J Fluoresc (2015) 25:1397–1402
DOI 10.1007/s10895-015-1630-1

ORIGINAL ARTICLE

Permethylated-β-Cyclodextrin Capped CdTe Quantum Dot and its Sensitive Fluorescence Analysis of Malachite Green

Yujuan Cao[1,2] · Jiongling Wei[1] · Wei Wu[1] · Song Wang[1] · Xiaogang Hu[1,2] · Ying Yu[1,2]

Received: 20 May 2015 / Accepted: 26 July 2015 / Published online: 7 August 2015

Abstract In the present work, the CdTe quantum dots were covalently conjugated with permethylated-β-cyclodextrin (OMe-β-CD) using 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride as cross-linking reagent. The obtained functional quantum dots (OMe-β-CD/QDs) showed highly luminescent, water solubility and photostability as well as good inclusion ability to malachite green. A sensitive fluorescence method was developed for the analysis of malachite green in different samples. The good linearity was 2.0×10^{-7}–1.0×10^{-5} mol/L and the limit of detect was 1.7×10^{-8} mol/L. The recoveries for three environmental water samples were 92.0–108.2 % with relative standard deviation (RSD) of 0.24–1.87 %, while the recovery for the fish sample was 94.3 % with RSD of 1.04 %. The results showed that the present method was sensitive and convenient to determine malachite green in complex samples.

Keyword Permethylated-β-cyclodextrin · Quantum dots · Malachite green · Fluorescence analysis · Water and fish samples

✉ Yujuan Cao
caoyj@scnu.edu.cn

[1] School of Chemistry and Environment, South China Normal University, Guangzhou 510006, China

[2] Guangzhou Key Laboratory of Analytical Chemistry for Biomedicine, South China Normal University, Guangzhou 510006, China

Introduction

Quantum dots (QDs) as novel fluorescent nano-materials, have attracted considerable attentions owing to their excellent optical properties including broad absorption, narrow emission, tunable emission, photostability and large extinction coefficients [1–3]. They have been widely applied in fluorescence sensor [4], bio-imaging [5], quantum device [6] and molecular biological application [7] in recent years. Water solubility and molecular recognition structures were essential for the application of QDs. To exploit sensing system which is based on QDs using fluorescence changes induced by molecular recognition at the surface of QDs is a topic of current interest.

β-Cyclodextrin (β-CD) is cyclic oligosaccharides made up of seven glucopyranose units through α-1,4-glucosidic bond linkages, it has a special molecular structure, that is, lipophilic internal cavity and hydrophilic external surface, to form host-guest inclusion complexes with many organic molecules [8]. β-CD-QDs emission properties were strongly modified by the non-covalent interactions between the surface anchored β-CD host and the molecular guest, providing a power molecular recognition system and had received much attention as fluorescence sensors [9]. Jia et al. [10] described a direct enzyme activity sensing nanobiosensor platform based on β-CD-functionalized CdTe QDs, and an alkaline phosphatase activity detection system was constructed based on the different quenching effect of the enzyme substrate and product on the modified QDs. Optical sensing and chiroselective sensing of different substrates were also reported using β-CD-functionalized CdSe/ZnS QDs based on a fluorescence resonance energy transfer (FRET) or an energy transfer mechanism [11, 12]. β-CD modified with 11-[(ethoxycarbonyl)thio] undecanoic acid was also used as a capping agent to prepare water-stable CdTe QDs and these modified QDs acted as

nanoprobes for acetylsalicylic acid and its metabolites, the limit of detect (LOD) was low to 8.5×10^{-9} mol/L [13]. Compared with natural β-CD, CD-derivatives can improve their performance such as better aqueous solubility, selectivity, bioavailability and higher binding capacities for most of poorly soluble materials. Among them, full methylation causes remarkable distortion of the β-CD macrocycle, increasing the water solubility as well as adjusting the molecular inclusion effect. In our previous work, the molecular recognition of mono-(6-mercapto)-β-cyclodextrin modified CdSe quantum dots with tyrosine enantiomers was investigated with theoretical calculation and fluorescence spectroscopy, and the functional β-CD/QDs showed better enantio-selectivity to *L*-tyrosine than that to *D*-tyrosine [14].

Malachite green (MG) has been extensively used as a topical fungicide and ectoparasiticide in fish farming, it is also used as a food coloring agent, a medical disinfectant and anthelminthic as well as a dye in silk, wool, leather, paper and acrylic industries [15]. Several studies [16, 17] had shown its hazardous and carcinogenic effects can cause irritation to the respiratory tract or gastrointestinal tract. The commercial use of MG is not permitted in the UE since 2002 and a minimum required performance limit (MRPL) at 2 $\mu g\cdot kg^{-1}$ has been established for the determination of MG residues in aquaculture products. The determination of residual MG in environmental water samples or fish had been carried out by liquid chromatography [18, 19] coupled to several detectors such as fluorescence detection and mass spectroscopy [20].

In the present work, permethylated-β-cyclodextrin capped CdTe quantum dots (OMe-β-CD/QDs) were synthesized, their fluorescence ability and inclusion effect were studied. A sensitive method was developed for the analysis of trace malachite green in environmental water and fish samples.

Experimental

Materials and Reagents

Tellurium (powder, 100 mesh, 99.99 %), $NaHB_4$ (96 %), malachite green (MG), leuco-malachite green (LMG), cadmium chloride ($CdCl_2\cdot2.5H_2O$, >99 %), ethanediamine 3-mercaptopropylacid (MPA), 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride (EDC) were purchased from Aladdin (Shanghai, China), β-cyclodextrin (β-CD) was purchased from Yongguang Industrial Corporation (Shanxi, China), it was recrystallized twice from water and dried under vacuum for 12 h at 95 °C before use. All chemicals were of analytical grade and used as received, with no additional purification. Double-distilled water was used throughout the work.

The phosphate buffered saline (PBS buffer) was prepared with disodium hydrogen phosphate and potassium dihydrogen phosphate, 1.0 mol/L NaOH was used to adjust the pH value.

Apparatus

UV–vis absorption spectra were recorded with a UV–vis 1700 spectrophotometer (Shimadzu, Japan). The fluorescence spectra were recorded on an F-2500 (Hitachi, Japan). The morphology of QDs was characterized by high resolution transmission electron microscopy (HRTEM) on a JEM-2100HR (JEOL, Japan). Fluorescence lifetime was recorded with FLS-920 (Edinburgh, UK), Fourier transform infrared (FT-IR) spectra (4000–400 cm^{-1} in KBr) were recorded on a PE Spectrum One FT-IR Spectrometer (CA, USA). The acidity was measured with a pH SJ-3 F pH meter (Leici, Shanghai, China).

Preparation of OMe-β-CD/QDs

The scheme of preparation of OMe-β-CD/QDs is shown in Fig. 1, including the following steps:

(1) Preparation of water-soluble MPA capped CdTe QDs

The preparation of MPA-capped CdTe QDs was based on previous method with slight modification [21]. Briefly, 20.6 mg of $CdCl_2\cdot2.5H_2O$ was dissolved in 100 mL of water and 18.8 μL of MPA was added under stirring, followed by adjusting the pH to 9.0 by dropwise addition of 1.0 mol/L NaOH solution. Under vigorously stirring, 90 μL of freshly prepared oxygen-free NaHTe solution was added into the above solution, the resulting mixture was then refluxed at 96 °C for 2 h.

(2) Preparation of mono-(6^A-N-ethylenediamine-6^A-deoxy)-permethylated β-CD [22]

Mono (6-(p-tolylsulfonyl)) permethylated β-CD (500 mg, 0.32 mmol) was added to a nitrogen saturated ethylenediamine (3.2 mmol) aqueous solution under stirring. The mixture was refluxed at 70 °C for 7 h, the resultant solution was cooled to room temperature and the excess ethylenediamine was removed under vacuum. Then water was added to the residue and the crude product was extracted using ethyl acetate, and then the extract was purified by silica gel using ethyl acetate-acetone (1:1, v/v) as eluent to afford white crystals. IR (cm^{-1}, KBr): 2928 (sp^3 C-H, s), 2831(−CH_2-, m), 1142 (C-N, m), 1038 (C-O-C, s).

(3) Preparation of CdTe QDs coated with OMe-β-CD

The preparation of CdTe QDs coated with β-CD was based on the approach for constructing an complex with CdTe QDs using the EDC reagent via the formation of amide between the carboxyl groups of QDs and the primary amine groups of OMe-β-CD [23]. Typically, MPA-capped CdTe QDs (50 mL), EDC (160 μL,

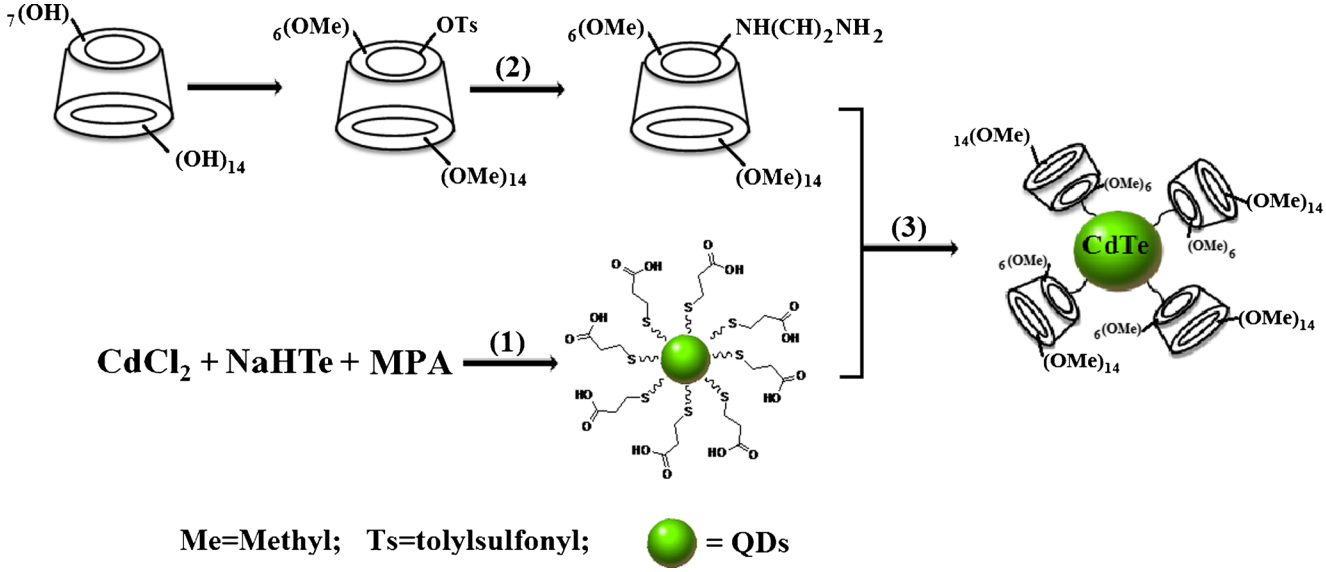

Fig. 1 The scheme of preparation of OMe-β-CD/QDs

0.1 mol/L), PBS buffer (pH 6.5, 0.01 mol/L, 120 μL) were mixed and the mixture was incubated at room temperature for 10 min with gentle stirring to activate the QDs. Then, the OMe-β-CD solution (10 mL, 2 mg/mL) was added and incubated for another 1.5 h at room temperature. Then the resultant solution was stored at 4 °C for overnight to allow the unreacted EDC to hydrolyze and lose its activity.

Methods

(1) Procedure for spectrum detection of MG

To a 10 mL calibrated test tube, 250 μL of the synthesized OMe-β-CD/QDs, 200 μL of PBS (pH=10.0) and an appropriate amount of MG was added into the tube in turn, then diluted with deionized water to 10 mL and mixed thoroughly with gentle shaking. After incubation for 5 min, the fluorescence spectra of these solutions were examined.

(2) Analysis of environmental water samples

The river water samples were collected from the Pearl River. The samples were filtered through Millipore membrane filter (0.2 μm pore size) to remove large solids, then transferred into pre-cleaned glass bottles and stored in a refrigerator.

Fresh fish was purchased from a local supermarket and separated from the skin and bones. Then it was crushed and homogenized with a mortar. Approximately 5.0 g homogenized tissue was extracted with 10.0 mL deionized water for 30 min, the extract was then centrifuged at 4000 rpm for 5 min and the supernatant was obtained for the further analysis.

Results and Discussion

Characterizations of OMe-β-CD/QDs

Figure 2 shows the UV–vis absorption (a, b) and photoluminescence (PL) (c, d) spectra of CdTe QDs before and after conjugated with OMe-β-CD in aqueous solution, respectively. The UV absorption of OMe-β-CD/QDs decreased slightly after conjugated with β-CD while the fluorescence emission intensity (FL) was remarkable increased. The maybe reason due to the fact that the interaction of QDs with OMe-β-CD passivated the surface of QDs and inhibits the radiationless recombination at the surface vacancies [24]. Furthermore, no clear shift in emission wavelength and the spectral width of the OMe-β-CD/QDs was almost the same as that of native CdTe QDs, which suggested that the OMe-β-CD/QDs in water retained the optical properties of the original QDs.

The shape and size of QDs were determined by HRTEM. The HRTEM images in Fig. 3 demonstrate that the CdTe QDs and OMe-β-CD/QDs were well monodispersed and spherical morphology, their average diameters were about 3.4 and 4.1 nm, respectively.

A common problem encountered in using water soluble, ligand protected QDs for practical applications was their low quantum yields (QYs). The QYs of the CdTe QDs and OMe-β-CD/QDs in aqueous solution were determined by comparison with that of Rhodamine B (QY=96 %, EtOH) at room temperature. After conjugated with OMe-β-CD, the defects on the surface of QDs were reduced and the QYs were enlarged from 64 to 74 %. Moreover, it was reported that the PL peak will shift to blue side with time under ultraviolet light irradiation due to photo-oxidation reaction [25]. In the present work, the photo-irradiation experiments of the QDs were performed

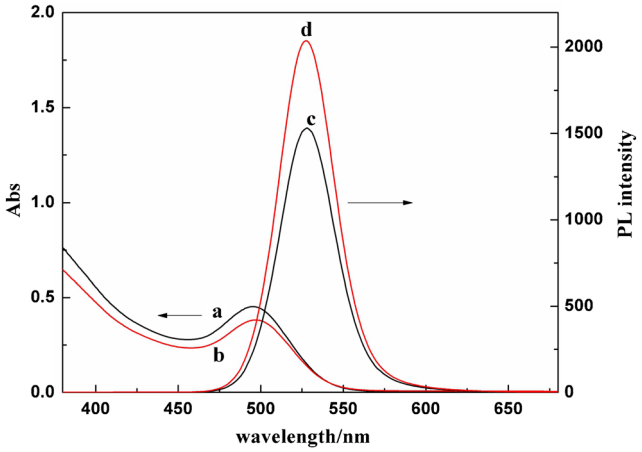

Fig. 2 UV/vis absorption and PL intensity of CdTe QDs (**a**, **c**) and OMe-*β*-CD/QDs (**b**, **d**)

under ambient condition and irradiation from a 365 nm ultraviolet lamp at certain time intervals. The modified OMe-*β*-CD/QDs showed good stability against light illumination, more than 80 % of the fluorescence response was obtained after the modified QDs were irradiated for more than 1 h.

Effects on the Fluorescence Intensity of OMe-β-CD/QDs

To study the specific fluorescence intensity of OMe-β-CD/QDs, malachite green (MG) was selected as the analyte and its concentration was kept at 1.0×10^{-6} mol/L, the effects of pH solution, ionic strength and concentration ratio of QDs to analyte were considered.

(1) Effect of pH

It is known that QDs are pH-sensitive. In this study, the effect of pH on the luminescent of OMe-*β*-CD/QDs was investigated in the range of 5.0-11.0. PBS solution was used to control the acidity of analytical system and ΔF (defined as F_0-F, where F_0 and F were the PL intensities of OMe-*β*-CD/QDs in the absence and presence of MG) was chosen as the response factor. The OMe-*β*-CD/QDs were not stable in acidic solution and a small ΔF occurred. On the other hand, the interaction between the MG and QDs can be enlarged in basic solution and the maximum value of ΔF was obtained when the pH value was 10.0. The MG had only a slight fluorescence quenching effect on QDs when the pH was higher than 10.0, so the optimum pH value of 10.0 was chose.

(2) Effect of ionic strength

The effect of ionic strength on the fluorescence intensity of OMe-*β*-CD/QDs was investigated by keeping the pH, the concentration of MG and OMe-*β*-CD/QDs while changing the volume of PBS. The value of ΔF enlarged with the increase of the volume of PBS before 200 μL, but it was greatly dropped down when the volume of PBS was larger than 300 μL. It is probably due to the fact that the solubility of MG in the high ionic strength PBS solution was reduced, resulting in the reduction of complexation effect between the MG and *β*-CD. Then, 200 μL PBS was selected in the following experiments.

(3) Effect of concentration ratio of OMe-β-CD/QDs to the analyte

The effect of concentration ratio of OMe-*β*-CD/QDs to MG was studied by keeping MG concentration at 1.0×10^{-6} mol/L and the pH 10.0. The results showed that the optimum concentration ratio was almost 1:1. When the added amounts of QDs were higher than this concentration, the value of ΔF began to decrease. From the reported experimental data with HNMR and theoretical calculation results [26, 27], one crystal violet molecule, which has very similar chemical structure to MG, was introduced into one *β*-CD molecule through its wide opening and one complete phenyl group was accommodated within its interior, the stoichiometry of the complex is 1:1. Our study in the present work also confirmed that the stoichiometry of the complex *β*-CD-MG is 1:1.

Fluorescence Quenching and Inclusion Mechanism

Fluorescence quenching mechanism is usually classified as either dynamic quenching or static quenching. The lifetime of fluorescence molecule on excited state has no change in the presence of quencher when static quenching takes place. Reversely, the fluorescence lifetime would be shorter if

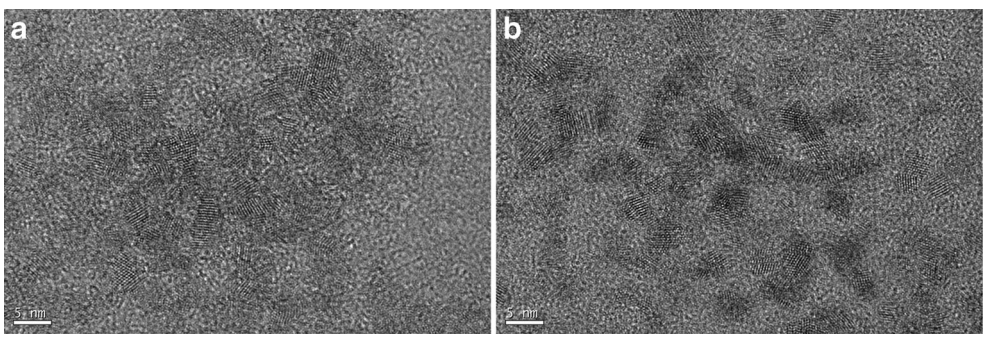

Fig. 3 HRTEM images of CdTe QDs (**a**) and OMe-*β*-CD/QDs (**b**)

dynamic quenching occurs [28]. As seen in Fig. 4, the fluorescence lifetime of OMe-β-CD/QDs has little difference, that is from 17.56 to 17.81 ns, with the increase of the amount of MG, suggesting the fluorescence quenching occurs by a static mechanism. Because of its inherent molecular structure, β-CD can form an inclusion complex with various guest molecules via non-covalent interaction. In this study, the added MG molecule was interacted with OMe-β-CD and a inclusion complex was formed between OMe-β-CD and MG. Then charge-transfer -induced photobleaching of QDs was occurred, which induces the fluorescence quenching of QDs. Similar results can also been observed in QDs system with amine groups, Ru-polypyridine complexes and azobenzene compounds [29].

Moreover, persubstitution of CDs may lead to structural modifications, associated with alteration of the physical properties such as the inclusion effect and selectivity. MG can be easily hydrolyzed in the body of animal and leuco-malachite green (LMG) is the primary metabolite of malachite green, they have highly similar chemical structures except MG has extended pi-delocalization. So, the selectivity of OMe-β-CD/QDs to MG and LMG was studied. Under the same experimental conditions, the PL intensity of OMe-β-CD/QDs to MG was three times than that to LMG, indicating the better selectivity of OMe-β-CD/QDs. The selectivity of the method for malachite green (MG) compared to its leuco-form was due to their different chemical structures and their interaction with the modified β-CD and the QDs. Compared to its neutral form, the cationic MG has two equivalent resonance structures, leading this cationic form have extended pi-delocalization with the methylated β-CD except the inclusion complexation [30], there also was an extra columbic interaction between the cationic MG with the residue anionic QD stabilized with MPA [31]. Moreover, the full methylation increased the hydrophilcity of β-CD, which was benefit for the hydrophilic MG than the hydrophobic LMG to form the inclusion complexes.

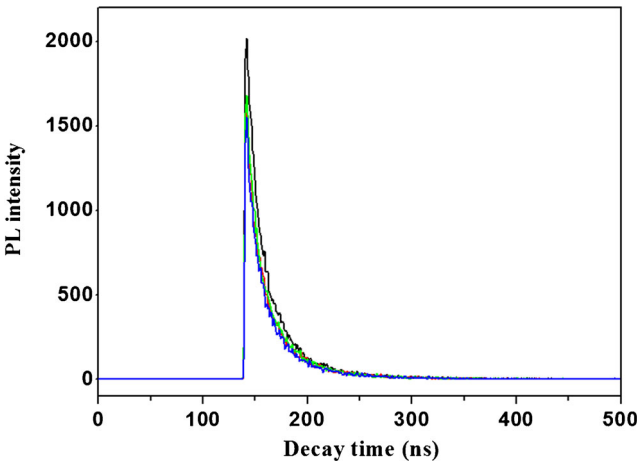

Fig. 4 Fluorescence decay curves (λ_{ex}=365 nm, measured at the maximum of the fluorescence) of OMe-β-CD/QDs in the absence and presence of malachite green using a mono-exponential function

Application to MG Analysis in Water and Fish Samples

The quenching effect of MG on the PL intensity of OMe-β-CD/QDs can be used to develop a method for the analysis of MG in a concentration dependence. A good linear relationship (Fig. 5) was observed up to the MG concentration as the following equation: F_0-F=320.7 [C]+195.3 (C: mol/L), where F_0 and F were the fluorescence intensities of OMe-β-CD/QDs in the absence and presence of MG, respectively. C was the concentration of MG. The linear range was from 2.0×10^{-7} to 1.0×10^{-5} mol L^{-1} with a correlation coefficient of 0.9963. The limit of detect (LOD) was 1.7×10^{-8} mol L^{-1} and the relative standard deviation established at six replicate was lower than 2.0 %.

To validate the new established method in real samples with complex matrix, environmental water and fish samples were selected for the analysis. The spiked MG could be accurately analyzed and the recoveries for MG in water samples ranged from 92 to 108 % with RSD of 0.24–1.87 %, the recovery of MG in fish was 94.3 % and its RSD was 1.04 %. In comparison with the reported chromatography method, for example, a graphene based solid phase extraction couple with ultra-performance liquid chromatography-tandem mass spectrometry for the determination of MG with LOD of 0.63 μg/kg and RSD lower than 5.0 % [18], the present work showed lower limit of detections and better precision, suggesting good potential of the present sensitive and simple method.

Conclusions

In summary, permethylated-β-cyclodextrin capped CdTe quantum dots (OMe-β-CD/QDs) were synthesized, it combined the fluorescence ability of QDs and the inclusion ability of β-CD. As a result of the remarkable changes of the fluorescent intensity for MG, it is possible for OMe-β-CD/QDs to

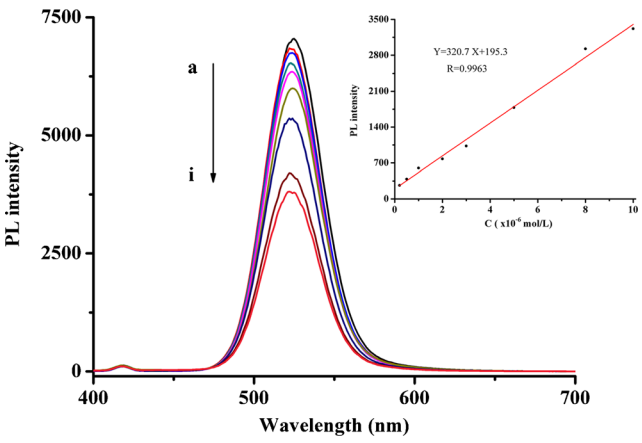

Fig. 5 PL spectra of OMe-β-CD/QDs with the addition of different MG concentrations. The MG concentrations added for spectrum (**a**) to (**i**) were 0, 0.2, 0.5, 1.0, 2.0, 3.0, 5.0, 8.0, 10.0×10^{-6} mol/L, respectively

selectively and sensitively detect MG. Under the optimum conditions, the relative PL intensity of OMe-β-CD/QDs was decreased with increasing MG concentration in range of 2.0×10^{-7}–1.0×10^{-5} mol/L, and the limit of detect was 1.7×10^{-8} mol/L. The proposed method was successfully applied to the determination of MG in real water samples and fish and satisfied results were obtained.

Acknowledgments We are grateful to Dr. Xiao-hua Xiao from Sun Yat-sen University for his helpful advice. This work was supported by the National Natural Science Foundation of China (No.21275056).

References

1. Reilly DJ (2013) Quantum dots: and then there were three. Nat Nanotechnol 8:395–396
2. Kershaw SV, Susha AS, Rogach AL (2013) Narrow bandgap colloidal metal chalcogenide quantum dots: synthetic methods, heterostructures, assemblies, electronic and infrared optical properties. Chem Soc Rev 42:3033–3087
3. Kikkeri R, Padler-Karavani V, Diaz S, Verhagen A, Yu H, Cao HZ, Langereis MA, De Groot RJ, Chen X, Varki A (2013) Quantum dot nanometal surface energy transfer based biosensing of sialic acid compositions and linkages in biological samples. Anal Chem 85:3864–3870
4. Zhang XQ, Li D, Wang C, Zhi X, Zhang CL, Wang K, Cui DX (2012) A CCD-based reader combined quantum dots-labeled lateral flow strips for ultrasensitive quantitative detection of anti-HBs antibody. J Biomed Nanotechnol 8:372–379
5. Zhang LM, Xing YD, He NY, Zhang Y, Lu ZX, Zhang JP, Zhang ZJ (2012) Preparation of graphene quantum dots for bioimaging application. J Nanosci Nanotechnol 12:2924–2928
6. Choi YJ, Kim YJ, Lee JW, Lee YH, Lim YB, Chung HW (2012) Cyto-/genotoxic effect of CdSe/ZnS quantum dots in human lung adenocarcinoma cells for potential photodynamic UV therapy applications. J Nanosci Nanotechnol 12:2160–2168
7. Wahab R, Yang YB, Umar A, Singh S, Hwang IH, Shin HS, Kim YS (2012) Platinum quantum dots and their cytotoxic effect towards myoblast cancer cells (C2C12). J Biomed Nanotechnol 8:424–431
8. Bavireddi H, Kikkeri R (2012) Glyco-β-cyclodextrin capped quantum dots: synthesis, cytotoxicity and optical detection of carbohydrate–protein interactions. Analyst 137:5123–5127
9. Vallafiorita-Monteoleone F, Daita V, Quarti C, Perdicchia D, Buttero PD, Scavia G, del Zoppo M, Botta C (2014) Light harvesting of CdSe/CdS quantum dots coated with β-cyclodextrin based host–guest species through resonant energy transfer from the guests. RSC Adv 4:28886–28892
10. Jia L, Xu JP, Li D, Pang SP, Fang Y, Song ZG, Ji J (2010) Fluorescence detection of alkaline phosphatase activity with β-cyclodextrin-modified quantum dots. Chem Commun 46:7166–7168
11. Tang B, Cao LH, Xu KH, Zhuo LH, Ge JC, Li QF, Yu LJ (2008) A new nanobiosensor for glucose with high sensitivity and selectivity in serum based on fluorescence resonance energy transfer (FRET) between CdTe quantum dots and Au nanoparticles. Chem Eur J 14:3637–3644
12. Han CP, Li HB (2008) Chiral Recognition of amino acids based on cyclodextrin-capped quantum dots. Small 4:1344–1350
13. Algarra M, Campos BB, Aguiar FR, Rodriguez-Borges JE, Esteves da Silva JCG (2012) Novel β-cyclodextrin modified CdTe quantum dots as fluorescence nanosensor for acetylsalicylic acid and metabolites. Mater Sci Eng 32:799–803
14. Cao YJ, Wu SS, Liang YZ, Yu Y (2013) The molecular recognition of β-cyclodextrin modified CdSe quantum dots with tyrosine enantiomers: theoretical calculation and experimental study. J Mol Struct 1031:9–13
15. Saha P, Chowdhury S, Gupta S, Kumar I, Kumar R (2010) Assessment on the removal of malachite green using tamarind fruit shell as biosorbent. Clean Soil Air Water 38:437–445
16. Chowdhury S, Mishra R, Saha P, Kushwaha P (2011) Adsorption thermodynamics, kinetics and isosteric heat of adsorption of malachite green onto chemically modified rice husk. Desalination 265:159–168
17. Guo ZY, Gai PP, Hao TT, Duan J, Wang S (2011) Determination of malachite green residues in fish using a highly sensitive electrochemiluminescence method combined with molecularly imprinted solid phase extraction. J Agric Food Chem 59:5257–5262
18. Chen LY, Lu YB, Li SY, Lin XJ, Xu ZM, Dai ZY (2013) Application of graphene-based solid-phase extraction for ultrafast determination of malachite green and its metabolite in fish tissues. Food Chem 141:1383–1389
19. Lopez-Gutierrez N, Romero-Gonzalez R, Plaza-Bolanos P, Martinez-Vidal JL, Garrido-Frenich A (2013) Simultaneous and fast determination of malachite green, leucomalachite green, crystal violet, and brilliant green in seafood by ultrahigh performance liquid chromatography–tandem mass spectrometry. Food Anal Methods 6:406–414
20. Zhang YY, Lai KQ, Zhou JL, Wang XC, Rasco BA, Huang YQ (2012) A novel approach to determine leucomalachite green and malachite green in fish fillets with surface-enhanced Raman spectroscopy (SERS) and multivariate analyses. J Raman Spectrosc 43:1208–1213
21. Li L, Qian HF, Fang NH, Ren JC (2006) Significant enhancement of the quantum yield of CdTe nanocrystals synthesized in aqueous phase by controlling the pH and concentrations of precursor solutions. J Lumin 116:59–66
22. Kang S, Chen Y, Shi J, Ma YH, Liu Y (2007) Synthesis of oligo(ethylenediamino) modified permethylated-β-cyclo-dextrins and their interactions with bovine serum albumin. Chem J Chin Univ 28:458–465
23. Wang SP, Mamedova N, Kotov NA, Chen W, Studer J (2002) Antigen/antibody immunocomplex from CdTe nanoparticle bioconjugates. Nano Lett 2:817–822
24. Zhao MP, Li JM, Du LY, Tan CP, Xia Q, Mao ZW, Ji LN (2011) Targeted cellular uptake and siRNA silencing by quantum-dot nanoparticles coated with β-cyclodextrin coupled to amino acids. Eur Chem J 17:5171–5179
25. Spanhel L, Haase M, Weller H, Henglein A (1987) Photochemistry of colloidal semiconductors. 20. Surface modification and stability of strong luminescing CDS particles. J Am Chem Soc 109:5649–5655
26. Garcia-Rio L, Leis JR, Mejuto JC, Navarro-Vazquez A, Perez-Juste J, Rodriguez-Dafonte P (2004) Basic hydrolysis of crystal violet in β-cyclodextrin surfactant mixed systems. Langmuir 20:606–613
27. Bernad-Bernad MJ, Gracia-Mora J, Diaz D, Mendoza Diaz G (1999) Molecular interactions and thermodynamic aspects of the complexation reaction between gentian violet and several cyclodextrin. J Incl Phenom Macrocycl Chem 34:1–18
28. Gan XJ, Liu SP, Liu ZF, Hu XL (2012) Determination of tetracaine hydrochloride by fluorescence quenching method with some aromatic amino acids as probes. J Fluoresc 22:129–135
29. Sykora M, Petruska MA, Acevedo JA, Bezel I, Meyer TJ, Klimov VI (2006) Photoinduced charge transfer between CdSe nanocrystal quantum dots and Ru-polypyridine complexes. J Am Chem Soc 128:9984–9985
30. Song LX, Bai L, Xu XM, He J, Pan SZ (2009) Inclusion complexation, encapsulation interaction and inclusion number in cyclodextrin chemistry. Coord Chem Rev 253:1276–1284
31. Ma Q, Cui HL, Su XG (2009) Highly sensitive gaseous formaldehyde sensor with CdTe quantum dots multilayer films. Biosen Bioelectron 25:839–844