CdSe/ZnS Quantum Dots As a Fluorescence Probes For Determination of Vitamin B₁

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Research Article

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Abstract

This paper presents a new and fast method for determination of vitamin B1 (thiamine) using functionalized CdSe/ZnS quantum dots (QDs) as a sensor. In this study the core-shell CdSe/ZnS QDs with thioglycolic acid capping agents were synthesized by wet chemical method in aqueous solution. Electronic absorption was applied for size determination of the QDs, the average diameters of the synthesized quantum dots were calculated using wavelength of the first excitonic absorption peak. The methods of FESEM and FTIR were also used for characterization of the prepared samples. The results indicated that vitamin B1 could effectively quench the QDs emission and the fluorescence intensity decreased linearly with the concentration of vitamin B1 ranging from 10^{-7} to 10^{-4} mol L $^{-1}$ with limit of detection of 2×10^{-8} mol L $^{-1}$. Determination of vitamin B1 in pills from two pharmaceutical companies were used as real samples using this method.

Introduction

Vitamin B1 (thiamine) is essential in carbohydrate metabolism and neural function. Thiamin is generally distributed in foods, but most contain only low concentrations of the vitamin. The richest sources are yeasts, liver and cereal grains. Severe thiamin deficiency results in the heart disease beriberi, nerve, loss of weight and irritability [1].

Quantum dots (QDs) are zero dimensional nanocrystals have smaller radius than bulk Bohr exciton radius [2]. The size of these nanoparticles is between molecules and bulk scale from 1 to 10 nm and often have spherical shape. Most of QDs are composed of the elements from II-IV, III-V and IV-VI groups of the periodic table of the chemical elements [3].

Individual electronic and optical properties of QDs that arise from quantum confinement and high surface area to volume ratio (SA/V) have caused their new technological applications [4]. QDs have wide applications including sensors [5], light emitting diodes [6], solar cells [7], lasers [8], medicine [9], imaging [10], photocatalysts [11] and antibacterial [12, 13].

The ability of QDs can be improved by capping them with different ligands; the capped QDs can be applied in biosystems owing to the hydrophilic nature of their surface.

It is promising that semiconductor nanocrystals also can be used as fluorescence probes [14–16] for chemical and biomedical applications. Up to now, various methods have been developed for the determination of thiamine, including, voltametric detection [17], high performance liquid chromatography (HPLC) [18, 19], spectrophotometric method [20, 21] and so on. However, these methods have some limitation such as complex operation and high cost. Compared with these methods, QDs fluorescence probe has many advantages like low cost, easy operation, low detection limit.

Capping agents have important role on the size of QDs their nucleation and particle growth process [22]. Thioglycolic acid (TGA) is a good capping agent. The functionalized CdSe/ZnS quantum

dots were used as chemical sensor of vitamin B1.

Experimental

2. 1. Reagents

All chemical compounds were reagent-grade and used as received without further purification. The following reagents are used for this synthesis: NaBH_4 , metallic selenium powder, $\text{CdCl}_2 \cdot 2\text{H}_2\text{O}$, NaOH , acetone, Na_2S , vitamin B1 and thioglycolic acid (TGA) were from Fluka chemical company, zinc acetate and CdSO_4 was purchased from Merk chemical company. Deionized water was used throughout.

2. 2. Instrumentation

UV-Visible spectra were obtained with the same spectral conditions on a UV-Vis spectrometer (PG instruments Ltd). The fluorescence spectra were recorded using a JASCO FP-8300 spectrofluorometer. The FTIR spectra were acquired by Fourier infrared spectrometry (AVATAR spectrophotometer) over the range $600\text{--}4000\text{ cm}^{-1}$ at room temperature. The pH value of the solutions was measured with 827 model of Metrohm pH meter. The images of the samples were performed on a field emission scanning electron microscopy coupled with energy dispersive X-ray spectrometer (FESEM/EDX) model TESCAN-MIRA3.

2. 3. Synthesis of TGA capped CdSe/ZnS QDs

In this work thioglycolic acid (TGA) was used as capping agent of for synthesise of CdSe/ZnS QDs via a wet chemical colloidal method in aqueous medium without using any organic solvent according to the previous reports [23]. Sodium hydrogen selenide (NaHSe) solution was synthesized in three necked flasks by dissolving 48 mg Se metallic powder and 453.6 mg NaBH_4 in 15 mL of deionized water, the clear solution was obtained after about 2 h [24]. The simple chemical reaction as follows:

Cd^{2+} solution was prepared by dissolving of 273.9 mg CdCl_2 in 285 mL deionized water. 74 μL of TGA was added to 95 mL of Cd^{2+} solution and the pH of solution was adjusted to 9 by stepwise addition of 1.0 M NaOH solution and were deoxygenated through bubbling N_2 gas for about 30 min and finally 5 mL of NaHSe solution was quickly injected into the reactant vessel. The solution was heated in water bath at 80°C under vigorous stirring under N_2 gas. The reaction as follows: The as-synthesized CdSe QDs were added to a solution that containing zinc acetate and TGA. The mixture was heated at boiling point of the the solution for 10 min and then 20 ml Na_2S solution was added dropwise. Finally the solution was refluxed for 1 h at 60°C . Thus, the core-shell TGA capped CdSe/ZnS QDs were obtained. Schematic presentation of the above reaction as follows:

Results And Discussion

3.1. Characterizations of the capped quantum dots

Capping agents are usually used in the functionalization of nanomaterials and could be used for the water solubilization and stabilization of QDs through steric stabilization, electrostatic repulsion, or a combination of both mechanisms [29, 30]. The capping agent should be covalently bonded to the QDs surface and S-containing capping agents are attached to the surface of the QDs through sulfur bonds and their functional groups control the surface characteristics of the QDs. Size determination of TGA capped quantum dots was monitored with sampling during the synthesis process of QDs, 6 mL of solution was taken and added excess amount of the acetone and then centrifuged (10000 rpm). The precipitate was washed and centrifuged for three times in order to remove free reagents and the salts in the quantum dots colloids. The QDs were dispersed in deionized water and then the UV-Vis spectra of the solution containing CdSe-TGA QDs were recorded and illustrated in Fig. 1. a.

The wavelengths of the first excitonic absorption of the quantum dots were extracted from the corresponding UV-Vis spectra ($\lambda = 468$ nm) and the size of CdSe QDs were obtained 2.08 nm by applying Eq. 2 [3].

$$D = (1.6122 \times 10^{-9}) \lambda^4 - (2.6575 \times 10^{-6}) \lambda^3 + (1.6242 \times 10^{-3}) \lambda^2 - (0.4277) \lambda + 41.57 \quad (2)$$

Where D (nm) is the diameter of a given quantum dot, and λ (nm) is the wavelength of the first excitonic absorption peak.

Absorption spectra of the CdSe-TGA QDs and core-shell CdSe/ZnS-TGA QDs are shown in Fig. 1.a. The red shift in the absorption peaks indicates the growth of ZnS shell on CdSe core and increasing the particle size. The morphology of the prepared TGA-capped core-shell CdSe/ZnS QDs was characterized by field emission scanning electron microscopy (FESEM) and illustrated in Fig. 1b. As can be observed the TGA-capped CdSe/ZnS QDs are mostly spherical shape with an average diameter of about 2.4 nm.

Figure 2. shows the powder XRD of TGA-capped CdSe/ZnS QDs. The characteristic zinc blend planes of 111, 220, and 311 located at 26.5°, 43.9° and 52.1° for CdSe/ZnS in the 10–60° 2 θ range are observed [25].

FTIR spectra of the TGA as well as capped QDs are presented in Fig. 3.

Signals at the wavenumbers of 2571 cm⁻¹ and 2363 cm⁻¹ in the pure thioglycolic acid (Fig. 5a) are associated to the SH group. These signals are almost disappeared in the spectrum of the CdSe/ZnS-TGA which specifies the -SH group is reacted with the surface of the QDs. The signals at 1226, 1383, 1574, and 3424 cm⁻¹ are related to the C = O stretching vibration, COO- symmetric stretching vibration, COO- asymmetric stretching vibration and, OH stretching vibration respectively [22]. The foregoing signals are shifted to the lower wavenumber in comparison with the pure TGA due to the attaching TGA with the QDs.

3.2. The effect of the concentration of thiamine on the fluorescence quenching

The band shape of fluorescence spectra of the quantum dots is significantly impacted by the size of the quantum dots [28]. The fluorescence spectra were recorded at the same spectral conditions with excitation wavelength of 480 nm. The trend of quenching on the fluorescence emission of TGA capped CdSe/ZnS QDs was recorded by adding various concentrations of thiamine to the solution and presented in Fig. 4a. It can be intuitively seen that the intensity of the peaks are diminished as the thiamine concentration increases from 0 to 100 μM . The quenching effect of thiamine can be described using the Stern-Volmer equation [?].

$$F_0/F = K_{SV}[Q] + 1$$

where F_0 and F are the fluorescence intensities in the absence and presence of quencher respectively and K_{SV} is the Stern-Volmer quenching constant. Here, F_0 and F are fluorescence emission of CdSe/ZnS QDs which measured at wavelength of 598 nm and $[Q]$ represents the concentration of thiamine. Figure 4b shows the Stern-Volmer plot, results indicate that there is a good linear relationship between the ratio of F_0/F and thiamine concentration with coefficient of determination (R^2) 0.994 and the linear range of 10^{-7} to 10^{-4} M. The Stern-Volmer quenching constant (K_{SV}) and the limit of detection ($3\sigma/S$) of TGA-capped CdSe/ZnS QDs with thiamine were obtained $6.77 \times 10^4 \text{ L M}^{-1}$ and $2 \times 10^{-8} \text{ M}$ respectively. The former figure of merit (the slope of plot) relies on the sensitivity which announces that this method has a good and favorable sensitivity for measuring of vitamin B1.

Besides the sensitivity requirement, high selectivity is also a key matter to be met in real sensors, especially when interfering substances coexist within the samples. To verify of the selectivity of the TGA capped CdSe/ZnS QDs probe for thiamine detection, the fluorescence signals from common interfering analytes including L-methionine, riboflavin, ascorbic acid, glucose and lactose were investigated and compared to that of thiamine (Fig. 5).

As clearly can be observed, the variation of the fluorescence intensity for all of substances are within the range of + 5 and - 5 percent except riboflavin whose change of the fluorescence intensity was much larger than 5%. This may be due to the functional group, which is similar to that of the capping agents affecting.

Table 1
presents the performance of the CdSe/ZnS Quantum dots as
a fluorescence probes for determination of vitamin B1 with
the other works

Methods	Detection limits (M)	Ref.
HPLC	3×10^{-6} M	[19]
Spectrophotometric method	1×10^{-6} M	[20]
Fluorimetric Method	2×10^{-6} M	[21]
Au/Graphene QDs FL probe	5×10^{-7} M	[35]
present study	2×10^{-8} M	

Communication of QDs and molecules powerfully influenced by their surface features at the QD-molecule interface.

Finally, two samples of pills from different pharmaceutical companies were selected as a real sample, the amount of vitamin B1 of those pills was determined using above method. The measured amounts of vitamin B1 were obtained near (with 3–4 % difference) as reported.

Conclusion

CdSe/ZnS QDs quantum dots were synthesized in aqueous solution using thioglycolic acid (TGA). The synthesized nanoparticles were characterized with the techniques of SEM, EDX, XRD and FTIR. On the basis of the results, a new method for measuring vitamin B1 would be introduced using TGA-capped CdSe/ZnS QDs probe as fluorescence sensor. The suggested method has good sensitivity, selectivity and limit of detection with reasonable linear range. (Table 1). The interfering examination specified measuring of vitamin B1 with this method is free from the other common interference.

Declarations

Funding ('Not applicable')

Conflicts of interest/Competing interests ('Not applicable')

Availability of data and material ('Not applicable')

Code availability ('Not applicable')

Authors' contributions (No funding from organization)

Ethics approval ('Not applicable')

Consent to participate (this work have done by graduate student only)

Consent for publication ('Not applicable')

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Figures

Figure 1

a) UV-Visible absorption spectra CdSe-TGA QDs and core-shell CdSe/ZnS-TGA QDs b) FESEM of core-shell CdSe/ZnS-TGA QDs

Figure 2

XRD pattern of TGA-capped CdSe/ZnS QDs

Figure 3

FTIR spectra (a) pure thioglycolic (TGA) and (b) CdSe/ZnS-TGA QDs.

Figure 4

a) Fluorescence emission spectra of TGA-capped CdSe/ZnS QDs ($\lambda_{\text{ex}}=480$ nm) with increasing amount of thiamine (0, 0.1, 0.2, 0.5, 2, 5, 10, 20, 50 and 100 μM), and (b) corresponding Stern–Volmer.

Figure 5

Effect of coexisting foreign substances on the fluorescence intensity of TGA-capped CdSe/ZnS QDs (concentration was 10^{-6} M) experiments were performed with the similar conditions and at room temperature)