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Development of Bromocresol Purple Immobilized Optical Sensor for the Determination of Dissolved Ammonia

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Abstract

In this work a fluorescent dye – bromocresol purple was immobilized to the xerogel prepared by the sol-gel technology. The effect of the solvent nature was explored to control the sensor properties and performance. Prepared final materials have shown stable and reproducible signals in a wide range of dissolved ammonia concentrations. Using i-butylalcohol leads to improved sensor properties because of the optimal match with the indicator dye with the immobilized environment. Developed optical ammonia sensors were investigated at different temperatures and their performance was also assessed.

Keywords: indicator; bromocresol purple; sol-gel; absorption; solvent; temperature

Introduction

Ammonia is one of the most abundant chemicals produced in the world. Most of the prepared ammonia is used to produce fertilizers. Moreover, ammonia is used by several industries (mining and metal manufacturing, the leather industry, etc.) [1]. As being very important chemical, ammonia is also one of the prevalent pollutants causing severe consequences [2]. The most notorious sources of ammonia "unwanted" ammonia emission come from nitrification, bacterial activity and anthropogenic (combustion of nitrogen containing compounds) [3,4].

Several methods have been exploited to control the dissolved ammonium concentration ranging from metal-oxide sensors to optical sensors. Although being highly selective, sensitive and cheap, electrochemical methods bear some drawbacks in regard to lifetime, stability and size [5,6]. Most electrochemical sensors' detection principle is based on changing the value of current on electrodes.

Optical sensors based on IR absorbance, UV-vis absorbance or fluorescence emission are being used for routine analysis for ammonia detection [7-11]. In one approach a semiconductor and fluorescence dual-mode sensor was developed using a metal-organic framework [12]. One can notice a tendency using of metal-organic frameworks for sensor construction. Recently ppb level of ammonia was reported using near-IR photoacoustic spectroscopy [13].

Among the optical methods, one of the simplest and cheapest are absorption based because of the detection scheme and preparation. Close scrutiny of papers dedicated to absorption based sensors reveals that all absorption based sensors share the similar scheme where change in color of a dye creates a signal. In order to achieve high sensitivity and good performance, choice of a dye and a substrate is imperative. Polymer or sol-gel materials have been used extensively in most cases. And sol-gel technology has been shown to be one of the most attractive methods to develop such materials.

Tuning of the sol-gel reaction can be fulfilled changing the nature of precursors, the molar ratios between the reactants, the nature of the solvent, the use of modifying agents, pH and curing temperature [14-16]. Among other parameters, the solvent nature was found one of the most strongly influencing. When used as a solvent, alcohols were found to strongly affect the photochemical and photophysical properties of the dopants [17-19].

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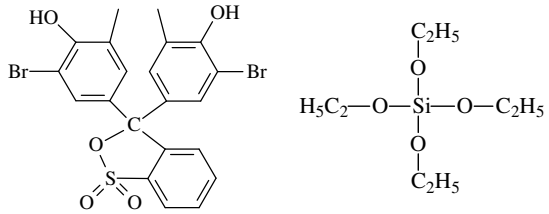
In this paper we aimed to exploit several alcohols to shape the properties of an optical sensors for dissolved ammonia in order to achieve a good sensor response and performance. By using the simple approach high sensitive optical sensor with a fast response time was developed.

Experimental

Materials and methods

Tetraethoxysilane (TEOS) was purchased from Haihang Industry Co., Ltd (PRC); ethanol (EtOH), bromocresol purple (BCP), hydrochloric acid (HCl) and nitric acid (HNO_3) were analytical grade and used without any further purification. All buffers and solutions were prepared using chemical pure grade reactants and doubly distilled water used as a solvent.



Scheme 1.Structure of BCP (*left*) and TEOS (*right*).

Standard solutions

Ammonia test solutions were prepared using 25% (mass) aqueous concentration of ammonia solution and consequently diluted to reach the desired concentration. Doubly distilled water was used to prepare all solutions throughout the experiment. In order to keep solution concentration constant, fresh test solutions were used in each experiment.

Preparation of sol-gel membranes

Sol-gel solutions were prepared to mix 4 ml of TEOS along appropriate amounts of C_2H_5OH, *i*-C_3H_7OH, 1-C_4H_9OH and *i*-C_4H_9OH for 30 minutes. The alkoxide to solvent ratio was maintained 1:4 in all experiments. 2.6 ml 0,01M HCl aqueous solution was added in order to start hydrolysis and condensation reactions. pH of the final solution was adjusted to 2. The resulting solution was mixed for 4 hours at room temperature. Then 80 µl of 0.1M BCP in C_2H_5OH solution was added and another 30 minutes was mixed. In order to study the solvent effect several sol cocktails were prepared and the content of such solutions is given in Table. 1.

Solution of sol then remained for 24 hours for aging. Microscope slides were taken and cut into 0.6×4 cm pieces. All glasses were activated in the aqueous solution of nitric acid for 1 hour and rinsed with ethanol and a copious amount of water before the flow coating process. Flow coating was performed using the pipette taking desired amounts of sol solution. After coating, glass slides were dried at 70 °C overnight. Preparation steps of samples are given in Scheme 2.

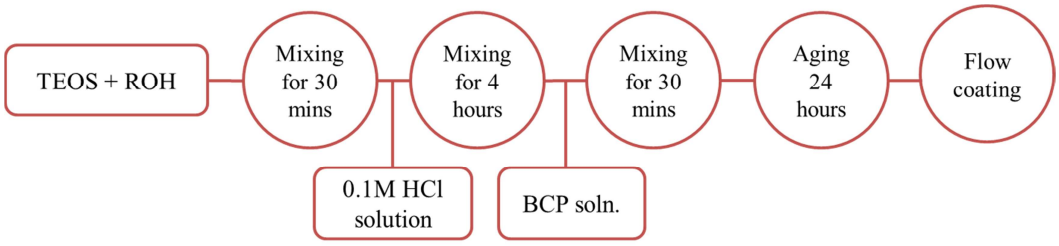
Sensor layers appeared transparent and microscopic examinations revealed no significant crack on the surface (Fig. 1).

Spectroscopic studies of prepared membranes

UV-vis spectrophotometer EMC-30PC-UV (EMC Labs Germany) was used to record the absorption spectra of the sensors. The surface of the sensor films was investigated using the light microscope Optika (Germany). Sensor membranes was rinsed in distilled water and dried before each experiment.

Results and discussion

After sensor films have been cured they possess dark yellow color because of BCP in acidic form. In order to evaluate substrate features,XRD studies were carried out. Fig. 2 shows one of the diffraction patterns of the sensor sample. This shows that all prepared films are almost amorphous structures. But there appears one small peak around 45º and during the heat treatment that peak stays constant. We also compared the XRD results sensor films prepared using other solvents excluding *i*- ButOH, and no peak was found. For this reason, we assumed that solvent also might affect the structure of the final film and formation of favorable environment for a dopant.



Scheme 2. Schematic diagram of sample preparation steps.

Table 1

Content of solutions used in this study (in molar ratios)

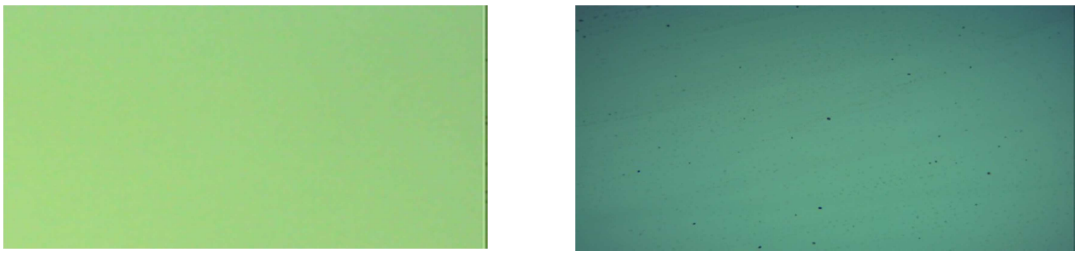
No	Alkoxide	Catalyst	C_2H_5OH	*i*-C_3H_7OH	1-C_4H_9OH	*i*-C_4H_9OH	H_2O
1	TEOS	HCl	3				4
2	TEOS	HCl	4				4
3	TEOS	HCl	5				4
4	TEOS	HCl	6				4
5	TEOS	HCl		3			4
6	TEOS	HCl		4			4
7	TEOS	HCl		5			4
8	TEOS	HCl		6			4
9	TEOS	HCl			3		4
10	TEOS	HCl			4		4
11	TEOS	HCl			5		4
12	TEOS	HCl			6		4
13	TEOS	HCl				3	4
14	TEOS	HCl				4	4
15	TEOS	HCl				5	4
16	TEOS	HCl				6	4

Dissolved ammonia detection analyses were made after one week prior the gelation process completed. Before and after the measurement's sensor samples were kept in a sealed polymer bag in order to protect them from deterioration. Upon immersing into the aqueous ammonia solution sensor films converted to violet color immediately. This shows pores of the sol-gel film perfectly fulfill to serve as a membrane for the selected indicator dye.

BCP reacts with the analyte - ammonia can be described by the following reaction:

$$HInd(s) + NH_3 \cdot H_2O\ (aq) \leftrightharpoons Ind^-\ (s) + NH_4^+\ (aq) + H_2O(l)$$

Where HInd is the acidic form of BCP and Ind^- is the deprotonated form of BCP, respectively. During the reaction the acidic form converts to the basic form and each form possesses different absorption maxima. Due to the hydrochloric acid aqueous solution was used as a catalyst during the sol-gel reaction, the final material is rich in protons. Thus



a) *b*)

Figure 1. Micrographs of undoped (*a*) and doped (*b*) films (×1000)

In order to evaluate the temperature effect, coated sensor membranes were dried at a range of different temperatures 30, 40, 50, 60, 70, 80, 90 and 100 °C. The optimal temperature was found to be 70 °C and sensors cured at this temperature showed the best performance. Below 70 °C higher content of water and alcohol molecules may interfere the strong interaction between silica the matrix and BCP dye. At higher temperatures absorption peak of BCP decreases again and it may be justified by the deterioration of inner environment of matrix. More interestingly, sensors cured up to 300 °C shown response to dissolved ammonia concentration meaning the matrix serves as a rigid protection for BCP dye.

sensor films without the heat treatment displayed only one maximum around of 430 nm. Heat treated sensor films containing BCP dye shows two absorption maxima 430 nm (strong) and 590 nm (weak) in distilled water. Presence of small amounts of dissolved ammonia causes increase in the intensity of the second peak and the first peak shows the blue shift.

Understanding of the solvent effect is more complex compared to the other parameters during the sol–gel reaction. Although the main role being to regulate the miscibility of the components present, alcohol used during the sol-gel process plays the role of a reactant through transesterification (alkoxy exchange) reactions:

$$Si(OC_2H_5)_4 + nROH \leftrightharpoons Si(OC_2H_5)_{4-n}(OR)_n + nC_2H_5OH$$

Alkoxy exchange found to be promoted in acidic environment and we kept pH of reaction media significantly low in order to study this effect. We have found out that the solvent not only changes the reaction rate, but also causes both the material property and consequently alters the photochemical properties of dopant immobilized. Being the type of the alcohol is one of the key factors, possible change in spectral properties of dye, in our case BCP come from different environment inside the prepared material.

Hydrolysis of TEOS has been found the rate determining step elsewhere [17]. When ethanol used as solvent, no significant change in reaction progress, since both alkoxide and solvent share similar groups (ethyl). Changes observed during the reaction also confirmed this deduction. Moreover, films prepared ethanol as solvent shown significantly thinner than other films.

Changing solvent to *i*-propanol caused to extended reaction time. Initially the viscosity of solution decreased. Then the viscosity gradually increased next 24 hours. Films coated after 96 hours gelation shown homogeneous surface and less cracks when investigated under microscope.

When 1-butanol was used as solvent, the phase boundary between TEOS, alcohol and water stayed up to 4 hours. Increase in catalyst concentration shown very little effect on hydrolysis time.

Films prepared using *i*-C_4H_9OH possesses interesting features. Having shorter reaction time and fast increase in viscosity are characteristic. This phenomenon may be explained partial change of alkoxy groups to butoxy groups and consequent formation of siloxane bridge. In this case films prepared between 24 to 48 hours shown improved properties. Microscopic examinations shown that surface of the thin films are homogeneous and have very few cracks. Especially membranes prepared in strong acidic conditions were superior to other membranes prepared at higher pH value.

Figure 3 displays the absorption spectra of BCP in different aqueous ammonia solutions. BCP shows an intense peak around 590 nm in the basic media. Increase in ammonia concentration also causes increase in the intensity of the peak. Calibration curve of the optical sensor for dissolved ammonia is shown in Figure 4. In the tested concentration range, a linear calibration curve was obtained.

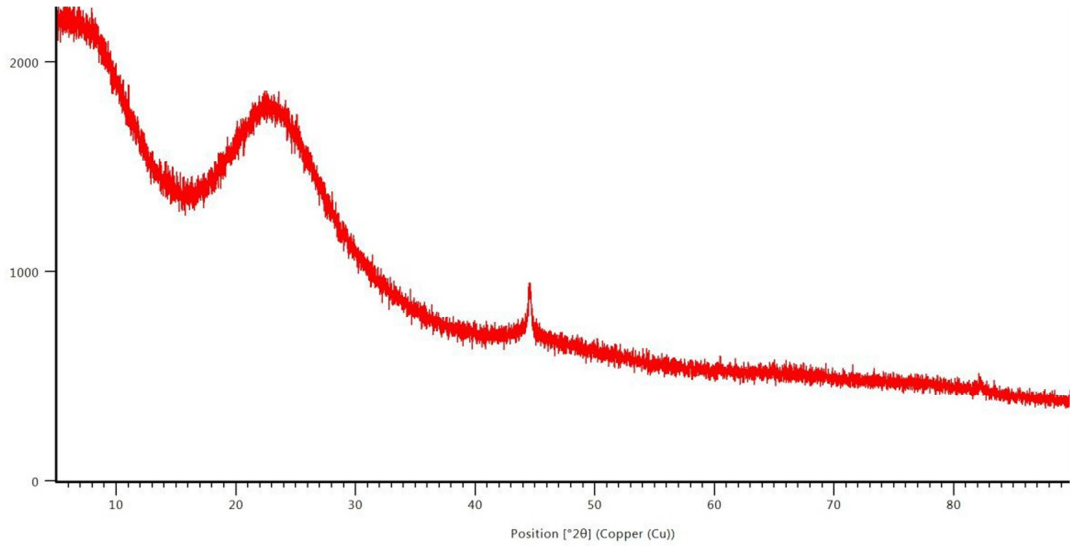


Figure 2: Powder XRD pattern of the prepared film

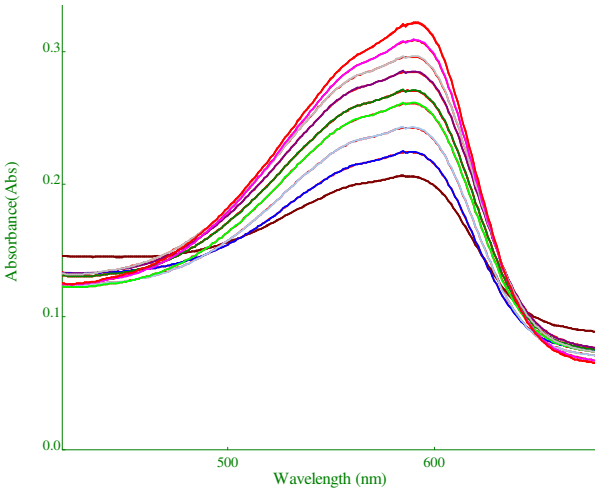


Figure 3: Absorption spectrum of BCP@TEOS sensor in different concentrations of aqueous ammonia (red – 1M, black – 0.2M). Intensity at 588 nm decreases as the concentration of ammonia decreases

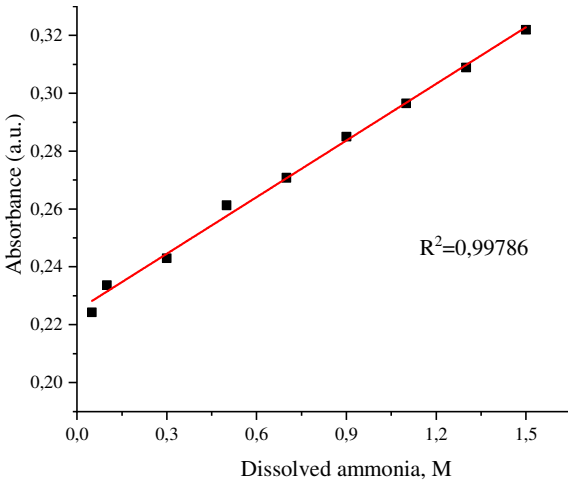


Figure 4: Calibration curve of BCP@TEOS sensors for aqueous ammonia detection.

The calibration curve of the sensor is shown in Figure 4. As can be seen from the figure, the absorbance and the concentration shows a good linear relationship in the range of 1M to 0.1M concentration. We also performed experiments with higher ammonia concentrations, but deviation was observed in the linear relationship. The possible reason may be related of saturation of the sensor film with $NH_{3(aq)}$ and regeneration of sensor films have little effect on the stable signal reproduction.

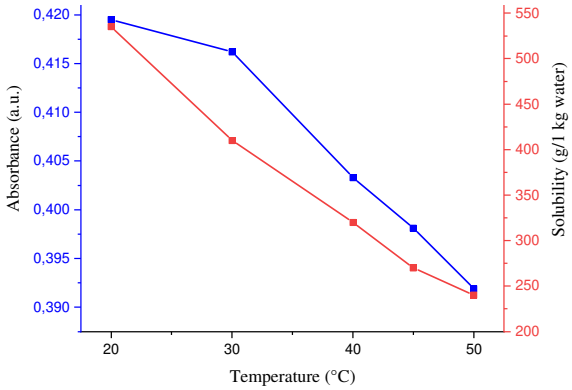


Figure 5: Sensor response of 2M dissolved ammonia at different temperatures

Elevated temperatures lead to decrease in solubility of gases in general and this trend also observes in the dissolution of ammonia in water. Figure 5 demonstrates this phenomenon. Rising the temperature causes to evaporation of ammonia molecules and we observed decline of the intensity of BCP around 590 nm. Moreover, Figure 5 shows a good relation between the sensor response and solubility of ammonia in water. Slow decrease of signal can be explained with 2M solution is still unsaturated.

Conclusions

Optical sensor for the determination of dissolved ammonia is developed using the sol-gel route. TEOS in the presence of BCP indicator and the catalyst was used to prepare thin films deposited on glass slides. The solvent nature was found to influence strongly the nature of the final films. The range of alcohols was tested to be suitable during the sol-gel reaction. The best results were obtained on optical ammonia sensors prepared using *i*-butanol as solvent which showed high UV-Vis absorbance and lowest leaching. BCP molecules were properly accommodated within silica network pores when the thin films were dried at 70 °C. Sensors showed stable response at long time intervals and reproducible signal to the concentration of dissolved ammonia.

Conflict of interest

Authors declare that they have no conflicts of interest.

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