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Naked-eye sensor for rapid determination of mercury ion

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ABSTRACT

A naked-eye paper sensor for rapid determination of trace mercury ion in water samples was designed and demonstrated. The mercury-sensing rhodamine B thiolactone was immobilized in silica matrices and the silica matrices were impregnated firmly and uniformly in the filter paper. As water samples flow through the filter paper, the membrane color will change from white to purple red, which could be observed obviously with naked eye, when concentration of mercury ions equals to or exceeds 10 nM, the maximum residue level in drinking water recommended by U.S. EPA. The color change can also be recorded by a flatbed scanner and then digitized, reducing the detection limit of Hg^{2+} down to 1.2 nM. Moreover, this method is extremely specific for Hg^{2+} and shows a high tolerance ratio of interferent coexisting ions. The presence of Na^{+} (2 mM), K^{+} (2 mM), Fe^{3+} (0.1 mM), Zn^{2+} (0.1 mM), Mg^{2+} (0.1 mM), Ni^{2+} (50 μM), Co^{2+} (50 μM), Cd^{2+} (50 μM), Pb^{2+} (50 μM), Cu^{2+} (50 μM) and Ag^{+} (3.5 μM) did not interfere with the detection of Hg^{2+} (25 nM). Finally, the present method was applied in the detection of Hg^{2+} in mineral water, tap water and pond water.

1. Introduction

Mercury is a widely distributed pollutant with broad toxicological profiles and exists in various forms (metallic, inorganic and organic salts). Inorganic mercuric ion is one of the most stable state of mercury [1] and is posing serious threat to the health of human beings. There are numbers of reports on the permanent damage of mercury to kidneys, digestive system, and nervous system [2]. Many countries and organizations have regulated the upper limit of Hg^{2+} for drinking water. For example, the United States Environmental Protection Agency (EPA) has set a maximum limit of 10 nM in drinking water [3]; whereas, the European Union and China permit a level of 5 nM Hg^{2+} in drinking water [4,5]. Many high-performance lab instruments can determine Hg^{2+} precisely down to sub ppb level, for example, atomic fluorescence spectrometry (AFS) [6], atomic absorption spectrometry (AAS) [7], inductively coupled plasma-mass spectrometry (ICP-MS) [8] and other electrochemical [9–13] and optic methods [14,15]. Extremely high sensitivity and specificity can be achieved by these methods. However, the routine running cost is very high, and special technical skills are also required for machine operation and sample pretreatment. In addition, some methods, especially the electrochemical methods, have obvious cross-talk interference among some ions. Thus, a rapid and simple method remains desirable for detection of Hg^{2+}.

Colorimetric sensor is one attractive approach for rapid and simple determination of Hg^{2+} [16–19], owing to its facile operation and simplicity. The color change can be easily caught by the naked eye and no special equipment is required. Besides those colorimetric sensors, some test strip methods based on DNA-functionalized gold nanoparticles [20–24] have also been developed for the one-step naked-eye detection of Hg^{2+}. These methods show great potential in rapid detection of Hg^{2+}, but further study is still needed to improve the stability, to simplify the strip operation conditions, and to prevent false results [20,21]. Compared to DNAzyme-AuNPs, molecule chemosensors are more stable [25–28].

Recently, we reported a reliable method for detection of trace Hg^{2+} by naked eye [29]. After Hg^{2+} preconcentration by dispersive liquid–liquid microextraction (DLLME), Hg^{2+} reacted with a highly selective molecule chemosensor and color change could be observed by naked eye. The preconcentration procedure was not straightforward enough for field Hg^{2+} screening. It would be necessary to develop a simple and single-step method for the determination of trace mercury with high sensitivity and selectivity. In recent years, a novel colorimetric determination method named colorimetric solid phase extraction (C-SPE) [30–33] has been developed. It complexes and concentrates analytes on a reagent-impregnated SPE membrane, and the resulting color change is then measured directly on the surface by a hand-held diffuse reflection spectra (DRS). By utilizing this technology, the

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elution step can be completely eliminated and the direct analysis of analyte on the surface of adsorbent-matrix is realizable. Due to its simplicity and rapidity for routine analyses, C-SPE provides another alternative for greener sample pretreatment.

In this paper, we developed a naked-eye paper sensor for rapid determination of Hg^{2+}. Hg^{2+} selective probe, rhodamine B thiolactone [36,37], were entrapped on porous silica matrix, and silica layer was impregnated in a filter paper. The water samples flowed through the membrane and the Hg^{2+} ions were captured by the rhodamine B thiolactone in silica matrices. The porous silica also acts as a preconcentrator for Hg^{2+} to improve the sensitivity effectively. The color change of the sensor membrane could be observed directly with naked eye at concentration level of 10 nM Hg^{2+} in water samples, and could be recorded by a home flatbed scanner [34,35] instead of DRS.

2. Experimental

2.1. Chemicals and materials

In this experiment, all regents were of analytical grade and used as received without further purification. Tetraethoxysilane (TEOS) and [3-(2,3-epoxypropoxy)]trimethoxysilane were obtained from ABCR GmbH & Co. KG and phenyltriethoxysilane (PTES) was from Alfa Aesar. Ascorbic acid and concentrated nitric acid (ultra pure, Hg≤0.0000005%) were from Jingchun Industry Co., Ltd. (Shanghai, China). Rhodamine B was from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Rhodamine B thiolactone was synthesized from rhodamine B and thiourea by two steps [36,37]. Deionized water was Wahaha deionized water (Hangzhou, China). The medium-speed qualitative filter paper from Hangzhou Special Paper Industry Co., Ltd. (Hangzhou, China) of Φ 7 mm was used as the substrate for silica matrices.

The standard stock solution of Hg^{2+} was prepared by dissolving the appropriate amount of mercury chloride salts in 2% (v/v) diluted HNO_3. Other metal ions, such as Cu^{2+}, Pb^{2+}, Cd^{2+}, Co^{2+}, Ni^{2+}, Fe^{3+}, Zn^{2+}, Mg^{2+}, K^{+}, Na^{+} and Ag^{+}, were in the form of their nitrate salts.

2.2. Preparation of sol–gel membrane

The sol–gel colloid formulation was prepared by mixing 1.2 mL of TEOS, 1.0 mL deionized water and 2.0 mL ethanol. The pH was adjusted to 2 by using 0.1 M hydrochloric acid to catalyze the hydrolysis of the silica precursors. After stirring for 3 h, 1.5 mL of 5 mM rhodamine B thiolactone was added and then the mixture was stirred for another 0.5 h. The filter paper was dipped in the sol–gel colloid solution for 5 min. After withdrawn from the solution, the membrane was dried in the air for 30 min (membrane 1). Membrane 2 and 3 were prepared in the same way as above, except that 0.15 mL PTES or [3-(2,3-epoxypropoxy)]trimethoxysilane was added in the silica precursors.

2.3. Sample collection and preparation

Mineral water bought from local supermarkets, tap water obtained from our laboratory and pond water from Dalian Institute of Chemical Physics were used as real water samples. The tap water was collected after flow of 5 min and the pond water was collected below 20 cm of water surface. All water samples were treated by the addition of 1.5 mL concentrated nitric acid per 1 L of water and kept in glass bottles. The sampling bottles had been cleaned with deionized water, dilute nitric acid and deionized water, in sequence. Water samples were stored at 4 °C and in dark. The water samples filtered with 0.45 μm cellulose acetate membrane (Millipore, Billerica, USA) were analyzed within 48 h after sampling. To avoid the oxidation of rhodamine B thiolactone probe in membrane, water samples were treated with ascorbic acid (5.7 μM) and then adjusted to pH 5 with 1.0 M acetate/acetic acid buffer solution.

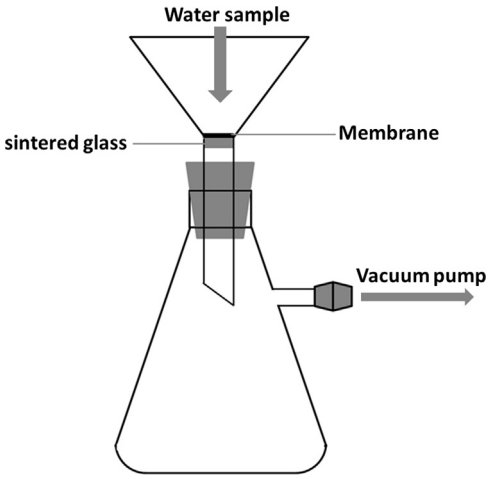

Fig. 1. The experimental set-up for mercury ion testing.

2.4. Procedures and data analysis

The mercury-sensing membrane was fixed on a sintered glass filter, as shown in Fig. 1. When the vacuum pump worked, water samples were pumped through the membrane at flow rate of about 30 mL min^{-1}. Then the membrane was picked and used for sensing experiments. Records of the membrane colors were performed on a commercial flatbed scanner. The blank-image was obtained with deionized water without Hg^{2+}. The average red, green and blue (RGB) values of the membranes were obtained from the center of the membranes (Φ 5 mm, 50% of the total size) using Adobe Photoshop™ software.

3. Results and discussion

3.1. Colorimetric response of Hg^{2+}

This colorimetric Hg^{2+} detection method is based on the complexation reaction between Hg^{2+} and rhodamine B thiolactone [36,37], and the formation of purple red product (Fig. 2). The silica matrix was chosen as the host material because of its large surface area, good stability and the adjustable hydrophobicity/-philicity. When water samples passed through the membrane, the filtration enhanced the complexing interaction probability between Hg^{2+} and rhodamine B thiolactone. The membrane coated with silica matrix serves as both a preconcentrator and a chromogenic reactor for Hg^{2+}. Therefore, the sensitivity of this method was improved significantly.

The colorimetric response change between sample-image and blank-image was normally expressed using Euclidean distance (ED), which was defined by the following formula.

$$ED = \sqrt{(\Delta R)^2 + (\Delta G)^2 + (\Delta B)^2}$$

In this experiment, the red and blue channels showed no significant color change while the green channel contributed almost 99% of the total color change. Therefore, the color signal change of green channel, instead of ED, was used for quantitative analysis throughout this experiment.