

CrossMark
click for updatesCite this: *Anal. Methods*, 2015, 7, 614

A novel fluorescence and resonance Rayleigh scattering probe based on quantum dots for the detection of albendazole†

Qin Li,^{*a} Xuanping Tan,^b Lingli Fu,^a Qu Liu^a and Weiwei Tang^a

Glutathione (GSH)-capped CdTe QDs with diameters of 3 nm were synthesised. The interaction between the QDs and albendazole (ABZ) was investigated by UV-vis absorption, resonance Rayleigh scattering (RRS) and fluorescence spectroscopy. Based on changes in the UV-vis absorption spectra of QDs and ABZ, we demonstrated that the QDs associated with ABZ to form new complexes. In pH 7.1 PBS buffer solution, the fluorescence intensity of QDs was effectively quenched by ABZ. The fluorescence quenching of QDs by ABZ mainly results from the QDs–ABZ complexes, and the electrostatic attraction played a major role in stabilising these complexes. Furthermore, the interaction between QDs and ABZ led to a remarkable enhancement in RRS, which was proportional to the ABZ concentration within a certain concentration range. The suitable reaction conditions, important factors as well as the influence of coexisting substances were studied. The possible reaction mechanism was also discussed.

Received 27th September 2014
Accepted 26th October 2014

DOI: 10.1039/c4ay02289k

www.rsc.org/methods

1 Introduction

In recent years, the exploration of systems capable of sensing and recognition based on semiconductor quantum dots (QDs) has attracted considerable interest in chemo/biosensing applications. This phenomenon is mainly due to the many advantages that QDs have over conventional organic and inorganic fluorescence materials, such as high quantum efficiency, photostability, and size-tunable optical properties.^{1–3} In addition, the large surface areas of QDs are favourable for attaching various ligands to obtain controllable properties.⁴ All of these properties make QDs excellent candidates for the development of novel and sensitive sensors in current research. Recently, progress in the controlled synthesis of high-quality QDs as well as in effective surface modifications^{5,6} have caused analytical chemists to explore QDs as promising optical labels for sensing and biosensing events.^{7,8} QDs are prone to exchange electrons or energy with their complementary partners (acceptors or donors) upon excitation. This behaviour can be engineered to signal the molecular recognition process as the presence of the target analytes can be transduced into detectable fluorescence signals. Quite a few sensing schemes based on fluorescence resonant energy transfer (FRET) or photoinduced electron transfer (PET) have been developed for detecting small

molecules and for tracing biorecognition events or biocatalytic transformations.^{8–14}

Since the resonance Rayleigh scattering (RRS) technique was first introduced in 1993 by Pastemack *et al.*,¹⁵ it has gradually gained recognition from analytical chemists.^{16–18} As a novel tool, RRS is characterised by high sensitivity, convenience in performance and simplicity in apparatus. It detects RRS signals with a common spectrofluorometer and has been widely employed in the designation of bio-assemblies and aggregation species.^{19–23} Recent studies have shown RRS is a valuable technique for the analysis of nucleic acids, proteins, and inorganic ions. In recent years, some people have used QDs as potential RRS probes.^{24,25}

Albendazole (ABZ, Fig. 6), a kind of high-efficiency anthelmintic, is a benzimidazole derivative that is widely used in veterinary and human medicine for the treatment of infections caused by helminths.^{26,27} After oral administration to domestic animal species and humans, ABZ readily undergoes first-pass metabolism in enterocytes and liver cells. The sequential products of this metabolism are albendazole sulphoxide, albendazole sulphone, and albendazole 2-aminosulphone.²⁸

Various methods such as high-performance liquid chromatography (HPLC),^{29,30} electrochemical oxidation,³¹ liquid chromatography-tandem mass spectrometry (LC-MS),³² liquid chromatography (LC)³³ and spectrofluorimetry^{34,35} have been used for the determination of ABZ. However, some of these methods are labour-intensive and require time-consuming sample pre-treatment or excessive labour costs. Compared with other analytical techniques, fluorescence methods that use QDs as probes are generally fast and economical for trace analysis.

^aChongqing Medical and Health School, Fuling, Chongqing 408100, P. R. China. E-mail: 13896550381@126.com; Tel: +86 18983311788

^bSchool of Chemistry and Chemical Engineering, Southwest University, Chongqing, 400715, China

† Electronic supplementary information (ESI) available. See DOI: 10.1039/c4ay02289k

To our knowledge, the application of QDs as probes for the quantitative determination of ABZ has not been reported to date. Herein, a sample, rapid, time-saving, low-cost and sensitive assay of ABZ was proposed based on the changes in the fluorescence signal of glutathione (GSH)-capped CdTe QDs for the first time. In addition, the RRS of the system changes at the same time as the changes in the fluorescence signal. In this work, we studied the interaction between CdTe QDs and ABZ. The results indicated that the fluorescence intensity of CdTe QDs was quenched at 560 nm in the presence of ABZ. The quenched intensity was proportional to the concentration of ABZ in the range of 0.264–4.752 $\mu\text{g mL}^{-1}$, with a detection limit of 88 ng mL^{-1} . At the same time, the RRS of CdTe QDs was enhanced in the presence of ABZ, and enhancement in RRS intensity was proportional to the concentration of ABZ in the range of 0–4.752 $\mu\text{g mL}^{-1}$, with a detection limit of 6.5 ng mL^{-1} . The optimum reactions and the influencing factors have also been examined. Finally, the method has been applied to determination of ABZ in commercial samples, and satisfactory results were obtained. The mechanism of the proposed reaction was also discussed.

2 Experimental

2.1 Reagents and apparatus

The main chemical reagents used in the present study were $\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$ (Shanghai Chemicals Reagent Co., Shanghai, China), Te powder (Sinopharm Chemical Reagent Co., Shanghai, China), glutathione (GSH, Aladdin Reagent Co., Shanghai, China), NaBH_4 (Tianjin Huanwei Fine Chemical Co., Tianjin, China), and albendazole (ABZ, Aladdin Reagent Co., Shanghai, China). PBS buffer solutions with different pH values were prepared by mixing 1/30 mol L^{-1} Na_2HPO_4 and 1/30 mol L^{-1} NaH_2PO_4 in different proportions. All reagents were of analytical grade and used without further purification.

A Hitachi F-2500 spectrofluorophotometer (Hitachi Company, Japan) was used to record the fluorescence and RRS spectra. A UV-2450 spectrophotometer (Tianmei Corporation, Shanghai, China) was employed to record the absorption spectra. Transmission electron microscopy (TEM) was carried out on a Hitachi-600 (Hitachi Company, Japan). A PHS-3C pH meter (Leici, Shanghai, China) was used to adjust the pH values of the aqueous solutions.

2.2 Methods

2.2.1 Synthesis of GSH-CdTe quantum dots. Solutions of aqueous colloids of GSH-CdTe QDs were prepared according to the previously described method.³⁶ Under N_2 atmosphere and magnetic stirring, tellurium powder (0.0383 g) was reacted with excessive sodium borohydride in deionised water to produce a colourless solution of sodium hydrogen telluride (NaHTe).

$\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$ (0.1028 g) and GSH (0.1844 g) were dissolved in 150 mL deionised water. Under magnetic stirring, the pH of the mixture was adjusted to 11.16 by the dropwise addition of NaOH solution (1 mol L^{-1}). The solution was de-aerated by N_2 bubbling for about 30 min. Under stirring, H_2Te gas generated

by the reaction of the solution of NaHTe with diluted H_2SO_4 (0.5 mol L^{-1}) was passed through the oxygen-free Cd^{2+} solution together with a slow nitrogen flow. The resulting solution was then heated to 369 K and refluxed under nitrogen for 1 h. A salmon pink CdTe solution was obtained. The concentration of GSH-capped CdTe QDs was 3.0×10^{-3} mol L^{-1} (determined by the Cd^{2+} concentration).

2.2.2 General procedure. To determine the ABZ by this novel sensor, 0.5 mL PBS buffer solution (pH 7.1), 0.5 mL above as-prepared GSH-CdTe QDs, and appropriate amount of ABZ were added into a 5.0 mL calibrated test tube, diluted with deionized water to the mark, and mixed thoroughly with gentle shaking. After incubation for 5 min, the RRS, fluorescence spectra of solution were examined.

3 Results and discussion

3.1 Characterisation and stability of aqueous CdTe QDs

As shown in Fig. S1(a),† the morphology of the as-prepared GSH-capped CdTe QDs was investigated by TEM. It is quite evident that these nanoparticles are close to spherical and uniform with an average diameter of 3.0 nm. The UV-vis absorption (curve 1) and fluorescence emission (curve 2) spectra of the as-prepared GSH-capped CdTe QDs are also shown in Fig. S1(b).† The UV-vis absorption spectrum shows a strong excitonic absorption in the ultraviolet region, and the characteristic absorption peak is located at 525 nm. Meanwhile, the symmetry and narrow FWHM (about 42 nm) seen in the fluorescence emission spectrum further confirm that the GSH-capped CdTe QDs were nearly monodisperse and homogeneous; the observed fluorescence band is centred at 560 nm (excitation 292 nm).

The fluorescence quantum yield (Φ_f) is one of the most fundamental properties of many fluorescent species. This quantity provides a direct measure of the efficiency of the conversion of absorbed photons into emitted photons.³⁷ Hence, the measurement of Φ_f is a key step in the characterisation of photoluminescent GSH-capped CdTe QDs. In this work, the Φ_f value of the GSH-capped CdTe QDs at room temperature was determined by comparison with that of Rhodamine 6G in ethanol solution assuming that its fluorescence quantum yield was 95%.^{38,39} The Φ_f of the GSH-capped CdTe QDs was then calculated by the following equation:

$$Y_u = Y_s \times \left(\frac{F_u}{F_s}\right) \times \left(\frac{A_s}{A_u}\right) \times \left(\frac{n_u^2}{n_s^2}\right) \quad (1)$$

where Y_u is the Φ_f of the sample solution to be measured and Y_s is the reference solution. F_u and F_s are the integral intensities, A_u and A_s are the absorption values, n_u and n_s stand for the refractive indexes of the solvents, and the subscripts “u” and “s” respectively refer to the samples and the standard. The result shows that the Φ_f of GSH-capped CdTe QDs was 41.8%.

3.2 Optimisation of the determination

3.2.1 Effect of acidity. In order to detect ABZ with the proposed sensor at physiological conditions, PBS buffer

solution was selected to control the acidity of the GSH-capped CdTe QDs–ABZ system. The effect of acidity on the system was investigated from pH 6.4 to 7.8 (Fig. 1(a)). The experimental results show that the optimal pH value was 7.1, which resulted in the maximum change in fluorescence intensity due to the ABZ-induced fluorescence quenching of GSH-capped CdTe QDs. Thus, to obtain a lower detection limit for ABZ, the pH of the solution system used in the experiment was set at 7.1.

3.2.2 Effect of the concentration of GSH-capped CdTe QDs.

The influence of the concentration of GSH-capped CdTe QDs on the fluorescence intensity of GSH-capped CdTe QDs–ABZ system was investigated by keeping ABZ concentration and pH value constant while changing the QD concentration (Fig. 1(b)). The results revealed that the optimum concentration of GSH-capped CdTe QDs was $3.0 \times 10^{-4} \text{ mol L}^{-1}$.

3.2.3 Effect of reaction time. The influence of reaction time on the fluorescence intensity of the GSH-capped CdTe QDs–ABZ system was studied. The results demonstrated that the reaction finished within 5 min, and that the fluorescence intensity was stable for more than 60 min. Therefore, the experiments were carried out after 5 min of reaction and finished within 1 h.

3.2.4 Effect of ethanol. The effect of ethanol on the fluorescence of GSH-capped CdTe QDs was investigated. The results showed that ethanol had no influence on the fluorescence intensity of GSH-capped CdTe QDs.

3.3 Fluorescence detection of ABZ based on QDs

In this work, the initial fluorescence spectra of GSH-capped CdTe QDs were recorded in the absence and presence of ABZ (Fig. 2). It was found that a progressive decrease in the fluorescence intensity of GSH-capped CdTe QDs was caused by ABZ. As the concentration of ABZ increased from 0.264 to $4.752 \mu\text{g mL}^{-1}$, the quenching intensity of QDs was enhanced. The calibration curve shown in the inset of Fig. 2 is the plots of the optical analysis of different concentrations of ABZ versus the quenching of the emission maximum of QDs. The linear regression equation is $\Delta F = 363.8C + 15.3$ (where C is the concentration of ABZ in $\mu\text{g mL}^{-1}$), and the correlation

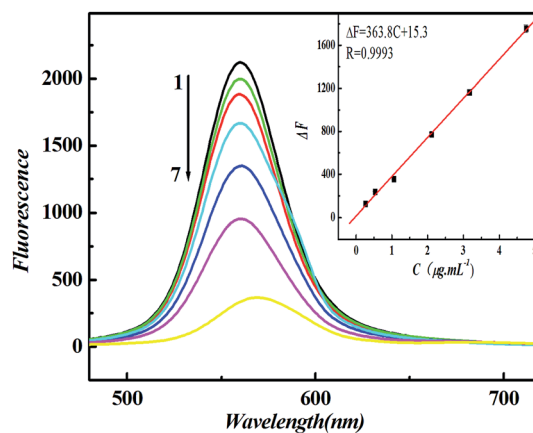


Fig. 2 Fluorescence spectra of GSH-capped CdTe QDs in the absence and presence of ABZ: from top to bottom, the concentrations of ABZ are 0, 0.264, 0.528, 1.056, 2.112, 3.168, 4.752 $\mu\text{g mL}^{-1}$ (GSH-capped CdTe QDs, $3.0 \times 10^{-4} \text{ mol L}^{-1}$; PBS buffer solution, 0.5 mL; pH 7.1). The inset is the linear plot of the quenched fluorescence intensity of GSH-capped CdTe QDs–ABZ system at 560 nm against the concentration of ABZ.

coefficient is 0.9993. The limit of detection defined by $3\sigma/K$, where σ is the standard deviation of the blank measurements ($n = 11$) and K is the slope of the calibration graph, is 88 ng mL^{-1} .

3.4 RRS detection of ABZ based on QDs

The RRS spectra of GSH-capped CdTe QDs and the GSH-capped CdTe QDs–ABZ complex are shown in Fig. 3. The experimental results show that the RRS intensity of the GSH-capped CdTe QDs was very weak. However, when GSH-capped CdTe QDs was mixed with trace amounts of ABZ, the RRS intensity was enhanced greatly, and the RRS spectrum was altered. The maximum RRS peak was observed at 390 nm. As shown in Fig. 3, the RRS peak of the GSH-capped CdTe QDs–ABZ system was gradually enhanced as the concentration of ABZ increased from 0 to $4.752 \mu\text{g mL}^{-1}$. That is, the RRS intensity of GSH-capped

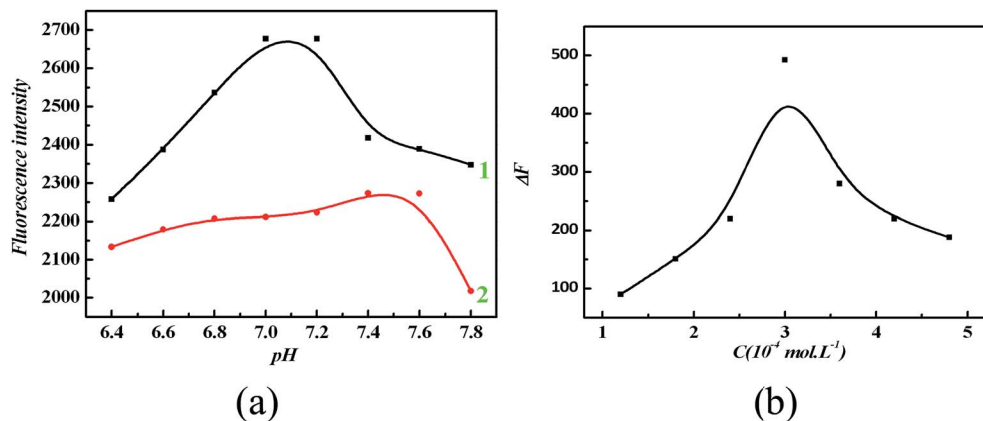


Fig. 1 (a) Effect of acidity on the GSH-capped CdTe QDs–ABZ system: curve 1 is the fluorescence intensity of QDs at different acidities; curve 2 is the fluorescence intensity of QDs in the presence of ABZ at different acidities. (b) Effect of the concentration of GSH-capped CdTe QDs on the fluorescence intensity of QDs after the addition of ABZ in PBS buffer solution.

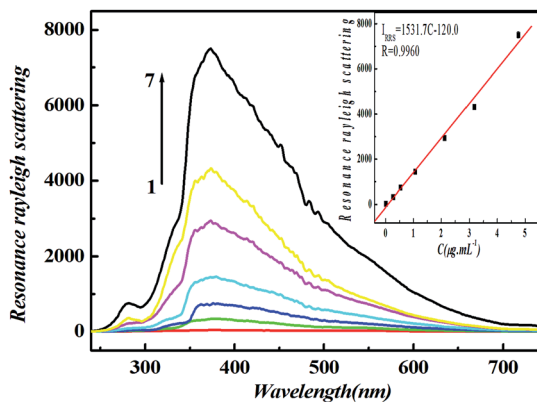


Fig. 3 RRS spectra of GSH-capped CdTe QDs in the absence and presence of ABZ: from bottom to top, the concentrations of ABZ are 0, 0.264, 0.528, 1.056, 2.112, 3.168, 4.752 $\mu\text{g mL}^{-1}$ (GSH-capped CdTe QDs, 3.0×10^{-4} mol L^{-1} ; PBS buffer solution, 0.5 mL; pH 7.1). The inset is the linear plot of the enhanced RRS intensity of the GSH-capped CdTe QDs–ABZ system at 390 nm against the concentration of ABZ.

CdTe QDs increased rapidly upon the addition of ABZ. As demonstrated in the inset of Fig. 3, a linear calibration plot of the RRS intensity against the concentration of ABZ was observed in the range of 0–4.752 $\mu\text{g mL}^{-1}$ with a correlation of 0.9960 and linear regression equation of $I_{\text{RRS}} = 1531.7C - 120.0$ (where C is the concentration of ABZ in $\mu\text{g mL}^{-1}$). An ABZ detection limit of 6.5 ng mL^{-1} was determined from $3\sigma/K$, where σ is the slope of the standard deviation of 11 repeated measurements of blank samples and K is the slope of calibration.

3.5 Mechanism of ABZ detection by GSH-capped CdTe QDs

Fluorescence quenching can proceed by different mechanisms that can usually be classified as either dynamic quenching or static quenching. Dynamic and static quenching can be distinguished by their differing dependences on temperature and viscosity. Dynamic quenching depends upon diffusion. Since higher temperatures result in larger diffusion coefficients, the bimolecular quenching constants are expected to increase with increasing temperature. In contrast, increased temperature is likely to result in decreased complex stability, thus resulting in lower values of the static quenching constants.

The phenomenon of fluorescence quenching is customarily described in terms of the following well-known Stern–Volmer equation:^{40,41}

$$F_0/F = 1 + K_{\text{SV}}[Q] \quad (2)$$

where F_0 and F are the fluorescence intensity in the absence and presence of the quencher (Q), respectively, K_{SV} is the Stern–Volmer quenching constant, and terms within square brackets

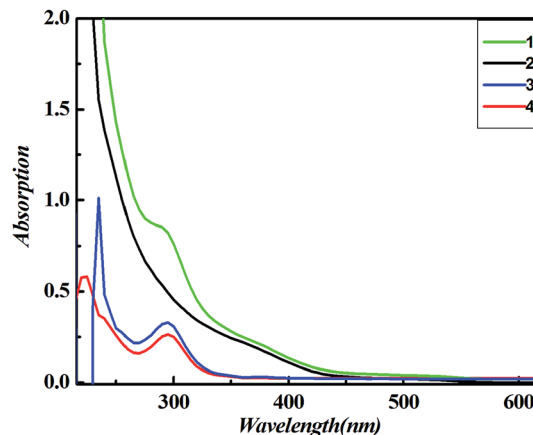


Fig. 4 UV-vis absorption spectra of: (1) mixed solution system (GSH-capped CdTe QDs and ABZ); (2) GSH-capped CdTe QDs; (3) ABZ (with GSH-capped CdTe QDs as the reference); and (4) ABZ (with distilled water as the reference). GSH-capped CdTe QDs, 3.0×10^{-4} mol L^{-1} ; ABZ, 1.056 $\mu\text{g mL}^{-1}$; PBS buffer solution, 1.0 mL; pH = 7.1.

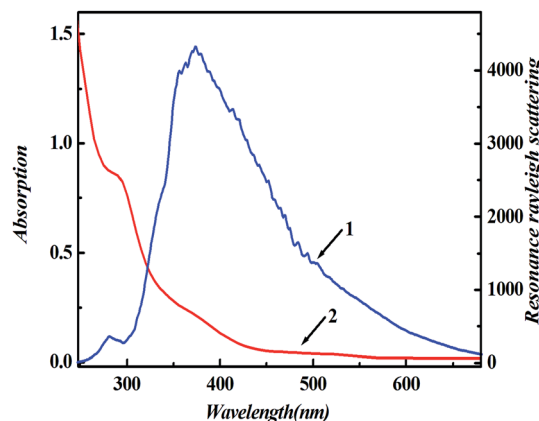


Fig. 5 Comparison of the RRS (curve 1) and absorption (curve 2) spectra of the GSH-capped CdTe QDs–ABZ system in PBS buffer solution at pH = 7.1 (GSH-capped CdTe QDs: 3.0×10^{-4} mol L^{-1} ; ABZ: 3.168 $\mu\text{g mL}^{-1}$).

Table 1 Stern–Volmer quenching constants for the interaction of GSH-capped CdTe QDs with ABZ at different temperatures in PBS buffer solution at pH = 7.1

Temperature (K)	Stern–Volmer linear equation	K_{SV} (L mol^{-1})	R^a	S.D. ^b
277	$F_0/F = 0.98 + 7.8 \times 10^4 [Q]$	7.8×10^4	0.995	0.0165
296	$F_0/F = 0.98 + 7.6 \times 10^4 [Q]$	7.6×10^4	0.995	0.0155
302	$F_0/F = 1.0 + 5.1 \times 10^4 [Q]$	5.1×10^4	0.997	0.0150

^a R is the correlation coefficient. ^b S.D. is the standard deviation for the K_{SV} values.

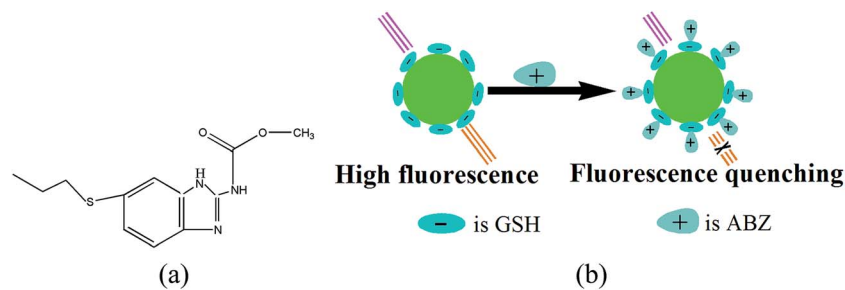


Fig. 6 (a) Molecular structure of ABZ and (b) model of the interaction between GSH-capped CdTe QDs and ABZ.

represent the concentrations of respective species. Herein, we have employed the Stern–Volmer equation (eqn (1)) to estimate the Stern–Volmer quenching constant (K_{SV}) at the three different studied temperatures (Fig. S2†); the data are compiled in Table 1. The results show that the Stern–Volmer quenching constant K_{SV} is negatively correlated with temperature, indicating that the probable quenching mechanism is static quenching rather than dynamic quenching.

One additional method to distinguish static and dynamic quenching is by the careful examination of the absorption spectra of the fluorophore. Collisional quenching (dynamic quenching) only affects the excited states of the fluorophore; thus, no changes in the absorption spectra are expected. On the contrary, ground-state complex formation will frequently result in the perturbation of the absorption spectrum of the fluorophore.⁴² For reconfirming that the probable fluorescence quenching mechanism of GSH-capped CdTe QDs by ABZ is static quenching, the UV-vis absorption spectra of the GSH-capped CdTe QDs–ABZ solution system were studied; the results are presented in Fig. 4. In the spectrum of pure GSH-capped CdTe QDs (curve 2), there is strong absorption in the UV area at wavelengths <400 nm, whereas the absorption in the visible region is relatively weak. Curve 4 shows the absorption spectrum of ABZ with distilled water as the reference, while curve 3 shows the absorption spectrum of ABZ with GSH-capped CdTe QDs as the reference. The comparison of curves 3 and 4 reveals an obvious spectral change, implying that there is a

strong interaction between GSH-capped CdTe QDs and ABZ. Namely, the quenching type is static quenching.

As illustrated in Fig. S3,† the RRS spectra of GSH-capped CdTe QDs–ABZ system were obtained. The RRS intensities of the separate GSH-capped CdTe QDs (curve 1) and ABZ (curve 2) were very weak. However, when they were mixed in PBS buffer solution (pH = 7.1), the RRS intensity was strongly enhanced (curve 3). These results indicated that the GSH-capped CdTe QDs interacted with ABZ due to the formation of GSH-capped CdTe QDs–ABZ complexes. In addition, as shown in Fig. 6, the RRS spectra of GSH-capped CdTe QDs with different concentrations of ABZ were measured. The RRS intensity of the GSH-capped CdTe QDs–ABZ system was directly proportional to the concentration of ABZ within a certain range. This indicated that the interaction between GSH-capped CdTe QDs and ABZ could increase the size and light scattering of a section of the complex. Thus, the scattering efficiency was increased correspondingly.⁴² According to above primary analysis, the RRS approach can be applied to the monitoring of ABZ as well.

In order to obtain more information about the interaction between GSH-capped CdTe QDs and ABZ, the possible reasons for the RRS enhancement were studied, and the results are discussed as follows:

3.5.1 Effect of absorption spectra on RRS. Since RRS is a scattering–absorption–rescattering process produced by the resonance of scattering and absorption, RRS spectra should be closely related to the absorption spectrum. As shown in Fig. 5,

Table 2 Effect of coexisting materials of the GSH-capped CdTe QDs–ABZ system in 1.0 mL PBS buffer solution at pH = 7.1 ($C_{ABZ} = 3.168 \mu\text{g mL}^{-1}$)

Coexistence materials	Concentration ($\mu\text{g mL}^{-1}$)	Relative error (%)	Coexistence materials	Concentration ($\mu\text{g mL}^{-1}$)	Relative error (%)
Al^{3+}	2.40	−3.8	Cl^-	100	+2.3
NH_4^+	80.0	+2.3	SO_4^{2-}	180	−1.5
Fe^{3+}	1.25	−5.0	CO_3^{2-}	116	+4.2
Ba^{2+}	41.7	−4.6	β -CD	56.8	−4.3
Co^{2+}	3.30	−3.6	Sucrose	50	−5.0
Cu^{2+}	5.00	−3.5	Tyrosine	40	−3.3
Na^+	140	+4.1	Phenylalanine	130	−4.9
K^+	125	+4.7	Leucine	80	+2.4
Mg^{2+}	1.75	−2.6	BSA ^a	2.2	+3.8
I^-	120	+2.8	HSA ^b	3.0	+3.7

^a BSA is Bovine serum albumin. ^b HSA is Human serum albumin.

Table 3 Results of real sample analysis indicating percentage recovery

Sample	Original found ($\mu\text{g mL}^{-1}$)	Added ($\mu\text{g mL}^{-1}$)	Total found ($\mu\text{g mL}^{-1}$)	R.S.D. (%) ($n = 5$)	Recovery (%)
1	1.056	0.500	1.579	2.13	101.5
2	1.056	1.000	2.027	2.54	98.6
3	1.056	2.000	3.041	1.98	99.5

the RRS spectrum of the GSH-capped CdTe QDs-ABZ system is situated in its absorption band, which resulted in the resonance-enhanced scattering.⁴³

3.5.2 Effect of the molecular volume. In neutral and weakly alkaline media, the water-soluble GSH-capped CdTe QDs carry negative charges in these experimental conditions (PBS buffer solution, pH = 7.1) because the isoelectric point of GSH is 5.93.⁴⁴ However, ABZ possesses an -NH- group that can easily react with H^+ in solution (*i.e.*, -NH- can be easily protonated in the neutral and weakly alkaline media). Therefore, ABZ can exist in the cationic form in neutral and weakly alkaline media (PBS buffer solution, pH = 7.1).⁴⁵ According to above primary analysis, the RRS will be enhanced.

With the above evidence including fluorescence spectra, Stern-Volmer curves, absorption spectra, and RRS spectra, we can demonstrate that the mechanism of the fluorescence quenching of GSH-capped CdTe QDs by ABZ was static quenching. In addition, in the experimental system ABZ interacted with GSH-capped CdTe QDs through electrostatic interactions. The reaction model is shown in Fig. 6.

3.6 Selectivity of the RRS method

In order to explore the selectivity of the RRS method using GSH-capped CdTe QDs as probes for ABZ detection in aqueous solution, the influences of foreign substances such as relevant metal ions, inorganic anions, and biomolecules on the determination of $3.168 \mu\text{g mL}^{-1}$ ABZ were investigated (Table 2). If the coexisting substances caused a relative error of less than $\pm 5\%$ in the RRS intensity change of the GSH-capped CdTe QDs, they were considered to have no interference with the detection of ABZ. Ions (NH_4^+ , Ba^{2+} , Na^+ , K^+ , I^- , Cl^- , SO_4^{2-} , CO_3^{2-} , $\beta\text{-CD}$) and biomolecules (sucrose, tyrosine, phenylalanine, leucine) did not interfere with the determinations, while Al^{3+} , Fe^{3+} , Co^{2+} , Cu^{2+} , Mg^{2+} , BSA, and HSA could be allowed at lower concentration levels without significant interference. These results indicated that the proposed method had high selectivity and might be applicable to the detection of ABZ in the quality control of bulk drugs and their pharmaceutical preparations with satisfactory results.

3.7 Analytical application

To confirm the feasibility of the proposed method for the determination of ABZ, it was applied to determine ABZ in commercial pharmaceutical dosages (albendazole tablet). The results are shown in Table 3. It can be seen that the relative standard deviation (RSD) is less than 3.0%, showing a good precision for this method. The results indicate that the

determination of ABZ using GSH-capped CdTe QDs as probe is sensitive and reliable.

4 Conclusion

In this work, we studied the interaction of GSH-capped CdTe QDs with ABZ by fluorescence, UV-vis absorption and RRS spectroscopy in PBS buffer solution at pH 7.1. The results indicated that the fluorescence quenching mechanism of GSH-capped CdTe QDs in the presence of ABZ is static quenching. The binding of ABZ to GSH-capped CdTe QDs was found to occur through electrostatic interaction. Moreover, the RRS intensity of GSH-capped CdTe QDs in the presence of ABZ was enhanced and was proportional to the concentration of ABZ within a certain concentration range. The RRS enhancement was assumed to result from the resonance-enhanced Rayleigh scattering effect and the increase in the molecular volume. Based on these results, the fluorescence quenching and RRS techniques for the determination of ABZ with the detection limits at the nanogram level were proposed. The RRS method has higher sensitivity than the fluorescence quenching method. Therefore, a novel, simple, time-saving, low-cost, highly sensitive and specific quantitative method based on the enhanced resonance scattering signals of GSH-capped CdTe QDs was developed for the detection of ABZ in pharmaceutical preparations (albendazole tablet) with satisfactory results.

Acknowledgements

This work was supported by a Chongqing Fuling district science and technology commission funded project (FLKJ, 2013ABB2088) and the National Natural Science Foundation of China (no. 21175015). All authors here express their deep thanks.

References

- Z. Chen and D. D. Wu, *Colloids Surf., A*, 2012, **414**, 174.
- P. P. Li, S. P. Liu, S. G. Yan, X. Q. Fan and Y. Q. He, *Colloids Surf., A*, 2011, **392**, 7.
- J. H. Wang, H. Q. Wang, H. L. Zhang, X. Q. Li, X. F. Hua, Z. L. Huang and Y. D. Zhao, *Colloids Surf., A*, 2007, **305**, 48.
- H. Yan and H. F. Wang, *Anal. Chem.*, 2011, **83**, 8589.
- Z. A. Peng and X. G. Peng, *J. Am. Chem. Soc.*, 2001, **123**, 183.
- A. L. Rogach, T. Franzl, T. A. Klar, J. Feldmann, N. Gaponik, V. Lesnyak, A. Shavel, A. Eychmuller, Y. P. Rakovich and J. F. Donegan, *J. Phys. Chem. C*, 2007, **111**, 14628.

- 7 J. M. Costa-Fernandez, R. Pereiro and A. Sanz-Medel, *TrAC, Trends Anal. Chem.*, 2006, **25**, 207.
- 8 R. Gill, M. Zayats and I. Willner, *Angew. Chem., Int. Ed.*, 2008, **47**, 7602.
- 9 J. P. Yuan, W. W. Guo, X. R. Yang and E. K. Wang, *Anal. Chem.*, 2009, **81**, 362.
- 10 B. Tang, L. H. Cao, K. H. Xu, L. H. Zhuo, J. H. Ge, Q. F. Li and L. Yu, *Chem.–Eur. J.*, 2008, **14**, 3637.
- 11 L. F. Shi, V. De Paoli, N. Rosenzweig and Z. Rosenzweig, *J. Am. Chem. Soc.*, 2006, **128**, 10378.
- 12 R. C. Somers, M. G. Bawendi and D. G. Nocera, *Chem. Soc. Rev.*, 2007, **36**, 579.
- 13 K. E. Sapsford, T. Pons, I. L. Medintz and H. Mattoussi, *Sensors*, 2006, 925.
- 14 I. Yildiz, M. Tomasulo and F. M. Raymo, *Proc. Natl. Acad. Sci. U. S. A.*, 2006, **103**, 11457.
- 15 R. F. Pastemack, C. Bustamante and P. Collings, *J. Am. Chem. Soc.*, 1993, **115**, 5393.
- 16 P. Bao, A. G. Frutos, C. Greef, J. Lahiri, U. Muller, T. C. Peterson, L. Warden and X. Y. Xie, *Anal. Chem.*, 2002, **74**, 1792.
- 17 T. Zhao, J. Y. Zhang, X. G. Cheng, X. G. Chen and Z. D. Hu, *J. Agric. Food Chem.*, 2004, **52**, 3688.
- 18 Y. F. Long, C. Z. Huang and Y. F. Li, *J. Phys. Chem. B*, 2007, **111**, 4535.
- 19 J. Ling, C. Z. Huang, Y. F. Li, Y. F. Long and Q. G. Liao, *Appl. Spectrosc. Rev.*, 2007, **42**, 177.
- 20 H. Q. Chen, F. G. Xu, S. Hong, *et al.*, *Spectrochim. Acta, Part A*, 2006, **65**, 428.
- 21 Z. G. Chen, L. Zhu, T. H. Song, J. H. Huang and Y. L. Han, *Anal. Chim. Acta*, 2009, **635**, 202.
- 22 J. M. de l Fuente, A. G. Barrientos, T. C. Rojas, J. Rojo, J. Canada, A. Fernandez and S. Penades, *Angew. Chem., Int. Ed.*, 2001, **40**, 2257.
- 23 J. Liu, W. Zhao, R. L. Fan, W. H. Wang, Z. Q. Tian, J. Peng, D. W. Pang and Z. L. Zhang, *Talanta*, 2009, **78**, 700.
- 24 P. Wu, T. Zhao, Y. F. Tian, L. Wu and X. D. Hou, *Chem.–Eur. J.*, 2013, **19**, 7473.
- 25 P. Wu, L. N. Miao, H. F. Wang, X. G. Shao and X. P. Yan, *Angew. Chem., Int. Ed.*, 2011, **50**, 8118.
- 26 V. J. Theodorides, R. J. Gyurik, W. D. Kingsbury and R. C. Parish, *Experientia*, 1976, **32**, 702.
- 27 Q. McKellar and E. Scott, *J. Vet. Pharmacol. Ther.*, 1990, **13**, 223.
- 28 G. C. Batzias and G. A. Delis, *J. Chromatogr. B: Anal. Technol. Biomed. Life Sci.*, 2004, **805**, 267.
- 29 Z. Wu, N. J. Medlicott, M. Razzak and I. G. Tucker, *J. Pharm. Biomed. Anal.*, 2005, **39**, 225.
- 30 D. Kitzman, K. J. Cheng and L. Fleckenstein, *J. Pharm. Biomed. Anal.*, 2002, **30**, 801.
- 31 A. L. Santos, R. M. Takeuchi and M. P. Mariotti, *Il Farmaco*, 2005, **60**, 671.
- 32 X. Y. Chen, L. Y. Zhao, H. Y. Xu and D. F. Zhong, *J. Pharm. Biomed. Anal.*, 2004, **35**, 829.
- 33 P. Chiap, B. Evrard, M. A. Bimazubute, P. de Tullio, Ph. Hubert, L. Delattre and J. Crommen, *J. Chromatogr. A*, 2000, **870**, 121.
- 34 K. Ganesh and K. P. Elango, *Spectrochim. Acta, Part A*, 2012, **93**, 85.
- 35 G. Y. Zhao, H. Wu, S. L. Dong and Li M. Du, *Chin. Chem. Lett.*, 2008, **19**, 951.
- 36 Y. F. Liu and L. J. S. Yu, *J. Colloid Interface Sci.*, 2009, **333**, 690.
- 37 C. Würth, M. G. González, R. Niessner, U. Panne, C. Haisch and U. Resch-Genger, *Talanta*, 2012, **90**, 30.
- 38 M. Grabolle, M. Spieles, V. Lesnyak, N. Gaponik, A. Eychmüller and U. Resch-Genger, *Anal. Chem.*, 2009, **81**, 6285.
- 39 L. Li, H. F. Qian, N. H. Fang and J. C. Ren, *J. Lumin.*, 2006, **116**, 59.
- 40 J. R. Lakowicz, *Principles of fluorescence spectroscopy*, Springer Press, New York, 3rd edn, 2006.
- 41 B. K. Paul and N. Guchhait, *Photochem. Photobiol. Sci.*, 2011, **10**, 980.
- 42 Z. X. Cai, G. X. Chen, X. Huang and M. H. Ma, *Sens. Actuators, B*, 2011, **157**, 368.
- 43 F. L. Tian, J. D. Yang, W. Huang, S. Zhou and G. Y. Yao, *Spectrochim. Acta, Part A*, 2013, **116**, 57.
- 44 H. P. Gong, S. P. Liu, P. F. Yin, S. G. Yan, X. Q. Fan and Y. Q. He, *Acta Chim. Sin.*, 2011, **69**, 2843.
- 45 T. S. Li, S. P. Liu, Z. F. Liu, X. L. Hu and L. P. Zhang, *Sci. China, Ser. B: Chem.*, 2009, **52**, 76.