

EFFECT OF ADDITIVE RATIO ON MICROSTRUCTURAL AND OPTICAL PROPERTIES IN ORGANIC AND INORGANIC MATRIX

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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.

General Terms

Sol-gel.

Keywords

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

1. 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.

Electrochemical sensor is the common conventional real time monitoring. However, electrochemical sensor has relatively high power consumption and vulnerable to cation ions interference. Differs from electrochemical sensor, optical sensor also has it set of disadvantages. The incompatibility between the dye and sensing materials limit the use of the optical sensor for

measuring ammonia in water. Sol-gel is a promising method to solve these problems encountered by electrochemical and optical sensors. Sol-gel offers several advantages such as low temperature process, fast sensor response, higher operational, higher shelf life time and potentially giving high homogeneous coating. Properties of sol-gel such as porosity, reactivity and stability also can easily be altered by controlling the process parameters.

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].

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].

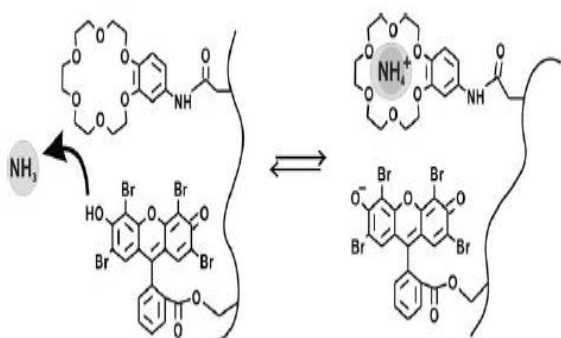


Fig. 1. 18-crown-6-ether act as cation trap for ammonia

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 analysed 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]. cell can be achieved.

2. 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. The characterization of the sensor film is done using Scanning Electron Microscope (SEM), UV-Vis spectrometer, Thermal Gravimetric Analyser (TGA) and Fourier Transform Infrared Spectroscopy (FTIR).

3. 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.

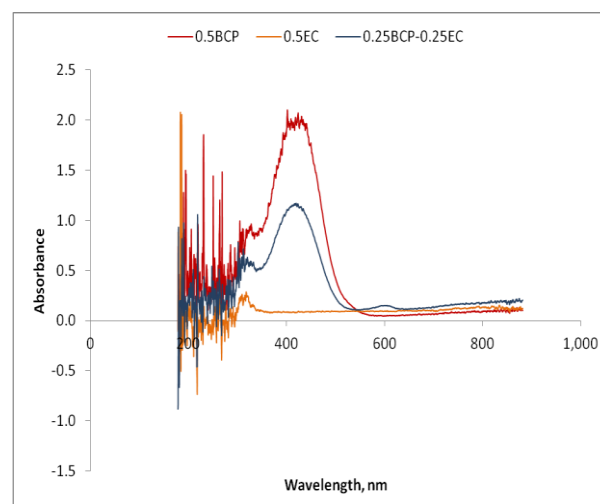


Fig. 2. Absorbance of VTES:TEOS sol-gel matrices with 0.5% BCP, 0.5% EC and 0.25% BCP+0.25% EC.

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].

Figure 4 shows the FTIR spectra of the sol-gel materials. The addition of BCP and EC influence the

FTIR spectra of VTES:TEOS sol-gel materials, which means these two dyes does have some reaction with the structure of silica network. The intensity of transmission band of Si-O-Si became dominant with increasing of network connectivity. The asymmetric stretching of Si-O-Si band is represents by transmission band around 775 cm-1, 1080 cm-1 and 1120 cm-1.

Transmission band around 910 cm-1 represent Si-OH bond, 1400 cm-1 represent Si-C bond, 1600 cm-1 is represent C=C bond while 3000 cm-1 is related to C-H bond [3]. Both C=C and C-H bonds can be influenced by the organic part VTES.

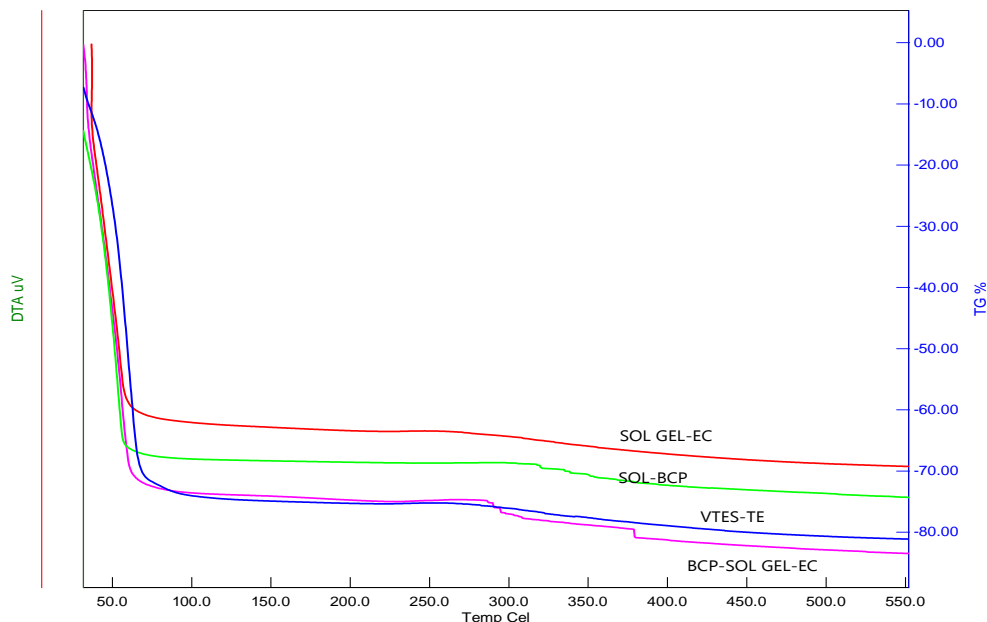


Fig. 3. TG curves of different sol-gel matrices composition with a heating rate of 5°C/min.

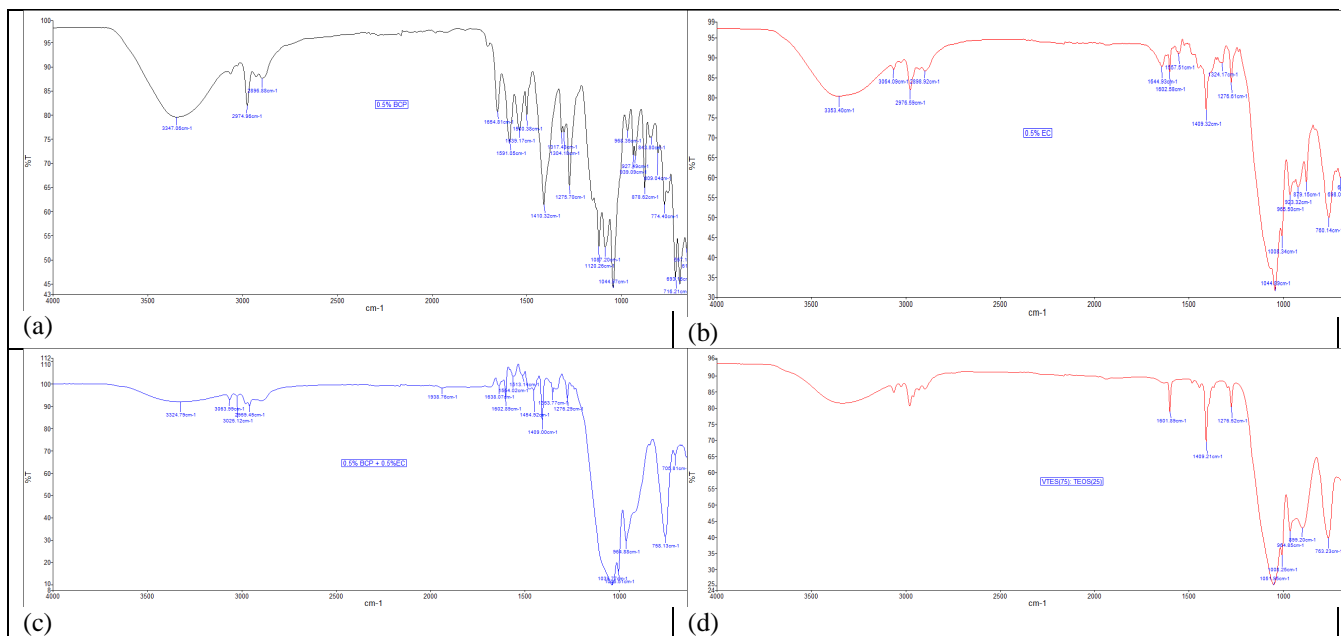


Fig. 4. FTIR spectra of VTES:TEOS sol-gel materials with (a) 0.5%BCP, (b) 0.5%EC, (c) 0.25%BCP+0.25%EC and (d) without any dye addition.

4. CONCLUSION

Cu foams are fabricated using MIM technique and employs SDP process to form interconnected pores. Cu foam specimens were divided based on the sintering schedules which are 450-850-950°C (specimen A) and

450-850°C (specimen B). Specimen A has lower density and higher porosity than specimen B which indicates that sintering at 950°C enhances the removal of K₂CO₃. Higher porosity in specimen A leads to decrease in strength, which is only 66.01 MPa compared to 110.93 MPa in specimen B. Higher

porosity in Cu foams is proven to enhance thermal conductivity since specimen A has higher thermal conductivity compared to B. Although specimen A has higher thermal conductivity, there is no significant difference compared to pure copper. This is probably due to formation of isolated pores apart from interconnected pores exhibited by the specimens.

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