β -Cyclodextrin functionalized molybdenum disulfide quantum dots as nanoprobe for sensitive fluorescent detection of parathion-methyl

Yinhui Yi^{a,b,d,*}, Wei Zeng^a, Gangbing Zhu^{a,c,**}

^a School of the Environment and Safety Engineering, Jiangsu University, Zhenjiang, 212013, PR China

^b State Key Laboratory of Chemo/Biosensing and Chemometrics, Hunan University, Changsha, 410082, PR China

^c Key Laboratory of Coastal Environmental Processes and Ecological Remediation, Yantai Institute of Coastal Zone Research, Chinese Academy of Sciences, PR China

^d Key Laboratory for Analytical Science of Food Safety and Biology, Ministry of Education, PR China

ARTICLE INFO

Keywords:

Parathion-methyl
Quantum dots
Cyclodextrin
Fluorescent sensing
Organophosphorus pesticides
Probe

ABSTRACT

Through modifying molybdenum disulfide quantum dots (MoS₂ QDs) with 3-aminophenyl boronic acid and functionalizing further with hydropropyl- β -cyclodextrin (β -CD), a novel nanoprobe based on β -CD functionalized MoS₂ QDs (β -CD-MoS₂ QDs) was developed for the fluorescent detection of parathion-methyl (MP). β -CD-MoS₂ QDs was characterized with various technologies including transmission electron microscopy, X-ray photoelectron spectroscopy, fluorescence and UV-Vis absorption spectra. As for MP detection, MP was hydrolyzed to p-nitrophenol (p-NP) under the alkaline conditions, and p-NP can enter into the β -CD cavity due to the host-guest recognition capability of β -CD, which then results the fluorescence quenching of nanoprobe. Based on this principle, an enzyme-free fluorescence sensing platform were constructed for MP. Under the optimal conditions, β -CD-MoS₂ QDs nanoprobe exhibits wide detection scope (0.01–18.0 ppm) and low detection limits (3.3 ppb) for MP detection. In addition, the nanoprobe has excellent selectivity for MP, and it can be applied to detect MP in real samples.

1. Introduction

Organophosphorus pesticides (OPs) are a cluster of organic pesticides which have been extensively utilized in agriculture due to the excellent ability to control pests and plant diseases [1–3]. The residues substances of OPs have been found to cause organ dysfunction, cancer disease and fetal anomaly even at very low concentration. Parathion-methyl (MP) is a typical OPs which incline to accumulate in food and water because of its bioaccumulation and low solubility [4]. According to the guidelines for drinking water quality ruled by World Health Organization, the concentration of MP in agricultural water ranges up to 1.7 nM increasing during summer months. Environmental Protection Agency (EPA) also regulates that the safe level of MP in drinking water is as follows: 0.11 μ M for longer term exposure of children, 1.1 μ M for 1 d or 10 d of exposure for children; and 7.6 nM for the adults lifetime exposure [5,6]. Therefore, developing sensitive detection method for MP is of great significance to ensure environment and food safety.

During the past years, several analytical techniques have been

designed to detect MP pesticide, such as gas chromatography, gas chromatography-mass spectrometry, chemiluminescence, surface-enhanced Raman spectroscopy [7], electrochemical analysis [8] and enzyme-linked immunosorbent assay [9]. Although the aforementioned methods are very important for detecting MP, their real applications are still restricted by some unavoidable shortcomings such as complex pre-treatment processes, high-cost and requiring skillful operation [10, 11]. Recently, some interesting works have been reported for detecting MP based on the fluorescence nanoprobe due to its unique advantages on cost, convenience and sensitivity. For instance, Xu et al. [12] established a fluorescence sensor based on the catalytic reaction of organophosphorus hydrolase for MP detection. Huang et al. [13] construct a biosensor based on acetylcholinesterase enzymatic reaction for OPs assay. However, most of the developed approaches for MP detection based on fluorescence nanoprobe generally depend on the catalytic or inhibitory effect of the enzyme, and the enzyme is relatively expensive and easily inactivated with short service life. For resolving this problem in MP detection, there are a few sensor arrays based on enzyme-free fluorescent nanoprobe have been proposed most recently [14], but

* Corresponding author. School of the Environment and Safety Engineering, Jiangsu University, Zhenjiang, 212013, PR China.

** Corresponding author. School of the Environment and Safety Engineering, Jiangsu University, Zhenjiang, 212013, PR China.

E-mail addresses: yyh1108@ujs.edu.cn (Y. Yi), zhgb1030@ujs.edu.cn (G. Zhu).

developing enzyme-free nanoprobe for the fluorescent detection of MP with high selectivity and sensitivity is still a challenge.

Transition metal chalcogenides attracted recently widespread attentions as a graphene-analogous two-dimensional nanomaterial which can exhibit uncommon and unique electronic, mechanical, optical, chemical and thermal properties [15,16]. Among these transition metal chalcogenides nanomaterials, molybdenum disulfide (MoS_2) has been exploited largely in the past years with important potential application as novel optical sensors, optoelectronic devices, batteries, transistors and catalysts. As is well-known, the optical properties from semiconductors relay mainly on the electronic band structure of nanomaterial [17]. When the indirect band gap from bulk MoS_2 (about 1.2 eV) transfer to direct band gap of monolayer MoS_2 (about 1.8 eV), the photoluminescent behavior from MoS_2 can be aroused [18,19]. In addition, when the lateral size MoS_2 nanosheets decrease to less than 10 nm to form MoS_2 quantum dots (MoS_2 QDs), the formed MoS_2 QDs can show strong fluorescence owing to the quantum confinement and edge effects, and MoS_2 QDs exhibit many unique superiorities such as low toxicity, environmentally friendly and easily functionalized [20]. Thus MoS_2 QDs have been widely applied in fluorescence determination of metal ion [21], hyaluronidase, pyrophosphate [20,22], etc. [23]. However, most fluorescence sensing platforms based on pure MoS_2 QDs usually exist several defects such as low selectivity and poor anti-interference [24], designing or bring in a new multifunctional molecule which has benign effects on the selectivity and sensitivity as well as other sensing performances of MoS_2 QD is thus highly interesting and important technologically.

β -Cyclodextrin (β -CD), a cyclic oligosaccharide consisted of 7 glucose units, is a well-known molecular host which is capable of including various organic molecules inside its cavity to form host-guest inclusion complex [25]. Because of its hydrophobic inner cavity, hydrophilic surface structure and molecular recognition property, β -CD has been widely used to develop various sensing platforms via host-guest interaction [26]. Thus, it's believed that the combination of the strong fluorescence properties from MoS_2 QD and high molecular recognition capabilities from β -CD can offer a novel pathway to construct highly sensitive and selective sensing platforms for different analytes including MP.

The previous studies demonstrated that MP can be hydrolyzed to p-nitrophenol (p-NP) under alkaline conditions [27], and p-NP can enter into the β -CD cavity via host-guest recognize between β -CD and p-NP [28]. Inspired by this insight, it's confirmed that the alliance of MoS_2 QDs and β -CDs can develop selective and sensitive fluorescent nanoprobe for MP via measuring the signaling changes produced by the entrance of p-NP into β -CD cavity. In the present study, β -CD

functionalized MoS_2 QDs (β -CD- MoS_2 QDs) was synthesized firstly and then used as a novel enzyme-free fluorescent nanoprobe for the detection of MP. As shown in Scheme S1, 3-aminophenylboronic acid (APBA) modified MoS_2 QDs was formed firstly via amidation reaction, which then couple with hydroxypropyl- β -CD to produce β -CD- MoS_2 QDs. Under the alkaline conditions, the target MP can be hydrolyzed to p-NP and sequentially the formed p-NP enters into β -CD cavity via host-guest recognize between β -CD and p-NP, which results the fluorescence from β -CD- MoS_2 QDs are effectively quenched (Scheme 1). Based on this principle, an effective and reliable sensing platform was constructed for MP. The experimental results demonstrated that the detection method based on β -CD- MoS_2 QDs probe for MP has high selectivity and sensitivity as well as wide linear range and low detection limit. It's believed the developed proposal has important potential applications for MP analysis and the produced β -CD- MoS_2 QDs nanoprobe has wide applications in the optical sensing.

2. Experiment

2.1. Materials and reagents

Sodium molybdate dihydrate ($\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$), 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide (EDC-HCl), APBA, glutathione, p-NP, hydroxypropyl- β -CD, N-hydroxysuccinimide (NHS), MP and other pesticides were purchased from Aladdin Industrial Co. Ltd. (Shanghai, China).

2.2. Characterization

The fluorescence spectrums were measured with F-7000 Spectrofluorometer (Shimadzu, Japan). UV-Vis absorption spectra were carried out on UV-Vis 2600 spectrophotometer (Shimadzu, Japan). X-ray photoelectron spectroscopy was measured on a K-Alpha 1063 (Thermo Fisher, U. K.). Transmission electron microscopy (TEM) was obtained using a JEM-3010 (Joel, Japan). The fluorescence lifetime was acquired by Horiba-Jobin-Yvon Fluorolog-3 spectrofluorometer (Horiba, Japan). Purification of β -CD- MoS_2 QDs was performed using a centrifuge 5804 R (Eppendorf, Germany).

2.3. Preparing MoS_2 QDs

MoS_2 QDs were synthesized via a modified process reported in previous work [15]. $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ (0.125 g) was dissolved in ultrapure water (12.5 mL) and adjusting its pH value to 6.5 with 0.1M HCl, then, the glutathione (0.215 g) and ultrapure water (25 mL) were added. After

Scheme 1. Schematic illustrations for (A) MP hydrolysis and (B) fluorescent sensing MP based on β -CD- MoS_2 QDs nanoprobe through host-guest recognition.

sonicating for about 10 min, the formed mixture solution was transferred into an autoclave (50.0 mL) and hydrothermally treated for one day at 200 °C. After cooled to room temperature, the large particles consisted of reaction solutions were removed through centrifugation. The pure MoS₂ QDs solution was stored in 4 °C.

2.4. Synthesis of β -CD-MoS₂ QDs

For synthesizing β -CD-MoS₂ QDs, the produced above MoS₂ QDs (20.0 mL) were added into 10.0 mL of ultrapure water, adjusting the pH value of the solution to 4.0. EDC·HCl (0.2 g) and NHS (0.2 g) were put into the MoS₂ QDs solution and stirred continuously for 30 min. Next, APBA (0.25 g) was added into the solution and heated at 100 °C for 12 h. Adjusting the pH value of the resulting solution to 9.0 with NaOH solution, and adding 0.35 g hydroxypropyl- β -CD into the solution for functionalizing MoS₂ QDs, the resulted mixed solution was heated continuously for 5 h at 100 °C. Finally, after purifying the obtained solution with 1000 Da dialysis bag for removing excessive EDC, NHS, APBA and β -CD, β -CD-MoS₂ QDs was obtained successfully.

2.5. Fluorescence detection of MP by β -CD-MoS₂ QDs

The analysis of MP was performed through the following steps. At first, MP (100.0 μ L) with a definite concentration was added into the solution of NaOH (35.0 mM) and incubated at 60 °C for 20 min to produce p-NP via hydrolytic action. Then, 10.0 μ L of β -CD-MoS₂ QDs was added into this mixed solution after adjusting its pH value to neutral with 5.0 mL PBS (pH 6.0). For achieving the fluorescence of MP, the fluorescence intensities at the excitation wavelength of 295 nm was measured.

2.6. Real samples detection

After crushing the edible portion of the real samples, a total of 25.0 g of each sample was mixed with acetonitrile solution (50.0 mL) and then the mixture was filtered. The collected solution was dried on a water bath and subsequently dissolved in a methanol solution. Next, MP with various concentrations were added to the treated samples and incubating at 60 °C for 20 min with NaOH solution (35.0 mM) to produce p-NP via hydrolytic action. Then, the hydrolyzed samples were added to 5.0 mL PBS and mixed with β -CD-MoS₂ QDs (10 μ L), the fluorescence intensity was measured at the excitation wavelength of 295 nm.

3. Results and discussion

3.1. Characterization of β -CD-MoS₂ QDs

The morphology and distribution of the obtained β -CD-MoS₂ QDs

were characterized by TEM, as shown in Fig. 1A, the picture displayed the uniformly dispersed of β -CD-MoS₂ QDs with an average diameter of $\sim$ 3 nm, which is in consistent with that of original MoS₂ QDs (Fig. S1). XPS spectrum was determined the surface element composition of β -CD-MoS₂ QDs, and the result are shown in Fig. 1B. The binding energy signal at 395.2 eV corresponded to N—C=O, which can confirmed the formation of an amide bond [29]. The peaks at 191.9 eV and 226.8 eV represented to B (—B—O—), and Mo, respectively [30,31]. Fig. S2A shows that the Mo 3d spectrum is deconvoluted into three peaks, which are located at 226.8 (S 2s), 228.0 (Mo 3d_{5/2}) and 231.8 eV (Mo3d_{3/2}), respectively [32,33]. From Fig. S2B, it can be found that the S 2p spectrum displayed S 2p_{3/2} and S 2p_{1/2} at 163 eV⁻¹ and 164 eV⁻¹, respectively, and the other two peaks in the spectrum are belong to S₂O₃²⁻ group [19]. In Fig. S2C, the B 1s spectrum shows two peaks appear at 191.0 eV⁻¹ for B—C, 191.9 eV⁻¹ for B—O [34,35]. The Fourier transform infrared spectroscopy (FT-IR) of β -CD-MoS₂ QDs was exhibited in Fig. S3, It's noted that the β -CD-MoS₂ QDs shows strong peaks of MoS₂ QDs at 3400 cm⁻¹, 1640 cm⁻¹ and 1036 cm⁻¹ ascribed to N—H stretching vibration, N—H bending vibration and B—O—H vibration, respectively. Meanwhile, the typical absorption features of β -CD for the coupled C—O—C stretching/O—H bending vibrations at 1146 cm⁻¹ and CH₂ stretching vibrations at 2915 cm⁻¹ can also be observed in β -CD-MoS₂ QDs. The results indicate that β -CD molecules were successfully linked covalently to MoS₂ QDs to produce β -CD-MoS₂ QDs nanoprobe through phenylboronic acid and amide bond.

The UV-vis displayed the different absorption spectrum between β -CD-MoS₂ QDs and MoS₂ QDs. The β -CD-MoS₂ QDs shows two remarkable absorption peaks at 238 nm and 289 nm, where no absorption peaks can be found for MoS₂ QDs (Fig. S4) [30]. Moreover,

Fig. 2. Fluorescence excitation and emission spectra of β -CD-MoS₂ QDs (solid line) and MoS₂ QDs (dashed line).

Fig. 1. (A) The TEM image and size distribution of β -CD-MoS₂ QDs; (B) the XPS spectrum of β -CD-MoS₂ QDs.

Fig. 2 reveals that the excitation and emission peaks of β -CD-MoS₂ QDs are greatly shifted compared to that of MoS₂ QDs, suggesting that the β -CD covalently link to the surface of APBA functionalized MoS₂ QDs through coupled effect between boronic acids and cis-diols. In summary, by comparing the XPS, UV-vis and fluorescence spectrum of β -CD-MoS₂ QDs and MoS₂ QDs, it's ensured that the β -CD-MoS₂ QDs fluorescent nanoprobe was successfully synthesized.

To further explore the stability of the as-prepared fluorescent nanoprobe, the fluorescence intensity of β -CD-MoS₂ QDs exposed to daylight for 8 h and in different concentrations of NaCl solution was measured. As illustrated in Fig. S5, no significant changes observed in the fluorescence intensity of β -CD-MoS₂ QDs under irradiation of daylight for 8 h or in a highly concentrated solution of NaCl. These results illustrate the synthesized β -CD-MoS₂ QDs possess excellent stability.

3.2. PET process between β -CD-MoS₂ QDs and p-NP

According to the previous study [36], p-NP is capable to enter the β -CD cavity to form a host-guest inclusion because of the large binding constant ($2.3 \times 10^3 \text{ M}^{-1}$) [37]. This process can close the distance between p-NP and β -CD-MoS₂ QDs, and can quench the fluorescence of β -CD-MoS₂ QDs. As shown in Fig. 3A, the fluorescence intensity of β -CD-MoS₂ QDs dramatically decreased with the addition of p-NP, which was consistent with resonance energy transfer (RET) or photo-induced electron transfer (PET) process [38]. For distinguishing whether the quenching effect is resulted from RET or PET, the fluorescence lifetime decay curve was further measured. As illustrated in Fig. 3B, the fluorescence lifetime of β -CD-MoS₂ QDs shows significant shorter after the addition of p-NP, which certificated that the quenching mechanism is related to PET [39]. Moreover, the absorption spectrum from p-NP and emission spectrum from β -CD-MoS₂ QDs verifies the hypothesis, as from Fig. S6, almost no overlap presents between the emission spectrum from β -CD-MoS₂ QDs and absorption spectrum from p-NP, which is inconsistent with the resonance energy transfer (RET) mechanism [40]. Therefore, the fluorescence quenching mechanism of p-NP for β -CD-MoS₂ QDs is attributed to PET process. Furthermore, an obviously blue-shift in fluorescence of β -CD-MoS₂ QDs is observed in the presence of p-NP. The blue shift might be attribute to the influence via host-guest interaction between p-NP and β -CD on the optical property of nanoprobe [41].

3.3. Fluorescence detection of MP based on β -CD-MoS₂ QDs

Based on the feature that MP can be hydrolyzed to produce p-NP under alkaline condition, and then the resulting p-NP can quench

efficiently the fluorescence of β -CD-MoS₂ QDs, the fluorescence detection of MP was carried out based on the β -CD-MoS₂ QDs nanoprobe. Firstly, the feasibility of the proposal was studied and the related results are exhibited in Fig. 4. For pure MoS₂ QDs (Fig. 4A), its fluorescence intensity only shows a very slight decrease in the presence of hydrolyzed MP. As for β -CD-MoS₂ QDs (Fig. 4B), its fluorescence intensity barely changed in the presence or absence of MP; however, it can be dramatically quenched in the present of hydrolyzed MP, suggesting the produced p-NP from the hydrolysis reaction of MP can entry into the β -CD cavity to quench the fluorescence intensity of β -CD-MoS₂ QDs. These results demonstrate that the fluorescence detection of MP based on β -CD-MoS₂ QDs is feasible.

To realize the best performance of β -CD-MoS₂ QDs for detecting MP, some experiment conditions were optimized. As illustrated in Fig. S7A, the absorbance intensity of MP at 400 nm reached the highest after the addition of 35 mM NaOH. However, as exhibited in Fig. S8, the fluorescence intensity of β -CD-MoS₂ QDs is dramatically decreased when the solution has a strongly alkaline (pH = 10.0). This phenomenon might be due to the broken of amide bond, and the β -CD molecules cannot connect with MoS₂ QDs. Thus, the pH of hydrolyzed MP solution was adjusted to neutral. Furthermore, the optimum for incubation time and temperature were also studied. As shown in Fig. S7B, the $(F_0 - F)/F_0$ (F_0 represents the background fluorescence of β -CD-MoS₂ without MP, and F represents the fluorescence of β -CD-MoS₂ with different MP concentrations) reaches a maximum when the reaction time reached 20 min. It is noted that the quenching efficiency reaches a maximum when the temperature of the system is 60 °C (Fig. S7C). Based on these observations, the analyte system was incubated at 70 °C for 20 min before the measurement for further experiments.

Under the optimum conditions, the usability of this fluorescent nanoprobe for sensitive detection of MP was measured. Fig. 5A shows the fluorescence intensity of β -CD-MoS₂ QDs gradually decreases with MP concentrations increasing from 0.01 ppm to 36.0 ppm. It can be observed a good linear relationship is presented between the fluorescence intensity and concentrations of MP ranging from 0.01 ppm to 18.0 ppm (Fig. 5B). The regression equation can be expressed as $(F_0 - F)/F_0 = 0.059[\text{MP}] + 0.085$, where R^2 is 0.992. The detection limit was estimated to be 3.3 ppb ($S/N = 3$). A comparison to previous methods for MP detection is shown in Table S1, which suggests that the β -CD-MoS₂ QDs based assay exhibits lower detection limit and wider linear range. More importantly, the proposed method is the first example to achieve sensitive detection of MP using a β -CD modified MoS₂ QDs through host-guest recognition without the addition of enzyme.

Fig. 3. (A) The fluorescence spectra of β -CD-MoS₂ QDs in the presence of different concentration of p-NP (0.0–12.00 μM); (B) time-resolved decay fitting line of β -CD-MoS₂ QDs in the absence and presence of p-NP (100 μM).

Fig. 4. (A) The fluorescence spectra of mere MoS₂ QDs in the absence (black line) and presence (red line) of hydrolyzed MP (80.0 ppm); (B) the fluorescence spectra of β -CD-MoS₂ in the presence of MP (160.0 ppm) and hydrolyzed MP (80 ppm). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

Fig. 5. (A) The fluorescence spectra of β -CD-MoS₂ with increasing concentration of MP in the range of 0.0–36.0 ppm; (B) the linear relationship between $(F_0 - F)/F_0$ and MP concentration. (Where F_0 represents the fluorescence of β -CD-MoS₂ without MP, and F represents the fluorescence of β -CD-MoS₂ with different MP concentration).

3.4. Selectivity and real application

To validate the selectivity of the proposed proposal for the determination of MP, the other organophosphorus pesticides (triazophos, dibrom, phosphamidon, glyphosate, methamidophos, dimethoate, phoxim, systox, and trichlorfon) were also analyzed using the β -CD-MoS₂ QDs fluorescent nanoprobe. As shown in Fig. S9, the fluorescence quenching efficiency of β -CD-MoS₂ QDs by MP (20.0 ppm) is prominent higher than other pesticides with relatively higher concentration (100.0 ppm). These results demonstrate that the proposed method is highly selective for distinguishing MP from other organophosphorus pesticides. Next, the practicality of the fluorescence nanoprobe for MP detection was investigated in real sample analysis including fruit and vegetable. Different concentration of MP (0.0, 1.0, 5.0 and 10.0 ppm) were spiked with processed apple and cucumber samples, the fluorescence was measured in a similar experiment procedure, and the results exhibit good recoveries ranging from 93.0% to 105.6% with a maximum RSD of 4.42% (Table S2), indicating that the proposed fluorescent nanoprobe has important potential applicability for the determination of MP in real samples.

4. Conclusions

In summary, this work developed an enzyme-free fluorescent nanoprobe based on β -CD-MoS₂ QDs for MP detection through host-guest recognize for the first time. By introducing β -CD molecules on the MoS₂ QDs surface, the formed novel β -CD-MoS₂ QDs nanoprobe can

exhibit the synthetic advantages from each component (e.g., excellent optical property of MoS₂ QDs and high molecular recognition performance of β -CD). Via the PET process, the p-NP molecules from MP hydrolysis under alkaline conditions can entry into the inner cavities of β -CD owing to its host-guest recognition and further quench the fluorescence of β -CD-MoS₂ QDs, thus a fluorescence sensing platform was constructed for MP. After optimizing various experimental conditions, the results show that the β -CD-MoS₂ QDs fluorescent nanoprobe presents excellent selectivity and sensitivity with wide linear range (three orders of magnitude) and low detection limit (3.3 ppb) toward MP detection. Furthermore, the developed nanoprobe can be applied successfully to the real food samples for MP analysis. It's believed that the β -CD-MoS₂ QDs probe can give a new sight for the selective and sensitive detection of MP and has potential for chem/biological analysis.

Credit author statement

Yinhui Yi: Supervision, Conceptualization, Methodology, Experiment, Writing- Reviewing and Editing. Wei Zeng: Experiment, Data curation, Writing-Editing. Gangbing Zhu: Validation, Writing- Reviewing and Editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

This work is supported by the National Natural Science Foundation of China (21607061), the CAS Key Laboratory of Coastal Environmental Processes and Ecological Remediation, YICCAS (Grant No.: 2020KFJJ16), the Opening Project of State Key Laboratory of Chemo/Biosensing and Chemometrics of Hunan University (2018019), the Open Project Program of Key Laboratory for Analytical Science of Food Safety and Biology, Ministry of Education (No. FS2008) and the Priority Academic Program Development of Jiangsu Higher Education Institutions, Collaborative Innovation Center of Technology and Material of Water Treatment.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.talanta.2020.121703>.

References

- [1] A. Samsidar, S. Siddiquee, S.M. Shaarani, A review of extraction, analytical and advanced methods for determination of pesticides in environment and foodstuffs, *Trends Food Sci. Technol.* 71 (2018) 188–201.
- [2] J.-W. Zhou, X.-M. Zou, S.-H. Song, G.-H. Chen, Quantum dots applied to methodology on detection of pesticide and veterinary drug residues, *J. Agric. Food Chem.* 66 (2018) 1307–1319.
- [3] B. Liu, G. Han, Z. Zhang, R. Liu, C. Jiang, S. Wang, M.-Y. Han, Shell thickness-dependent Raman enhancement for rapid identification and detection of pesticide residues at fruit peels, *Anal. Chem.* 84 (2012) 255–261.
- [4] W. Zhu, W. Liu, T. Li, X. Yue, T. Liu, W. Zhang, S. Yu, D. Zhang, J. Wang, Facile green synthesis of graphene-Au nanorod nanoassembly for on-line extraction and sensitive stripping analysis of methyl parathion, *Electrochim. Acta* 146 (2014) 419–428.
- [5] C. Esen, J. Czulak, T. Cowen, E. Piletska, S.A. Piletsky, Highly efficient abiotic assay formats for methyl parathion: molecularly imprinted polymer nanoparticle assay as an alternative to enzyme-linked immunosorbent assay, *Anal. Chem.* 91 (2019) 958–964.
- [6] S. Lan, X. Wang, Q. Liu, J. Bao, M. Yang, H. Fa, C. Hou, D. Huo, Fluorescent sensor for indirect measurement of methyl parathion based on alkaline-induced hydrolysis using N-doped carbon dots, *Talanta* 192 (2019) 368–373.
- [7] H. Wu, Y. Luo, C. Hou, D. Huo, Y. Zhou, S. Zou, J. Zhao, Y. Lei, Flexible bipyramid-AuNPs based SERS tape sensing strategy for detecting methyl parathion on vegetable and fruit surface, *Sensor. Actuator. B Chem.* 285 (2019) 123–128.
- [8] Y. Li, J. Liu, Y. Zhang, M. Gu, D. Wang, Y.Y. Dang, B.C. Ye, Y. Li, A robust electrochemical sensing platform using carbon paste electrode modified with molecularly imprinted microsphere and its application on methyl parathion detection, *Biosens. Bioelectron.* 106 (2018) 71–77.
- [9] C. Zhang, H. Cui, Y. Han, F. Yu, X. Shi, Development of a biomimetic enzyme-linked immunosorbent assay based on molecularly imprinted polymers on paper for the detection of carbaryl, *Food Chem.* 240 (2018) 893–897.
- [10] H. Li, X. Yan, G. Lu, X. Su, Carbon dot-based bioplateform for dual colorimetric and fluorometric sensing of organophosphate pesticides, *Sensor. Actuator. B Chem.* 260 (2018) 563–570.
- [11] F. Zhang, Y. Liu, P. Ma, S. Tao, Y. Sun, X. Wang, D. Song, A Mn-doped ZnS quantum dots-based ratiometric fluorescence probe for lead ion detection and "off-on" strategy for methyl parathion detection, *Talanta* 204 (2019) 13–19.
- [12] X. Yan, H. Li, Y. Yan, X. Su, Selective detection of parathion-methyl based on near-infrared CuInS₂ quantum dots, *Food Chem.* 173 (2015) 179–184.
- [13] S. Huang, Y. Yao, X. Chu, Y. Liu, Q. Xiao, Y. Zhang, One-Step Facile Synthesis of nitrogen-doped carbon dots: a ratiometric fluorescent probe for evaluation of acetylcholinesterase activity and detection of organophosphorus pesticides in tap water and food, *J. Agric. Food Chem.* 67 (2019) 11244–11255.
- [14] A. Zheng, C. Shen, Q. Tang, C.-B. Gong, C.-F. Chow, Catalytic chemosensing assay for selective detection of methyl parathion organophosphate pesticide, *Chem. Eur. J.* 25 (2019) 9643–9649.
- [15] L. Liu, G. Zhu, W. Zeng, B. Lv, Y. Yi, Highly sensitive and selective "off-on" fluorescent sensing platform for ClO⁻ in water based on silicon quantum dots coupled with nanosilver, *Anal. Bioanal. Chem.* 411 (2019) 1561–1568.
- [16] K. Zhang, H. Zhou, Q. Mei, S. Wang, G. Guan, R. Liu, J. Zhang, Z. Zhang, Instant visual detection of trinitrotoluene particulates on various surfaces by ratiometric fluorescence of dual-emission quantum dots hybrid, *J. Am. Chem. Soc.* 133 (2011) 8424–8427.
- [17] H. Zhu, H. Zhang, Y. Xia, Planar Is Better: Monodisperse three-Layered MoS₂ quantum dots as fluorescent reporters for 2,4,6-trinitrotoluene sensing in environmental water and luggage cases, *Anal. Chem.* 90 (2018) 3942–3949.
- [18] W. Dai, H. Dong, B. Fugetsu, Y. Cao, H. Lu, X. Ma, X. Zhang, Tunable fabrication of molybdenum disulfide quantum dots for intracellular microRNA detection and multiphoton bioimaging, *Small* 11 (2015) 4158–4164.
- [19] F. Sarpong, P. Otengdarko, M.K. Golly, L.P. Amenorfe, M.T. Rashid, C. Zhou, Comparative study of enzymes inactivation and browning pigmentation of apple (*Malus domestica*) slices by selected gums during low temperature storage, *J. Food Biochem.* 42 (2018).
- [20] W. Gu, Y. Yan, C. Zhang, C. Ding, Y. Xian, One-step synthesis of water-soluble MoS₂ quantum dots via a hydrothermal method as a fluorescent probe for hyaluronidase detection, *ACS Appl. Mater. Interfaces* 8 (2016) 11272–11279.
- [21] J. Ma, H. Yu, X. Jiang, Z. Luo, Y. Zheng, High sensitivity label-free detection of Fe³⁺ ion in aqueous solution using fluorescent MoS₂ quantum dots, *Sensor. Actuator. B Chem.* 281 (2019) 989–997.
- [22] R. Zeng, Z. Luo, L. Zhang, D. Tang, Platinum nanzyme-catalyzed gas generation for pressure-based bioassay using polyaniline nanowires-functionalized graphene oxide framework, *Anal. Chem.* 90 (2018) 12299–12306.
- [23] Z. Wang, J. Lin, J. Gao, Q. Wang, Two optically active molybdenum disulfide quantum dots as tetracycline sensors, *Mater. Chem. Phys.* 178 (2016) 82–87.
- [24] G.M. Durán, C. Abellán, A.M. Contento, A. Ríos, Discrimination of penicillamine enantiomers using β -cyclodextrin modified CdSe/ZnS quantum dots, *Microchimica Acta* 184 (2017) 815–824.
- [25] Y. Yi, D. Zhang, Y. Ma, X. Wu, G. Zhu, Dual-signal electrochemical enantiospecific recognition system via competitive supramolecular host-guest interactions: the case of phenylalanine, *Anal. Chem.* 91 (2019) 2908–2915.
- [26] A. Mondal, N.R. Jana, Fluorescent detection of cholesterol using beta-cyclodextrin functionalized graphene, *Chem. Commun.* 48 (2012) 7316–7318.
- [27] J. Zhang, J. Wang, L. Yang, B. Liu, G. Guan, C. Jiang, Z. Zhang, Ligand replacement induced chemiluminescence for selective detection of an organophosphorus pesticide using bifunctional Au-Fe₃O₄ dumbbell-like nanoparticles, *Chem. Commun.* 50 (2014) 15870–15873.
- [28] Ronit Freeman, Tali Finder, LiLy Bahshi, I. Willner, β -cyclodextrin-modified CdSe/ZnS quantum dots for sensing and chiroselective analysis, *Nano Lett.* 9 (2009) 2073–2076.
- [29] Mai Luo, Yifan Hua, Yiran Liang, Jiajun Han, Donghui Liu, Wenting Zhao, P. Wang, Synthesis of novel β -cyclodextrin functionalized S, N codoped carbon dots for selective detection of testosterone, *Biosens. Bioelectron.* 98 (2017) 195–201.
- [30] C. Tang, Z. Qian, Y. Huang, J. Xu, H. Ao, M. Zhao, J. Zhou, J. Chen, H. Feng, A fluorometric assay for alkaline phosphatase activity based on beta-cyclodextrin-modified carbon quantum dots through host-guest recognition, *Biosens. Bioelectron.* 83 (2016) 274–280.
- [31] Wei Zeng, Lirong Liu, Yinhu Yi, Yuntao Wu, Ning Sun, Baohe Lv, G. Zhu, A double signal nanoprobe based on molybdenum disulfide quantum dots, *Microchem. J.* 150 (2019).
- [32] S. Xu, D. Li, P. Wu, One-pot, facile, and versatile synthesis of monolayer MoS₂/WS₂ quantum dots as bioimaging probes and efficient electrocatalysts for hydrogen evolution reaction, *Adv. Funct. Mater.* 25 (2015) 1127–1136.
- [33] M. Li, L. Zhang, X. Fan, M. Wu, Y. Du, M. Wang, Q. Kong, L. Zhang, J. Shi, Dual synergistic effects in MoS₂/pyridine-modified g-C₃N₄ composite for highly active and stable photocatalytic hydrogen evolution under visible light, *Appl. Catal. B Environ.* 190 (2016) 36–43.
- [34] X. Zhou, X. Gao, F. Song, C. Wang, F. Chu, S. Wu, A sensing approach for dopamine determination by boronic acid-functionalized molecularly imprinted graphene quantum dots composite, *Appl. Surf. Sci.* 423 (2017) 810–816.
- [35] S. Xu, S. Che, P. Ma, F. Zhang, L. Xu, X. Liu, X. Wang, D. Song, Y. Sun, One-step fabrication of boronic-acid-functionalized carbon dots for the detection of sialic acid, *Talanta* 197 (2019) 548–552.
- [36] Zhixing Zhang, Jie Zhou, Yun Liu, J. Tang, W. Tang, Cyclodextrin capped CdTe quantum dots as versatile fluorescence sensors for nitrophenol isomers, *Nanoscale* 7 (2015) 19540–19546.
- [37] Q. Sun, S. Fang, Y. Fang, Z. Qian, H. Feng, Fluorometric detection of cholesterol based on beta-cyclodextrin functionalized carbon quantum dots via competitive host-guest recognition, *Talanta* 167 (2017) 513–519.
- [38] L. Jia, J.P. Xu, D. Li, S.P. Pang, Y. Fang, Z.G. Song, J. Ji, Fluorescence detection of alkaline phosphatase activity with beta-cyclodextrin-modified quantum dots, *Chem. Commun.* 46 (2010) 7166–7168.
- [39] Z.-Y. Lin, Y.-C. Kuo, C.-J. Chang, Y.-S. Lin, T.-C. Chiu, C.-C. Hu, Highly sensitive sensing of hydroquinone and catechol based on β -cyclodextrin-modified carbon dots, *RSC Adv.* 8 (2018) 19381–19388.
- [40] M.I. Halawa, F. Wu, T.H. Fereja, B. Lou, G. Xu, One-pot green synthesis of supramolecular-cyclodextrin unfunctionalized gold nanoclusters and their application for highly selective and sensitive fluorescent detection of dopamine, *Sensor. Actuator. B Chem.* 254 (2018) 1017–1024.
- [41] C. Tang, J. Zhou, Z. Qian, Y. Ma, Y. Huang, H. Feng, A universal fluorometric assay strategy for glycosidases based on functional carbon quantum dots: β -galactosidase activity detection in vitro and in living cells, *J. Mater. Chem. B* 5 (2017) 1971–1979.