Sol–gel derived highly selective optical sensor for sensitive determination of the mercury(II) ion in solution

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ABSTRACT

We report a versatile optical sensor by incorporating the indicator dye 4-phenyl-2,6-bis(2,3,5,6-tetrahydrobenzo[b][1,4,7]trioxononin-9-yl)pyrylium perchlorate into a sol–gel layer. The proposed optical sensor that is stable, fast and highly selective to Hg^{2+} ions shows a significant absorbance signal change on exposure to an aqueous solution containing mercury(II) ion. The sensing film is able to determine mercury(II) ion in aqueous solution with a high selectivity over a wide dynamic range between 1.52×10^{-9} and 1.70×10^{-2} M, at pH 5, and a lower detection limit of 1.11×10^{-9} M. Validation of the assay method revealed excellent performance characteristics for Hg^{2+} ions over a wide variety of other metal ions, including good selectivity, long-term response stability and high reproducibility. Applications, for the direct determination of mercury(II) in real samples, gave the results with good correlation with the data obtained by using cold vapor atomic absorption spectrometry.

1. Introduction

Recent years, we have seen an increasing interest in the development of optical chemical sensors for heavy metal ions. In addition, an ideal chemical sensor will possess adequate selectivity, sensitivity, lower detection limits, be easy to calibrate, be robust and stable over the long-term. On the other hand, real sensors that meet all these ideals are rare. Sol–gel chemistry represents an alternative method for preparing optodes that offers a low temperature method for synthesizing materials that are either totally inorganic in nature or both inorganic and organic [1,2]. Compared with organic polymer coatings, the sol–gel films manifest advantages such as optical transparency, tunability of physical characteristics, low chemical reactivity and high mechanical stability as well as good compatibility with different substrates to be coated [3].

The sol–gel technique involves a complex reaction, especially when different materials are added to the matrix. Typically, the sol–gel process involves a metal alkoxide such as tetraethoxysilane (TEOS), water, and a second solvent, which are mixed thoroughly to achieve homogeneity on a molecular scale. The particles develop in the colloidal sol cross-link to form a gel, which is subsequently dried to form a three-dimensional porous glass. Doping of sol–gel materials with organic or biological molecules has been widely studied and has shown interesting and unique properties [4–9]. Meanwhile,

during the past decade, the development of optical chemosensors for the determination of heavy metal ions has become a rapidly expanding area of analytical chemistry [10,11].

Mercury is one of the heavy metals, which are highly toxic. Nowadays, determination of trace amounts of mercury in environmental samples is of great importance due to its high toxicity, accumulative and persistent character in the environment and living organisms. Mercury is generally found at very low concentration in the environment. Humans and other organisms can absorb mercuric ion readily. It may cause kidney toxicity, neurological damage, paralysis, chromosome breakage, and birth defeats. One of the routes of incorporation of mercury into the human body is drinking water [12]. Thus, in recent years, a number of optodes with different optical principles have been reported for the determination of mercury [11,13–20]. In addition, a wide range of other analytical methods has been used for the determination of mercury in real samples. They range from polarography to spectrophotometry [21–23], inductively coupled plasma (ICP) spectroscopy [24,25], anodic stripping voltammetry [26], neutron activation analysis [27,28], atomic fluorescence spectrometry [29,30] and cold vapor atomic absorption spectrometry [31]. To date, not many studies have been reported on mercury-detecting sol–gel derived optical sensors except for a few papers [17,32].

The present work describes the production and characteristics of a sensitive and highly selective sol–gel thin film, to detect trace level of Hg(II) in aqueous solution, in which the recently synthesized spectrophotometric reagent 4-phenyl-2,6-bis(2,3,5,6-tetrahydrobenzo[b][1,4,7]trioxononin-9-yl)pyrylium perchlorate is incorporated in a sol–gel derived thin film glass.

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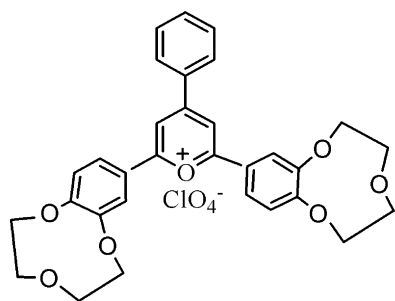*E-mail address:* a.yari@ymail.com (A. Yari).

Fig. 1. The structural formula of the sensing material, LX.

2. Experimental

2.1. Materials and reagents

All reagents (all from Merck) were of analytical reagent grade and used as purchased without further purification, except for vacuum drying. The selected sensing material, 4-phenyl-2,6-bis(2,3,5,6-tetrahydrobenzo[b][1,4,7]trioxononin-9-yl)pyrylium perchlorate (LX, Fig. 1), was prepared as described elsewhere [33]. The sol–gel precursor's TEOS, absolute ethanol (EtOH), Tritton X-100, hydrochloric acid (HCl), standard buffer solutions (pHs 4.0, 7.0 and 10.0) for pH-meter calibration, glass slides and potassium hydroxide (KOH) were also purchased from Merck. The metal cations tested were of their nitrate salt. Aqueous solutions were prepared from doubly distilled and deionized water.

2.2. Instrumentation

Spectroscopic measurements were made using a Shimadzu 1650 PC UV–vis spectrophotometer with 1.0-cm quartz cells. A Jenway 3020 (UK) pH-meter was used to measure of pH. A cold vapor atomic absorption spectrometry system (CV-FAAS) including an AA 670 Shimadzu atomic absorption spectrometer with an air/acetylene flame was used for measurement of mercury contents of the samples.

2.3. Sensor fabrication

We prepared the sol–gel thin film according the general procedure described in literature [34]. In this work, the formation of a silica sol–gel from the alkoxide TEOS in EtOH, and H_2O was performed. A sol–gel stock solution was prepared from a mixture of 2 mL TEOS, 0.5 mL 0.1 M HCl, 1 mL deionized water, 2 mL EtOH, 3–4 drops of Triton-X 100 and 28 mg of indicator (LX) in a polyethylene vial. The solution was then stirred for 12 h with a magnetic stirrer at 30 °C. The sensors were constructed by casting the surface of microscope glass slide (2 cm × 2 cm) with the sol–gel solutions via spin coating process by using a spinning device (rpm 1000) in a duration time of 30 s. Before casting, the glass slide surface were roughened and washed with a KOH–EtOH solution. The surfaces were then rinsed with water, acetone, ethanol, and finally with water. After the coating and drying, the glass slides were cut into appropriate sizes to be mounted in a 1.0 cm quartz cell for absorbance measurements.

2.4. General procedure

The glass slide was mounted in the diameter direction of the photometric measuring cell. The volume capacity of the cell was ca. 4 ml. A stock solution of 1.0×10^{-3} M Hg^{2+} was prepared by dissolving exactly weighed amounts (with an accuracy of 0.00001 g) of mercury(II) nitrate, $Hg(NO_3)_2 \cdot 2H_2O$, diluted with distilled water
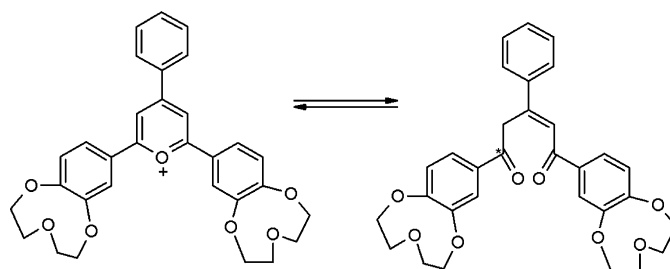
Scheme 1. Pyrylium salt (LX) could undergo ring opening when dissolves in the solution.

and standardizing with a EDTA solution [35]. Lower concentrations of solutions were obtained by serial dilution of the stock solution. Standard solutions containing the metal cation were added sequentially into the system by a micropipette (with 2-μL step) and the absorbance data were recorded at $\lambda_{max} = 550$ nm. The limiting absorbencies A_0 and A_c were determined with the optode in contact with (1.0×10^{-2} M) and without Hg^{2+}. By plotting the calibration curve of the absorbance values versus the logarithmic concentration of mercury ion (pHg), the unknown mercury(II) concentration can be read. All measurements were carried out at the room temperature.

3. Results and discussion

3.1. Spectrophotometric study of the solution

As we have already reported [36] for a PVC membrane, to explore the properties of LX as an optically sensing material for the metal cation, various metal ions tested in a preliminary experiment. It was found that the addition of proper amounts of Hg^{2+} to an acetonitrile solution of LX results in a fast change in the color of the solution from pale orange to red indicative of selective complex formation of the ligand with Hg^{2+} ions in the solution. The formation constants values, K_1 and K_2, of the resulting complexes were $(2.44 \pm 0.01) \times 10^5$ and $(3.57 \pm 0.01) \times 10^7$, respectively. Furthermore, in a preliminary experiment we found that the data collected to construct the molar ratio plot (not shown) of the interaction between the ligand (L) and the Hg(II) ions in the film are best fitting to the corresponding theoretical curve for the 1:1 (metal:ligand) model of the resulting complex. Therefore, this suggests that a 1:1 nature of the complex exists between Hg^{2+} and the ligand (L) in the film and the reasonable equilibrium constant evaluated as $(3.21 \pm 0.01) \times 10^3$.

Pyrylium salt (LX) could undergo ring opening when dissolves in the solution (Scheme 1). A similar behavior for ring opening and ring closure of different pyrylium compounds has already been reported in literature [37]. Ring closure in the presence of metal ions is most likely due to the Lewis acid character of the metals, when coordinated to the crown-oxygen atoms, that might enhance the electrophilic character of the C* carbon [38]. Thus, the formation of the pyrylium cation is triggered by electron withdrawing event in remote sites (crown-ether rings).

3.2. Effect of the pH of the solution

As the sol–gel processes and the mechanism of the reactions are profoundly affected by many factors, such as the size of the alkoxide reagent on silicon and the solution pH [39] the effect of the pH of the solution, in which the sensor is applied, is also a critical factor that must be considered definitely. The response curve data were obtained by measuring the absorbance values for Hg^{2+} 4.0×10^{-4} M at different pH values and the results are shown in Fig. 2. From this
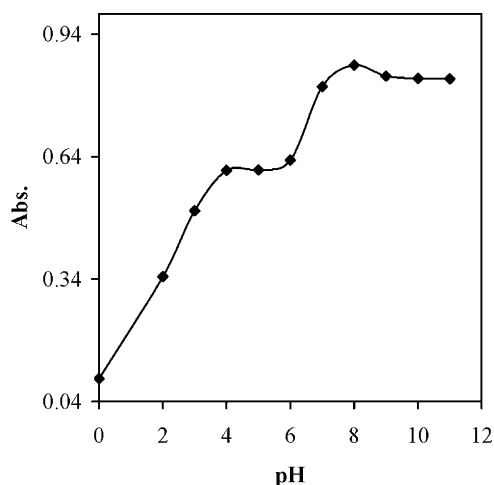
Fig. 2. The effect of pH values on the response function of the optical film in the presence 4.0×10^{-4} M of Hg^{2+} ions, at $\lambda_{max} = 550$ nm.

figure, we see that the pH of the solution has no considerable effect on the response of the film in two pH ranges 3.5–6.0 and 7.5–11.0. The pH 5.0 was selected as the best solution pH because of the acidic condition in the solution and preventing the precipitation of the mercury(II) ions as hydroxides. Among some buffer-systems tested, the sodium citrate/citric acid system was used as the proper buffer solution throughout.

3.3. Spectral characteristics

After LX was incorporated in the thin film through the sol–gel process, the spectral responses of the film, on exposure the mercury(II) ion in the solution, is demonstrated in Fig. 3 and the spectral pattern of the ligand–metal interaction in the film remained similar to those occurred in the organic solvent [36]. From this figure, the ligand shows a strong change in its electronic absorption spectra about 482 nm as growing a new and strong absorption peak at about 550 nm, with a clear isosbestic point at 496 nm. This remarkably spectral changes can be attributed to the extraction of Hg^{2+} into the L-containing sol–gel film and the effective interaction between the mercury(II) ion and the ligand L in the film. This is the basis of the optical sensing device in this investigation. Therefore, the
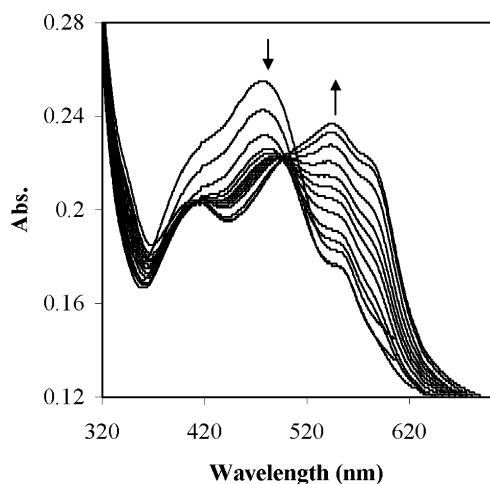
Fig. 3. Absorption spectra for the titration of the ligand, L incorporated into the film, with the increasing amounts of Hg^{2+} ions (0.0–1.0) $\times 10^{-3}$ M in aqueous solution, at pH (5).
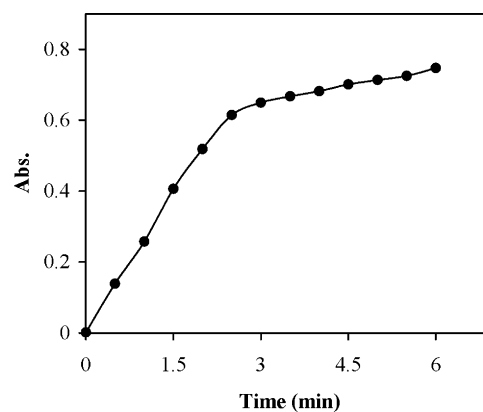
Fig. 4. The time-dependence response characteristics of the optical film, immersed in a citrate-buffer solution containing 6.67×10^{-5} M Hg^{2+}, at $\lambda_{max} = 550$ nm.

wavelength 550 nm was used in all subsequent absorbance measurements.

3.4. Performance characteristics

3.4.1. Time-dependence response characteristics of the film

As we know, the time required to response of the sensor towards a certain concentration of the measuring ion, the response time value ($t_{95\%}$) of the sensor when reaches to 95% of its final value (steady state) [40], is one of the main parameters that must be determined experimentally. Fig. 4 demonstrates the time-dependent response characteristics of the optical film, which immersed in a buffer solution containing 7.67×10^{-5} M Hg^{2+}. This figure shows that the shortest response time of the film is about 3 min in which the sensor is able to monitor reversibly and reproducibly the mercury(II) ions.

The reusability of the optode was studied by repeating six cycles of Hg(II) measurements from the two different standard samples. The reversibility of the optical film was calculated by the absorptions collected from the measurements of the buffer solutions containing 1.0×10^{-6} and 1.0×10^{-3} M Hg^{2+}. The results are shown in Fig. 5. As can be seen from this figure, the system was highly reversible. The evaluated %RSDs were of ±0.020 and ±0.026 for the lower and the higher Hg^{2+} concentrations, respectively.

The film was used periodically over a period of 3 months. Over this period, using the optode in contact with a mercury(II) solution (1.0×10^{-4} M) for 1 h per day, the absorbance signal of the optical film changed no more than 5% and no considerable leach of the
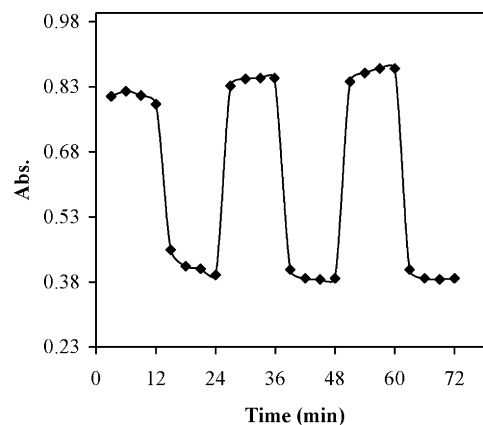
Fig. 5. The reversibility of the optical film from the absorbance measurements (at $\lambda_{max} = 550$ nm) of two buffer solutions containing 2.0×10^{-6} and 2.0×10^{-3} M Hg^{2+}, bottom and top, respectively.

ligand was detected during the measurement of sample solution. We think the high lipophilic property; enough long branches of L and the delocalization of its electronic structure should increase the stability of incorporation in the sol–gel derived film and provide a long lifetime.

3.4.2. Analytical response capabilities of the optical film

Here, some analytical capabilities of the optical film such as the stability, the reproducibility, the linear concentration dynamic range and the limit of detection are investigated.

As mentioned in the previous section, the film was used frequently over a period of 3 months. Over this period, the film exhibited a good stability with a dynamic range deviation of less than 1.0%, when the mercury(II) ion solutions were measured. We found that mildly washing the film by distilled water regenerates its response function perfectly.

The response curves of optical sensors are usually depicted as the normalized absorption α as a function of the metal-ion concentration [41]. The measured absorption is converted into α by Eq. (4), in which A_0 is the initial absorption of the film, A_c the highest absorption power of the film in the presence of the metal ion, and A is the measured absorbance at the desired maximum wavelength. At this wavelength, the only absorbing species is the complex Hg-L, α is equal to the molar fraction of the complex. From Beer's law, we assume the normalized absorbance value α is related to the measured absorbance as follows:
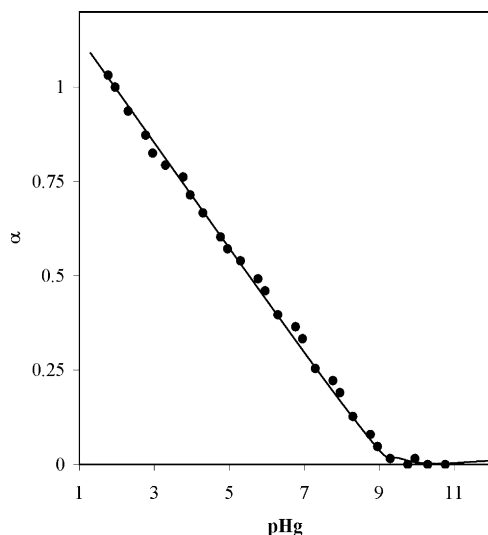
$$a = \frac{(A - A_0)}{(A_c - A_0)} \tag{4}$$

As can be seen from Fig. 6, the calibration curve plot including the normalized absorption response of the film (α) against logarithmic concentration of Hg^{2+} (pHg) gives a wide concentration measurable range from 1.52×10^{-9} to 1.70×10^{-2} M of Hg^{2+} in the solution.

In order to assess the possible analytical application of the sensing method, the lower limit of detection 1.11×10^{-9} M was evaluated from the intersection of the two segments of the calibration graph of the film response at its lowest part.

3.4.3. Selectivity

Obviously, the selectivity is one of the most important properties of the response of a sensor. This property represents the
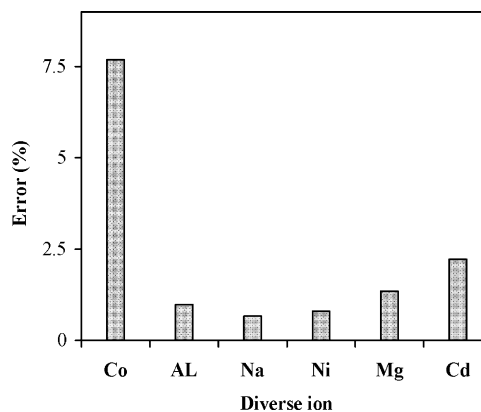
Fig. 7. Effect of some diverse cations on the optode response to the mercury(II) ion.

preference of a sensor to response to the primary ion with respect to the potentially interfering ions. To investigate the selectivity of the proposed film if the resulting tolerated relative error is defined as error (%) = $[(A - A_i)/A] \times 100$, in which A_i denotes the absorbance of the film in the presence of the interfere [41], we will be able to evaluate the selectivity of the film towards the Hg^{2+} ion over the interfering ions in the solution. The selectivity of the optode was tested for the determination of Hg(II) in the presence of other interfering cations namely Co(II), Ni(II), Al(III), Mg(II), Na(I) and Cd(II). The results are summarized in Fig. 7, in which the concentration of the interfering ion was 100 times as much the primary ion (Hg^{2+}, 1.67×10^{-5} M). As seen, the relative errors are lower the reasonable level, 2.5%, except for the case of cobalt(II) for which the relative error is about 7.5%. Such minor interferences could be due to massive existence of the cation in the solution and enforcement of the exchange equilibrium to the other side of the interface. On the average, the optode does not have a significant selectivity towards other cations, making it feasible for practical application in mercury(II) ion measurements.

3.5. Determination of Hg^{2+} concentration in samples

To test the practical application of the present sensor, applications for direct determination of mercury(II) in two samples including a cyanidic garbage from an electrocoating manufactory and a resinic black mud were carried out. The samples collected were first acidified with HNO_3 and then filtered through a packed filter to remove oils and other organic impurities. Under the optimal conditions for the proposed optode, the obtained data were collected. As shown in Table 1, which summarizes six measurements for each case by following the standard addition calibration method, the results are in good agreement with data obtained by CV-FAAS. In addition, the proposed mercury(II)-selective optode was found to work well under laboratory conditions where mercury ions were accurately determined with the proposed film when it was used as an indicator device for the titration of a solution of Hg^{2+} with EDTA.

Fig. 6. The calibration curve plot of the optimized film including the normalized absorption response (α) against the logarithmic concentration of Hg^{2+} (pHg), at pH (5).

Table 1
Determination of mercury(II) concentration (%) in real samples of six replicate measurements using standard addition method.

Sample	CV-FAAS	Proposed sensor	STD
Cyanidic garbage	3.88	3.79	±0.04
Resinic black mud	1.16	1.08	±0.03

4. Conclusions

The results reported in this work clearly demonstrate the ability of a ligand containing crown sub-units to coordinate Hg(II) metal ion in the sol–gel derived film. Since the ligand bearing a suitable light sensitive moiety, its changes at the electronic level was able to use it as a good chemosensor for Hg^{2+} metal ion by exploiting the absorption effect on the light absorption of the sensitive moiety upon interaction with metal centers. Furthermore on the basis of the results discussed in this paper, the proposed Hg(II) ion-selective optode has many advantages including outstanding wide dynamic range, good response time, very low detection limit, high selectivity and good reproducibility. It was applied to determine the concentration of mercury(II) ions in real samples.

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