Simultaneous Determination of Heavy Metals Using Array Based Optical Chemical Sensor

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ABSTRACT

A sol-gel optical chemical sensor encapsulated with complexing agents for simultaneous detection of selected heavy metals such as chromium and iron in aqueous media was fabricated. The sensor was prepared by acid catalyzed copolymerization of tetramethoxysilane(TMOS) and starch. 300μL of TMOS and starch mixture was load to the 96 well plate and then the gelation was completed within 2 hours. The composition of TMOS and starch, pH and detection range of heavy metals were optimized. 100μL of environmental and laboratory samples spiked with heavy metals were used to evaluate the application of the chemical sensor array to real samples. The chemical sensor exhibited high specificity in identifying multiple analytes. No obvious cross-interference was obtained when a 96 Well plate sensor array was used for simultaneous analysis of multiple samples in the presence of multiple analytes. The snesor array showed high reproducibility and relative standard deviation of 5%(n=10) was obtained. The developing reaction time was completed within at least 20 minutes. The detection limit of selected heavy metals was between 10 to 50μM by naked eye or Well plate reader. The physical properties have been investigated by various technique such as FTIR, XRD, SEM, TG-DTA to obtain information on chemical, structural and morphological composition of the layer.

Keywords: sol-gel, heavy metals, optical chemical sensor array

1 INTRODUCTION

Heavy metals are ubiquitous in natural and contaminated environments. Due to their toxicity, the potential risk of heavy metals to human health and ecology has received much attention. Although various classical methods such as atomic absoption spectrophotometry (AAS), inductively coupled plasma atomic emission spectrophotometry (ICP-AES), and inductively coupled plasma mass spectrometry (ICP-MS), UV-VIS spectrophotometry, potentiometry (ISE), and amperometry, the development of chemical sensors or biosensors for the determination of heavy metals is still required due to the possibility of rapid and in situ with little pretreatment [1-3]. From the point of view of optical sensing for heavy metal detection, one of the advantages of sol-gel materials is the possibility of using a large variety of chelating agents as receptors, which facilitates selective sensing. A key step in developing the chemical sol-gel sensor is the immobilization of chelating agent. There are three most widely used methods for immobilization: (a) adsorption of chelating agents onto a solid substrate; (b) covalent binding which involves the formation of permanent chemical bonds between sensing agents and a support; and (c) encapsulation or entrapment of chelating agents within a polymeric matrix. It seems that the encapsulation method avoids the disadvantages an combines the advantages of the first two methods [4]. Sol-gel is an optically transparent glass-like material produced by the hydrolysis and polycondensation of silicone alkoxides. Recently, inkjet printing technology for sol-gel materials and devices has been reported, and screen-printing technology for the fabrication of disposable biosensors and chemical sensors has been reviewed. In this work, a chelating agent entrapped optical chemical sensor fabricated by sol-gel technique for the rapid determination of heavy metals was developed. The preparation procedure of sol-gel sensor including sol-gel composition, gelation time, reaction condition on Well plates was optimized. The feasibility study for fabrication of chemical sensor by using inkjet printer was carried out.

2 EXPERIMENTAL PROCEDURE

The sol-gel preparation procedure was

similar to the method described elsewhere with minor modifications(1). The acid catalyzed sol solution was first prepared by mixing 2.2mL of TMOS and 0.54mL of 1mM HCl in a glass vial and then sonicated for 30min at room temperature to complete the hydrolysis step. Separately, 1mL of 1% chelating agent-0.4% starch, 6.4mL of 5mM Tris buffer at pH 8.9 was mixed to form the starch catalyzed chelating agent solution(SC solution). The SC solution was added into 2mL of sol solution and 200μL of the mixture was loaded to the Well plate for 2 hrs to complete the gelation process. Two heavy metals including Cr(VI) and Fe(II) were selected in this study. An aliquot of 100μL of metal solution was added to sol-gel plate and the absorbance was evaluated by naked eye or Well plate reader, and the data was recorded by PC. 1,10-phenanthrolin for Fe(II) and diphenylcarbazide for Cr(VI) was used each as a complexing agent.

3 RESULTS AND DISCUSSION

3.1 Chemical composition of the sensing sol-gel material

Sol-gel inorganic material with different proportions of the precursor TMOS was prepared by hydrolysis and copolymerization. The copolymerization was carried out in the presence of starch. The composition of TMOS and starch was optimized in respect of gelation time and composition to give maximum sensitivity for Fe(II)-1,10 phenanthroline complex. The gelation time took long with increasing the amount of SC solution described in experimental section. When the volume ratio of TMOS and SC solution was 1:1, sol-gel sensor was formed within 15min similar to sol-gel glass formed by Tsai et. al[1]. When the volume ratio of them comes to 1:5 or 1:6, the gelatiom time was extended to take 2 hours. It appeared that the ratio of 1:5 or 1:6 was preferred to that of 1:1 to prevent the clogging of nozzle during shutting the TMOS and SC solution using inkjet printer modified for fabrication of chemical sol-gel sensor. Variation of the concentration for starch from 0.1 to 0.4% in SC solution gave increment of around 20% in absorbance of metal complex. It seems that the starch concentration affects not only the pore size of sol-gel matrix but also the gelation time. Further SEM study is needed for the explanation of the phenomena.

3.2 Reaction time of metal complex on sol-gel sensor

To study the reaction time of metal ion loaded on sol-gel sensor, after the preperation of sol-gel sensor under the optimum condition, the response of chemical sensor array for Fe(II) ion in 96 Well plate was tested. Figure 1 shows the response of the response of the chemical sensor at various concentrations of Fe(II) prepared by 1 mM acetate buffer at pH 4. The absorbance increased from 0.011 to 0.10 as the concentration increased from 1.00E-6 to 1.00E-4. After loaded, the reaction was completed within 1.5 hours, and the consistence in absorbance was represented with elapsed time up to 8 hours.

3.3 Interference studies

Studieds were carried out to determine whether other cations interfere with the Fe(II) and Cr(VI) analysis. The absorption spectra of the Fe(II)-1,10-phenanthroline (phen) complex and Cr(VI)-diphenylcarbazide (DPC) complex have maximum absorbance at 510nm and 540nm, respectively. Ten species of 0.1mM interference cations were added to a distilled water, and the absorbance was compared to that for a solution containing only 0.1mM Fe(II) or 0.1mM Cr(VI). The results of these studied are presented in Table 1. The relative absorbance of interference cations relative to that of Fe(II)-phen complex shows the relative absorbance range from ND to 3%, and in case of Cr(VI)-DPC complex, the relative absorbance range from ND to 1%. These mean that the selective determination for Fe(II) and
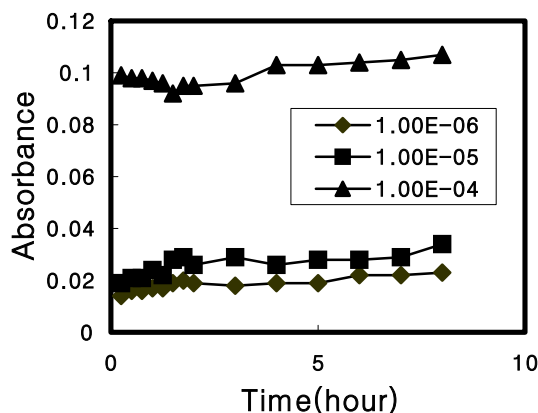

Figure 1: Variation of absorbance for Fe(II)-1,10-phenanthroline complex on sol-gel chemical sensor with loading time.

Table 1: Comparison of relative absorbance

for Fe(II) and Cr(VI) complex relative to interference cations

Interference Cations	Fe(II)-phen*	Cr(VI)-DPC**
Al^{3+}	0.06	0.089
Cd^{2+}	0.24	0.049
Co^{2+}	1.32	0.416
Cu^{2+}	0.32	ND
Fe^{2+}	100	ND
Fe^{3+}	2.34	1.196
Hg^{2+}	2.83	ND
Cr^{6+}	0.24	100
Mn^{2+}	0.14	ND
Pb^{2+}	ND	0.048
Zn^{2+}	0.37	0.059

* phen: 1,10-phenanthroline
**DPC: diphenylcarbazide

Cr(VI) by chemical sensor array based on sol-gel glass makes possible.

3.3 Determination of Fe(II) and Cr(VI)

Two heavy metals of Fe(II) and Cr(VI) were investigated by the optimized chemical sensor array based on sol-gel glass. 100µL of environmental and laboratory samples spiked with heavy metals were used to evaluate the application of the chemical sensor array to real samples. The chemical sensor exhibited high specificity in identifying multiple analytes. No obvious cross-interference was obtained when a 96 Well plate sensor array was used for simultaneous analysis of multiple samples in the presence of multiple analytes. The snesor array showed high reproducibility and relative standard deviation of 5%(n=10) was obtained. As shown in Figure 2, a linear line with respect to Fe(II) concentration was obtained. Regression equation of calibration for Fe(II) is as follows:

Absorbance = 0.0113[C] + 0.001 (R^2 = 0.9997)

Detection limit of 0.5µM for Fe(II) by Well plate reader and 10µM for Fe(II) by naked eyes was obtained. The optimal pH for CrIVI)-DPC complex is between pH 1 and 3 as shown in Figure 3. As shown in Figure 4, a linear line with
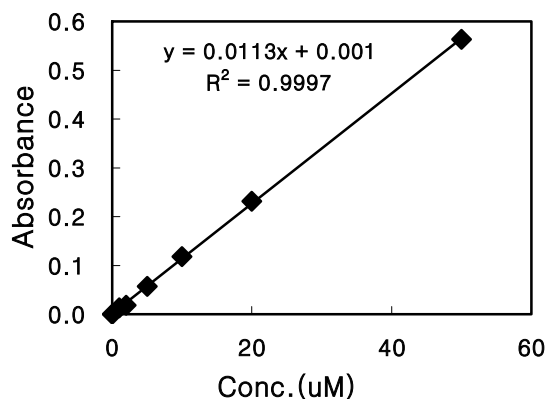

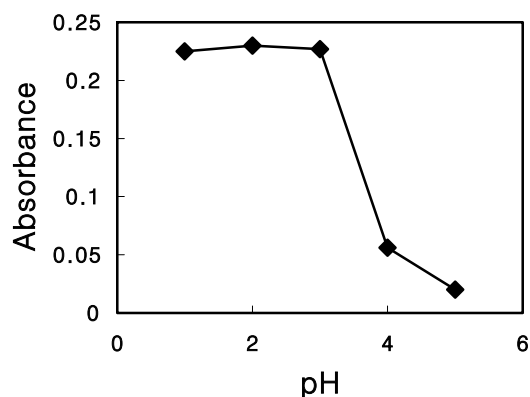Figure 2: Calibration curve for Fe(II)-1,10-phenanthroline complex on sol-gel chemical sensor..

Figure 3: Variation of absorbance for Cr(VI)-diphenylcarbazide complex on sol-gel chemical sensor with reaction pH.
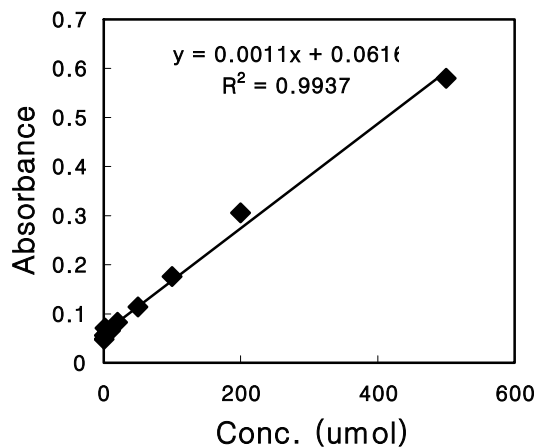

Figure 4. Calibration curve for Cr(VI)-diphenyl carbazide on sol-gel chemical sensor.

respect to Cr(VI) complex was obtained. Regression equation of calibration for Cr(VI) is as follows:

Absorbance = 0.0011[C] + 0.06 (R^2 = 0.9937)

Detection limit of 0.5µM for Cr(VI) by Well plate reader and 5µM for Cr(VI) by naked eyes was obtained.

ACKNOWLEGMENT

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