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Cu^{2+}-modulated cysteamine-capped CdS quantum dots as a turn-on fluorescence sensor for cyanide recognition

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ABSTRACT

A new fluorescence sensor for detection of cyanide ions (CN^-) in aqueous media based on the recovered fluorescence of cysteamine capped CdS quantum dots [Cys-CdS QDs]-Cu^{2+} system was proposed. The fluorescence intensity of Cys-CdS QDs was quenched by Cu^{2+} due to the binding of Cu^{2+} to cysteamine on the surface of the QDs. The degree of fluorescence quenching was proportional to the concentration of Cu^{2+}. However, in the presence of CN^-, the fluorescence intensity of Cys-CdS QDs was found to be efficiently recovered. Experimental results showed that the pH of the buffer solution and the concentration of Cu^{2+} affected the fluorescence intensity upon adding CN^-. Under the optimal condition, the recovered fluorescence intensity was linearly proportional to the increasing CN^- concentration in the range 2.5–20 μM. The limit of detection and the limit of quantification were found to be 1.13 μM and 3.23 μM, respectively. In addition, among the tested ions, only CN^- could turn on the fluorescence intensity suggesting that the [Cys-CdS QDs]-Cu^{2+} system was a highly selective sensor for CN^-. Moreover, this proposed sensor was demonstrated to detect CN^- in drinking water with satisfactory results.

1. Introduction

Anion sensing has received considerable attention due to their important roles in biological, environmental, and industrial processes. Among various anions, cyanide (CN^-) is the most toxic inorganic anion [1]. It strongly interacts with active sites of cytochrome a_3 and inhibits the cellular respiration in mammalian cells [2,3]; as a result even its small amount is very lethal to human body. Despite its acute toxicity, cyanide is used in many industries such as metal plating, metal mining and plastics manufacture [4] and it does not easily decompose in the environment. As a consequence, accidental cyanide release in wastewater or rivers may lead to serious contamination of groundwater and drinking water. Therefore, it is necessary to develop an efficient and reliable sensing system for detecting cyanide from contaminant sources.

Nowadays, various analytical methods have been developed for the determination of cyanide ions such as chromatographic [5,6], fluorometric [7,8], flow injection [9,10] and electrochemical [11,12] analyses. Among these methods, fluorescence spectrophotometry is the most promising tool due to its intrinsically high sensitivity, low cost, easy detection and especially suitability as a diagnostic tool for biological concerns.

To date, a large number of fluorescence sensors for cyanide have been developed [13–17]. Among these sensing systems, synthetic organic dyes are usually used as fluorescence reporters. However, the relatively tedious synthesis and purification, low fluorescence quantum yields, low solubility in aqueous media, and poor photostability of organic fluorophores are limited for many applications [18].

Nanocrystalline quantum dots (QDs) have attracted considerable attention in recent years due to their unique and suitable optical characteristic for chemical and biological sensing such as high-quality fluorescence, the broad excitation and size-tunable fluorescence spectrum, relatively high quantum yields and photochemical stability [18–20]. These properties provide better advantages over conventional organic fluorophore in fluorescent applications, resulting in increasing the use of QDs as the fluorescent transducer in the new analytical chemistry direction. Recently, QDs-based sensors have been reported for the optical sensing of many metal ions (e.g. Cu^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+}, and Ag^+) [21–25], small organic molecules (e.g. butylamine) [26], organic pollutants (e.g. paraoxon and polycyclic aromatic hydrocarbons) [27,28] and small biological molecules (e.g. tyrosine and cysteine) [29]. However, most of these approaches work in a "turn-off" mode and their selectivities are still a major problem as

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the interactions of the metal ions and small molecules with QDs surface are not specific enough and many species can also affect the surface state of QDs in the turn-off mode. To improve the selectivity, several ion-specific ligands have been designed and appended onto the surface of QDs to provide a "turn-on" mode. Although QD-based fluorescence "turn-on" sensors were reported [30–34], the detection of cyanide by QD-based turn-on fluorescence sensors mode is rarely found [35,36]. For instance, Touceda-Varela et al. [35] reported the combination of hydrophobic CdSe QDs and $CuCl_2$ as a turn-on fluorescence cyanide probe. However, the use of toxic and volatile organic solvents limited the application of the developed method for a practical cyanide sensor. Recent studies by Shang et al. [36] showed a fluorescence turn-on sensor for selective detection of cyanide ions using the recovered fluorescence intensity of CdTe QDs which was quenched by Cu^{2+}. This sensor could work in pure aqueous media and possessed a low detection limit.

Herein, we report a new fluorescence turn-on sensor for selective detection of cyanide ions (CN^-) based on the recovered fluorescence intensity of the cysteamine capped CdS quantum dots [Cys-CdS QDs]-Cu^{2+} system. The fluorescence of Cys-CdS QDs is firstly quenched by Cu^{2+}, and then selectively recovered by cyanide ions based on the high copper–cyanide affinity. Possible parameters affecting the quenching ability of Cu^{2+} and the fluorescence recovery by CN^- are explored. Moreover, selectivity of the sensor toward cyanide ion is also studied and compared with those of other anions. In addition, the proposed sensor is used to determine cyanide ions in water samples with satisfactory results.

2. Experimental

2.1. Chemicals

All reagents used 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 ($Na_2S \cdot H_2O$), potassium cyanide, potassium fluoride and sodium carbonate were received from BDH. Potassium chloride and sodium sulfite were obtained from Merck. Potassium bromide, potassium nitrate, potassium sulfate, di-potassium hydrogen phosphate and tris-hydroxymethyl-methylamine were received from Univar. Potassium chlorate was purchased from Fluka. Copper (II) nitrate hexahydrate, potassium iodide, sodium acetate, and sodium nitrite were obtained from Carlo Erba. Ultrapure water (18.2 MΩ cm) was obtained from a Millipore water purification system.

2.2. Instrumentations

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

2.3. Synthesis of cysteamine capped CdS quantum dots (Cys-CdS QDs)

Cysteamine capped CdS QDs were prepared in aqueous solution using the method described previously [37] with modification. Briefly, $CdCl_2 \cdot H_2O$ (1.8824 g, 9.35 mmol) was dissolved in 100 mL of Milli-Q water in a three-necked round bottom flask, and cysteamine hydrochloride (5.3113 g, 46.75 mmol) was successively added with stirring. After stirring the mixture solution under nitrogen atmosphere for 30 min, pH of the solution was carefully adjusted to 6.5 by adding 1 M NaOH. In a different flask, $Na_2S \cdot H_2O$ (0.7297 g, 9.35 mmol) was dissolved in 10 mL of deionized water. The Na_2S solution was subsequently added into the reaction mixture under nitrogen. After refluxing at 75 °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 0.0636 M. Colloidal quantum dots were stored at room temperature. No precipitation was observed over a one month period.

2.4. Fluorescence quenching of Cys-CdS QDs by Cu^{2+}

To study the fluorescence quenching of Cys-CdS QDs by Cu^{2+}, the following general procedures were carried out. A stock solution of 1.0 mM $Cu(NO_3)_2$ was prepared. To a 10 mL volumetric flask, 100 μL of the quantum dots solution was added followed by the addition of stock $Cu(NO_3)_2$ to the given concentration level. The mixture was made to a final volume of 10.00 mL with 0.05 M Tris–HCl buffered pH 9.0. 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.

2.5. Fluorescence recovered by cyanide ion

To study the effect of cyanide ions on the fluorescence restoration from the Cu^{2+}-modulated Cys-CdS QDs system ([Cys-CdS QDs]-Cu^{2+}), the following procedure was carried out. A stock solution of KCN (1.0 mM) was prepared by dissolution of solid KCN in ultrapure water. To a 10 mL volumetric flask, 100 μL of quantum dots solution was added following by adding 400 μL of 1 mM Cu^{2+}. The mixture was diluted to about three quarters of the total volumetric flask with 0.05 M Tris–HCl buffer pH 9.0. Then, KCN stock solution was added and the mixture was further diluted to the mark with 0.05 M Tris–HCl buffer pH 9.0. The pH of the mixture after adding CN^- was always checked to make sure that the pH of the mixture did not exceed the buffer capacity. The solution was mixed thoroughly, and left for 10 min before recording the fluorescence spectrum.

2.6. Interference studies

To evaluate the selectivity of the proposed cyanide assay, following procedures were carried out. An individual stock solution of various anions (1.0 mM) was prepared by dissolution of an anion salt in ultrapure water. To a 10 mL volumetric flask, 100 μL of the quantum dots solution was added following by adding 400 μL of 1 mM Cu^{2+}. The mixture was diluted to about three quarters of the total volumetric flask with 0.05 M Tris–HCl buffer pH 9.0. Then, the stock solution of anions was added, and the mixture was further diluted to the mark with 0.05 M Tris–HCl buffer pH 9.0. The solution was mixed thoroughly, and left for 10 min before recording the fluorescence spectrum.

3. Results and discussion

3.1. Characterization of the synthesized Cys-CdS QDs

The water-soluble cysteamine functionalized CdS QDs (Cys-CdS QDs) were successfully synthesized according to the procedure described in the experimental section. The optical properties of Cys-CdS QDs were characterized and the results are shown in Fig. 1.

The first absorption peak indicated that the band gap of the synthesized quantum dots has shifted to higher energies as a consequence of the quantum confinement [38]. The absorbance edge of nanocrystals was 420 nm and the band gap was calculated to be 2.95 eV. The fluorescence emission maximum of Cys-CdS QDs was obtained at 525 nm when excited by the wavelength of 360 nm. The synthesized Cys-CdS QDs exhibited long emission wavelengths and a high Stokes shift between the excitation and emission wavelengths (more than 150 nm), providing a simplified fluorescence measurement with a high quantum yield [39]. The fluorescence spectrum showed relatively a symmetric and narrow emission band, suggesting that the synthesized Cys-CdS QDs were nearly homogeneous and monodisperse [40]. The fluorescence spectrum did not exhibit a tail on the longer wavelength side, suggesting that the synthesized quantum dots possessed good fluorescence properties.

Furthermore, the morphology of Cys-CdS QDs was also elucidated by TEM as shown in Fig. 2. The shape of the synthesized particles was close to spherical, and the particles have a uniform distribution with an average size of about 4.16 ± 0.86 nm. From the optical and morphological properties of the synthesized particles, Cys-CdS QDs possessed good nanoparticle characteristics and could be a potential probe in chemical sensors application.

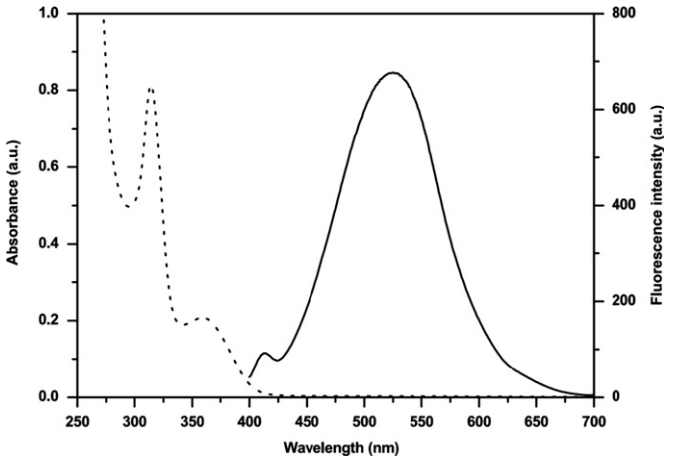

Fig. 1. Absorbance spectrum (——) and fluorescence emission spectrum (—) of cysteamine capped CdS QDs ($\lambda_{em}/\lambda_{ex}$=525/360 nm).

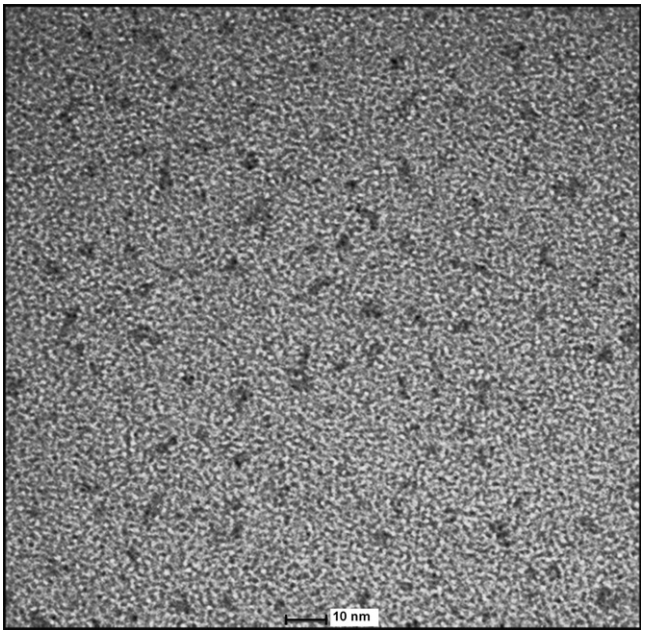

Fig. 2. TEM image of the synthesized Cys-Cds QDs.

3.2. Modulating the fluorescence intensity of Cys-CdS QDs by Cu^{2+}

The sensing of metal ions based on quantum dots as a sensing material was reported in many published papers. Detections of heavy metal and transition metal ions could be carried out by the fluorescence quenching approach [21,23,24,41–44]. Cu^{2+} was mainly a type of ions which strongly affected the fluorescence quenching of the quantum dots [23,43–45]. Moreover, it was well known that Cu^{2+} could react with CN^- ions to form a very stable complex [46]. Therefore, in this work Cu^{2+} was chosen as the fluorescence modulation ion for preparing a CN^- sensor.

The fluorescence intensity of Cys-CdS QDs in the presence of various concentration of Cu^{2+} in 0.05 M Tris–HCl buffer pH 9.0 is shown in Fig. 3. The unexpected result showed that the fluorescence intensity of Cys-CdS QDs was enhanced at low Cu^{2+} concentration ($Cu^{2+} < 10$ μM). On the other hand, the fluorescence intensity of Cys-CdS QDs was further quenched upon increasing the concentration of Cu^{2+}. The fluorescence enhancement of QDs at low Cu^{2+} concentration may stem from the decreasing of the small crystal defect on the surface of original quantum dots by Cu^{2+} ions. Meanwhile, a large redshift of fluorescence spectra (from 525 nm to 557 nm) was observed after adding 10 μM Cu^{2+}. This result implied the increasing diameter due to the formation of small particles around the surface of QDs and was pertinent to the size-tuning fluorescence spectra of QDs [47].

When the concentration of Cu^{2+} was higher than 10 μM, the fluorescence intensity of Cys-CdS QDs was reduced in conjunction with a large redshift of the emission peaks (up to 70 nm). This quenching may be due to the coordination of Cu^{2+} to the amine group of the capping molecule on the surface of Cys-CdS QDs [48]. Fluorescence quenching by Cu^{2+} may stem from the facilitating of nonradiative e^-/h^+ recombination on the surface of Cys-CdS QDs through an effective electron transfer process between surface amine groups and Cu^{2+} [39]. These results implied that there were two types of Cu^{2+} on the surface of Cys-CdS QDs. We expected that the coordinated Cu^{2+} on the quantum dots surface would form a reversible complex which could undergo a competitive equilibrium with cyanide ions.

It has been reported that pHs of the solution not only affect the fluorescence intensity of the QDs but also play an important role in the interaction of QDs with other molecules [25,49]. The main reason is most capping molecules possessing weak acid or weak base properties. Therefore, the solution pH controls the net charge on the quantum dots surface. The effect of different pH values on the fluorescence intensity of Cys-CdS QDs in the absence and presence of Cu^{2+} was investigated in the range of pH 7.5–9.5. The pHs of solution were varied by adjusting the pH of 0.05 M Tris–HCl buffer. The results are shown in Fig. 4. It was found that the pH of the solution did not significantly affect the fluorescence intensity of the synthesized Cys-CdS QDs in the studied pH range as shown in Fig. 4A. This result showed that the synthesized quantum dots could be used in a wide pH range.

On the other hand, the solution pH strongly affected the fluorescence quenching efficiency of Cys-CdS QDs by Cu^{2+} as shown in Fig. 4B. The quenching efficiency significantly increased when increasing solution pHs from 7.5 to 9.0, and leveled off from pH 9.0 to 9.5. The enhancement of the quenching efficiency when increasing solution pH may be due to the deprotonation of amine group on the surface of QDs. This led to the increasing coordination ability of amine groups toward Cu^{2+} on the quantum dots surface.

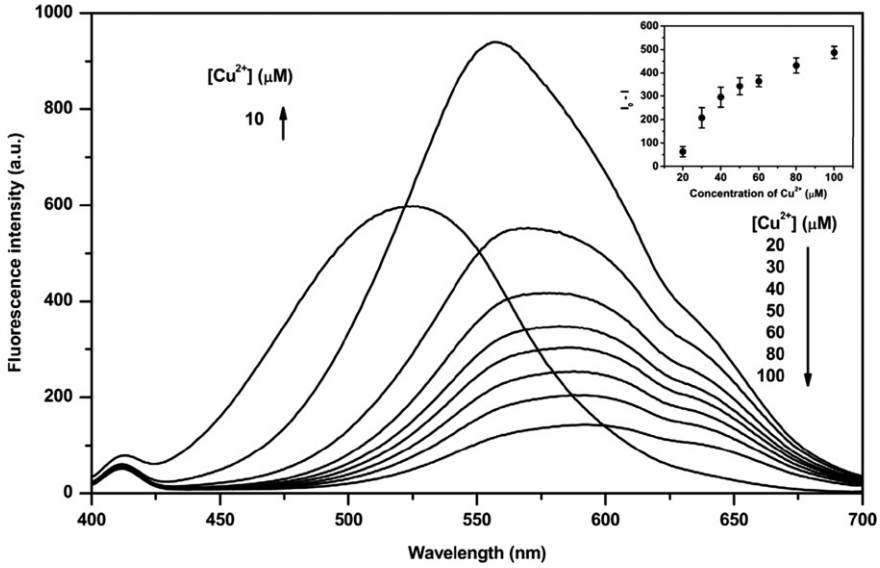

Fig. 3. Fluorescence quenching of Cys-Cds QDs upon addition of Cu^{2+}. The inset shows the relationship between $I_0 - I$ and Cu^{2+} concentration (where I_0 and I are fluorescence intensities of QDs in the absence and presence of Cu^{2+}, respectively).

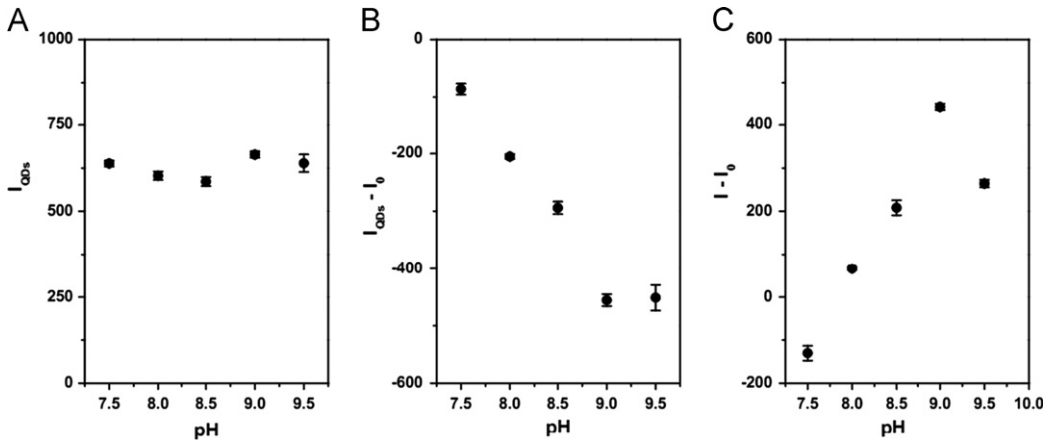

Fig. 4. Effects of pH on fluorescence intensity of Cys-Cds QDs (A), fluorescence quenching efficiency of Cys-Cds QDs by Cu^{2+} (50 μM) (B), and subsequent recovery of the fluorescence intensity by KCN (40 μM) (C).

3.3. Recovery of fluorescence intensity of Cu^{2+}-modulated Cys-CdS QDs by CN^-

According to the results in the previous section, the fluorescence quenching of Cys-CdS QDs was attributed to the coordination of Cu^{2+} to the amine group at the surface of QDs. Consequently, the fluorescence intensity of [Cys-CdS QDs]-Cu^{2+} could be restored by introducing CN^- to extract Cu^{2+} from Cys-CdS QDs surface by forming a stable $[Cu(CN)_n]^{(n-1)-}$ complex [46].

Although this concept was applied to [MSA-CdTe QDs]-Cu^{2+} (mercaptosuccinic acid: MSA) by Shang et al. [36], the sensing mechanism seemed to be different from that in this work. In that report, there was no discernible change in the shape of the fluorescence spectrum that accompanied quenching, except a slight redshift at higher Cu^{2+} concentration. In contrast, in our work the fluorescence spectrum showed a significant redshift only when Cu^{2+} added (over 70 nm) but did not show any spectrum shifts with other metal ions. The change of fluorescence spectrum occurred at a longer wavelength than the emission wavelength of the original quantum dots. Moreover, working at longer wavelength has lower potential interferences. This characteristic definitely gave a better selectivity in detecting CN^-.

Before studying the fluorescence recovery ability of [Cys-CdS QDs]-Cu^{2+} by CN^-, we firstly explored the effect of CN^- toward the original Cys-CdS QDs. It was found that CN^- did not significantly affect the fluorescence intensity of Cys-CdS QDs. This pointed out that we could not use unmodified quantum dots as a CN^- probe. Then, the experiment was carried out with the [Cys-CdS QDs]-Cu^{2+} system as a CN^- sensor platform. As shown in Fig. 5(A), the fluorescence intensity which was quenched by Cu^{2+} gradually increased upon increasing CN^- concentration. However, the shapes of the fluorescence spectra did not change (from the [Cys-CdS QDs]-Cu^{2+} spectrum). Furthermore, the emission spectra did not return to the original spectrum of Cys-CdS QDs. This implied that CN^- did not interact with Cu^{2+} from the surface of Cys-CdS QDs but it removed Cu^{2+} coordinating to the surface capping molecules of Cys-CdS QDs.

The photos under UV illumination were taken to show the turn-off–on procedure. Since the concentration of the Cys-CdS QDs used in this work was very low, the emission light cannot be observed using a camera. Therefore, concentrations of the sensors

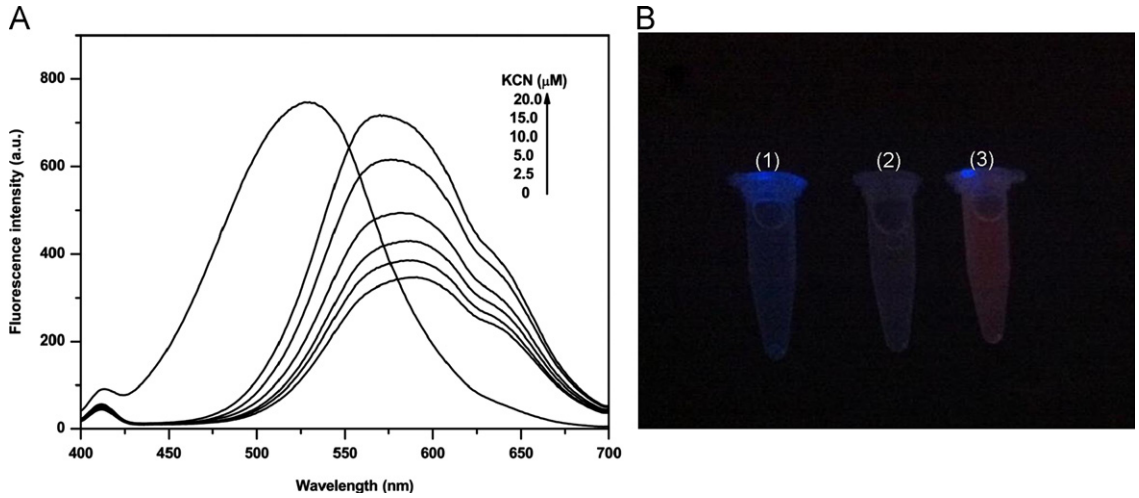

Fig. 5. (A) Fluorescence emission spectra of Cys-Cds QDs containing 40 μM Cu^{2+} in the presence of different concentrations of KCN. (B) Photos under UV illumination, Cys-CdS QDs (1), [Cys-CdS QDs]-Cu^{2+} before (2) and after (3) adding CN^-.

(Cys-CdS QDs and Cu^{2+}) for taking photos were increased to twice as the concentration used in the spectrofluorometer. Fig. 5(B) exhibits the emission light observed from three different systems: (1) Cys-CdS QDs , (2) [Cys-CdS QDs]-Cu^{2+} and (3) [Cys-CdS QDs]-Cu^{2+} after adding CN^-. The original QDs emitted the fluorescence light after UV illumination which was turned off upon adding Cu^{2+}. After adding CN^- into the [Cys-CdS QDs]-Cu^{2+} solution, the emission light can be turned on again with a different color from the original QDs. This observation corresponds well with the redshift of the spectrum from that of the original QDs obtained by the spectrofluorometer.

3.4. Factors affecting fluorescence restoration by CN^-

Basically, a sensor working in a "turn-on" mode is usually more sensitive than in a turn-off approach since the enhanced fluorescence nature of the signal transduction affords a much better signal-to-noise ratio for the sensing scheme [50]. As mentioned above, the fluorescence enhancement of [Cys-CdS QDs]-Cu^{2+} system could be utilized to develop an optical probe for detecting cyanide ions. In order to obtain the best sensing sensitivity, we then investigated various possible parameters that affected the detection sensitivity.

3.4.1. Effect of pH

According to the previous section, the pH of the solution strongly affected the fluorescence quenching ability of Cu^{2+} toward the synthesized Cys-CdS QDs. The same experiment was carried out for investigating the effect of solution pH on the fluorescence restoration ability of CN^-. To obtain an optimum pH, the influence of pH was studied by using 0.05 M Tris–HCl buffer and the solution pH varied from 7.5 to 9.5. The result is shown in Fig. 4C. The recovery of fluorescence intensity was significantly enhanced with the increasing of pH from 7.5 to 9.0, and then decreased markedly with further increasing pH. The optimal pH for the fluorescence recovery was at pH 9.0. This result showed that the formation of $[Cu(CN)_n]^{(n-1)-}$ complex strongly depended on the solution pH. Therefore, 0.05 M Tris–HCl buffer solution of pH 9.0 was chosen as a solvent medium for the running assay.

3.4.2. Concentration of Cu^{2+}

The concentration of Cu^{2+} in the running assay was also found to be an essentially important factor affecting the fluorescence recovery by CN^-. If the solution contained an excessive amount of

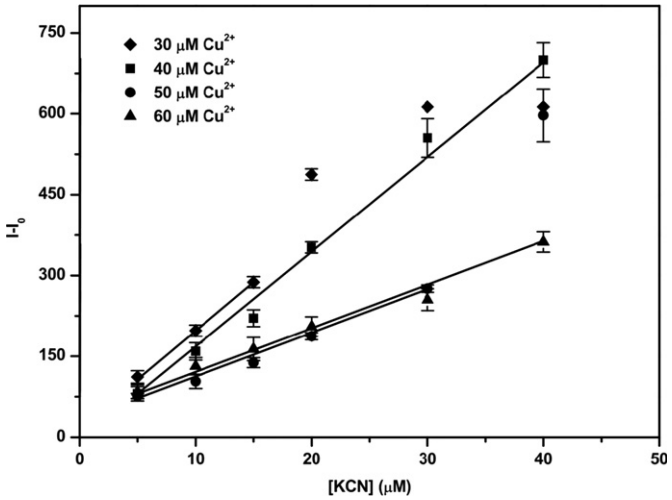

Fig. 6. Effect of the concentration of Cu^{2+} added on the recovered fluorescence intensity.

Cu^{2+}, some of the cyanide ions would complex with free Cu^{2+}. Therefore, the free cyanide ions reacting with Cu^{2+} on the quantum dots surface would decrease. On the contrary, if the solution contained an insufficient amount of Cu^{2+}, the working range and sensitivity of the sensor would be limited. Therefore, the concentration of Cu^{2+} was optimized in the concentration range of 30–60 μM. As shown in Fig. 6, at the concentration of Cu^{2+} higher than 40 μM the sensitivity of the sensor seemed to drop. It implied that on exceeding 40 μM a lot of free Cu^{2+} ions existed in the running assay and could affect the detection sensitivity. On the other hand, when using 30 μM Cu^{2+} as modulated ions, the working concentration range was narrower than using 40 μM Cu^{2+}. This may stem from the insufficient Cu^{2+} species on the quantum dot surface leading to the inefficient complexation with CN^- at the higher CN^- concentration. Therefore, to obtain the highest detection sensitivity, 40 μM of Cu^{2+} was selected for modulation of the fluorescence of Cys-CdS QDs.

3.5. Selectivity of the proposed turn-on fluorescence sensor for cyanide ions

Generally, selectivity is a crucial characteristic for most sensors. Especially, in the fabrication of anion sensors, the selectivity

of the sensors is still a challenging subject because the specific interactions between an anion and the sensor are difficult to design. Thus, several common anions, including F^-, Cl^-, Br^-, I^-, NO_3^-, CH_3COO^-, SO_4^{2-}, HPO_4^{2-}, ClO_3^-, NO_2^-, SCN^-, CO_3^{2-} and SO_3^{2-}, were then tested with the proposed sensor. The optimized condition for the detection of CN^- was applied in the presence of each individual anion at the same concentration. As can be seen in Fig. 7, only CN^- was able to turn on the fluorescence of the [Cys-CdS QDs]-Cu^{2+} probe. On the other hand, for the other tested anions, a slight quenching of the fluorescence intensity of the [Cys-CdS QDs]-Cu^{2+} probe was found. The selectivity of this sensor may be attributed to the operation in turn-off followed by turn-on signal strategy, providing double sources of the selectivity. The first reason is that the selectivity resulted from the selective quenching by Cu^{2+}. In addition, the selectivity was obtained from the strong copper–cyanide complex which could discriminate cyanide and other anions. Finally, the sensors based on turn-on approach were more advantageous than on the turn-off mode because a few species could turn on the fluorescence intensity of the quantum dots. These results suggested that the proposed sensor platform provided good selectivity toward CN^- by the fluorescence turn-on mechanism.

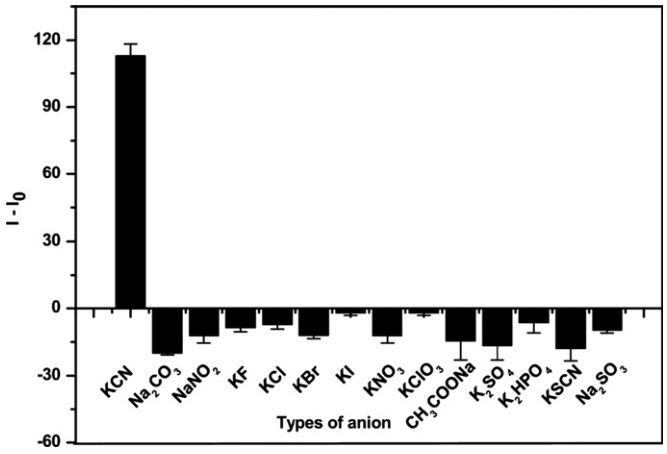

Fig. 7. Fluorescence turn-on selectivity to various anions.

3.6. Analytical performance of the proposed sensor

In order to apply the proposed sensor as the cyanide sensing probe, it is important to evaluate the analytical performance of the new method. The linear working concentration range of the sensors was first evaluated under optimal condition by increasing the cyanide concentration as a function of the different fluorescence intensities ($I-I_0$) between before (I_0) and after (I) the addition of cyanide ions. As shown in Fig. 8, the sensor showed good linear relationship between the recovered fluorescence intensity and the concentration of CN^-. The regression equation was found to be $I-I_0=17.46[CN^-, \mu M]-4.005$ ($r^2=0.992$) within the working concentration range 2.5–20 μM. 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 analyte giving the fluorescence intensity equal to $I_0-3\times$ standard deviation of I_0, while the LOQ was measured as the concentration of analyte giving the fluorescence intensity equal to $I_0-10\times$ standard deviation of I_0 [51]. The LOD and LOQ of the proposed sensor were 1.13 μM and 3.23 μM, respectively. The repeatability of the present method was then evaluated. The relative standard deviation from the detections of 15 μM CN^- for 10 replicates was found to be only 3.6%. This result suggested that the proposed Cu^{2+}-QDs sensor exhibited a very good repeatability.

3.7. Applications of the proposed sensor for cyanide detection in drinking water

To confirm the usability, the present method was applied to determine CN^- ions in the drinking water as a model sample. Three types of drinking water samples were used for demonstrating the method feasibility under the optimum condition. The water samples were buffered with 0.05 M Tris–HCl buffer pH 9.0 and spiked with known amount of cyanide ions (0, 5, 10 and 15 μM). Each concentration level was carried out three times.

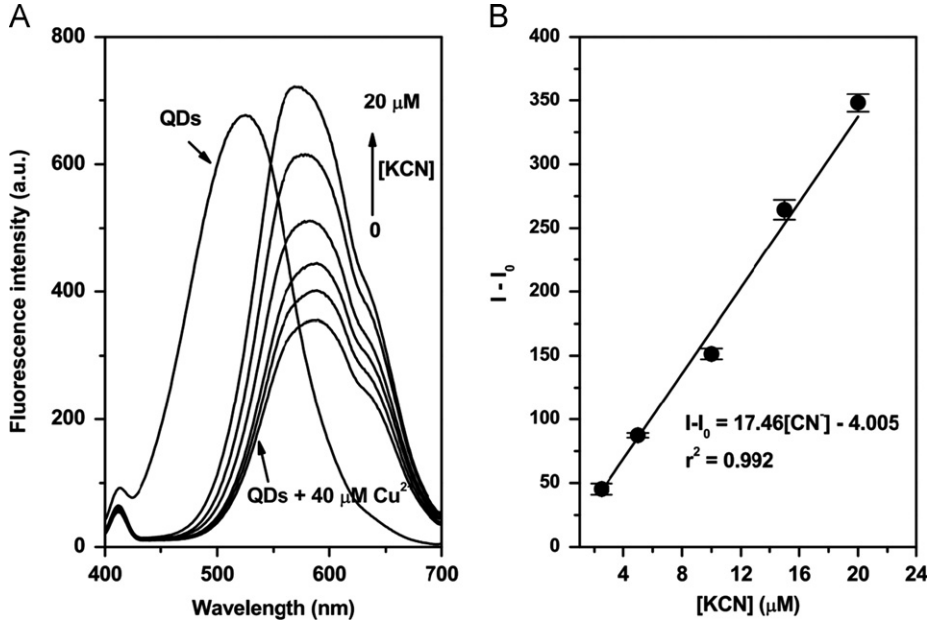

Fig. 8. Fluorescence emission spectra of Cu^{2+}-modulated Cys-Cds QDs in the presence of cyanide ions at various concentrations (A) and the corresponding calibration curve (B).

Table 1
Recovery data for the detection of cyanide ions in spiked drinking water samples ($n=3$).

Samples	Spiked (μM)	Found (μM)[a]	Recovery (%)	RSD (%)
Drinking water 1	5.0	4.85 ± 0.09	96.94 ± 1.73	1.78
	10.0	10.10 ± 0.30	100.99 ± 2.95	2.92
	15.0	15.70 ± 0.27	104.67 ± 1.78	1.70
Drinking water 2	5.0	4.73 ± 0.20	94.52 ± 3.98	4.21
	10.0	10.33 ± 0.09	103.28 ± 0.86	0.83
	15.0	15.39 ± 0.37	102.61 ± 2.49	2.42
Drinking water 3	5.0	4.72 ± 0.25	94.39 ± 4.94	5.24
	10.0	11.05 ± 0.64	110.49 ± 6.43	5.82
	15.0	15.84 ± 0.22	105.57 ± 1.43	1.36

[a] Mean ± SD.

The results are listed in Table 1. For unspiked samples, the fluorescence intensity was not significantly recovered. This indicated that the concentrations of cyanide ions in these drinking water samples were less than the LOD level. However, the cyanide ions in the spiked samples were detected by the proposed method. The recoveries of spiked cyanide ions were obtained in the range 94–110% with a satisfying analytical precision (RSD $\leq$ 6%). These results, thus, validated the reliability and practicality of this method.

4. Conclusion

In summary, we successfully developed a turn-on fluorescence sensor for cyanide ions. The sensor was based on the utilizing of nanocrytalline cysteamine capped CdS QDs which were effectively quenched by Cu^{2+}. The fluorescence intensity was recovered upon adding CN^- to remove Cu^{2+} ions from the surface of the quantum dots by forming a strong copper–cyanide complex. The proposed method showed good selectivity toward cyanide ions over other anions and could be efficiently applied to detect cyanide in drinking water samples with satisfactory results.

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