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ORIGINAL PAPER

A novel method for methimazole determination using CdSe quantum dots as fluorescence probes

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Abstract A novel method has been developed for methimazole analysis based on the quenching of fluorescence emission from CdSe quantum dots by methimazole. Under optimum conditions, the calibration graph was linear over the range of 50 nM to 5 μM (r^2=0.990). The limit of detection (S/N=3) was 30 nM. The R.S.D. for ten determinations of 500 nM methimazole was 3.4%. The method was applied to determine methimazole in tablets and rat urine, and the results were satisfactory, i.e. consistent with those of gas chromatography–mass spectrometry. The possible cause of fluorescence quenching is due to the exchange of surface capping organic molecules of quantum dots induced by methimazole.

Keywords CdSe quantum dots · Methimazole · Determination

Introduction

Methimazole (2-mercapto-1-methylimidazole) is an orally active drug widely used for the treatment of hyperthyroidism in human beings [1]. It has been found that methimazole may cause some side effects such as nephritis, liver cirrhosis or the decrease of white blood cells in the blood, etc. [2]. Methimazole has been prohibited in animal production in many countries, since it is illegally applied to animals to obtain a higher live weight gain for economic interests. The introduction of methimazole into the human food chain not only can lead to meat quality reduction, but also cause serious health implications to human beings [3]. Therefore, the detection of methimazole is of great importance in many areas including clinical chemistry, nutrition, as well as pharmaceutical formulations. Up to now, some methods based on various analytical procedures have been described for the determination of methimazole, such as liquid chromatography, reversed-phase high-performance liquid chromatography and high-performance liquid chromatography–mass spectrometry [4–6], gas chromatography–mass spectrometry (GC–MS) [7], potentiometric and voltammetric [8–9], flow-injection spectrophotometric [10], resonance light scattering spectroscopy [11], etc. However, these methods have their own limits, like expensive instruments, high cost, robust sample handling, and so on. It is necessary to develop simple, accurate and sensitive methods for the determination of methimazole.

The fluorescence (FL) probe method has attracted substantial interest in analytical chemistry since it is simple, sensitive and rapid [12]. As a kind of novel FL probe, quantum dots (QDs) have always been used in biology and medicine, recently especially in analytical chemistry [13]. So far, many papers have focused on the detection of metal ions with QDs via analyte-induced changes in photoluminescence [14]. However, little attention has been paid to the use of QDs as FL probes for drug detection. Based on the quenching of the FL of CdSe QDs by spironolactone, Liang et al. presented a simple, rapid and specific method for spironolactone determination, which considered that the changed surface-bound organic molecules of QDs were induced by spironolactone [15]. Lately, CdTe QDs as pH-sensitive FL probes were described for the determination of

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tiopronin by Wang et al. [16]. These researches revealed that QDs can be used as FL probes for drug molecules based on the changes of their luminescent properties. In this paper, the determination of methimazole based on FL quenching of CdSe QDs induced by methimazole is reported, and the method is successfully applied to the determination of methimazole in tablets and rat urine. The possible mechanism of reaction is also discussed.

Experimental

Reagents and chemicals

Selenium powder (200 mesh, 99.99%), CdO (99%), hexane (99%), methanol (99%), chloroform (99%), stearic acid (99%) were purchased from Shanghai Chemical Reagent Co., Ltd. (Shanghai, China, http://www.scrcc1.online.sh.cn) and used as received without any further purification. Methimazole tablets were obtained from Beijing Taiyang Pharmaceutical Industry Co., Ltd. (Beijing, China, http://www.taiyangpharm.com). Dioctylamine (DOA, 90%), methimazole (98%), tri-n-octylphosphine (TOP, 90%), tri-n-octylphosphine oxide (TOPO, 90%) and hexadecylamine (HDA, 90%) were purchased from Aldrich (Milwaukee, WI, http://www.sigmaaldrich.com). All other chemicals used were of analytical-reagent grade.

Apparatus

The FL and the resonance light scattering (RLS) spectra were obtained on a Perkin-Elmer Model LS-55 luminescence spectrometer equipped with a 20 kW xenon discharge lamp as a light source. The excitation wavelength was 380 nm. The ultraviolet and visible (UV–Vis) absorption spectra were obtained on a Thermo Nicolet Corporation Model evolution 300 UV–visible spectrometer. The Raman spectra were obtained with an inVia micro-Raman spectroscopy system (Renishow, UK), equipped with an He–Ne laser excitation source emitting a wavelength at 633 nm. GC–MS was obtained with a Varian CP-3800 gas chromatography/saturn 2200 MS system (Varian, USA).

Procedure

CdSe QDs were prepared according to the method reported previously, with some modifications [17]. Briefly, 0.016 g CdO and 0.32 g stearic acid were heated to 150 °C under nitrogen atmosphere. After CdO was completely dissolved, the mixture was kept in air to cool to room temperature. In the meantime, 2.4 g TOPO and 2.4 g HDA were added to the flask, and then the mixture was heated to 320 °C under nitrogen atmosphere. At this temperature, the selenium solution, prepared previously by dissolving 0.10 g selenium powder in 0.81 g TOP and 1.6 g DOA in a nitrogen-filled dry-box, was quickly injected into the reaction flask. After injection of the stock solution, the reaction temperature was maintained at 280 °C for 2, 4, 7 min for 2.6, 2.9, 3.3 nm diameter CdSe QDs. Monodisperse CdSe QDs were purified by precipitation, centrifugation, and decantation and re-dispersed in hexane, before keeping in the dark until further use.

Methimazole was dissolved in chloroform and diluted to an appropriate concentration with hexane. The FL, RLS and UV–Vis absorption spectra were obtained by adding different concentrations of methimazole to the CdSe QDs solution, then diluted with hexane to the mark and stirred for 15 min prior to FL measurements. The FL intensity was measured with the following settings on the spectrofluorometer (excitation wavelength (λ_{ex}), 380 nm; excitation slit (EX), 10.0 nm; emission slit (EM), 5.0 nm). The Raman spectra were based on a spectral range of 500–2,000 cm^{-1}. The samples were measured on quartz slides, and each spectrum was obtained in 10 s×3 collection times.

Sample preparation procedures

For the pharmaceutical analysis, ten tablets were weighed and powdered in a mortar. The average weight of a tablet was calculated. The powder was dissolved in chloroform/hexane (1:9 (*v*/*v*)) solution, and insoluble excipients and concomitants were removed from solution by centrifugation at 10,000 rpm for 8 min [15]. The solution was kept in the dark until further use. For the rat urine analysis, fresh rat urine was collected from small white Kunmin rats (25 g) within 24 h after a daily dose of 10 mg/kg for 3 days. Then the urine was extracted with chloroform (10 ml), centrifuged, separated and evaporated to dryness under a slow stream of nitrogen. The extracts were dissolved in chloroform/hexane (1:9 (*v*/*v*)) and the recommended procedure was applied [5, 7, 18].

Results and discussion

Characterization of CdSe QDs

The prepared CdSe QDs were characterized by the UV−Vis and FL spectra (Fig. 1). It can be seen that the line widths of the FL spectra are narrow (with the full width at half-maximum about 30 nm), which showed that as-prepared CdSe QDs were nearly monodisperse and homogenous [19]. The particle sizes and concentrations of the as-prepared CdSe QDs were calculated according to the calculation method specified in the literature [20]. The results showed that the particle diameters of the prepared

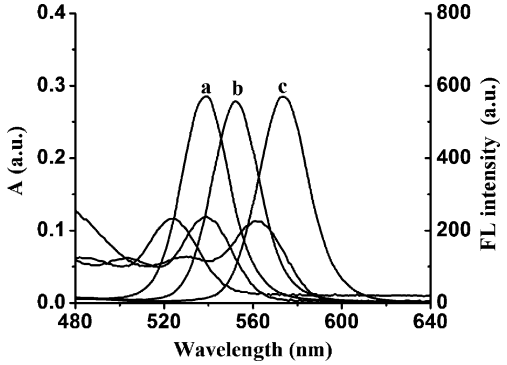

Fig. 1 UV–Vis absorption and FL spectra of CdSe QDs with different diameters (*a* 2.6 nm, *b* 2.9 nm, *c* 3.3 nm)

CdSe QDs were 2.6, 2.9, 3.3 nm and had concentrations of 16, 14, and 8.1 μM, respectively. In comparison to the FL emission of Rhodamine 6G (95%), the quantum yields of as-prepared CdSe QDs were 20% (2.6 nm), 18% (2.9 nm) and 17% (3.3 nm), respectively.

Effect of reaction time

Initial experiments demonstrated that the reaction between methimazole and CdSe QDs was slow. In order to make CdSe QDs and methimazole react sufficiently and save time, the FL intensity was collected after a fixed time (15 min).

Effect of sizes of CdSe QDs

Size effect is a basic characteristic of semiconductor nanoparticles. Many papers have shown the size-dependent property of semiconductor nanoparticles. In this study, the size effect on FL emission from CdSe QDs in the presence of methimazole was also investigated (Fig. 2). As shown in Fig. 2, the FL emission from different sizes of CdSe QDs gradually decreased with increasing amounts of methimazole. Also, slight red shifts of FL emission from CdSe QDs were observed. When the concentration of methimazole was more than 50 μM, almost all the emissions were quenched.

To further investigate the effect of sizes of CdSe QDs, the data was analyzed using the Stern–Volmer equation:

$$I_{\max}/I = 1 + K[Q]$$

Where $I_{\max}$ is the FL intensity of fluorophore in the absence of quencher; I is the FL intensity of fluorophore when the quencher is present at concentration $[Q]$; K is the Stern–Volmer constant. Table 1 demonstrates the good linear relationships between $I_{\max}/I$ and methimazole. The linear ranges depend on the size of the QDs (2.6, 2.9 and 3.3 nm) and are in the range of 50 nM to 5 μM, 100 nM to 5 μM, and 100 nM to 2.5 μM, respectively. The quenching constants (K) are 6.7, 3.4 and 2.7×10^6 L mol^{-1}. It was found that decreasing the CdSe diameter from 3.3 to 2.6 nm caused an increment in the values of K, indicating a systematic dependence of quenching on CdSe size. On the other hand, the value of the detection limit of small diameter CdSe was smallest. To summarize, FL experiments showed that the strength of interactions between CdSe and methimazole can be ordered: 2.6> 2.9>3.3 nm CdSe. This can be attributed to the fact that smaller QDs facilitated better surface coverage of methimazole, and thus a higher quenching efficiency of methimazole can be implemented as compared to larger CdSe QDs.

In this paper, the 2.6 nm diameter CdSe QDs was used as the FL probe for the determination of the methimazole sample. In optimum conditions, the methimazole concentration versus QDs FL gave a linear response with an excellent 0.990 correlation coefficient, between 50 nM and 5 μM, and the limit of detection (S/N=3) was 30 nM. The relative standard deviation for ten determinations of 500 nM methimazole was 3.4%.

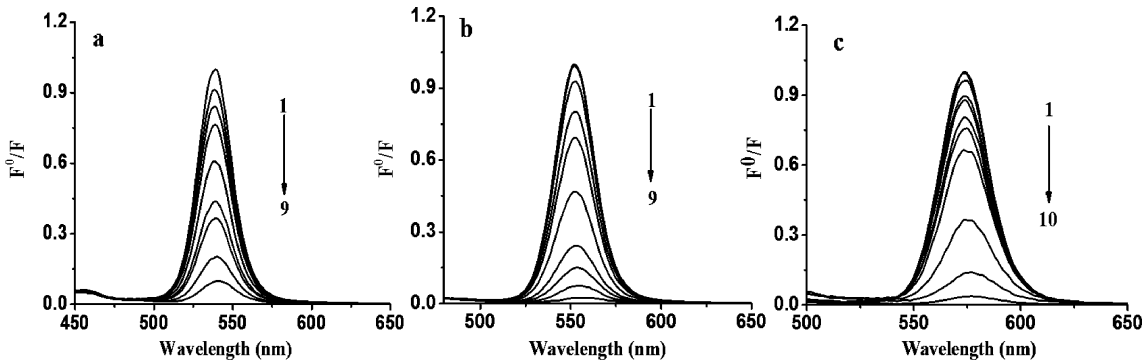

Fig. 2 FL response of CdSe QDs to addition of methimazole. λ_{ex}= 380 nm. **a** CdSe QDs: 2.6 nm; methimazole from 1 to 9: 0.0, 0.05, 0.25, 0.5, 1.5, 5.0, 7.5, 15, 50 μM; **b** CdSe QDs: 2.9 nm; methimazole from 1 to 9: 0.0, 0.1, 0.15, 0.25, 0.5, 0.75, 1.0, 2.5, 50 μM; **c** CdSe QDs: 3.3 nm; methimazole from 1 to 10: 0.0, 0.1, 0.25, 0.5, 0.75, 1.0, 1.5, 2.5, 3.0, 50 μM; The concentrations of CdSe QDs was 0.16 μM

Table 1 Stern–Volmer equations based on FL quenching in the system

The sizes of CdSe QDs (nm)	Regression equations	Correlation coefficients
3.3	$F_0/F=1+2.7\times10^6$ [Q]	0.987
2.9	$F_0/F=1+3.4\times10^6$ [Q]	0.976
2.6	$F_0/F=1+6.7\times10^6$ [Q]	0.990

F_0 and F are the FL intensity of CdSe in the absence and presence of methimazole, respectively; [Q] is the concentration of methimazole

Effect of methimazole on the RLS spectra of CdSe QDs

The RLS theory indicates that the increase in the extent of particle aggregation is one of the main reasons for the RLS enhancement [21]. Previous reports had proved that CdSe QDs become larger in the presence of amines, where a significant increase in RLS intensity was observed [19]. In this paper, the effects of methimazole on the RLS spectra of different sizes of CdSe QDs were also explored (Fig. 3). As shown in Fig. 3, increasing the concentration of methimazole gradually enhanced the scattering signal of CdSe QDs in the 300–500 nm wavelength range. The similar mechanism of larger particles of CdSe QDs being formed in the presence of methimazole can be used to explain the phenomenon in this paper. It was also found that decreasing the CdSe diameter from 3.3 to 2.6 nm caused a stronger enhancement of the RLS intensity. The result was in accordance with the effects of methimazole on the FL emission from different sizes of CdSe QDs. Both of the results show that the interactions between methimazole and CdSe QDs present a systematic dependence on CdSe size, namely, the smaller of the sizes of QDs, the more sensitive the method.

Application

Interference experiments for methimazole determination with the presented method showed that potential interferents have hardly any effect on FL emission of CdSe QDs (supplementary material). Later, the application of the elaborate method for methimazole determination was extended to methimazole tablets and rat urine samples. Parallel measurements were carried out with five similar samples by both the present method and GC–MS in this study [7]. The results obtained by this method were in good agreement with those of GC–MS, which are given in Table 2. In comparison with the other previous methods, the results obtained by the present method were satisfactory (Table 3).

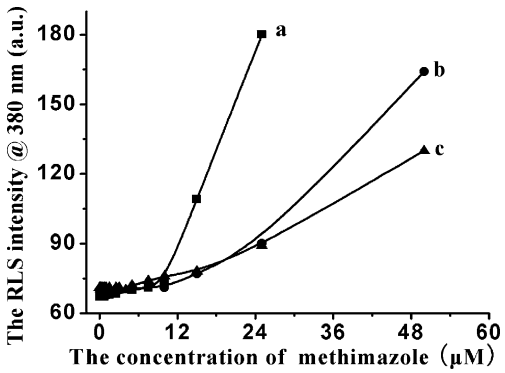

Fig. 3 RLS intensity of different sizes of CdSe QDs at 380 nm versus the concentration of methimazole (*a* 2.6 nm, *b* 2.9 nm, *c* 3.3 nm)

The mechanism of reaction

Several mechanisms for the quenching of FL emission from QDs are possible, including energy transferring, charge diverting, and surface absorption, surface bound complexation equilibrium attraction [14, 19], and others. In this study, with sulphydryl in methimazole, the surface of CdSe QDs may be changed after adding methimazole to the QDs solution, which may be the reason of the quenching of the FL emission from CdSe QDs.

To explore the mechanism of reaction, the UV–Vis absorption spectra of CdSe QDs were investigated in the absence and presence of the methimazole (Fig. 4). As shown in Fig. 4, methimazole had no absorption in the 300–700 nm wavelength range. So the quenching of FL emission of CdSe QDs was not attributed to the absorption of the emission wavelength by methimazole. A red-shift can be observed for the absorption spectra of CdSe QDs when adding methimazole to CdSe QDs solutions, which can be explained by the larger particles of CdSe QDs having formed in the presence of the methimazole. This result was in agreement with the study of the effect of methimazole concentration on the RLS spectra of CdSe QDs, and the aggregation of CdSe QDs might cause the FL quenching [19].

Raman spectroscopy is routinely used to investigate changes in the properties of nanoparticles [22]. The Raman spectra of normal CdSe QDs (a), CdSe QDs in the presence of methimazole (b) and methimazole (c) are given in Fig. 5. The bands at 837, 1,055, 1,134, 1,155, 1,297 and 1,442 cm^{-1} seen in spectrum (a) were associated with normal CdSe QDs. The bands at 837 cm^{-1} originate from

Table 2 Determination of methimazole in tablets and rat urine with this method and GC–MS

Sample	This method		GC–MS [7]
	Average value	RSD (%) (N=5)	
Rat urine	340 (μg·L^{-1})	3.5	342 (μg·L^{-1})
Tablets[a]	5.02 (mg/tablet)	3.2	4.99 (mg/tablet)

[a] The claimed values is 5 mg/tablet

Table 3 Comparison of the present method with published results for methimazole determination

Methods	Sample	Linear range & LODs	Comments	Reference
FI-CL	Tablets	17.5–876 μM; 8.75 μM	pH<7.0; interferents: cysteine, lysine, histidine, arginine, ascorbic acid, Co(II), Ni(II) and Cr(VI) etc.	[10]
Voltammetric	Tablets & human synthetic serum samples	1.0–100 μM; 0.5 μM	pH=7.0; interferents: thiols; samples without prior separation	[9]
Potentiometric	Tablets	1.0–700 μM; 0.5 μM	pH>7; drug samples without prior separation	[8]
RLS	Not mentioned	43.8 nM–2.28 μM; 2.01 nM	pH=5.2; interferents: thiols;	[11]
HPLC	Urine	2.0–10.0 μM; 1.0 μM	pH=5.5; Samples without prior separation or preconcentration	[6]
GC–MS	Urine	Not mentioned; 50 nM	Organic system; samples with prior extraction and derivatization	[7]
HPLC–MS	Thyroid tissue & meat	Not mentioned; detection capability 20 $\mu g \cdot kg^{-1}$	Organic system; samples with prior extraction and derivatization	[5]
LC	Human synthetic serum samples	2.19–43.8 μM; 1.31 μM	pH=7.5; samples with prior derivatization	[4]
This method	Tablets & rat urine	50 nM–5.0 μM; 30 nM	Organic system; interferents: thiols; drug samples without prior separation; rat urine with prior extraction	

the CH_3 wagging modes, and those at 1,055 and 1,134 cm^{-1} were ascribed to the C–N stretch vibrations from HDA and DOA, respectively [23]. The peaks at 1,155, 1,297 and 1,442 cm^{-1} were assigned to P = O stretch vibrations, $(CH_2)_n$ torsional vibrations and H–C–H bend vibrations, respectively [24]. In comparison, the Raman peaks of CdSe QDs at 1,155 cm^{-1} almost disappeared in the presence of methimazole (spectrum b), indicating that TOPO at the surface of QDs were partially replaced. Besides, the peaks at 837, 1,055, 1,297, 1,134 and 1,442 cm^{-1} became weak, which might be attributed to the decrease of the long-chain alkyl compounds. Further information was also provided by the appearance of peaks at 520 and 1,367 cm^{-1}, which might be due to methimazole being bonded on the surface of CdSe QDs.

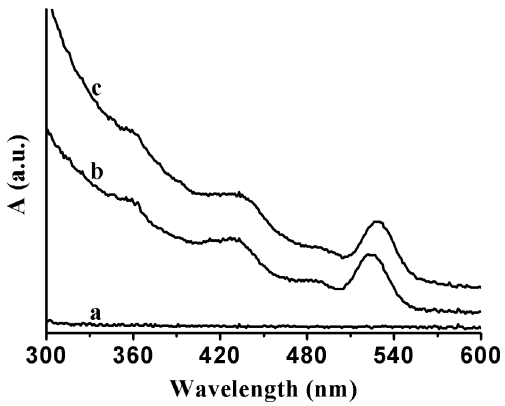

Fig. 4 UV–Vis absorption spectra of *a* 50 μM methimazole, *b* 160 nM CdSe QDs (2.6 nm) and *c* 0.16 μM CdSe QDs+50 μM mol L^{-1} methimazole

Normal methimazole exhibited four strong bands at 692, 1,270, 1,346 and 1,478 cm^{-1} (spectrum c). The peak at 692 cm^{-1} was assigned to C–S–H in-plane bending vibrations, and the peak at 1,270 cm^{-1} belonged to CH in-plane deformation (δ(CH)) mode. The later two bands (1,346 and 1,478 cm^{-1}) were both from imidazole ring stretching modes. In addition, some minor bands were also evident at 526 cm^{-1} (N–C–S in-plane bending vibrations), 910 cm^{-1} (ring in-plane deformation), 1,109 cm^{-1} (CH in-plane deformation and ring), 1,152 cm^{-1} (ring breathing) and 1,579 cm^{-1} (ring stretching) [25–27]. In comparison to spectrum (b) and (c), the peaks at 692 cm^{-1} almost disappeared in (c) and new peaks appeared at 520 and 1,367 cm^{-1} in (b). It is known that the Cd–S bond is much stronger than the Cd–N or Cd–P bond [17, 20]. Therefore, the disappearance of the peaks at 692 cm^{-1} was ascribed to the binding of methimazole on the surface of CdSe QDs

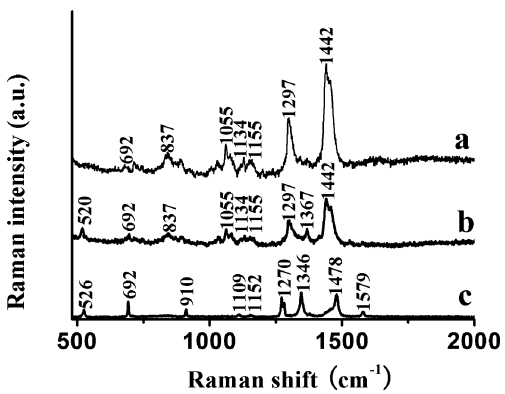

Fig. 5 Raman spectra of *a* CdSe QDs (2.6 nm), *b* CdSe QDs + methimazole, *c* methimazole

according to the Cd–S bond after adding methimazole to the CdSe QDs solutions. Then new N–C–S in-plane bending vibrations appeared on the surface of CdSe QDs at the peak of 520 cm^{-1} with a slight blue shift due to the changes of environment. The appearance of the peak at 1,367 cm^{-1}, which was due to imidazole ring stretching vibrations, was yet more evidence for methimazole present on the surface of QDs. The changes of peaks at 1,109 and 1,152 cm^{-1} were not obvious because the peaks overlap between methimazole and CdSe QDs. The disappearance of the peak at 1,270 cm^{-1} might be attributed to the changes of environment of the ring when it was on the surface of CdSe QDs. The changes of the bands at 910, 1,346, 1,478 and 1,579 cm^{-1} indicated that there were interactions between the imidazole ring and CdSe QDs, which might also cause the surface exchanges. In a word, the results of the Raman spectra indicated that the surface capping organic molecules of CdSe QDs were exchanged in the presence of methimazole.

As we know, the passivation of surface capping molecules plays a vital role in improving the FL efficiency of QDs, because it can eliminate the surface traps, which is the most common reason causing poor luminescence efficiency, according to the non-radiative recombination of light-generated charge carriers at these traps [28]. In this study, CdSe QDs with very strong passivation effect stabilized by TOPO/HDA groups, exhibited very high FL efficiency. However, after adding methimazole to CdSe QDs solutions, the surface molecules of CdSe QDs were shown to have been exchanged with methimazole, which might change the previous perfect surface passivation attained by capping a TOPO/HDA layer and cause the increase of surface defects. In addition, the exchanges of the surface molecules induced by methimazole might cause the reduction of stereo-hindrance effect provided by long-chain alkyl compounds. This may result in the aggregation of QDs, and then make surface traps increase. According to non-radiative recombination of light-generated charge carriers at these surface traps induced, the FL emission from CdSe QDs was quenched. Therefore, the possible quenching mechanism was due to the surface capping organic molecules of CdSe QDs being exchanged after adding methimazole to the QDs solutions.

Conclusions

In summary, the FL and RLS response of different sizes of CdSe QDs to methimazole was investigated in detail. It was found that the strength of interactions between CdSe and methimazole was systematically dependent on the size of CdSe QDs. Furthermore, the small size CdSe QDs were successfully used as a novel and highly sensitive FL probe for the determination of methimazole. Quenching of the FL emitted by the synthesized CdSe QDs allows the detection of methimazole concentration as low as 30 nM, thus affording a very sensitive detection system for this drug molecule. In addition, the method was applied to determine methimazole in tablets and rat urine, and the results were satisfactory. The possible quenching mechanism was due to the surface capping organic molecules of CdSe QDs being exchanged after adding methimazole to the QDs solutions.

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