

A Novel Method for the Selective Determination of Silver (I) Ion

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Abstract: Water-soluble CdSe quantum dots (QDs) capped by bovine serum albumin (BSA) is described as selective silver (I) ion probe based on their fluorescence (FL) quenched by silver ion at pH 5.7. The detection limit is 3×10^{-7} mol L⁻¹ for silver ion. The interference was also investigated.

Keywords: Quantum dots, silver(I) ion, determination.

Semiconductor quantum dots (QDs) present considerable advantages over bulk single-crystal semiconductors¹. As a result of quantum confinement, they have unique optical and electronic properties such as broad excitation spectra, narrow, symmetric and tunable emission spectra². In addition, QDs exhibit high photobleaching threshold and excellent photostability. They are starting to attract considerable attention as novel fluorescence probes in recent years³⁻⁶. Recently, Chen and Rosenzweig⁷ demonstrated the first example of copper and zinc ion analysis by utilizing CdS luminescent quantum dot capped by different ligands in aqueous media. Peng *et al.*⁸ reported the photoluminescence of CdSe QDs incorporated into polymer thin films upon photoradiation, which was responded reversibly and rapidly to environmental changes such as the properties of the gases. The responses of the fluorescence (FL) properties of the QDs to different gases are due to the interactions between the gas molecules and the surface atoms of the inorganic QDs. They thought it is potentially possible to develop sensitive and simple sensors based on high-quality semiconductor QDs with different gases. Bard *et al.*⁹ showed and discussed enhancement of the fluorescence of CdSe QDs dispersed in CHCl₃ by oxygen passivation of surface states.

Until now, few reports have been explored for silver ion^{10, 11}. In this paper, we have used luminescent CdSe quantum dots capped by BSA as selective silver ion probe and got good results.

Experimental

CdSe QDs were synthesized and purified according to the procedures reported by Peng *et al.*¹². CdO and stearic acid were heated briefly to 150°C under Ar flow. After CdO

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completely dissolved, the mixture was allowed to cool to room temperature, trioctylphosphine oxide (TOPO) and hexadecylamine were added, and the mixture was heated to 320°C under Ar flow. At this temperature, the Se solution in trioctylphosphine (TOP) and dioctylamine was swiftly injected into the reaction flask. The reaction was stopped 5 min after the injection, and heat was immediately removed. After purification by precipitation, centrifugation, and decantation, the vacuum-dried CdSe QDs were redispersed in hexane and kept in the dark for future use. Water-soluble CdSe QDs were synthesized according to the scheme reported by our group¹³. Briefly, 1~3 mg of CdSe QDs were homogeneously dispersed in 1 mL of hexane then precipitated with anhydrous methanol; centrifuging, washing and redissolving the precipitate in about 1 mL of hexane; and then mixing 50 mg of BSA with QDs in hexane, grinding for about 2 minutes in a mortar. After complete evaporation of hexane, 2 mL of 0.1 mol L⁻¹ citric acid buffer (pH 5.7) was added. The prepared suspension contained superfluous BSA, BSA-capped CdSe QDs and some QDs of aggregation. Superfluous BSA was removed with ultracentrifugation at 18000 rpm, the supernatant was discarded and the QDs-BSA and agglutinated QDs were resuspended in citric acid buffer, centrifuging again at about 5000 rpm to remove agglutinated QDs. Aliquot solutions were used for ion response measurements.

Results and Discussion

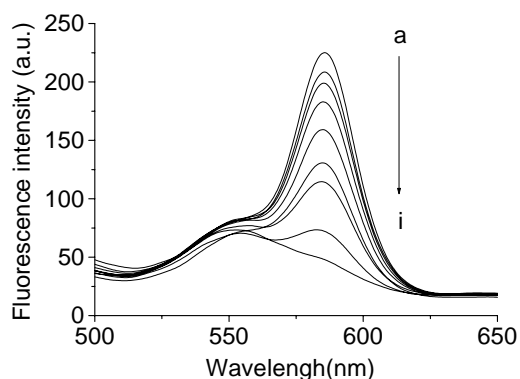
The CdSe QDs diameters were 3.4 nm, which were determined from the correspondence of the absorption spectrum with the particle diameter¹⁴. The spectrum of BSA-QDs shows typical emission peak centered at 582 nm (excitation 388 nm), which is commonly attributed to the recombination of the charge carriers within surface states¹. The quantum yield of these CdSe QDs in hexane ranges from 30% to 50%, but dramatically decreased by capping their surface with BSA. The quantum yield reduces from 30~50% to 5~10%. This decrease is in agreement with previous studies¹⁵.

The emission spectra of BSA-QDs and its fluorescence titration with silver ion were recorded in 0.1 mol L⁻¹ citric acid buffers at pH 5.7, the results are shown in **Figure 1**. When silver ion was added to the solution of BSA-QDs, a significant decrease of the CdSe QDs emission was observed. **Figure 2** describes the silver ion concentration dependence on the FL intensity of BSA-QDs. It can be seen that the FL intensity decreases with the increase in silver ion concentrations, which allows determining free silver ion concentration. It was found that silver ion quench the FL intensity of BSA-QDs in a concentration dependence that is best described by a Stern-Volmer-type equation:

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

F and F₀ are the FL intensities of the BSA-QDs at a given silver ion concentration and in a silver ion-free solution. Q is the silver ion concentration. **Figure 2** shows a Stern-Volmer quenching curve describing F₀/F as a function of silver ion concentration. K_{SV} is found to be 4.9×10⁴ L mol⁻¹.

Figure 1 Fluorescence emission spectra changes of BSA-capped CdSe QDs upon the addition of silver ion in citric acid buffer at pH 5.7



a. BSA-capped CdSe QDs in 0.1 mol L⁻¹ citric acid buffer at pH 5.7, b. a+8×10⁻⁷ mol L⁻¹ Ag⁺, c. a+2×10⁻⁶ mol L⁻¹ Ag⁺, d. a+4×10⁻⁶ mol L⁻¹ Ag⁺, e. a+1×10⁻⁵ mol L⁻¹ Ag⁺, f. a+ 2×10⁻⁵ mol L⁻¹ Ag⁺, g. a+4×10⁻⁵ mol L⁻¹ Ag⁺, h. a+6×10⁻⁵ mol L⁻¹ Ag⁺, i. a+8×10⁻⁵ mol L⁻¹ Ag⁺.

Figure 2 A Stern-Volmer plot effectively describes the silver ion concentration dependence on the fluorescence intensity of BSA-capped CdSe QDs with a Stern-Volmer constant K_{SV}=4.9×10⁴ L mol⁻¹

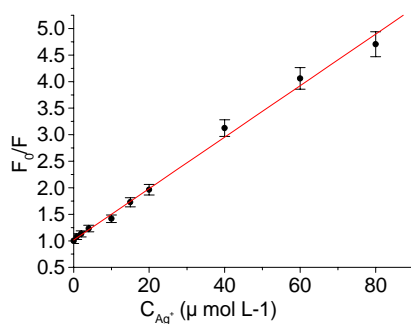
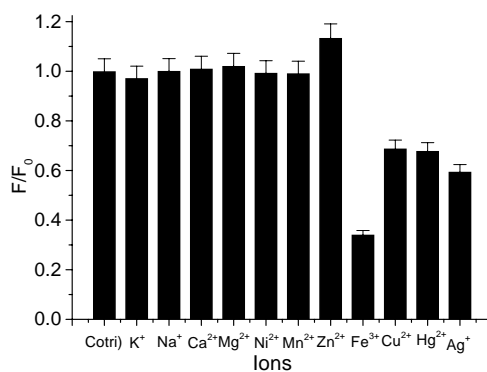


Figure 3 Effect of different ions on the fluorescence of BSA-CdSe QDs



The concentrations of copper, silver and mercury ions are 0.01 mmol L⁻¹, others are 1 mmol L⁻¹.

The response of BSA-capped CdSe QDs to cations is shown in **Figure 3**. Among other ions investigated, alkali, alkaline earth ions, Mn^{2+} , Co^{2+} , Cd^{2+} have less effect on BSA-QDs fluorescence, while Cu^{2+} , Hg^{2+} and Fe^{3+} also show strong quenching of BSA-QDs fluorescence. On the contrary, Zn^{2+} showed slight fluorescence enhancement. The interference of iron ion with silver ion detection is eliminated by adding fluoride ions to form the colorless complex FeF_6^{3-} . BSA can bind Cu^{2+} and Hg^{2+} specifically, with intrinsic affinity constants on the order of $10^{11} \text{ L mol}^{-1}$ and 10^7 L mol^{-1} for BSA- Cu^{2+} and BSA- Hg^{2+} complexes, respectively¹⁶⁻¹⁸, which reduce the reaction speed of copper and mercury ions with CdSe QDs much more than that of silver ion. It was demonstrated that the interference of copper and mercury ions with silver ion could be eliminated by kinetic fluorescence assay in the presence of large amount of free BSA.

Acknowledgments

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