

Impact of Bromocresol Purple in Organic and Inorganic Matrix on Optical Properties

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Abstract - Sol-gel matrix derived from from organic and inorganic moieties offer interesting features such as chemical and mechanical stability. Mixture of organic vinyltriethoxysilane (VTES) and inorganic tetraethoxysilane (TEOS) produce sol-gel matrices with improvement in density, flexibility and optical properties. Bromocresol purple and 18-crown-6-ether are added into the sol-gel mixture with 75:25 of VTES to TEOS ratio. The effect of incorporated bromocresol purple and 18-crown-6-ether to the sol-gel matrices is study using SEM, TGA, FTIR and UV-Vis. It is found that sol-gel matrices incorporated with bromocresol purple and 18-crown-6-ether improves response sensitivity and has the prospect to be developed as a new sensing materials. After a while a pH-sensitive indicator bromocresol purple (BCP) and surfactant were incorporate into the sol-gel mixture. The percentage of sodium dodecyl sulfate (SDS) and polyethylene glycol (PEG) which act as surfactant were varied to observe the effect of improving host material's nanostructure as well as the interaction between BCP and sol-gel matrices. The absorption peak of the BCP dye changed significantly in the presence of surfactant compared to pure VTES: TEOS mixture (control) in the range of 400 to 450nm.

Keywords- Sol-gel, optical sensor, bromocresol purple, ether crown.

I. INTRODUCTION

Ammonia, NH₃ is a common substance in major industrial application, specifically in production of fertilizers. However, ammonia could create potential hazards to human and ecosystems if its quantity in atmosphere is not properly controlled. Ammonia in water at trace level higher than 25 µg/l is known to be toxic to various organisms [1, 2]. Therefore, fast and real time detection of ammonia concentration are important for environmental chemistry.

Sol-gel materials known as organically modified silicates (ORMOSILs) offers interesting features such as chemical and mechanical stability, excellent sensitivity and exhibit low limit of detection when doped with colorimetric or fluorometric indicators. ORMOSILs are organic-inorganic hybrid materials in which the structure of silica network can be modified by the presence of organic groups. It is reported that combination of organic vinyltriethoxysilane (VTES) and inorganic tetraethoxysilane (TEOS) can be used to make protective, hard and crack-free coating on substrates [3, 4]. Organic part of the hybrid materials can improve adhesion between coating and polymer substrate meanwhile inorganic part can increase hardness of the coating and remain unaltered during sol-gel process, acting as network modifiers that terminate the silica network [1]. TEOS is used as precursor for sol-gel preparation since the refractive index of the porous silica film produced is less than the fibre core [5].

Bromocresol purple (BCP) has been widely used as sensing layer for ammonia detection [1, 5-9]. BCP is

characterized by refractive index higher than the waveguide core refractive index and become highly absorbing for a considered wavelength upon ammonia encountered [7]. BCP also is chemically more stable and has a good resistance to oxidation compared to indicators. It is also reported that BCP enhance interaction between ammonia molecules and the dye molecules [5]. However, BCP dye is subjected to potential leaching from the matrix that prevents stability [4, 10]. The incorporation of BCP into VTES-TEOS sol-gel may help to prevent leaching from occurring and has been proven to increase thermal stability of BCP [1].

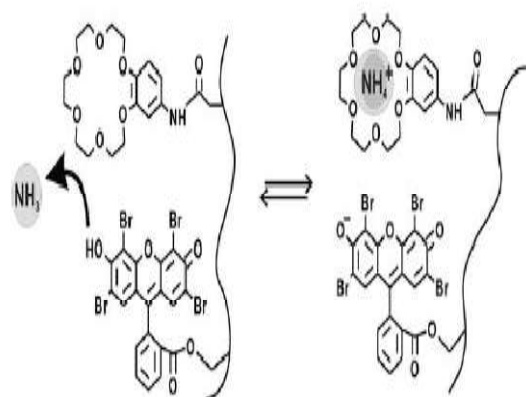


Fig. 1. 18-crown-6-ether act as cation trap for ammonia

Although BCP is a common material for ammonia detection, it is also selective towards other cations (K⁺, H⁺, etc). Thus, other cations may influence data analysis

process and this will be a critical problem especially when employed as water sensor. Adding 18-crown-6-ether (EC) into the solution helps to enhance ammonia detection. This is because EC acts as cation repellent and only attract ammonia. Ammonia is known to fit perfectly into the polar cavity of EC and form hydrogen bonds with the oxygen atoms of the ether such as shown in Figure 1 [10].

The purpose of this study is to develop organic-inorganic sol-gel materials which could be used for ammonia detection in water at $\mu\text{g/l}$ level. BCP and EC is added into the sol-gel by means of enhancing the properties of the sol-gel and increase sensitivity towards ammonia. Therefore, the characteristics of sol-gel with BCP, EC and BCP-EC addition will be analyzed respectively. Based on previous study, the ratio of VTES:TEOS is fixed at 3:1. This is because as VTES proportion increase, surface hydrophobicity also increase which effectively block H_2O molecules and only allowing ammonia ions to penetrate the porous matrices. Higher amount of VTES also reduce BCP decomposition rate, reduce brittleness and improves adhesion between the coatings and the films [1, 3]. Further study is done to observe the effect of surfactant on physical properties of sol gel film. Bromocresol Purple (BCP), an organic dye, was incorporated into VTES and TEOS precursors with different surfactant ratios of SDS and PEG. The sol-gel precursor mixtures were then drop-casted on slide glasses to form thin films and subsequently undergone heat treatment. BCP doped sol-gel matrices absorption spectral and physical properties of the matrices were analyzed.

II. METHODS AND MATERIALS

Vinyltriethoxysilane and tetraethoxysilane is mixed with 3:1 ratio and stirred for one hour to provide precursor solution for sol-gel preparation. Sol-gel solution is prepared by hydrolysis process of the precursor with ethanol as the solvent and deionized water (pH 5) as the catalyst with 1:4:2 ratios of precursor, ethanol and deionized water respectively. The precursor solution is mixed with ethanol, stirred for one hour and then deionized water is added and the solution is stirred overnight at room temperature to ensure homogeneous mixing.

After that, sol-gel solution is mixed with the dye, which is 0.5% BCP, 0.5 EC and 0.25%BCP + 0.25% EC respectively. Then the solution is mixed for one hour. The sensor film is prepared on slide glasses using spin-coating method for 30 seconds to produce even and homogeneous coating. The samples undergone heat treatment at 60°C for 24 hours.

For the next study, 0.02% of BCP was added to either SDS or PEG of variable percentages of 0.5%, 1%, 1.5%, 2% and 2.5% with respect to the total volume of the prepared sol and stirred for one hour. All mixtures produced yellowish color. Thin film was fabricated on 8 x

25 mm slide glass by dropping an average of $80\mu\text{l}$ of the mixture which then slowly moved across the glass to produce flat films. Samples were placed inside an oven for heat treatment at a temperature of 60°C for 24 hours.

III. RESULTS AND DISCUSSION

All the coating films are very transparent, uniform and have a smooth surface regardless of their compositions. The presence of BCP, EC and BCP+EC in VTES:TEOS sol-gel matrices are confirm using UV-Vis spectrometer. Based on Figure 2, the corresponding peak around 400 nm for both sol-gel matrices with 0.5%BCP and 0.25%BCP+0.25%EC represent absorption band for BCP. Although absorption band of EC is not evident in 0.5%EC, the peak represent EC is can be found in 0.25%BCP+0.25%EC which is around 600 nm.

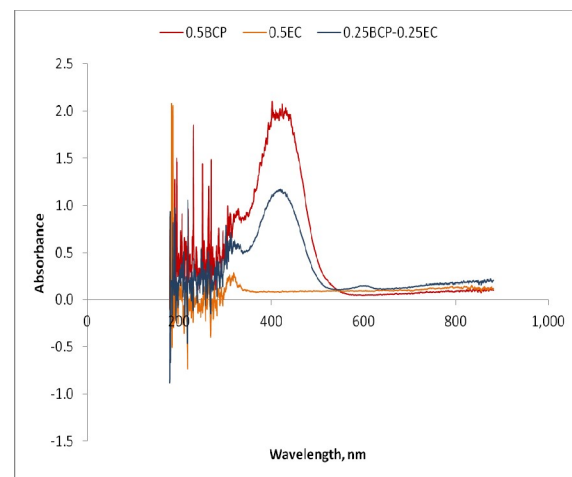


Fig. 2. Absorbance of VTES:TEOS sol-gel matrices with 0.5%BCP, 0.5%EC and 0.25%BCP+0.25%EC.

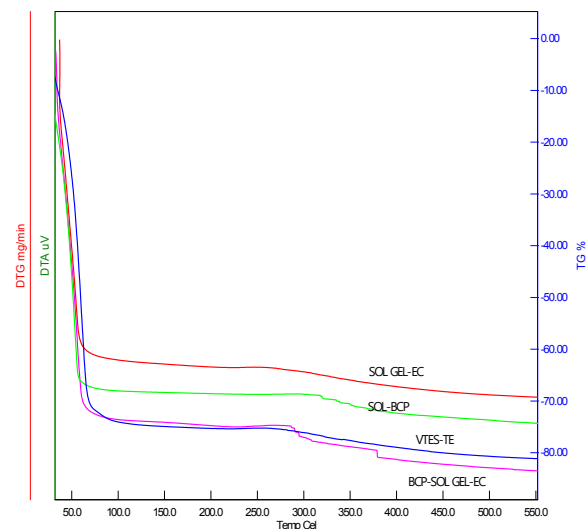


Fig. 3. TG curves of different sol-gel matrices composition with a heating rate of 5C/min.

TG curves shown in Figure 3 shows that all the sol-gel matrices experience rapid weight loss during heating up to 70°C due to evaporation of volatile products such as water and ethanol. However, it is found that VTES:TEOS sol-gel matrices has slower weight loss rate compared to sol-gel with addition of BCP, EC and BCP+EC. At around 300°C, sample of VTES:TEOS, 0.5%EC and 0.25%BCP+0.25%EC gradually experienced weight loss due to the decomposition of organic VTES. However, decomposition of VTES for sample of 0.5%BCP is delayed and only started to experienced weight loss around 320°C to 330°C. This is probably due to its thermal stability after being incorporated into VTES:TEOS sol-gel matrices [1].

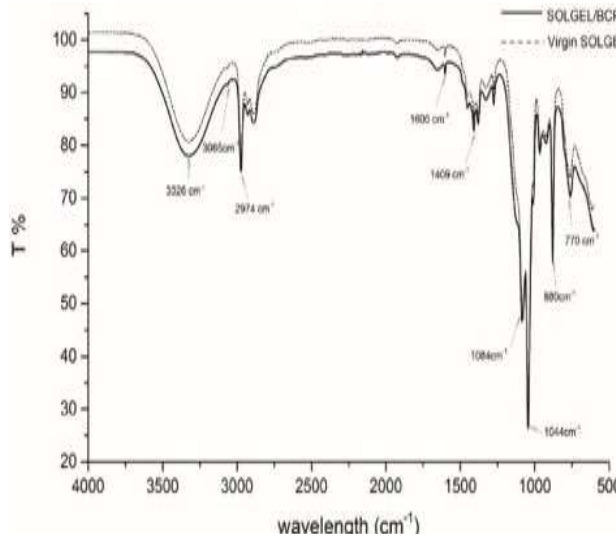


Fig. 4. FTIR spectra of immobilized BCP and virgin sol-gel.

Figure 4 shows the FTIR spectra of the immobilized BCP and the pure (control) sol-gel materials. There is no significant spectral difference between immobilized BCP and the pure sol-gel because the silica network dominates the spectra. The presence of BCP dye can be determined by the FTIR spectrum where a =C–H stretch in aromatics is observed at 3100-3000 cm⁻¹ which is typical representation of the aromatics of BCP structure. Asymmetric stretching of Si-O-Si bands are represented by transmission band around 770 cm⁻¹, 1044 cm⁻¹ and 1184 cm⁻¹ respectively. Transmission band around 880 cm⁻¹ represents Si-OH bond, Si-C bond at 1409 cm⁻¹, C=C bond at 1600 cm⁻¹ whilst 3065 cm⁻¹ belongs to C-H bond. Both C=C and C-H bonds can be influenced by the organic part of VTES. Addition of BCP influences the FTIR spectra of VTES:TEOS sol-gel materials, which shows that a reaction has occurred between the dopant and the silica network.

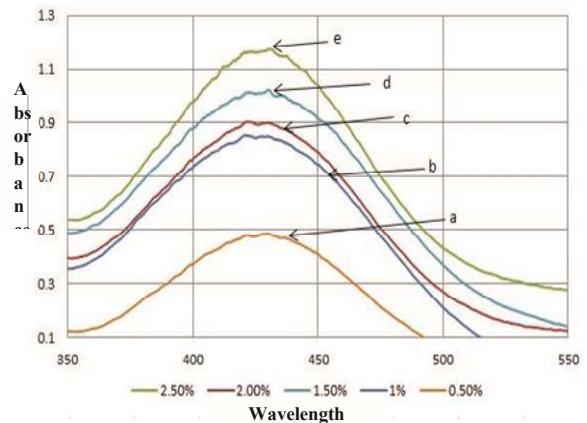


Fig. 5. Absorption spectra of immobilized BCP/PEG at different volume ratio of PEG:(a) 0.5 %, (b) 1%, (c) 1.5% (d) 2%, and (e) 2.5%.

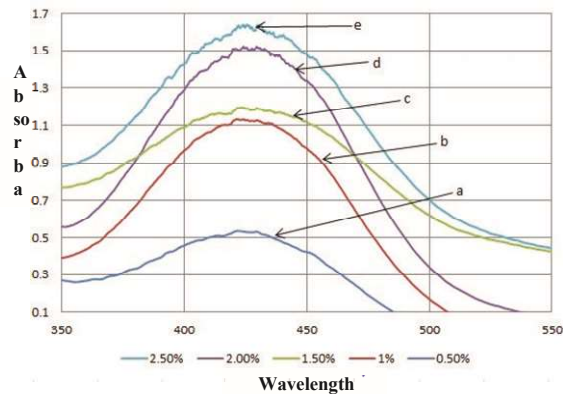


Fig. 6. Absorption spectra of immobilized BCP/SDS at different volume ratio of SDS:(a) 0.5 %, (b) 1%, (c) 1.5% (d) 2%, and (e) 2.5%.

Absorption spectra were analyzed to verify the presence of BCP and to determine the effect of surfactant toward silica network. Different ratios of SDS, and PEG surfactants (0.5%-2.5%) versus its absorption spectral are presented in Fig. 5 and Fig. 6 respectively. By examining the absorption spectra at around $\lambda_{max} = 430-435$ nm, absorption peak for each formulations can be determined, which was due to the yellowish color of the coated film, which indicates the presence of BCP. It was found that increasing surfactant's concentration (PEG and SDS) increases the absorbance where 2.5% concentration gives the maximum value. This result implies that increasing surfactant's concentration will increase the number of binding sites available in the surfactant.

IV. CONCLUSION

Further study on Bromocresol Purple (BCP), in the presence of anionic SDS and non-ionic PEG surfactants shows that the nature of the matrix does not only affect the

optical properties of BCP but also increases the stability of the dye. The sol-gel derived matrices with the presence of surfactant provide the dye with an improved sufficient rigid surrounding environment.

V. ACKNOWLEDGEMENTS

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