluorescent probe. Meanwhile, the P–O bond on the surface of P-CDs can prove that phosphorus has been doped into carbon dots successfully.

Figure S3 (Supporting Information) exhibits the emission spectra of P-CDs excited at different wavelengths. When the excitation wavelength is increased, the emission peak is red-shifted. The excitation-dependent property of P-CDs is consistent with that of CDs reported by previous literature.²⁹ The surface of the P-CDs has different functional groups, which can lead to a series of emissive traps between $\pi$ and $\pi^*$ states of C=C.²⁹ The emission is dominated by a surface energy trap when a certain excitation wavelength illuminates the P-CDs. Another corresponding surface state emissive trap will become dominant when the excitation wavelength changes. With increasing excitation wavelength, the emission behavior would be different, which leads to the excitation-dependent property.²⁹ In addition, the QY of P-CDs is 3.8% by calculation at 350 nm, using quinine sulfate as a standard. Compared to other CDs (Table S1, Supporting Information), the P-CDs have a relatively low QY.

Photoluminescence mechanism of P-doped C-dots

In the previous reports, functional groups, surface defects, quantum confinement effect, and free zig-zag sites might result in photoluminescence emission.³⁰,³¹ As can be seen from the FTIR spectrum, the surface of the P-CDs has different groups, like C-O-C, C=O, and C-OH, which can induce emissive traps between $\pi$ and $\pi^*$ states of C=C group.²⁷ The specific structure on the surface of the P-CDs would induce the formation of diverse surface defects, and then the surface defects can form diverse emission sites on the P-CDs.³² When the P-CDs are excited, the surface defects would catch exciton, and release energy in the formation of photon emission. Hence, the photoluminescence of the P-CDs is ascribed to the radiative recombination of electron traps and surface defects on the P-CDs surface.

Optimization of P-doped C-dots synthesis conditions

Some synthesis conditions, such as the reaction temperature, response time, and the molar ratio of reactants were optimized to acquire the optimal fluorescence properties of P-CDs. Figure S4 (Supporting Information) shows that the molar ratio of $\beta$-cyclodextrin to sodium pyrophosphate influences the fluorescence intensity of P-CDs. When the molar ratio is 4:1, the fluorescence of the P-CDs is the strongest. Thus, the optimized molar ratio of $\beta$-cyclodextrin to sodium pyrophosphate is 4:1. In addition, the influence of different phosphorus sources was explored. As shown in Fig. S5 (Supporting Information), sodium pyrophosphate as the
phosphorus source is better than phosphoric acid, so we chose sodium pyrophosphate as the phosphorus source for P-CDs. Meanwhile, the fluorescence intensity of P-CDs is stronger than that of C-dots without phosphorus being doped.

The low temperature results in an incomplete reaction of β-cyclodextrin with sodium pyrophosphate, so the fluorescence intensity is very weak (Fig. S6, Supporting Information). With increasing temperature, the reaction is more thorough, which leads to an increased yield of P-CDs. Furthermore, we can obtain the bright fluorescent P-CDs by increasing the heating time (Fig. S7, Supporting Information). It is conceivable that longer heating time can enhance carbonization and polymerization of the reagents, which can enhance the fluorescence intensity of the system. But given energy and cost saving, a final reaction temperature of 180 °C and a time of 10 h were selected for further experiments.

Detection of PA with P-CDs

To obtain the optimal PA detection conditions, the pH value, P-CDs concentration, and incubation time were optimized. The influence of the pH on the quenching effect of PA was explored in the Tris-HCl buffer by supervising the variation of the fluorescence quenching efficiency \((i.e., (F_0 - F)/F_0)\), where \(F_0\) and \(F\) represent the fluorescence intensities of P-CDs in the presence and absence of PA, respectively and concentration of PA from 0 to 100 μM, and the inset shows the linear range for PA in the 0.1 – 10 μM range. Conditions: P-CDs, 1.7% (v/v); Tris-HCl buffer, pH 7.0; excitation, 350 nm; emission, 440 nm.

Fig. 3 (A) Fluorescence quenching efficiency of P-CDs with PA (5 μM) in Tris-HCl buffer with different pH values. (B) Normalized fluorescence intensity of P-CDs with PA at different incubation times. Conditions: P-CDs, 2% (v/v); Tris-HCl buffer, pH 7.0; excitation, 350 nm; emission, 440 nm.

Detection of PA with P-CDs

To obtain the optimal PA detection conditions, the pH value, P-CDs concentration, and incubation time were optimized. The influence of the pH on the quenching effect of PA was explored in the Tris-HCl buffer by supervising the variation of the fluorescence quenching efficiency \((i.e., (F_0 - F)/F_0)\), where \(F_0\) and \(F_0\) represent the fluorescence intensities of P-CDs in the presence and absence of PA, respectively. Figure 3A shows that the quenching efficiency does not obviously change in the pH range of 7.0 – 9.1. Hence, changing pH value has almost no influence on the detection result. As a result, pH 7.0 Tris-HCl buffer was chosen for the experiment.

The effect of the reaction time on the fluorescence quenching efficiency of the P-CDs system for the detection of PA was investigated. After the addition of PA for 13 min, the quenching rate becomes constant, and can keep stable for at least 45 min (Fig. 3B), which indicates that a stable sensing platform for PA can be established. Thus, we selected 13 min as the optimal reaction time for a reliable and sensitive sensing system for PA detection.

To ensure that the sensing system can be utilized for detecting PA, we tested the fluorescence intensities of P-CDs with adding PA at different concentrations under the optimal experimental conditions. As shown in Fig. 4A, the fluorescence of P-CDs at 440 nm is quenched when the concentration of PA is increased. Figure 4B displays the relationship between the fluorescence intensities of P-CDs and the concentrations of PA. The sensor displayed a two-stage linear relationships (\(R^2 = 0.999\)) between the intensity ratio \((F_0 - F)/F_0\) and the concentration of PA.
from 0.1 to 0.9 μM and 0.9 to 10 μM (the inset of Fig. 4B).
Also, a two-stage linear relationship between the change in fluorescence intensity and the concentration of analyte can also be observed in some literature. The detection limit (defined as 3σ/slope) of the sensing system was estimated to be 82 nM. Meanwhile, a comparison of the previously reported sensing platforms (e.g., CDs, AuNCs, and QDs) for PA detection is summarized (Table S2, Supporting Information). It can be seen that our method has several obvious advantages in the preparation and detection processes compared to other reports, such as low cost, simple synthesis, and good sensitivity in the aqueous medium with a lower detection limit.

Selectivity study of P-CDs for PA detection
The selectivity of the P-CDs for detecting PA was investigated in the presence of non-nitroaromatic, nitroaromatic, non-aromatic compounds, and various metal ions, respectively. The fluorescence of the P-CDs is obviously decreased with the addition of 10 μM PA, whereas other compounds (2,4-DNT, m-DNB, p-NT, o-NT, p-DHB, o-DHB, NB, BA, MB, AN, PHE, 2,4-DNP, and TNT) do not exhibit obvious fluorescence change (Fig. 5A). Figure S8 (Supporting Information) displays the excitation and emission spectra of P-CDs and the absorption spectra of the other analytes. The absorption spectra of the analytes have hardly any overlap, except for that of PA with the fluorescence spectrum of P-CDs, which illustrates that the P-CDs have a good selectivity toward PA. Furthermore, the fluorescence responses of the P-CDs were also evaluated in the presence of various metal ions such as Mg²⁺, Co²⁺, Ag⁺, Fe³⁺, Ni²⁺, Zn²⁺, Mn²⁺, Cu²⁺, Na⁺, Li⁺, Hg²⁺, Al³⁺, Fe²⁺, Pb²⁺, and Cr³⁺. Figure 5B exhibits that the fluorescence intensity of the P-CDs has hardly any change upon the addition of metal ions. It can be seen that the P-CDs-based fluorescent probe exhibits superior selectivity towards PA. The results suggest that the sensing system can serve as a reliable and helpful method to detect PA in an aqueous medium.

With the purpose of exploring the reason that the P-CDs had a high selectivity for detecting PA, we investigated the quenching mechanism. Generally, the fluorescence quenching is mainly attributed to two ways: (1) the formation of donor-acceptor charge-transfer complex, (2) IFE or fluorescence resonance energy transfer (FRET). As illustrated in Fig. 6, the fluorescence lifetime changes from 2.487 to 2.482 ns after the addition of PA. The result suggests that the fluorescence lifetime has nearly no change with the addition of 20 μM PA, which is consistent with some previous reports. The possibility of a quenching mechanism ascribed to FRET was ruled out. Meanwhile, the high selectivity toward PA can also be attributed to the IFE. Furthermore, the fluorophores and the receptors need not link by chemical bonds in this sensing system, which only made use of the fluorophores and the receptors as such. The above property made the quenching process more flexible and simpler. Figure S10 (Supporting Information) exhibits that any new absorption peaks are not found after the addition of PA, which suggests that the ground-state complex is not formed. Hence, the fluorescence quenching mechanism of the P-CDs was attributed to IFE between PA and P-CDs. Moreover, according to the previous reports, cyclodextrins show a great affinity for nitroaromatic compounds, such as nitrophenols. Thus, β-cyclodextrin might form the host–guest complexation with picric acid, which is beneficial to the fabrication of the sensing system.

Application in water samples
To verify the practicality of this probe, the as-prepared P-CDs were used for detecting PA in the Jialing River water and the tap water samples. As PA was not found in the water samples, we tested the pre-treated samples that were spiked with the standard
PA solutions. The recoveries of PA in the water samples varied from 102.6 to 106.7% (Table S3, Supporting Information) and the relative standard deviations (RSDs) ranged from 1.16 to 3.53%. The above result indicates a good repeatability of the proposed method. Hence, the as-prepared P-CDs exhibit a potential application for detecting PA in the real water samples.

Conclusions

A sensitive and selective sensing system has been developed for the detection of PA using blue fluorescent P-CDs as the nanoprobe prepared with β-cyclodextrin and sodium pyrophosphate. To date, phosphorus-doped CDs have been rarely reported. We synthesized successfully P-CDs by one-pot hydrothermal method in this work. Phosphorus doped enhanced the fluorescence intensity of the CDs. The obtained P-CDs with a mean diameter of 2.8 nm have the fluorescence QY of 3.8%. We have proved the fluorescence quenching mechanism of P-CDs for detection of PA, which is ascribed to inner filter effect. The fluorescent probe has a low detection limit of 82 nM for PA. The P-CDs have been used for the sensitive and selective determination of PA in real samples without more chemical modification. The selectivity and sensitivity of this system, accompanied by its other properties, make it offer a reliable and beneficial platform for the low-cost, rapid, sensitive, and environmentally friendly sensing applications for PA in an aqueous medium.

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Supporting Information

This material is available free of charge on the Web at http://www.jsac.or.jp/analsci/.

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