www.elsevier.com/locate/talanta

Fluorescent Sensor for Indirect Measurement of Methyl Parathion Based on Alkaline-induced Hydrolysis Using N-Doped Carbon Dots

Shiyu Lan, Xianfeng Wang, Qingyan Liu, Jing Bao, Mei Yang, Huanbao Fa, Changjun Hou, Danqun Huo

PII: S0039-9140(18)30900-7
DOI: https://doi.org/10.1016/j.talanta.2018.08.083
Reference: TAL19004

To appear in: *Talanta*

Received date: 7 January 2018
Revised date: 9 August 2018
Accepted date: 29 August 2018

Cite this article as: Shiyu Lan, Xianfeng Wang, Qingyan Liu, Jing Bao, Mei Yang, Huanbao Fa, Changjun Hou and Danqun Huo, Fluorescent Sensor for Indirect Measurement of Methyl Parathion Based on Alkaline-induced Hydrolysis Using N-Doped Carbon Dots, *Talanta,* https://doi.org/10.1016/j.talanta.2018.08.083

Fluorescent Sensor for Indirect Measurement of Methyl Parathion Based on Alkaline-induced Hydrolysis Using N-Doped Carbon Dots

Shiyu Lan[a1], Xianfeng Wang[a1], Qingyan Liu[a], Jing Bao[a], Mei Yang[a], Huanbao Fa[c], Changjun Hou[a,b*], Danqun Huo[a*]

[s]Key Laboratory of Biorheology Science and Technology, Ministry of Education, College of Bioengineering, Chongqing University, Chongqing, 400044, China

[b]National Key Laboratory of Fundamental Science of Micro/Nano-Device and System Technology, Chongqing University, Chongqing, 400044, China

[c]College of Chemistry and Chemical Engineering, Chongqing University, Chongqing, 400044, China

houcj@cqu.edu.cn

huodq@cqu.edu.cn

[*]Corresponding authors. Tel.: +862365112673; fax: +862365102507.

[1] Those authors contribute equally to the article

Abstract

High-performance measurement of methyl parathion (MP) is of great importance in both agricultural and environmental surveillance. Herein, we presented a facile fluorescent biosensor to indirectly measure MP using N-doped carbon dots (N-CDS) based on the inner filter effect (IFE). Methyl parathion was employed as the substrate of alkaline-catalytic hydrolysis, and p-nitrophenol (p-NP) was obtained by rapid the hydrolysis reaction under strong alkaline conditions without enzymes. Interestingly, the absorption band of p-NP appeared at 403 nm, which presented an overlapping spectrum with the excitation of N-CDs (410 nm). Due to its strong molar absorptivity, p-NP played the part of a powerful absorber in IFE to influence the excitation of fluorophore (N-CDs). Through the competitive absorption, the fluorescence intensity of N-CDs decreased extremely. With optimum conditions selected, the fluorescent sensor presented a concentration-dependent fluorescent response (ΔF) to MP ranging from 0.075 to 15 ppm (R^2 =0.9956). The limit of detection was calculated to be 1.87 ppb (S/N=3) with good selectivity. Successful measurement of MP in spiked river water and apple samples demonstrated that as-proposed optical sensor provided an alternative strategy for real applications in environmental and food safety control.

Keywords: fluorescent biosensor; methyl parathion; carbon dots; inner filter effect

1 Introduction

Methyl parathion (MP) has been extensively used in agriculture to reduce crops production decline caused by insect attack.[1] However, the cumulative use of pesticides in agriculture has generated numerous concerns about food safety. It is well known that the persistence, bioaccumulation and toxicity of MP inhibit the activity of cholinesterase enzyme, resulting in the disturbance to regulation of acetylcholine.[2, 3] To make matters worse, continuous damage to the nervous system can be caused by MP, resulting in organ dysfunction and eventually death. It has been demonstrated that intakes of MP in food and drinking water are also possible incentives of some hematological diseases including decreased hemoglobin count, RBC contraction and impairment of heme biosynthesis.[4] Given the toxicity to human health, the amount of MP in related food stuff has been restricted by many regulations set by official organizations around the world.[5] Thus, development of convenient and reliable sensors for MP analysis is useful in environmental and food safety monitoring.

Accordingly, different quantitative strategies such as gas chromatography (GC)[6, 7], high-performance liquid chromatography (HPLC)[8], gas chromatography-mass spectrometry (GC/MS)[9, 10], ELISA[11, 12] and surface-enhanced Raman spectroscopy[13, 14] have been developed to realize sensitive and selective MP detection. Although the aforementioned techniques demonstrated excellent accuracy and sensitivity, their application are still challenged by some unavoidable disadvantages such as high cost, complex pre-treatment, requirement of skillful operation, which restrict their application in real-time field.

Currently, a number of electrochemical and optical sensors for MP have been developed and most of them involve enzyme catalytic reaction or enzyme inhibition reaction.[15-18] Organic phosphorus hydrolase (OPH)[15, 19, 20] and acetyl cholinesterase (AChE)[18, 21, 22] are the two major common enzymes to construct biosensors for MP detection. However, the activity of enzyme might be inhibited by the different detection conditions and solvent species.[23] Besides, relatively expensive enzyme and difficulties in immobilization of enzymes allow another hindrance to their wide application. In view of above-mentioned setbacks, enzyme-free fluorescent sensor might provide a useful alternative for MP measurement.[24-26] Yet most enzyme-free sensors for organophosphorous pesticide

measurement mainly rely on the direct response via the secondary bond including hydrogen bond and Van der Waals' force, which present the eurytopic effects towards most organophosphorous pesticide.[27, 28] Therefore, false-positive results were frequently observed in presence of interfering compounds in complex samples and not all performances of sensors have been actualized in terms of sensitivity, interference immunity and stability.

Recently, inner filter effect (IFE) based fluorescent sensor is proven to be an alternative method in trace detection due to its easy fabrication and high sensitivity.[29-32] Generally, by matching the absorption of analyte (absorbers) and the excitation/emission of fluorophore, the fluorescence could be quenched through the competitive absorption. Therefore, the measurement procedure in the IFE was realized through suitable absorber-fluorophore paired with the optical spectrum, which avoids the modification of quantum dot or establishing of any covalent linking between the absorber and a fluorophore.[33] Unlike other fluorescent detection mechanisms such as photoinduced electron transfer (PET) or fluorescence resonance energy transfer (FRET), The IFE does not involve any electron or energy transfer process, which makes our assay more facile.[34] Additionally, the analytical absorption signal is converted to the fluorescence signal, which provides flexibility and simplicity on probe construction.

Accordingly, methyl parathion can be hydrolyzed under alkaline conditions without any additions of other reagents or enzyme.[35, 36] This process involves the formation of p-nitrophenol with a strong absorbance at 403 nm, which presents a promising and cost-effective technique for enzyme-free detection of MP. In the meantime, as a new fluorescent nanomaterial, carbon quantum dots (CDs) exhibit satisfactory advantages like unique optical properties, excellent biocompatibility and low cost of fabrication, which have been rapidly exhumed for chemical analysis.[33, 34] To date, it has not yet been reported to measure MP using CDs via IFE. Herein, N-doped carbon dots were applied to develop a new fluorescent sensor to realize simple, enzyme-free, low-cost and effective detection of MP. As shown in schematic 1, N-CDs were successfully prepared by one-pot hydro-thermal process without any modifications. The obtained N-CDs emitted green fluorescence at 510 nm after excitation at 410 nm and acted as the fluorescent signal generator. Upon addition of MP under

strong alkaline condition, the formation of p-nitrophenol (p-NP) was promoted by rapid hydrolysis of MP. Simultaneously, the color of the mixture changed from colorless to yellow. Subsequently, fluorescence inner filter effect occurred between p-NP and N-CDs, leading to significant fluorescence quenching of N-CDs. In such a design, a reliable measurement of MP was realized by non-enzymatic process.

2 Materials and Methods

2.1 Reagents and Instruments

Ethylenediamine (EDA) and catechol employed as the main reagents for the preparation of N-CDs were purchased from Aladdin (Shanghai, China). Other conventional reagents including sodium hydroxide, hydrochloric acid (37.5%) and phosphate buffer (PBS) were obtained from Changzheng Chemical Reagent Co., Ltd, China. Methyl parathion and other pesticides were obtained from Chongqing Pesticide Chemical (Group) Co., Ltd. Deionized water with a resistivity of 18.25 MΩ*cm was used to prepare all aqueous solutions. All the pH measurements were performed on a PHS-25C pH-meter (Shanghai).

2.2 Syntheses of N-CDs

According to former study, one-pot hydrothermal process was applied to prepare water-soluble N-CDs.[29] Briefly, the catechol solution with a final concentration of 10.8 mg/ml was prepared using absolute ethanol. After mixing the as-prepared catechol solution (25 ml) with ethylenediamine (300 μl), the mixture was incubated at room temperature for 15 min, and then transferred into to a 50 ml Teflon autoclave and heated to 200 ℃ for 10 h. After cooled to room temperature, the large particles consisted of reaction solutions were wiped out via centrifugation at 10000 rpm for 15 min. To remove unreacted small molecules, a 500 Da dialysis membrane was employed to purify as-obtained supernatant for 36 h. The final N-CDs solutions were diluted 100 times and stored in dark for further use.

2.3 Characterization

Fluorescence spectrophotometer (Perkin Elmer LS55) and UV-Vis spectrophotometer (TU-1901) were applied to collect the fluorescence and UV-vis absorption spectra. The

surface morphology and size dimension of N-CDs were recorded by TECNAI G2 F20 transmission electron microscope (FEI, Holland). Atomic force microscope (AFM) image was performed on MFP-3D (Asylum Research, America). The chemical groups on the surface of N-CDs were identified by a Nicolet 6700 FTIR spectrometer (Thermoelectric Scientific Instruments). The elemental composition of N-CDs was studied on an EX-CALIBUR X-ray photoelectron spectroscopy (Jordan Valley). X-ray diffraction (XRD) analysis was performed on D/MAX-1200 X-ray diffractometer (RIGAKU Corporation) to solve the crystal structure of N-CDs.

2.4 The IFE-Based fluorescent detection of methyl parathion

Measurement of MP using the IFE-based fluorescent sensor was executed through the following procedures. 30 μl N-CDs solutions with a certain concentration of $7.28*10^{-3}$ mg/ml were first mixed with 2.92 ml of PBS buffer (0.2 M, pH 12.0) in a 5 ml tube and shaken thoroughly to form a well-distributed precursor. Subsequently, different concentrations of MP (50 μl) solutions were successfully added into the mixture and incubated at 70 ℃ for 25 min to ensure full response. The fluorescence intensity of the mixture at 510 nm was collected for quantitative analysis of MP.

2.5 Practicability and real applications

To explore the performance of the as-present sensor in practicability, interfering compounds were introduced to investigate the stability and selectivity. Typically, cider obtained from squeeze of fresh apple samples (20 g) was diluted 5 times with PBS buffer (0.2 M, pH 12.0). Different concentrations of MP (1.0, 5.0, and 10.0 ppm) were spiked into the cider samples and measured directly using the sensor under optimized conditions. Similarly, the water samples, collected from Chialing River, were filtered and spiked with MP standards of 1.0, 5.0, and 10.0 ppm, respectively. Thereafter, those water samples were detected in a similar procedure.

3 Results and discussion

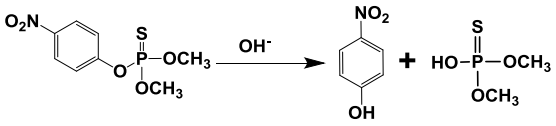
3.1 Materials characterization

In the present study, N-doped CDs synthesized with catechol and ethanediamine were employed as fluorescent signal output. The surface morphology and size of N-CDs were characterized by transmission electron microscope (TEM). As can be seen from Fig.1A, all N-CDs particles showed a uniform dispersion with a relatively narrow size distribution around 3~5 nm. The AFM images (Fig. S1) also exhibit a similar result to the TEM measurement and the heights of N-CDs were about 3.5 nm, indicating that the as-prepared N-CDs were nearly spherical in shape. Diffraction peak appeared at $2\theta = 25.3°$ in XRD pattern (Fig. 1B) matches well with the characteristic peak of (0 0 2) facet of graphene, indicating that the sp^2-hybridized carbon consisted in N-CDs. The surface groups of the as-prepared N-CDs were identified by FT-IR. As shown in Fig. 2, a clear and strong peak observed at 3409.28 cm^{-1} is indicative of υ(O-H, N-H). It demonstrats that abundant hydroxyls and amidogens were bonded on the surface of N-CDs, making them water-soluble. Two strong absorption peaks at 2931.41 cm^{-1} and 2852.49 cm^{-1} are associated with the stretching vibrations of CH_3– bond and –CH_2– bond. Particularly, characteristic stretching vibration band of C=O bond and C=C bond appear at 1636.54 cm^{-1}. The peaks emerged at 1452.67 cm^{-1} and 1349.33 cm^{-1} are assigned to the stretching vibrations of C–N bond and C-N= bond, respectively. The absorption peak at 1230.73 cm^{-1} belongs to the stretching vibrations of C–O groups. XPS was further performed to identify the surface composition and elements analysis. The characteristic peaks of C 1s, N 1s and O1s could be observed at 285.1 eV, 399.6 eV and 532.7 eV in full scan XPS spectrum of N-CDs (Fig. 3A), clearly supporting the successful nitrogen doping into carbon quantum dots. As shown in high resolution XPS of C 1s region (Fig.3B) , four different peaks at 284.8 eV, 285.9 eV, 287.5 eV and 288.8 eV suggest the different existences of C=C (graphitic structure, sp^2 hybridization), C-N (sp^3 hybridization), C-O (sp^3 hybridization) and C=O (sp^2 hybridization). Meanwhile, for N 1s spectrum, three different peaks observed in Fig.3 C could be attributed to N-H (398.8 eV), C=N (399.8 eV) and C-N (401.1 eV) bonds respectively, which further demonstrates the successful nitrogen doping in carbon quantum in accordance with the result of FT-IR. As

shown in Fig.3D, different chemical states of oxygen existing in N-CDs are assigned to O-H (530.9 eV), C-O (532.2 eV), and C=O (533.3 eV), respectively. Those observations indicate a good N-CDs quality in view of distribution, topography and crystal structures. The as-prepared N-CDs with green emission at 510 nm exhibits a strong fluorescence after excitation at 410 nm (Fig. S2). The fluorescence signal of N-CDs remained constant at the pH below 10. Meanwhile, a slight decreasing fluorescence response intensity was observed as increasing pH ranged from 11 to 14 (Fig. S3 B). Quinine sulfate was employed as a reference to calculate the quantum yield (QY) of the N-CDs (Supporting Information). The nitrogen-doped quantum dots is endued a higher QY of 10.8% than that of recently reported CDs.[37-40]

3.2. Principle of detecting assay based on IFE

Fluorescence inner filter effect, as a promising sensing technique, is frequently applied for various chemical detection. It occurs from a spectra overlap between the excitation or emission spectra of fluorescent materials and the absorption spectra of absorber.[34, 41] Thus, an extreme fluorescence quenching caused by the strong absorption of absorber provides an alternative platform for facile and sensitive detection. In the present study, p-nirophenol was employed as an absorber at 403 nm for indirect measurement of MP based on inner filter effect. This strategy was realized by alkaline catalytic hydrolysis of MP resulting in the formation of p-nirophenol with solutions color change to yellow (Fig. S4) according to the following chemical equation.[36, 42] The present system provides a relatively high hydrolysis efficiency (87.2%, Supporting Information) of MP under the optimal conditions.



In this study, the sensing mechanism of the IFE-based fluorescent sensors for MP analysis was illustrated in Fig.4. N-CDs exhibited a strong green fluorescence at 510 nm under the excitation of 410 nm. Concurrently, the maximum absorption peak of p-nirophenol centered at 403 nm, which well overlapped with the excitation of the as-prepared N-CDs (Shown in Fig.4A). As depicted in Fig.4B, upon addition of MP into reaction solutions in acidic

condition, a slight fluorescence quenching was observed, suggesting a negligible detection influence on fluorescence of N-CDs under strong acid environment. While, for an alkaline system with a pH of 12, the addition of MP led to a dramatic decrease of fluorescence intensity concomitant with a color change to yellow. This phenomenon could be explicated by that P-NP was released in the mixture from rapid hydrolysis of MP under strong alkaline environment and the inner filter effect occurred between p-NP and N-CDs. All these results mentioned above demonstrated that the IFE-based sensor could be used to quantitative analysis of MP.

3.3 Optimization of the experimental conditions

Several pivotal factors including pH, reaction time and temperature were investigated to improve the performance of the developed sensor for MP detection. As the most critical factor to improve the hydrolysis reaction of MP, the influence of pH on the detection system was evaluated (Fig.5A). When pH was lower than 7, the fluorescent response (ΔF) could not be observed resulting from the good stability of N-CDs and MP under acid conditions. Meanwhile, a gradually increasing fluorescence response was obtained with the increase of pH from 7 to 12. The maximum response occurred at the pH of 12, but further increase of pH led to no clear changes in ΔF. Therefore, pH of 12 was chosen in the following-up study.

Commonly, the kinetics or equilibrium of a reaction was determined by temperature and reaction time. Fig. 5B presents a positive correlation between the fluorescent response and the temperature range from 20 to 70 ˚C. It could be seen that the increase in collision frequency caused by the kinetic energy escalation expedited the hydrolysis rate of MP in higher temperature. Above 70˚C, no clear changes in ΔF were observed and this temperature was selected as the optimal detection condition. A typical time-dependent response was plotted from 5 min to 25 min in Fig. 5C. The largest change in ΔF was obtained at 25 min, indicating an equilibrium of hydrolysis reaction at this time. Therefore, 25 min of reaction time was selected as the preferred time for later experiments (Fig. S5).

3.4 Analytical performance for detection of methyl parathion

The sensitivity of present strategy was studied by recording the fluorescent response of the

IFE-based sensor to different concentrations of MP under optimal detection conditions. As shown in Fig. 6, the fluorescent intensity decreased gradually with increasing amount of MP. Simultaneously, the original green color of detection system diminished under the UV lights with the concentration of MP over 1.0 ppm, which could be easily distinguished by naked eyes. The generated ΔF presented a well-defined linear relationship (ΔF = 44.76*C + 19.50, R^2=0.9956) with the concentration of MP ranging from 0.075 to 15.0 ppm and the detection limit was calculated to be 1.87 ppb (S/N=3). Since p-NP effectively quench the fluorescence of N-CDs without heating procedure. For MP measurement, a heating procedure is needed to trigger the hydrolysis reaction for quenching the fluorescence. Therefore, for sample with co-existing p-NP, we just need to monitor the fluorescence intensity before and after heating to calculate the concentration of MP (Fig. S7B).

The IFE-based sensor exhibited a relatively higher sensitivity compared with other reported fluorescent methods listed in Table 1. Admitted that the methods based on immunological reaction and enzyme inhibition had lower LODs than that of this work, the present method focused on providing an alternative way for MP measurement. The detection procedure was realized by alkaline catalytic hydrolysis without any addition of other reagents or enzyme. Therefore, the proposed method presented the advantage of low cost and it had a better stability.

Additionally, evaluation on the stability of as-proposed sensor was tested by long-term monitoring the fluorescent intensity at specified conditions. As shown in Fig. S8, after stored at 4℃ for more than 1 month, the fluorescent signal of N-CDs remained 91% of its initial intensity, suggesting the relative good stability of the proposed method. Besides, we investigated the reproducibility by testing different batches of sensors upon reaction with 15.0 ppm MP under optimal detection conditions. Insignificant fluctuation in different batches with the maximum relative standard deviations (RSD) of 3.86% indicated that the measurement was repeatable enough for detecting of MP.

3.5 Selectivity and real application

To examine the performance of the IFE based sensor in selectivity, a number of structural similar pesticides including carbendazim (CB), deltamethrin (DT), triazolone (TA),

chlorpyrifos (CR), isoprocarb (IP), celoprofen (CP), omethoate (OM), malathion (MT), phorate (PR), phlogide (PG), aldicarb (AD), trichlorfon (TC), methamidophos (MT), glyphosate (GP) were selected as the interference chemicals and tested under the optimum conditions. As summarized in Fig. 7, a full fluorescence quenching of N-CDs only induced by MP with a low concentration of 15.0 ppm. The resultant responses in ΔF caused by other tested pesticides were observed in a negligible extent even with a concentration of 150.0 ppm. Except for methyl parathion, none of the interfering chemicals could be hydrolyzed to initiate the inner filter effect, which demonstrated the as-present sensor excellent selectivity.

To verify the practical application, the IFE-based sensor was tested using apple sample and river water spiked with MP in a similar procedure. The testing results shown in Table 2 exhibited an acceptable validation accuracy ranging from 97.6 % to 104.3 % with a maximum RSD of 4.03 %, suggesting the feasibility for real sample analysis.

Conclusion

In summary, an IFE-based fluorescent sensor was successfully developed for efficient measurement of methyl parathion. It was achieved by the inner filter effect between N-CDs and p-nitrophenol obtained from alkaline hydrolysis of methyl parathion. This technique not only provided a facile detection choice for MP free of enzymes, but also circumvented the tedious modification of carbon quantum dots. Excellent performance also demonstrated the sensitivity and stability of the IFE-based sensor. In addition, the practical application of the presented sensor on real samples exhibited an acceptable recovery with a RSD around 4.03 %. All the results obtained above made the present sensor an effective approach for on-line detection of methyl parathion.

Acknowledgement

The authors would like to acknowledge the financial support obtained from Chongqing science and technology commission (CSTC2015shmszxl20097), Key Technologies R&D Program of China (No. 2014BAD07B02), Chongqing Graduate Student Research Innovation

Project (CYB17037), the workstation in Sichuan Province (GY2015-01), and sharing fund of Chongqing university's large equipment.

References

[1] J.-C. Wei, J. Hu, J.-L. Cao, J.-B. Wan, C.-W. He, Y.-J. Hu, H. Hu, P. Li, Journal of Agricultural and Food Chemistry, 64 (2016) 932-940.

[2] J. Tian, Q. Dong, C. Yu, R. Zhao, J. Wang, L. Chen, Journal of Agricultural and Food Chemistry, 64 (2016) 4280-4287.

[3] F.M. Buratti, M.T. Volpe, A. Meneguz, L. Vittozzi, E. Testai, Toxicology and Applied Pharmacology, 186 (2003) 143-154.

[4] S.K. Rastogi, V.K. Singh, C. Kesavachandran, Jyoti, M.K.J. Siddiqui, N. Mathur, R.S. Bharti, Indian journal of occupational and environmental medicine, 12 (2008) 29-32.

[5] N. Tiwari, A. Asthana, K. Upadhyay, Spectrochimica Acta Part a-Molecular and Biomolecular Spectroscopy, 101 (2013) 54-58.

[6] K.H. Holmgren, T. Gustafsson, A. Ostin, Journal of Chromatography B-Analytical Technologies in the Biomedical and Life Sciences, 1033 (2016) 97-105.

[7] Z. Witkiewicz, E. Sliwka, S. Neffe, Trac-Trends in Analytical Chemistry, 85 (2016) 21-33.

[8] S.B. Mammana, P. Berton, A.B. Camargo, G.E. Lascalea, J.C. Altamirano, Electrophoresis, 38 (2017) 1334-1343.

[9] K. Seebunrueng, Y. Santaladchaiyakit, S. Srijaranai, Talanta, 132 (2015) 769-774.

[10] C.K. Zacharis, C. Christophoridis, K. Fytianos, Journal of Separation Science, 35 (2012) 2422-2429.

[11] H. Ouyang, L. Wang, S. Yang, W. Wang, L. Wang, F. Liu, Z. Fu, Analytical Chemistry, 87 (2015) 2952-2958.

[12] X. Yan, H. Li, Y. Yan, X. Su, Analytical Methods, 6 (2014) 3543-3554.

[13] J. Chen, Y. Huang, P. Kannan, L. Zhang, Z. Lin, J. Zhang, T. Chen, L. Guo, Anal Chem, 88 (2016) 2149-2155.

[14] W. Fang, X. Zhang, Y. Chen, L. Wan, W. Huang, A. Shen, J. Hu, Analytical Chemistry, 87 (2015) 9217-9224.

[15] X. Yan, H. Li, X. Wang, X. Su, Talanta, 131 (2015) 88-94.

[16] B. He, Y.-L. Mao, Y. Zhang, W. Yin, C.-J. Hou, D.-Q. Huo, H.-B. Fa, Nano, 12 (2017).

[17] J. Jiang, H. Zhang, C. Wang, Y. Xu, International Journal of Electrochemical Science, 11 (2016) 5481-5489.

[18] L. Peng, S. Dong, W. Wei, X. Yuan, T. Huang, Biosens Bioelectron, 92 (2017) 563-569.

[19] A. Mishra, J. Kumar, J.S. Melo, Biosensors & Bioelectronics, 87 (2017) 332-338.

[20] X. Yan, H. Li, Y. Yan, X. Su, Food Chemistry, 173 (2015) 179-184.

[21] J. Gong, Z. Guan, D. Song, Biosensors & Bioelectronics, 39 (2013) 320-323.

[22] Y. Shen, F. Yan, X. Huang, X. Zhang, Y. Zhang, C. Zhang, J. Jin, H. Li, S. Yao, Rsc

Advances, 6 (2016) 88096-88103.

[23] J. Bao, C. Hou, Y. Zhang, Q. Li, D. Huo, M. Yang, X. Luo, Journal of the Electrochemical Society, 162 (2014) B47-B51.

[24] X. Yue, P. Han, W. Zhu, J. Wang, L. Zhang, Rsc Advances, 6 (2016) 58771-58779.

[25] F.-m. Liu, Y.-q. Du, Y.-m. Cheng, W. Yin, C.-j. Hou, D.-q. Huo, C. Chen, H.-b. Fa, Journal of Solid State Electrochemistry, 20 (2016) 599-607.

[26] D. Zhang, D. Yu, W. Zhao, Q. Yang, H. Kajiura, Y. Li, T. Zhou, G. Shi, Analyst, 137 (2012) 2629-2636.

[27] Y. Tan, I. Ahmad, T.-X. Wei, Chinese Chemical Letters, 26 (2015) 797-800.

[28] Y. Zhao, W. Zhang, Y. Lin, D. Du, Nanoscale, 5 (2013) 1121-1126.

[29] W. Kong, D. Wu, L. Xia, X. Chen, G. Li, N. Qiu, G. Chen, Z. Sun, J. You, Y. Wu, Anal Chim Acta, 973 (2017) 91-99.

[30] H.-Q. Chen, Y. Wu, F. Yuan, J. Xu, Y.-Y. Zhang, L. Wang, Journal of Luminescence, 141 (2013) 33-37.

[31] J. Guo, H. Li, M. Xue, M. Zhang, X. Cao, Y. Luo, F. Shen, C. Sun, Food Analytical Methods, 7 (2014) 1247-1255.

[32] J. Guo, X. Liu, H. Gao, J. Bie, Y. Zhang, B. Liu, C. Sun, Rsc Advances, 4 (2014) 27228-27235.

[33] S. Lu, G. Li, Z. Lv, N. Qiu, W. Kong, P. Gong, G. Chen, L. Xia, X. Guo, J. You, Y. Wu, Biosensors and Bioelectronics, 85 (2016) 358-362.

[34] G. Li, H. Fu, X. Chen, P. Gong, G. Chen, L. Xia, H. Wang, J. You, Y. Wu, Analytical Chemistry, 88 (2016) 2720-2726.

[35] M.S. Mulla, L.S. Mian, J.A. Kawecki, Residue reviews, 81 (1981) 1-172.

[36] J. Zhang, J. Wang, L. Yang, B. Liu, G. Guan, C. Jiang, Z. Zhang, Chem. Commun., 50 (2014) 15870-15873.

[37] N. Xiao, S.G. Liu, S. Mo, N. Li, Y.J. Ju, Y. Ling, N.B. Li, H.Q. Luo, Talanta, 184 (2018) 184-192.

[38] V.A. Ansi, N.K. Renuka, Sensors and Actuators B-Chemical, 264 (2018) 67-75.

[39] Y. Dong, J. Shao, C. Chen, H. Li, R. Wang, Y. Chi, X. Lin, G. Chen, Carbon, 50 (2012) 4738-4743.

[40] J. Zhang, J. Yan, Y. Wang, Y. Zhang, Journal of Nanoscience and Nanotechnology, 18 (2018) 4457-4463.

[41] M. Zheng, Z. Xie, D. Qu, D. Li, P. Du, X. Jing, Z. Sun, Acs Applied Materials & Interfaces, 5 (2013) 13242-13247.

[42] N. Fahimi-Kashani, A. Rashti, M.R. Hormozi-Nezhad, V. Mahdavi, Analytical Methods, 9 (2017) 716-723.

[43] Q. Sun, Q. Yao, Z. Sun, T. Zhou, D. Nie, G. Shi, L. Jin, Chinese Journal of Chemistry, 29 (2011) 2134-2140.

[44] A.Y. Kolosova, J.H. Park, S.A. Eremin, S.J. Kang, D.H. Chung, Journal of Agricultural and Food Chemistry, 51 (2003) 1107-1114.

[45] R.S. Chouhan, A.C. Vinayaka, M.S. Thakur, Analytical and Bioanalytical Chemistry, 397 (2010) 1467-1475.

[46] W. Song, H.-J. Zhang, Y.-H. Liu, C.-L. Ren, H.-L. Chen, Chinese Chemical Letters, 28 (2017) 1675-1680.

[47] J. Hou, J. Dong, H. Zhu, X. Teng, S. Ai, M. Mang, Biosensors & Bioelectronics, 68 (2015) 20-26.

Fig. 1 TEM image (A) and XRD (B) of as-prepared N-CDs.

Fig. 2 FT-IR spectrum of N-CDs.

Fig.3 Wide-scan XPS spectrum of N-CDs (A). XPS survey of C 1s (B), N 1s (C) and O 1s (D).

Fig.4 (A) Fluorescence property of N-CDs and Uv-Vis absorption spectrum of p-nitrophenol; Inset: Images of N-CDs solutions under ultraviolet (right) and visible (left) light. (B) Fluorescence spectra of N-CDs and N-CDs incubated with MP (pH 12 and pH<7).

Fig.5 Fluorescent responses of IFE-based sensor to MP versus pH (A), temperature (B) and reaction time (C).

Fig. 6 (A) Fluorescence intensity of N-CDs with increasing concentrations of MP from 0 ppm to 15.0 ppm. (B) Corresponding linear relationship between fluorescent responses to different concentrations of MP.

Fig. 7 (A) Fluorescence emission spectra of N-CDs in the presence of MP (15.0 ppm) and other interfering pesticides (150.00 ppm); (B) Relative response of different interfering pesticides to the proposed detection method.

Scheme 1. Illustration of IFE-based fluorescent sensor for methyl parathion using N-doped carbon quantum dots.

Fig. 1

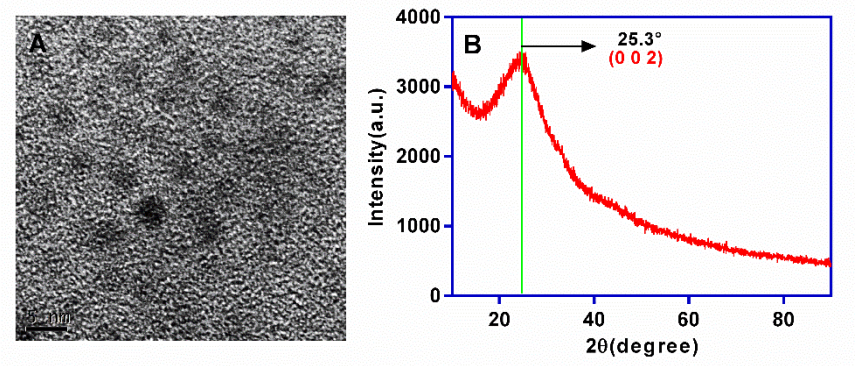


Fig. 2

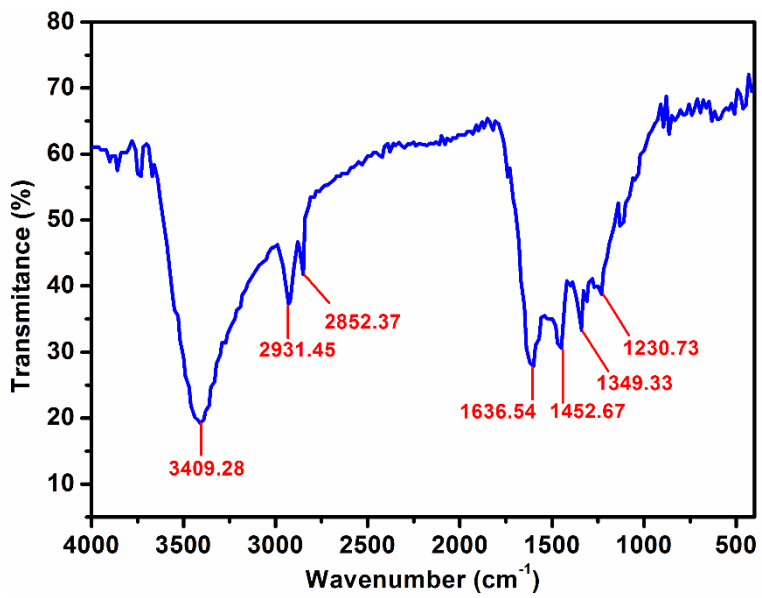


Fig.3

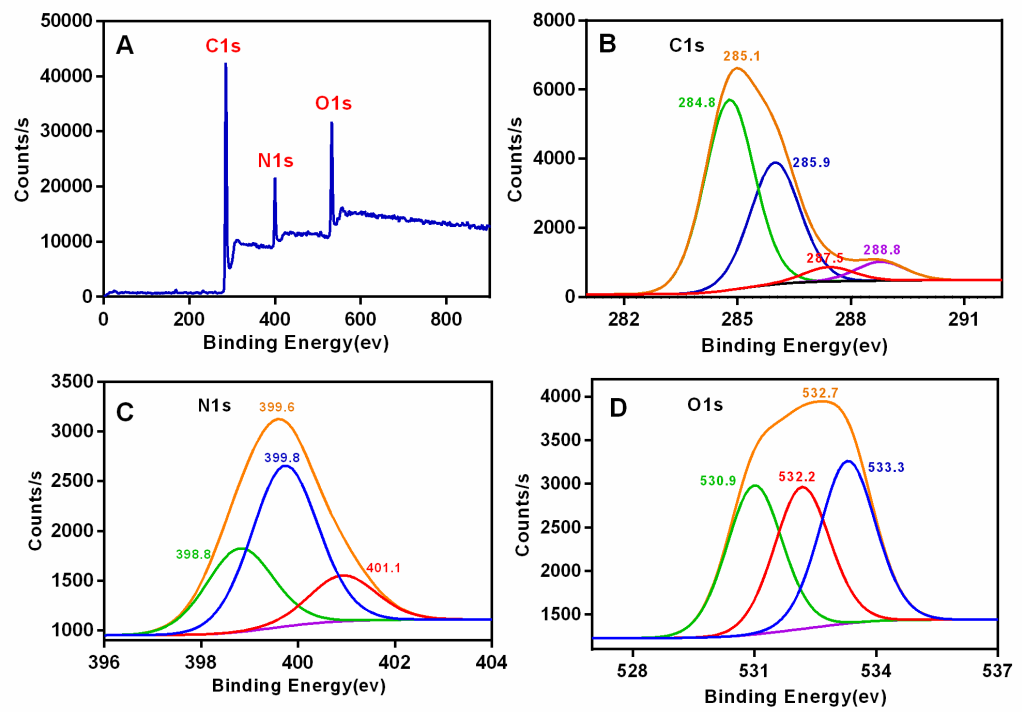


Fig.4

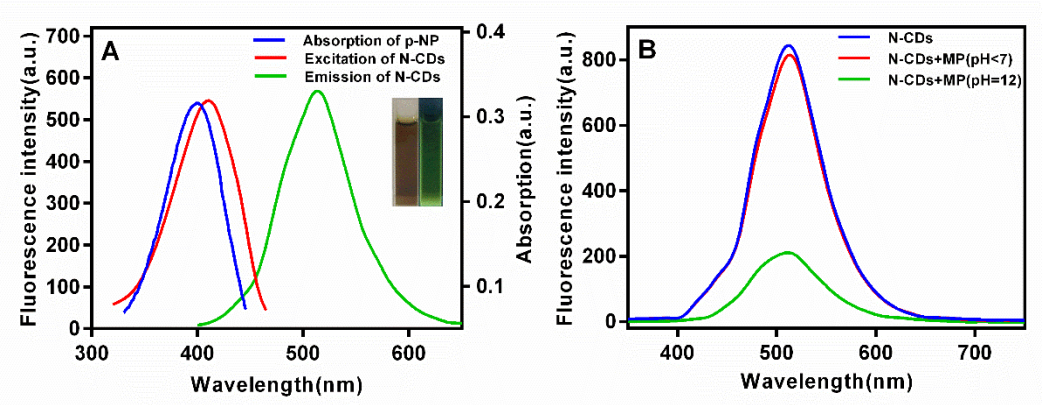


Fig.5

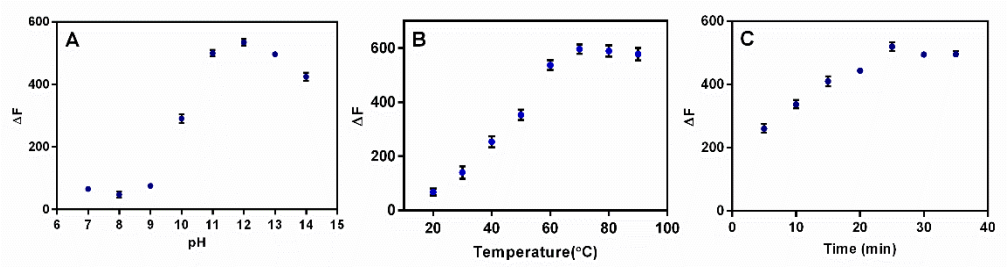


Fig. 6

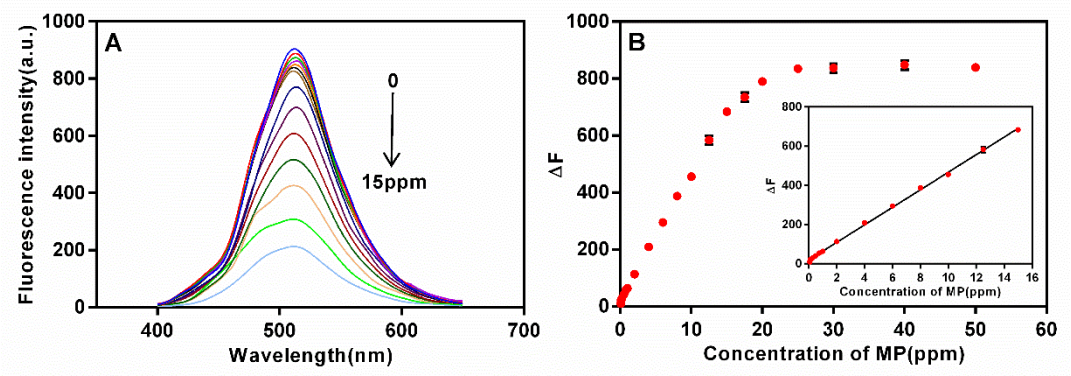
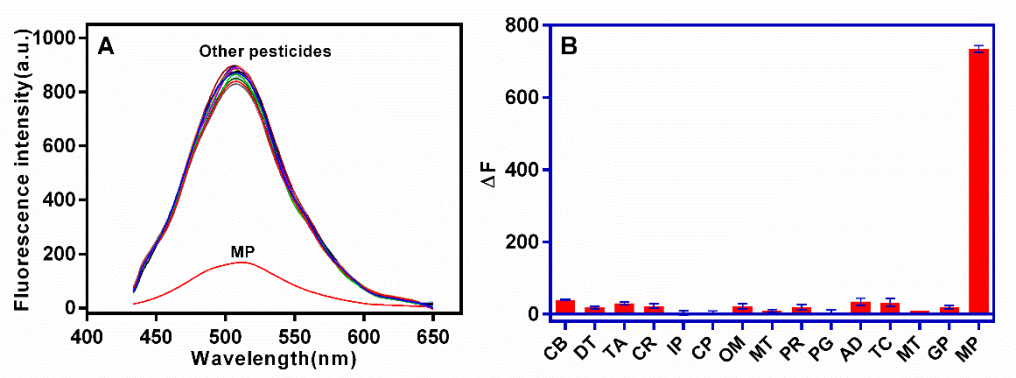
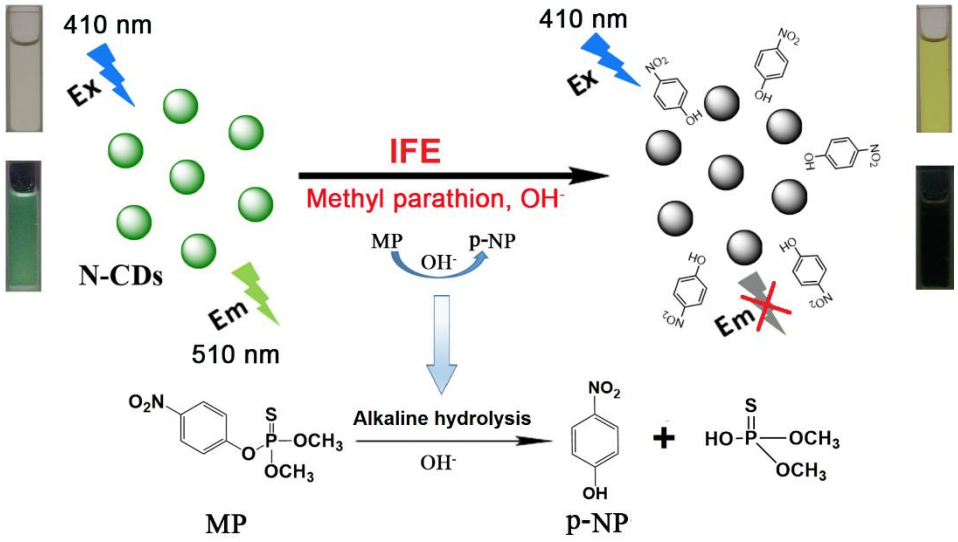


Fig. 7



Scheme 1



Graphical Abstract

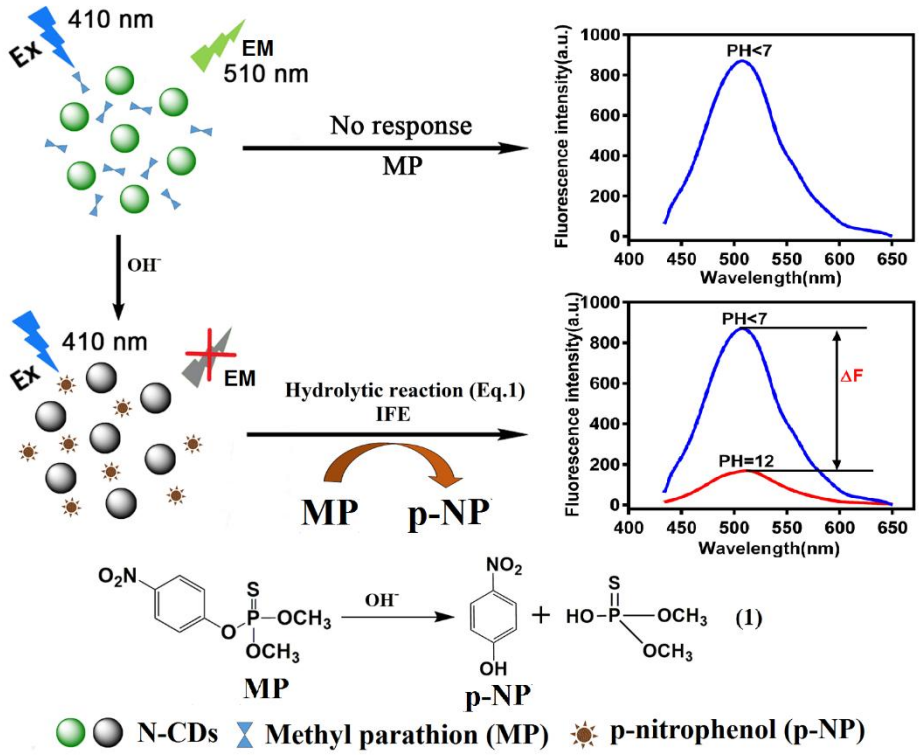


Table 1 A comparison of present IFE-based fluorescent sensor with other fluorescent sensors for measurement of MP

Method	Label/probe	LOD	Ref.
Molecular Imprinting	CdSe@SiO_2@MIP	4 ppb	[43]
Fluorescence Polarization Immunoassay	Monoclonal antibodies	15 ppb	[44]
Immunological reaction	BSA–CdTe QDs	0.1 ppb	[45]
Enzyme catalyzed hydrolysis	CdTe/OP hydrolase	18.00 ppb	[15]
Enzyme catalyzed hydrolysis	CuInS2/OP hydrolase	15.79 ppb	[20]
Enzyme catalyzed hydrolysis	N-CDs/MP hydrolase	88.96 ppb	[46]
Enzyme inhibition	Tyr-CDs	0.013 ppb	[47]
Alkaline catalytic hydrolysis	N-CDs (IFE)	1.87 ppb	This work

Table 2 Detection of MP concentrations in real applications

	Spiked (ppm)	Founded (ppm)	RSD (%)	Recovery (%)
Apple	0	Not found	/	/
	1	0.987	2.12	98.7
	5	5.081	4.03	101.6
	10	10.271	3.52	102.7
River water	0	Not found	/	/
	1	1.043	2.73	104.3
	5	5.034	3.49	100.7
	10	9.758	3.08	97.6

Highlights:

- N-doped carbon dots were innovatively introduced as fluorescent signal readout for measurement of methyl parathion.
- This strategy realized the quantitative analysis for MP via enzyme-free process rather than enzymatic hydrolysis of MP.
- This work could serve as a good model for the design of new fluorescence biosensors based on inner filter effect.
- MP was successfully measured in river water and apple sample with high selectivity and satisfactory detection limit.