J Fluoresc (2011) 21:1123–1129
DOI 10.1007/s10895-010-0788-9

ORIGINAL PAPER

Aqueous Synthesis of CdTe/CdSe Core/Shell Quantum Dots as pH-Sensitive Fluorescence Probe for the Determination of Ascorbic Acid

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Received: 13 August 2010 / Accepted: 9 December 2010 / Published online: 16 December 2010

Abstract By controlling the reflux time and the quantity of the shell materials, different sizes of thioglycollic acid (TGA) modified CdTe/CdSe core/shell quantum dots were synthesized in aqueous solution. This type of QDs was used for sensitive and selective determination of ascorbic acid in commercial tablets. Under optimal conditions, a good linearity was observed between the relative fluorescence (FL) intensity and the concentration of ascorbic acid in the range of 4.0 to 64.0 μg/mL with a correlation coefficient of 0.9968. The limit of detection was 2.4 μg/mL. This method was applied to the determination of the ascorbic acid in Vitamin C tablets and Vitamin C Yinqiao pills, and satisfactory results were obtained.

Keywords Aqueous · CdTe/CdSe · Ascorbic acid · pH-sensitive · Fluorescent

Introduction

Colloidal semiconductor nanocrystals, also named quantum dots, have been attracting extensive attention in the last decade. Due to their unique electronic and optical properties, they have been showing great potential especially in labeling, imaging and detection in biological and bioimaging applications [1–5]. Compared with traditional organic dyes, quantum dots (QDs) have unique optical advantages such as broad excitation spectra, tunable, narrow and symmetric emission spectra, high resistance to photo- and chemical degradation and high photostability [6–8], which make them a new type of luminescent materials as an alternative to organic dyes.

QDs are traditionally synthesized in organic solution using the high boiling point solvent of trioctylphosphine oxide (TOPO) or trioctylphosphine (TOP) [9, 10], but this method is complex, time consuming and toxic. Moreover, QDs synthesized in organic solution have to be transferred to aqueous solution by surface modification to meet the need of biological applications, which usually results in a significant decrease of the photoluminescence quantum yield (PL QY) and fluorescence stability of the QDs [2, 11, 12]. QDs can also be synthesized in aqueous solution, which is simpler, less expensive, less toxic and biocompatible [13]. Since aqueous phase synthesis of thioglycerol capped CdTe QDs was reported in 1996 for the first time [14], a variety of water soluble single core QDs have been successfully synthesized, but they are not so satisfying in all kinds of properties. Epitaxial growth of a semiconductor shell out of the single core quantum dots resulting in core/shell QDs is a useful ways to improve the quality of water dispersed QDs [15, 16]. Surface defects and nonradiative decay of the QDs can be reduced through this way. In recent years, the synthesis of core/shell QDs in aqueous media has been of great interest to many researchers. Up to now, several kinds of core/shell QDs have been synthesized in aqueous solution. But the CdTe/CdSe QDs have been seldom reported [17, 18].

Previous researches showed that fluorescence intensity of QDs varies with the pH change of the system. Susha AS et al. found that thioglycolic acid capped CdTe nanocrystals

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was pH sensitve in certain pH range and pointed out the potential use of water-soluble CdTe nanocrystals as pH sensor [19]. Yu et al. have used modified QDs as pH probe for the detecting of reaction kinetic study of hydrolysis of glycidyl butyrate catalyzed by porcine pancreatic lipase (PPL) [20]. Wang YQ et al. have studied mercaptopmpionic acid (MPA) modified CdTe QDs as pH sensor for the determination of tiopronin [21]. However, the studies of QDs as pH sensors and their applications are still very limited. Therefore, further and deeper researches are expected.

Ascorbic acid, also named Vitamin C, is a kind of important nutrient that can only be supplied by food but is crucially important for human body. It plays an important role in variety of biological events, such as collagen formation, amino acid metabolism, ion absorption [22] and so on. It is also an essential addictive in food processing industry. However, excessive intake of ascorbic acid can result in diarrhea, hyperacidity and kidney calculi [23]. Up to now, many techniques have been developed for the determination of ascorbic acid in food and tablets, including HPLC [24], flow injection analysis [25], potentiometry [26], spectrofluorimetry [27], enzymatic method [28], etc. Because of their simplicity and low cost, spectrofluorimetric methods have been used wildly in recent years. As of yet, however, no work has been reported for the determination of ascorbic acid using QDs as pH sensitive fluorescence probe.

In this paper, TGA capped CdTe/CdSe core/shell QDs have been prepared in aqueous solution and their optical properties and structural were characterized. By using this type of QDs as a pH-sensitive fluorescence probe, we developed a simple and rapid method for the selective determination of ascorbic acid. The proposed method was successfully applied in the determination of ascorbic acid in Vitamin C tablets and Vitamin C Yinqiao pills.

Experimental

Apparatus

All fluorescence measurements were made with RF-5301PC fluorescence spectrophotometer (Shimadzu, Japan) equipped with a 1 cm quartz cell. The absorption spectra were measured on a TU-1901 UV–vis Spectrophotometer (Beijing Purkinje General Instument Co., LTD, Beijing, China) using a 1 cm quartz cell. pH measurements were performed on pHs-3 C (Leici Analytical Instrument Factory, Shanghai, China). Powder X-ray diffraction (XRD) was taken on a D/max-2400 X-ray powder diffractometer (Rigaku, Japan) with Cu Kα radiation (λ=1.54056 Å). The sample was placed on the glass slide, and the scanning range was from 10° to 70°.

Materials

$CdCl_2 \cdot 2.5H_2O$ and Te powder were purchased from Sinopharm Chemical Reagent Co., Ltd. Se was obtained from Shanghai Meixing Chemical Co., Ltd. $NaBH_4$ was obtained from Shanghai Guangming Chemical Co., Ltd, China. Thiogycolic acid (TGA, 90%) was from Tianjin Guangfu Fine Chemical Research Institute, China. Ascorbic acid was purchased from Xi'an Chemical Reagents Factory, China. Vitamin C tablets and Vitamin C Yinqiao pills were bought from local drug store. All chemicals used are of analytical reagent grade without further purification. Distilled water was used throughout the whole work.

Preparation of CdTe QDs

TGA-modified CdTe QDs were synthesized in aqueous solution according to a previous method [29] with some modification. In brief, 4 mL of $CdCl_2 \cdot 2.5H_2O$ (0.1 mol/L) was diluted to 100 mL in a three-necked flask in the presence of 60 μL TGA as stabilizing agent, then the pH of the mixture was adjusted to 9.5 with NaOH (1.0 mol/L), followed by deaeration with N_2 for at least 30 min. 2 mL of freshly prepared NaHTe solution was injected into the Cd precursor solution dropwise under vigorous stirring. The molar ratio of Cd^{2+}:TGA:Te was fixed at 1:2:0.25. Then the mixture was refluxed at 100 °C for 3 h under N_2 atmosphere protection to promote the growth of QDs. The final concentration of the QDs was 1×10^{-3} mol/L according to the concentration of Te. The products were precipitated by 200 mL of acetone, thus the redundant Cd^{2+} and TGA were removed through centrifugation at 12,000 rmp for 5 min. The obtained precipitate was dried in N_2 atmosphere.

Stock Solutions for Shell Growth

The Cd precursor was prepared as follows: 10 mL Cd^{2+} (0.1 mol/L) and 150 μL TGA was dissolved in 15 mL H_2O. Then, the pH of the solution was adjusted to 11.2. The concentration of Cd^{2+} was 0.04 mol/L. 2 mL of 0.025 mol/L freshly prepared NaHSe solution under the protection of N_2 was used as Se precursor.

Preparation of CdTe/CdSe QDs

The dried CdTe QDs was re-dispersed in 100 mL distilled water in a three-necked flask and then the solution was deaerated by N_2 bubbling for 40 min. The resulting mixed

solution was heated to 75–80 °C under the protection of N_2 atmosphere.

2.5 mL of oxygen-free Cd precursor and 2.0 mL Se precursor was injected into the hot solution by dropwise addition with syringes simultaneously followed by several hours of reflux to promote the growth of the CdSe shell. Then, 2.0 mL of the reaction solution was taken out for the determination of its optical properties. This was defined as the 1 layer. Same procedure was repeated for the growth of the second layer. Using this method, CdTe with 1～4 layers of CdSe was finally synthesized.

Sample Treatment

For the pharmaceutical analysis, ten pills of Vitamin C tablets were weighed and powdered in a mortar. Average weight of each tablet was calculated and certain part of the powder was weighed and transferred into a 10 mL volumetric tube and diluted to the mark. The mixture was extracted in an ultrasonic bath for 15 min followed by centrifugation at 15,000 rpm for 10 min to remove the insoluble excipients. The supernatant was used for the following analysis.

For Vitamin C Yinqiao pills, the sugar-coats was removed. Then, the pills were powdered and proper quantity of the powder was transferred into a 10 mL volumetric tube and diluted to the mark, the following procedure was the same as Vitamin C tablets.

Analytical Procedure

200 μL of the CdTe/CdSe QDs was transferred into a 10 mL volumetric tube and diluted to the mark with distilled water and mixed thoroughly. Then the pH of the mixed solution was adjusted to 8.5 with 0.1 mol/L HCl. 2 mL of the mixed solution was titrated by successive adding 4.0 μL of 2.0 mg/mL ascorbic acid solutions. The fluorescence emission spectra were recorded from 220 to 770 nm (excitation wavelength 360 nm) using 5/5 nm slit widths.

All the experiments were performed at room temperature.

Results and Discussion

Characterization of CdTe and CdTe/CdSe Core/Shell QDs

Figure 1 depicted the fluorescence spectra and colour change of CdTe and CdTe with various thickness of CdSe shell. As can be seen in Fig. 1(a), the emission band of the bare-core CdTe was narrow and symmetrical with a sharp emission peak at 556 nm. With the growth of the shell thickness from 1 to 4 layers, a significant red shift of the maximum emission wavelength from 556 nm to 637 nm was obtained, and the colour of the reaction solution changed from green to yellow, red and deep red finally (Fig. 1(b)). This red shift can be attributable to the size increase of the QDs by overcoating CdTe with CdSe shell. Also, it can be seen from Fig. 1, with the growth of the shell, the full width at half-maximum (FWHM) gradually become wider. We concluded that this was caused by the Ostwald ripening of the QDs [30] and the distribution of the core/shell QDs with different shell thickness [31].

The synthesized CdTe/CdSe core/shell QDs exhibited good stability, when stored in darkness at 4 °C, the fluorescence intensity can kept stable for 3 months.

Figure 2 showed the UV/vis adsorption spectra of the CdTe and differnent sizes of CdTe/CdSe QDs. The maximum absorbance of CdTe was 512 nm. When the QDs were coated with CdSe, the absorption spectra were found to be redshifted during the shell growing process. The maximum absorbance was at 595 nm when the CdSe shell was 4 layers. This can be explained by the quantum

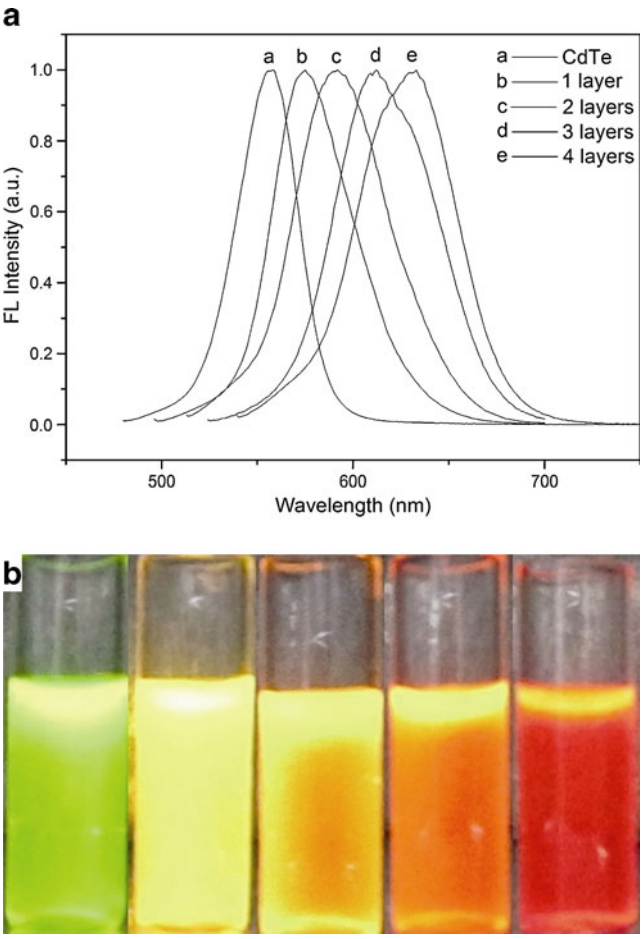

Fig. 1 Fluorescence spectra of CdTe and CdTe QDs with different thickness of the CdSe shell (**a**) and photograph of the nanocrystals under the irradiation of a UV lamp (**b**)

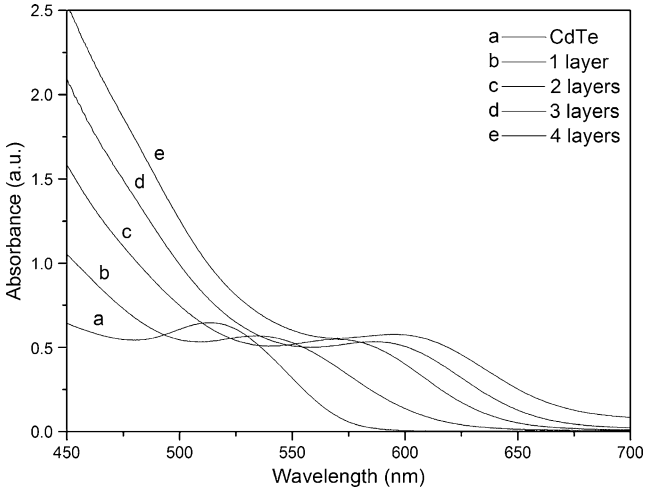

Fig. 2 UV/vis adsorption spectra of CdTe and CdTe QDs with different thickness of the CdSe shell

size effect theory: The maximum absorbance shifts to lower energy when the size of the QDs increases [32].

The formation of the CdSe shell was further supported by XRD results. The XRD patterns of CdTe and CdTe/CdSe with different shell thickness are present in Fig. 3. The broad peaks are typical for nanoparticles. The diffraction pattern of the bare-core CdTe QDs is consistent with that of bulk cubic CdTe structure. The three strong peaks at 23.7°, 39.8°, and 46.5° corresponded to the (111), (220) and (311) planes, respectively. It demonstrates that the prepared quantum dots have a zinc blende structure. By increasing the shell thickness of the CdTe/CdSe QDs, the diffraction pattern shifted to the higher angle. The diffractive peaks of the CdTe/CdSe QDs are between the cubic CdTe and cubic CdSe QDs. No separated CdSe diffraction peaks were observed, which indicated the formation of the core/shell structure. The results were similar with the CdTe/CdS and CdTe/CdSe core/shell structures reported previously [31, 33].

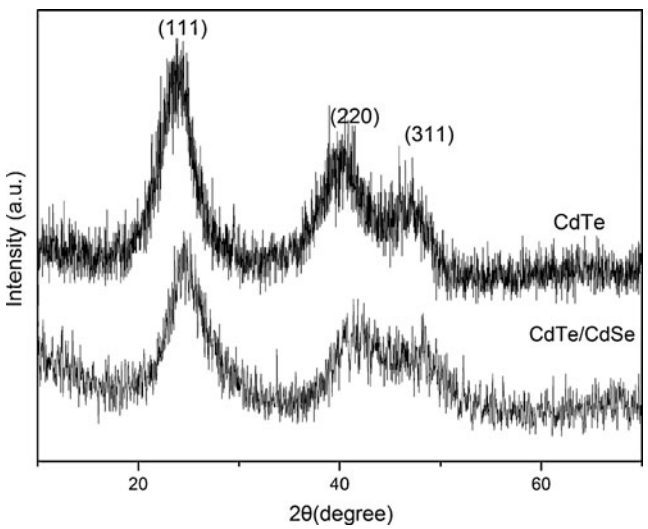

Fig. 3 X-ray diffraction patterns of CdTe and CdTe/CdSe QDs with 4 layers thickness of CdSe shell

Relationship Between pH and Fluorescence Intensity of the QDs

It has been reported that pH values greatly influence the fluorescence intensity of QDs. Here, the relationship between different pH values and the fluorescence intensity of CdTe/CdSe QDs was studied. Fluorescence intensity of QDs diluted in NaH_2PO_4-Na_2HPO_4 buffer solutions with different pH was recorded. As can be seen from Fig. 4, fluorescence intensity of the QDs kept increasing as the pH values changed from 4.3 to 8.5, and then decreased with the pH values continued to increase. A slightly red-shift of the maximum emission peak was observed when the pH value was low (See inset of Fig. 4). According to that, the pH range of 4.3 to 8.5 was selected for the determination of ascorbic acid.

Fluorescence Quenching of QDs Caused by Ascorbic Acid

Ascorbic acid is a weak acid in aqueous solution. In order to ascertain whether the fluorescence quenching was mainly caused by the pH change due to the adding of ascorbic acid, effect of ascorbic acid on the fluorescence intensity of the core/shell QDs diluted by 0.05 mol/L NaH_2PO_4-Na_2HPO_4 (pH 8.5) buffer solution was studied. As shown in Fig. 5, the fluorescence intensity of the QDs changed very slightly with the addition of ascorbic acid. Also, the pH change was measured while the concentration of ascorbic acid increased. The experiment results showed that the pH decreased slightly from 8.53 to 8.39 when the concentration

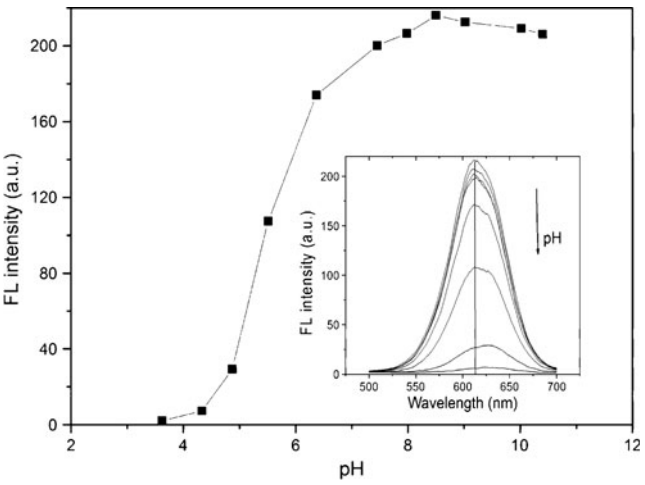

Fig. 4 Effect of pH on the fluorescence intensity of the CdTe/CdSe QDs. The pH values were 3.62, 4.33, 4.87, 5.51, 6.37, 7.45, 7.98, 8.50, 9.02, 10.02 and 10.40; Inset: The FL spectra of the QDs from pH 8.50 to 4.33

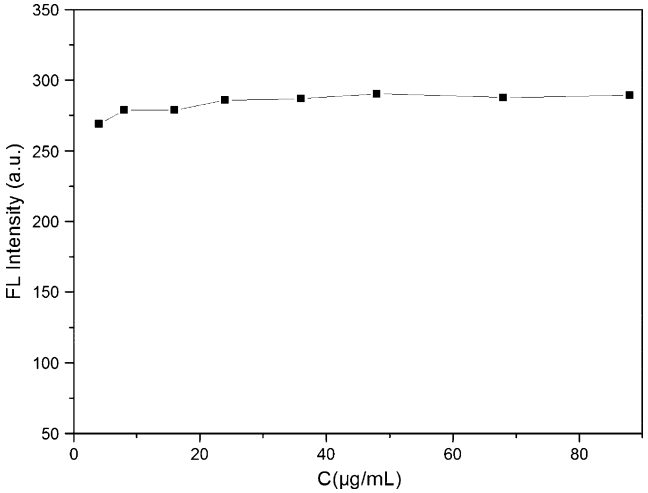

Fig. 5 Effect of ascorbic acid on the fluorescence intensity of the QDs in the NaH_2PO_4-Na_2HPO_4 buffer solution with pH 8.5

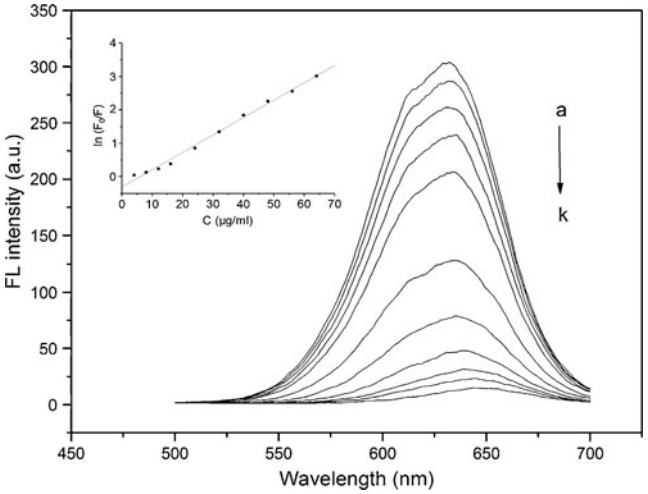

Fig. 6 FL spectra of the CdTe/CdSe QDs in the presence of different concentration of ascorbic acid. The final concentration of the ascorbic acid was (*a*) 0, (*b*) 4.0, (*c*) 8.0, (*d*) 12.0, (*e*) 16.0, (*f*) 24.0, (*g*) 32.0, (*h*) 40.0, (*i*) 48.0, (*j*) 56.0, and (*k*) 64.0 μg/mL; Inset: Calibration curve for the fluorescence quenching of the QDs by ascorbic acid. [QDs] = 2.0×10^{-5}mol/L

of ascorbic acid increased from 0 to 80.0 μg/mL. So it was concluded that the pH change caused by the addition of ascorbic acid induced the fluorescence quenching of the QDs.

Optimization of the Analytical Procedure

Effect of Temperature and Reaction Time

Since the temperature of the reaction system did not affect the fluorescence intensity greatly, room temperature was selected for convenience. According to the experiments, the fluorescence intensity of the system can reached equilibrium immediately after intensive mixing and changed slightly in 15 min. We finally chose 1 min after intensive mixing as the best reaction time.

Effect of the Concentration of the CdTe/CdSe QDs

The optimal concentration of the QDs should given the highest sensitivity and the widest linear range of response to the target analyte. The experimental results indicated that when the concentration was low, significant fluorescence quenching can be obtained and the sensitivity was relatively high. When the concentration increased, the fluorescence intensity became stronger and the linear range was wider. To give consideration to both the sensitivity and the linear range, 2.0×10^{-5} mol/L (referring to the concentration of corresponding bare-core CdTe) was finally employed as the best QDs concentration throughout the experiment.

Calibration and Sensitivity

A serial fluorescence spectra of QDs in the presence of different amount of ascorbic acid was recorded under the optimal reaction conditions. As shown in Fig. 6, with the gradual addition of ascorbic acid, a significantly fluorescence quenching and a gradual red-shift of the emission peak were observed, especially for high concentration of ascorbic acid. And the pH of the system was 8.47, 7.69, 6.81, 4.73, 4.44, 4.28 while the ascorbic acid concentration was 0, 4.0, 12.0, 32.0, 48.0, 64.0 μg/mL separately. The results further confirmed the conclusion that the fluorescence quenching was caused by the pH change.

There was a good linearity between $\ln(F_0/F)$ and C (concentration of ascorbic acid, μg/mL) in the range between 4.0 to 64.0 μg/mL with a correlation coefficient of 0.9968 (See inset of Fig. 6). The regression equation was $\ln(F_0/F) = 0.052C - 0.312$. The limit of detection (calculated following the 3σ IUPAC criteria) was 2.4 μg/mL. The relative standard deviation for a set of 6 measurements of 10.0 μg/mL ascorbic acid was 2.2%, which indicated that this method has good precision and accuracy.

Table 1 Effect of foreign substances on the QDs-ascorbic acid system under optimal condition. [Ascorbic acid]=8.0 μg/mL

Coexisting substance	Concentration (μg/mL)	Change of F (%)
Glucose	200	−4.22
β-CD	50	−3.26
SDS	180	−1.90
Urea	30	−3.14
Sodium citrate	50	3.19
Ammonium tartrate	80	3.73
NaCl	300	−4.59
NH_4Cl	40	−3.27

Table 2 The determination results of the real samples (n=5)

Sample	Labled value (μg/mL)	Average found (μg/mL)	R.S.D.%	Added	Total found (μg/mL)	Recovery (%)
Vitamin C tablets	15.0	14.96	1.4	15.0	30.76	105
	15.0	15.10	1.8	25.0	39.93	99
Vitamin C Yinqiao pills	–	13.10	3.7	25.0	38.50	102

Effect of Foreign Substance

In order to assess the selectivity of the proposed method, effect of foreign substances on the fluorescence intensity of the CdTe/CdSe QDs system containing 8.0 μg/mL ascorbic acid was evaluated. Experiments results showed that some metal ions, such as Cu^{2+}, Zn^{2+}, Hg^{2+} can severely interfere with the determination due to their intensely interaction with QDs. But, their concentrations in the tablets are always very low, and could hardly interfere with the fluorescence intensity of the systems. Several excipients that are often in presence of the commercial tablets were tested and the results were showed in Table 1. The tolerance concentrations of these excipients were much higher than their concentrations in the tablets. Therefore, we can conclude that this method has high selectivity and can be applied in the determination of ascorbic acid in tablets.

Quenching Mechanism

There have been many researches on the relationship between the fluorescence intensity of QDs and the pH. As the fluorescence quenching of the CdTe/CdSe QDs caused by ascorbic acid was mostly because of the pH change of the system caused when ascorbic acid was added. We deduced that when ascorbic acid was added, pH of the system decreased, leading to the deconstruction of the Cd^{2+}-TGA complexes' annulus due to the protonation of the surface-binding thiolates [34]. Then part of the TGA dissociated from the surface of the QDs and the aggregate of the uncapped QDs given rise to the fluorescence quenching [35] and the red-shift of the emission peak to longer wavelength.

Analytical Applications

To demonstrate the proposed method was feasible, it was applied to the determination of ascorbic acid in commercial Vitamin C tablets and Vitamin C Yinqiao pills. The results obtained by standard addition method were showed in Table 2. It can be seen that the RSD was lower than 3.7% and the average recovery of the real samples was between 99% and 105%, which indicated that the proposed method can meet the requirement of microanalysis and was practical for the determination of ascorbic acid in commercial tablets.

Conclusion

In summary, TGA modified CdTe/CdSe core/shell QDs with different shell thickness was directly synthesized in aqueous solution. The obtained core/shell structure nanoparticles exhibited great stability. It was found that ascorbic acid can effectively quench the fluorescence intensity of such QDs. Based on this phenomenon, it was used as fluorescent probe for the sensitive and selective determination of ascorbic acid for the first time, and satisfactory results were obtained.

Acknowledgements This work was supported by the National Natural Science Foundation of China (Nos. 20875040, J0730425).

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