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Selective turn-on fluorescence sensor for Ag^+ using cysteamine capped CdS quantum dots: Determination of free Ag^+ in silver nanoparticles solution

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ABSTRACT

Cadmium sulfide quantum dots capped with cysteamine (Cys–CdS QDs) were demonstrated as a selective fluorescence probe for sensing of free trace silver ions. The fluorescence intensity of the Cys–CdS QDs can be enhanced only in the presence of free Ag^+ and the fluorescence spectrum was slightly red shift from the original spectra. In addition, the fluorescence intensities were linearly increased upon increasing Ag^+ concentration. At the optimized condition for Ag^+ detection, when adding other metal ions to the Cys–CdS QDs solution, fluorescence spectra of Cys–CdS QDs did not change significantly revealing good selectivity of the sensors towards Ag^+. The working linear concentration range was found to be 0.1–1.5 μM with LOD of 68 nM. The proposed sensor was then applied to detect free Ag^+ in the silver nanoparticles solution. The results showed that the proposed sensor can be efficiently used with good accuracy and precision providing the simple method for detection of free Ag^+ in silver nanoparticles of quality control products.

1. Introduction

Nanoparticles play an important role in the development of nanoscience and nanotechnology due to new properties as compared to the conventional bulk materials. Silver nanoparticles (AgNPs) are one of the most interesting nanomaterials used in a variety of applications such as antibacteria agents in textiles industry [1]. Even though AgNPs are used for their antimicrobial properties, their toxicity is not yet clear whether due to the release of free silver ions (Ag^+), AgNPs or a combination of both species [2–4]. Basically, silver nanoparticles can be synthesized from the reduction of silver nitrate solution with several reducing agents [5–7]. Thus, it is possible that Ag^+ still remains in the solution. This may cause a lower effectiveness of the synthesized nanoparticles solution. Moreover, free Ag^+ can possibly be released from O_2-oxidized AgNPs [8]. Therefore, it is important to know the amount of free Ag^+ in the silver nanoparticles solution.

There are a few papers reporting the method of nanoparticles speciation probably due to the difficulty of measurements using conventional instrumental analysis. Recently, an excellent review regarding the silver nanoparticles analysis has been published [9]. In 2008, our group demonstrated a successful use of silver ion selective electrode (Ag^+–ISE) for determination of free Ag^+ and total Ag in the silver nanoparticles [10]. The detection principle was based on the fact that the Ag-ISE can respond to only free silver ions. In 2009, this work was extended to fabricate a glucose biosensor by using AgNPs as a redox marker [11]. Determinations of free Ag^+ in the AgNPs solution by several spectroscopy techniques were also reported. Guo and coworker reported a 2-mercaptoisonicotinic acid (2-MNA) functionalized Au nanoparticles (2-MNA-AuNPs) sensor for highly sensitive and selective detection of Ag^+ in aqueous solution in terms of the recognizable changes of the surface-enhanced raman scattering (SERS) spectra [12]. In addition, the combination of ion-exchange technique (IET), centrifugal ultrafiltration and single particle inductively coupled plasma mass spectrometry (SP ICP-MS) were demonstrated to determine very low concentrations of free Ag^+ in commercial AgNPs [8].

Fluorescence sensor is one of the useful techniques for the detection of free Ag^+. Nowadays, nanocrystalline semiconductors or quantum dots attract great attention from chemists as a new class of the inorganic fluorophores due to the unique superior properties than the classical organic fluorophores. Cadmium sulfide quantum dots with different capping molecules (CdS QDs) are one of the most popular quantum dots used as metal ion sensor probes. Recently, several types of quantum dots used as a sensor probe for detection of

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Ag^+ have been reported [13–18]. However, the reported sensors always worked by the fluorescence quenching approach which was frequently caused by many possible species especially heavy metal ions [19–28]. Thus far, a few QDs-based sensors in which fluorescence intensity was enhanced by Ag^+ have been reported [19,29–31].

Recently, a fluorescent method for determination of Ag^+ has been reported in the system of BSA absorption on the CdSe quantum dots modified with mercaptoacetic acid [13]. Peptide-coated CdS quantum dots were synthesized for photoluminescence detection of silver ions and copper ions [32]. However, both methods possessed relative low sensitivity and high detection limit owing to the quenching of optical signals of the quantum dots. Haram and coworker reported the use of water soluble CdSe capped with citrate for sensing of metal ions [14]. The fluorescence response of citrate capped CdSe towards ten different metal cations were studied. Among them, Ag^+ ions showed large quenching of the fluorescence intensity. The water-soluble CdS QDs surface modified with L-cysteine were prepared by one step synthesis [29]. Fresh L-cysteine and functionalized CdS QDs were combined to give a novel and highly sensitive fluorescence probe for optical recognition of silver ions. Citrate-capped CdSe quantum dots were demonstrated as a selective quenching sensor of Ag^+ [14]. Moreover, a novel strategy for selective detection of Ag^+ based on the red-shift of emission wavelength of TGA-CdTe QDs was reported [33]. Under optimal conditions, a linear relationship did exist between the red-shift of the emission and the concentration of Ag^+.

From intensive reviews with available resources, there has been no report focusing on the determination of free Ag^+ in AgNPs solution by the fluorescence quantum dots. Herein, we report a fluorescent turn-on sensor for selective detection of silver ions (Ag^+) based on the unmodified cysteamine capped CdS quantum dots (Cys–CdS QDs). The fluorescence intensity of Cys–CdS QDs can be enhanced only in the presence of Ag^+. Possible parameters affecting the enhancement ability of Ag^+ are investigated. Moreover, selectivity of the sensor towards other metal ions is also reported. In addition, the proposed sensor is, for the first time, used to determine free Ag^+ in AgNPs solution with satisfactory results.

2. Experimental

2.1. Chemicals

All reagents were of analytical grade and used without further purification. Cadmium chloride ($CdCl_2 \cdot H_2O$) was obtained from Riedel-deHaen. Cysteamine hydrochloride was purchased from Sigma. Sodium sulfide ($Na_2S.H_2O$) and silver nitrate were received from BDH. Ferric nitrate nonahydrate, lead (II) nitrate, nickel nitrate hexahydrate and zinc nitrate hexahydrate were purchased from Fluka. Sodium acetate and sodium hydroxide were obtained from Carlo Erba Reagents. Glacial acetic acid was purchased from QRec. Ultrapure water (18.2 MΩ cm) was obtained from a Millipore water purification system. Water colloids of high concentration silver nanoparticles (10,000 ppm) were synthesized via the chemical reduction process from previous reports [11] and diluted with pure water to the appropriate concentration before using.

2.2. Synthesis of cysteamine capped CdS quantum dots (Cys–CdS QDs)

Cysteamine capped CdS QDs were prepared in aqueous solution using the method described previously [34]. Briefly, $CdCl_2 \cdot H_2O$ (1.8812 g, 9.34 mmol) was dissolved in 100 mL of pure water in a round bottom flask, and cysteamine hydrochloride (2.1245 g, 18.7 mmol) was successively added (dissolved in 5 mL of pure water) with stirring and purging nitrogen for 30 min. Then, the solution pH was carefully adjusted to pH 6.5 by adding 1 M NaOH dropwise. In a separate funnel, $Na_2S \cdot H_2O$ (0.7296 g, 9.35 mmol) was dissolved in 5 mL of pure water. The Na_2S solution was subsequently added into the reaction mixture under nitrogen. After refluxing at 65 °C under nitrogen for 1 h, a bright yellow colloid was obtained. The concentration of colloidal quantum dots was calculated using the original cadmium source and found to be 0.0710 M. Colloidal quantum dots were stored at room temperature. No precipitation was observed over a one month period.

2.3. Instrumentations

Fluorescence spectra were recorded using a RF-5301PC spectrofluorometer (Shimadzu). The slit width used for both excitation and emission were 5 nm. Absorption spectra of the quantum dots solution was measured on an Agilent HP 8453 UV–vis spectrophotometer. The transmission electron microscopy (TEM) images of the Cys–CdS QDs were carried out on Tecnai G^2-20 (FEI, Netherlands) under the accelerating voltage of 200 kV. Measurements of pH were carried out using a UB-10 UltraBasic pH meter (Denver Instrument).

2.4. Determination of Ag^+ by Cys–CdS QDs

To a 10 mL volumetric flask containing 100 μL of the quantum dots solution was added the stock solution of Ag^+ to the desired concentration levels. The mixture was made to a final volume of 10.00 mL with 100 mM acetic-acetate buffer at pH 4.6. The solution mixture was then incubated at room temperature for 10 min. The fluorescence intensity was measured at $\lambda_{em}/\lambda_{ex}$= 525/360 nm. The fluorescence intensity of Cys–CdS QDs was assigned as F_0. The fluorescence intensity after adding Ag^+ was assigned as F. The different intensity ($F-F_0$) was plotted versus the concentration of Ag^+ to obtain a calibration curve.

2.5. Interference studies

To evaluate the selectivity of the proposed sensor, the following procedure was carried out. An individual stock solution of various metal ions (0.1 mM) was prepared by dissolution of a metal salt in ultrapure water. To a 10 mL volumetric flask containing 100 μL of the quantum dots solution was added 300 μL of 0.1 mM of a metal ion (final concentration of 3 μM). Then, the volume of the mixture was adjusted with 100 mM acetic-acetate buffer solution pH 4.6, and the mixture was left for 5 min before recording the fluorescence spectrum.

2.6. Applications for determination of free Ag^+ in AgNPs solution

To measure free Ag^+ in AgNPs solution, AgNPs solution was firstly diluted to 10 ppm by ultrapure water because the original solution was relatively concentrated. To a 10 mL volumetric flask containing 100 μL of Cys–CdS QDs solution was added 80 μL of 10 ppm AgNPs and diluted with a small amount of 100 mM acetic-acetate buffer. The concentration of free Ag^+ can be calculated using the standard calibration curve. For standard addition method, an appropriate volume of 1.0 mM Ag^+ solution was added into the mixture of 100 μL of Cys–CdS QDs and 80 μL of 10 ppm AgNPs. Then the volume of the mixture was adjusted with 100 mM acetic-acetate buffer solution pH 4.6, and the mixture was left for 5 min before recording the fluorescence spectrum. The concentration of free Ag^+ can be calculated from the linear equation obtained from the standard calibration curve.

3. Results and discussion

According to our previous reports, the cysteamine capped cadmium sulfide quantum dots (Cys–CdS QDs) were synthesized and completely characterized [34]. The synthesized quantum dots were used as a sensitive and selective cyanide sensor. The fluorescence intensity of Cys–CdS QDs can be selectively quenched by Cu^{2+} and recovered again by CN^-. The degree of fluorescence recovery can be directly related to the concentration of CN^-. When studying of the interactions between Cys–CdS QDs and various metal ions, the preliminary results showed that Ag^+ gave different spectroscopic results compared to other tested metal ions (condition: 100 mM acetic-acetate buffer pH 4.6). The fluorescence intensity was enhanced by Ag^+ but did not show a significant change for other tested metal ions. Therefore, this sensor was highly selective and sensitive toward Ag^+ by direct interactions on the Cys–CdS QDs surface. We further explore several parameters that can affect the sensor efficiency in details.

3.1. Characteristics of the Cys–CdS QDs

Absorption and emission spectra of Cys–CdS QDs are shown in Fig. 1. The Cys–CdS QDs showed the important characteristic of the nanocrystalline quantum dots which are better than the classical organic fluorophore. The wide absorption spectra can be observed in the range of ultraviolet wavelength to around 390 nm. The onset absorption peak at 390 nm can be used to confirm that the synthesized particles are different from the similar bulk materials (CdS) and related to the band gap energy of 3.18 eV. The corresponding emission spectra which were excited at 360 nm showed the maximum fluorescence intensity at 525 nm. The large Stokes shift between the maximum absorption wavelength and the emission wavelength (more than 150 nm) can be observed. This characteristic is not always observed when using organic fluorophores. Moreover, this characteristic can be useful for the analytical method using fluorescence measurements due to the elimination of spectrum overlap. The fluorescence spectrum shape exhibited a symmetric and narrow emission spectra signifying that the Cys–CdS QDs were nearly homogeneous and monodisperse [35].

We have further investigated the effect of cysteamine toward the fluorescence intensity of the QDs. Therefore, we have synthesized Cys–CdS QDs with different mole ratios between Cd and cysteamine using exactly the same procedure. The mole ratios between Cd and cysteamine were increased 0.5 and 1.0 times and decreased 0.5 times for 1:3, 1:4, and 1:1 mol ratios, respectively. The absorbance and fluorescence spectra at each cysteamine levels were shown in Fig. S1 (ESI).

The results showed that when decreasing the amount of cysteamine to be lower than 1:2 ratio (Cd:Cys by mole), the Cys–CdS QDs cannot be synthesized. In addition, when increasing the amount of cysteamine the fluorescence intensity of the resulted QDs was increased. However, the fluorescence spectra were broader than that of the ratio 1:2 used in this work.

The size and shape of the Cys–CdS QDs were characterized by TEM as shown in Fig. 2. From the TEM image, it was clearly seen that the Cys–CdS QDs used in this work possessed the size of 3.6 ± 1.2 nm ($N=72$) and a lower particle size distribution. Therefore, the synthesized Cys–CdS QDs showed excellent nanoparticle characteristics and could be used to fabricate Ag^+ sensors.

3.2. Fluorescence enhancement of Cys–CdS QDs by Ag^+

In this work, we fabricate the fluorescence turn-on sensors based on the Cys–CdS QDs for detection of Ag^+. The preliminary experiment is carried out by adding 1 μM Ag^+ into the solution of 0.71 mM Cys–CdS QDs in 100 mM acetic-acetate buffer pH 4.6. The results are shown in Fig. 3a. In the presence of only 1 μM of Ag^+ the fluorescence intensity of the original quantum dots is enhanced ca. 2 times with the same spectrum shape and a relatively small red shift.

Enhancement of the fluorescence intensity of the QDs by Ag^+ has been examined extensively by Zhu [29] and Wang [30]. Basically, Ag^+ could coordinate to thiols on the surface of Cys–CdS QDs due to its strong affinity towards RSH and RS^- compounds. The complex of Ag^+ and RS^- which was adsorbed on the surface of the quantum dots can enhance the recombination fluorescence of the QDs by the creation of more radiative centers at the CdS/Ag–SR complex microheterojunctions and stimulation blocking of nonradiative e^-/h^+ recombination defect sites on the surface of QDs. Moreover, the relatively small red shift in the spectra after adding Ag^+ suggests the increase in size of the particles by the creation of more radiative centers or new radiative centers from the complex of Ag^+ and cysteamine absorbed on the surface of Cys–CdS QDs. The result from the emission spectrum corresponds well to the result from the absorption spectrum. As

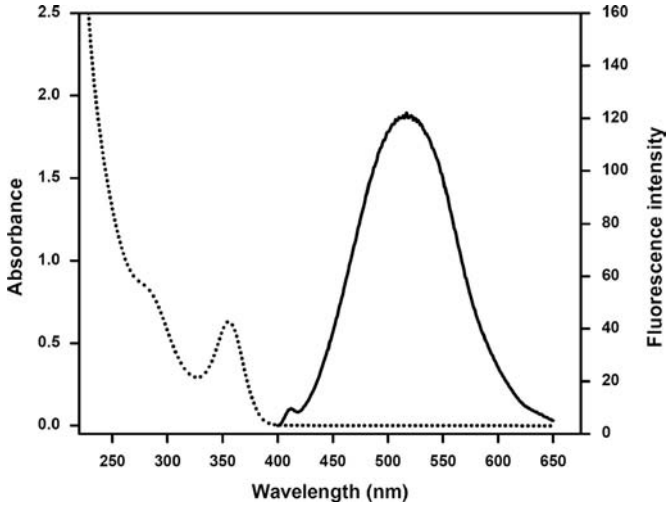

Fig. 1. Absorption spectrum (⋯) and fluorescence spectrum (—) of the Cys–CdS QDs. Excitation wavelength and emission wavelength are 360 nm and 520 nm, respectively. (Concentration of Cys–CdS QDs: 0.71 mM).

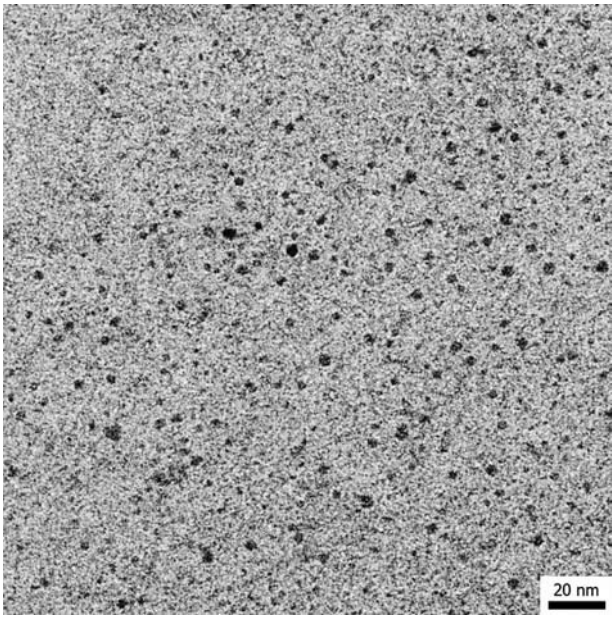

Fig. 2. TEM image of the synthesized Cys–CdS QDs.

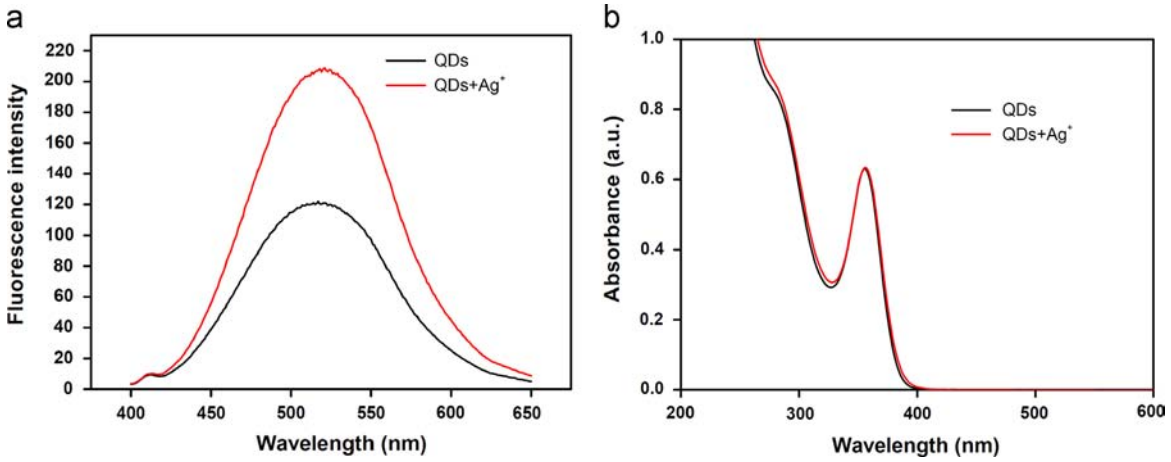

Fig. 3. (a) The enhancement of the fluorescence intensity of 0.71 mM Cys–CdS QDs in the presence of 1 μM Ag^+ in 100 mM acetic-acetate buffer pH 4.6. (b) Absorption spectra of 0.77 mM Cys–CdS QDs before and after addition of 5 μM Ag^+.

shown in Fig. 3b, after the addition of Ag^+ (5 μM), the absorbance spectra of the Cys–CdS QDs is identical to the original spectrum with a relatively small red shift. This behavior occurs only on the material with the particle size smaller than its own Bohr exiton radius [36,37].

The binding of Ag^+ on the QDs surface may be explained by Langmuir-type binding isotherm. The fluorescence intensity of the QDs increases with the increasing concentration of Ag^+ which occupies the binding sites on the QDs surface. Therefore, the surface of the nanoparticles consists of a finite number of binding sites and each of the binding sites can be occupied by only one Ag ion. The linear relationship of the Langmuir-type binding isotherm is expressed in the following equation [29,30]:

$$\frac{[Ag^+]}{F} = \left(\frac{1}{B \times F_{max}}\right) + \left(\frac{1}{F_{max}}\right)[Ag^+] \quad (1)$$

F and F_{max} are fluorescence intensity obtained at a given Ag^+ concentration and the maximum fluorescence intensity, respectively and B is the binding constant.

From this relationship, if the binding of Ag^+ on the QDs surface obey the Langmuir-type binding isotherm, a plot of $[Ag^+]/F$ as a function of $[Ag^+]$ should be linear. The plotting result agrees with this isotherm as shown in the plot in Fig. S2 (ESI). The regression equation is $[Ag^+]/F = 0.0006 + 0.0029[Ag^+]$ ($\times 10^{-6}$ mol L^{-1}). By fitting the linear equation with the experimental data, the binding constant B can be calculated and is found to be 4.83 with the correlation coefficient of 0.9785. This behavior suggests that the probability of binding more than one Ag ion to the surface of an individual nanoparticle is negligible in this work.

From the preliminary results, it can be concluded that the Cys–CdS QDs can be used as fluorescence probe for Ag^+ sensing by fluorescence enhancement strategy. For the best sensor efficiency, optimized conditions are further investigated.

3.3. Effect of concentration of Cys–CdS QDs on the detection of Ag^+

The concentration of nanoparticles in fabricated sensors plays an important role in the detection sensitivity. This behavior stems from the quantum confinement effect of nanoparticles which is related to their size. Basically, the synthesized particles are not exactly the same size, and therefore some particle size distribution may be expected. From the nature of these nanoparticles, at higher concentration of quantum dots, the emission light from smaller particles may absorb by the larger particles. Therefore, the fluorescence intensity will not directly relate to quantum dots concentration. On the other hand, if the solution is more dilute, the amount of the sensor would be limited and affect the sensor sensitivity. Therefore, the concentration of quantum dots must be studied.

The concentration of Cys–CdS QDs was varied from 0.35 to 3.54 mM by controlling the solution pH at 4.6 by 100 mM acetic-acetate buffer. The fluorescence intensities increased when the concentration of Cys–CdS QDs increased from 0.35 to 2.12 mM due to the higher number of nanoparticles in the solution (Fig. 4a). However, upon further increasing the concentration of Cys–CdS QDs beyond 2.12 mM, the fluorescence intensities did not increase.

The higher fluorescence intensity is needed for sensor fabrication and the sensitivity of the sensor should also be accounted for. Therefore, 1 μM of Ag^+ was added into various Cys–CdS QDs concentrations, and the difference of the fluorescence intensities after and before ($F - F_0$) addition of Ag^+ was compared as illustrated in Fig. 4b. The highest detection sensitivity was obtained at lower concentrations of Cys–CdS QDs. However, the precision at 0.71 mM Cys–CdS QDs was better than the precision at 0.35 mM Cys–CdS QDs. The concentration of Cys–CdS QDs at 0.71 mM was then used for further investigation.

3.4. Effect of the solution pH on the fluorescence enhancement by Ag^+

The effect of the solution pH towards the fluorescence enhancement of Cys–CdS QDs by Ag^+ was studied. The experiment was carried out by adjusting 100 mM acetic-acetate buffer containing 0.71 mM Cys–CdS QDs and 1 μM Ag^+ to the desired pH. Basically, the capping molecule used in this work is a weak base (primary amine). Therefore, the charge on the quantum dots surface should depend on degree of protonation of the amino groups. Changes in surface charge always affect the electron–hole recombination process which reflects by the fluorescence intensity of the quantum dots. Moreover, surface charge may affect interactions between interested species and the quantum dots surface. Thus, the solution pH of the running assay must be studied. The fluorescence spectra of 0.71 mM Cys–CdS QDs at different solution pHs (adjusted the pH of 100 mM acetic acid solution) are shown in Fig. 5a. At pH 4.6, the Cys–CdS QDs provided the highest intensity while pHs above and below 4.6 decreased the fluorescence intensity. When adding 1 μM of Ag^+, the fluorescence intensity of Cys–CdS QDs was enhanced for all studied pHs (Fig. 5b). The highest fluorescence enhancement efficiency was also found at pH 4.6.

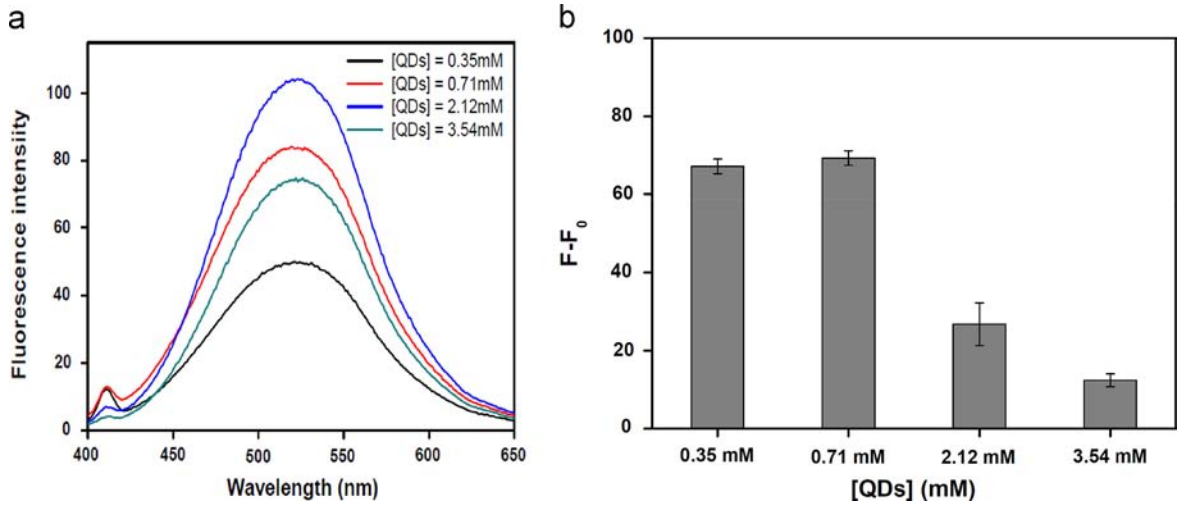

Fig. 4. (a) Fluorescence spectra of the Cys–CdS QDs at different concentrations in 100 mM acetic-acetate buffer pH 4.6. (b) Effect of concentration of Cys–CdS QDs on the enhancement of the fluorescence intensity in the presence of 1 μM silver ion in 100 mM acetic-acetate buffer pH 4.6.

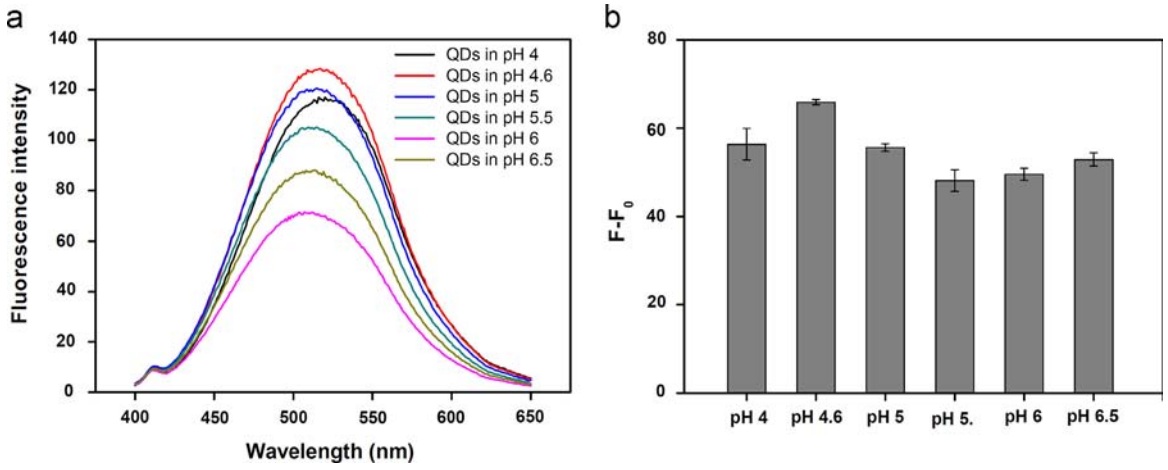

Fig. 5. (a) Fluorescence spectrum of the Cys–CdS QDs at different solution pH in 100 mM acetic-acetate mixture. (b) Effect of pH on the enhancement of fluorescence intensity of Cys–CdS QDs in the present of 1 μM Ag^+ in 100 mM acetic-acetate buffer.

3.5. Selectivity of the sensor

Selectivity is the most important characteristic of a new proposed sensor. Ideally, the sensor should respond solely to interesting analytes without interfering from other species. Basically, the selectivity of the Ag^+ sensor can be obtained from the formation of a complex by a specific design ligand. We have reported the use of new ionophores based calix [4] arene incorporated in plasticized polymeric membrane as a selective sensor for Ag^+ by a potentiometric approach [10,38]. In this work the proposed sensor works by the coordination of Ag^+ to the quantum dots surface containing the thiol group. Therefore, the possible interfering ions that can interfere the detection of Ag^+ should be ions that can interact on the quantum dots surface by the same manner. The selectivity of the proposed sensors is depicted in Fig. 6. The fluorescence spectra of the Cys–CdS QDs in the presence of various metal ions are shown in Fig. 6a. It can be seen that the fluorescence spectra of the Cys–CdS QDs in the presence of most tested ions except Cu^{2+} and Hg^{2+} did not show any significant change from the original spectrum. In the case of Cu^{2+}, the emission spectrum exhibited a change in the spectrum shape, and the spectrum shifted to the longer wavelength (red shift) [34]. The comparison of the degree of fluorescence change which resulted from the addition of possible interfering ions is shown in Fig. 6b. It is clearly seen that only Ag^+ can enhance the fluorescence intensity of Cys–CdS QDs significantly, and other metal ions do not response to this probe. Furthermore, the sensor selectivity was evaluated by mixing other metal ions with Ag^+, and the fluorescence intensity was determined by the proposed sensor. The results shown in Fig. 6c confirmed that Ag^+ could be determined in the presence of other metal ions by the proposed sensor.

3.6. Merits of the proposed sensor on the detection of free Ag^+

The proposed sensor was optimized to obtain the best sensor sensitivity. The response of the sensor towards the change of Ag^+ concentration was evaluated using the optimized condition. The fluorescence spectra of Cys–CdS QDs at different concentrations of Ag^+ are shown in Fig. 7. Upon increasing Ag^+ concentration from 0.1 to 1.5 μM, the fluorescence intensities linearly increased as a function of the increasing Ag^+ concentration. It should be noted that the spectrum shape was the same but a relatively small red shift was observed. Moreover, the degree of fluorescence enhancement as a function of Ag^+ concentration is shown in the inset of Fig. 7. The sensor thus showed a good linear relationship between the fluorescence intensity enhancement $(F-F_0)$ and the concentration of Ag^+. The regression equation was found to be $F-F_0=74.71[Ag^+, \mu M]-0.91$ $(r^2=0.9971)$ with the working concentration range of 0.1–1.5 μM.

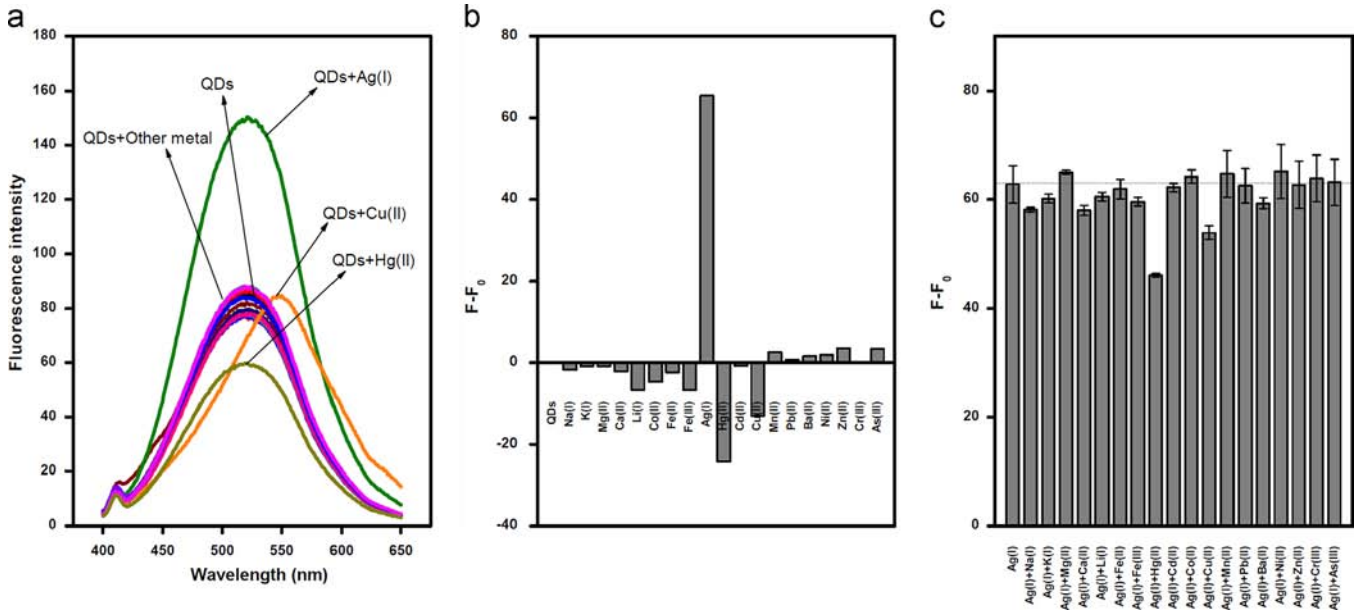

Fig. 6. (a) Fluorescence spectra of 0.71 mM Cys–CdS QDs with different metal ions in 100 mM acetic-acetate buffer pH 4.6. (b) The corresponding fluorescence intensity difference between before (F_0) and after (F) adding various metal ions to be a final concentration of 3 μM, (except Ag^+ (1 μM) and Na^+, K^+, Ca^{2+}, Mg^{2+} (1 mM)). (c) Different fluorescence intensity before (F_0) and after (F) adding the mixture of 1 μM of Ag^+ and coexist metal ions (except Na^+, K^+, Ca^{2+}, Mg^{2+} used at 1 mM).

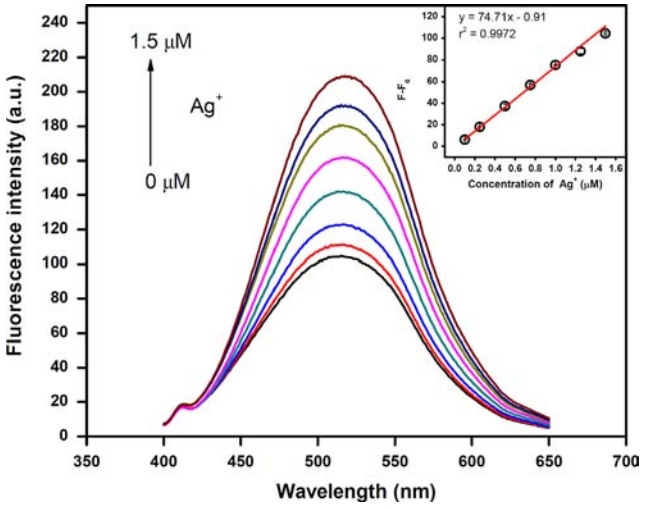

Fig. 7. Fluorescence spectra of 0.71 mM Cys–CdS QDs containing various concentration of Ag^+ range of 0.10–1.50 μM in 100 mM acetic-acetate buffer pH 4.6, (inset) the corresponding calibration curve.

The limit of detection (LOD) and limit of quantitation (LOQ) were also evaluated to demonstrate the limitation of the sensor. The LOD was calculated as the concentration of an analyte giving the fluorescence intensity equal to 3 × standard deviation of F_0, while the LOQ was measured as the concentration of an analyte giving the fluorescence intensity equal to 10 × standard deviation of F_0. The LOD and LOQ of the proposed sensor were 68 nM and 0.2 μM, respectively. The repeatability of the present method was also evaluated. The relative standard deviation from the detection of 0.25 μM Ag^+ for five replicates was found to be only 2.61%. The results suggested that the proposed sensor exhibited very good repeatability.

3.7. *Applications of the sensor for detection of free Ag^+ in the AgNPs solution*

Basically, atomic spectroscopy is a suitable technique for the analysis of trace metals. However, direct determination does not provide the chemical information of the metal species in the samples. Especially, in the case of the AgNPs solution which is composed of suspended colloidal nanoparticles and free Ag^+ ions. If the AgNPs solution is directly injected into the atomizer, total concentration of Ag in the solution will be obtained. This information seems not to be enough for the quality evaluation of nanoparticles. Therefore, the determination of each chemical species in nanoparticles solutions must be developed.

In our previous reports, we have successfully developed the first Ag^+ selective polymeric membrane electrode for speciation analysis of silver species in the AgNPs solution [10]. Furthermore, we have developed a new Cd^{2+} selective polymeric membrane electrode and used it in the analysis of CdS QDs [39].

In this work, the Cys–CdS QDs can selectively respond to free Ag^+ in the solution by fluorescence enhancement strategy. Therefore, it may be used to sense the remaining free Ag^+ in the AgNPs solution. However, in order to investigate the effect of the sample matrix and the method feasibility, the generation of signal (degree of fluorescence enhancement) from the increasing of Ag^+ in the solution containing AgNPs by the optimized sensor was evaluated. If the signal generated from standard free Ag^+ in the solution containing AgNPs similar to the generation from the increasing of Ag^+ in the buffer solution, the interference from the matrix of the AgNPs solution would be negligible. The results in Fig. 8a and b showed the fluorescence change upon the increment of Ag^+ in the solution with and without AgNPs, and the corresponding fluorescence change as a function of concentration is shown in Fig. 8c. Fluorescence changes based upon the addition of standard Ag^+ and AgNPs are in the same direction. This result showed that there was free Ag^+ remaining in the AgNPs solution and could interact with Cys–CdS QDs in the same manner as the free Ag^+ added. The linear line developed from standard Ag^+ in the solution without AgNPs superimposed on the line developed from the addition of Ag^+ in the solution with AgNPs implying that the matrix of AgNPs solution did not affect the detection of the remaining free Ag^+. In addition, the interference from the absorption of the suspended nanoparticles was not observed. Therefore, the Cys–CdS QDs sensor can be applied to detect the remaining free Ag^+ in the AgNPs solution.

Since the concentration of the AgNPs solution was quite high and the proposed sensor was very sensitive, the dilution was needed to

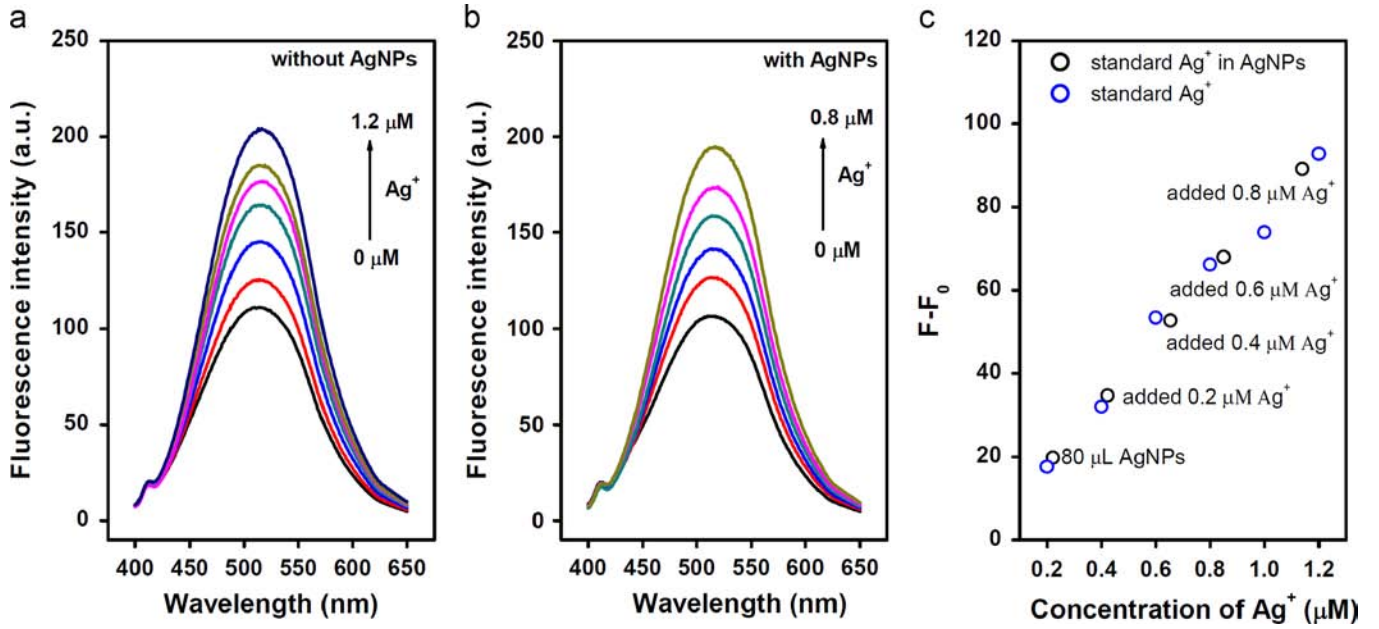

Fig. 8. Fluorescence spectra of Cys–CdS QDs at various concentrations of Ag^+ in the absence (a) and in the presence (b) of 0.08 ppm of concentrated AgNPs solution diluted to 10 mL in acetic-acetate buffer pH 4.6. (c) Comparison between the calibration curves of the fluorescence response of Ag^+ and the system containing AgNPs.

Table 1
Determination of Ag^+ in AgNPs solution by Cys–CdS QDs.

Method	Added Ag^+ (μM)	Found (μM) ($\pm$SD, n=4)	%Recovery ($\pm$SD, n=4)	%RSD
Standard curve	–	0.204 ± 0.016	–	–
	0.400	0.658 ± 0.011	109 ± 2	1.9
	0.800	1.100 ± 0.003	110 ± 3	2.3
Standard addition	–	0.198 ± 0.022	–	–

make a suitable Ag^+ concentration level. The concentration of free Ag^+ in diluted nanoparticles was determined by the calibration curve. Moreover, in order to test the method accuracy, the concentration of free Ag^+ in AgNPs solution was also evaluated by the standard addition method. The concentrations of free Ag^+ in AgNPs solution obtained by both methods are summarized in Table 1. The recoveries of spiked Ag^+ were obtained in the range of 109–110% with a satisfying analytical precision (%R.S.D.≤3). In addition, the concentration of free Ag^+ in the AgNPs solution determined by the direct calibration curve and standard addition method were not significantly different. Therefore, the accuracy of the proposed sensor was acceptable.

4. Conclusion

The fluorescence sensor for the detection of free Ag^+ using unmodified Cys–CdS QDs was successfully developed. In the presence of Ag^+, the fluorescence intensity of Cys–CdS QDs was increased as a linear function of Ag^+ concentration. The fabricated sensor showed good selectivity and sensitivity towards the detection of Ag^+ compared to other tested metal ions. The working linear concentration range was found to be 0.1–1.5 μM with the limit of detection (LOD) and limit of quantification (LOQ) of 68 nM and 0.2 μM, respectively. The proposed sensor was applied to detect free Ag^+ in the AgNPs solution with satisfactory results.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.talanta.2013.06.053.

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