CrossMark

ORIGINAL ARTICLE

Specific Fluorescence Probe for Direct Recognition of Dimethoate Using Molecularly Imprinting Polymer on ZnO Quantum Dots

Behrouz Vahid[1] iD

Abstract ZnO quantum dots (QDs) based molecularly imprinting polymer (MIP)-coated composite was described for specific detection of the dimethoate (DM) as a template. The MIP was synthesized by simple self-assembly of 3-aminopropyl triethoxysilane (APTES) monomers and tetraethyl ortho-silicate as cross linking agent in the presence of template molecules. The used imprinting course can improve the tendency of the prepared QDs toward the DM template molecules. The MIP-coated ZnO QDs showed a strong fluorescence emission which undergoes a quenching effect in the presence of DM. So, a selective probe could be designed based on these composites to recognize DM in water samples. Under optimized experimental conditions, a linear relationship between the emission intensity of MIP-coated ZnO QDs and concentration of DM, in the range of 0.02–3.2 mg L^{-1} with a detection limit of 0.006 mg L^{-1}. Combination of high specificity of MIP element and distinct fluorescence features of ZnO QDs provides a sensitive and selective recognizing method for pesticide detection. The developed method was successfully applied for the determination of DM contamination in environmental water samples.

Keywords ZnO quantum dots · Molecularly imprinting polymer · Dimethoate · Pesticide · Fluorescence quenching

✉ Behrouz Vahid
behrouz_vahid@iaut.ac.ir; behrouz.vahid@gmail.com

[1] Department of Chemical Engineering, Tabriz Branch, Islamic Azad University, Tabriz, Iran

Introduction

Organophosphorous pesticides (OPs), as a wide series of toxic compounds, prevent the activity of acetylcholinesterase, which play an important role in nerve functions of insects, humans, and other animals [1]. OPs have been widely applied to control pests [2]. The usage of pesticides leads to the introducing of their residues in environmental water and soils. This can also result in contamination of vegetables and fruits [3] and finally, OPs can entry human body and cause serious side effects. It is demonstrated that pesticides can have mutagenic and carcinogenic effect and cause many diseases [3]. So, to provide a healthful and safe environment for humans, we need a sensitive and efficient screening technique for the recognition of trace pesticides in environmental samples. Dimethoate (O,O-dimethyl-S-methylcarbamoylmethyl phosphorodithioate, DM) is one of the important pesticides, which is applied for destroying an extensive variety of insects and acari in agriculture products. The chemical structure of DM is showed in Fig. 1. The maximum acceptable limit of DM in environment is in the range of few μg/kg [2]. DM and other pesticides is commonly quantified by chromatographic based techniques or immunoassays [2, 4–8] which are more expensive, complicated and laborious. Thus, developing a simple, cost-effective and rapid method for the determination of pesticides is a challenge for researchers.

Fluorescence techniques with high sensitivity can be assigned as a useful case for this purpose. They have unique interesting features such as simplicity, high speed, and low-cost. Fluorescence sensors based on quantum dots (QDs), have been recently reported for many of important analytes which have several advantages to other developed methods. High luminescent QDs have widely applied in analytical areas to sense several organic and inorganic compounds [9] that is because of their unique features [10, 11] such as high photo-stability, narrow emission with a high quantum efficiency,

Springer

H_3C—O—$\overset{\overset{S}{\|}}{P}$
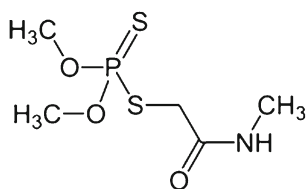
H_3C—O—S—CH$_2$—C(=O)—NH—CH$_3$

Fig. 1 Chemical structure of dimethoate

broad absorption spectrum and large Stokes shift [11–13]. They have quanum-size effect that's mean the emission wavelength is dependent to the diameter of nanomaterial [14–16]. These unique advantages make QDs superior to common organic fluorescent materials. More specific, ZnO QDs with high quantum yield, broad excitation spectrum and a narrow emission spectrum have been exploited by many researchers in chemosensors [16–21]. According to the Fonoberov and Balandin studies [14, 22], ZnO QDs with a size of less than 7 nm can exhibit a tunable fluorescence emission [14, 15]. Furthermore, they are non-toxic, bio-compatible, cheap, eco-friendly and can be synthesized by a simple and cost-effective process and so, they are superior to other QDs [14, 15, 23–26]. These properties make ZnO QDs as an interesting material in fluorescence-based probes. They have been applied in many studies leading to excellent analytical features.

Molecular imprinting as a potent procedure for the synthesis of particular polymeric receptors with high tendency to specific analytes, is interesting in sensor designing owing to its great selectivity, high physical strength and thermal stability along with an easy and low-cost preparation method [2, 11, 27–32]. Molecularly imprinted polymers (MIPs) are usually created based on the co-polymerization of certain monomers and cross-linkers in the presence of specific template molecules. The presence of template in the polymerization process leads to its trapping in polymer matrix, which can be removed by suitable washing methods. The created molecularly imprinted polymers have specific sites for rebinding template molecules [27]. The binding between MIP sites and template molecules is based on the key-lock principle, providing high selectivity and specificity for template. The high selectivity of MIPs-based methods along with a simple preparation process make them preferable to immunosorbents, increasing their applications area. The combination of the specific recognition features of MIPs and the outstanding advantages of QDs-based fluorescence detection methods can be an attracting analysis technique for the selective detection of important analytes [33–43].

To the best of our knowledge, there is no report for the determination of DM based on MIPs-functionalized ZnO QDs. Here, a selective probe based on MIP-coated ZnO QDs was developed for the rapid recognition of DM in environmental samples. ZnO QDs were synthesized via a simple mixing method and applied as an efficient support for MIPs due to their high luminescence and other aforementioned

advantages. The MIP shell are produced on the surface of ZnO QDs by self-assembly of 3-aminopropyl triethoxysilane (APTES) and tetraethyl orthosilicate (TEOS) in the presence of DM as template. The created MIP-coated ZnO QDs composite could specifically bind to DM molecules, and in this format, the fluorescence emission of ZnO QDs undergoes a diminishing effect proportional to DM concentration. So, it is applicable for the accurate and sensitive determination of DM which provided a low detection limit. The offered probe was used to the determination of DM in some environmental water samples. The method is more economical and sensitive in comparison with common chromatographic and immuno-based techniques. Figure 2 shows the schematic design for developed MIP-based probe for the determination of DM.

Experimental

Reagents and Apparatus

Dimethoate (DM), Zinc acetate dihydrate (Zn(OAc)$_2$.2H$_2$O), 3-aminopropyl triethoxysilane (APTES) and tetraethyl orthosilicate (TEOS) were all from Sigma Aldrich (Germany) and were applied without any purification. Ethanol and KOH were obtained from Merck (Germany). All the used materials were of analytical grade. All solutions were prepared in deionized water (Kasra CO., Iran).

Fluorescence (FL) experiments were accomplished by using a Shimadzu RF-5301 PC spectrofluorometer. UV-visible absorption spectra were achieved by UV-1800 spectrophotometer (Shimadzu). The size and morphology of synthesized QDs were investigated by Transmission electron microscopy (TEM, Leo 906, Zeiss, Germany). A Tensor 27 FTIR spectrometer (Bruker, Germany) was used to achieve Fourier transform infrared (FTIR) spectra.

Synthesis of ZnO Quantum Dots

Preparation of ZnO quantum dots was performed by a simple and rapid method [26]. Briefly, a certain amount of Zn(OAc)$_2$.2H$_2$O (0.001 mol) was added to 100 mL ethanol and ultra-sonication was used to its dissolving. 10 mL ethanol containing 2.8 mmol KOH was added slowly to Zn(OAc)$_2$ solution at room temperature. The solution was vigorously stirred during the KOH addition. ZnO QDs was gradually formed as a white suspension after about 1 h, which was then precipitated by its centrifugation (10,000 rpm) for 15 min. The obtained QDs were dispersed in ethanol and then were centrifuged to eliminate unreacted reagents. The rinsing process was repeated for several times. In order to increase the stability of obtained QDs in aqueous solution, they were modified by using APTES. ZnO QDs (0.04 g) were dispersed in 50 mL ethanol and then APTES solution (0.5 g in 5 mL ethanol) was

Fig. 2 Schematic design of offered probe for the determination of DM, based on MIP-coated ZnO QDs
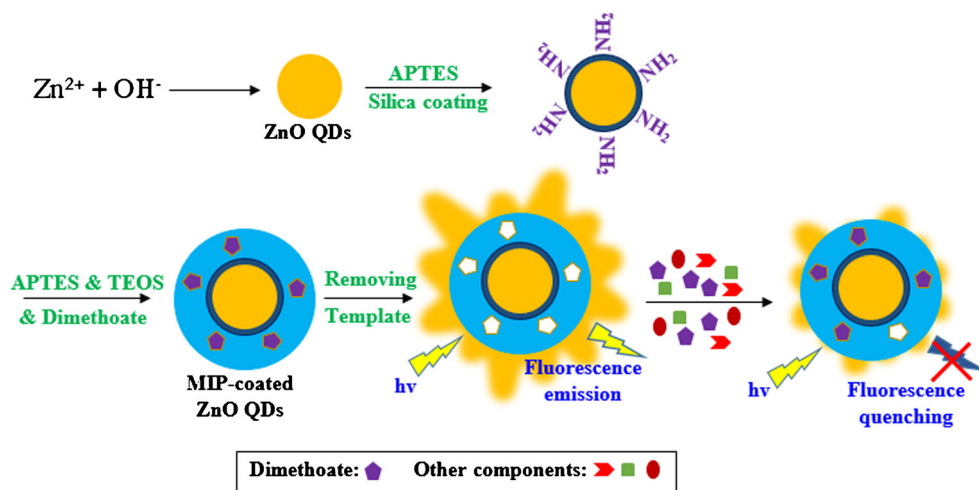
drop-wisely added, followed by addition of 0.2 mL distilled water. The mixture was stirred for another 1 h without its heating and then, coated QDs were separated by centrifugation (10,000 rpm, 10 min). Again, to remove excess precursors, QDs were twice redisposed and then precipitated by their centrifugation. The yellow emission which was observed from obtained solution under UV radiation, confirmed the success synthesis of ZnO QDs. The QDs were completely washed and dispersed in deionized water for future experiments.

Synthesis of MIP-Coated ZnO Quantum Dots

In order to prepare the MIP coating layer on the surface of ZnO QDs, 500 μL of APTES (as the main monomer) and 20 mL of DM (as the template molecules) solution (containing 250 mg DM in ethanol) were mixed and stirred for 30 min. Then, TEOS (2 mL) was added as the cross-linking monomer. After 5 min stirring, certain amounts of prepared ZnO QDs (600 mg) as well as 2 mL of 8% $NH_3 \cdot H_2O$ were added. The solution was stirred for another 16 h. Also, for control experiments, non-imprinted polymer (NIP)-coated ZnO QDs was obtained by the same way, but in the absence of template. Finally, the produced modified ZnO QDs were centrifuged and rinsed with ethanol for three times to remove template molecules and get approximately the identical FL emission intensity from NIP and MIP-QDs.

Fluorescence Determinations

Fluorescence studies for the determination of DM were performed at room temperature in a batch system. The synthesized MIP-capped ZnO QDs (500 μL, 100 mg L^{-1}) were added to certain volumes of DM standard or sample solutions in a 5 mL volumetric flask. The pH of solution was adjusted to about 7 by adding 500 μL Tris buffer. The solution was effectively mixed and its final volume was increased to 5 mL by deionized water. Finally, the fluorescence emission intensity of solution was measured at maximum emission wavelength of ZnO QDs (λ_{em} = 520 nm and λ_{ex} = 374 nm).

Sample Preparation

To assess the practical applicability, some environmental water samples were used for the determination of DM by developed probe. No further pretreatments was performed for samples. Just, each sample was cleaned by 220 nm micro-porous filter to remove suspended particles. Also, to study the recovery of probe, certain volumes of DM standard solution were spiked into samples before any pretreatment. The fluorescence intensity of DM solutions can be related to its concentration using a calibration graph plotted for standard solutions.

Results and Discussion

Characterization of Synthesized ZnO QDs

Surface structure of synthesized ZnO QDs and MIP-ZnO QDs was investigated by FTIR spectra (Fig. 3a). FTIR spectrum of ZnO QDs contains clear peaks at about 3412 and 1522 cm^{-1} which are related to N-H bonds. The peak at 2948 cm^{-1} is for well-known symmetric C-H vibrations. Two peaks at 1110 and 1021 cm^{-1} show Si-O bonds, and a characteristic peak at 505 cm^{-1} indicates the Zn-O bonds [44]. In FTIR spectrum of MIP-capped ZnO QDs, the peaks of Si-O and N-H were strengthened and a peak at 1611 cm^{-1} was appeared which is related to C = C bonds. Also, the peak of Zn-O bonds at about 500 cm-1 was weakened because of the coating of a polymeric layer on its surface. These changes confirm the MIP placing on the surface of ZnO QDs.

TEM images of ZnO QDs and MIP-coated ZnO QDs were indicated in Fig. 3b and c. As it is clear, mono-dispersed spherical ZnO QDs with a diameter size of about 2–8 nm were obtained. Also, the average size of MIP-coated QDs was

Fig. 3 **a** FT-IR spectra for ZnO QDs and MIP-ZnO QDs; **b**, **c** TEM images for ZnO QDs (**b**) and MIP-ZnO QDs (**c**), the insets show the size distribution of QDs; and d) XRD pattern for ZnO QDs
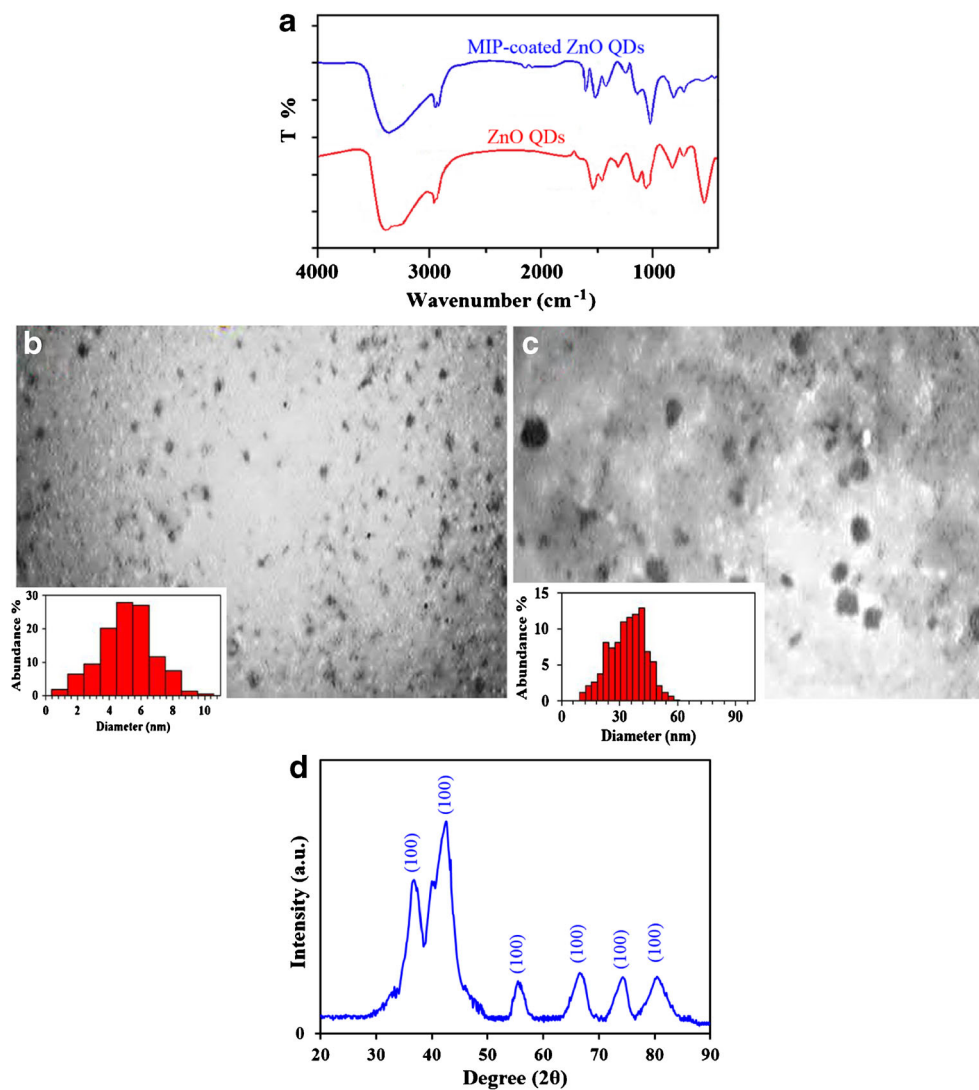
about 35 nm and so, it can be considered an about 20 nm layer of MIP on the QDs. Also, XRD analysis was applied to investigate the crystallinity of QDs, which indicated some clear intense peaks showed in Fig. 3d. The observed peaks confirmed the crystalline structure of obtained QDs with the size in nanometer range. Also, there isn't any additional peak which indicates that the synthesized ZnO QDs are free from any impurity. The size of obtained particles was calculated to be 5.93 nm by using Debye Scherrer formula [44].

Furthermore, UV-visible absorption spectrum of prepared ZnO QDs is indicated in Fig. 4a. The spectrum showed a shoulder at about 315 nm. Comparing to bulk ZnO, there is a clear shift to shorter wavelengths in absorption spectrum of QDs which can be related to their nanometer size [44]. On the other hand, the synthesized QDs showed an intense fluorescence emission at 536 nm (λ_{ex} = 389 nm). The stability and quantum yield of the fluorescence emission were investigated for prepared MIP-coated QDs. The results showed a stable emission (Fig. 4b) with a quantum yield of 13%. It can be

observed from Fig. 3b that the florescence emission intensity of MIP-coated ZnO QDs remains constant during 50 day after their synthesis. The relative standard deviation (RSD) of 0.48% was acquired by 20 repetitive determination of the emission intensity for the aqueous solution of MIP-coated ZnO QDs every 10 min. The silica coating of ZnO QDs is the chief cause of the stable emission.

Basis of Developed Probe

MIP-capped ZnO QDs were used as recognition element for a specific pesticide. ZnO QDs can act as optical readout and lead to intensification of obtained signal. The stability of synthesized QDs was enhanced by their coating with APTES hydrolysis reaction which leads to reduction of surface defects of QDs. Furthermore, in order to increase selectivity for DM and remove the interfering effect of other compounds, the MIP recipient was employed on the surface of ZnO QDs. It was done by self-assembling of APTES monomers on the
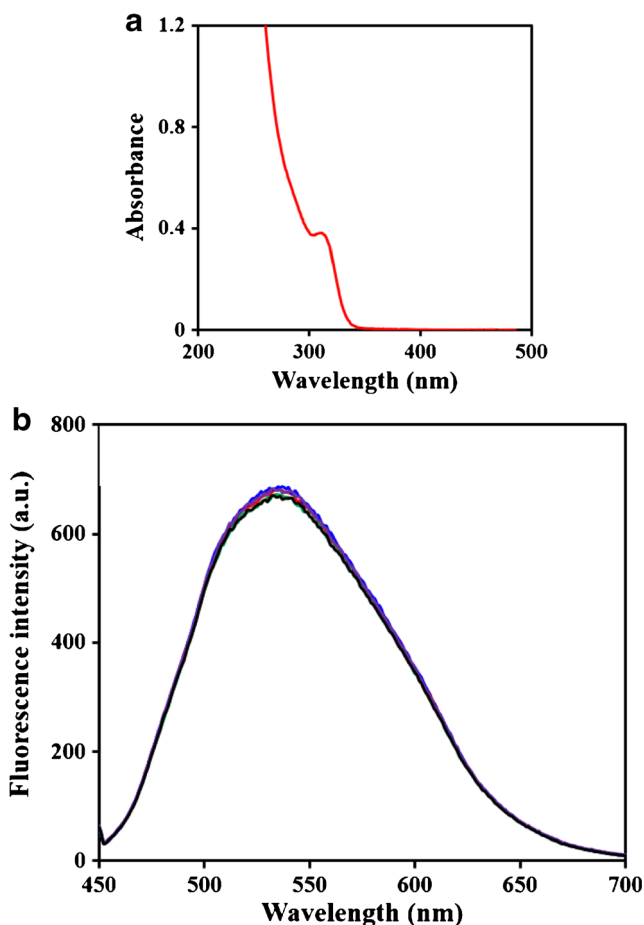
Fig. 4 **a** Absorption spectrum of MIP-coated ZnO QDs; **b** Emission spectra for MIP-coated ZnO QDs recorded in different times after their synthesis (10 min, 10 h, 3 day and 15 day)

Fig. 5 Fluorescence emission spectra for (**a**) NIP-coated ZnO QDs and (**b-d**) MIP coated ZnO QDs before (**b**) and after (**c**) template removal; (**d**) Fluorescence emission spectrum for template removed MIP-coated ZnO QDs in the presence of 2.5 mg L^{-1} DM

amino capped-ZnO QDs in the presence of TEOS as cross-linking agent and DM as template molecules. The amino groups on the surface of the APTES-modified QDs can support the template molecules to enter the designed MIP shell during the imprinting polymerization stage. The template molecules were non-covalently entrapped into the polymer and after eliminating the template, specific sites with a shape and functional groups matching to the DM molecules were shaped in the polymer matrix. Also, NIP-coated ZnO QDs were synthesized to further investigation of selectivity. Study of the fluorescence emission of MIP-coated ZnO QDs showed a relatively strong emission peak at about 536 nm with an excitation wavelength of 389 nm. In the presence of templates, MIP-coated QDs had a weaker emission intensity which was remarkably restored after template removal (Fig. 5). The fluorescence intensity of the MIP-coated QDs without templates was almost equal to that of the NIP-coated QDs. This indicate the complete removal of template molecules from the MIP sites on the surface of QDs.

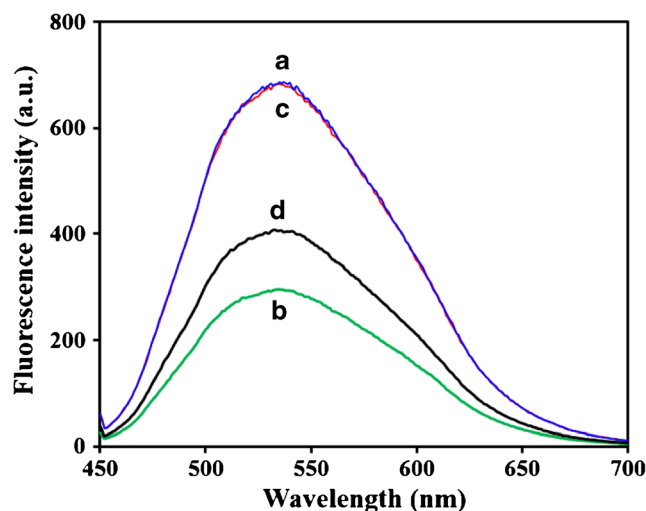Observations showed that the MIP-coated QDs can be practically applied to facile and rapid recognition of DM in aqueous media without any preconcentration stage. Decrease in fluorescence intensity of MIP-coated QDs in the presence of DM used as the probe signal, and concentration of DM in a sample can be obtain by using standard addition method.

Optimization of Experimental Condition for DM Determination

In order to obtain a high sensitive probe for DM, the effect of some important factors including the pH of determination media and incubation time were investigated.

The pH effect on the fluorescence response of MIP-coated QDs was studied in the range of 4–12 (Fig. 6a). As the results showed, the fluorescence signal decreased in very low or high pHs and a pH between 5 and 8 is suitable for determination process. The low fluorescence response outside of this range can be explained as follows: The high concentration of H+ or OH- can affect the functional group of MIP sites and therefore, decrease their tendency for template molecules. Also, ZnO QDs in the center of probe, may be affected in very low or high pH values. In result, their fluorescence emission would be changed. Experiments showed that Tris buffer in a relatively low concentration (0.5 mmol L^{-1}) was useful for pH adjusting. Other buffers such as phosphate quenched the fluorescence of ZnO QDs and were not suitable.

In order to study the effect of incubation time on the response of probe, MIP-coated ZnO QDs were exposed to DM in a constant concentration for different time scales and then, the fluorescence intensity was recorded (Fig. 6b). A rapid quenching effect was observed in the emission of QDs by addition of DM. The fluorescence intensity was decreased in first 5 min and then remained constant. This result show that the interaction of DM molecules with created specific sites on

Fig. 6 **a** Fluorescence response of MIP-coated ZnO QDs for 1.2 mg L^{-1} DM in different pH values, **b** Fluorescence intensity of MIP-coated ZnO QDs after their exposing to 1.2 mg L^{-1} DM in different times
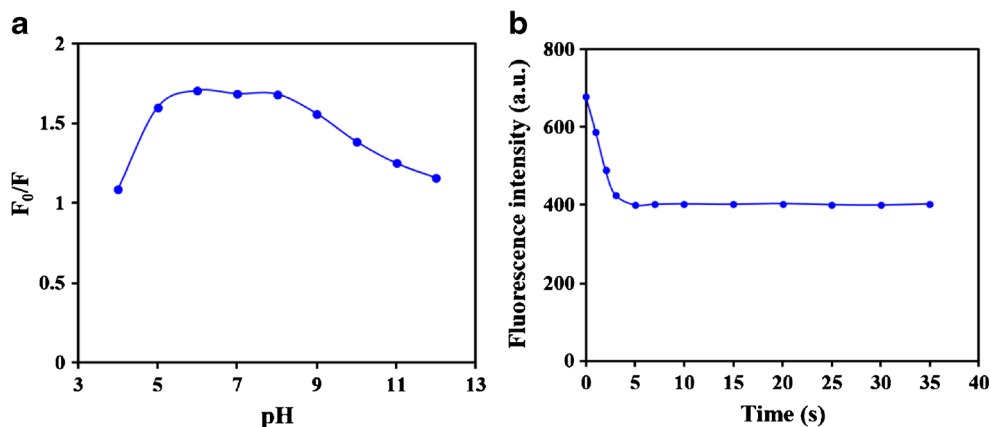
MIP matrix occur with high speed. So, an incubation time of 7 min was considered for all experiments.

Effect of DM Concentration on the FL of MIP-Coated ZnO QDs

The fluorescence of MIP-coated QDs showed a sensible decrease in the presence of DM in trace concentrations (Fig. 7a). Based on this observation, a sensitive and selective method was designed for the determination of DM in aqueous media. The calibration graph was obtained as the response of QDs to DM, F_0/F, against to the concentration of DM (C) in mg L^{-1} (F_0 and F show the fluorescence intensity of MIP-coated ZnO QDs in the absence and presence of DM, respectively). The obtained linear range was 0.02–3.2 mg L^{-1} with a regression equation of $F_0/F = 0.551C + 0.983$ ($R^2 = 0.9995$) (Fig. 7b). The limit of diction (LOD) for method was achieved 0.006 mg L^{-1}. On the other hand, the reducing effect of analyte on the fluorescence emission of MIP-coated ZnO QDs can be described by electron transfer process [44]. Analyte molecules on the MIP sites near the QDs can trap the excited electron leading to decrease of excited QDs. Figure 2 explains the entire procedure for the determination of DM.

The reproducibility of the developed method was investigated by calculating relative standard deviation (RSD) for seven replicate determinations of 0.1 and 1 mg L^{-1} DM which were obtained 2.31 and 1.67%, respectively.

Selectivity

To investigate the probable interfering effect of some species present in the real samples on the offered determination probe, increasing quantities of them were added into a DM solution (0.2 mg L^{-1}) and determination process was accomplished according the general procedure. The results in Table 1 showed that the most of the examined species have not considerable interfering effect on the signal of probe. The tolerable concentration ratios for interferences mentioned in Table are for relative error of <5%. The amounts of most of

tested substances in real samples are below their tolerable levels and so, no interferences were observed in DM determination.

Furthermore, the effect of some similar compounds with DM for example other organophosphates have been studied. Figure 8a shows the response of developed probe for the 10 mg L^{-1} solutions of these compounds. No considerable
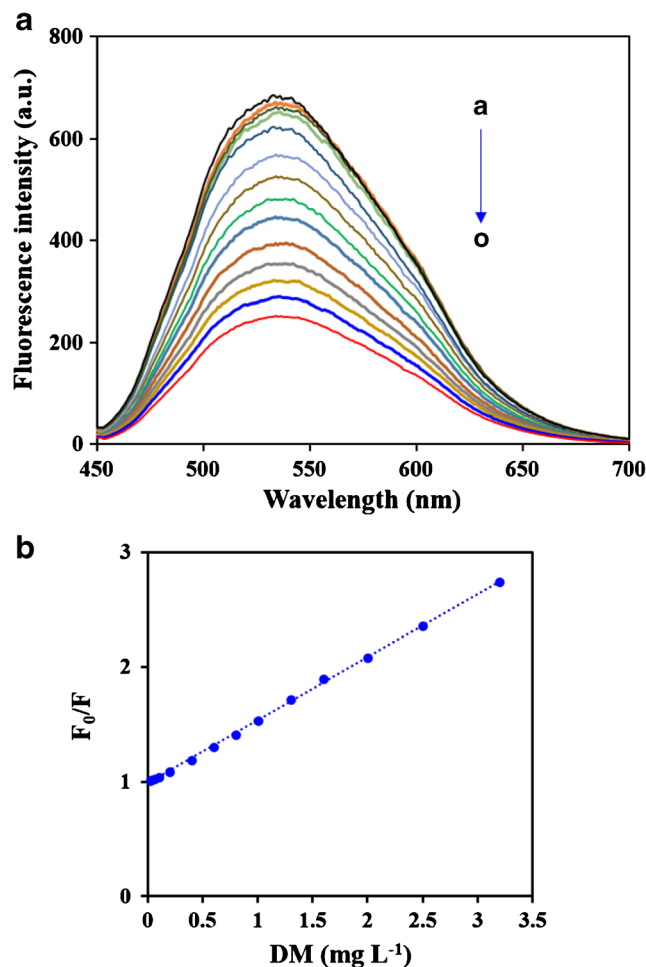

Fig. 7 **a** Fluorescence intensity of MIP-coated ZnO QDs in the presence of different concentrations of DM and **b** corresponding calibration graph

Table 1 Interference of different species on the determination of 1 mg L^{-1} DM (in optimum condition)

Coexisting substance	Tolerance limit (interference to analyte ratio)
Na^+, K^+, Ca^{2+}, Cl^-, NO_3^-	1500
Al^{3+}, Mn^{2+}, CO_3^{2-}, PO_4^{3-}, Oxalate	1100
HCO_3^-, CH_3COO^-, SO_4^{2-}, Mg^{2+}	900
Cu^{2+}, Ni^{2+}, Fe^{2+}, Fe^{3+}, Cr^{3+}	350
Glucose, Ascorbic acid, Uric Acid	260
Citrate, Glutathione	150
I^-, Zn^{2+}, Pb^{2+}, Cd^{2+}	70
Cysteine, Hg^{2+}	50

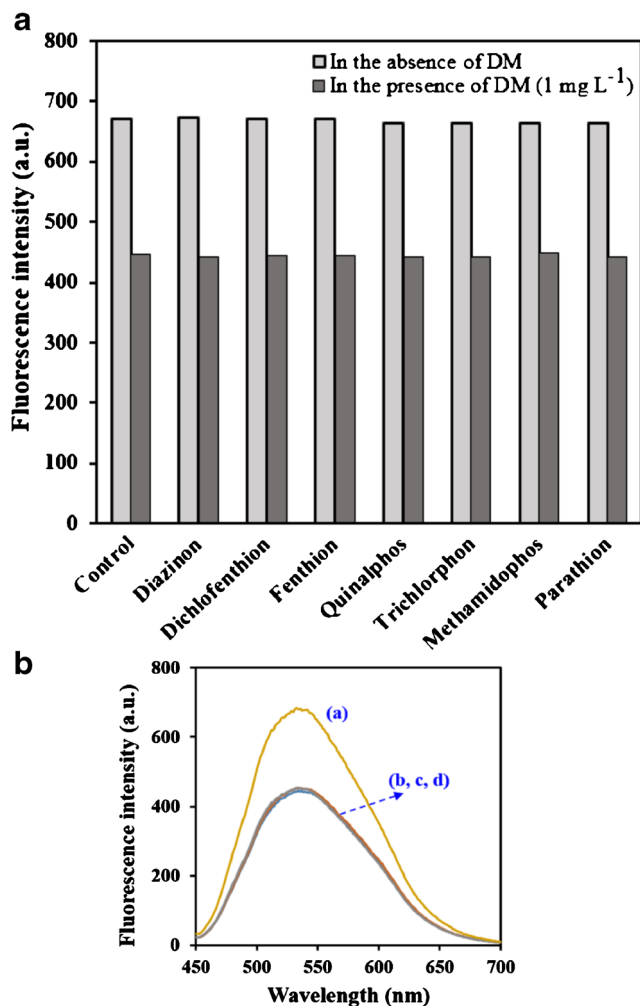effect was observed on the fluorescence of MIP-coated ZnO QDs from examined compounds. It can be explained by specific sites produced in the presence of DM as template. The functional groups in these sites are matching to the DM chemical structure. This shows the great selectivity of present sensor for DM. The ZnO QDs without MIP shell on their surfaces show a sensible response for about all of examined organophosphates.

Also, three different water samples (including deionized water, tap water and river water) have been applied to prepare the analyte solution with constant concentration (1 mg L^{-1}). The response of probe for the prepared solutions was recorded (Fig. 8b) which showed no obvious difference between three examined solution. So, developed method is applicable for the determination of pesticides in real water samples.

Analysis of Real Samples

The presented system was applied for DM quantification in environmental water samples (Table 2). For more validation of method, certain quantities of DM standard were added into samples prior to preparation stages, and then DM was followed according to the described method in Experimental section. As can be seen from the results (Table 2), the obtained recoveries were acceptable.

Conclusions

The ZnO QDs coated with MIP have been applied to recognize a specific pesticide in water samples. The MIP created on the surface of ZnO QDs using the co-plymezation of APTES and TEOS in the presence of DM as template molecules. So, recipient sites molecules can be created in the polymer matrix which is specific for DM providing the selective interaction of MIP-coated QDs with DM. Adsorption of DM molecules on the MIP sites leads to an efficient electron transfer from ZnO QDs to DM which quench the FL emission of ZnO QDs. The developed technique has more advantages such as high selectivity and sensitivity. This provide a rapid, cost-effective,

Fig. 8 **a** Effect of different organophosphates on the signal of MIP-coated ZnO QDs developed for DM; **b** fluorescence emission of MIP-coated ZnO QDs in the presence of 1 mg L^{-1} DM [*a*: absence of DM, *b*: DM in deionized water, *c*: DM in tap water and *d*: DM in river water]

Table 2 Results of DM determination in the water samples by established system

Sample	Add (mg L^{-1})	Found [a] (mg L^{-1})	Recovery % ± RSD	t-statistic [b]
River Water (1)	0	ND	-	-
	0.10	0.098 ± 0.002	97.67 ± 1.59	2.65
	0.30	0.294 ± 0.004	98.11 ± 1.19	2.79
River Water (2)	0	ND	-	-
	0.20	0.193 ± 0.004	96.59 ± 1.96	3.05
	0.50	0.498 ± 0.004	99.67 ± 0.70	0.82

[a] Mean of three determinations ± standard deviation, [b] t-critical = 3.18 for $n = 3$ and $P = 0.05$

simple and safe system for the detection of DM in the linear range of 0.02–40 mg L^{-1} with a LOD of 0.006 mg L^{-1}. The method displays good specificity for DM in the presence of other similar compounds.

References

1. Liang H, Song D, Gong J (2014) Signal-on electrochemiluminescence of biofunctional CdTe quantum dots for biosensing of organophosphate pesticides. Biosens Bioelectron 53:363–369

2. Lv Y, Lin Z, Feng W, Zhou X, Tan T (2007) Selective recognition and large enrichment of dimethoate from tea leaves by molecularly imprinted polymers. Biochem Eng J 36:221–229

3. Tadeo JL, Sanchez-Brunete C, González L (2008) Pesticides: classification and properties. In: Tadeo JL (ed) Analysis of pesticides in food and environmental samples. CRC Press, Taylor & Francis Group LLC, Boca Raton, pp 1–35

4. Khan BA, Farid A, Asi MR, Shah H, Badshah AK (2009) Determination of residues of trichlorfon and dimethoate on guava using HPLC. Food Chem 114:286–288

5. Bagyalakshmi J, Kavitha G, Ravi TK (2011) Residue determination of dimethoate in leafy vegetables (spinach) using RP-HPLC. Int J Pharm Sci Res 2:62–64

6. Barrek S, Olivier P, Marie-Florence GL (2003) Determination of residual pesticides in olive oil by GC–MS and HPLC–MS after extraction by size-exclusion chromatography. Anal Bioanal Chem 376:355–359

7. Polgár L, Kmellár B, García-Reyes JF, Fodor P (2012) Comprehensive evaluation of the clean-up step in QuEChERS procedure for the multi-residue determination of pesticides in different vegetable oils using LC-MS/MS. Anal Methods 4:1142–1148

8. Salm P, Taylor PJ, Roberts D, de Silva J (2009) Liquid chromatography–tandem mass spectrometry method for the simultaneous quantitative determination of the organophosphorus pesticides dimethoate, fenthion, diazinon and chlorpyrifos in human blood. J Chromatogr B 877:568–574

9. Cui L, He XP, Chen GR (2015) Recent progress in quantum dot based sensors. RSC Adv 5:26644–26663

10. Chan WC, Nie S (1998) Quantum dot bioconjugates for ultrasensitive nonisotopic detection. Science 281(5385):2016–2018

11. Ren X, Chen L (2015a) Preparation of molecularly imprinted polymer coated quantum dots to detect nicosulfuron in water samples. Anal Bioanal Chem 407:8087–8095

12. Xu SF, Lu HZ, Li JH, Song XL, Wang AX, Chen LX, Han SB (2013) Dummy molecularly imprinted polymers-capped CdTe quantum dots for the fluorescent sensing of 2,4,6-trinitrotoluene. Appl Mater Interfaces 5:8146–8154

13. Zhang Z, Li JH, Wang XY, Shen DZ, Chen LX (2015) Quantum dots based mesoporous structured imprinting microspheres for the sensitive fluorescent detection of phycocyanin. Appl Mater Interfaces 7:9118–9127

14. Hagura N, Ogi T, Shirahama T, Iskandar F, Okuyama K (2011a) Highly luminescent silica-coated ZnO nanoparticles dispersed in an aqueous medium. J Lumin 131:921–925

15. Hagura N, Takeuchi T, Takayama S, Iskandar F, Okuyama K (2011b) Enhanced photoluminescence of ZnO–SiO₂ nanocomposite particles and the analyses of structure and composition. J Lumin 131:138–146

16. Fonoberov VA, Alim KA, Balandin AA, Xiu F, Liu J (2006) Photoluminescence investigation of the carrier recombination processes in ZnO quantum dots and nanocrystals. Phys Rev B 73:165317

17. Segets D, Gradl J, Taylor RK, Vassilev V, Peukert W (2009) Analysis of optical absorbance spectra for the determination of ZnO nanoparticle size distribution, solubility, and surface energy. ACS Nano 3:1703–1710

18. Asok A, Gandhi MN, Kulkarni AR (2012) Enhanced visible photoluminescence in ZnO quantum dots by promotion of oxygen vacancy formation. Nano 4:4943–4946

19. Xiong HM, Shchukin DG, Möhwald H, Xu Y, Xia YY (2009) Sonochemical synthesis of highly luminescent zinc oxide nanoparticles doped with magnesium (II). Angew Chem Int Ed 48:2727–2731

20. Xu X, Xu C, Shi Z, Yang C, Yu B, Hu J (2012) Identification of visible emission from ZnO quantum dots: excitation-dependence and size-dependence. J Appl Phys 111:083521

21. Zhao D, Song H, Hao L, Liu X, Zhang L, Lv Y (2013) Luminescent ZnO quantum dots for sensitive and selective detection of dopamine. Talanta 107:133–139

22. Fonoberov VA, Balandin AA (2004) Origin of ultraviolet photoluminescence in ZnO quantum dots: confined excitons versus surface-bound impurity exciton complexes. Appl Phys Lett 85:5971–5973

23. Wu YL, Lim CS, Fu S, Tok AIY, Lau HM, Boey FYC, Zeng XT (2007) Surface modifications of ZnO quantum dots for bio-imaging. Nanotechnology 18:215604

24. Qu F, Santos DR, Dantas NO, Monte AFG, Morais PC (2004) Effects of nanocrystal shape on the physical properties of colloidal ZnO quantum dots. Phys E 23:410–415

25. Patra MK, Manoth M, Singh VK, Gowd GS, Choudhry VS, Vadera SR, Kumar N (2009) Synthesis of stable dispersion of ZnO quantum dots in aqueous medium showing visible emission from bluish green to yellow. J Lumin 129:320–324

26. Ren X, Chen L (2015b) Quantum dots coated with molecularly imprinted polymer as fluorescence probe for detection of cyphenothrin. Biosens Bioelectron 64:182–188

27. Singh K, Mehta SK (2016) Luminescent ZnO quantum dots as an efficient sensor for free chlorine detection in water. Analyst 141:2487–2492

28. Chen LX, Xu SF, Li JH (2011) Recent advances in molecular imprinting technology: current status, challenges and highlighted applications. Chem Soc Rev 40:2922–2942

29. Garcia R, Freitas AMC (2011) Application of molecularly imprinted polymers for the analysis of pesticide residues in food—a highly selective and innovative approach. Am J Anal Chem 2(08):16

30. Bedwell TS, Whitcombe MJ (2016) Analytical applications of MIPs in diagnostic assays: future perspectives. Anal Bioanal Chem 408:1735–1751

31. Martins N, Carreiro EP, Simões M, Cabrita MJ, Burke AJ, Garcia R (2015) An emerging approach for the targeting analysis of dimethoate in olive oil: the role of molecularly imprinted polymers based on photo-iniferter induced "living" radical polymerization. React Funct Polym 86:37–46

32. Vasapollo G, Sole RD, Mergola L, Lazzoi MR, Scardino A, Scorrano S, Mele G (2011) Molecularly imprinted polymers: present and future prospective. Int J Mol Sci 12:5908–5945

33. Tang J, Xiang L (2016) Development of a probe based on quantum dots embedded with molecularly imprinted polymers to detect parathion. Pol J Environ Stud 25:787–793

34. Abbasifar J, Samadi-Maybodi A (2016) Selective determination of atropine using poly dopamine-coated molecularly imprinted Mn-doped ZnS quantum dots. J Fluoresc 26:1645–1652

35. Huy BT, Seo MH, Zhang X, Lee YI (2014) Selective optosensing of clenbuterol and melamine using molecularly imprinted polymer-capped CdTe quantum dots. Biosens Bioelectron 57:310–316

36. Chantada-Vázquez MP, Sánchez-González J, Peña-Vázquez E, Tabernero MJ, Bermejo AM, Bermejo-Barrera P, Moreda-Piñeiro A (2016) Synthesis and characterization of novel molecularly imprinted polymer–coated Mn-doped ZnS quantum dots for specific fluorescent recognition of cocaine. Biosens Bioelectron 75:213–221

37. Amjadi M, Jalili R, Manzoori JL (2015) A sensitive fluorescent nanosensor for chloramphenicol based on molecularly imprinted polymer-capped CdTe quantum dots. Luminescence 31:633–639

38. Ge S, Lu J, Ge L, Yan M, Yu J (2011) Development of a novel deltamethrin sensor based on molecularly imprinted silica nanospheres embedded CdTe quantum dots. Spectrochim Acta A 79:1704–1709

39. Liu J, Chen H, Lin Z, Lin JM (2010) Preparation of surface imprinting polymer capped Mn-doped ZnS quantum dots and their application for chemiluminescence detection of 4-nitrophenol in tap water. Anal Chem 82:7380–7386

40. Wei F, Wu Y, Xu G, Gao Y, Yang J, Liu L, Zhou P, Hu Q (2014) Molecularly imprinted polymer based on CdTe@ SiO$_2$ quantum dots as a fluorescent sensor for the recognition of norepinephrine. Analyst 139:5785–5792

41. Wang HF, HeY JTR, Yan XP (2009) Surface molecular imprinting on Mn-doped ZnS quantum dots for room-temperature phosphorescence optosensing of pentachlorophenol in water. Anal Chem 81:1615–1621

42. Zhang W, He XW, Chen Y, Li WY, Zhang YK (2011) Composite of CdTe quantum dots and molecularly imprinted polymer as a sensing material for cytochrome c. Biosens Bioelectron 26:2553–2558

43. Zhao Y, Ma Y, Li H, Wang L (2011) Composite QDs@MIP nanospheres for specific recognition and direct fluorescent quantification of pesticides in aqueous media. Anal Chem 84:386–395

44. Singh K, Chaudhary GR, Singh S, Mehta SK (2014) Synthesis of highly luminescent water stable ZnO quantum dots as photoluminescent sensor for picric acid. J Lumin 154:148–154