Talanta 93 (2012) 398–403

Contents lists available at SciVerse ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

Enhanced fluorescence sensing of melamine based on thioglycolic acid-capped CdS quantum dots

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ARTICLE INFO

Article history:
Received 8 October 2011
Received in revised form 23 February 2012
Accepted 25 February 2012
Available online 3 March 2012

Keywords:
Melamine
Thioglycolic acid
CdS QDs
Fluorescence enhancement

ABSTRACT

A sensitive and simple method for the determination of melamine (MA) was developed based on the fluorescence enhancement effect of MA for thioglycolic acid-capped (TGA-capped) CdS quantum dots (QDs). Under optimum conditions, a good linear relationship was obtained from 2.0×10^{-9} to 5.0×10^{-5} M. The detection limit was 1.0×10^{-9} M, which was much lower than the safety limit (2.5 ppm in USA and the UK; 1 ppm for infant formula in China). The solution pH, the adding sequence of the buffer solution and MA and surface modifiers of CdS QDs greatly influenced the enhancement extent of MA for CdS QDs. The fluorescence enhancement was attributed to the surface passivation of the surface states of QDs by amine group of MA. The method was applied to detect MA in raw milk with satisfactory results. The proposed method manifested several advantages such as high sensitivity, short analysis time, low cost and ease of operation.

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1. Introduction

Melamine (2,4,6-triamino-1,3,5-triazine, MA) is a heterocyclic triazine organic compound containing nitrogen, which has been widely used in polymer resins or as raw material in chemical industry. Owning to its high nitrogen level (about 66% nitrogen by mass) and low cost, MA was illegally added in the infant formula and pet food by unethical manufacturers to enhance the apparent crude protein value [1,2] because the Kjeldahl method cannot differentiate MA from protein molecules. However, MA cannot be absorbed metabolically by animals, which could lead to crystallization and subsequent tissue injury, such as urolithiasis and bladder cancer [3,4]. Therefore, there is an increasing demand for effective and reliable methods to detect MA.

Nowadays, the available techniques for MA detection include gas chromatography (GC) [5], liquid chromatography (LC) [6,7], capillary electrophoresis (CE) [8,9] and capillary electrophoresis coupled with UV or MS detector [10,11]. However, many of these assays are not readily adaptable to routine analysis because many of these methods are time-consuming and require relatively expensive and complicated instruments. So, the development of simple, rapid, sensitive and low-cost assay for MA has become increasingly attractive.

Quantum dots (QDs) has unique and superior optical properties including high photobleaching threshold, good chemical stability, size-tunable photoluminescence spectra, broad absorption, and narrow emission wavelengths [12], which makes them the focus of current research for the development of novel sensitive sensors. The luminescence of QDs is extremely sensitive to their surface states. The direct interaction between certain analytes and the surface of QDs can influence the efficiency of the electron-hole recombination process [13]. On this basis, simple and sensitive fluorescence sensors were developed. Many analytes, such as metal ions [14–17], trinitrotoluene [18], hydrogen peroxide [19], phenols [20] and some drugs [21,22] could quench fluorescence (FL) of QDs, based on which "turn-off" sensors were developed. It seemed that surface states that acted as nonradiative recombination centers could be easily produced on the surface of QDs by solvents and/or the analytes, thus, the FL of QDs were quenched. In comparison with the FL quenching mode, where a variety of factors rather than analytes can induce the ultimate FL "off" state, the FL "turn-on" mode seems to be more preferable due to the reduction of the chance of false positives. That is to say, the "turn-on" systems based on QDs have better selectivity than "turn-off" sensors. However, "turn-on" probes based on the direct interaction between the analytes and QDs was rarely reported [23–25].

In this report, a novel "turn-on" sensor for MA was developed based on MA-induced fluorescence enhancement of TGA-capped CdS QDs in acidic solutions. In acidic solution, TGA detached from the surface of CdS QDs, resulted in FL quenching. MA contains amine group, which can provide electron to bind with the defect sites and passivate the QDs, leading to the restoration of the fluorescence. The fluorescence enhancement extent of CdS QDs by MA was related to the surface modifier of QDs. This method showed the

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doi:10.1016/j.talanta.2012.02.062

advantage of fast, simple and sensitive. To the best of our knowledge, no report concerning quantum dots based nanosensor for the determination of MA was reported. The CdS QDs-MA system with greatly enhanced fluorescence intensity may also find potential applications in other sensitive sensing systems.

2. Experimental

2.1. Reagents

$CdCl_2 \cdot 2.5H_2O$ was purchased from Shanghai Jinshan Tingxin Chemical Plant (Shanghai, China). $Na_2S \cdot 9H_2O$ was purchased from Shanghai Lingfeng Chemical Reagent Co., LTD (Shanghai, China). Melamine, TGA, sodium citrate and L-cysteine hydrochloride were all purchased from Sinopharm Chemical Reagent Co., LTD (Shanghai, China). All other chemicals used were of analytical grade. A 0.1 M phosphate buffer solution (PBS) was prepared using NaH_2PO_4 and Na_2HPO_4 and used as the medium for QD solutions. The pH values of PBS were from 2.0 to 9.0. All solutions were prepared with distilled water.

2.2. Apparatus

Fluorescence spectra were measured on Cary Eclipse Fluorescence spectrophotometer (Varian Co., LTD, USA). UV–Vis absorption spectroscopic measurements were carried out using a TU-1901 spectrophotometer (Beijing Purkinje General Instrument Co., Ltd., Beijing, China). The pH of the PBS was measured with a glass electrode connected to a PHS-3 C pH meter (Shanghai, China).

2.3. Synthesis of CdS QDs

TGA-capped CdS QDs were synthesized in aqueous solution using a modified procedure [26]. A 1.3 mL of 0.15 M TGA solution and 80 mL of 0.001 M $CdCl_2$ solution was mixed in a round bottom flask. Then, 3 mL of 0.1 M NaOH was added into the above mixture dropwise and the pH value of the solution reached about 8.0. With the continuous drop of NaOH into the mixture of Cd^{2+} and TGA, white precipitation emerged at first, and then the white precipitation disappeared and finally clear solution formed. This was due to the different dissociation extent of carboxylate and sulfhydryl group at different pH, leading to Cd–thio complexes with different structure formed [27]. After the solution was bubbled with high pure nitrogen for 20 min, 20 mL of 0.002 M Na_2S was added into the flask, and the mixture was allowed to react at room temperature for 20 min under nitrogen atmosphere.

In order to investigate the effect of surface modifiers of CdS QDs for MA sensing, L-cysteine (Cys)-capped and Citrate (Cit)-capped CdS QDs were also synthesized. Cys-capped CdS QDs [28] were synthesized using the same procedure described above for TGA-capped CdS QDs by replacing TGA with the same concentration of L-cysteine hydrochloride. Cit-capped CdS QDs [23] were synthesized using our previously reported method.

2.4. General procedure for MA detection

In order to determine MA, 0.5 mL of standard solution of MA and 0.2 mL of PBS (pH = 3.0) was mixed in a 5-mL calibrated test tube, and then 0.25 mL TGA-capped CdS QDs was added and the mixture was diluted to volume with deionized water and shaken completely. Finally, the fluorescence intensity of the solution was measured with the excitation wavelength of 357 nm and an emission maximum was obtained at 490 nm.

The method was also used to determine MA in real samples by standard addition method. The raw milk was pretreated as reported procedures [29]. The raw milk was purchased from local supermarkets. 1 mL of acetonitrile, 1 mL of CCl_3COOH, and 7 mL of water were added into 2.0 mL of raw milk. Then the mixture in a centrifuge tube was ultrasonically extracted for 20 min and then centrifugated at 5000 rpm for 20 min. The obtained supernatant was filtered two times. The filter liquor was diluted as a 1:10 ratio with deionized water and the diluents were used for the preparation of MA solution and MA detection. For the detection of MA in real samples, 0.5 mL of the as-prepared MA solution and 0.2 mL of PBS (pH = 3.0) was mixed in a 5-mL calibrated test tube, and then 0.25 mL TGA-capped CdS QDs was added and the mixture was diluted to volume with the diluents and shaken completely. The fluorescence intensity of the solution was recorded at 490 nm.

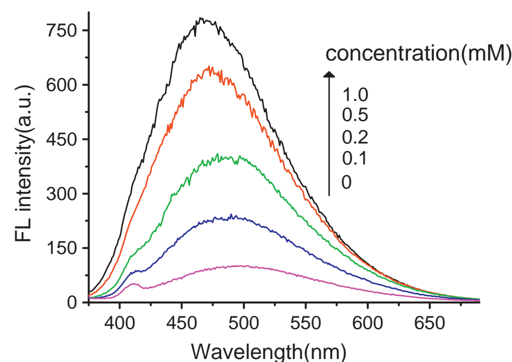

Fig. 1. Fluorescence spectra of the TGA-capped CdS QDs in the presence of different concentrations of MA at the pH value of 3, from bottom to top, the concentration of the MA were ($\times 10^{-3}$ M) 0, 0.1, 0.2, 0.5, 1.0, respectively. (For interpretation of the references to color in text, the reader is referred to the web version of this article.)

3. Results and discussion

3.1. Fluorescence enhancement of TGA-capped CdS QDs by MA

When excited at 357 nm, TGA-capped CdS QDs showed a dominant broad emission band centered at ~490 nm along with a shoulder at ~410 nm. The shoulder at ~410 nm was attributed to the excitonic emission of CdS nanocrystallites [30]. The strong and broad emission observed at longer wavelengths (490 nm) was attributed to trap state emission arising from surface trap states of CdS nanocrystallites [31]. The as-prepared TGA-capped CdS QDs were very stable in water for at least 6 months without notable precipitation in dark under 4 °C. In our experiment, it was found that the fluorescence intensity of TGA-capped CdS QDs could keep stable for about 20 days. After that, the fluorescence of TGA-capped CdS QDs gradually decreased.

Luminescence spectroscopy is well-known to be very sensitive towards small changes of the surface chemistry of the semiconductor nanoparticles [32]. As shown in Fig. 1, MA could drastically increase the fluorescence intensity of TGA-capped CdS QDs. With the increased concentration of MA, a slight blue shift occurred from 490 to 470 nm in the presence of 1.0×10^{-3} M MA.

In this work, MA could greatly enhance the fluorescence intensity of CdS QDs at pH values under 4.0 (Fig. 2A). At solution pH of 3.0, the maximum fluorescence enhancement factor (I/I_0) was observed. Where, I and I_0 represented the fluorescence intensity of CdS QDs in the presence and absence of MA, respectively. As can be seen in Fig. 2B, CdS QDs showed much weaker fluorescence intensity in the solutions with lower pH values (such as at pH of 3.0 and 4.0). When the solution pH was further decreased to 2.0, almost no fluorescence was observed for CdS QDs. The surface modifier (TGA) could enhance the fluorescence intensity of QDs through its surface passivation effects at high solution pH [23], but the case may

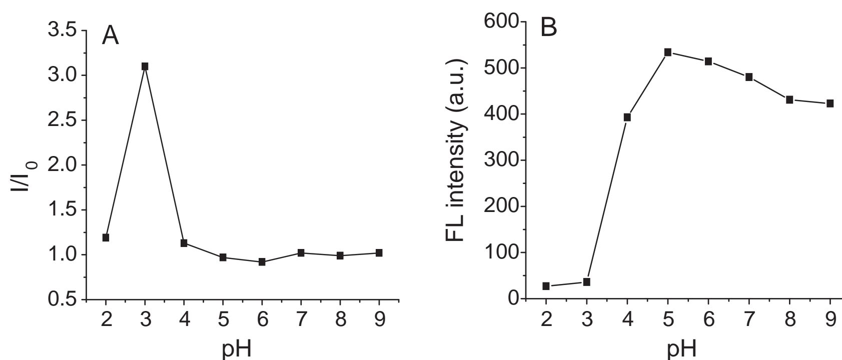

Fig. 2. (A) Effects of different pH of PBS on fluorescence enhancement (I/I_0) of CdS QDs by MA. (B) Effects of the pH of PBS on the fluorescence intensity of TGA-capped CdS QDs.

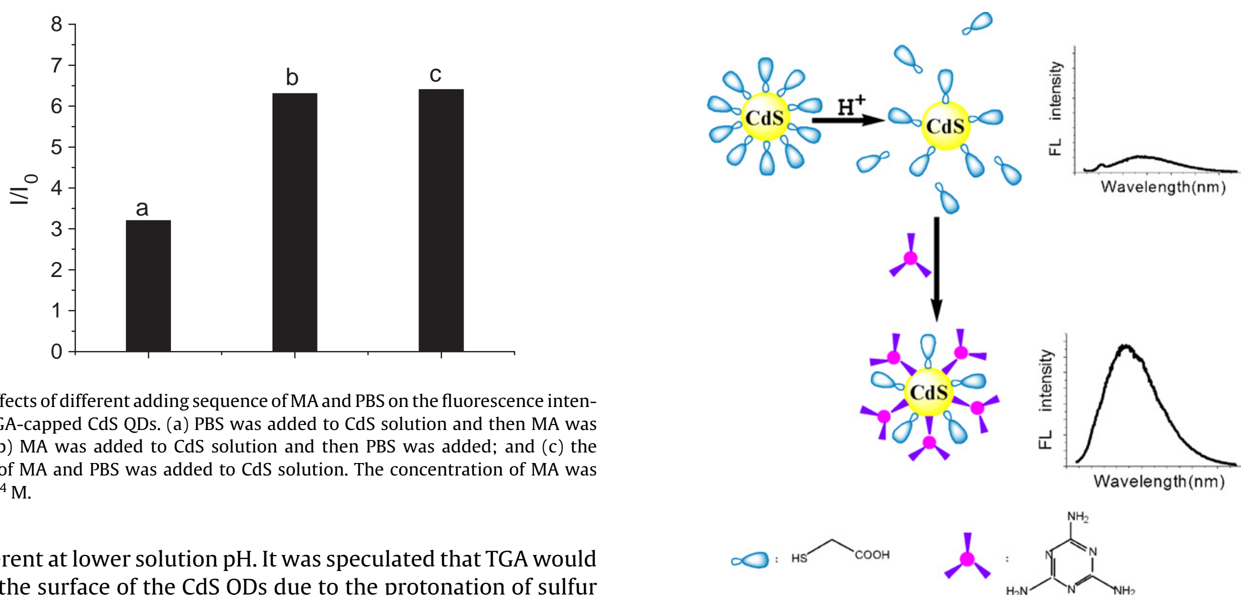

Fig. 3. Effects of different adding sequence of MA and PBS on the fluorescence intensity of TGA-capped CdS QDs. (a) PBS was added to CdS solution and then MA was added; (b) MA was added to CdS solution and then PBS was added; and (c) the mixture of MA and PBS was added to CdS solution. The concentration of MA was 5.0×10^{-4} M.

Scheme 1. Scheme illustrating the interaction of MA with TGA-capped CdS QDs.

be different at lower solution pH. It was speculated that TGA would fall off the surface of the CdS QDs due to the protonation of sulfur group at lower pH (3.0 and 4.0), forming thiols. The loss of the TGA from the surface of QDs induced surface defects, which facilitated the non-radiation recombination, leading to fluorescence decrease. Furthermore, it was also reported that thiols can decrease the fluorescence intensity of QDs due to the hole-trapping capacity of mercaptan groups [33]. As a result, TGA-capped CdS QDs showed weaker fluorescence intensity at lower solution pH.

It was reported that compounds containing amine group could enhance the fluorescence intensity of QDs [34]. Amine group could bind to the surface of CdS QDs through the N—Cd bond, which can eliminate the surface defects as efficient traps, thus, increased emission intensity was observed. The emission spectrum of the CdS QDs blue-shifted after the addition of MA (Fig. 1), indicating that MA bound to lower energy sits and this binding raised the site energy [35] of CdS QDs.

It was found that the adding sequence of MA and PBS into the solution of TGA-capped CdS QDs had great impact on the fluorescence enhancement extent of CdS QDs induced by MA. The fluorescence enhancement factor (3.2 fold) when PBS and MA were sequentially added to CdS QDs was much lower than that (6.3 fold) when MA was added first and then PBS was added (Fig. 3). When PBS was added to CdS QDs, which could lead to the protonation of TGA and the detachment of TGA from the surface of QDs, thus, aggregated QDs may form due to the loss of negative charges on QDs' surface. The aggregated QDs may not interact effectively with MA. If MA was added to CdS QDs' solution first, the vacancy sites on the surface of QDs due to detachment of TGA induced by PBS was occupied by MA promptly, leading to effective passivation of QDs by MA. If the mixture of MA and PBS was added to CdS QDs solution, similar FL enhancement factor was obtained as that when MA was added first and then PBS was added, which also indicated that the presence of MA in QDs solution was favorable for its effective substitution for the protonated TGA on the surface of QDs.

The possible detection mechanism for MA was illustrated in Scheme 1.

In this work, the volumes of the PBS and QDs solution on the fluorescence enhancement by MA were also investigated. The results are shown in Fig. 4A and B. The maximum enhancement ratio was obtained when the PBS and QDs solution with the volumes of 0.2 mL and 0.25 mL, respectively. As a result, 0.2 mL of PBS and 0.25 mL QDs solution were used for MA detection. In addition, it was found that the addition of MA could promptly induce FL enhancement of the QDs, indicating that the reaction between MA and the QDs was very fast.

3.2. Fluorescence detection of MA with TGA-capped CdS QDs

Under the optimum detection conditions, the MA concentration dependence of the fluorescence intensity of TGA-capped CdS QDs is shown in Fig. 5A, which showed that the emission intensity of TGA-capped CdS QDs increased as a Sigmoid curve in response to MA. When the concentration of MA reached the 1.0×10^{-3} M, the enhancement of the fluorescence intensity achieved a platform

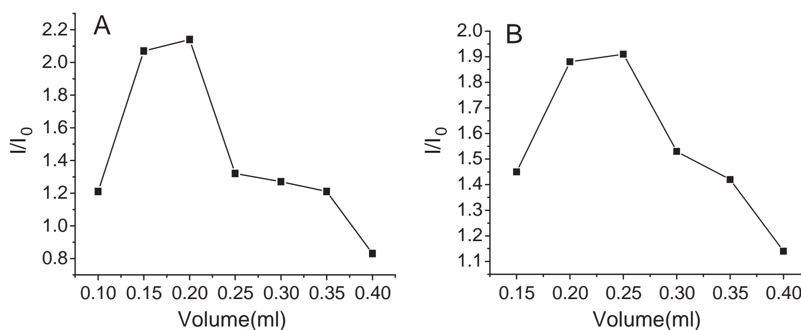

Fig. 4. (A) Effect of the volume of PBS on fluorescence enhancement. (B) Effect of the volume of the CdS QDs solution on the fluorescence enhancement. The concentration of MA is 1.0×10^{-4} M.

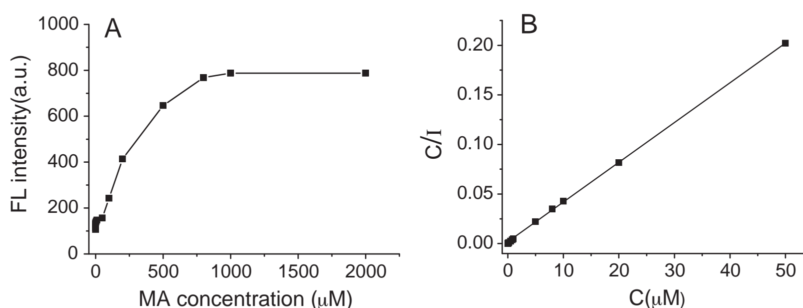

Fig. 5. (A) Effect of the concentration of MA on the fluorescence of TGA-capped CdS QDs. (B) Langmuir-binding isotherm relationship between fluorescence enhancement and the concentration of MA.

due to the saturation of binding sites. Moreover, the concentration dependence of the luminescence intensity follows the binding of MA to the surface of the TGA-capped CdS QDs and is effectively described by a Langmuir-type binding isotherm [14] as shown in Fig. 4B. The equation can be linearized to take the following form:

$$\frac{C}{I} = \frac{1}{BI_{\max}} + \left(\frac{1}{I_{\max}}\right) C$$

where $I_{\max}$ and I are the maximum fluorescence intensity in the presence of MA and the fluorescence intensity at a given MA concentration, respectively. C is the concentration of MA and B is the equilibrium binding constant. The linear range was from 2.0×10^{-9} to 5.0×10^{-5} M. The data fitting gave the correlation coefficient of 0.999 and the equilibrium binding constant of 2.2. The remarkable Langmuirian fit suggested that it was probable that more than one MA molecules bound to the surface of an individual QDs. The much smaller binding constant than that of cysteine bound to CdS QDs indicated a weaker binding affinity of MA to TGA-capped CdS. This observed weaker binding ability of MA for QDs was consistent with that of the reported weak interaction between amine and QDs [34]. A detection limit of 1.0×10^{-9} M was obtained on the basis of three times the standard deviation of eleven replicate measurements of the fluorescence intensity of the blank samples. The detection limit (1.0×10^{-9} M≈0.13 ppb) for MA was much lower than the safety limit (2.5 ppm in USA and the UK; 1 ppm for infant formula in China) [36]. In addition, the method was more sensitive than current colorimetric [37–40] and fluorescent [41] methods using organic probes.

The influence of other substances including Ca^{2+}, K^{+}, urea, vitamin C (Vc), vitamin B (Vb), alanine (Ala), methionine (Met), tryptophane (Trp), lysine (Lys), leucine (Leu), isoleucine (Ile), valine (Val), phenylalanine (Phe), Zn^{2+}, Fe^{2+}, Fe^{3+} and cyanuric acid (CA) on the fluorescence of TGA-capped CdS QDs was investigated, as shown in Fig. 6. It was observed that the investigated substances had almost no effect on the fluorescence intensity of TGA-capped

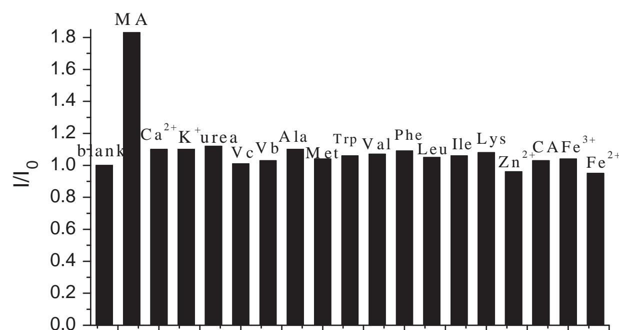

Fig. 6. Effect of MA and other relevant analytes on the fluorescence intensity of TGA-capped CdS QDs. The concentration of MA was 5.0×10^{-6} M. For others the concentration was 5.0×10^{-4} M and the concentration of Ca^{2+} was 3.3×10^{-4} M.

CdS QDs. Especially, high concentration of Ca^{2+} (3.3×10^{-3} M) also did not affect the fluorescence intensity of TGA-capped CdS QDs. The result indicated that the selectivity of this method was acceptable.

Table 1
Results of the determination of the MA in raw milk.

Original amount (μM)	Added (μM)	Found mean[a]	Recovery (%)	CV (%)
0	0.05	0.050	100	2.1
0	0.08	0.082	102	1.7
0	0.50	0.49	98	2.7
0	0.80	0.80	100	3.1
0	6.0	7.0	106	2.5
0	8.0	7.8	98	2.3
0	20.0	19.8	99	1.9

CV = relative standard deviation.
[a] The mean of three experiments.

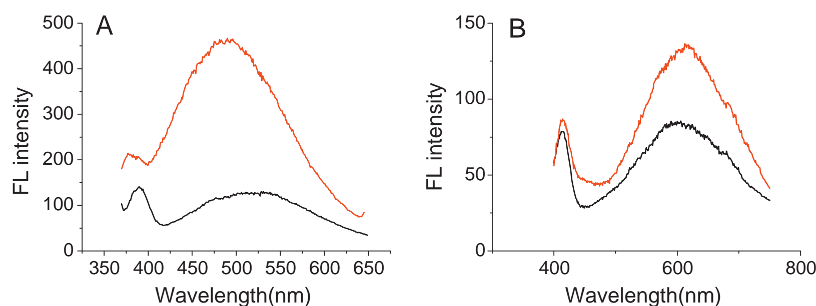

Fig. 7. Fluorescence spectrum of the Cys-capped CdS QDs (A) and Cit-capped CdS QDs (B) in the absence (a) and presence of 1.0×10^{-3} M MA (b).

3.3. Detection of MA in real samples

In order to validate the reliability of the proposed method, pretreated real liquid milk which spiked with different concentration of MA were detected according to the procedure described in Section 2.4. The results in Table 1 indicated that the recovery of the melamine was in the range of 98–106%. The result was indicated that this method could be applied successfully to the determination of MA in pretreated liquid milk products.

3.4. Effects of surface modifiers on fluorescence enhancement of CdS QDs by MA

Besides TGA-capped CdS QDs, Cys-capped and Cit-capped CdS QDs were also synthesized in order to investigate the effect of surface modifiers on fluorescence enhancement of CdS QDs by MA. As shown in Fig. 7, the same concentration of MA had a much less fluorescence enhancement extent for Cys-capped or Cit-capped CdS QDs than that of the TGA-capped CdS QDs. The fluorescence intensity increased by 7.8 fold for TGA-capped CdS QDs in the presence of 1.0×10^{-3} M MA while that was 3.7 and 1.6 fold for Cys-capped and Cit-capped CdS QDs, respectively. It was speculated that the amino of the L-cysteine would have competition role in the process of MA binding to the surface of the QDs. Thus, a smaller enhancement factor was observed for Cys-capped CdS QDs than that of Cit-capped CdS QDs. Blue-shift in the emission spectra was observed for TGA-capped and Cys-capped CdS QDs in the presence of MA. However, a little red-shift was observed for Cit-capped CdS QDs after its interaction with MA. So, there might be a different interaction between MA and Cit-capped CdS QDs from the interaction between MA and TGA-capped or Cys-capped CdS QDs. By investigating the absorption spectra, it was found that the characteristic absorption peak (at 235 nm) of C=N group of MA nearly vanished after the interaction between and MA and Cit-capped CdS QDs (Fig. S1, supplementary information), indicating that MA interacted with Cit-capped CdS QDs mainly through the heterocyclic N atom. The characteristic absorption peak of C=N group of MA almost did no change when MA interacted with TGA-capped or Cys-capped CdS QDs (Figs. S2 and S3, supplementary information). We speculated that the MA interacted with TGA-capped and Cys-capped CdS QDs mainly through the primary amine (NH_2) group. Due to that the primary amine group had much enhanced fluorescence effect for QDs than that heterocyclic N atom [34], much higher fluorescence enhancement factor was obtained for TGA-capped and Cys-capped CdS QDs than that of Cit-capped CdS QDs. The different interaction mode for Cit-capped CdS QDs and TGA-capped/Cys-capped CdS QDs may be due to the different surface state of QDs synthesized using different surface modifiers.

4. Conclusion

In summary, a simple and sensitive melamine sensor was developed using TGA-capped CdS QDs. The sensing mechanism was based on the passivation of surface states of TGA-capped CdS QDs through the amine group of MA, which led to fluorescence enhancement. Under the optimum conditions, the detection limit for melamine was 1.0×10^{-9} M. The method was applied to detect melamine in raw milk with satisfactory results. MA could lead to much higher fluorescence enhancement for TGA-capped CdS QDs than that of cysteine-capped and citrate-capped CdS QDs. The CdS QDs-MA system with much enhanced fluorescence intensity may find potential applications in the design of other sensitive fluorescence sensors.

Acknowledgements

This work was supported by The National Natural Science Foundation of China (Nos. 21005031 and 20903048), the Fundamental Research Funds for the Central Universities (JUSRP211A10), the Opening Foundation of the State Key Laboratory of Analytical Chemistry for Life Science of Nanjing University (KLACLS1008) and the Youth Scientific Foundation of Jiangnan University (No. 2009LQN11).

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.talanta.2012.02.062.

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