Optical Probe for Determination of Chromium(III) Ion in Aqueous Solution Based on Sol-Gel-Entrapped Lucigenin Chemiluminescence

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A method to determine chromium(III) ion in aqueous solution by chemiluminescence method using a lucigenin entrapped silica sol-gel film has been studied. An optical probe for chromium(III) ion has been prepared by entrapping lucigenin into silica sol-gel film coated on a glass support by dip coating. The chromium(III) optical sensor is based on the catalytic effect of chromium(III) ion on the reaction between lucigenin and hydrogen peroxide in basic solutions. The effects of Nafion, DMF and Triton X-100 were investigated to find the optimum condition to minimize cracking and leaching from the probe. The effects of pH and concentrations of lucigenin and hydrogen peroxide on the chemiluminescence intensity were investigated. The chemiluminescence intensity was increased linearly with increasing chromium(III) concentration from 2.5×10^{-4} M to 8.0×10^{-7} M and the detection limit was 4.0×10^{-7} M.

Key words : Sensor, Sol-gel, Chromium(III), Chemiluminescence

1. Introduction

Chromium exists in environmental water and seawater in two different oxidation states, Cr(III) and Cr(VI). Thermodynamic calculations predict that in oxygenated natural waters chromium should exist almost exclusively as Cr(VI), with the predicted species being CrO_4^{2-}, and Cr(III), existing as the aquahydroxy species $Cr(OH)^+(H_2O)_4^{1-2)}$. In two oxidation states, Cr(III) and Cr(VI), it differs significantly in biological and toxicological behavior. The degree of toxicity depends on the chemical form. Cr(III) is considered an essential trace element for the proper functioning of living organisms. On the other hand, water soluble Cr(VI) is extremely irritating and toxic to human body tissue owing to its oxidizing potential and easy permeation of biological membranes[3-4].

There are a few analytical techniques that have sufficient sensitivity for direct determination of trace levels of chromium in various sample. The most common techniques used include atomic absorption spectrometry(AAS) employing flame or electrothermal atomization[5-6], inductively coupled plasma mass spectrometer(ICP-MS), and inductively coupled plasma atom emission spectrometer(ICP-AES)[7-14]. But all these analytical techniques can only yield information on the total concentrations. Techniques are used in the determination of chromium in real samples, the separation and preconcentration of chromium species are also required. Traditional methods for separation and preconcentration of chromium species are mainly based on coprecipitation[15-16], solid–liquid extraction[17], solvent extraction[18-19], and chromatography[20]. All these methods have the disadvantage of introducing additional laborious and time-consuming sample manipulation steps with the associated well-known sources of error. Capillary electrophoresis (CE) with UV detection has been used to determine Cr(VI) and Cr(III), after chelating with organic ligands to form all anionic complexes[21]. Unfortunately, the sensitivity of this method is not sufficient. Chemiluminescence (CL) is well known for high sensitivity and low detection limits. The application of CL for the analysis of chromium(III) in natural water has been reported[22-24]. These methods were based on the chromium(III)-catalysed oxidation of luminol by hydrogen peroxide in a basic aqueous solution.

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The concentration of Cr(III) can be obtained by direct measurement, but the total concentration of chromium involves a previous reduction the Cr(VI) to Cr(III) with hydrogen peroxide in acidic solution. Finally, the concentration of Cr(VI), Cr(III) and total concentration of chromium was determined in samples of water containing different amounts of chromium[25].

Sol-gel technology, in which a multicomponent solution undergoes gelation to form a useful rigid network of the oxides present, has the potential to produce optical transparency, mechanical stability, chemical stability, low temperature, tailored glasses, and thus a range of highly suitable substrates for the variety of fiber optic chemical sensors. Many compounds can be entrapped into sol-gel matrix. The applications include sensors, where sol-gel are used as matrices for optodes of chemical optical sensors or biosensors [26-28].

In this paper, based on catalytic effect of chromium(III) to the lucigenin-H_2O_2 CL system, an optical probe for chromium(III) ion has been prepared by entrapping lucigenin into silica sol-gel film coated on a glass support by dip coating. The effects of Nafion, DMF and Triton X-100 on film formation were investigated to find the optimum condition to minimize cracking and leaching from the probe. The effects of pH and concentrations of lucigenin and hydrogen peroxide on the chemiluminescence intensity were investigated.

2. Experimental Methods

2.1 Materials

Tetraethyl orthosilicate(TEOS) was obtained from Sigma(St. Louis, MO, USA) and Bis-N-methylacridium nitrate(lucigenin) was purchased from aldrich(Milwaukee, WI, USA). Hydrochloric acid and ethanol were obtained from Duksan Chemical (Inchon, Korea). All the other chemicals were of analytical reagent grade and were used as received. Deionized water was obtained by means of a Millipore (Bedford, MA, . USA) Milli-Q water system and used throughout the whole experiment.

2.2 Apparatus

A flow system consisted of two peristaltic pumps (Ismatec Model MS-4 Reglo/6-100, Glattbrugg-Zürich, Switzerland). One (P1)

delivered hydrogen peroxide. The other (P2) delivered buffer solution in the flow system. An aliquot of 100 μl of sample was injected by a six-way injection valve into the carrier stream of buffer solution. A mixture of P1 stream was mixed with a mixture of P2 stream in a Y-shaped element connected to a 50 cm mixing coil. The solution passed through a mixing coil was introduced to a flow cell on which a 8.0 mm diameter sol gel film coated on glass. The water stream pumped by P1 was used for rinsing a mixing coil and a flow cell. PTFE tubing (0.8 mm i.d.) was used to connect all the components of this system. A bifurcated optical fiber bundle (Model 77533, Oriel, Stratford, CT, USA) was screwed to a flow cell for the position of the sensing tip of the optical fiber to be the same for each measurement. The flow cell was housed in a laboratory made light tight chamber to remove all the unnecessary stray light. One end of the fiber bundle was fixed at 10 mm before the emission port and the other end at 10 mm before the excitation port of the cell compartment of a spectrofluorometer (Model FL111, Spex, Edison, NJ, USA). A Hamamatsu Model R928 photomultiplier tube were used. The voltage used for the photomultiplier tube was 900 V.

2.3 Immobilization of lucigenin

The preparation procedure of sol-gel stock solution was a modified method of 2.2 ml tetraethylorthosilicate TEOS, 0.7 ml H_2O and 50 ml 0.1 M HCl were mixed in a glass vial. The mixture was stirred for 3 h in which the hydrolysis and condensation of TEOS occurred. Then, a clear sol-gel stock solution was obtained. 0.5 ml sol-gel stock solution and 0.5 ml of 2.0 mg lucigenin solution were mixed and placed on a 8.0 mm diameter glass plate, which were pretreated in H_2O_2-H_2SO_4(1:1) solution for 30 min and rinsed with distilled water followed by dried at $100^{\circ}C$ oven for 24 hr, to form a sol-gel film that was enclosed in a glass vessel to age at room temperature for a week. During this period, lucigenin was encapsulated in the gel's network formed by the polymerization of silanol groups in the sol. To prevent the film from cracking, Nafion, DMF and Triton X-100 were also added and tested respectively.

2.4 Measurement procedure

Flow lines were inserted into hydrogen peroxide, carbonate buffer, respectively. Then, 100 µl of sample was injected into the carrier stream of carbonate buffer which mixed with released H_2O_2 stream. When mixed solution reached the flow cell, react with immobilized lucigenin to produce a CL signal.

3. Results and discussion

3.1 Film surface morphologies

Atomic force microscopy is a powerful method for studying the surface morphologies of films. Fig. 1. show pretreated glass surface and film surface entrapped with lucigenin. The surface entrapped with lucigenin form a more granulated surface with many small details.
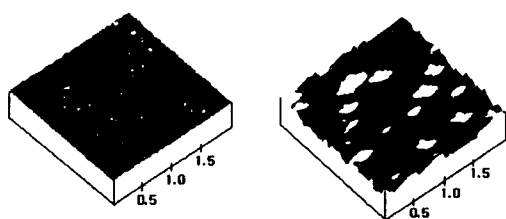

Fig. 1. The AFM patterns of the surface morphologies of the silica films: (A), slide glass; (B), lucigenin entrapped in a silica sol-gel film.

3.2 Optical property and leaching of immobilized lucigenin

The lucigenin when incorporated in the sol-gel matrix prepared from 100 % TEOS modified with 0.1 % Triton X-100 show no visible cracks and only about 1-2 % leaching by dipping the layer into continuous flow of distilled water over the period of 3 h. According to Brinker, addition of surfactant provides a further homogeneity. In the presence of a surfactant increases the molecular mass and decreases the inner tensions in the glass during condensation, as a result the cracks do not form.

Immobilized lucigenin under sol-gel preparation conditions, the emission maximum has little shift in solution and for about 1 µm in TEOS-based layers (Fig. 2), but the ratio of emisson peaks of lucigenin had slightly changed. The nature of the interaction of the luminophore with the sol-gel has not been fully investigated yet, although similar observations have been already published. It seems that the microenvironment

that is not homogenous in sol-gel matrices exerts the effect on the emission maximum and intensity.
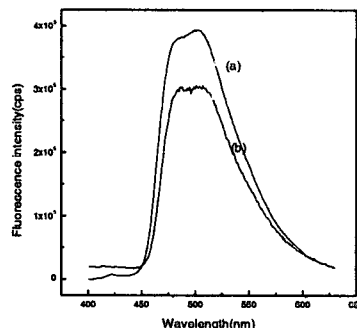

Fig. 2. Fluorescence spectra of lucigenin(λex, 369.0 nm) in pH 8 buffer solution: (a), 1×10^{-6} M; b), 2 mM entrapped in a silica sol-gel film.

3. 3 pH effects on CL intensity

The CL intensity was dependent on pH. Experiments were performed with a different ratio of hydrogen carbonate and carbonate. As shown in Fig. 3., the CL intensity was increased with increasing pH value, reaching a maximum at 11.9. When pH value higher than 12.5 by addition of 1.0 M NaOH, the CL emission was totally quenched.
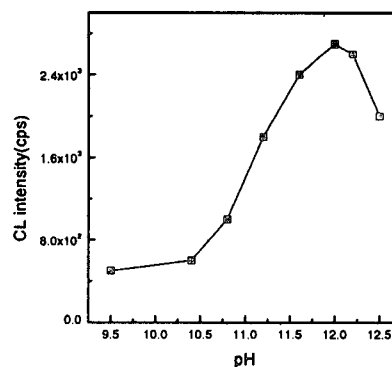

Fig. 3. Effect of pH on CL intensity in flow system: [H_2O_2], 2.0 M; λem, 500 nm.

3. 4 Optimization of reaction conditions

A series of experiments were conducted to establish optimum analytical variables in a flow injection system. The parameters optimized included flow rates, the distance between valve and flow-cell and reagents concentrations. Since

this CL reaction is very fast, higher total flow rates are favorable for the sensitivity. A total flow rate of 4.5 ml/min was recommended because a higher flow rate than 4.5 ml/min showed constant signals. The distance between valve and flow-cell should be as short as possible to avoid unnecessary dispersion. In this paper, this distance was about 20 cm and limited by the construction of a light-tight box. The influence of the concentration of hydrogen peroxide on the emission intensity was shown in Fig. 4. The CL intensity increased with the raising of the concentration of hydrogen peroxide in the range of 10 mM-2.0 M, and reached a plateau at a higher concentration. Thus a 2 M hydrogen peroxide was selected for subsequent experiments.
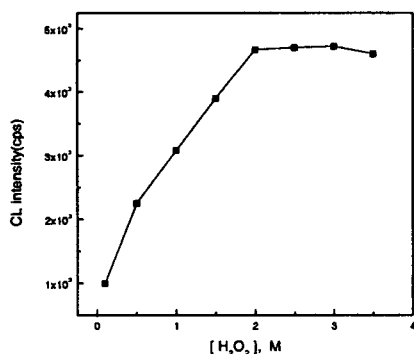

Fig. 4. Effect of H_2O_2 concentration on CL intensity in flow system: pH 11; [Cr(III)], 5×10^{-6} M; λem, 500 nm.

3.5 Response time

The response time of sensor system, apart from sensitivity and sensing range, is one of the most crucial aspects for sensor implementation. The response time of the sensor prepared with the sol gel film is shorter than 1 min showed in Fig. 5. Fig. 5. show chemiluminescence signal increases rapidly when reagents reached on the surface of sol-gel film. But the signal decreased more slowly than in aqueous reaction system. These results can be understood by considering the microscopic structure of the silica host. Reaction in porous, inorganic solids can be significantly more complex than that observed in aqueous solution because diffusion rates will strongly depend on both pore structure and surface interactions. The rate and the manner at which reagents move

around in these porous solids is important for investigations that rely on the ability of the entrapped reagent to undergo conformational changes or react with another species that must diffuse from solution into the gel. Given that the silica surface has a net negative charge, positively charged chromium(III) can be electrostatically adsorbed on the pore wall, while negatively charged HO_2^- diffused more slowly to the sol gel inside, showing tailed CL signal.
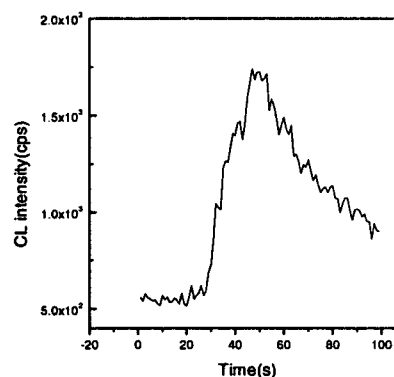

Fig. 5. Response time of the sensor prepared with the sol gel film: [Cr(III)], 2×10^{-6} M.

3. 6 Performance of the flow sensor

Under the above optimum conditions, the calibration curve was obtained for chromium(III) determination by plotting the graph of the CL signal versus Cr(III) concentration, which gave linear ranges from 2.5×10^{-4} M to 8.0×10^{-7} M and the detection limit was 4.0×10^{-7} M. The reproducibility of this CL sensor was studied by injecting 5.0×10^{-6} M Cr(III) nine times. Fig. 6. gives the result. The relative standard deviation (RSD) was 3.9 %.

4. Conclusions

In this flow sensor, as CL reagent lucigenin immobilized in a sol-gel matrix, which exhibited excellent characteristics in terms of chemical inert and optical transparency. It offered several advantages, such as operational convenience, instrumental simplification, reducing the reagent consumption. These permit the flow sensor to operate in a very simple and cheap way, and make the operation very convenient.
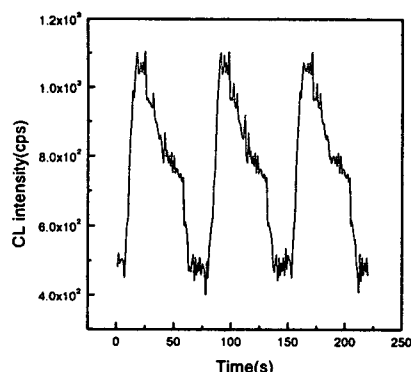
Fig. 6. Reproducibility of sensor CL response: [Cr(III)], 1×10^{-6} M.

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