

Chemical sensors based on hydrophobic porous sol-gel films and ATR-FTIR spectroscopy

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Abstract

A new chemical sensor based on attenuated total reflectance-Fourier transform infrared (ATR-FTIR) spectroscopy has been fabricated by coating an ATR crystal with a hydrophobic mesoporous silica film. The highly porous coating can extract hydrophobic analytes, such as benzene, from aqueous solutions and concentrate them inside the film. The enrichment of the analytes inside the film provides the sensor with enhanced sensitivity. The hydrophobic porous film can efficiently exclude water from the region probed by the evanescent wave, thus eliminating the spectral interference due to water absorption bands. Measurement of nitrogen adsorption and desorption isotherms of the films using surface acoustic wave techniques has been used to characterize the pore structure of the films. Relationships between the structure of the porous film and sensor performance are discussed.

Keywords: FTIR; ATR; Sol-gel; Thin film; Optical sensor; Chemical sensor

1. Introduction

Various techniques have been developed to detect organic compounds in water, including spectroscopic methods such as fiber optic evanescent wave spectroscopy (FEWS) [1–5] and attenuated total reflection-Fourier transform infrared spectroscopy (ATR-FTIR) [6–8]. ATR-FTIR is a well-developed spectroscopic technique that uses a waveguide, through which the IR radiation passes, placed in contact with the sample [9–11]. A fraction of infrared radiation propagates out of the waveguide in the form of an evanescent wave. The evanescent wave can be absorbed by analytes causing attenuation of the totally reflected beam inside the ATR crystal. The IR absorption spectrum is obtained by detecting the attenuated radiation leaving the ATR crystal. This technique has been used in various applications, such as studying the adsorption of proteins [15], degradation of polymers [12–14], diffusion of small molecules into polymer films and sensing of organic pollution in aqueous media [7–9]. The use of ATR-FTIR techniques to sense trace organic con-

tamination in aqueous systems has the advantage of being able to detect a wide variety of analytes in a short time. However, the strong interference by water and relatively high detection limit (which is constrained by the small volume of solution probed by the evanescent wave) has limited the applications of ATR-FTIR spectroscopy.

Many attempts have been made to improve the detection limit and decrease the water interference by coating the ATR crystals or optical fibers with organic polymer coatings [1–8]. The hydrophobic polymer coatings extract and concentrate the analytes within the coatings and repel water from the region probed by the evanescent wave to eliminate the spectral interference. Small amounts of organic chemicals in water can be detected in this fashion, but the diffusion resistance of polymer coatings is relatively high, and thus the response and recovery times of the sensors are too long for many practical applications [12,16]. Furthermore, detection is limited to those molecules that are able to diffuse into the polymer.

We have attempted to develop a new sensor with low detection limits, fast response times and general applicability. The strategy used is based on the fabrication of a hydrophobic coating with low diffusion resistance and

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high transparency throughout the majority of the infrared spectral region. This was accomplished by depositing a porous hydrophobic silica film on an ATR crystal by sol-gel processing. Sol-gel processing has been widely used to prepare porous materials (bulk and thin films) under mild reaction conditions [17]. It is based on hydrolysis and condensation reactions of ceramic precursors (e.g. tetraethoxysilane (TEOS), tetramethoxysilane (TMOS)) in an aqueous, alcohol or other medium. Various types of porous films with controlled thickness and structure can be prepared by spin coating or dip-coating [17]. Although organic dye doped sol-gel films have been used for detecting metal and hydrogen ions by evanescent wave sensing techniques [18-21], sol-gel films, to our knowledge, have not been experimentally used to sense organic chemicals in water. In this paper, we report the fabrication of a new ATR-FTIR spectroscopic sensor that can detect organic chemicals in aqueous media with short response times and low detection limits. The techniques described have the potential to be extended to the fabrication of fiber optic chemical sensors for remote monitoring.

2. Experimental

The gel was prepared by copolymerizing tetraethylorthosilicate (TEOS, Aldrich Chemical Co.) with ethyltrimethoxysilane (ETES, Gelest Chemical Co.) in ethanol and water media with an acid catalyst (hydrogen chloride) at 50°C until gelation occurred. The gelation time was approximately 1 week and the molar ratios of the reactants are TEOS/ETES/water/ethanol/HCl (1:1.5:3.8:0.4). The wet gel was derivatized with trimethylchlorosilane (TMCS, Gelest Chemical Co., 0.4 mol% in hexane) according to Prakash et al. [28]. The TMCS-derivatized gel was then sonicated for 10 min in hexane to obtain the sol. The films were prepared in a nitrogen atmosphere by dip-coating the ATR substrates from the sonicated sol with a coating speed of 19.2 cm min⁻¹. The films were then heated to 400°C with a heating rate 1°C min⁻¹ in air and held at 400°C for a total of 3 h. Surface modification of the films was conducted under a nitrogen atmosphere. The coated-ATR substrates were placed in a flask containing 50 µl of octyltrichlorosilane, 30 ml of carbon tetrachloride and chloroform mixture (3:2 v/v) and 30 ml of dodecane and reacted with sonication for 4 h at room temperature. The surface modified waveguides were then washed with benzene several times and heated at 170°C for 8 h.

The refractive index and thickness of the coated films were measured using ellipsometry (Gaertner Scientific Corporation, Model L116C) assuming that the absorption coefficient is zero at $\lambda = 632.8$ nm. The thicknesses were confirmed by scanning electron microscopy (SEM) of cross-sections of films on silicon substrates coated under the same experimental conditions as described above.

Sol-gel films, identical to those deposited on the Si waveguides, were deposited on surface acoustic wave (SAW) substrates for the purpose of estimating surface area, pore size, pore size distribution and total pore volume [29]. The SAW devices (97 MHz) on ST-quartz with Ti-primed Au transducers were designed and fabricated at Sandia National Laboratories [22]. The measurements were conducted at 77 K by measuring the frequency shifts of the SAW device configured as the feedback element of an oscillation circuit during adsorption and desorption of nitrogen. The amount of nitrogen adsorbed as a function of relative pressure was determined from the frequency change, assuming that the SAW frequency is only perturbed by a mass loading variation [22]. Nitrogen adsorption isotherms at 77 K were obtained by plotting the amount of nitrogen adsorbed versus the corresponding relative pressure of nitrogen. Surface areas, pore size and pore size distributions were estimated by using the Brunauer-Emmet-Teller (BET) equation and the BJH (Barett, Joyner, and Halenda) algorithm [23].

IR spectral data were collected using a Nicolet model 800 infrared spectrometer equipped with a mercury cadmium telluride (MCT) detector. The silicon ATR crystals used in these studies were 55 × 10 × 3 mm with 45° beveled ends and mounted in an Varimax horizontal ATR apparatus (International Crystals Laboratory, Garfield NJ). A Teflon trough bolted to the top of the ATR crystal was constructed to hold aqueous samples. The top of the trough could be opened, and a pipette was used to introduce or remove the samples. Benzene (527 ppm, reagent grade) in de-ionized water was used as a model analyte.

3. Results and discussion

3.1. Characterization of the porous film

The nitrogen adsorption experiment is the traditional method used to characterize porous materials [25]. The materials are, however, generally in the form of a powder. The chemical and physical conditions used to form a bulk xerogel powder can be very different than those used to form a thin film, and hence the pore structure can be very different in these two types of materials. Also, the amount of nitrogen adsorbed in a thin film is very small compared with that in the xerogel powder, hence surface acoustic wave techniques were chosen to measure the nitrogen adsorption isotherms. Fig. 1 shows the nitrogen adsorption isotherm (77 K) of the surface-modified porous film obtained using the SAW measurement. The type IV isotherm suggests that the film has a mesoporous structure [25]. The pore size and pore size distribution of the film can be obtained by using the desorption branch of the isotherm and the model of Barrett, Joyner, and Halenda (BJH model) [23]. Fig. 2 shows the BJH pore volume versus pore diameter distribution of the film obtained by the desorption isotherm. The average pore size r is esti-

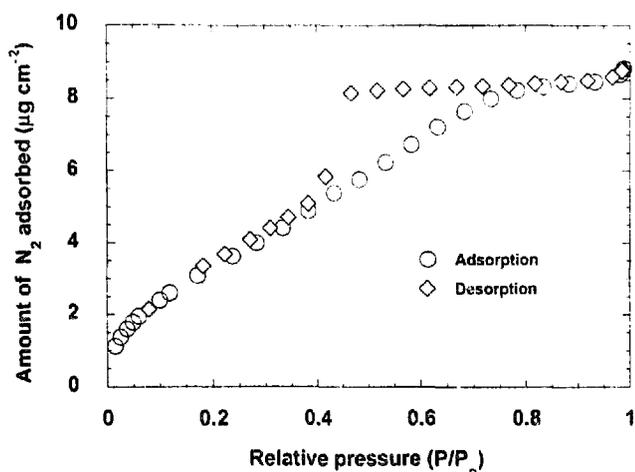


Fig. 1. Nitrogen adsorption and desorption isotherms (77 K) of the surface-modified, hydrophobic porous film. The isotherms were obtained using surface acoustic wave techniques.

mated using $r = 4V/S$, where V is the BJH desorption pore volume, and S is the BJH desorption surface area (assuming a cylindrical pore shape). This results in an average pore diameter of 29 Å. However, this model is based on a cylindrical pore shape, whereas the actual pore shape is irregular. The details of the structure of the surface-modified porous thin films are summarized in Table 1.

3.2. ATR-FTIR spectroscopy

ATR-FTIR spectroscopy is based on the interaction of analytes with an infrared evanescent wave propagating out of the waveguide. The attenuation of the electric field amplitude, E , in rare media (the film or the solution when using an uncoated waveguide) can be described as $E = E_0 \exp(-Z/d_p)$, where E_0 is the electric field amplitude at the waveguide–film (solution) interface, Z is the distance from the waveguide surface, and d_p is the penetration

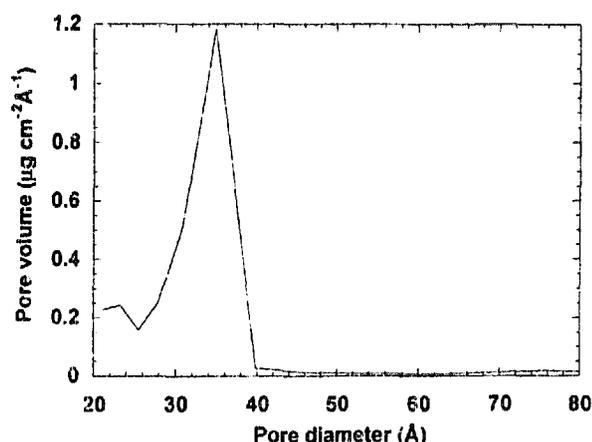


Fig. 2. Pore volume versus pore diameter distribution of the porous sol-gel film. The data in the plot were obtained by using the desorption isotherm in Fig. 1 and by applying the algorithm of Barrett, Joyner and Halenda (BJH).

Table 1

Structure of the surface-modified porous sol-gel film

Thickness (Å)	Refractive index	BET surface (cm ² cm ⁻²) ^a	Pore diameter (Å)	Porosity (%)
3835 ± 145	1.42 ± 0.02	141	29	30

Porosity was estimated by the amount of nitrogen adsorbed (9.5 µg cm⁻²) on the film and the film thickness 0.39 µm, assuming that the density of nitrogen at 77 K is 0.8 g cm⁻³.

^acm² of the BET surface area per cm² area of the ATR coating film.

depth. The penetration depth is the perpendicular distance from the waveguide/film (or solution) interface at which E is equal to E_0/e , and is given by

$$d_p = \frac{\lambda}{2\pi n_1 \left[\sin^2 \theta - \left(\frac{n_2}{n_1} \right)^2 \right]^{1/2}}$$

where λ is the wavelength of the IR radiation in vacuum, θ is the angle of incidence of the radiation at the waveguide–film interface, and n_1 and n_2 are the refractive indexes of the dense (ATR crystal) and rare media, respectively. In our experiments, $n_1 = 3.42$, $n_2 = 1.42$, and $\theta = 45^\circ$, so that the penetration depth can be estimated to be 0.23 µm at 3400 cm⁻¹ or 0.52 µm at 1500 cm⁻¹. If the hydrophobic surface of the sol-gel film prevents water entering the pores, one would expect the strong water absorption bands in the infrared to be significantly attenuated, especially if the film thickness is as large, or larger, than the penetration depth. Fig. 3 compares the response of sensors prepared with a sol-gel film (b) and without a sol-gel film (c) to a sample of pure water. Fig. 3 also contains the spectrum obtained from a sol-gel coated waveguide in contact with nitrogen prior to the surface modification step. Note that there are small CH₂ and CH₃ features (2900 cm⁻¹) due to the incomplete pyrolyzation of the organic components in the sol-gel film. The increased CH₂ and CH₃ features in spectrum b are the result of the surface modification. The water bands near 3400 cm⁻¹ and 1700 cm⁻¹ are significantly attenuated when the ATR crystal is coated with the porous hydrophobic film. The thickness of the film is between the values of the penetration depths calculated at 3400 cm⁻¹ and 1500 cm⁻¹. A slightly thicker film might completely eliminate the water absorption bands, although the increase of thickness may also increase sensor response time.

Fig. 4 shows the steady state responses of two waveguide sensors, one with and the other without the sol-gel film, to a 527 ppm solution of benzene. A comparison of the benzene triplet intensity between 3000 cm⁻¹ and 3100 cm⁻¹ [26] indicates a signal en-

hancement of about a factor of 10^3 for the sol-gel film coated waveguide relative to the uncoated waveguide. This large enhancement suggests that the porous hydrophobic film is an excellent choice for fabrication of ATR-FTIR chemical sensors for use in aqueous environments.

The mechanism of the signal enhancement may be due to adsorption of benzene onto the hydrophobic surface of the porous film. It is well known that hydrophobic organic compounds will preferentially separate from an aqueous solution into a hydrophobic region such as that provided by an organic polymer [1–8]. It is likely that benzene diffuses into the hydrophobic porous film resulting in a concentration enhancement relative to the bulk solution. As shown in Table 1, the BET surface area of the porous film is much greater than the surface area of the waveguide, i.e. $141 \text{ cm}^2 \text{ cm}^{-2}$ (surface area of the film per cm^2 of the waveguide surface). This suggests that the porous film provides a matrix that can accommodate a large amount of absorbed benzene. Pore size may also affect the adsorption of benzene in the coated films. A decrease of the pore radius will increase the interaction between the pore wall and benzene and thus favor the adsorption of benzene in the film [25]. However, if the pore size is so small that benzene cannot enter the pores, the benzene will be excluded from the region probed by the evanescent wave and a diminished signal, relative to an uncoated waveguide, would be expected. For example, a sol-gel film with an approximate pore diameter of 5 \AA and a thickness of $0.3 \mu\text{m}$, prepared using an organic template approach [24], was coated onto an ATR crystal, but the resulting sensor showed almost no signal for benzene.

We have not characterized the response time of the sensor to benzene, but a response time experiment has been performed using benzonitrile as the analyte [27]. We

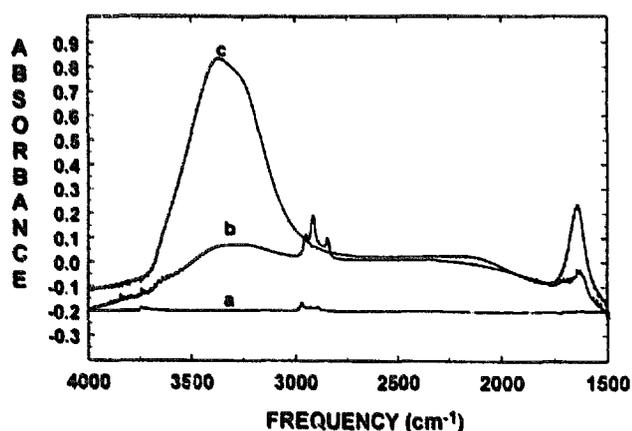


Fig. 3. The ATR-spectrum of the porous film in nitrogen and the infrared spectra of the water response obtained by ATR-FTIR spectroscopic sensors. (a) The spectrum of the porous film (without hydrophobic surface-modification) in a nitrogen atmosphere. (b) The spectrum obtained from the ATR-FTIR spectroscopic sensor prepared with a hydrophobic sol-gel film when the sensor is placed in pure water. (c) The spectrum of the water response obtained by the ATR-FTIR spectroscopic sensor prepared without a hydrophobic sol-gel film.

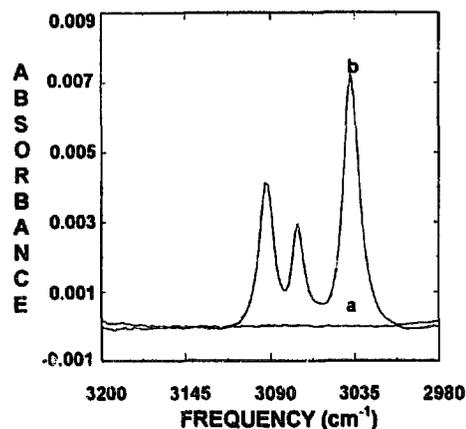


Fig. 4. The response to benzene dissolved in water (527 ppm) produced by the ATR-FTIR spectroscopic sensor with and without the hydrophobic porous film. (a) A spectrum obtained by the ATR-FTIR spectroscopic sensor prepared without a hydrophobic sol-gel film. (b) A spectrum obtained by the ATR-FTIR spectroscopic sensor prepared with a hydrophobic sol-gel film.

believe that the response time of the sensor to benzene should be similar to that measured for benzonitrile. The sensor response time was measured in a relatively simple experiment. The sensor was first immersed in water. The water was removed and rapidly replaced with 100 ppm benzonitrile and eight scans were collected. The time required for the sample introduction and data collection was approximately 6 s. Eight additional scans were immediately collected. The signal following the first data collection was identical to the second, indicating that the benzonitrile in the porous film had reached equilibrium within the initial 6 s. The analogous experiment, except replacing the benzonitrile solution with pure water, indicated an equally rapid washing of the benzonitrile from the sensor. The response speed of the sensor is mostly determined by the diffusion resistance of benzonitrile in the solution and the porous film, as well as the interaction of benzonitrile and the hydrophobic surface coating. It depends on the hydrophobicity, pore size, film thickness, and pore connectivity. Increasing the pore size and pore connectivity or decreasing the film thickness will decrease the response time. Compared to the sensors prepared using organic polymer films, the sol-gel coated sensors have much lower diffusion resistance and thus much shorter response times. Moreover, the non-swelling property of the inorganic film material (i.e. silica) provides the sensors with excellent recovery behavior, which makes it possible to employ the sensor as a real time monitor in a situation when the analyte concentrations might be continuously varying.

4. Conclusion

We have prepared a new chemical sensor to detect low concentrations of benzene in water using ATR-FTIR and

a waveguide coated with a hydrophobic, porous sol-gel film. The hydrophobic film repels water from the region probed by the evanescent wave, thus eliminating the spectral interference due to the strong water absorption bands. The hydrophobic porous films adsorb hydrophobic molecules, such as benzene, from dilute aqueous solutions enriching the analyte concentration in the porous film. Rapid response times and recovery times have been demonstrated. This new chemical sensor can be potentially used to continuously monitor trace organic contamination in aqueous samples. This principle can also be used to prepare fiber optic chemical sensors thus making remote sensing possible.

Acknowledgements

This work is supported by NASA under contract NAG10-0160 and by the Semiconductor Research Corporation under contract MJ-573. The authors would like to thank Teresa Bohuszewicz for assistance with the SAW measurements.

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