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An organically modified sol–gel membrane for detection of lead ion by using 2-hydroxy-1-naphthaldehydene-8-aminoquinoline as fluorescence probe

Liangqia Guo, Songchen Hong, Xucong Lin, Zenghong Xie, Guonan Chen *

Ministry of Education Key Laboratory of Analysis and Detection Technology for Food Safety (Fuzhou University), Department of Chemistry, Fuzhou University, Fuzhou, Fujian 350002, China

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Abstract

A fluorescent reagent, 2-hydroxy-1-naphthaldehydene-8-aminoquinoline (HNAAQ) was synthesized, and an organically modified sol–gel membrane for detection of lead ion by using HNAAQ as fluorescence probe was fabricated. Under the optimum conditions, by a coplanar effect and the degree of molecular conjugation due to the complexation of Pb^{2+} with HNAAQ the relative fluorescence intensity I_{100}/I_0 of the sensing membrane is linearly increased over the Pb^{2+} concentration range of 1.9×10^{-7} to 1.9×10^{-4} mol/L with the detection limit of 8.3×10^{-8} mol/L. The preparation of this organically modified sol–gel membrane and its characteristics were investigated in detail.

Keywords: Sol–gel; Sensor; Lead ion

1. Introduction

Measuring and controlling the concentration of heavy metals is an important subject from an environmental point of view. Lead is a common environmental contaminant. All forms of lead are toxic and adversely affect reproductive, nervous, immune, cardiovascular systems as well as developmental processes in children [1]. Once introduced into the body, lead is a potent neurotoxin that can interfere with brain development [2], slow nerve conduction velocity [3], and trigger behavioral problems [4]. The lead level in the blood is considered toxic when it is ≥480 nM [5]. Several analytical techniques, such as atomic absorption spectrometry (AAS) [6,7], inductive coupled plasma atomic emission spectrometry (ICP-AES), anodic stripping voltammetry [8], inductive coupled plasma-mass spectrometry (ICP-MS) [9,10] are available for the quantification of lead. However, maintenance and operation cost of these techniques are expensive and require adequate expertise or sample treatment [11]. Therefore, these techniques are often limited to use in laboratory only [11]. Reliable, low cost, quick analytical techniques that permit real-time sampling of Pb^{2+} are important in the fields of environmental monitoring, clinical toxicology, wastewater treatment, and industrial process monitoring.

The use of ion-selective electrodes (ISEs) for the detection of lead has received much interest, and many ionophores have been investigated. Calix[4]arene derivatives [11–14], carbamates [15], cyclic amides/oxamides [16], anthraquinone derivatives [17], crown ether derivatives [18–20], ETH 5435 [21], porphyrin derivatives [22], macrocyclic ionophore [23], pyridinecarboximide derivatives [24], schiff base complex [25–29] have been used for lead-ISEs. How to minimize the interference of other cations such as Hg^{2+}, Ag^{+}, and Cu^{2+} is the major challenge for ISEs [13].

Fluorescent chemosensors capable of selectively recognizing cations have potential analytical applications in many fields, such as chemistry, biology, and medicine [30]. Fluorescence imaging with Pb^{2+}-sensitive chemosensors can, in principle, provide information with spatial and temporal resolution. The major challenges to achieving this goal are creating systems that are selective for Pb^{2+} and can function in water [31]. Most of the fluorescent chemosensors for cations are composed of a cation recognition unit (ionophore) together with a fluorogenic unit

* Corresponding author. Tel.: +86 591 87893315; fax: +86 591 83713866.
E-mail address: gnchen@fzu.edu.cn (G. Chen).

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(fluorophore) and are called fluoroionophores [30]. An effective fluorescence chemosensor must convert the event of cation recognition by the ionophore into an easily monitored and highly sensitive light signal from the fluorophore [32,33]. Recently, Pb^{2+}-responsive fluorescent probes based on peptide [34], protein [35], DNAzyme [36–39], polymer [40], and small-molecule [31,41–51] scaffolds have been reported. These fluorescence chemosensors show high sensitive for Pb^{2+}, but most of these systems have limitations, which include the interference of other metal ions [41–42], and/or a lack of water solubility, requiring the use of organic [43,48,50] or aqueous organic solvent mixtures [41,42,44]. Furthermore, these systems were still on the state of prototype and could not realize the real time and on-line determination for Pb^{2+} in the environment.

A fluorescent reagent 2-hydroxy-1-naphthaldehydene-8-aminoquinoline (HNAAQ) [41,52–54] has been reported and used for determination of lead [41] based on its chelation reaction. The fluorescent intensity of the complex was obviously increased by a coplanar effect and the degree of molecular conjugation owing to the presence of naphthalene and quinoline rings at both ends of the reagent molecule. This method showed a high sensitivity for lead ion, but this system was developed in water–ethanol mixture medium. In this paper, we utilized HNAAQ as the fluorescent probe, a fluorescent sensing membrane based on organically modified sol–gel for detection of lead ion was developed. The preparation and characteristics of sol–gel membranes were investigated in detailed.

2. Experimental

2.1. Reagents

8-Aminoquinoline and 2-hydroxy-1-naphthaldehyde were obtained from ACROS without further purification before use. Dimethyl diethoxysilane (DEOS) was purchased from Sigma. Tetramethoxysilane (TMOS) was from organic silicon new material Co., Ltd. of Wuhan University of China. $Pb(NO_3)_2$ (A.R.) was purchased from Huanqiu chemical factory of Jiangyan, China. Ammonia–ammonium chloride buffer solution (pH 9.0) was used. All other reagents used were analytical reagent or above. All water used in the experiment was Millpore pure water.

2-Hydroxy-1-naphthaldehydene-8-aminoquinoline (HNAAQ) was prepared according to the literatures [52,53] with slight modification. Briefly, a 1.44 g (0.01 mol) amount of 8-aminoquinoline was dissolved in 10 ml of absolute ethanol. The solution was heated to slightly reflux. To this solution, 1.72 g (0.01 mol) of 2-hydroxy-1-naphthaldehyde was added and the mixture was refluxed for 4 h. The mixture was then cooled to room temperature and recrystallized from ethanol. Orange–red sheet crystals were obtained (yield 72%).

The melting point (WI-1 micro-melting point apparatus) of HNAAQ is $215 \pm 0.5\,^{\circ}C$. The infrared spectra of 2-hydroxy-1-naphthaldehyde, 8-aminoquinoline and HNAAQ (KBr discs) were obtained on Perkin–Elmer 2000 FTIR spectrophotometer. The peaks of $\nu_{C=O}$ at $1640\,cm^{-1}$ of 2-hydroxy-1-naphthaldehyde and ν_{N-H} at 3420 and $3515\,cm^{-1}$ of 8-aminoquinoline both disappear from the spectrum of HNAAQ. In the spectrum of HNAAQ, a peak at $1628\,cm^{-1}$ ($\nu_{C=N}$) appears. Elemental analysis (Perkin–Elmer 240 analyzer) gave a composition of—C: 80.32%, H: 4.82% and N: 9.26%, which is in good agreement with the theoretical composition of HNAAQ—C: 80.51, H: 4.73 and N: 9.39%.

A stock lead ion solution (100 mg/L) was prepared by dissolving lead nitrate in acidified water. HNAAQ stock solution (5.0×10^{-5} mol/L) was prepared by dissolving 0.01492 g of HNAAQ in 1000 ml of absolute ethanol.

2.2. Sol–gel membrane preparation

20 mm × 20 mm glass slices were immersed in concentrated nitric acid for 24 h and then were dealt with ultrasonic treatment in water and ethanol by KQ118 ultrasonic cleaning apparatus (Kunshan ultrasonic instrument Co., Ltd., China). Finally dried at 100 °C for 1 h before use.

The sol–gel membranes were prepared similar to the literature [55] with a slight modification. The first step in the sol–gel preparation was mixing of TMOS and DMOS (silicon alkoxide precursor), ethanol (solvent), formamide (drying control chemical additive, DCCA), nitric acid (acid-catalyst for hydrolysis) and water by a QL-901 vortex instrument (Jiangsu Haimen Qilin Medical Appliance Co., China). The mixture was heated up and stirred for 30 min at 60 °C by a DF-101B heat and magnetic stirring apparatus (Zhejiang Yueqing Yuecheng Electrical Appliance Co., China). Hydrolysis and condensation took place and the sol was formed. Then an appropriate amount of HNAAQ solution (1.0×10^{-6} mol/L) was added and the mixture were stirred at 70 °C for 10 min. Seventy-five microliter of the mixture was transferred onto a 20 mm × 20 mm glass slice and dried at room temperature for gelation and aging the sample. The sample was then dried in the oven at 60 °C for 12 h in a DZF-1B vacuum drying oven (Shanghai Yuejin Medical Appliance Co., China) and yielding the final product of sol–gel sensing membrane. The sol–gel membranes were soaked in a NH_3–NH_4Cl buffer (pH 9.0) for 30 min before test.

2.3. Characterization of sol–gel membrane

The fluorescence intensities of the sol–gel membranes were determined with a spectrofluorimeter (Varian, Eclipse) with excitation and emission wavelength of 298 and 355 nm, respectively. A calibration curve of the relative fluorescence intensity I_{100}/I_0 versus Pb^{2+} concentration was plotted, where I_0 and I_{100} were the fluorescence intensity of the sol–gel membrane in the absence and presence of lead ion, respectively.

3. Results and discussions

3.1. Optimization of sol–gel sensing membrane

As to the matrix of sensing membrane, sol–gel-derived glass has been a promising matrix due to its mechanical and chemical stability, and optical transparence [56]. Precursor sol for preparation of sol–gel membrane was prepared from a solu-