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# Hydrothermal synthetic mercaptopropionic acid stabled CdTe quantum dots as fluorescent probes for detection of $Ag^+$

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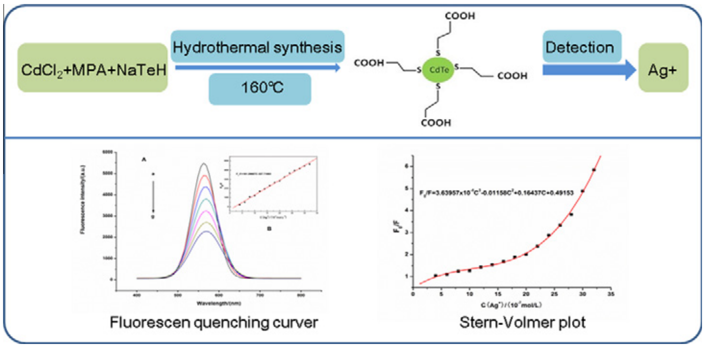
## HIGHLIGHTS

- MPA stabled CdTe QDs were successfully synthesized by hydrothermal method.
- Research the effect of different metal ions on fluorescence intensity of CdTe QDs.
- $Ag^+$ could effectively quench the CdTe QDs fluorescence intensity.
- A rapid, simple and specific method of detection $Ag^+$ was proposed.
- The method of detecting $Ag^+$ had a wide linear range and low detection limit.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Mercaptopropionic acid (MPA) capped CdTe quantum dots (QDs) with particle size 3 nm have been successfully synthesized in aqueous medium by hydrothermal synthesis method. And the effects of different metal ions on MPA capped CdTe QDs fluorescence were studied using fluorescence spectrometry. The results demonstrated that at the same concentration level, $Ag^+$ could strongly quench CdTe QDs fluorescence, and the other metal ions had little effect on CdTe QDs fluorescence except $Cu^{2+}$. On the basis of this fact, a rapid, simple, highly sensitive and selective method based on fluorescence quenching principle for $Ag^+$ detection in aqueous solution was proposed. Under optimal conditions, the quenched fluorescence intensity ($F_0$–$F$) increased linearly with the concentration of $Ag^+$ ranging from $4 \times 10^{-7}$ to $32 \times 10^{-7}$ mol $L^{-1}$. The limit of detection for $Ag^+$ was $4.106 \times 10^{-8}$ mol $L^{-1}$. The obtained plot of $F_0/F$ versus $[Ag^+]$ was an upward curvature, concave towards the *y*-axis, rather than a straight line. The modified form of the Stern–Volmer equation was third order in $Ag^+$ concentration. According to the modified Stern–Volmer equation, it can be inferred that dynamic quenching and static quenching simultaneously occurred when $Ag^+$ interacted with MPA capped CdTe QDs. At the same time other factors might also influence the quenching process. Based on this study, hydrothermal synthesized MPA capped CdTe QDs with particle size 3 nm may be used as a novel fluorescence probe to quantificationally and selectively detect $Ag^+$.

## Introduction

Quantum dots (QDs), as special semiconductor nanoparticles [1] have received much attention over past decades because of their unique optical and electronic properties [2–7], such as broad excitation spectra, symmetric and narrow tunable emission spectra and

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excellent photostability [8,9]. In recent years, with the developments of water-soluble QDs preparation and surface-modification, QDs have been widely used as fluorescence labels in biosensing, bio-analyses, cell labeling, animal imaging, and biomedical fields [10–13]. Meanwhile, considerable attentions have also been focused on the researches of chemical sensing for small molecules [14,15] and ions [16,17], with QDs via analyte-induced fluorescence changes [18]. Up to now, there are many reports on the effects of different metal ions on the fluorescence of QDs based on different mechanisms. For example, Chen and Rosenzweing [19] first respectively used thioglycerol capped CdS QDs and cysteine capped CdS QDs as fluorescent probes to detect $Cu^{2+}$ and $Zn^{2+}$. Cai et al. [20] and Chen et al. [21] respectively found that L-cysteine modified CdS and CdSe QDs had the fluorescence response to $Hg^{2+}$. Ali et al. [22] selectively detected $Pb^{2+}$ respectively using the synthetic glutathione stabled CdTe and CdSe/ZnSe QDs as fluorescent probes based on fluorescence quenching principle. Some researchers have reported that $Zn^{2+}$, $Mn^{2+}$ and $Cd^{2+}$ could increase the fluorescence quantum yield of CdS or ZnS QDs [23–25], and $Zn^{2+}$ could enhance the fluorescence intensity by binding to the surface of the CdTe QDs [26]. Besides, some heavy metal ions, such as $Cu^{2+}$ and $Hg^{2+}$, effectively quench the fluorescence of QDs [2]. Some reports also demonstrated that $Ag^+$ could effectively effect the fluorescence of cadmium chalcogenide (CdS, CdSe or CdTe) nanoparticles [2,27–30].

In many studies, QDs with different composition have different fluorescence properties. Even though the QDs have the same composition, different synthesis conditions also result in different fluorescence properties of QDs. The same cadmium chalcogenide (CdS, CdSe or CdTe) quantum dots modified by different stabilizator, also have different surface structures and different fluorescence properties. So those QDs have different interactions with different metal ions, which leads to different influences on QDs fluorescence. In our work, mercaptopropionic acid (MPA) capped CdTe quantum dots (QDs) with particle size 3 nm were successfully synthesized in aqueous medium by hydrothermal synthesis method. And the effects of different metal ions on the CdTe QDs fluorescence were studied. The experimental results demonstrated that at the same concentration level, $Ag^+$ could strongly quench the CdTe QDs fluorescence and made the CdTe QDs fluorescence intensity decrease 99.97%. And the other metal ions had little effect on the CdTe QDs fluorescence except $Cu^{2+}$. On the basis of this fact, a rapid, simple, highly sensitive and selective method based on fluorescence quenching principle for $Ag^+$ detection in aqueous solution was proposed. Under optimal conditions, the quenched fluorescence intensity ($F_0$–$F$) increased linearly with the concentration of $Ag^+$ ranging from $4 \times 10^{-7}$ to $32 \times 10^{-7}$ mol $L^{-1}$. The limit of detection for $Ag^+$ was $4.106 \times 10^{-8}$ mol $L^{-1}$. The obtained plot of $F_0/F$ versus $[Ag^+]$ was an upward curvature, concave towards the $y$-axis, rather than a straight line. The modified form of the Stern–Volmer equation was third order in $Ag^+$ concentration. According to the modified Stern–Volmer equation, it can be inferred that dynamic quenching and static quenching simultaneously occurred when $Ag^+$ interacted with MPA capped CdTe QDs. At the same time, other factors might also influence the quenching process. Based on this approach, MPA capped CdTe QDs with particle size 3 nm may be used as a novel fluorescence probe to quantificationally and selectively detect $Ag^+$.

## Experimental

### Reagent

Tellurium powder (99.9%), Sodium borohydride ($NaBH_4$, 99%), Sodium hydroxide (NaOH, 99%) and Cadmium chloride ($CdCl_2 \cdot 2.5H_2O$, 99%) were purchased from Tianjin recovery fine chemical industry research institute (China). $K_2HPO_4 \cdot 3H_2O$, $KH_2PO_4$, KCl, $MgCl_2 \cdot 6H_2O$, $ZnCl_2$, NaCl, $MnCl_2 \cdot 4H_2O$, $FeCl_3 \cdot 6H_2O$, $CoCl_2 \cdot 6H_2O$, $NH_4Cl$, $FeSO_4 \cdot 7H_2O$, $CaCl_2 \cdot 2H_2O$, $BaCl_2 \cdot 2H_2O$, $N_2NiO_6 \cdot 6H_2O$, $AgNO_3$, $Cu(NO_3) \cdot 3H_2O$ were acquired from Guoyao Chemical Reagent Company (Shanghai, China). 3-mercaptopropionic acid was purchased from Aladdin. Methanol and acetone were purchased from Shanghai SuYi chemical reagent Co. Ltd. (China). All the chemicals were of analytical grade and were used as received without further purification. All the solutions were prepared with double deionized water (DDW) purified by a Millipore Milli-Q Purification System. PBS buffer solutions with different pH values were used in the experiment.

### Apparatus

Fluorescence measurements were performed using a F-7000 spectrofluorometer (Hitachi, Japan) equipped with a plotter unit and a quartz cell (1 cm × 1 cm), and the slit width was set at 5 nm at room temperature under ambient conditions. pH values were measured with a model PHS-3C pH meter (Leici Analytical Instrument Factory, Shanghai, China).

### Hydrothermal synthesis of MPA capped CdTe QDs

Luminescent CdTe QDs capped with MPA were prepared according to the procedure reported in the literature [18] with little modification. In a typical synthesis, $2.0 \times 10^{-3}$ mol of $CdCl_2 \cdot 2.5H_2O$ was dissolved in 100 mL of DDW, and $4.8 \times 10^{-3}$ mol of MPA was added under stirring, followed by adjusting the pH to 9.0 by dropwising 1 mol $L^{-1}$ NaOH. The solution was deaerated by $N_2$ bubbling for 30 min. Under vigorous stirring, $1.0 \times 10^{-3}$ M freshly prepared oxygen-free NaHTe was injected to the above solution. Afterward, the final mixture solution was continually stirred vigorously and bubbled with $N_2$ atmosphere for 20 min, then transferred to a 50 mL hydrothermal synthesis reaction kettle with PTFE inner liner. The hydrothermal synthesis reaction kettle was put into a 160 °C oven, and heated 80 min. The concentration of CdTe QDs solution was estimated from the absorption spectra using molar absorptivity at first maximum for QDs of this size reported by Peng's group [31]. The obtained CdTe QDs solution was purified by size-selective precipitation and centrifugal separation with the purpose of removing the unreacted reactants.

### The influence of different metal ions on the MPA capped CdTe QDs fluorescence intensity

The common metal ions: $Cu^{2+}$, $Ag^+$, $K^+$, $Mg^{2+}$, $Zn^{2+}$, $Na^+$, $Mn^{2+}$, $Fe^{3+}$, $Co^{2+}$, $NH_4^+$, $Fe^{2+}$, $Ca^{2+}$, $Ba^{2+}$, $Ni^{2+}$, were selected and respectively prepared their stock solutions, all in a concentration of 0.04 mol $L^{-1}$.

Into a series of 10 mL colorimetric tubes were added 0.1 mL of purified CdTe QDs solution, 0.1 mL of 0.2 mol $L^{-1}$ phosphate buffer solution (PBS, pH 6.6) and 0.02 mL of 0.04 mol $L^{-1}$ different metal ions stock solution sequentially. The mixture was diluted to the mark with DDW, shaken thoroughly and equilibrated for 10 min. Reference solution was the same without any ions added. The fluorescence intensity of the solution was recorded at 575 nm with the excitation wavelength of 400 nm. Both slit widths of excitation and emission were 5 nm.

### Procedure for spectrofluorometric detection of $Ag^+$

Into a 10 mL colorimetric tube 0.5 mL of purified CdTe QDs solution, 0.1 mL of 0.2 mol $L^{-1}$ phosphate buffer solution (PBS, pH 6.6) and certain amounts of $Ag^+$ were sequentially added. The mixture was diluted to the mark with DDW, shaken thoroughly and equilibrated for 10 min. Reference solution was the same without