

An eco-friendly molecularly imprinted fluorescence composite material based on carbon dots for fluorescent detection of 4-nitrophenol

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Abstract We on report an eco-friendly molecularly imprinted material based on carbon dots (C-dots) via a facile and efficient sol–gel polymerization for selective fluorescence detection of 4-nitrophenol (4-NP). The amino-modified C-dots were firstly synthesized by a hydrothermal process using citric acid as the carbon source and poly(ethyleneimine) as the surface modifier, and then after a sol–gel molecular imprinting process, the molecularly imprinted fluorescence material was obtained. The material (MIP-C-dots) showed strong fluorescence from C-dots and high selectivity due to the presence of a molecular imprint. After the detection conditions were optimized, the relative fluorescence intensity (F_0/F) of MIP-C-dots presented a good linearity with 4-NP concentrations in the linear range of $0.2 - 50 \mu\text{mol L}^{-1}$ with a detection limit ($3\sigma/k$) of $0.06 \mu\text{mol L}^{-1}$. In addition, the correlation coefficient was 0.9978 and the imprinting factor was 2.76. The method was applicable to the determination of trace 4-NP in Yangtze River water samples and good recoveries from 92.6–107.3 % were obtained. The present study provides a general strategy to fabricate materials based on C-dots with good fluorescence property for selective fluorescence detection of organic pollutants.

Keywords Molecular imprinting · Sol–gel · Eco-friendly material · Quenching · Stern–Volmer plot · Selective recognition

Introduction

4-Nitrophenol (4-NP) has been listed by the U.S. Environmental Protection Agency (U.S.EPA) as the priority environmental pollutant due to its wide use in agriculture and drug production [1, 2]. Thus, developing effective analytical methods for the detection of the 4-NP is very important. Until now, many traditional detection methods, such as electrophoresis and electrochemical methods, [3] chromatographic techniques [4] and high performance liquid chromatography (HPLC) [5] have been applied to detect trace 4-NP in real samples. However, these methods suffer from expensive reagents, time consuming, tedious sample pretreatment and possible production of secondary pollutants. Therefore, it is still a challenge to develop a simple, rapid and selective method for the determination of the 4-NP in real samples.

Quantum dots (QDs) have attracted much attention in the scientific community because of their unique properties, such as good photostability, narrow emission spectra and broad absorption spectrum [6, 7]. However, most traditional QDs contain heavy metals, such as Cd, and their applications are thus limited due to the toxicity and potential environmental risk of the heavy metals. As one type of QD substitutes, carbon dots (C-dots) were discovered in single-walled carbon nanotubes in 2004 [8]. Compared with the traditional QDs, C-dots exhibit advantages, including low toxicity, excellent photostability, easy preparation, and good water solubility [9–11]. Substantial research has been reported on analytical and detecting

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applications of C-dots based on the excellent fluorescence property. Lu et al. used pomelo peel as the carbon source to synthesize C-dots by hydrothermal treatment for the detection of Cu^{2+} [12]. Huang et al. prepared a new C-dots material by a one-pot microwave-assisted hydrothermal treatment using histidine as the carbon source for the detection of Fe^{3+} [13]. Gao et al. used water-soluble amino-functionalized C-dots as a fluorescence probe for the detection of Hg^{2+} in aqueous solution [14]. However, fluorescent detection based on QDs often confronts with the interference of the coexisting substances. A feasible method to enhance the selectivity of fluorescent detection is the use of molecular imprinting technology (MIT) [15].

MIT is a versatile and well-established strategy to obtain three-dimensional cross-linked polymers with tailor-made recognition sites [16]. The resulting molecularly imprinted polymers (MIPs) are prepared by the polymerization of functional monomers, cross-linkers and initiators in the presence of the template molecules [17]. Subsequently, the removal of template molecules from the three-dimensional cross-linked polymers leaves behind specific recognition sites with complementarity to the original template [18]. Due to the good stability, high selectivity and satisfactory practicability, MIPs have been widely used in many applications, including drug delivery and controlled release, [19] extraction and separation, [20] chemical material [21] and catalysis [22]. Recently, many effective MIPs-based QDs materials have been reported, which combined the advantages of high selectivity of MIPs and high sensitivity of fluorescence detecting from QDs [23]. We reported previously on the use of MIPs on Mn-doped ZnS QDs for selective fluorescence detection of 2,4,5-trichlorophenol, 2,6-dichlorophenol and 2,4-dichlorophenol, [24–26] and the use of MIPs on Octadecyl-4-vinylbenzyl-dimethyl-ammonium chloride-modified CdTe QDs for specific recognition and fluorescence detection of bifenthrin and λ -cyhalothrin [27, 28]. Here, we synthesized a novel MIPs fluorescence material based on polyamine-functionalized C-dots using a simple room-temperature sol–gel method for the fluorescence detection of target molecules.

In the present work, we report on a facile approach for the formation of a fluorescent material by coating an imprinted polymer layer on the surface of C-dots by a sol–gel process. Polyamine-functionalized C-dots were first synthesized by hydrothermal process using citric acid as the carbon source and poly (ethylenimine) as the surface modifier. Then 4-NP, 3-aminopropyltriethoxysilane (APTES) and tetramethoxysilane (TEOS) were chosen as the template molecule, functional monomer and cross

linker, respectively. After a sol–gel molecular imprinting process and a solvent extraction process, the MIP-C-dots fluorescence material was obtained. The synthesized nanomaterial was characterized by transmission electron microscopy (TEM), Fourier transform infrared spectroscopy (FTIR) and spectrofluorometer, and then used for selective recognition and fluorescence detection of the target molecule 4-NP. To the best of our knowledge, MIPs-capped C-dots for fluorescence detection of 4-NP has not been reported. Finally, this material was demonstrated as a simple, rapid and selective detection system for determination of 4-NP in real samples.

Experimental

Materials

All chemicals were of at least analytical grade. Citric acid, branched poly(ethyleneimine) (PEI) (MM 1800 Da), ammonia solution (25–28 %), tetraethoxysilane (TEOS) and 3-aminopropyltriethoxysilane (APTES) 4-nitrophenol (4-NP), 2-nitrophenol (2-NP), 2,4,6-trinitrotoluene (TNT), 2,4,5-trichlorophenol (2,4,5-TCP) were all purchased from Aladdin reagent Co., Ltd. (Shang Hai, China, www.aladdin-reagent.com). Ethanol was obtained from Sinopharm Chemical Reagent Co., Ltd. (Shang Hai, China, www.sinoreagent.com). Double distilled water was used during the whole experiment process.

Instrumentation

The morphologies were observed by a transmission electron microscope (TEM, JEOL, JEM-2100). Fourier transform infrared (FT-IR) spectra were recorded using Nicolet NEXUS-470 FTIR apparatus (USA). The fluorescence spectra of the C-dots and eco-friendly fluorescence material were obtained by a spectrofluorometer (Cary Eclipse) equipped with a quartz cell and a plotter unit.

The synthesis of polyamine-functionalized C-dots

Polyamine-functionalized C-dots were synthesized based on the procedure described in the literature with some modifications [29]. Briefly, 2.0 g of citric acid and 1.0 g of PEI were dissolved in 30 mL of deionized water, and the mixture was then transferred into a 50 mL Teflon-lined autoclave and heated at 200 °C for 5 h. After the reaction, the autoclave was cooled to room temperature, and the mixture was centrifuged at 12,000 rpm for 15 min to remove the large

dots. Finally, the C-dots were dried and re-dispersed in deionized water at the concentration of 50 g/L.

Synthesis of MIP-C-dots and NIP-C-dots

0.02 mmol of 4-NP template was dissolved in 10 mL of ethanol, mixed with 0.08 mmol of APTES (functional precursor), and then 100 μL of C-dots was added and stirred for 1.0 h. Subsequently, 0.4 mmol of TEOS (cross-linker) and 100 μL of $\text{NH}_3 \cdot \text{H}_2\text{O}$ (catalyst) were added to the reaction flask, and the mixture solution was kept stirring for another 12 h. The resultant MIP-C-dots were collected by centrifugation (8000 rpm, 5 min) and washed with ethanol several times to remove any free reagents. The 4-NP templates in the imprinted polymer were extracted with ethanol, until no 4-NP can be detected by using UV spectrometer. Finally, the MIP-C-dots were dried at 50 $^\circ\text{C}$ under a vacuum overnight. As a control, the non-imprinted fluorescence materials (NIP-C-dots) were also prepared using the same method but without the addition of 4-NP.

Fluorescence measurement

All the fluorescence measurements were performed under the same conditions: the slit widths of the emission and excitation were both 10 nm, and the excitation wavelength was set at 350 nm with a recording emission range of 390–540 nm. The MIP-C-dots were dispersed in deionized water to get the stock solution (100 mg L^{-1}). 4-NP and other phenols were dissolved in ethanol to get the analyte stock solutions (1.0 mmol L^{-1}), respectively. In a 5.0 mL tube, a given concentration of 4-NP solution was added to a certain volume of a solution of the MIP-C-dots, and then the mixture was diluted to volume with deionized water. After incubation, the testing solution was transferred to a quartz cell for the following fluorescence detection.

Fig. 2 (a) Emission spectra of the C-dots at different excitation wavelengths from 280 to 420 nm, and (b) FL spectra of 4-NP@MIP-C-dots (1), MIP-C-dots (2), NIP-CQDs (3)

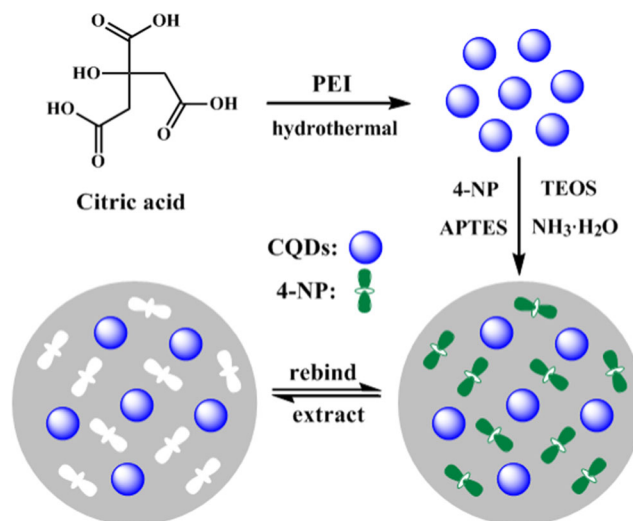
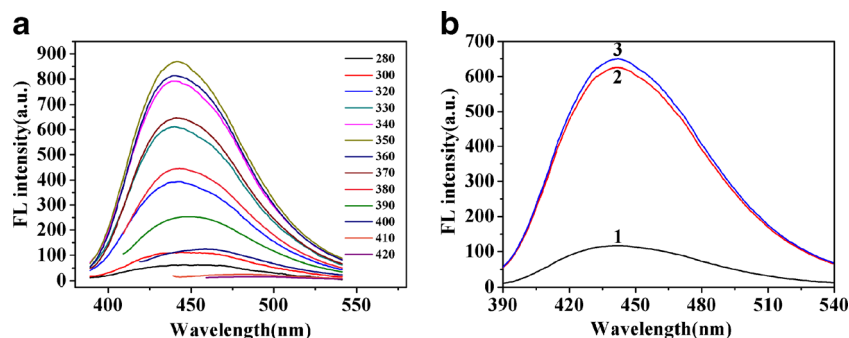


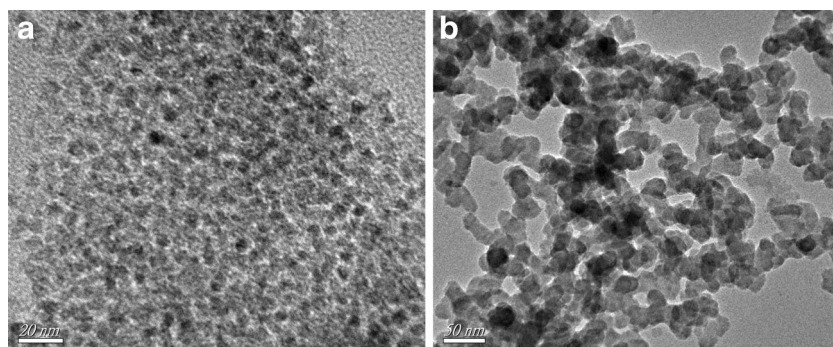
Fig. 1 Schematic illustration for the preparation of MIP-C-dots

Results and discussion

Preparation and characterization of C-dots and MIP-C-dots

The general scheme for the preparations of C-dots and MIP-C-dots are illustrated in Fig. 1. Firstly, amino-functionalized C-dots (see Figure S1) with high fluorescence property were synthesized via a facile and effective hydrothermal method. Citric acid and poly (ethylenimine) were used as the carbon source and surface modifier, respectively. Subsequently, the sol-gel molecular imprinting method was chosen as a simple and appropriate way to fabricate the MIP-C-dots. As shown in Fig. 1, 4-NP, APTES, TEOS and $\text{NH}_3 \cdot \text{H}_2\text{O}$ were used as template molecule, functional monomer, cross-linking agent and catalyst, respectively. After a copolymerization of the C-dots, APTES, 4-NP, and TEOS, the polymeric networks around the 4-NP molecules and C-dots were formed. The C-dots and APTES were interacted with 4-NP via the hydrogen bond interaction and van der Waals

Fig. 3 TEM images of C-dots (scale bar: 20 nm) (a) and MIP-C-dots (scale bar: 50 nm) (b)



force. After the removal of the templates by solvent extraction, the MIP-C-dots with specific imprinted cavities were obtained.

The fluorescence spectra of the amino-functionalized C-dots are shown in Fig. 2a. It can be found that when the excitation wavelength was set at 365 nm, the maximum emission wavelength was at 460 nm. Thus, excitation wavelength at 365 nm and emission wavelength at 460 nm were used in the further experiments. As shown in Fig. 2b, the fluorescence intensity of 4-NP@MIP-C-dots was about 18 % of that of NIP-C-dots; after 4-NP was removed by solvent extraction, the fluorescence intensity of MIP-C-dots was restored to 96.3 % of that of NIP-C-dots, which indicated that 4-NP was removed cleanly from the polymer matrix.

The morphology of C-dots and MIP-C-dots were investigated by TEM. As shown in Fig. 3a, the amino-functionalized CQDs are uniform and microspherical particles with the size about 4.5 nm. As shown in Fig. 3b, MIPs-CQDs exhibited spherical structure and the diameters were about 20 nm, indicating that the CQDs were coated with silica and the MIPs-CQDs were successfully synthesized.

FT-IR spectra of MIP-C-dots and NIP-C-dots were shown in Fig. 4. It can be found that the MIP-C-dots and NIP-C-dots showed similar spectrum owing to the same composition. The broad peak around 1097 cm^{-1} and the

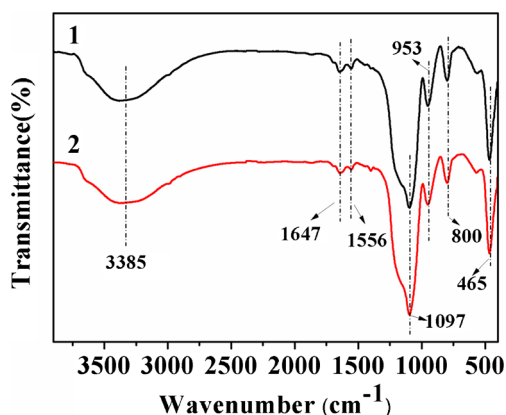


Fig. 4 FT-IR spectra of MIP-C-dots (1) and NIP-C-dots (2)

characteristic peaks at 800 and 465 cm^{-1} are attributed to the Si–O–Si asymmetric stretching and the Si–O vibrations, respectively. The bands at 3385 , 1647 and 1556 cm^{-1} were assigned to the stretching vibration of N–H, indicating the presence of amino group. All the bonds further confirmed that the material was successfully synthesized by the sol-gel condensation of the silane reagents.

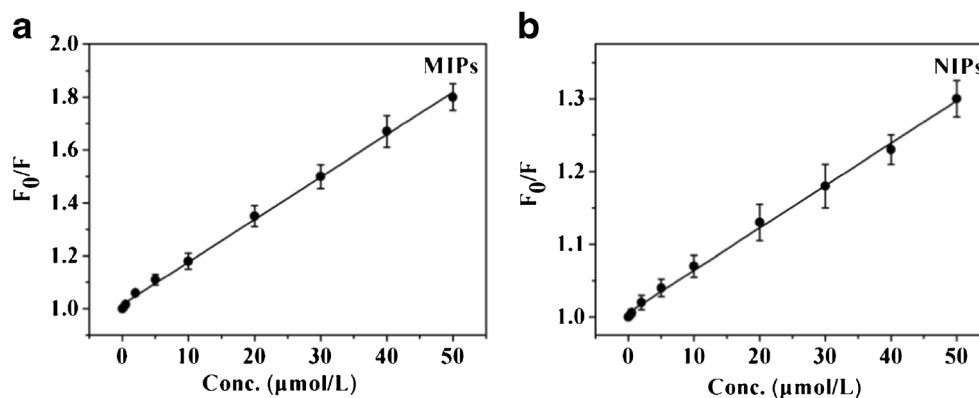
Fluorescence detection of 4-NP by MIP-C-dots

The following parameters were optimized: the concentration of MIP-C-dots and the detection time. Respective data and Figures are given in the Electronic Supporting Material. The following experimental conditions were found to give best results: (a) the optimum concentration of MIP-C-dots was about 2.0 mg L^{-1} ; (b) 2 min was determined as the optimal detection time. Under the optimal condition, the capability of the MIP-C-dots for quantitative determination of 4-NP was further studied. After incubation of MIP-C-dots with different concentrations of 4-NP for 2 min, the test was implemented. As a control, NIP-C-dots with different concentrations of 4-NP were also researched. The detection system was based on the fluorescence quenching between C-dots and 4-NP. Moreover, the quenching mechanism of this fluorescence detection system can be described as follows: In the synthesis process of MIP-C-dots, many tailor-made recognition sites with complementarity to 4-NP (template molecule) were produced, and the specific imprinted cavities can generate a strong adsorption of 4-NP; based on the hydrogen bonding interactions between the template molecules and polymer matrix, the template 4-NP can easily close to the fluorescent material and lead to the fluorescence quenching behavior which can be explained as the electron transfer from C-dots to 4-NP. The fluorescence quenching followed the Stern–Volmer equation.

$$F_0/F = 1 + K_{sv}[c] \quad (1)$$

F_0 and F are the fluorescence intensities of the MIP-C-dots in the absence and presence of the target molecule 4-NP,

Fig. 5 The Stern–Volmer plots for MIP-C-dots (a) and NIP-C-dots (b) with different concentrations of 4-NP in test solution



respectively. K_{SV} is the quenching constant, and $[c]$ is the concentration of 4-NP. In addition, the ratio of $K_{SV,MIP}$ and $K_{SV,NIP}$ is defined as the imprinting factor (IF) to evaluate selectivity. The Stern–Volmer plots of MIP-C-dots and NIPs-C-dots with different concentrations of 4-NP were shown in Fig. 5a and b, respectively. The plot shown in Fig. 7a can be described by the following equation: $F_0/F = 0.01605 [c] + 1.01593$, the $K_{SV,MIP}$ was $16,050 \text{ M}^{-1}$ and the correlation coefficient was 0.9978. The linear calibration curve was obtained in the range of $0.2\text{--}50 \mu\text{mol L}^{-1}$ with a detection limit ($3\sigma/k$) of $0.06 \mu\text{mol L}^{-1}$. As shown in Fig. 7b, the $K_{SV,NIP}$ was about 5820 M^{-1} and the correlation coefficient was 0.9970. After being calculated, a high imprinting factor (IF) of 2.76 was obtained, indicating that MIP-C-dots can selectively recognize the template molecule 4-NP.

Selectivity study

Firstly, the interference of potentially interfering ions was studied. It can be found from the Table S1 that all of the potentially interfering ions have no effect on the FL intensity of the MIP-C-dots. Then the other three substances (2-NP, TNT and 2, 4,5-TCP) were chosen to evaluate the selectivity of

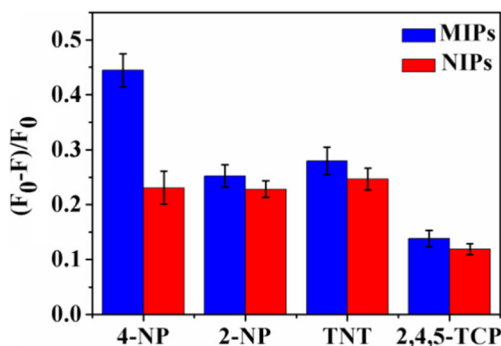


Fig. 6 Quenching efficiencies of MIP-C-dots and NIP-C-dots for 4-NP and other substances

MIP-C-dots. As shown in Fig. 6, the MIP-C-dots have a strong response to the template molecule 4-NP, and the fluorescence quenching amount of the MIP-C-dots for 4-NP was larger than others. After being calculated, the difference in the quench efficiency ($(F_0-F)/F_0$) of MIP-C-dots and NIP-C-dots were 0.2136, 0.0242, 0.0330, 0.0190 at $50 \mu\text{mol L}^{-1}$ for the four phenols (4-NP, 2-NP, TNT and 2,4,5-TCP), respectively. Based on the above results, it can be found that MIP-C-dots had specific recognition ability for 4-NP and the specificity was probably due to the existence of the imprinted cavities in the MIP-C-dots. In addition, other target molecules were not bound firmly into the imprinted cavities, and there were no specific recognition sites in the NIP-C-dots.

Analytical applications in real sample

To prove the applicability of the method, the nano material was used for the determination of 4-NP in Yangtze River water samples. The samples were filtered and stored in clean containers. As no response to 4-NP was found in the Yangtze River water samples, a recovery study was implemented and the corresponding analysis results were listed in Table 1. Owing to the excellent performance of the MIP-C-dots, good recoveries from 92.6 to 107.3 % were obtained. It can be found that the MIP-C-dots had good recognition ability to

Table 1 Recovery of 4-NP in Yangtze River samples ($n=3$)

Sample	Concentration taken ($\mu\text{mol L}^{-1}$)	Found ($\mu\text{mol L}^{-1}$)	Recovery (%)	RSD (%)
1	5	4.63	92.6	4.7
2	10	10.73	107.3	3.6
3	15	15.81	105.4	2.7
4	20	19.26	96.3	4.1
5	30	29.37	97.9	3.3
6	40	41.12	102.8	3.8

Table 2 Different methods of detection 4-NP

Analytical methods	Analytical ranges ($\mu\text{mol L}^{-1}$)	LODs (nmol L^{-1})	Reference
Hybrid inorganic-organic coated Pt electrode	30–90	8216	[30]
Cu ₂ O nanoparticles modified Pt rotating ring-disk electrode	10–100	100	[31]
Functionalized mesoporous silica fluorescent material	3.5–9.0	726	[32]
Carbon nanotube film electrode	1.0–35	120	[33]
DTD/Ag NP based carbon paste electrode	1.0–100	252	[34]
Hydrodynamic differential pulse voltammetry	10–1000	100	[31]
fluorescent carbon dots	0.1–50	28	[35]
MIP-C-dots fluorescent material	0.2–50	60	This work

provide accurate values of 4-NP concentrations on unknown water samples. Thus, this eco-friendly fluorescence material can be used as an effective tool for rapid and accurate analysis of real samples.

Many good works about analytical method for 4-NP detection have been reported and some of them were summarized and compared with our work in Table 2. It can be found that the methodology had wide linear range and low detection limit. Compared with electrochemical methods, fluorescence analysis method has a lot of advantages, such as good stability, low cost, simplicity, high sensitivity and test rapidity. For the MIP-C-dots detection system, the selectivity was significant improved but the sensitivity was low. The reason can be described as follow: during the polymerization process, cross-linkers formed the main polymer layer, and the interaction sites between functional monomers and template molecules were comparatively far less.

Conclusions

In summary, we developed a simple and efficient strategy to fabricate the eco-friendly molecularly imprinted fluorescence material based on C-dots for selective fluorescence detection of 4-NP. The prepared MIP-C-dots integrated the merits of the fluorescence property of C-dots and selectivity of MIPs. The material has a good linear range and detection limit, which provided a reliable method to detection of 4-NP in a real environment. Furthermore, it is suggested that a novel generation of eco-friendly fluorescence material based on C-dots can be fabricated by using this strategy.

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Compliance with ethical standards The author(s) declare that they have no competing interests

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