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CdTe quantum dot-based pH-sensitive probes for ascorbic acid determination

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TGA-modified CdTe quantum dots were used as pH-sensitive probes for the determination of ascorbic acid in aqueous solutions. The fluorescence of the water-soluble QDs could be irreversibly quenched by H^+ and the fluorescence intensity of the water-soluble QDs decreased linearly as the pH decreased in the range of 6.45~8.22. Based on this phenomenon, a simple, rapid and specific method for the quick determination of ascorbic acid was proposed. Under optimum conditions, the relative fluorescence intensity was linearly proportional to the concentration of ascorbic acid between 1.25×10^{-5} and 1.00×10^{-4} mol/L with correlation coefficient of 0.9981. The limit of detection was 3.6×10^{-6} mol/L. The relative standard deviation (RSD) was 2.1% for a 3.75×10^{-5} mol/L ascorbic acid. As an application, the proposed method was successfully applied to the analysis of ascorbic acid in medical samples including drug tablets and injection solutions, and the results were consistent with those obtained by oxidation–reduction titration method. In addition, the quenching mechanism was also described. CdTe QDs were found to be a satisfactory pH-sensitive probe that could serve as the potential development of fluorescence sensors.

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Keywords: CdTe quantum dots, pH sensitive, Fluorescence quenching, Ascorbic acid, Determination

1. Introduction

Colloidal semiconductor nanocrystals (NCs), also called quantum dots (QDs), have attracted tremendous attentions in the past two decades because of their high emission quantum yields, good chemical and photo stability, size-tunable emission profiles and narrow spectral bands in comparisons with conventional organic fluorophores [1-3]. Recently, the great advances in the surface chemistry of QDs allow them to be effective in practical applications, such as multicolor biological imaging and detection [4-11].

In recent years, QDs have attracted considerable attention as novel ion probes. Chen and Rosenzweig demonstrated the first example of Cu(II) and Zn(II) ions analysis by utilizing CdS luminescent QDs capped by different ligands in aqueous media [12]. Liu FC et al demonstrated a highly selective and sensitive approach for detection of Cu^{2+} based on the fluorescence quenching of PDDA/GSH-QDs composites [13]. Susha et al the first proposed water-soluble CdTe QDs would be developed into promising pH-sensitive probes [14]. Yu DH et al found QDs to be a satisfactory pH probe that could indicate for enzymatic hydrolysis of paraoxon [15]. It was found that a subtle perturbation of the surface property of QDs could result in a dramatic change in their fluorescent emission properties. Xia YS et al investigated the interaction of several cationic surfactants with CdTe QDs modified with thioglycolic acid (TGA) [16]. The results showed that cationic surfactants dramatically quenched the fluorescence of CdTe QDs. The extent of quenching was linearly proportional to the concentration of cationic surfactants from 2.0×10^{-7} to 7.0×10^{-6} mol/L, the detection limit was 0.5×10^{-6} mol/L with correction coefficient 0.997. The above study results are in consistence with that based on the view point of surface chemistry, all the quenching processes of QDs are the result of surface structure change of QDs.

To the best of our knowledge, there are only a few reported on pH sensitive probes. It was also found that only a few reports involving in QDs as probes for the determination of pharmaceutical. Wang YQ et al used CdTe as pH sensitive probe for determination tiopronin [17]. It was found that the quenching degree of CdTe QDs with concentration of tiopronin was linear in the range of 0.15~20 μg/mL with correlation coefficient of 0.998. The limit of detection was 0.15 μg/mL. Sun JF et al established a novel CdSe quantum dots-based technology platform in aqueous solution for the determination of vitamin B1 [18]. The linear relationship was observed between 5.00 and 40.0 $\mu g\cdot ml^{-1}$ with a correlation coefficient of 0.9963 for vitamin B1 determination and the detection limit of 70 $ng\cdot ml^{-1}$.

Ascorbic acid is a weak acid, which are an unsaturated lacton (Fig. 1) and a vital vitamin in human nutrition. It plays an important role in maintaining human health, which is known to protect against most aging-related and chronic diseases, such as cardiovascular disorders and

cancer. Commonly, the human body cannot synthesis ascorbic acid by itself. The standard content of ascorbic acid in pharmaceutical is considered a fundamental marker of the quality and value. Therefore, a reliable and easy method was needed for the determination of ascorbic acid. Numerous titrimetric [19, 20], electroanalytic [21, 22], and spectrometric [23, 24] methods for ascorbic acid determination have been proposed so far. In this work, a new method for the determination of ascorbic acid was proposed, which takes advantage of CdTe QDs as pH-sensitive probes, based on fluorescence quenching extent of CdTe QDs caused by pH changes when adding ascorbic acid in aqueous medium.

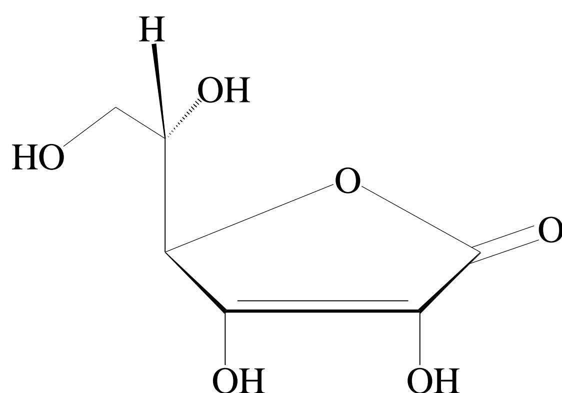


Fig. 1. Structural formula of ascorbic acid.

2. Experimental section

2.1 Instruments

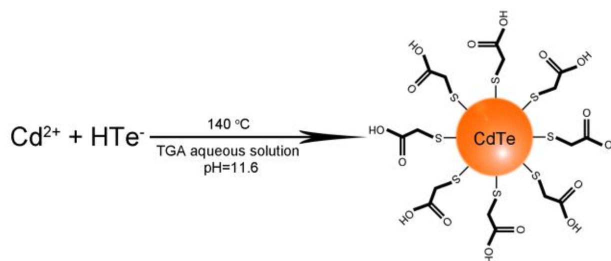
Fluorescence spectra were obtained on a LS-55 luminescence spectrometer (Perkin-Elmer, USA). Absorption spectra were recorded on a UV-2100 spectrometer (Rui Li Analytical Instrument Co., Beijing, China). Two cuvettes of 1 cm path length were used to measure the fluorescence spectra and absorption spectra, respectively. All optical measurements were performed at room temperature under ambient conditions. pH measurements were made using a pH meter (pH-3C; Hangzhou, China).

2.2 Reagents and materials

Thioglycolic acid, sodium borohydride (96%), tellurium powder (99.99%) was purchased from the Company of Chemical Reagent in Shanghai, China. Cadmium chloride was purchased from the Beijing Chemical Plant, China. Sodium hydroxide and hydrogen chloride were obtained from Shenyang Huabo Company, China. All chemicals reagents used in the experiments obtaining commercially were of analytical grade and were used without further purification, and double distilled water was used throughout the experiments.

2.3 Sythesis of CdTe QDs

The TGA-capped CdTe QDs were synthesized based on our group previous literature reports [25]and briefly described as follows. The synthesis reaction was expressed as following equation:



NaHTe solution was produced by reaction of sodium borohydride with tellurium powder in the circumstance of ice bath and vigorously stirred continuously until the black tellurium powder disappeared and sodium tetraborate white precipitation appeared on the bottom of the flask instead. Subsequently, thioglycolic acid, as a stabilizer, was injected into nitrogen-saturated 2×10^{-2} mol/L $CdCl_2$ aqueous solution at pH value of 11.6. The molar ratio of Cd^{2+}:Te^{2-}:TGA was fixed at 1:0.5:2.5. The whole process was in the presence of surrounding with N_2 and ice bath. Finally, The CdTe precursors were transfered into a pot of polytetraflourethylene. The stable photoluminescent CdTe QDs of different sizes were synthesized at temperature controllable cabinet drier via heating some time at 140°C. The concentration of CdTe QDs was estimated to be 5.0×10^{-3} mol/L according to the final concentration of NaHTe.

2.4 Reaction of ascorbic acid with CdTe QDs

200 μL CdTe QDs was diluted with 5.8 mL double distilled water. Transfer 100 μL QDs into nine 5.0 mL tubes，respectively. Then 0, 50, 100, 150, 200, 250, 300, 350, and 400 μL with the concentration of 1.0×10^{-3} mol/L ascorbic acid solutions were added to the tubes, respectively, and the total volume of the mixed solution was made up to 4.0mL with double distilled water. It should be emphasized that the ascorbic acid was readily oxidized in the presence of oxygen. In this condition, the fluorescence spectra were measured in turn within 10 min at room temperature to obtain relative stable and accurate fluorescence intensity. The luminescence intensity of the solution was recorded at 520 nm with excitation wavelength at 360 nm. Both slit widths of excitation and emission were 10 nm.

2.5 Sample treatment

Tests were carried out on the determination of samples of one tablet and of one injection samples. Both of tablets and injections were obtained from local drugstores. For the determination of ascorbic acid in pharmaceutical, twenty ascorbic acid tablets were weighted and powdered in a mortar. After calculating the average weight of one tablet, representative portions of the 0.1216 g powder (about 0.1 g ascorbic acid) was dissolved in 50 mL water, at maximum speed, insoluble excipients were removed via qualitative filter paper filtering. Filter paper and the residue washed twice with pure water. Then, the solutions were transferred into 250 ml volumetric flask, diluted to mark with distilled water. As to injection, 200 μl of it was transferred exactly into a 100-ml volumetric flask, and diluted to the mark with distilled water.

3. Results and discussion

3.1 Characterization of CdTe QDs

Using the above process, CdTe QDs were prepared, and their absorption and photoluminescence spectra are shown in Fig. 2. It can be seen that the photoluminescence spectrum relative symmetric and narrow, revealing that the as-prepared CdTe QDs posed well monodisperse and homogenous. According to the following empirical formula [26], the particle size of as prepared CdTe QDs could be estimated from their corresponding excitonic absorption peaks.

$$D = (9.8127 \times 10^{-7})\lambda^3 - (1.7147 \times 10^{-3})\lambda^2 + (1.0064)\lambda - 194.84.$$

Where D (nm) is the size of the given CdTe QDs, and λ (nm) is the wavelength of the first excitonic absorption peak of the corresponding sample. The results indicated that the average diameter of CdTe QDs was 1.87 nm.

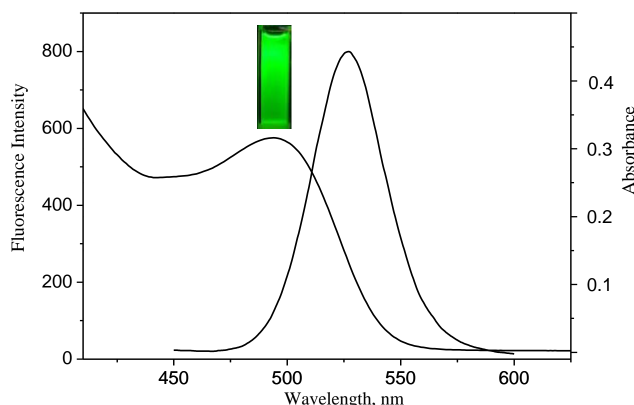


Fig. 2. Absorption and fluorescence emission spectra of CdTe QDs.

3.2 Fluorescence quenching caused by ascorbic acid

In our study, effect of concentration of ascorbic acid on fluorescent intensity of CdTe QDs was investigated in pure water medium CdTe QDs medium. As is shown in Fig. 3, with the addition of different concentrations of ascorbic acid solutions, the fluorescence intensity of CdTe QDs were quenched obviously, as well as the emission peak shifted red. It was found that ascorbic acid quenched the fluorescence intensity of CdTe QDs in a concentration dependence that possesses a good linear relationship, which was shown in the inset of Fig. 3. Herein, the dependence between QDs fluorescence intensity and the concentration of ascorbic acid was established.

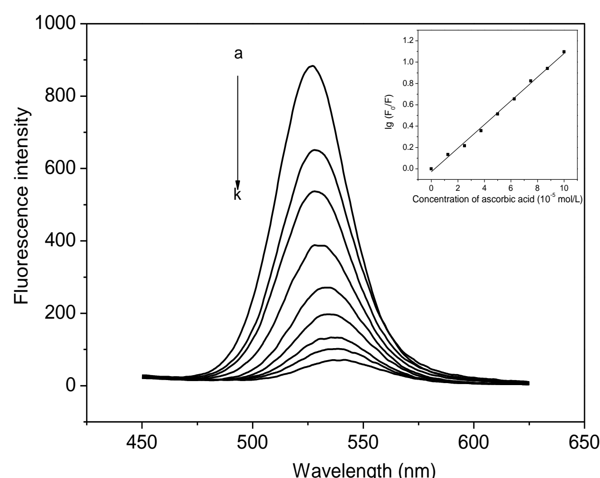


Fig. 3. Effect of concentration of ascorbic acid on fluorescent intensity of CdTe QDs (Curve a ~ k, the final concentration of ascorbic acid was 0, 1.25×10^{-5}, 2.50×10^{-5}, 3.75×10^{-5}, 5.00×10^{-5}, 6.25×10^{-5}, 8.75×10^{-5} and 1.00×10^{-4} mol/L, respectively).

3.3 Effect of reaction time

Just as demonstrated in our initial experiments, ascorbic acid quenching of CdTe QDs reached equilibrium within 3 min, and the fluorescence signal kept stable for more than 20 min in the room temperature, which was shown in Fig. 4. Based on this phenomenon, we chose 5 min as the optimum reaction time for recording the fluorescence intensity.

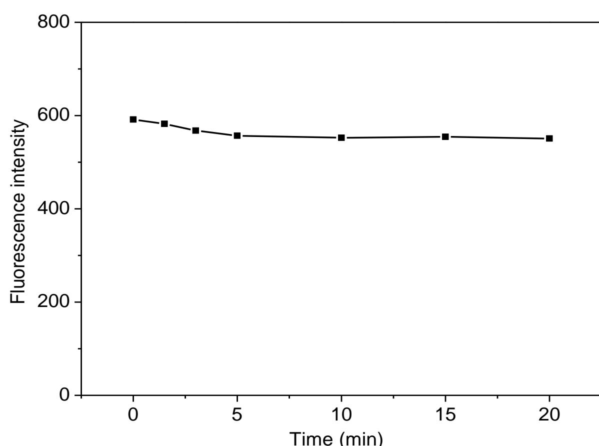


Fig. 4. Effect of reaction time on fluorescence intensity of CdTe QDs.

3.4 Effect of medium pH

It has been demonstrated that the fluorescence intensity of water-soluble QDs sensitizes with pH values [27]. However, the effect of pH on the fluorescence response of CdTe QDs in aqueous solution varied with different reports [28-30]. As shown in Fig. 5, the fluorescence intensity of QDs under different pH values were investigated using 0.05 mol/L PBS buffers in the range between 4.92 and 11.47，which confirmed the above finding. It was found that the fluorescence intensity of QDs linearly increased by 2.40 fold with pH varying from 6.45 to 8.22, as shown in the inset of Fig. 5. The results obtained from this study showed pH in the interval of 6.45 to 8.22, the fluorescence signals of CdTe QDs were sensitive to H^+.

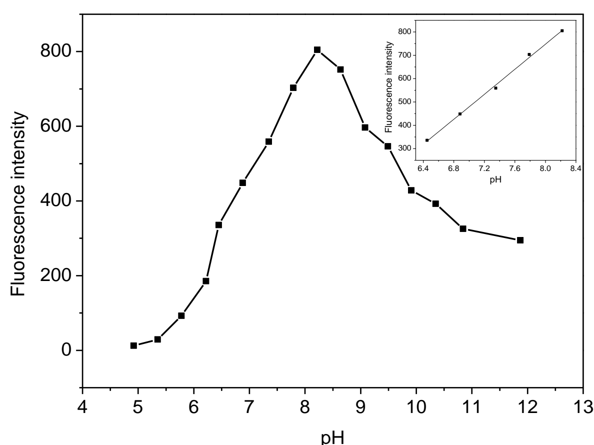


Fig. 5. Relationship between fluorescence intensity of QDs and pH values.

3.5 Effect of the CdTe QDs concentration and size

As to the concentration of CdTe QDs, either too high or too low could not obtain optimum detection results. When the concentration of QDs was too high, the relative magnitude of quenching effect by lower concentration of ascorbic acid decreased, namely, relatively higher concentration of ascorbic acid will be needed to quench the QDs. Under this condition, the sensitivity for detecting ascorbic acid will be reduced. However, when the concentration of QDs was too low, QDs were not quantitatively quenched by a given concentration range of ascorbic acid, that is, the relative limited QDs quenched by higher concentration of ascorbic acid. Thus, the linear range will be decreased; even the ascorbic acid in the system can not be detected accurately, which was shown in Fig. 6. Based on these factors, 4.17×10^{-6} mol/L of CdTe QDs was adopted. It is well known that the small sized CdTe QDs possess more effective quenching efficiency than the larger ones, according to the previous literature reported by Scaiano group [31]. Herein, it was found that the smaller sized CdTe QDs were more suitable for constructing sensitive and selective H^+ sensing system. Based on our investigations, the smaller sized CdTe QDs were chosen for further experiments to obtain higher analytical sensitivity.

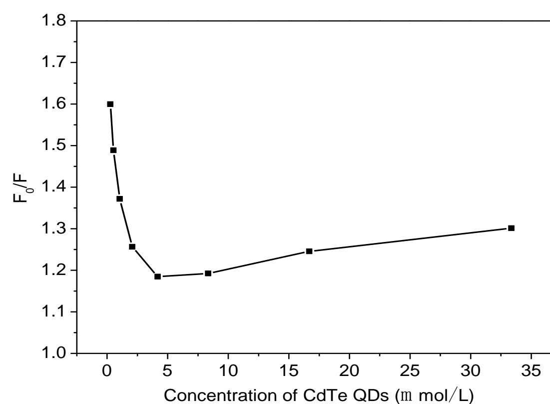


Fig. 6. Quenching of ascorbic acid of 2.5×10^{-5} mol/L on fluorescence intensity of CdTe QDs of different concentration.

3.6 Effect of coexisting substances

In order to evaluate other possible interferences in practical application system, a systematic investigation of the interferences of coexisting substances on the the determination of ascorbic acid was carried out. The response of CdTe QDs to relevant species was shown in Table 1. Glucose, sucrose, starch, EDTA, SDS, magnesium stearate, and fructose, which commonly co-exit with ascorbic acid, were found to show little interference. High concentration of Cl^-, I^-, Mg^{2+}, Ca^{2+}, Fe^{2+}, Zn^{2+}, and Al^{3+} did not produce any noticeable effect on the

fluorescence intensity of CdTe QDs. On the other hand, Fe^{3+} and some heavy metal ions, such as Cu^{2+}, Hg^{2+}, Ag^{+}, Pb^{2+} and Cd^{2+} interfered the fluorescence signal of CdTe QDs strongly. Generally, the amount of metal ions in the pharmaceutical samples was strictly limited, usually controlling in the level of below 1μg/mL, and the sample was diluted before determination. Thus, the interferences in the process of determination of ascorbic acid could be ignored.

Table 1. Influences of coexisted substances.

Coexisting substance	Coexisting concentration (10^{-5} mol/L)	Change of F (%)	Coexisting substance	Coexisting concentration (10^{-5} mol/L)	Change of F (%)
K^{+}, I^{-}	100	+3.61	Cd^{2+}, Cl^{-}	5.0	+16.9
Mg^{2+}, Cl^{-}	80	-3.47	Pb^{2+}, NO_3^{-}	5.0	-15.6
Ca^{2+}, Cl^{-}	80	+3.53	Hg^{2+}, Cl^{-}	5.0	-21.7
Al^{3+}, Cl^{-}	80	+4.95	Glucose	50	+4.75
Zn^{2+}, SO_4^{2-}	80	+3.28	Sucrose	50	+2.42
Fe^{2+}, Cl^{-}	80	-4.47	Fructose	50	+4.76
Fe^{3+}, Cl^{-}	5.0	-12.0	EDTA	50	+2.38
Ag^{+}, NO_3^{-}	5.0	-13.7	Magnesium stearate	50	+3.24
Cu^{2+}, Cl^{-}	5.0	-15.4	Starch	Saturated solution	-3.49

Concentration of ascorbic acid:2.5×10^{-5} mol/L.

3.7 Calibration curve and detection limit

Under the optimal conditions mentioned before, we established relationship between concentration of ascorbic acid and the fluorescence quenching extent which caused by ascorbic acid. It was found that ascorbic acid quenched the fluorescence intensity of CdTe QDs in a concentration dependence that wasn't fit for the conventional Stern-Volmer plot, which was shown in Fig. 7a. Herein, the dependence between QDs fluorescence intensity and the concentration of ascorbic acid is best described by a modified Stern-Volmer equation [18]: $\lg(F_0/F) = 0.111\ C - 0.029$, where F_0 and F are the fluorescence intensity of CdTe QDs in the absence and the presence of ascorbic acid, respectively, which is shown in Fig. 7b. The results show that the change of relative fluorescence intensity and the concentration of ascorbic acid possess a good linear relationship in the concentration range from 1.25×10^{-5} to 1.0×10^{-4} mol/L with a correlation coefficient of 0.9981. The relative standard deviation (n=11) for 3.75×10^{-4} mol/L is 2.1%. Following the 3σ IUPAC criteria, the detection limit of 3.6×10^{-6} mol/L can be obtained, where σ is the standard deviation of blank signal (n=11). The results show that the present method exhibits good sensitivity and reproducibility.

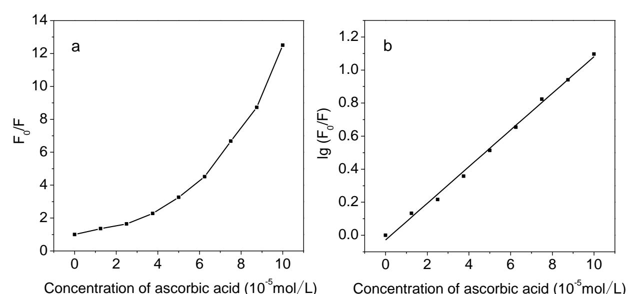


Fig. 7. Modified Stern-Volmer plot of ascorbic acid concentration dependence of the fluorescence quenching degree.

4. Determination of real samples

The concentrations of ascorbic acid in commercial tablets and injections were determined by the standard-curve method which was shown in Fig. 6b. Drug samples were all purchased from a local drugstore. Before the following fluorescence measurement, As to the commercial tablets, 250 μL of 4.17×10^{-6} mol/L CdTe QDs solution was transferred to 10-mL colorimetric tube, then 125-μL treated sample solution were added subsequently and diluted to 10 mL with pure water, well mixed. After that, the fluorescence measurement was carried out by setting the excitation wavelength at 360 nm. Both of the

excitation and emission slits were set at 10 nm. The results are shown in Table 2 and each value was the average of five determinations. The recovery test was carried out in each instance by adding 25, 30, 35 μL ascorbic acid (10^{-2} mol/L) standard solution to 125 μL sample solution in three different levels and kept the total volume to 10 mL with pure water before measurement, well mixed, other procedures were the same as before. As to the injections, procedures were the same as former. The recoveries of the tablelets and injections were in the range of 95~102% and 93~107%, respectively. As shown in Table 3 and 4, the determination results achieved by this method were in good agreement with oxidation–reduction titration standard method which proposed by Pharmacopoeia of China [32]. Statistical T-test and F-test revealed no significant difference between the content found by both methods (α = 0.05). It is clear that the determination of drug samples is reliable and practical.

Table 2. Determination of ascorbic acid in real samples (n=5).

Sample	Vc found (10^{-5} mol/L)	RSD (%)	Vc added (10^{-5} mol/L)	Total found (10^{-5} mol/L)	Recovery (%)
Vc tablets	2.81	1.41	2.5	5.19	95.2
			3.0	5.73	97.5
			3.5	6.36	101.4
Vc injections	3.54	2.40	3.0	6.35	93.7
			3.5	7.19	104.3
			4.0	7.81	106.7

Table 3. Analytical results for determination of ascorbic acid in Vc tablets (n=5).

Vc tablets	Repeat determination (mg/tablet)					Average (mg/tablet)	R S D (%)
Titration method	100.1	101.6	103.4	99.6	103.5	101.6	1.8
This method	100.0	100.4	97.2	99.7	97.9	99.0	1.4

Table 4. Analytical results for determination of ascorbic acid in Vc injections (n = 5)

Vc injections	Repeat determination（mg/mL）					Average (mg/mL)	R S D (%)
Titration method	125.7	126.6	127.3	129.2	128.4	127.4	1.1
This method	123.6	127.9	122.6	121.9	128.2	124.8	2.4

5. Mechanism

In the process of determination ascorbic acid, we found that when the concentration of ascorbic acid was lower than 1.25×10^{-5} mol/L, the fluorescence intensity of CdTe QDs was strengthened. On the other hand, as the concentration of ascorbic acid increased from 1.25×10^{-5}~1.00×10^{-4}mol/L, the fluorescence intensity of CdTe QDs was quenched significantly and the emission spectrum was red-shifted, As the concentration of ascorbic acid was higher than 1.00×10^{-4}mol/L, the fluorescence intensity of CdTe QDs was hardly detected. Based on the above phenomenon, the probable fluorescence increasing mechanism can be explained as the hydrogen bond interaction between the hydroxyl of ascorbic acid and carboxyl of CdTe QDs surface. With the increase of ascorbic acid, the quenching effect was stronger than hydrogen bond interaction. Herein, the probable quenching mechanism can be explained as follows: First, it was reported that small cations can pass through the shell layer and interact with the core [33]. In our thesis, it also may be that not all particles of QDs are perfectly capped with the

shell and the added H^+ can pass through the shell layer and interact with the core. Further more, the added H^+ leading to a portion of TGA dissociated from the nanoparticle surface, resulting in a lower surface charge, and the uncapped QDs trended to aggregate [17]. Third, the addition of H^+ may cause reversible reaction and Te is oxidized by oxygen and precipitated from the solution. The schematic diagram of quenching mechanism between CdTe QDs and ascorbic acid were shown in Fig. 8. By far, the mechanism is no verdict. But from the viewpoint of surface chemistry, all the quenching processes of QDs maybe the result of surface structure change of QDs. The shift of the emission peak may result from the conjugation between CdTe nanoparticles and H^+, and the increased surface electric charge may increase the orientation polarization rate and the Stokes shift [15].

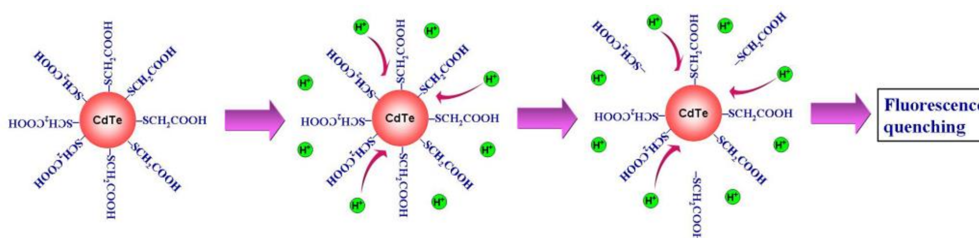


Fig. 8. The schematic diagram of quenching mechanism between CdTe QDs and ascorbic acid.

6. Conclusions

Water-soluble CdTe QDs are found to be a satisfactory pH probe that could have potential applications in chemical and biochemical sensing. Herein, we have established a simple novel method for quick, accurate and sensitive determination ascorbic acid based on fluorescence quenching of CdTe QDs. The quenching process was described by a modified Stern–Volmer type equation. The effects of the size and concentration of the QDs, and pH value on the determination of ascorbic acid were discussed. The proposed method have been applied to determination of ascorbic acid in commercial tablets and injections，which agreed with the oxidation–reduction titration result and the labeled value，suggesting that the method is reliable and practical. It is feasible to develop a simple assay kit for determination of ascorbic acid without using expensive instrumental set-up. These results point out the potential use of water-soluble CdTe QDs as selective pH sensors.

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References

[1] H. Weller, Angew. Chem. Int. Ed., **32**, 41 (1993).
[2] A. P. Alivisatos, J. Phys. Chem., **100**, 13226 (1996).
[3] X. G. Peng, L. Manna, W. D. Yang, etal, Nature. **404**, 59 (2000).
[4] J. E. Katari, V. L. Colvin, A. P. Alivisatos, J. Phys. Chem., **98**, 4109 (1994).
[5] H. Zhang, Z. Zhou, B. Yang, etal, J. Phys. Chem. B. **107**, 8 (2003).
[6] X. J. Ji, C. S. Wang, J. M. Xu, etal, Langmuir. **21**, 5377 (2005).
[7] M. Bruchea, M. Moronne, P. Gin, etal, Science. **281**, 2013 (1998).
[8] B. Dubertret, P. Skourides, D. J. Norris, etal, Science. **298**, 1759 (2002).
[9] D. R. Larson, W. R. Zipfel, R. M. Williams, etal, Science. **300**, 1434 (2003).
[10] J. K. Jaiswal, H. Mattoussi, J. M. Mauro, etal, **21**, 47 (2003).
[11] W. C. Chan, S. M. Nie, Science. **281**, 2016 (1998).
[12] Y. F. Chan, Z. Rosenzweig, Anal. Chem., **74**, 5132 (2002).
[13] F. C. Liu, C. C. Shen, W. L. Tseng, J. Chin. Chem. Soc., **58**, 707 (2011).
[14] A. S. Susha, A. M. Javier, W. J. Parak, etal, Colloids Surf. A: Physicochem. Eng. Asp., **281**, 40 (2006).
[15] D. H. Yu, Z. Wang, Y. Liu, etal, Enzyme Microb. Tech., **41**, 127 (2007).
[16] X. L. Diao, Y. S. Xia, T. L. Zhang, etal, Anal. Bioanal. Chem., **388**, 1191 (2007).
[17] Y. Q. Wang, C. Ye, Z. H. Zhu, etal, Anal. Chim. Acta. **610**, 50 (2008).
[18] J. F. Sun, L. H. Liu, C. L. Ren, etal, Microchim. Acta. **163**, 271 (2008).
[19] M. A. Koupparis, P. Anagnostopoulou, H. V. Malmstadt, Talanta, **32**, 411 (1985).
[20] A. M. K. Al-Rikabi, F. M. Al-Jabri, T. M. Al-Mothefer, Anal. Lett., **23**, 273 (1990).
[21] L.G. Shaidarova, I. A. Chelnokova, A. V. Gedmina, et al, Anal. Chem., **64**, 36 (2009).
[22] G. F. Wang, J. G. Sun, W. Zhang, etal, Microchim. Acta. **164**, 357 (2009).
[23] S. Birghila, V. Popescu, S. Dobrinas, etal, Rev. Chim., **54**, 289 (2003).

[24] S. Uršić, S. Luterotti, D. Ljubas, Anal. Chem., **369**, 719 (2001).
[25] M. Y. Li, Y. X. Ge, Q. F. Chen, et al, Talanta. **72**, 89 (2007).
[26] W. W. Yu, L. H. Qu, W. Z. Guo, et al, Chem. Mater., **15**, 2854 (2003).
[27] Y. Wang, Z. Tang, M. A. Correa-Duarte, et al, J. Phys. Chem. B. **108**, 15461 (2004).
[28] M. Tomasulo, I. Yildiz, F. M. Raymo, J. Phys. Chem. B. **110**, 3853 (2006).
[29] M. Y. Gao, S. Kirstein, H. Mohwald, J. Phys. Chem. B. **102**, 8360 (1998).
[30] H. Zhang, Z. Zhou, B. Yang, J. Phys. Chem. B. **107**, 8 (2003).
[31] M. Laferrière, R. E. Galian, V. Maurel, etal, Chem. Commun., **257** (2006).
[32] National Commission of Chinese Pharmacopoeia. The Pharmacopoeia of People's Republic of China, Chemistry Industry Publishing Press, Beijing, China, **2**, 669 (2005).
[33] H. Y. Xie, J. G. Liang, Z. L. Zhang, etal, Spectrochimi. Acta, Part A. **60**, 2527 (2004).

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