Journal Name RSC

ARTICLE

Glycine-Functionalized Carbon Quantum Dots as Chemiluminescence Sensitization for Detection of M-phenylenediamine

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Abstract: A novel sensing system has been designed for m-phenylenediamine detection based on carbon quantum dots (CQDs)-improved chemiluminescence (CL) in Luminol-potassium permanganate ($KMnO_4$) system. The CQDs were synthesized by pyrolyzing the mixture of citric acid (CA) and glycine (Gly). Under the action of CQDs and $KMnO_4$, the luminol can be oxidized by the synergy which makes the chemiluminescence intensity increase significantly. In this work, it has been demonstrated that this facile methodology can offer a rapid, sensitive and reliable detection of m-phenylenediamine with a detection limit as low as 1.02×10^{-3} g/L and a dynamic range from 2.0×10^{-3} to 3.0×10^{-1} g/L, which shows a promising application prospect.

Keywords: CQDs, sensitization, chemiluminescence, m-phenylenediamine detection

Introduction

CQDs are one kind of nano materials that inherently fluoresce at specific wavelengths in the visible, enabling a number of potential applications to be realized[1]. The CQDs appear to be almost sphere-shaped with a size generally less than 10 nm, belonging to the zero-dimensional carbon nanomaterials[2-4]. Because of the carbon element is one of the basic elements in life and has a wide source, the carbon nano materials cost less and have no or smaller toxicity to organism. Currently there are two main kinds of methods to realize CQDs synthesis, namely synthesis method from top to bottom and from bottom to top. The top-bottom synthesis method refers to etching or stripping carbon nanoparticles from larger carbon skeleton (such as carbon target) to obtain CQDs, including electrochemical oxidation[5], laser ablation[6], electric arc discharge[1] and so on. While the bottom-top method refers to getting carbon precursors first by burning, heating[3] and microwave[7], then producing CQDs by chemical oxidation, and finally be separated and purified, including chemical oxidation[8], pyrolysis[9], microwave-assisted[10], carrier synthesis[11], etc. But most of the methods are faced with the problem of low fluorescence quantum yield or high equipment cost.

M-phenylenediamine is a kind of industrial dye, mainly used in hair dyes and cement coagulant. As a typical of aromatic amine water pollutants, it is difficult to degrade in the water, and its toxicity is also very terrible. M-phenylenediamine is an internationally recognized as “Three Causes” material which can cause mutagenic effect, cancer and teratogenic effect. Inhaling the steam or dust of M-phenylenediamine can cause asthma and other respiratory diseases, although it is not easy to inhale due to its small volatility. However, it will show strong toxicity if taken orally, causing methemoglobin hematic disease, hypoxia, cyanosis and also causing damage to the central nervous system, cardiovascular system, etc. Now the commonly used methods to detect the content of m-phenylenediamine are Griess-saltzmanmethod[12] and H-acid colorimetric method[13], while both of which have low sensitivity. Therefor it is necessary to develop a simple effective detection method.

In this paper, we put glycine and citric acid into the reaction kettle to complete the synthesis of high quality with amino modified CQDs by using high temperature pyrolysis[14]. And found theGly-CQDs has increased the sensitivity of luminol-potassium permanganate chemiluminescence system. Based on such effect a new method for the determination of m-phenylenediamine in the water hasbeen built, which is proved to be sensitive, fast and easy to operate.

Experimentalsection

Materials

CA (Nanjing chemical reagent co., LTD, AR), Gly (Yika biotech, Nanjing, BR), the above two reagents are used for the preparation of Gly-CQDs. Luminol (Aladdin, Shanghai, China), KMnO4 (Chemical reagent factory, Nanjing, AR), Sodium hydroxide (NaOH) (West long chemical co., LTD, AR). All other reagents were of analytical grade and used as received. Doubly distilled water was used throughout the whole experiments process. The artificial sea water was obtained in the laboratory.

Synthesis of Gly-CQDs

Herein, the Gly-CQDs were synthesized directly by pyrolyzing the mixture of CA and Gly. Briefly, 3.6 g of CA and 1.5 g of Gly were dissolved in a 80 mL beaker with 30 mL doubly distilled water andthen heated at 200 ℃ for 4 hours using a reaction kettle. When the color of the liquid turned to wine red and the solution exhibited strong blue emission under the excitation of 365 nm, it suggested the formation of CQDs. Finally, the obtained CQDs were purified by extracting with N-butyl alcohol. The purified Gly-CQD solution was dried and stored under 0 ℃ before further study.

Quantum yield measurements

The quantum yield of the Gly-CQDs was measured by the following equation[15]: Qu=Qs [As/Au][nu2/ns2][Fu/Fs]. Where Q is the quantum yield, F is the measured integrated emission intensity, A is the optical density, which is measured by UV-Vis spectrophotometer, and n is the refractive index. The subscript s refers to the reference fluorophore of known quantum yield, such as quinine sulfate (QS) used in present work. And the subscript u refers to the sample of unknown quantum yield. In this work, the fluorescence quantum yield of the Gly-CQDs is higher than 27%.

Instrumentation

Transmission electron microscopy (TEM) measurements were performed on an electronic microscope (JEM-2100 120KV). UV/vis absorption spectra were recorded by a UV/vis spectrophotometer (UV 2100). Fluorescence spectra of the prepared Gly-CQDs were obtained by an FL spectrophotometer (RF-5301PC). Fourier transform infrared (FT-IR) spectra were obtained on an FT-IR spectrophotometer (FTIR-8400S, Shimadzu), X-ray photoelectron spectroscopy (XPS) data for C1s of the Gly-CQDs solution deposited on a glass substrate was measured by a PHI 5000 Versa Probe^{TM} XPS system for determining the composition and chemical bonding configurations. A flow injection CL analyzer (IFFM-E) was used to detect the m-phenylenediamine concentration of the water sample.

Analysis of a real sample

The preparation procedure of stock solution of luminol (1.0×10^{-2}mol/L) was listed as follows: first dissolved 0.1772 g luminol in NaOH aqueous solution (0.1 mol/L),which wasthen diluted with 0.1 mol/L NaOH to 100 mL. The obtained solution was stored in the refrigerator (keep 2-6℃) without light. The stock solution of $KMnO_4$ (5.0×10^{-2}mol/L) was prepared as shown below: dissolved 0.79 g $KMnO_4$ in water and diluted it with doubly distilled water to 100 mL. The solution of Gly-CQDs (0.2g/L): 20 mg of Gly-CQDs were dissolved in 100 mL glass flask volumetric with water, and adjusted the pH to 7.0, finally diluted it to 100 mL with doubly distilled water. M-phenylenediamine standard solution (0.66g/L): 165 mg of m-phenylenediamine were dissolved in 250 mL brown glass flask volumetric and diluted it to the calibration with doubly distilled water. The water samples were collected from the river in campus, artificial sea water, drinking water and tap water respectively. The samples were filtered through a 0.22 μm membrane (Millipore) prior to the detection. Added 1 mL m-phenylenediamine standard solution to each sample and then diluted them to 30 mL with themselves. The luminol (2.0×10^{-4}mol/L)-$KMnO_4$ (1.25×10^{-3}mol/L)-CQDs (0.2g/L) CL system was designed for the detection of m-phenylenediamine.

The flow injection CL analysis system was shown in Figure 1. It consisted of two peristaltic pumps, a injection valve, a flow cell, a photomultiplier tube and a CL luminescence analyzer. The doubly distilled water was injected into each pipeline before the experiment. When the baseline was zero, injected luminol, $KMnO_4$, doubly distilled water and doubly distilled water into the system and recorded the CL signal I_1. Replacing one of the doubly distilled water pipelines with the CQDs solution after the baseline was stable. And the CL signal was I_2. Finally, replace another doubly distilled water pipeline with the samples to record the CL signal I_3. Used relative luminous intensity ΔI ($\Delta I=I_2-I_3$) for quantitative analysis.

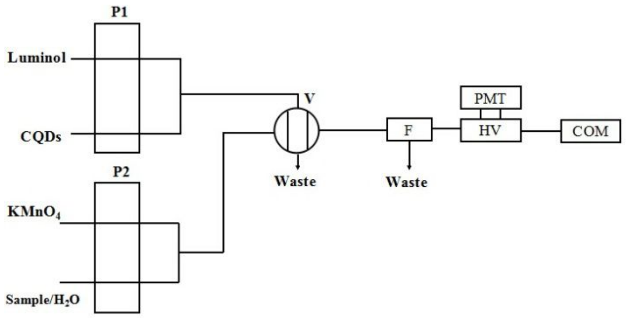


Figure 1. Flow injection CL analysis system (P1、P2: peristaltic pumps, V: injection valve, F: flow cell, PMT: photomultiplier tube, HV: negativepressure, COM: computer)

Results and discussion

Characterization

The Gly-CQDs synthesized by the above method are monodisperse nanoparticles of near spherical morphology[16] and about 5-10 nm in size (see Figure 2). The solution of Gly-CQDs emits blue light (485 nm) when excited with 380 nm UV beam (see Figure 3(a)). The blue fluorescent (FL) of Gly-CQDs were proposed to be produced by the ordered sp^2 clusters within the sp^3 C-O matrix. The Gly-CQDs exhibited a broad UV-Vis absorption below 600nm without any obvious peak, indicating that those sp^2 clusters contained in Gly-CQDs were uniform in size. The FT-IR spectrum was also used to characterize the Gly-CQDs. As shown in Figure 3(b), the Gly-CQDs have many characteristic absorption bands of Gly (NH of 3458 and 1628 cm^{-1}, CH_2 of 2936 cm^{-1}, CN of 1186 cm^{-1}), but nearly no characteristic absorption of CA. These results indicate that CA might be mostly carbonized during the pyrolysis, while the Gly kept stable. Furthermore, a new sharp peak associate with amide linkage (-CONH-) found at 1713 cm^{-1} indicates that abundant Gly should be coated at the surface of the CQDs by the amide linkages. The XPS result shows that the as-prepared Gly-CQDs contain mainly carbon, nitrogen and oxygen (see Figure 3(c)). Furthermore, the characteristic peak of C-C sp2 appearing at 284.3 eV suggests that abundant graphite structures should be contained in the obtained Gly-CQDs (see Figure 3(d)).

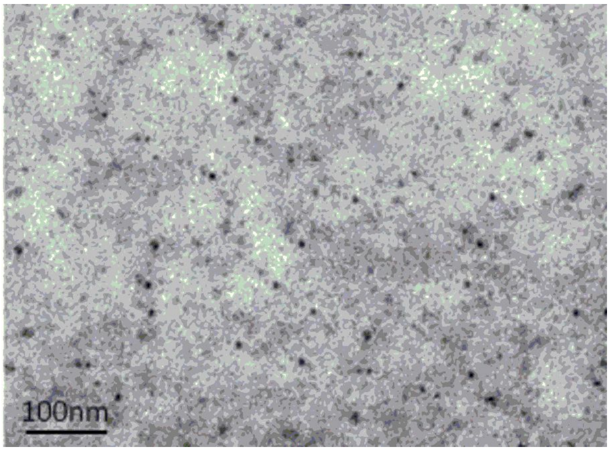


Figure 2. TEM image of CQDs

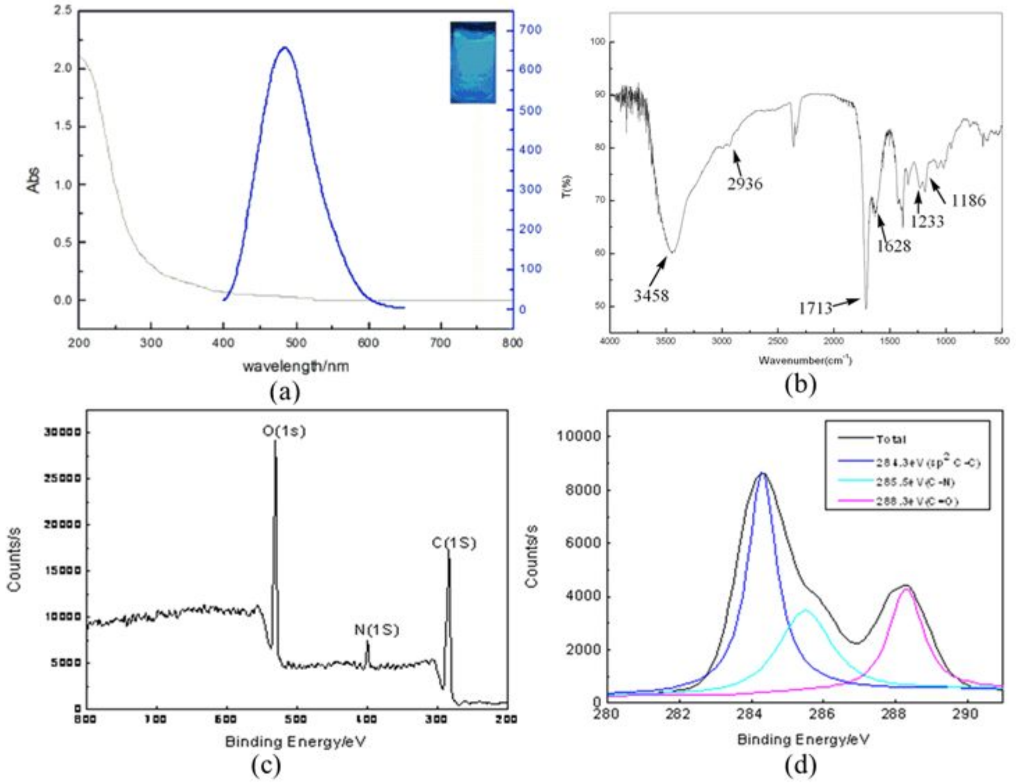
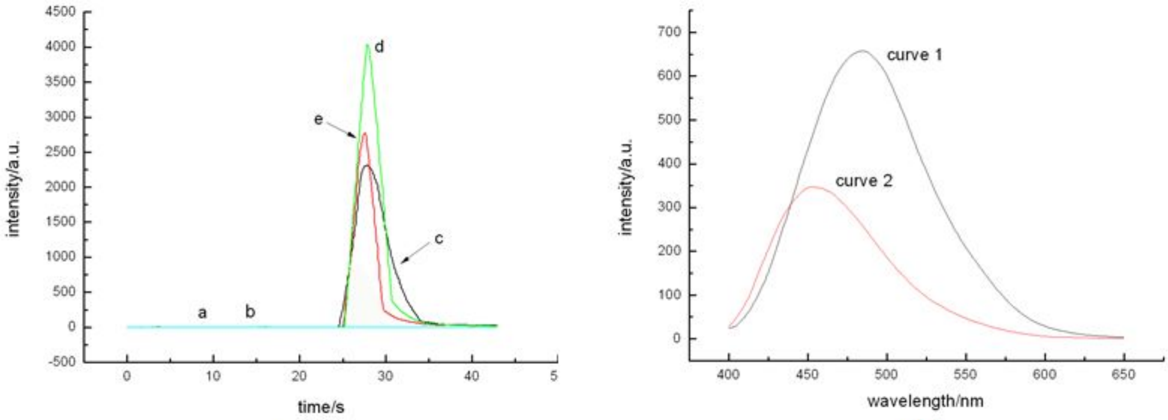


Figure 3.(a) UV-Vis absorption spectra and emission spectra of the Gly-CQDs with the excitation of 380 nm. Inset: Photographs of the solution of Gly-CQDs taken under 365 nm UV light, (b) FTIR spectra of Gly-CQDs, (c) XPS survey obtained for Gly-CQDs, (d) XPS-C1s spectra obtained for Gly-CQDs

Detection mechanism

As shown in Figure 4, the curve 1 and 2 are the fluorescence emission spectra of luminol-$KMnO_4$-CQDs CL system and luminol-$KMnO_4$-CQDs-m-phenylene diamine CL system respectively. The maximum emission wavelength of the two system is both about 450 nm, which is similar to that in the luminol-$KMnO_4$ CL system. It indicates that the excited state of the luminol acid radical ion returning to the ground state with the release of energy in the form of photons[17-18]. The CL is produced by this way and CQDs themselves do not produce the CL. Curve a and b can't detect the CL intensity, and the intensity of c is weak while that of d is significantly stronger. This further illustrates that luminol is the only luminescent material in the system and the CQDs have played an important role in sensitization effect. The CQDs-luminol system and the CQDs-$KMnO_4$system cannot produce CL. According to the literature[19-22], the luminol-$KMnO_4$-CQDs CL system mechanism is as follows (Figure 5). Under the alkaline condition, Luminol (A) is oxidized by $KMnO_4$ and produces luminol acid radical ion (B). The excited state of B returns to the ground state and the CL is produced (Figure 4(a)-c). At the same time, the CQDs gain the energy which is released from the interaction of $KMnO_4$ and CQDs with high quantum efficiency and turn into the CQDs*. Under the reaction of CQDs* and $KMnO_4$, B can be further oxidized by the synergy and produce C which makes the CL intensity increase significantly (Figure 4(a)-d). In this work, CQDs* acted as catalyst that is involved in the oxidation reaction. Namely, in the process of the formation of CQDs*, CQDs$^{\cdot -}$ tranfered the electron to $KMnO_4$, which accelerated the decomposition to produce a variety of active intermediates that could oxidate luminol efficiently. Due to the m-phenylenediamine having strong reducibility, it can react with $KMnO_4$ and consume the $KMnO_4$ in the luminol-$KMnO_4$-CQDs CL system. The strong CL intensity of the system can be quenched obviously (Figure 4(a)-e).



(a) (b)

Figure 4. (a) is CL signal intensity (a is CQDs-luminol-water, b is CQDs-KMnO$_4$-water, c is luminol-KMnO$_4$-water, d isluminol-KMnO$_4$ -CQDs, e is luminol-KMnO$_4$-CQDs-m-phenylene diamine), (b) is fluorescence spectra (curve 1 and 2 are the fluorescence spectrum curves of luminol-KMnO$_4$-CQDs CL system and luminol-KMnO$_4$-CQDs-m-phenylene diamine CL system respectively.)

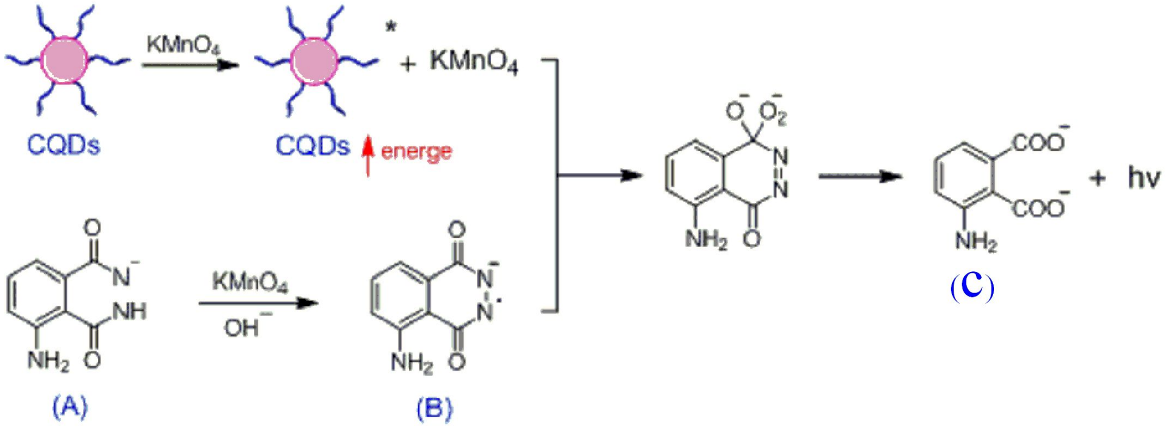


Figure 5. Luminol-KMnO4-CQDs CL mechanism

Establishment of the CL sensing method for m-phenylenediamine

In this work, we tested different reactant mixing sequence such as (luminol+KMnO$_4$)+(CQDs+m-phenylenediamine) 、 (luminol+CQDs)+(KMnO$_4$+m-phenylene diamine) and (luminol+m-phenylenediamine)+(KMnO$_4$+CQDs), and obtained the CL intensity. The results shows that the CL intensity of (luminol+CQDs)+(KMnO$_4$+m-phenylene diamine) is the strongest and stablest. So we choosed this mixing sequence. The reaction alkalinity is depending on the concentration of NaOH aqueous solution which is used to dissolve the luminol. As shown in Figure 6-a, the other experimental conditions remained unchanged, with the increasing of concentration of NaOH, △I is also rising. When the concentration reaches 0.1 mol/L, the value of △I is the highest. But when the concentration is greater than 0.1 mol/L, △I is lower. This phenomenon may be due to the strong alkaline inhibit the reaction. Finally, 0.1 mol/L NaOH is chosen for the dissolution of the luminol.

As the only luminescent material in this experiment, luminol concentration is another key factor which affects the sensing system. That is because it influences the CL intensity, sensitivity and linear range in the whole system. As shown in Figure 6-b, in the range of 1.0×10^{-4} to 1.0×10^{-3}mol/L, when the concentration reaches 2.0×10^{-4}mol/L, the value of △I is the highest. While when the concentration is greater than 2.0×10^{-4}mol/L, △I is lower. The reason is that with the increase of the concentration of luminol, the risk of the excited state of ions collision is rising after the chemical reaction. This results in a quenching effect. As the oxidant in this system, KMnO$_4$ has a significant influence on CL intensity (see Figure 6-c). With the increase of concentration of KMnO$_4$, △I is also rising. And the value of △I is highest when the concentration is 1.25×10^{-3} mol/L.

In this paper, the Gly-CQDs has obvious sensitization effect in Luminol-KMnO$_4$ CL system. Detecting the △I to study the effect of CQDs concentration on this system. As shown in Figure 6-d, in the range of 10 to 200 μ g/mL, with the increasing of the CQDs concentration, △I increased, but stabilized gradually. It can be known that the system's CL intensity is relatively insensitive to the change of CQDs concentration when it is higher than 0.2g/L. Therefore, the concentration of Gly-CQDs should be chosen in the sensitive and linear response range, i.e., 0.2g/L.

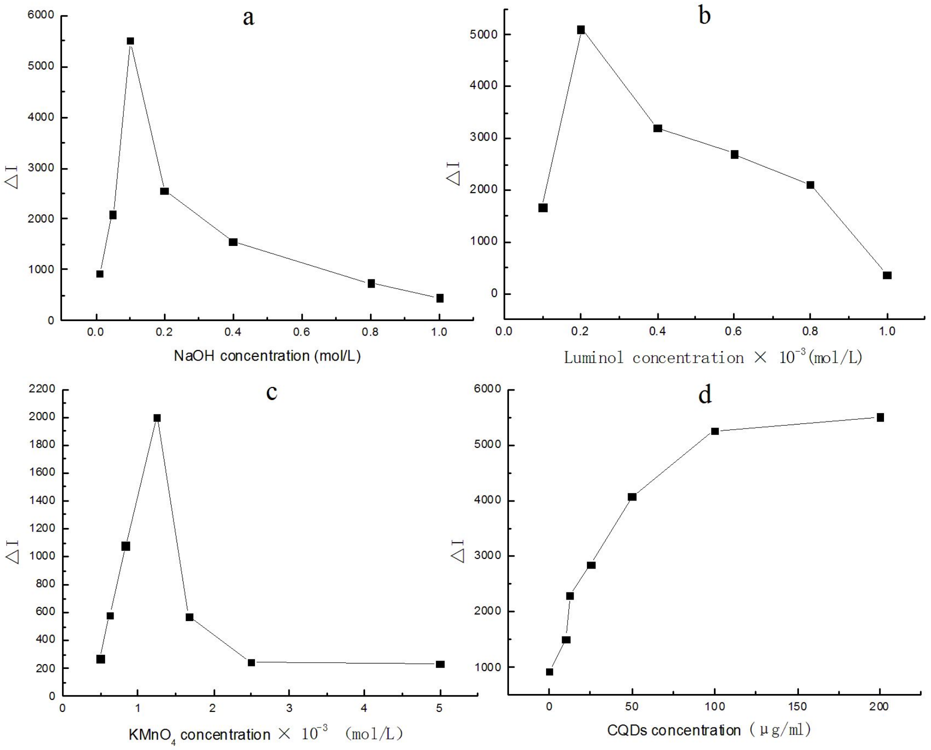


Figure 6. Effect of reagent concentration (a, b, c, d is the influence of NaOH concentration, luminol concentration, $KMnO_4$ concentration, CQDs concentration respectively)

The interference of coexisting substance

The selectivity of this luminol-$KMnO_4$-CQDs CL sensing system was also estimated. According to the above experimental method, adding different kinds of the intefering substances to detect the CL spectrum in the complex system under the m-phenylenediamine concentration of 8.0×10^{-3} g/L. As shown in Table 1, besides m-phenylenediamine, the effects of 12 other kinds of ions, including Na^+, Cl^-, K^+, I^-, sodium oxalate, NH_4^+, Ca^{2+}, Mg^{2+}, SO_4^{2-}, EDTA, CA and Cu^{2+}, on the CL response of the system were investigated. Within the error range of 5%, 1000 times of Na^+, Cl^-, K^+ and I^-, 800 times of sodium oxalate, 100 times of NH_4^+, 50 times of Ca^{2+}, Mg^{2+} and SO_4^{2-}, 10 times of EDTA and the same amount of Cu^{2+}, Co^{2+}, Ni^{2+} don't interfere with the detection of m-phenylenediamine.

Table 1. Selectivity of luminol-$KMnO_4$-CQDs CL system

Coexisting substance	Amount (times)
NaCl, KI	1000
sodium oxalate	800
NH_4Cl	100
$CaCl_2$, $MgSO_4$	50
EDTA, CA	10
$CuSO_4$	1
$CoCl_2$	1
Ni SO_4	1

The linear response range, detection limit, accuracy and recovery rate

As mentioned above, the addition of m-phenylenediamine changes the system with strong CL intensity (luminol-$KMnO_4$-CQDs) into a system without CL intensity (luminol-$KMnO_4$-CQDs-m-phenylene diamine), or the addition of m-phenylenediamine decreases the concentration of the luminol-$KMnO_4$-CQDs. Apparently, there should be some useful relationship between the m-phenylenediamine concentration and the quenched CL which can be adopted for quantitative analysis of m-phenylenediamine. The linear response range, accuracy and detection limit of the sensing system are measured under the optimum experimental conditions. It shows a good correlation between the $\triangle$ I and the concentration of m-phenylenediamine in the range from 2.0×10^{-3} to 3.0×10^{-1} g/L via the following equation: $\triangle I=3 \times 10^{8}C-226.31$ ($R^2=0.9992$), where C is the concentration of m-phenylenediamine. The detection limit of m-phenylenediamine (at a S/N of 3) was calculated to be 1.02×10^{-3} g/L. Under the m-phenylenediamine concentration of 8.0×10^{-3} g/L, the RSD was 0.83% (n=11). Theresults show that the luminol-$KMnO^4$-CQDs system with strong CL activity has very promising application in the detection of m-phenylenediamine. Taking a certain amount of distilled water, and then adding suitable amount of m-phenylenediamine standard solution as the test solutions. The concentrations of them were 1.6×10^{-2},2.0×10^{-2}, 2.4×10^{-2} g/L respectively. Each of them needs three copies. The control was prepared by the same method without m-phenylenediamine. Detecting the CL spectra by the flow injection method mentioned above to test the recovery rate. The results can be seen in Table 2, all the recovery rates of the samples were located within 95.80% to 105.5%, and therefore the method can be used for the determination of m-phenylenediamine in water.

Table 2. The recovery rate of m-phenylenediamine

Sample amount (g/L)	Measured amount (g/L)	Recovery rate (%)	Average recovery rate (%)	RSD (%)
1.6×10^{-2}	1.68×10^{-2}	105.0	104.2	0.9
	1.65×10^{-2}	103.1		
	1.67×10^{-2}	104.4		
2.0×10^{-2}	2.11×10^{-2}	105.5	103.7	1.6
	2.05×10^{-2}	102.5		
	2.06×10^{-2}	103.0		
2.4×10^{-2}	2.30×10^{-2}	95.80	97.70	1.8
	2.35×10^{-2}	98.00		
	2.38×10^{-2}	99.20		

Application

The application of this sensing system for detecting m-phenylenediamine in a sample was further evaluated. According to the experimental method above,adding some m-phenylenediamineinto the water from Ming Lake （China Pharmaceutical University, Jiangsu, China）, drinking water（Wahaha, Zhejiang, China）, tap water and sea water respectively. Detecting the simulation samples and the results were shown in table 3. The value is consistent with the result obtained by the kinetic spectrophotometry method, namely, 9.85×10^{-5}g/L, 6.01×10^{-5}g/L, 1.12×10^{-5}g/L,9.43×10^{-5}g/L in the river water, drinking water, tap water and sea water respectively. The relationship between m-phenylenediamine and ΔI in the luminol-$KMnO_4$-CQDs CL system suggests promising applications in analytical chemistry.

Table 3. The results of the simulation samples

Sample	Sample amount （g/L）	Measured amount （g/L）	Content （g/L）	Average content （g/L）
River water	2.2×10^{-2}	2.49×10^{-2}	9.79×10^{-5}	9.76×10^{-5}
		2.49×10^{-2}	9.68×10^{-5}	
		2.49×10^{-2}	9.82×10^{-5}	
Drinking water	2.2×10^{-2}	2.37×10^{-2}	5.65×10^{-5}	6.10×10^{-5}
		2.38×10^{-2}	6.10×10^{-5}	
		2.40×10^{-2}	6.55×10^{-5}	
Tap water	2.2×10^{-2}	2.51×10^{-2}	1.04×10^{-4}	1.06×10^{-4}
		2.52×10^{-2}	1.06×10^{-4}	
		2.52×10^{-2}	1.07×10^{-4}	
Sea water	2.2×10^{-2}	2.48×10^{-2}	9.25×10^{-5}	9.58×10^{-5}
		2.47×10^{-2}	9.08×10^{-5}	
		2.51×10^{-2}	1.04×10^{-4}	

Conclusions

The Gly-CQDs were synthesized by pyrolysis method. The CL intensity of the luminol-$KMnO_4$ system increased significantly under the action of CQDs. The interaction mechanism between ΔI and m-phenylenediamine was studied using the flow injection CL analysis system. After optimization of the experimental conditions, an excellent CL sensing system has been developed for the detection of m-phenylenediamin in aqueous solutions, which indicates promising applications in the environmental water samples.

Acknowledgements

This work was supported by the following foundations and projects: The natural science foundation of Jiangsu Province Youth Fund (BK20130646), Jiangsu Key Lab of Environmental Engineering Open Foundation (KF2012008), Doctor Scientific Research Foundation from China Pharmaceutical University (2012ZJ13002),The Research and Innovation Project for Graduate Students Academic Degree of Colleges and Universities of Jiangsu Province (KYZZ_0185), National Undergraduate Training Programs for Innovation and Entrepreneurship (02420152), the Fundamental Research Funds for the Central Universities (JKPZ2013017) and the Qinglan project(2014).

Notes and references

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