

CuInS₂ Quantum Dots-based Off/On Probe for Detection of Cetyltrimethylammonium Bromide and L-Cysteine

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Abstract. We developed a convenient method for cetyltrimethylammonium bromide (CTABr) detection based on the quenching phenomenon of CuInS₂ quantum dots. There existed a good linear relationship between the fluorescence intensity of CuInS₂ quantum dots and CTABr concentration from 0.08 μmol/L to 6.0 μmol/L with a detection limit of 25 nmol/L. The quenched fluorescence intensity of CuInS₂ quantum dots by CTABr could be recovered by L-cysteine, which could be also used to detect L-cysteine from 0.05 to 100 μmol/L with a detection limit of 20 nmol/L.

1. Introduction

L-Cysteine (Cys) plays a vital role in a series of physiological processes [1]. Multifarious techniques have been utilized for the detection of Cys [2]. In recent two decades, fluorescence assays for Cys based nanosensors have attracted great attentions due to the practicality and convenience for operation [3].

Semiconductor quantum dots (QDs) have attracted more attentions in the past two decades due to their unique physicochemical properties. In recent years, QDs such as CdTe, CdSe, etc, capped by stabilizing agents such as organophosphate or thiols, were generally reported to be utilized in bimolecular recognition, ion detection, DNA and protein analysis [4-6]. CuInS₂ QDs was a new I-III-VI nanomaterial with low toxicity to organism [7]. According to previous report, mercaptopropionic acid (MPA)-capped CuInS₂ QDs were prepared [8].

Cetyltrimethylammonium bromide (CTABr), as cationic surfactants, can promote nucleic acid and acid polysaccharide precipitation from the low ionic strength of solution, so it could be used in the separation and purification of DNA and polysaccharide. During the past two decades, CTABr was also used in the synthesis of mesoporous materials. Although CTABr has been applied in many fields, it was also reported as a pollutant in water due to its high toxicity to human body and animals.

Herein, we used CuInS₂ QDs for the fluorescent detection of CTABr and Cys. The fluorescence of CuInS₂ QDs would be obviously quenched by CTABr, and then recovered in the presence of Cys. Based on the fluorescent turn off/on process, we proposed a convenient method for determination of CTABr and Cys with high selectivity and sensitivity.

2. Experiment Section

2.1. Synthesis of CuInS₂ QDs

MPA-capped CuInS₂ QDs was prepared on the basis of previous report [8].



2.2. Fluorescent Detection of CTABr

CuInS₂ QDs solution (0.3mL, 1.5mmol/L), PBS (0.2mL, 0.1 mol/L pH 9.0) and different amount of CTABr solution were successively added into a 2 ml test tube, diluted to the mark with deionized water, and then incubated for 5 minutes.

2.3. Fluorescent Detection of Cys

CuInS₂ QDs solution (0.3mL, 1.5mmol/L), PBS (0.2mL, 0.1mol/L pH 9.0) and a certain amount of CTABr solution were added into a 2 ml test tube, and then equilibrated for 5 minutes. Different amount of Cys were added into the test tube, diluted to the mark with deionized water. The fluorescence spectra were recorded after 15 minutes incubations.

3. Results and Discussions

3.1. Fluorescence Quenching by CTABr

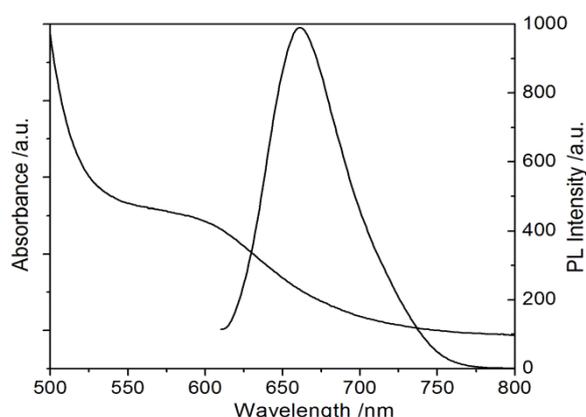


Figure 1. The Fluorescence Emission and UV-Vis Absorption Spectra of the CuInS₂ QDs Solution

As shown in Figure 1, the prepared CuInS₂ QDs displayed a symmetrical fluorescence emission peak at 660 nm and absorption peak around 570nm, which were consistent with previous report [8].

In recent years, a lot of works have reported the effect of cationic surfactant on the PL of QDs. Herein, we investigated systematically the effects of CTABr on CuInS₂ QDs. Figure 2A Curve a showed the temporal evolution of the fluorescence intensity of CuInS₂ QDs with 6μmol/L CTABr. The fluorescence intensity sharply reduced after the addition of CTABr in 5 minutes, and reached equilibrium.

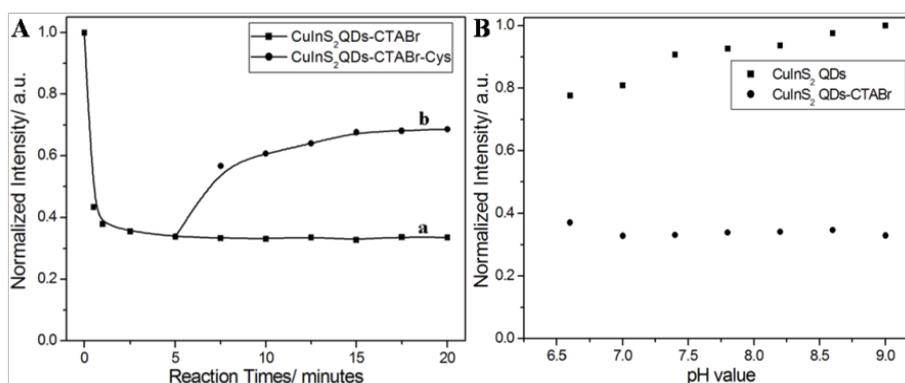


Figure 2. (A) (a) Fluorescence quenching of CuInS₂ QDs by 6μmol/L CTABr at different incubation time. (b) Fluorescence recovery of CuInS₂ QDs-CTABr system (incubating 5 minutes) by addition of 100μmol/L Cys with increasing incubation times. (B) Fluorescence intensity of CuInS₂ QDs without or with 6μmol/L CTABr in different pH environments

We studied the effects of pH on the fluorescence intensity of CuInS₂ QDs in the range of 6.6-9.0. Figure 2B showed the fluorescence intensity of CuInS₂ QDs solution increased along with the increase of pH from 6.6 to 9.0, which was because that the thiol (-SH) of the stabilizer MPA was easy to be proton in acid medium. The CuInS₂ QDs can remain stable in alkali environments, and the pH has a little influence on the fluorescence of CuInS₂ QDs-CTABr in the range of 6.6-9.0. Considering the stronger electrostatic interactions between the surfaces of CuInS₂ QDs and CTABr in alkali environment, pH 9.0 PBS was used in the next experiments.

Figure 3A showed the fluorescence emission spectra of CuInS₂ QDs with various CTABr concentrations. The fluorescence intensity of CuInS₂ QDs gradually reduced with CTABr concentration enrichment. Figure 3A Inset showed that there was a good linear relationship between $(F_0-F)/F_0$ (F_0 or F was the fluorescence intensity of the CuInS₂ QDs without or with CTABr, respectively) and CTABr concentration in the range of 0.08-6.0 μmol/L, which can be described as follow:

$$(F_0-F)/F_0=0.088+0.099[\text{CTABr}], \mu\text{mol/L} \quad (1)$$

The regression coefficient is 0.998 with 0.02 μmol/L mol/L detection limit for CTABr. The cationic surfactant CTABr can bind to the surface of CuInS₂QDs via electrostatic interactions, which would induce the aggregation and the fluorescence quenching of CuInS₂QDs.

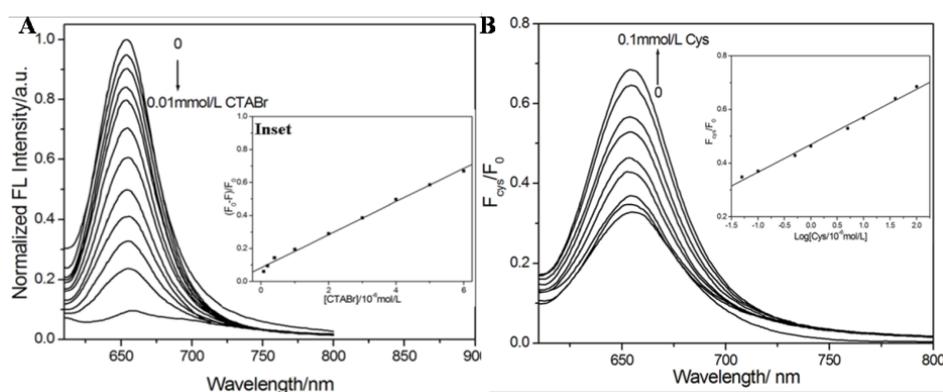


Figure 3. (A) Fluorescence spectra of CuInS₂ QDs upon the addition of different concentration of CTABr from 0 to 10 μmol/L. Inset: The plot of FL intensity versus the concentration of CTABr. (B) Fluorescence spectra of CuInS₂ QDs-6 μmol/L CTABr system upon the addition of different concentration of Cys from 0 to 0.1 mmol/L. Inset: The plot of F_{cys}/F_0 versus the logarithm of Cys concentration. PBS: 10 mmol/L phosphate buffer solution (pH 9.0)

3.2. Effect of Foreign Substance on the Fluorescence Quenching By CTABr

We investigated the influence of various metal ions and foreign molecule on the determination of CTABr. As shown in Table 1, high concentration of metal cation Na⁺, K⁺, Ca²⁺, Mg²⁺, Ba²⁺ have no remarkable effects. The short chain tetraalkylammonium such as L-carnitine and acetylcholine and the common chelating agent tartaric acid and sodium citrate also nearly have no interference on the determination process.

3.3. Fluorescence Recovery by Cys

The quenched fluorescence of CuInS₂ QDs by CTABr could be recovered by Cys. Figure 2A Curve b offered the temporal evolution of the fluorescence of CuInS₂ QDs quenched by CTABr after the addition of Cys. The FL of CuInS₂ QDs was quenched by CTABr for 5 minutes, and then the quenched fluorescence recovered after the addition of Cys, and reached equilibrium after 15 minutes. Figure 3B showed that the quenched fluorescence by CTABr was sensitive to Cys. The fluorescence intensity was recovered as the Cys concentration increased from 0 to 100 μmol/L. The relationship between F_{cys}/F_0 (F_{cys} is the FL of the CuInS₂ QDs-6 μmol/L CTABr system with different concentration of Cys,

and F_0 is the original FL of CuInS₂ QDs) and the logarithm of Cys concentration in the range of 0.05-100 μmol/L can be described as the following equation:

$$F_{\text{cys}}/F_0 = 0.470 + 0.103 \text{Log}[\text{Cys}], \mu\text{mol/L} \quad (2)$$

The regression coefficient is 0.997 with 0.025 μmol/L detection limit for Cys.

Table 1. Tolerance of foreign substance (The concentration of CTABr is 6 μmol/L)

Coexisting substance	Tolerance ratios	Change of fluorescence(%)
Na⁺	1000	-2.1
K⁺	1000	+1.9
Mg²⁺	100	-4.7
Ca²⁺	100	+2.6
Ba²⁺	100	+4.3
L-carnitine	500	+4.9
Acetylcholine	100	-1.5
Tartaric acid	1000	-1.7
Sodium citrate	1000	-2.0

Compared with the previous works about fluorescent detection for Cys, our method has the lower detection limit and similar dynamic range. As previous reports, Cys has strong binding ability to QDs. The CTABr adsorbed on MPA-capped CuInS₂ QDs would be replaced by Cys, which changed the surface charges of CuInS₂ QDs. The repulsion of the same charges and the steric hindrance effect would prevent the CTABr from fluorescence quenching of QDs, which induced the fluorescent recovery of CuInS₂ QDs.

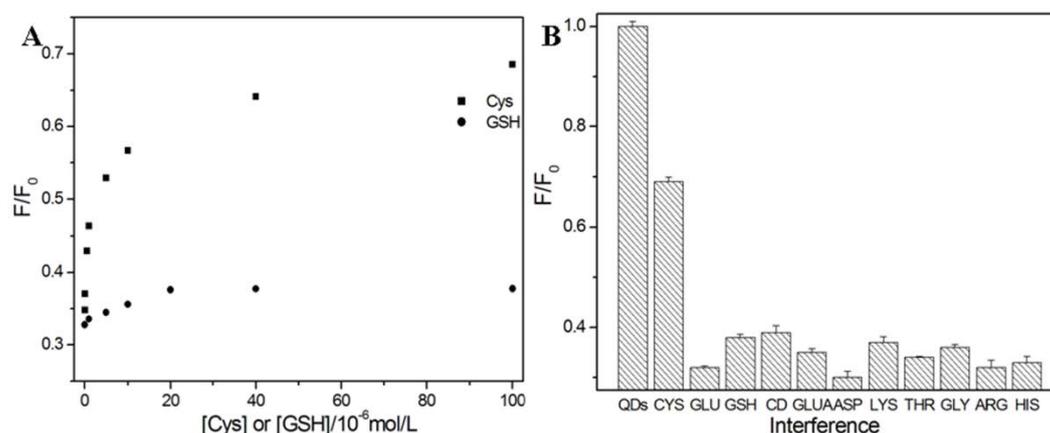


Figure 4. (A) The fluorescence intensity of CuInS₂QDs quenched by CTABr with different concentration of L-cysteine and glutathione in the range from 0-0.1 mmol/L. (B) Effect of a series of 0.1 mmol/L biomolecule such as L-cysteine (Cys), glucose (GLU), glutathione (GSH), cyclodextrin (CD), glutamic acid (GLUA), aspartate (ASP), lysine (LYS), threonine (THR), glycine (GLY), arginine (ARG), histidine (His) on the fluorescence intensity of CuInS₂ QDs quenched by CTABr solution

The study on the competition between Cys and glutathione (GSH) was illustrated in Figure 4A. The quenched fluorescence by CTABr could restore to 69% of the original fluorescence with 0.1 mmol/L Cys. The fluorescence recovery with 0.1 mmol/L GSH is not very ideal, which is because that the

CTABr molecules prevent the higher molecule weight GSH molecule from closing to the surface of CuInS₂QDs due to the steric hindrance effect. As shown in Figure 4B, the presence of other amino acid only produced small effects on the fluorescence intensity.

4. Conclusions

In summary, the prepared CuInS₂ QDs was successfully used to detect CTABr and Cys. This method avoids complicated surface modification and operations, and has simple operation and excellent selectivity.

5. Acknowledgements

This work was supported by the National Training Program of Innovation and Entrepreneurship for Undergraduates (201910145108) and Fundamental Research Funds for Central Universities (N182410001).

6. References

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