

## Investigation of dye-doped sol–gels for ammonia gas sensing

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### Abstract

Sol–gel films doped with fluorescein (FL) and phenol red (PR) dyes were evaluated for their responses to ammonia gas. In a steady state, the sensors respond to the gas-phase ammonia evolved from ammonium hydroxide solutions in the range of  $5 \times 10^{-6}$  to 0.05 M for FL-doped gels, and  $10^{-4}$  to 1 M for PR-doped gels. The sensors have high selectivity for ammonia against larger amines and moderate selectivity against methyl and ethylamines. The FL-gel exhibits rapid and reproducible response to dry  $\text{NH}_3$  gas samples of 9–50 ppm, while PR-gel is insensitive to ammonia in this low concentration range. The life-times of the sensors are over a year.

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### 1. Introduction

Optical sensors using sol–gels have attracted great attention to researchers because of their optical transparency, ruggedness, ease of fabrication and most of all, the possibility to be used directly for gas sensing in micro- and remote-samples [1,2]. Many pH dyes have been entrapped in sol–gels for the sensing of pH and acid–base gases including  $\text{CO}_2$  and  $\text{NH}_3$  [3–14]. In general, dye leaching was a major problem for pH sensors based on dyes entrapped in sol–gel.

In our laboratory, we have found a sol–gel process for doping a high concentration of phenol red. The resulted sol–gel responds to proton concentrations in the pH range 6–12 [15], has a very long life-time, and has high reproducibility and a fast response. The gel also showed high sensitivity and fast response to moisturized hydrochloric acid gas [16]. Further experiments showed that this phenol red-doped gel responded very rapidly to ammonia gas. Thus we have processed sol–gels doped with lower  $\text{p}K_a$  dyes, to design high sensitivity and stable sol–gels for the sensing of ammonia gas. Sol–gels doped with fluorescein have good stability in the solution phase and are very stable in gas phase. With the high molar absorptivity and lower  $\text{p}K_a$  value of fluorescein,

the sensor showed much higher absorbance signal changes and a lower detection limit with a rapid response, compared to previously reported sensors based on polymer membranes [17–20] and other sol–gel sensors using different processing techniques [11–14,20].

Ammonia is a volatile, basic, compound and dissolves readily in water. It is produced in nature by a variety of organisms and by human industrial, agricultural, and social activities. The commercial product is an aqueous solution with about 33 wt% ammonia at 20 °C, household ammonia ranges in concentration from 5 to 10 wt% ammonia. Although ammonia contributes significantly to the nutritional needs of plants and biological systems, the gas itself is caustic and can cause serious health damage [21,22]. Occupational safety and health administration (OSHA) has set a 15 min exposure limit for gaseous ammonia of 35 ppm by volume in the environmental air and an 8 h exposure limit of 25 ppm by volume. Exposure to very high concentrations of gaseous ammonia can result in lung damage and death [22]. Thus many efforts have been put forth geared towards awareness, the proper control, detection and quantification of ammonia in the range of 100–0.1 ppm levels. In this paper, we describe two dyes-doped sol–gels that respond to ammonia gas in a wide range of concentration levels in wet and dry gas samples. The response is based on the direct acid–base reaction between the dyes in the sol–gels and the ammonia gas diffused into the matrix.

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## 2. Experimental

### 2.1. Reagents

Fluorescein, phenol red, tetraethoxysilane (TEOS), ethanol (99.9%), ammonia and amine hydrogen chloride salts were obtained from Aldrich. Phenyltriethoxysilane (Ph-triEOS) was purchased from Gelest, Inc. All the other chemicals were commercially available products. Standard solutions and buffers were prepared with de-ionized water. Certified NH<sub>3</sub> gas in nitrogen samples were from Messer MG Industries (Morrisville, PA).

### 2.2. Preparation of sol–gel coated slides

The FL-sols were prepared by mixing 10.0 mg fluorescein, 2.00 mL of tetraethoxysilane (TEOS), 25 μL of phenyltriethoxysilane (Ph-triEOS), 0.80 mL of 0.1 M hydrochloric acid and 2.50 mL of ethanol. The PR-sol was prepared by mixing 4.00 mL of TEOS, 200 μL of Ph-triEOS, 1.60 mL of 0.1 M of HCl, and 20.0 mg of PR, 5.00 mL of ethanol (99.9%, v/v) as a co-solvent. The mixtures were stirred at room temperature for 20 min. Two hundred microliters of the sol was placed on a pre-cleaned microscopic slide (7.5 cm × 2.5 cm × 1 mm) and then spin cast at 500–3000 rpm for 30 s. The resulting single side coated sol–gel glasses were dried and stored at room temperature. Measurements were made at least 2 weeks after the sol–gels had been made to ensure stable gel composition. Smaller sol–gel glass slides were cut from the coated glasses in order to be placed into the standard cuvette (0.9 cm × 2.5 cm) or in a flow cell (1.2 cm × 4 cm). The thickness of the sol–gel glass films was approximately 1 μm when measured by scanning electron microscopy.

### 2.3. Solution preparations

One molar NH<sub>4</sub>Cl and amine hydrogen chloride solutions were prepared from the corresponding salts and were used to prepare all the other solutions by serial dilution with de-ionized water. The ranges of the serial dilutions were 10<sup>-1</sup> to 10<sup>-5</sup> M.

The testing solutions were 1:1 mixtures of the above salts solution and 2 M NaOH. In the steady-state mode the volume of base (NaOH) was fixed at 50 μL. In the flow mode, 10 mL of base was used to generate a long-term flow of the gases.

### 2.4. Optical cell and sampling

In the steady-state measurement, the sol–gel membrane was secured to the wall of a standard polyethylene cuvette with the sample (Fig. 1). Fifty microliters of the ammonium chloride (NH<sub>4</sub>Cl) and 50 μL sodium hydroxide (NaOH) were added into the cuvette carefully using a micropipette not to disturb the sensor. An empty cuvette with an uncoated glass slide was used as a reference for a double beam UV–vis spectrophotometer.

When using the flow mode, a slide was fixed in a flow cell with a sol–gel coating as the inner wall of the sample cell. The ammonia gas was introduced from the inlet gas tube, passed the sol–gel membrane, then exited to the waste trap (1 M HCl solution). The

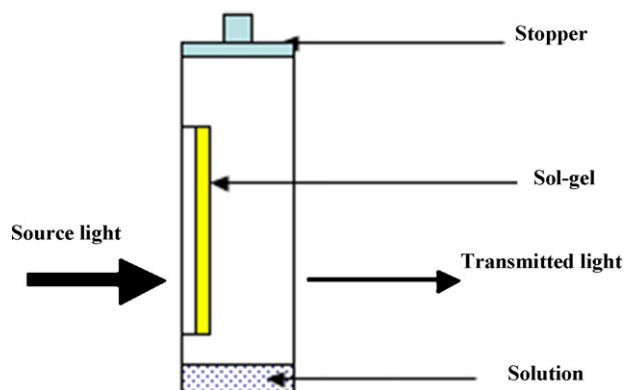


Fig. 1. Schematic of the measuring cell for steady-state response to NH<sub>3</sub> gas over the NH<sub>4</sub>Cl/NaOH solution mixture with the sol–gel coated glass slides fixed on the wall of a standard cuvette.

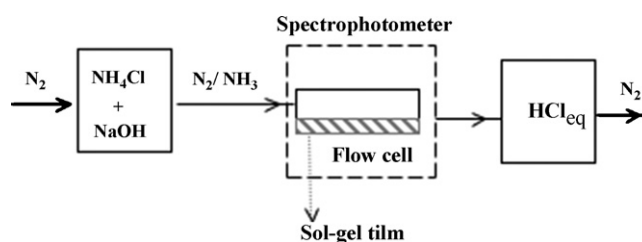


Fig. 2. Schematic of the device for the sol–gel coated glass slide response to NH<sub>3</sub> gas purged out from an NH<sub>4</sub>Cl/NaOH solution with N<sub>2</sub> gas.

wet ammonia gas was produced from 10 mL ammonia salts and 10 mL NaOH, and purged with N<sub>2</sub> gas (Fig. 2). Dry ammonia gas was supplied directly from the compressed NH<sub>3</sub>/N<sub>2</sub> gas mixture.

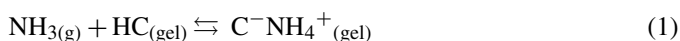
### 2.5. Optical measurements

Absorbance measurements were recorded on a UV–vis double beam (DU-2, Shimadzu) spectrophotometer. All quantitative measurements were made at 490 nm for FL-gel and 560 nm for PR-gel. The spectrophotometer was zeroed at 700 nm with the sol–gel coated glass slides in air. The absorbance was taken 2 min after the sample was introduced. The slides were used at room temperature dry and at humidity of 60–70%. All measurements and pre-calibration operations were carried out at room temperature (~23 °C).

## 3. Results and discussion

### 3.1. Response principle

Fluorescein and phenol red are pH-sensitive dyes; in solution and in the sol–gel, the dyes deprotonate from pH 5 to 10 and 6 to 10, respectively. The colors of the sol–gels change from yellow to pink. When the gels were exposed to ammonia gas in air, they rapidly changed color from yellow to pink. The sol–gel membrane response to ammonia gas can be described using the equations below:



Here HC is the protonated form of the dye, and  $C^-$  is the deprotonated form. The reaction equilibrium constant depends on the  $pK_a$  value of the dye; a higher  $K_a$  value results in a larger degree of deprotonation of the dye:

$$K_{eq} = \frac{[C^-][NH_4^+]}{[NH_3][HC]} = \frac{K_{aInd}}{K_{aNH_4^+}} \quad (2)$$

The sol-gel absorbance ( $A$ ) would be dependent on the dye concentration and the position of the deprotonation equilibrium. Higher ammonia concentration would result in a higher degree of deprotonation of the dye, and a greater change of the absorbance. By using relative absorbance  $\alpha$  [23] to represent the fraction of the deprotonated form ( $[C^-]$ ) in the total dye concentration ( $C_T$ ) in the  $\alpha$  can be related to the absorbance value at a given wavelength as follows

$$\alpha = \frac{[C^-]}{C_T} = \left( \frac{A - A_0}{A_1 - A_0} \right) \quad (3)$$

where  $A_0$  and  $A_1$  correspond to the absorbance of the completely deprotonated and protonated dye, respectively. The  $\alpha$  value will be dependent only on the  $NH_3$  gas concentration in the samples, but not on the sol-gel thickness or dye concentration in the sol-gel.

### 3.2. Steady-state ammonia response

As shown in Fig. 1, in the steady-state measurement, the sol-gel glass was secured onto the wall of the standard cuvette, 0.5 cm above the bottom. Then a volume of 50  $\mu$ L of 2 M NaOH was carefully introduced into the cuvette, followed by addition of a volume of 50  $\mu$ L of  $NH_4Cl$ , and their reaction liberates  $NH_3$  gas. When  $NH_4Cl$  concentration increases, the color of the slides gradually change to pink, and the absorbance around 450–520 nm increases (see Fig. 3 for FL-gel). The absorbance at 490 nm versus log of the logarithmic concentration of  $NH_4Cl$  is depicted in the response curve in Fig. 4. For a 50  $\mu$ L  $10^{-5}$  M solution of  $NH_4Cl$ , if all the  $NH_3$  produced

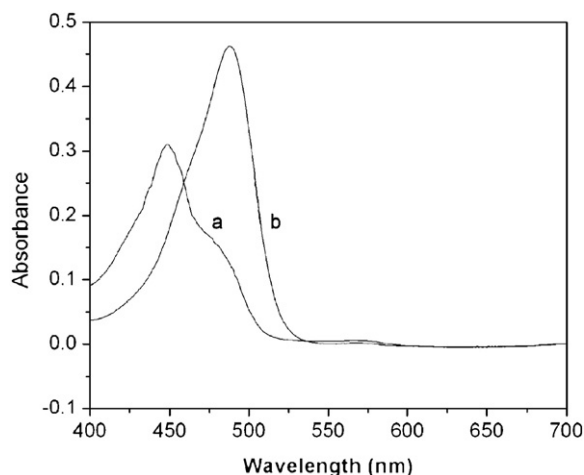


Fig. 3. Absorption spectra of the fluorescein-doped sol-gel in (a) air and (b) over a 50  $\mu$ L 0.05 M  $NH_4Cl$ /50  $\mu$ L 2 M NaOH solution.

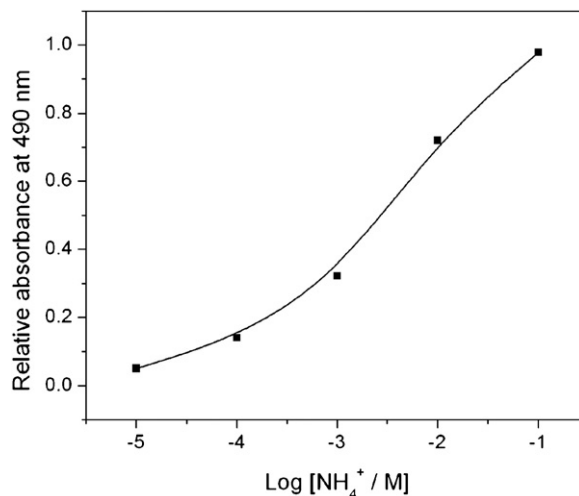


Fig. 4. Absorbance at 490 nm of FL-gel vs. logarithmic  $NH_4^+$  concentration with 1 M NaOH as background in steady-state response. Solution volume:  $NH_4Cl$  50  $\mu$ L, 2 M NaOH 50  $\mu$ L.

by adding 2 M NaOH is liberated into the air in the cuvette ( $V=4$  mL in volume), the ammonia gas concentration ( $C_{NH_3}$ ) in the overhead sample is calculated to be about 3 ppm (using  $P_{NH_3} = nRT/V$  and  $C_{NH_3} = P_{NH_3}/P_{air}$ ). Considering the solubility of ammonia in the solution is very high, the  $NH_3$  vapor in the gas should be less than 3 ppm. Thus the detection limit of the sol-gel towards ammonia gas should be on the low ppm level.

The absorption spectra of the PR-gel (not shown) in ammonia gas resemble the deprotonation of the dye in high pH buffer solutions as reported earlier [15]. However, due to the higher  $pK_a$  of phenol red, the PR-gel response to ammonia is much less sensitive than the FL-doped gel, as predicted from Eqs. (1) and (2). The response curve for PR-gel under the same conditions of sampling for FL-gel is shown in Fig. 5. The response range is from  $10^{-4}$  M to 1 M  $NH_4OH$ . This sensor can be used for higher

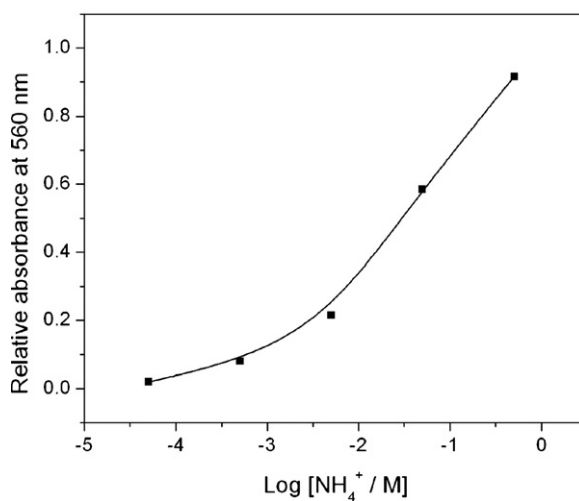


Fig. 5. Absorbance at 560 nm of PR-gel vs. logarithmic  $NH_4^+$  concentration with 1 M NaOH as background in steady-state response. Solution volume:  $NH_4Cl$  50  $\mu$ L, 2 M NaOH 50  $\mu$ L.

Table 1  
Response time ( $t_{95\%}$ ) of FL-gel to headspace gases over mixed solutions of various concentrations of  $\text{NH}_4\text{Cl}$  and 2 M NaOH (volume ratio of 1:1)

Concentration (M)	Time (s)
0.00001	100
0.0001	95
0.001	82
0.01	63
0.1	50

ammonia or ammonium salt concentration determinations. The maximum absorbance change is less than half of the change of FL-based sensor, partly due to the lower molar absorptivity of phenol red.

The response speed of the sensors depends on the concentration of  $\text{NH}_4\text{OH}$  in the test solutions. The response is slower with low concentration and faster with higher concentration, as shown in Table 1.

The recovery times of the sol-gel membranes were relatively slow when only exposed to air (about 5 min). The fastest way to reset the membranes is to immerse the membrane in an acid solution, pH 4, followed by washing with de-ionized water and drying thoroughly.

### 3.3. Response to amines

Using the same method to prepare and test the sol-gels, the responses of the sensors to various amines were evaluated by introducing 50  $\mu\text{L}$  0.1 M amine chloride solutions into the cuvette and subsequently adding 50  $\mu\text{L}$  of 2 M NaOH. The response of these sol-gel sensors in relative absorbance units to the gases of these solutions are shown in Table 2. As can be seen in the table, the sol-gels did not show significant responses towards most alkylamines except for the two relatively small methylamine and ethylamine. It is presumed that the small size of the methyl and ethylamines allows them to penetrate easily into the sol-gel pores to interact with the dyes. The weak responses to diethyl amine and triethylamine may be because these molecules are either too bulky or too hydrophobic to diffuse into the sol-gel pores. The small response to pyridine may be due to its low  $\text{p}K_{\text{a}}$  value; the weak base cannot deprotonate the dyes.

Table 2  
Relative absorbance of the sensors when exposed to headspace gas over a mixed solution of 0.1 M ammonia or amine hydrochloride salts and 2 M NaOH (volume ratio of 1:1)

Base	FL-gel $\alpha$ at 490 nm	PR-gel $\alpha$ at 560 nm
Ammonia	0.92	0.7
Methylamine	0.32	0.25
Ethylamine	0.25	0.20
Propylamine	0.12	0
Pyridine	0.085	0
Diethylamine	0.057	0
Triethylamine	0.009	0

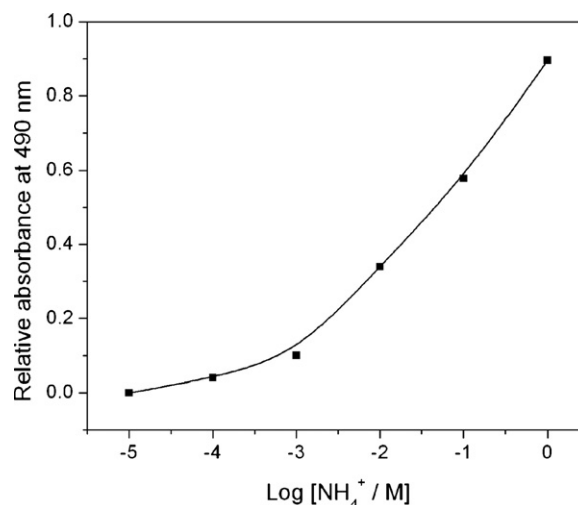


Fig. 6. Response curve of the FL-gel coated glass slide in a flow cell to  $\text{NH}_3$  gas purged from various  $\text{NH}_4\text{Cl}$  solutions in 1 M NaOH background with nitrogen gas.  $\text{N}_2$  flow rate: 90 mL/min.

### 3.4. Flow-through cell response to $\text{NH}_3$ from solutions purged by $\text{N}_2$ gas

To evaluate the response behavior and applicability of the sol-gel-based optical sensor to  $\text{NH}_3$  gas in a flow system, experiments were performed using a device as sketched in Fig. 2. The sol-gel coated glass slide was placed in a flow cell, and gases generated by bubbling  $\text{N}_2$  gas (90 mL/min) through various ammonium chloride solutions (10 mL) mixed with 2 M NaOH (10 mL). The response to ammonia gas in the flow structure is inferior to the steady-state response. When the same  $\text{NH}_4\text{Cl}$  concentration was mixed with NaOH, the same concentration of  $\text{NH}_3$  gas was expected to be produced. However, the response in the flow mode is about ten times less sensitive than the steady-state mode (see Figs. 4 and 6). Here, the  $\text{NH}_3$  gas is diluted with a fast flow of  $\text{N}_2$  gas, thus ammonia in purging gas has a much lower concentration than in the steady state even at the similar concentration.

### 3.5. Flow-through cell response to dry $\text{NH}_3/\text{N}_2$ gas mixture

In order to find the exact detection limit towards  $\text{NH}_3$  gas, certified gas samples from Messer, Inc., PA, were used. The  $\text{NH}_3$  concentrations were 9.7 and 46.6 ppm diluted in  $\text{N}_2$ . Real-time responses of the FL-gel sensor to the two gases mixtures are shown in Fig. 7. The response times are about 1 min.  $\text{NH}_3$  gas of 9.7 ppm resulted in 37% of the relative absorbance change of the FL-gel, while  $\text{NH}_3$  gas of 46.6 ppm gas gave a 77% of the relative absorbance change. This suggests that the FL-gel can respond to ammonia in the range of 0–100 ppm. Unlike the response to the HCl gas of a PR-doped gel [16], the ammonia response of the sol-gel film does not require the presence of moisture.

The PR-doped gel is less sensitive, and no observable absorbance change was recorded when exposed to the above mentioned ammonia gas samples.

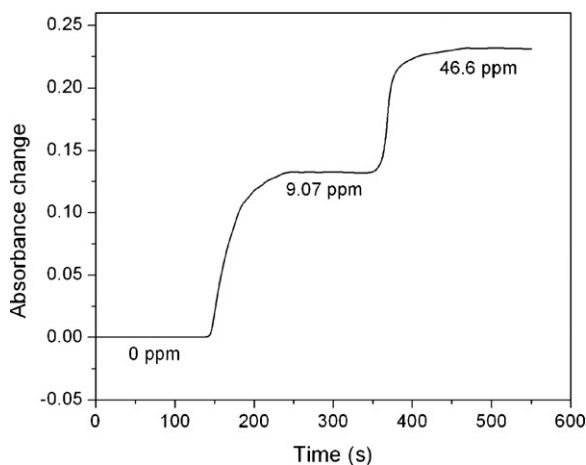


Fig. 7. Real-time response of FL-gel at 490 nm to two certified  $\text{NH}_3$  gas samples in  $\text{N}_2$ . Flow rate: 90 mL/min.

#### 4. Conclusion

A sensitive and selective ammonia sensor has been developed using fluorescein dye doped in sol–gels. The sensor exhibits fast response and a low detection limit (ppm level) to dry or moisturized ammonia samples. Thus the FL-gel has high potential for practical monitoring of low levels of ammonia gas.

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