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A label free Ag^+ sensing method via in situ formation of metal coordination polymer

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ABSTRACT

Metal ions sensing play critical roles in environmental monitoring and in biology. In this assay, we report the development of a facile fluorometric method for the sensing of Ag^+ ions via the in situ formation of metal coordination polymer, based on the selective interactions of GSH with Ag^+. The formation of coordination polymer with net multiple negative charges in an aqueous buffer solution (Tris-HAc, pH 9.0) resulted in aggregation and fluorescence quenching of a cationic perylene probe. The difference in emission intensity spurred us to develop a new strategy for sensing Ag^+ ions. The proposed Ag^+ detection method is simple, convenient, selective and sensitive, and can be used for Ag^+ detection in lake water samples.

Introduction

Silver ions are toxic to aquatic life [1,2]. It has been extensively employed in the photographic and imaging industry. There are approximately 2500 tons of silver released into the environment annually [3]. It is thus important to monitor its level in the ecosystem [4,5]. Many sensitive and selective detection technics have been developed to detect silver, such as the fluorometry [6–8], colorimetry [9–11], electrochemiluminescence [12], atomic absorption/emission spectroscopy [13–15], inductively coupled plasma mass spectroscopy (ICP-MS) [16,17], and ion-selective electrode based methods [18,19]. However, most methods have certain disadvantages, such as the need for large-scale and costly instruments, professional and technical personnel, complex synthesis of sensing materials, etc [7,8]. Facile and efficient Ag^+ detection techniques are still in demand.

Glutathione (GSH) is a tripeptide that can be synthesized in the body from the amino acids L-cysteine, L-glutamic acid, and glycine. It is a thiol group containing short peptide. The study of interactions between metal ions and amino acids has attracted extensive attentions for sensing related applications in recent years [20–25]. Thiol-containing amino acid or peptide and certain monovalent metal ions [M(I), M: Cu, Ag, Au] can form coordination polymers, which provides the foundation for a number of chemo- and bio-sensing applications.

Herein we report the development of a fluorometric method for the selective sensing of Ag^+ ions via the in situ generation of coordination polymer based on the selective interactions of GSH and Ag^+. The formed coordination polymer is polyanion in nature in an aqueous buffer solution at pH 9.0. It could induce the self-assembly of a cationic perylene probes and cause significant probe fluorescence quenching, which could be used for the quantification of Ag^+ ions. The probes synthesized have good fluorescence performance and high fluorescence quantum yield, which provides high sensitivity for the sensing of Ag^+ ions. In addition, the proposed Ag^+ detection method is simple, convenient, and selective and could be also used for Ag^+ detection in various lake water samples with satisfied results.

Experimental section

Materials

Glutathione was obtained from Sangon Biotechnology Co. Ltd. (Shanghai, China). Silver nitrate was purchased from Shanghai

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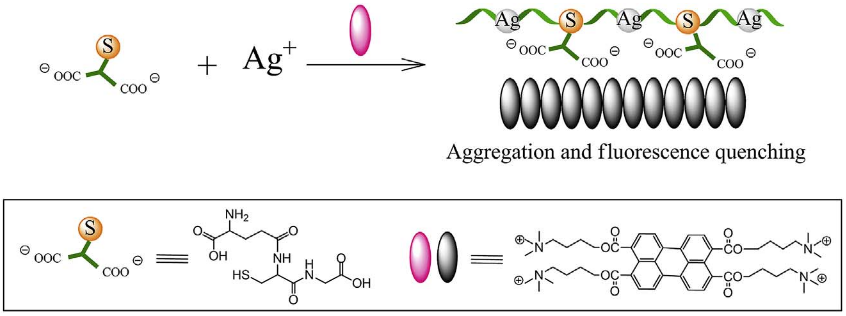

Scheme 1. Schematic representation of fluorescence sensing of Ag^+ ions based on the in situ formation of metal coordination polymer.

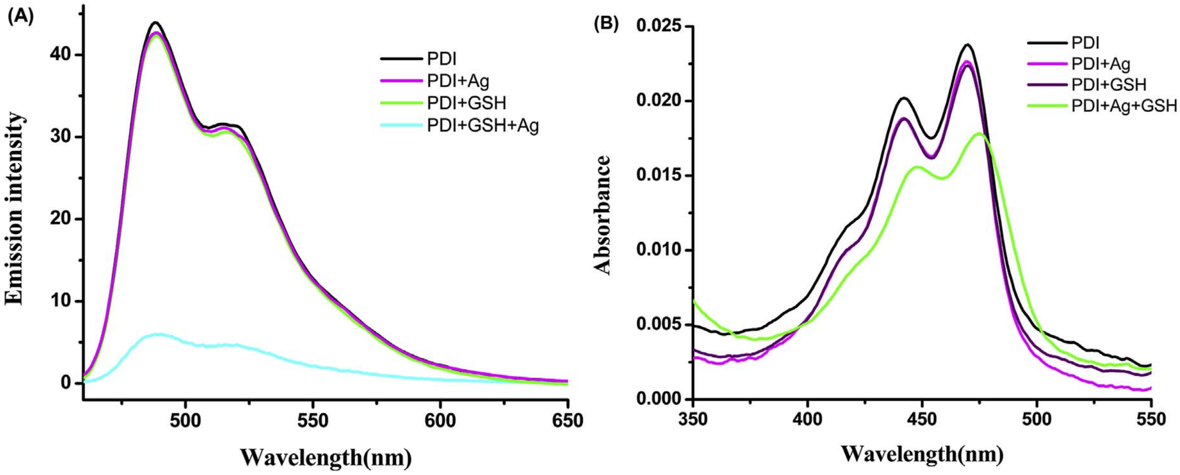

Fig. 1. Fluorescence emission (A) and UV–vis absorption (B) spectra of the probe (0.9 μM) under different conditions: 1) the probe only; 2) the probe + GSH; 3) the probe + Ag^+; 4) the probe + GSH + Ag^+. GSH and Ag^+ concentration: 100 μM each. Buffer: 10 mM Tris-HAc, pH 9.0.

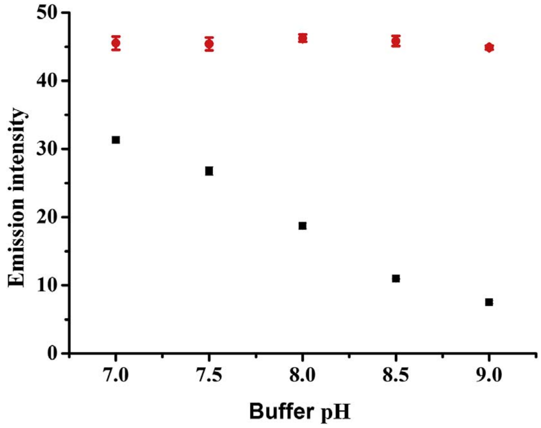

Fig. 2. Effect of assay buffer pH value on the fluorescence emission of the probe. (Round): the probe + GSH; (Square): the probe + GSH + Ag^+. Conditions: 10 mM Tris-HAc; GSH: 100 μM; Ag^+: 100 μM.

Chemical Reagent Co., LTD (Shanghai, China). All other reagents were of analytical grade and used without further purification. Water was doubly distilled and purified by a Milli-Q system (Millipore, Billerica, MA, USA).

Instrumentation

Fluorescence experiments were carried out on a Fluoromax-4 spectrofluorometer (Horiba Jobin Yvon Inc., USA). Sample solutions were excited at 442 nm and fluorescence emission spectra were recorded. Slits for excitation and emission were both of 2 nm. All emission spectra were collected at an ambient temperature of 22 °C.

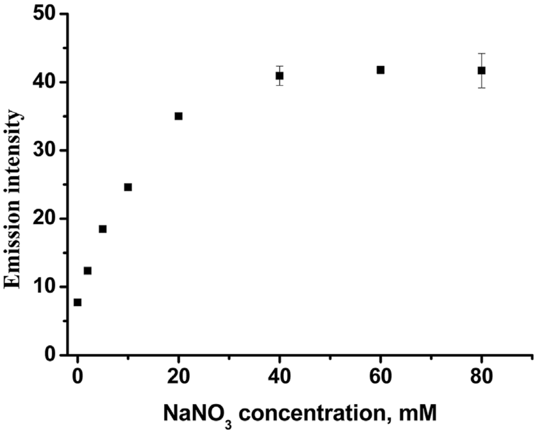

Fig. 3. The influence of $NaNO_3$ concentration on the fluorescence emission of the probe. Conditions: GSH and Ag^+: 100 μM each; buffer: 10 mM Tris-HAc, pH 9.0.

Procedures

25 μL of GSH (1 mM) and different concentrations of Ag^+ were mixed in a buffer solution (10 mM Tris-HAc, pH 9.0). Then, 25 μL of the probe was added (total sample volume: 275 μL), and the emission spectra were recorded.

Selectivity assay

The procedures of selectivity assay were the same as the detection of Ag^+ except that a number of other metal ions were employed.