

CHARACTERIZATION OF SOL-GEL FILM FOR DISSOLVED AMMONIA SENSING¹⁾

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Abstract Optical sensing films using organically modified silicates (omosils) as a matrix for the determination of ammonia in water based on immobilized a fluorescent indicator aminofluorescein (AF) have been investigated. The sensing film was stability for 6 months. The detection limit of ammonia for different kind of homosils precursors ranges from 0.01 to 0.5 $\mu\text{g}\cdot\text{ml}^{-1}$ (S/N 2). The response time was less than 10 min.

Keywords ammonia, homosils, seawater, aminofluorescein

1 Introduction

The development of reliable, reversible, inexpensive devices for the detection of ammonia both in the gas phase and dissolved in liquids is currently an active area of research. Fiber optic ammonia sensors have been developed for measuring low concentrations of ammonia in aqueous solutions^[1-3]. Recently, methods with indicator immobilization technique are of large interest for fiber optic probes. Silicones^[4], Teflon^[5] and plasticized poly(vinyl chloride)^[2] are considered to be good polymer materials to immobilize an ammonia indicator owing to their high permeability for ammonia and their impermeability to ions. With the development of sol-gel science and technology, one of the attractive features of the sol-gel process is that it makes the preparation of numerous types of new organic-inorganic hybrid materials possible under the mild conditions^[6-8].

Organically modified silicates (omosils) are kinds of such materials in which organic fragments are built into silicon-oxide networks. A typical process of preparing such homosils is by cohydrolyzing from a mixture of a tetraalkoxysilane and an alkyl-substituted silicon alkoxides. Owing to the nonhydrolyzing alkyl groups structurally acting as a network modifier that terminates the silicate networks, many desired properties have been achieved by these new hybrids for a range of applications. The apparent change of brittleness may be one of the most important advantages of homosils, which makes them more suitable as matrices for chemical sensing.

This study attempts to apply a covalent binding between aminofluorescein (AF) and (glycidyl-oxypropyl)trimethoxysilane (GLYMO) to homosil based ammonia sensor materials that were prepared by varying the ration of TMOS and organically modified sol-gel precursor, methyltrimethoxysilane (Me-TriMOS), phenyltrimethoxy-silane (Ph-TriMOS), dimethyldimethoxysilane (DiMe-DiMOS),

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diphenyldimethoxysilan (Diph-DiMOS). The resulting materials were tested for their response to pH and the dissolved ammonia of seawater samples.

2 Experimental

2.1 Chemical and standard solution

Methyltrimethoxysilane (TMOS), phenyltrimethoxysilane (Ph-TriMOS), dimethyldimethoxysilane (DiMe-DiMOS), diphenyldimethoxysilane (Diph-DiMOS), (glycidyoxypropyl)-trimethoxysilane (GLYMO) and aminofluorescein (AF) were obtained from Fluka (Buchs, Switzerland). All other chemicals were of guaranteed grade. Twice-distilled deionized water was used throughout.

The stock standard ammonia solution was prepared by dissolving ammonium chloride in $0.1 \text{ mol} \cdot \text{l}^{-1}$ sodium phosphate buffer of pH 8.0. The concentration of free ammonia was calculated by use of the Henderson-Hasselbach equation, which at pH 8.0 and 25°C is: $[\text{NH}_4\text{Cl}] = [\text{NH}_3] \{1 + 10^{(\text{pH} - \text{pK}_a)}\} / 10^{(\text{pH} - \text{pK}_a)}$

2.2 Apparatus

For fluorescence spectra and measurements, a Hitachi F-4500 spectrofluorometer was used. The sensing film was placed on the middle side of the detection cell, light from the Xenon source passed through the excitation monochromator ($\lambda_{\text{excit}} = 498\text{nm}$), and was directed onto the sensing layer at an angle of typically 45° . The fluorescence intensity was measured in synchronous fluorimetry ($\Delta\lambda = 25 \text{ nm}$) form by using a photomultiplier. The experimental results were processed by a PC.

3 Results and discussion

3.1 Fluorescence study of AF in various ormosils

Constant addition of AF was mixed into different ormosils, prepared by varying the ratio of TMOS and organosilicon precursor. The excitation and emission spectra of AF doped ormosils films prepared during this study show the peaks centered at 485nm and 505nm, respectively. Before measurements, the sensing films were conditioned by storing them in distilled water for 24h to obtain a stable baseline. The ammonia and pH responses of AF sensing film were found to depend on the ratio of TMOS and the different organosilicon precursors in ormosil. The fluorescent responses of ammonia were enhanced, but a significant decrease in occurred pH with the increase of organosilicon precursor addition since the polarity of organosilicon precursor based ormosil is decreased with the increasing of organosilicon precursor addition. Obviously, a more hydrophobic material can be obtained on addition of a higher concentration of organosilicon precursor, which causes a higher response to ammonia and a lower response to pH.

The experimental results summarized in Table 1 shows that ormosils film with molar ratios as TMOS : Me-TriMOS (1 : 3); TMOS : Ph-TriMOS (1 : 1.5); TMOS : DiMe-DiMOS (1 : 1.1) or TMOS : DiPh-DiMOS (1 : 1) displays the most sensitive fluorescent response to AF. The polarity decrease with the size increase of the substituent for all ratios by the comparison of Me-TriMOS, Ph-TriMe and DiMe-DiMOS, DiPh-DiMOS, and the difference in R- concentration affects the sensitivity of the or-

omosils sensing film on ammonia for their different ratio to reach the maximum response. Diphenyl substituent omosils introduce the most obvious polarity decrease. The sensing film exhibits an excellent linear response to dissolved ammonia at room temperature.

The calibration curve for S₂₋₁, S₂₋₂, S₂₋₃ and S₂₋₄ sensing film was linear for ammonia concentration from 0.1 to 20 $\mu\text{g}\cdot\text{ml}^{-1}$, 1.0 to 20 $\mu\text{g}\cdot\text{ml}^{-1}$, 0.5 to 80 $\mu\text{g}\cdot\text{ml}^{-1}$, and 0.5 to 20 $\mu\text{g}\cdot\text{ml}^{-1}$, respectively. S₂₋₁ sensing film gives the lowest detection limit, but contributes the narrowest linear range. The reproducibility of the sensing film was determined by measurement cycles between ammonia concentration from 0 to 10 $\mu\text{g}\cdot\text{ml}^{-1}$, and the reproducibility is found to be 3.5%, 4.3%, 3.2% and 3.8% for S₂₋₁ to S₂₋₄ film, respectively. The response time required to achieve 95% of the full fluorescent response is about 2.0min, 5.6min, 4.0min and 10min when going from distilled water to 5 $\mu\text{g}\cdot\text{ml}^{-1}$ ammonia solution and the time needed for returning to the sensing line is all 10min for the films.

Table 1 The maximal responses on NH₃ of different omosils sensing films

Omosils film	Molar ratio (Organosilicon:TMOS)				IOD ($\mu\text{g}\cdot\text{ml}^{-1}$)	Linear range ($\mu\text{g}\cdot\text{ml}^{-1}$)
	Me-TriMOS	Pr-TriMOS	DiMe-DMOS	DiPh-DMOS		
S ₂₋₁	3:1				0.01	0.1-10
S ₂₋₂		3:2			0.8	1.0-20
S ₂₋₃			6:5		0.5	0.5-80
S ₂₋₄				1:1	0.5	0.5-20

3.2 Stability

The stability of the sensing films was found to depend on GLYMO addition. Steady leaching of AF out of the sol-gel sensing film was observed over 7 days of continuous operation in water. GLYMO was selected as an immobilization sol-gel reagent because it can be coupled rather easily to the amino-group of AF. The covalent immobilization sensing film provided a long-term mechanical and chemical stability because covalently bound indicators are hardly washed out. Sol-gel precursors with covalently immobilized AF were prepared by mixing of AF and GLYMO, and leaving it for 12h at room temperature. No leaching was found for sensing films.

The response to ammonia remained the same over a period of 6 months. The initial fluorescence intensity of films which were kept under dry condition decreased about 15% compared with films stored in distilled water, but the response to ammonia remained the same over a period of 6 months. As reason for this, it can be considered that a more dense structure of the omosil network resulted in the absence of water due to an incomplete hydrolysis on these layers.

4 Conclusion

Organically modified silicate materials provide a convenient host matrix for the immobilization of AF for ammonia sensing application. The presented work describes the behaviors of fluorescent re-

sponse between AF and ammonia in ormosils film, and the detection limits, response times and stability of the different organosilicon precursor based ormosil sensing films were studied.

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氨溶胶-凝胶传感膜的特性

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