Chinese Chemical Letters 25 (2014) 261–264

Contents lists available at ScienceDirect

Chinese Chemical Letters

journal homepage: www.elsevier.com/locate/cclet

Original article

Determination of silver ion based on the redshift of emission wavelength of quantum dots functionalized with rhodanine

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ARTICLE INFO

Article history:
Received 7 August 2013
Received in revised form 9 September 2013
Accepted 26 September 2013
Available online 17 November 2013

Keywords:
Quantum dots
Silver
Redshift
Rhodanine

ABSTRACT

A simple and selective method for the determination of silver ions was developed by utilizing the red-shift in emission wavelength of the core–shell CdSe/CdS quantum dots (QDs) functionalized with rhodanine upon the addition of Ag^+. A linear relationship was observed between the shift and the increase in concentration of Ag^+ in the range of 0.0125–12.5 μmol/L. The mechanism of the red-shift was investigated and suggested that the coordination between Ag^+ and rhodanine on the QDs surface caused an increase of particle size, which resulted in the red-shift of the QDs' emission wavelength. A detection limit of 2 nmol/L was achieved. The developed method showed superior selectivity and was successfully applied to the determination of silver in environmental samples.

1. Introduction

Quantum dots (QDs) possess attractive optical properties, including broad excitation and narrow emission spectra, size-tunable emission profiles, high photoluminescence quantum yields, and excellent photochemical stability [1]. These unique properties of QDs show considerable advantages over traditional organic fluorophores [2] in the application of analytical chemistry, resulting in the increased use of QDs in various areas [3–8]. Chen and Rosenzweig [5] reported for the first time that CdS QDs modified with different ligands could be used as luminescent probes for the determination of Zn^{2+} and Cu^{2+}. Subsequently, dozens of QDs-based fluorescent methods were reported for the detection of various heavy metals [6–8].

Most of the reported methods were based on the quenching or enhancement of fluorescence intensity of QDs upon the addition of heavy metal ions. They exhibited distinct advantages, including high sensitivity and low cost. However, these methods often suffered from interference caused by co-existing ions. In order to alleviate the interference, QDs functionalized with diethyldithiocarbamate, dithizone, and xylenol orange were synthesized and used recently for the determination of Cu^{2+} and Pb^{2+} in our laboratory [9–11].

In this study, a novel strategy was proposed for the selective detection of Ag^+, which was based on the red-shift in emission wavelength of QDs upon the addition of Ag^+. Core–shell CdSe/CdS QDs functionalized by rhodanine (Rd) were synthesized and used as the fluorescence probe. Rd is often used as the silver reagent in molecular absorption spectrophotometry due to its specific and strong Ag^+ binding capability. The objective of this study is to develop a sensitive and selective method for the detection of silver ions by exploring the unique properties of QDs and the specificity of Rd.

2. Experimental

Fluorescence spectra were acquired on an F-2500 fluorescence spectrophotometer (Hitachi, Japan). AU-2810 spectrophotometer (Hitachi, Japan) was used to obtain ultraviolet–visible absorption spectra. FTIR spectroscopic measurements were carried out using Nicolet FTIR-6700 spectrophotometer (Nicolet, Japan). An Allegra 64R high-speed refrigerated centrifuge (Beckman, USA) was used to separate particles from solution. The pH values were measured by a Delta 320 pH-meter (Mettler Toledo, Switzerland). An AA240FS atomic absorption spectrometer (Varian, USA) was used in the verification test. Deionized water was produced by a Milli-Q system (Millipore, USA) and used for preparing solutions. All chemicals used were purchased from Sinopharm Chemical Reagent Co. and were of analytical-reagent grade, except for nitric acid which was of MOS grade.

Rd-functionalized QDs were synthesized in two steps. In the first step, the core–shell CdSe/CdS QDs capped by thioglycolic acid (TGA) were prepared according to a previously reported method [12]. In the second step, Rd-functionlized QDs were prepared by

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http://dx.doi.org/10.1016/j.cclet.2013.10.029

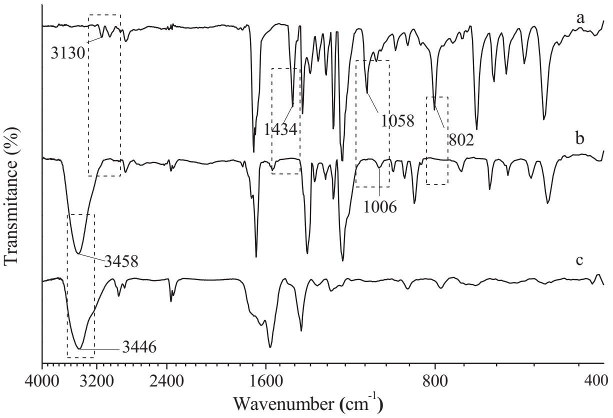

Fig. 1. FT-IR spectra of free rhodanine (a), Rd-functionalized QDs (b) and TGA-QDs (c).

mixing 5 mL of 250 μmol/L rhodanine ethanol solution and 5 mL of 1.2 μmol/L TGA-QDs in a phosphate buffer solution (PBS, pH 8.0). The mixture was stirred for 4 h, allowing Rd to be attached to the QDs through the coordination between Rd and cadmium on QDs surface. The QDs were separated from the bulk solution for purification by precipitation of the particles with acetone and centrifugation. The separated QDs were redispersed in 10 mL of pH 8.0 PBS solution and stored in dark at 4 °C for further use.

For the detection of Ag^+, 100 μL of standard, or sample solution, and 200 μL of the synthesized QDs were added into 700 μL of 20 mmol/L PBS (pH 8.0) and mixed for 20 min at 25 °C. The fluorescence intensity and the emission wavelength were then measured at an excitation wavelength of 380 nm.

3. Results and discussion

Rhodanine on the QDs surface played an important role in the present study. To investigate whether rhodanine was bonded on the surface of the core–shell CdSe/CdS QDs capped by TGA, the FT-IR study of Rd-functionalized QDs was conducted. As shown in Fig. 1(a), the IR absorption bands at 3130 cm^{-1}, 1434 cm^{-1} and 802 cm^{-1} could be attributed to N–H group vibration of rhodanine. These bands were not observed in Fig. 1(b), indicating that the N–H group of rhodanine had been replaced by cadmium to form Rd–Cd complex. On the other hand, the IR characteristic peak of C=S of rhodanine was shifted from 1058 cm^{-1} (Fig. 1(a)) to 1006 cm^{-1}(Fig. 1(b)), due to the formation of the Cd–S bond between sulphur of C=S of rhodanine and cadmium on the QDs surface. The strong vibration band of the O-H group at 3446 cm^{-1} in Fig. 1(c) and 3458 cm^{-1} in Fig. 1(b) clearly indicated that TGA had still remained on the QDs surface rendering the Rd-functionalized QDs water-soluble. The absence of the N–H related peaks in Fig. 1(b) and the shift of the C=S peak provided the evidence of the formation of Rd–Cd complex and confirmed rhodanine had been bound to the surface of QDs.

In theory, the more rhodanine molecules were bonded on the surface of QDs, the more complexation sites for Ag^+ were introduced and thus, higher sensitivity could be achieved for Ag^+ determination. However, increasing the amount of rhodanine could cause higher quenching of the fluorescence intensity and lower solubility of the Rd-funtionalized QDs. When the concentration of rhodanine reached 350 μmol/L, precipitation was observed in the solution. Thus, a solution of 250 μmol/L rhodanine in ethanol was used here for the preparation of Rd-functionalized QDs. The resulting Rd-functionalized QDs exhibited high optical stability without obvious decrease of fluorescence intensity or shift of emission wavelength over 3 months.

Fig. 2(a) shows the fluorescence spectra of the Rd-functionalized QDs in the presence of Ag^+ with different concentrations. An obvious red-shift of the emission wavelength was observed upon the addition of Ag^+. The red-shift of the emission wavelength can be attributed to the coordination between Ag^+ and rhodanine on the QDs surface [13] and, subsequently, the increase of the particle size [2,14]. To investigate the mechanism, the ultraviolet absorption spectra of the Rd-functionalized QDs were examined after adding various amounts of Ag^+. As shown in Fig. 3, the spectra displayed a gradual red-shift with the increase of Ag^+ concentration, indicating the formation of Rd–Ag^+ at the Rd-functionalized QDs surface and the increase of the particle size [15,16].

To further confirm the mechanism, Ag^+ was added to the solution containing QDs without functionalization by rhodanine. Very little change of emission wavelength was observed when

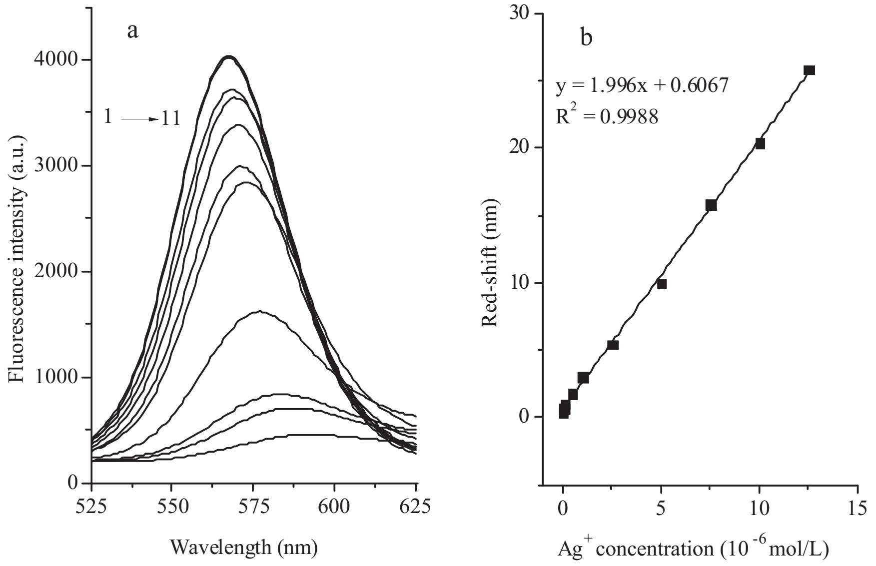

Fig. 2. Fluorescence spectra of Rd-functionalized QDs after adding different concentrations of Ag^+ (a) and the linear relationship between the red-shift of emission wavelength of the QDs and Ag^+ concentration (b). The concentrations of Ag^+ added for spectrum (1) to (11) were 0, 0.0125, 0.075, 0.1, 0.5, 1, 2.5, 5, 7.5, 10, 12.5 μmol/L, respectively.