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Carbon nanodots sensitized chemiluminescence on peroxomonosulfate–sulfite–hydrochloric acid system and its analytical applications

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ABSTRACT

In the present work, new water-soluble fluorescent carbon nanodots (C-dots) were prepared in a facile microwave pyrolysis approach in minutes by combining glycine and polyethylene glycol 200 (PEG 200). Transmission electron microscopy (TEM) measurements showed that the resulting C-dots had diameters of about 3 nm. ^{13}C NMR spectra further confirmed the presence of carbons (sp^2 and sp^3) indicating a nanocrystalline core of the resulting C-dots with hydroxyl of PEG 200 covered outside. It was discovered that the prepared C-dots could dramatically enhance the chemiluminescence (CL) intensity of potassium peroxomonosulfate–sodium sulfite–hydrochloric acid (PSHA) reactions. UV–vis absorption and photoluminescence (PL) spectra indicated that the C-dots sensitized enhancements originated from their energy transfer and electron-transfer annihilation effects on the CL system. When the concentration of C-dots was 4×10^{-5} M, and those of $KHSO_5$, Na_2SO_3 and HCl were 1×10^{-2} M, an excellent performance was obtained. The C-dots sensitized CL system was successfully applied to the determination of aliphatic primary amines in real water samples with satisfactory results.

1. Introduction

Recently, C-dots have been paid great attention in many fields [1–5]. They are discrete and almost spherical nanoparticles with sizes below 10 nm. They can be bought inexpensively and easily in bulk by many methods (for example, electrochemical oxidation of graphite or multiwalled carbon nanotubes, one-step pathway of microwave pyrolysis approach, etc.) [6–13]. They have many luminescent properties such as strong optical absorption in the UV region [14–16], photoluminescence produced with photoexcitation [17–19], and electrochemiluminescence (ECL) generated by electron injection [8,15,20]. They have many other amazing characteristics: size and wavelength-dependent luminescence emission, resistance to photobleaching, and ease of bioconjugation without toxicity and environmental hazard. Besides these outstanding advantages, the most commendable fact is that they are covered with hydrophilic hydroxyl of PEG 200 from outside. Therefore they have good solubility in water, which greatly deepens their applications as many reactions occur in aqueous phase systems [21–26].

Water soluble aliphatic primary amines (i.e. C1: methylamine, C2: ethylamine, C3: n-propylamine, C4: n-butylamine, and C5: n-pentylamine) are degradation products of biological systems, such as amino acids and proteins. They are widely distributed in the environment as the byproducts of industrial and agricultural activities. Residues of these amines are hazardous to human health due to their pungent and irritant odor to skin, eyes, etc. [27–29]. But in certain environmental water, the quantities of aliphatic primary amines are too small to be detected. Thus, a rapid and sensitive technique for the detection of aliphatic primary amines in water samples is very necessary.

CL technique is a cheap and simple optical detection system. It has low background noise, low detection limit, and wide working range [30–33]. It has been proven effective in rapid and sensitive measurements at ultra-trace levels. Recently, the CL detection technique has widely incorporated C-dots in many CL systems, which broadens its application fields [34–38].

In this paper, water-soluble C-dots were prepared easily in a facile microwave pyrolysis approach in minutes. Incorporated with these C-dots, a novel PHSA CL system was developed. It consists of C-dots, sulfite, hydrochloric acid and peroxomonosulfate ($KHSO_5$). $KHSO_5$ is an inexpensive, commercially available potassium carotate. It acts as a provider of excited singlet oxygen ($^1O_2$) in many CL systems [39–41]. Investigation indicated that C-dots had apparent sensitization effects on the PHSA CL system. Possible mechanism of C-dots sensitized PHSA CL system was proposed. Further investigation indicated that the CL enhancements of C-dots could be inhibited by the addition of aliphatic primary amines. This inhibited method exhibited a linear range

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from 1×10^{-9} to 1×10^{-5} M with detection limits from 2.5×10^{-10} to 3.3×10^{-9} M. The proposed CL system was successfully applied for the determination of aliphatic primary amines in water samples.

2. Experimental

2.1. Chemicals and materials

Ultra-purification water was prepared with a Compact Ultrapure water system (18.3 MΩ cm). The analytical reagent-grade chemicals were used throughout. A solution of $KHSO_5$ was prepared daily by dissolving a triple salt ($K_2SO_4\cdot KHSO_4\cdot 2KHSO_5$, Alfa, Ward Hill, USA) in water. Na_2SO_3 and HCl were obtained from Tianjin Kaitong Chemicals Co. (Tianjin, China). They were also prepared daily. PEG 200 and glycerol were obtained from Shantou Xilong Chemical Factory (Guangdong, China). Glycine (assay ≥ 99%) was from Dingguo Changsheng Biotechnology Co., Ltd. (Beijing, China). Aliphatic primary amines (i.e. methylamine, assay 30–33%; ethylamine, assay 65–70%; n-propylamine, assay ≥ 98.5%; n-butylamine, assay ≥ 99%; and n-pentylamine, assay ≥ 97%) were from Sigma-Aldrich Co. (USA).

2.2. Apparatus

C-dots were synthesized within an 800 W microwave oven (Galanz G8023CSL-K3, Galanz Group, Guandong, China). Static CL measurements were performed with an ultra-weak CL analyzer (Institute of Biophysics, Chinese Academy of Sciences, Beijing, China). A flow CL analyzer (Lumiflow LF-800, Microtech NITI-ON, Funabashi, Japan) was used in flow injection CL measurements. PL spectra were examined by a F-7000 fluorescence spectrophotometer (Hitachi, Japan). UV–vis absorption spectra were achieved with a Model UV-2100s Spectrophotometer (Shimadzu, Japan). Particle sizes and morphologies of C-dots were measured by a transmission electron microscope (TEM, Tecnai G^2 20S-Twin, FEI Company, USA) at 200 kV. The TEM samples were prepared by casting a drop of C-dots solution in nanopure water onto a 300-mesh holey carbon-coated copper grid for observation. ^{13}C NMR spectra were collected with a JNM-ECX 400 MHz spectrometer (JEOL Ltd., Japan) by dissolving 30 mg of C-dots in 0.5 mL deuterated water. Ultrasonic instrument (KQ-500DB, 500 W, Kun Shan Ultrasonic Instruments Co., Ltd.) was used for mixing solutions well.

2.3. Synthesis of C-dots

C-dots were synthesized according to Ref. [10] with little modification. Briefly, PEG 200 (1 mL) and glycine (1 mM) were added into glycerin (5 mL). Then they were mixed well by an ultrasonic instrument. Next, the mixture was heated for 6 min in a microwave oven. Increasingly, the color of the heated solution changed from colorless to dark brown. Then the solution was dialyzed for 4 days. Finally, a light green powder was prepared and labeled as C-dots. It was then dried in a vacuum rotary evaporator and stored in a refrigerator at 4 °C for future use (Fig. 1).

2.4. Procedure for PSHA dynamic CL

To investigate the dynamic properties of the PSHA CL system, a static injection CL analysis was carried out in a 3 mL quartz glass cuvette by a batch method. Every time before static CL measurement was taken, the analyzer was run for 10 min in order to obtain a good mechanical and thermal stability. After that, a solution of Na_2SO_3 (100 μL) was added to the mixture of $KHSO_5$ (100 μL) and C-dots (100 μL) in the cuvette. Immediately, a solution of HCl (100 μL) was injected into it too. The CL intensity was displayed and integrated instantly with the luminescence analyzer. The analyzer was run at a 0.01 s sample interval and −1.2 kV PMT work voltage.

2.5. Procedure for PSHA CL

A flow injection analysis (FIA) was employed to perform the C-dots sensitized PSHA CL system (Fig. 2). Two peristaltic pumps were used to deliver four flowing streams in this FIA method. PTFE (polytetrafluoroethylene) tubing (0.8 mm i.d.) was used as the delivery channel. The sample injection part was a six way valve which was equipped with a 100 μL sample loop. A spiral

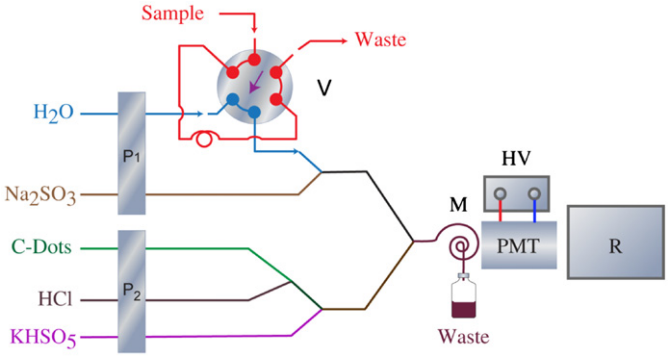


Fig. 2. Schematic diagram of FIA CL system. P_1 and P_2, peristaltic pump; V, six-way injection valve; M, CL flow cell; W, waste; HV, negative high-voltage power supply; PMT, photomultiplier tube detector; and R, luminescence analyzer controlled by personal computer.

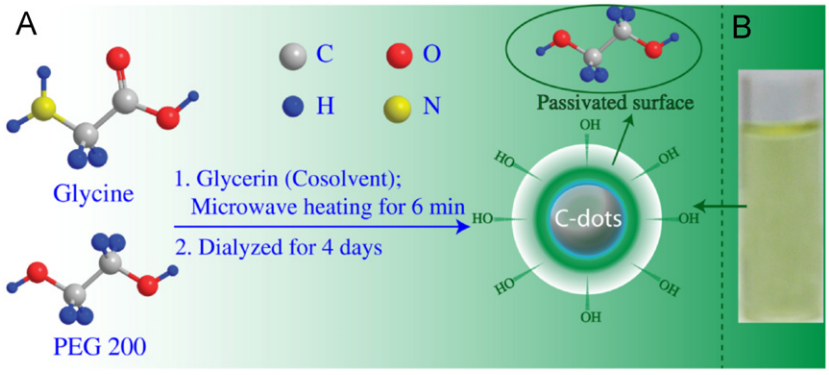


Fig. 1. (A) Schematic illustration for the synthesis of C-dots and (B) photo of light green product after being dialyzed for 4 days. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

flow cell made of organic glass with an inner diameter of about 1 mm was placed on the top window of a photomultiplier tube (PMT, Hamamatsu, Japan). PMT was used as a detector of CL signals. Prior to running, the FIA instrument was rinsed out thoroughly for about 20 min to get a stable baseline record. The flow rates of all lines were set at 1 mL min^{-1}. In the sample injection procedure, 100 μL Na_2SO_3 solution was injected into a carrier stream, and then mixed with the mixture formed from other three lines: C-dots, HCl, and $KHSO_5$. The final mixture then reached the flow cell and immediately produced CL emission. Distance between the final mixing point and flow cell was about 5 cm. The produced CL signal was detected and recorded by a computerized flow CL analyzer. Data acquisition and treatment were performed with the Lumiflow software which was run under the Windows XP system.

2.6. Procedure for inhibited CL detection of aliphatic primary amines

Fig. 2 depicts the lab-built FIA CL detection system. In the scheduled procedure, the flow rates of the detection system were fed at 1 mL min^{-1}. Firstly, the FIA CL detection system was washed well until a stable baseline signal was achieved. A 100 μL sample solution was injected into the carrier stream and then mixed with Na_2SO_3 solution. Finally, all carrier solutions merged and flowed into a flow cell, accompanied with an inhibited CL signal. The concentration of samples was quantified by the relative decreased CL intensity.

3. Results and discussion

3.1. Characterization of C-dots

The UV–vis absorption spectra and PL spectra of six synthesized C-dots under different microwave heating times are shown in Fig. 3A and B. The spectra c and d in Fig. 3A displayed strong absorptions of C-dots at about 470 nm, while the others showed almost no (a and f) or weak absorptions (b and e). The C-dots (c) were then selected as the sensitizer of the PHSA CL system. Fig. 3B displayed the PL spectra of the selected C-dots with a maximum emission at around 502 nm. Based on the facts above, it is suggested that under short microwave heating time (less than 6 min) C-dots were not shaped well or only small parts were shaped (showing weak or no absorption in UV spectra, as shown in spectra a and b of Fig. 3A). But longer the microwave heating time (more than 8 min) C-dots underwent, lesser the absorption C-dots had (spectra e and f of Fig. 3A). This was probably due to the carbonation of nanocrystalline core of C-dots and PEG 200. Usually, C-dots had high activities in solution with passivation layers of PEG 200 covering outside. After being heated for a long time, the carbonation of C-dots and PEG 200 damaged the structure and thus caused the loss of activities of the C-dots.

^{13}C NMR spectra of the C-dots are shown in Fig. 4A. The peaks below 80 ppm arose from PEG 200, the outside passivation layer of C-dots. In detail, the peaks at 61.5 and 72.8 ppm (Fig. 4A) were attributed to terminal α and β C (sp^3) of PEG 200; the peak at 70.5 (Fig. 4A) was assigned to the methylene carbon (sp^3) of the main chain [42]. The peaks centered at 135 ppm (Fig. 4A) were ascribed to the polycyclic carbons (sp^2) of the C-dots [5]. Thus, C-dots consisted most probably of nanocrystalline cores with graphitic carbons (sp^2) inside and PEG 200 with hydrophilic functional groups of hydroxyl outside. These outward groups enabled C-dots to have a good water-solubility and wide applications. The inset of Fig. 4A displayed the TEM images of C-dots. The particles of C-dots were mostly spherical and dispersed rather evenly on the surface of the TEM copper grid, with sizes averaging about 3.0 nm.

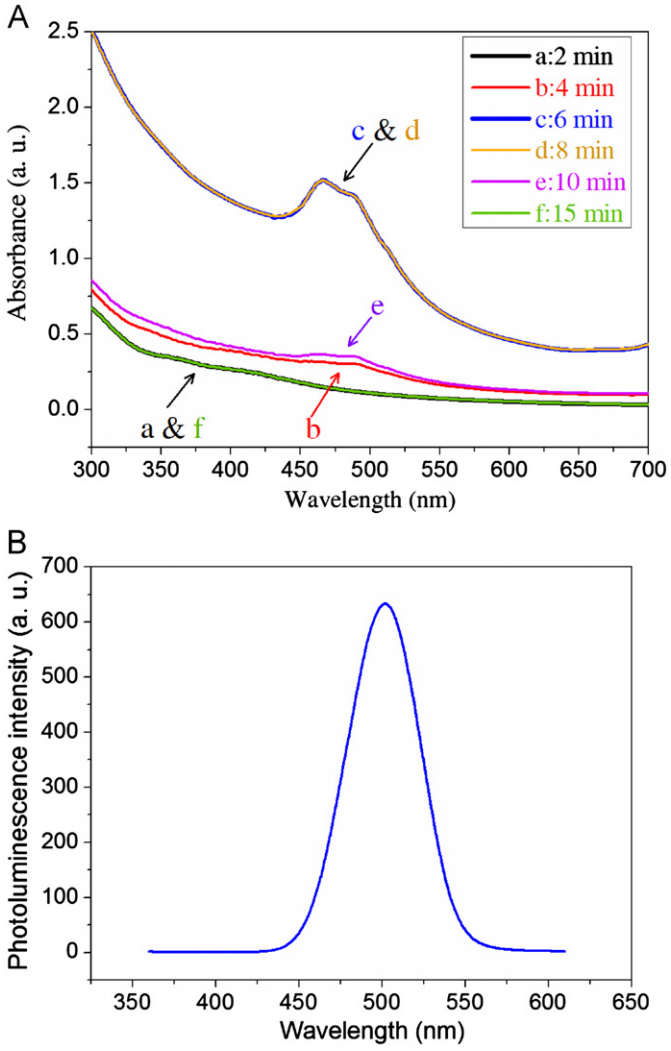


Fig. 3. Optical property of C-dots. (A) Absorption spectra of C-dots synthesized under different microwave heating times; a–f: 2–15 min of microwave heating time. Spectra a and f, as well as c and d almost overlapped each other. (B) PL spectra of selected C-dots synthesized under 6 min of microwave heating time; excitation wavelength: 470 nm.

3.2. Dynamic CL profiles of the PSHA CL

The dynamic profiles of PHSA with and without C-dots sensitized CL systems were acquired in a static injection analysis. Results demonstrated that the CL reactions were very quick (Fig. 4B). After the CL reaction began, the CL intensity reached a maximum up to 1247 counts at about 2 s for the PHSA system (Fig. 4B) and 40,508 counts at about 3.5 s for the PHSA-C-dots system (Fig. 4B). Obviously, the CL intensity of the PHSA-C-dots system was far stronger (about 33 times) than that of the PHSA system. The C-dots showed great sensitization effects on the PHSA CL system.

3.3. FIA CL profile of the PSHA CL system before and after being sensitized by C-dots

Concentrations of PHSA-C-dots CL system were then systematically investigated to achieve optimal conditions (Table 1). The best concentration of C-dots was 4×10^{-5} M. And the concentrations of $KHSO_5$, Na_2SO_3 and HCl were 1×10^{-2} M. Under optimal conditions, the FIA CL profile of the PSHA CL system before (Fig. 5A) and after (Fig. 5B) being sensitized by C-dots was obtained. Results in Fig. 5 displayed great sensitized enhancement

effects of the C-dots on the PSHA CL system. The running mode of FIA CL analysis was shown in Fig. 2.

3.4. Interferences

The influence of common ions was studied by preparing solutions containing C1 (1×10^{-7} M). The tolerable concentration ratios for interference level at 5% were over 1000-fold for Na^+, Ca^{2+}, Mg^{2+}, CO_3^{2-} and SO_4^{2-}, 100-fold for K^+, Fe^{3+}, NO_3^-, and Cl^-, and 10-fold for Cu^{2+}, NH_4^+, and $H_2PO_4^-$, respectively. Most ions caused no interferences at the concentrations of lower than 1×10^{-4} M. Ions such as CO_3^{2-}, NH_4^+ at the concentrations higher than 1×10^{-4} M had negative effects thanks to their influence on the pH value of the CL system.

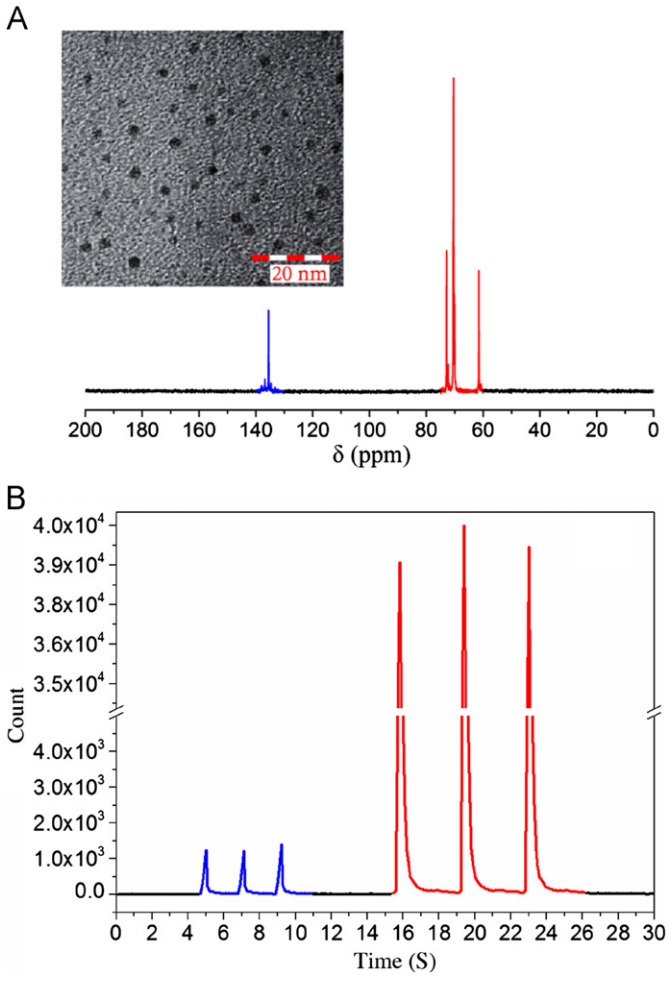
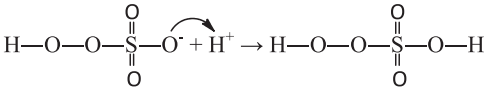


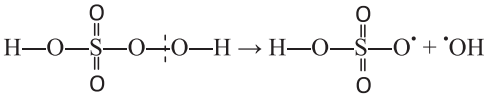
Fig. 4. ^{13}C NMR spectra of C-dots in D_2O. Inset: TEM pattern of C-dots (A) and dynamic profiles for the PHSA CL system with and without C-dots (B). Blue peaks in profile B: 100 μL of 1×10^{-2} M Na_2SO_3 solution was injected firstly into a mixture of 100 μL 1×10^{-2} M $KHSO_5$ solution and 100 μL water, and then 100 μL 1×10^{-2} M HCl solution was injected as quickly as possible; red peaks in profile B: 100 μL 1×10^{-2} M Na_2SO_3 solution was injected firstly into a mixture of 100 μL 1×10^{-2} M $KHSO_5$ and 100 μL 4×10^{-5} M C-dots solutions, and then 100 μL 1×10^{-2} M HCl solution was injected as soon as possible; high voltage: −1.1 kV; sample interval, 0.1 s. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

3.5. Possible mechanism of C-dots enhanced CL reaction

$KHSO_5$ is a powerful organic oxidant under acidic conditions [39]. In the present system, HSO_5^- was acidified firstly to form peroxymonosulfurous acid H_2SO_5 (Reaction 1). H_2SO_5 was unstable and very apt to decompose to hydroxyl radical ($HO^\bullet$) and bisulfite radical ($HSO_4^\bullet$) (Reaction 2). Next, hydroxyl radical ($HO^\bullet$) combined with itself to form hydrogen peroxide (H_2O_2) (Reaction 3) [43]



(1)



(2)

$$^\bullet OH + {}^\bullet OH \rightarrow H_2O_2 \quad (3)$$

In addition, sulfite (SO_3^{2-}) was also acidified to form bisulfite ion (HSO_3^-) (Reaction 4). HSO_3^- was further oxidized by hydrogen peroxide (H_2O_2) to produce $HSO_3^\bullet$ (Reactions 5 and 6) [44,45]. Two

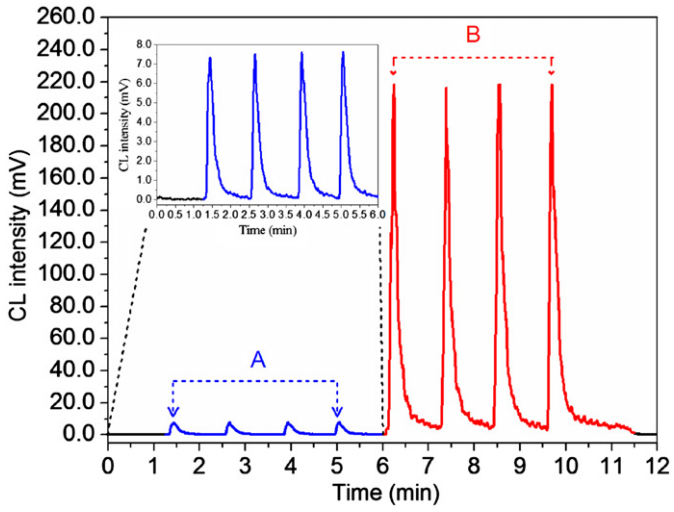


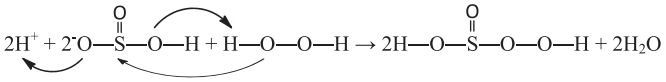
Fig. 5. FIA CL profile of the PSHA CL system before (blue peaks in group A) and after (red peaks in group B) being sensitized by C-dots. Solutions of $KHSO_5$, Na_2SO_3 and HCl were all 1×10^{-2} M and the C-dots solution was 4×10^{-5} M; flow rate: 1 mL min^{-1}; high voltage, −0.8 kV. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Table 1
Optimization of the reaction concentrations.

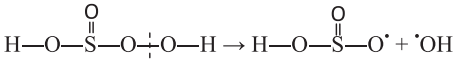
$KHSO_5$		Na_2SO_3		HCl		C-dots	
Concn (M)	CL intensity (count)	Concn (M)	CL intensity (count)	Concn (M)	CL intensity (count)	Concn (M)	CL intensity (count)
1×10^{-5}	1.3×10^3	1×10^{-5}	1.2×10^3	1×10^{-5}	1.4×10^3	4×10^{-6}	1.1×10^3
1×10^{-4}	16.7×10^3	1×10^{-4}	15.3×10^3	1×10^{-4}	18.9×10^3	4×10^{-5}	12.2×10^3
1×10^{-3}	27.1×10^3	1×10^{-3}	26.4×10^3	1×10^{-3}	28.3×10^3	4×10^{-4}	30.7×10^3
1×10^{-2}	39.3×10^3	1×10^{-2}	39.1×10^3	1×10^{-2}	39.7×10^3	4×10^{-3}	40.5×10^3
1×10^{-1}	39.4×10^3	1×10^{-1}	39.2×10^3	1×10^{-1}	39.6×10^3	4×10^{-2}	40.3×10^3

$HSO_3^{\bullet}$ radicals combined immediately to generate $S_2O_6^{2-}$ which finally decomposed to generate an excited intermediate SO_2^* (Reactions 7 and 8) [46]

$$H^+ + SO_3^{2-} \rightarrow HSO_3^- \quad (4)$$



(5)



(6)

$$2HSO_3^{\bullet} \rightarrow S_2O_6^{2-} + 2H^+ \quad (7)$$

$$S_2O_6^{2-} \rightarrow SO_4^{2-} + SO_2^* \quad (8)$$

SO_2^* is an important intermediate. It has a wide emission spectra range of 450–600 nm [47]. This range overlapped well with the absorption band and the excitation wavelength of the sensitizer C-dots (Fig. 3A and B). Therefore, the excited SO_2^* could pass its energy to the sensitizer C-dots. And a CL resonance energy transfer occurred between SO_2^* (donors) and acceptors (C-dots) (Reaction 9). The excited C-dots (C-dots*) finally returned to their ground states with production of CL emissions (Reaction 10) [48]

$$SO_2^* + \text{C-dots} \rightarrow SO_2 + \text{C-dots}^* \quad (9)$$

$$\text{C-dots}^* \rightarrow \text{C-dots} + h\nu \quad (10)$$

At the same time, H_2O_2 reacted with $^{\bullet}OH$ to form $HO_2^{\bullet}$ (Reaction 11) [47]. $HO_2^{\bullet}$ was unstable. It decomposed to intermediate radicals H^+ and $O_2^{\bullet -}$ (Reaction 12) [48]. These intermediate radicals further reacted with C-dots to produce C-dots$^{\bullet +}$ and C-dots$^{\bullet -}$ by the processes of hole and electron injection (Reactions 13 and 14). C-dots in excited state were then formed by electron-transfer annihilation processes between C-dots$^{\bullet +}$ and C-dots$^{\bullet -}$ (Reaction 15) [48]

$$^{\bullet}OH + H_2O_2 \rightarrow HO_2^{\bullet} + H_2O \quad (11)$$

$$HO_2^{\bullet} \rightarrow H^+ + O_2^{\bullet -} \quad (12)$$

$$^{\bullet}OH + \text{C-dots} \rightarrow {}^-OH + \text{C-dots}^{\bullet +} \quad (13)$$

$$O_2^{\bullet -} + \text{C-dots} \rightarrow O_2 + \text{C-dots}^{\bullet -} \quad (14)$$

$$\text{C-dots}^{\bullet +} + \text{C-dots}^{\bullet -} \rightarrow \text{C-dots}^* + \text{C-dots} \quad (15)$$

Also, electron transfer processes occurred between H_2O_2, radical $^{\bullet}OH$ and the intermediate C-dots$^{\bullet -}$ (Reactions 16 and 17) to generate the excited C-dots*, as did the radical $O_2^{\bullet -}$ (Reaction 18). Finally, CL emissions were produced from the return of the excited C-dots* to their ground states (Reaction 10). The main points of the possible CL reaction mechanisms were briefly illustrated in Fig. 6

$$^{\bullet}OH + \text{C-dots}^{\bullet -} \rightarrow {}^-OH + \text{C-dots}^* \quad (16)$$

$$H_2O_2 + \text{C-dots}^{\bullet -} \rightarrow 2\,{}^-OH + \text{C-dots}^* \quad (17)$$

$$O_2^{\bullet -} + \text{C-dots}^{\bullet +} \rightarrow O_2 + \text{C-dots}^* \quad (18)$$

$$2SO_3^{2-} + O_2 \rightarrow 2SO_4^{2-} \quad (19)$$

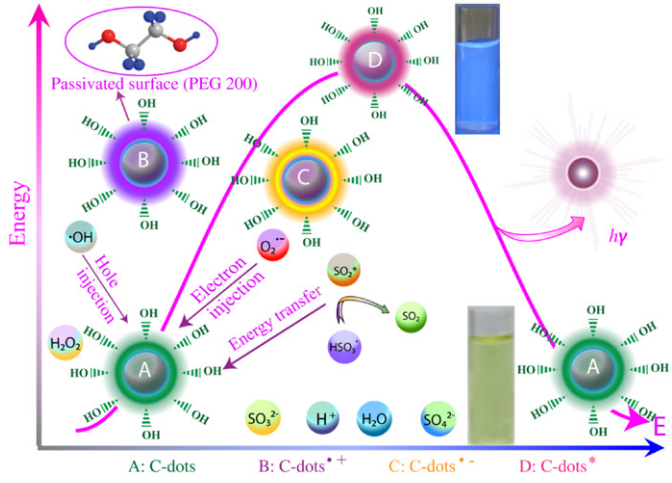


Fig. 6. Schematic illustration for the possible CL reaction mechanisms.

3.6. Analytical performance

As a means of analysis, the inhibited CL system was often applied for sensitive trace analysis in different fields. Having strong sensitization effects, C-dots were chosen as sensitizers of the PHSA CL system for the detection of water soluble aliphatic primary amines (C1, C2, C3, C4, and C5). The FIA CL analysis mode designed as that shown in Fig. 2 was employed in the test. Under optimized conditions, calibration curves of relative CL intensities versus concentrations of the amines were obtained. The linear range was from 1×10^{-9} to 1×10^{-5} M (Table 2). All the equations showed good correlations. They demonstrated linear responses over the tested concentrations. The relative CL intensities had been obtained by subtracting the blank from the maximum peak. They increased linearly with the concentrations of amines. The relative standard deviations (R.S.D.) for 5 parallel determinations of five amines C1, C2, C3, C4, and C5 were 5.9%, 2.6%, 6.0%, 7.6% and 4.7%, respectively. The detection limits achieved based on 100 μL of solution of calibrators are also given in Table 2. Compared with the official method [49–51], the proposed method exhibited excellent agreement in detection limits. Fig. 7 displayed a typical FIA CL profile for the determination of standard amine solution with a concentration of 8×10^{-5} M. Under this same concentration, the strong CL signals

Table 2
Analytical performance of the proposed inhibited CL system for the determination of water soluble aliphatic primary amines.

Analyte[a]	Linear range (M)	Calibration curve	Correlation coefficient	Detection limit (M)	
				Proposed method[b]	Official method
C1	2×10^{-7}–1×10^{-5}	$\Delta I = 15.5C + 24.2$	R2 = 0.998	3.3×10^{-9}	1.6×10^{-7}
C2	1×10^{-7}–1×10^{-5}	$\Delta I = 6.2C + 63.4$	R2 = 0.989	1.1×10^{-9}	1.8×10^{-8}
C3	1×10^{-8}–1×10^{-6}	$\Delta I = 56.6C + 104.6$	R2 = 0.988	3.3×10^{-10}	1.2×10^{-8}
C4	1×10^{-9}–1×10^{-6}	$\Delta I = 9.9C + 138.6$	R2 = 0.997	2.6×10^{-10}	5.5×10^{-8}
C5	1×10^{-9}–1×10^{-6}	$\Delta I = 84.9C + 148.4$	R2 = 0.998	2.5×10^{-10}	2.3×10^{-8}

[a] C1: methylamine, C2: ethylamine, C3: n-propylamine, C4: n-butylamine, and C5: n-pentylamine.
[b] Conditions: amine, 8×10^{-5} M, $KHSO_5$, Na_2SO_3 and HCl were all 1×10^{-2} M and the C-dots solution was 4×10^{-5} M; flow rate: 1 mL min^{-1}; high voltage, −0.8 kV.

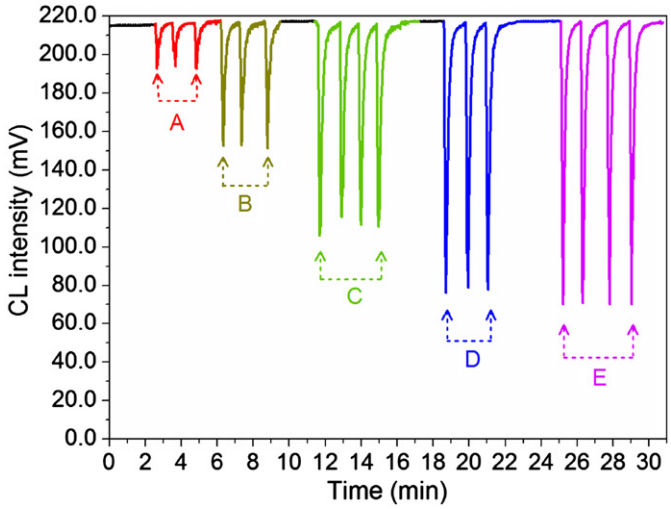


Fig. 7. A typical inhibited FIA CL profile for the determination of water soluble aliphatic primary amines (8×10^{-5} M). A: methylamine; B: ethylamine; C: n-propylamine; D: n-butylamine; and E: n-pentylamine. Analysis mode: Fig. 1B; solutions of $KHSO_5$, Na_2SO_3 and HCl were all 1×10^{-2} M and the C-dots solution was 4×10^{-5} M; flow rate: 1 mL min^{-1}; high voltage: −0.8 kV.

Table 3
Determination results for four water soluble aliphatic primary amines in real water samples.

Sample[a]	Method[b]	Found concentration (ng mL^{-1})				
		C1	C2	C3	C4	C5
T1	Proposed	–	–	–	–	–
	Official	–	–	–	–	–
T2	Proposed	18.9	25.7	39.0		
	Official	30	20.1	24	27	26.7
T3	Proposed	5.3	5.9	46.7	–	–
	Official	8.8	–	8.8	3.5	0.2
T4	Proposed	190.2	357.4	177.3	111.8	121.7
	Official	30	20	<5	<5	–

[a] T1: tap water, T2: sewage, T3: lotus pond water and, T4: industrial waste water from a factory.
[b] Conditions in proposed method: $KHSO_5$, Na_2SO_3 and HCl were all 1×10^{-2} M and the C-dots solution was 4×10^{-5} M; flow rate: 1 mL min^{-1}; high voltage, −0.8 kV.

of the PHSA-C-dots system were increasingly inhibited with the increments of the carbon chains of amines (Fig. 7). This increasing trend was well consistent with the variation of reductive properties of the amines. The CL inhibition probably resulted from the reductive consumption of the oxidant H_2O_2 by amines during the CL reactions. The above experiments indicated that the C-dots sensitized PHSA CL system could be used for the determination of aliphatic primary amines in water samples.

4. Inhibited CL determination of aliphatic primary amines

The proposed inhibited FIA CL system was then tested with real water samples with unknown amine concentrations. The water samples were labeled, respectively, as T1 (tap water), T2 (sewage), T3 (lotus pond water) and T4 (industrial wastewater from a factory). All the samples were collected, filtered through microporous membrane (aperture: 0.45 μm) and acidified to pH 2 with HCl. Prior to the analysis, the samples were alkalized to pH 10.5 with NaOH. The results were compared with the official values (Table 3) [49–51]. For sample T1 (tap water), no amines were detected. But for sample T4 (industrial wastewater from a factory), the results showed higher concentrations of amines than that of others, demonstrating severe amine contaminations in sample T4. Above results demonstrated that the C-dots sensitized PHSA CL system responded sensitively to water soluble aliphatic primary amines. It could be utilized as a rapid and sensitive detection system. After combining with other analysis techniques such as HPLC and CE, it could further be used for simultaneous detections of numerous compounds.

5. Conclusions

In summary, water soluble fluorescent C-dots were prepared. These C-dots had potential effects on the PSHA CL system. TEM and ^{13}C NMR spectra indicated that C-dots had nanocrystalline cores inside and PEG 200 with hydrophilic groups of hydroxyl covered outside. UV spectra displayed strong absorption spectra of C-dots at about 421 nm, while their PL spectra showed a maximum emission at 502 nm. The CL enhancements of C-dots were supposed to be originated from the processes of electron-transfer annihilation and resonance energy transfers. These transfers occurred between C-dots and active radicals produced by CL reactions of the PSHA system. Aliphatic primary amines were able to inhibit the CL signals of the C-dots sensitized PSHA CL system. Based on the findings, the C-dots sensitized PSHA CL system was then developed for the determination of aliphatic primary amines in real water samples. This work is important on the investigations of new and efficient catalysts for CL reactions. The C-dots sensitized CL system is promising in broadening analytical applications in various fields such as bioanalysis, catalysis, etc.

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