

CdS Quantum Dots as Fluorescent Probes for Detection of Naphthalene

Zhengyu Yan, Yan Yu, Jianqiu Chen

Abstract—A novel sensing system has been designed for naphthalene detection based on the quenched fluorescence signal of CdS quantum dots. The fluorescence intensity of the system reduced significantly after adding CdS quantum dots to the water pollution model because of the fluorescent static quenching mechanism. Herein, we have demonstrated the facile methodology can offer a convenient and low analysis cost with the recovery rate as 97.43%–103.2%, which has potential application prospect.

Keywords—CdS quantum dots, modification, detection, naphthalene.

I. INTRODUCTION

WITH the development of science and technology and the improvement of people's living standard, an increasing number of waste and toxicant is produced every moment in daily life and industrial activities, which aggravates environmental pollution and makes it become one of the three major global crises. Polycyclic aromatic hydrocarbons (PAHs) are one kind of fused ring compounds which contain two or more than two benzene rings arranged in linear, angular or clustered forms. As a typical kind of persistent organic pollutants (POPs), PAHs are the product of pyrolysis and incomplete combustion of organic matter, which widely exist in the environment [1]. 70%-90% of the human and animal cancer lesion cases are caused by chemicals in the environment, and the largest kind of carcinogenic chemicals are PAHs [2].

Just because PAHs can cause serious environmental pollution and threat to human health, many countries have added PAHs into the list of priority control pollutants. The traditional detection method for PAHs is chromatography [3], such as Culotta [4] using GC-MS to analyze the PAHs concentration and distribution of surface sediment in Stagnone lagoon in Italy. And Zhang [5] employed dispersive liquid-liquid microextraction-HPLC method for the determination of PAHs in environmental water samples. Although using chromatography for the determination of organic pollutants has several advantages such as high sensitivity, good precision and having the ability to respectively determine a variety of compounds and isomers with similar structure, this kind of analysis method needs to extract the

determinants from the samples and remove the impurity contamination during pretreatment. This process (extraction, purification, concentration and derivation) is very complicated. A high level of laboratory and equipment is required to satisfy such pretreatment. In addition, it's also a time-consuming and expensive process. All the above make it difficult to adapt to the large number of samples and field test occasions. Therefore, it's imperative to find a rapid, sensitive, cheap and effective detection method.

Naphthalene is one of the most important PAHs in industry with the simplest structure. Both the US EPA and China put naphthalene as the first PAHs on the list of priority control pollutants due to its huge harm to human health. As a new type of materials, quantum dots have several incomparable characteristics such as long strong fluorescence lifetime, good ability to resist drifting, wide absorption spectrum, narrow emission and easy to do surface modification. The analyte can be detected by investigating the change of the luminescence properties caused by the interaction between quantum dots and analyte [6]. This paper takes naphthalene as representative to study the interaction between CdS quantum dots and naphthalene by the research of the change of fluorescence spectrum, exploring a new detection method of PAHs. The results show that the quantum dots have great application value in the field of environmental detection.

II. EXPERIMENTAL SECTION

A. Materials

CdCl₂ solution (0.02 mol/L), Na₂S solution (0.2 mol/L), thioglycolic acid (TGA) (V/V: 10%), PEG400 (polyethyleneglycol) (V/V: 25%), Isopropanol, ethanol, naphthalene (0.1 g/L), HCl solution (0.1 mol/L), NaOH (0.1 mol/L), NaCl (1 mol/L). All other reagents were of analytical grade and used as received. Doubly distilled water was used throughout the experiments.

B. Synthesis of CdS Quantum Dots

The CdS quantum dots were synthesized by CdCl₂ and other reagents according a method that has been described elsewhere [7]. Briefly, 10 mL CdCl₂ solution (0.02 mol/L) was diluted with doubly distilled water to 20 mL. Then 0.33 mL 10% (V/V) TGA was added. The pH of the solution was adjusted to 7 by titrating 1 mol/L NaOH solution. Before the mixture was ultrasounded by 40 kHz for 15 min at room temperature, 0.5 mL Na₂S (0.2 mol/L) was added. Finally, the CdS quantum dots were obtained by heating 10 min at 75°C.

Zhengyu Yan is with the Institute of China Pharmaceutical University, China (phone: 86-025-86185150; fax: 86-025-86185150; e-mail: 779061285@qq.com).

Yan Yu is now with the Department of Analytical Chemistry, China Pharmaceutical University, China (phone: 86-025-86185150; fax: 86-025-86185150; e-mail: yuyanhappy123@163.com).

Jianqiu Chen is with the Institute of China Pharmaceutical University, China (Corresponding author: phone: 86-025-86185150; fax: 86-025-86185150; e-mail: 745815879@qq.com).

C. Modification of CdS Quantum Dots

2 mL CdS quantum dots solution prepared as above and 4 mL PEG400 (V/V: 25%) as modifier were mixed and ultrasounded by 40 kHz at room temperature. The reaction proceeded for 10min.

D. Size Selective Precipitation of CdS Quantum Dots

1 mL CdS quantum dots solution was added to 0.25 mL, 0.5 mL, 0.75 mL and 1 mL isopropyl alcohol respectively and obtained the precipitation. Then the same volume isopropyl alcohol is added to the supernatant after extraction and completed precipitation. The precipitation is dried and dissolved in 2 mL doubly distilled water as test solution before further study.

E. Analysis of a Real Sample

The water samples were collected from the river in the campus, drinking water, tap water. The samples were filtered through a 0.22 μm membrane (Millipore) after precipitating for 24 hours. Then the samples are centrifugated by 4000 r/min and the supernatant is obtained. Aliquots (100 μL) of the samples were spiked with standard naphthalene solution (100 μL , concentration 0.1010 mg/mL). The spiked samples were then diluted to 1000 μL with doubly distilled water containing PEG400-capped CdS quantum dots solution (500 μL) and reacted for 10 min at room temperature. The control samples without CdS quantum dots were obtained as above. All the samples were analyzed using the developed sensing technique.

F. Instrumentation

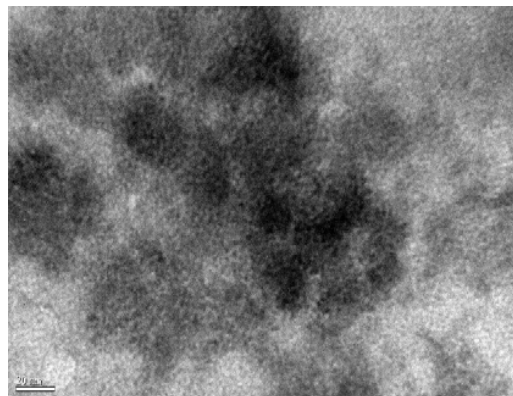
High-resolution transmission electron microscopy (HRTEM) measurements were performed on an electronic microscope (JEM-200CX). UV/vis absorption spectra were recorded by a UV/vis/NIR spectrophotometer (UV 2100). Fluorescence spectra of the prepared CdS quantum dots were obtained by an FL spectrophotometer (RF-5301PC).

III. RESULTS AND DISCUSSION

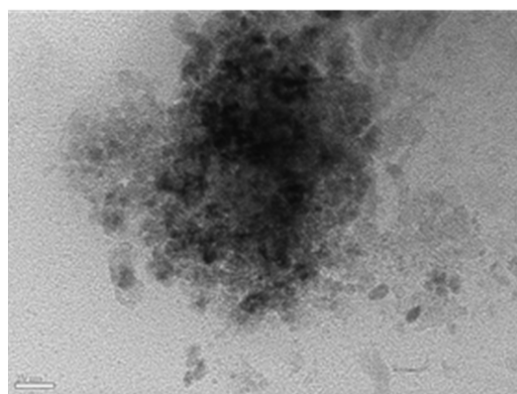
A. Characterization

The CdS quantum dots synthesized by the previously reported method [7] are monodisperse nanoparticles of near spherical morphology and about 3 nm in size (Fig. 1 (a)). Under the excitation of 519 nm, the CdS quantum dots solution exhibits strong emission with an FL quantum yield higher than 22.5%. They are well capped by PEG400 (Fig. 1 (b)). The organic coating can be seen on the outside of the CdS quantum dots.

Fig. 2 is the fluorescence emission spectra of CdS quantum dots solution which was modified. We can see that the fluorescence properties of PEG400-CdS quantum dots are improved; indicating that this modified method effectively eliminates the surface defects of the CdS quantum dots. The PEG400 and CdS quantum dots reacted with 2:1 (V/V) can get the best result according to the fluorescence intensity.



(a) CdS quantum dots



(b) PEG400-CdS quantum dots

Fig. 1 TEM for different quantum dots

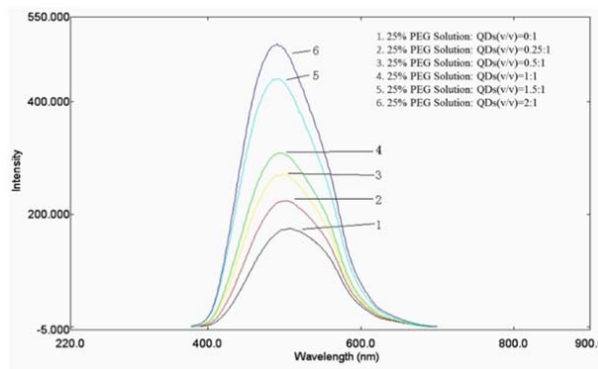


Fig. 2 FL spectra of different proportions of reaction

B. Establishment of Extraction Method for CdS Quantum Dots

The size selective precipitation of CdS quantum dots were obtained as 2.4 said. Through size selective precipitation the fluorescence emission wavelength of the CdS quantum dots supernatant blue shifted (see Fig. 3).

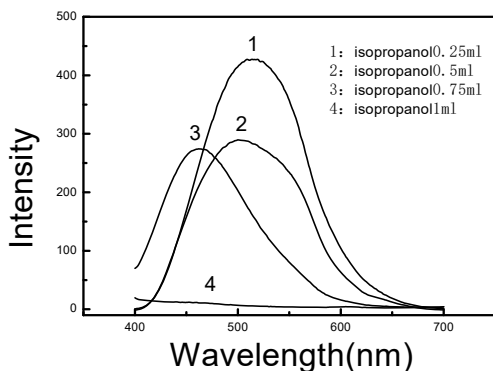


Fig. 3 The FL spectra of the size selective precipitation of CdS quantum dots

This is because that with increasing the addition of isopropanol, quantum dots size from large to small precipitated in turn and fluorescence emission peak sharpening gradually. The figure can also illustrate that the size selective precipitation can improve the quantum dot monodispersity effectively. And because of the quantum dots supernatant being precipitated and extracted, the fluorescence intensity decreased, which can reflect the content of quantum dots of various sizes in the mother solution. In general, the same volume of isopropanol can be used to make the CdS quantum dots precipitate completely in this paper.

C. Study on the Stability of CdS Quantum Dots

The CdS quantum dots solution was stored at 4°C without light in the refrigerator and measured the fluorescence emission at 1 month, 3 months respectively. The original solution and the solution which placed 1 month, 3 months are all clear and yellowish green. Fig. 4 indicates that the fluorescence intensity of the CdS quantum dots synthesized in this paper is stable for the applications in analytical chemistry.

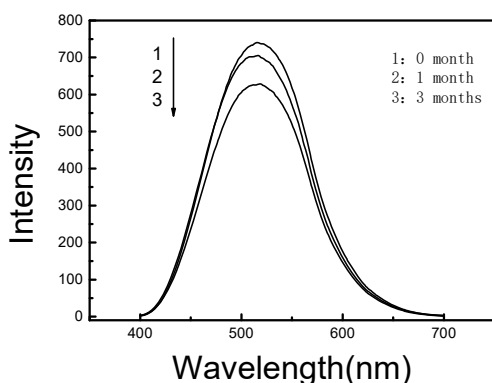


Fig. 4 The stability of the CdS quantum dots

The position of the fluorescence peak has not changed significantly, which indicated that the time has little effect on the particle size. The fluorescence intensity decreased little illustrates that TGA as the stabilizer can prevent the aggregation of CdS quantum dots and increase the water

solubility.

The fluorescent properties of CdS quantum dots can maintain stability may be as time goes by, the aging process leads to the particle surface reaction, thereby eliminating the more surface defects [8]. At the same time, the CdS quantum dots are stored in low temperature, the molecular movement speed slow and reduce the molecular collision probability, internal and external conversion decreased, and the non-radiative transition is reduced, so as to improve the efficiency of fluorescence. So the CdS quantum dots stored without light in refrigerator contribute to the stability of the quantum dots.

D. FL Quenching Mechanism

Fluorescence intensity is significantly reduced after adding a certain amount of CdS quantum dots in the naphthalene. CdS quantum dots for naphthalene are fluorescence quenchers. According to the literature [9], the fluorescence quenching process can usually be divided into static quenching, dynamic quenching and non-radiation energy transfer quenching. And dynamic quenching and static quenching can be described by Stern-Volmer equation and Lineweaver-Burk equation respectively. The equations are as follows:

Stern-Volmer equation:

$$I_F^0/I_F = 1 + K_{SV}c = 1 + K_q\tau_0c \quad (1)$$

Lineweaver-Burk equation:

$$(I_F^0 - I_F)^{-1} = (I_F^0)^{-1} + K_{LB}^{-1}(I_F^0)^{-1}c^{-1} \quad (2)$$

I_F^0 is the fluorescence intensity of the pure naphthalene solution, I_F is the fluorescence intensity of naphthalene solution after addition of the quencher, c is the total concentration of the quencher, K_{SV} is the quenching constant of Stern-Volmer, which reflects the dose-effect relationship between the biological macromolecules and the fluorescent quencher when they diffuse and collide to reach the dynamic equilibrium, K_q is the rate constant of bimolecular dynamic quenching, K_{LB} is the complex formation constant in static quenching procedure, which reflects the dose-effect relationship between the quencher and the biological macromolecules when they reach to balance, τ_0 is the life expectancy of the fluorescence molecule without quencher.

Determined the fluorescence intensity in the naphthalene solution with different CdS quantum dots concentration and used the experimental data to make Stern-Volmer curve and Lineweaver-Burk double reciprocal curve respectively. The curves were fitted to obtain the linear equations (the following equations were measured at room temperature):

Stern-Volmer curve:

$$I_F^0/I_F = 4.532 \times 10^6 c + 0.9872 \quad (R^2=0.9880) \quad (3)$$

Lineweaver-Burk curve:

$$(I_F^0 - I_F)^{-1} / (I_F^0)^{-1} = 2.321 \times 10^{-7} c^{-1} + 0.9820 \quad (R^2=0.9981) \quad (4)$$

As we can see, the linear relation according to Lineweaver-Burk equation is better than Stern-Volmer equation does. It indicates that CdS quantum dots as fluorescence quencher for naphthalene is more in line with the static quenching.

In addition, the experiments were at 20°C and 40°C Stern-Volmer curves can be obtained by the data as follows:

20 °C (Stern-Volmer curve):

$$I_F^0 / I_F = 4.316 \times 10^6 c + 0.9468 \quad (R^2=0.9865) \quad (5)$$

40 °C (Stern-Volmer curve):

$$I_F^0 / I_F = 4.450 \times 10^6 c + 0.9920 \quad (R^2=0.9809) \quad (6)$$

The slope of Stern-Volmer curve fitting equations were 4.316×10^6 , 4.532×10^6 , 4.450×10^6 at 20°C, 25°C (room temperature) and 40°C respectively. The slope is similar, which illustrating that the temperature has little effect on the CdS quantum dots quenching effect of naphthalene fluorescence characteristics and indicating that CdS quantum dots as fluorescence quencher for naphthalene is more in line with the static quenching. But the mode of action is needed to be studied further.

E. Establishment of the FL Sensing Method for Naphthalene

Due to the solubility of naphthalene in water is very low and the naphthalene content in environment is low too (usually using g/L, ng/L unit level), adding some naphthalene to the water to obtain the environmental samples and using them to study the method of detecting polycyclic aromatic hydrocarbons by CdS quantum dots.

With the increasing of NaCl concentration, ionic strength in this system is increasing too. To study the effect of ionic strength on the fluorescence system, the fluorescence intensity of naphthalene is detected. According to the above experimental method, adding 1 mol/L NaCl solution of different volume to detect the fluorescence spectrum in the complex system. As shown in Fig. 5, with increasing of ionic strength, the characteristic fluorescence of naphthalene decreased, but stabilized gradually, and the extent of decreasing is slight. So there is no need to add NaCl in the system when measuring the quantity relationship.

Using the HCl (0.1 mol/L) and NaOH (0.1 mol/L) to adjust the pH of the solution. And detect the fluorescence intensity of naphthalene based on the above method (see Fig. 6). When the pH was 6.5, the fluorescence intensity was strongest. So the solution system was detected under the condition of pH 6.5.

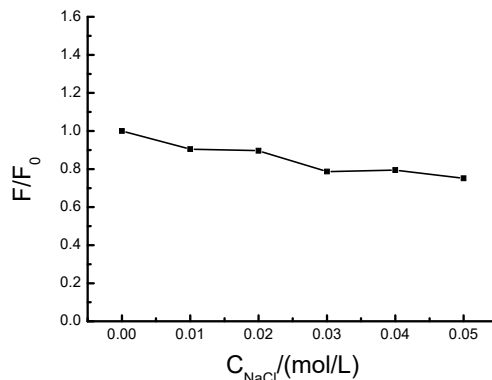


Fig. 5 The effect of ionic strength

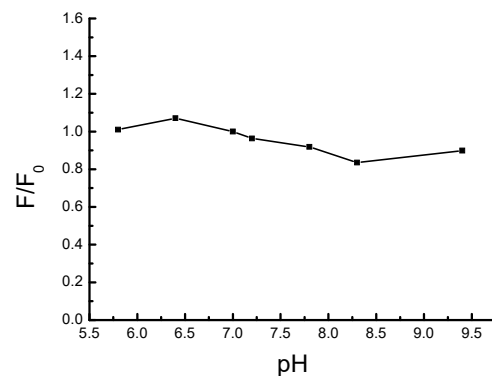


Fig. 6 The effect of pH

Take a certain amount of distilled water, adding 50 μl, 100 μl and 200 μl naphthalene solution (0.1010 mg/mL) respectively, each of them need three copies, and mixed with 500 μl CdS quantum dots solution. Finally add distilled water to 1mL as the test solution. The control was prepared by the same method without CdS quantum dots. The mixture was reacted for 10 min at the room temperature. The fluorescence spectra under the excitation of 286 nm is detected to test the recovery rate. The results can be seen in Table I, all the recovery rate of the samples was 97.43%–103.2%, so the method can be used for the determination of naphthalene in water.

TABLE I
THE RECOVERY RATE OF NAPHTHALENE

Sample amount (mg/mL)	Measured amount (mg/mL)	Recovery rate (%)	Average recovery rate (%)	RAD (%)
	0.005044	99.88		
0.005050	0.005072	100.4	101.2	1.8
	0.005213	103.2		
	0.009862	97.64		
0.01010	0.009840	97.43	98.44	1.6
	0.01012	100.2		
	0.02039	100.9		
0.02020	0.02069	102.4	100.9	1.4
	0.02010	99.50		

F. Application

Some naphthalene is added to the water in the river of the

campus, drinking water and tap water respectively according to the experimental method above. The detected simulation samples and the results were shown in Table II. The relationship between CdS quantum dots and naphthalene suggests promising applications of CdS quantum dots in analytical chemistry.

TABLE II
THE RESULTS OF THE SIMULATION SAMPLES

Sample	Sample amount (mg/mL)	Measured amount (mg/mL)	Content (mg/mL)	Average content (mg/mL)	RAD (%)
River water	0.01010	0.01125	0.01150	0.01125	2.1
		0.01120	0.01103		
		0.01122	0.01124		
Drinking water	0.01010	0.01069	0.005932	0.005827	2.0
		0.01068	0.005844		
		0.01067	0.005706		
Tap water	0.01010	0.01201	0.01913	0.01892	2.0
		0.01195	0.01848		
		0.01201	0.01913		

(content= (measured amount - sample amount)/volume, in this experiment, the volume is 0.1 mL.)

IV. CONCLUSION

The modification and extraction methods of the CdS quantum dots were investigated in this paper. The results were that the poly organic coated CdS-PEG quantum dots system which greatly improves the fluorescence properties of the CdS quantum dots and the efficient extraction method of the CdS quantum dots was obtained successfully. The interaction mechanism between CdS quantum dots and naphthalene was studied using the fluorescence spectrometry. The results showed that the fluorescence quenching of naphthalene with CdS quantum dots belonged to static quenching. After optimization of the experimental conditions, an excellent FL sensing system has been developed for the detection of naphthalene in aqueous solutions, which indicates promising applications in the environmental water samples.

ACKNOWLEDGMENT

The authors thank the support of the Fundamental Research Funds for the Central Universities.

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