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SENSORS

Characterization of Octaethyl Porphyrin Thin Films with Application to Determination of Volatile Organic Compounds

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ABSTRACT
Metal-free octaethyl porphyrins and octaethyl zinc porphyrins were used to fabricate thin films via spin coating. The film quality was evaluated by ultraviolet-visible spectroscopy. Surface plasmon resonance was employed to characterize the thin films for sensing of volatile organic compounds. The metal-free porphyrin thin films were sensitive for acetone and chloroform due to the shapes, sizes, and dipole moments of these molecules. The metallated porphyrin thin films interacted slightly with the volatile compounds.

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Acetone; octaethyl porphyrins; spin coating; surface plasmon resonance

Introduction

High concentrations of toxic gases have been introduced into the atmosphere due to increased industrial production in recent years. Sensitive, selective, and low cost sensors have been developed to monitor these emissions. Organic materials have been investigated for sensors due to their simple, low cost synthesis, and wide range of physical and chemical properties that can be tailored by changing the composition.

Porphyrins include a broad π-electron cloud with semiconducting properties and provide intense absorption in the ultraviolet-visible region that suggest application as optical gas sensors. Porphyrin provide large spectral shifts upon ligand binding and significant interaction with gas molecules providing colorimetric changes that allow application for optical sensing (Giancane and Valli 2012). Previous reports have incorporated porphyrins using absorption spectroscopy in the ultraviolet-visible region (Richardson et al. 2005). This work has shown that metal-free porphyrins may be used for nitrogen dioxide determination sensing at sub-parts per million concentrations. By modification of substituents in the meso positions, improvements in the sensitivity and response time of the resulting porphyrin films were obtained. The introduction of a metal atom inside the porphyrin ring structure (Arnold et al. 2002; Brittle et al. 2008) and functionalizing the peripheral positions of the porphyrin ring (Gulino et al. 2006) was shown to enhance gas sensing. Recent studies have shown that porphyrin derivatives are well-suited for integration with optical fiber technology, critical for remote sensing within hazardous environments (Martelli et al. 2009; Bahrampour et al. 2013).

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Optical fiber sensing allowed the determination of ions (Zhang et al. 2002), volatile organic compounds (Jarzebinska et al. 2012), and oxygen (Tsukada et al. 2003; Wang et al. 2014).

Octaethyl porphyrins have also been used as active layers to detect volatile organics employing optical methods. Measurements with 2-propanol, ethanol, acetone, and cyclohexane vapor of Langmuir Blodgett thin films of octaethyl porphyrins revealed a signature for the analytes (Akrajas, Salleh, and Yahaya 2002). Octaethyl porphyrins were employed as odor sensors when exposed to capsicum (Salleh and Akrajas 2002) and tea (Chen et al. 2013). In our previous study, the gas sensing performance of the Langmuir-Blodgett thin films fabricated from metal free 2, 3, 7, 8, 12, 13, 17, 18-octaethyl-21H, 23H-porphine and its derivatives containing iron chloride, cobalt, and magnesium were characterized by the quartz crystal microbalance (QCM) for volatile organic compounds (Capan, Tarımcı, and Capan 2010). The Langmuir-Blodgett films were sensitive to volatiles. The primary sensing mechanism was proposed as the interaction between the gas molecules and the central metal atom or conjugated π-electron system. Atomic force microscopy showed the influence of the surface morphology on the gas sensing properties. A larger surface area for the thin films caused higher response in gas sensing (Çaycı et al. 2011).

Surface plasmon resonance is an optical technique employed for chemical sensing. Under the optimum conditions, the reflectivity of a thin metal film is extremely sensitive to optical variations in the adjacent medium because surface plasmons are sensitive probes of boundary conditions (Liedberg, Nylander, and Lunström 1983). In this study, the spun thin films of metal free octaethyl porphine and its derivative octaethyl zinc porphyrin were fabricated. These thin films have been exposed to saturated concentrations of benzene, toluene, ethanol, methanol, chloroform, dichloromethane, carbontetrachloride, and acetone. The goal of this work was to characterize the influence of zinc on gas sensing (Capan, Tarımcı, and Capan 2010; Çaycı et al. 2011). This study involves the investigations on the gas sensing properties of the octaethyl porphyrin thin films. Surface plasmon resonance was employed because it is more sensitive than the quartz crystal microbalance. To the best of our knowledge, the gas sensing properties of octaethyl porphyrin and octaethyl zinc porphyrin thin films to acetone have not been previously reported. The metal-free octaethyl thin film was sensitive to chloroform and acetone while the metallated thin film was insensitive to all compounds. The results were characterized in terms of the shape, size, and dipole moment of the analytes. The poor interaction of the metallated thin film may be due to reduced π-stacked aggregation of the molecules on the surface compared with the metal-free films.

Experimental

Chemicals

The 2, 3, 7, 8, 12, 13, 17, 18-Octaethyl-21H, 23H-porphine and 2, 3, 7, 8, 12, 13, 17, 18-Octaethyl-21H, 23H-porphine zinc(II) porphyrins, designated as octaethyl porphyrin and octaethyl zinc porphyrin, respectively, were purchased from Sigma Aldrich and used without further purification (Capan, Tarımcı, and Capan 2010). Benzene (99.8%), toluene (99.8%), ethanol (99.8%), methanol (99.9%), chloroform (99.5%), dichloromethane (99.8%), carbontetrachloride (99.5%), and acetone (99.9%) were purchased from Sigma Aldrich and used without further treatment. To obtain saturated concentrations of these compounds in the gas phase, 5 mL of were placed in a 10- mL glass flask for two hours at room temperature and a syringe was used to directly inject the vapor into a gas cell. The saturated concentrations of acetone and chloroform were 270,000 ppm and 230,000 ppm, respectively.

Thin film fabrication and characterization

Porphyrin solutions (0.2 mg/ml) were prepared in chloroform. A schematic of the spin coater (Specialty Coating Systems Spincoat G3P-8 model) is presented in Figure 1. The substrate was connected with a vacuum holder to fix the on a rotating table moved by a digital controller. When the solution was dispensed on the table, the solution interacted with the substrate to form a thin layer. The 100 µL of porphyrin solution was dispensed on the substrate rotating at 2,000 rpm for two minutes. The film was allowed to stand for at least thirty minutes before measurements were initiated. Ultraviolet-visible spectra were collected with the thin films fabricated on glass slides. For gas sensing, the thin films were fabricated on 50 nm gold coated glass (Biosuplar, 20 × 20 mm, thickness of 1 mm). Previous measurements have shown that a sharply defined thickness of 55 ± 5 nm is required to achieve optimum surface plasmon resonance excitation and sensitivity (Neff et al. 2006). Both substrates were cleaned with chloroform in an ultrasonic bath for ten minutes.

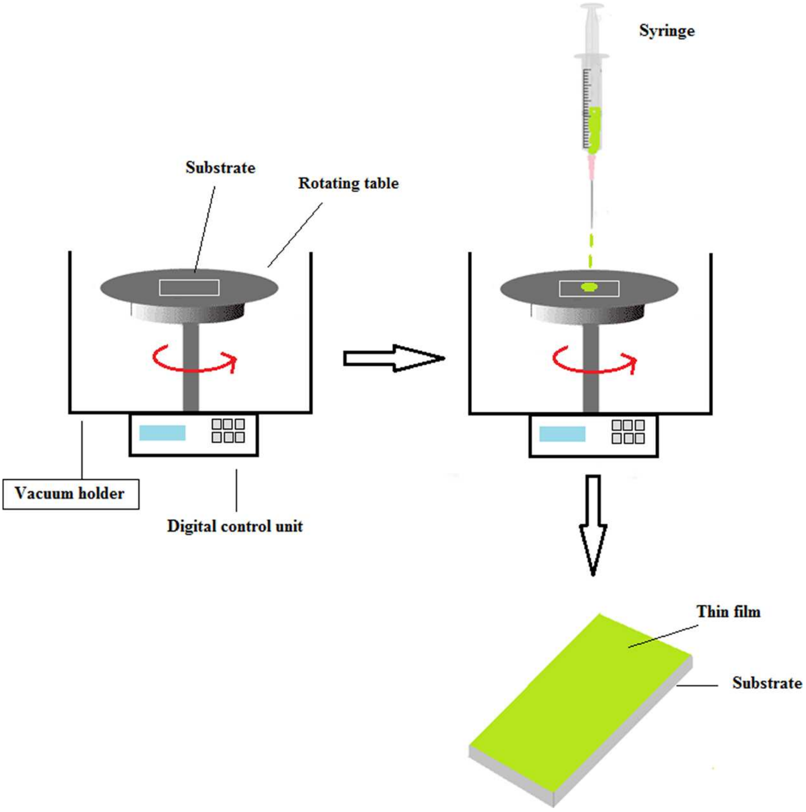

Figure 1. Schematic of the spin coater.

Ultraviolet-visible spectroscopy was used for the characterization of thin films from 250 to 850 nm using an Ocean Optics source (DH-2000-BAL Deuterium Tungsten light source) and spectrometer (USB4000) in absorbance mode.

Gas sensing

The surface plasmon resonance instrument (Biosuplar 6) measured light intensity versus the angle of incidence between a metal and a dielectric was employed to characterize the gas sensing performance of the thin films. A schematic of the system is presented in Figure 2. Glass slides with dimensions 20 mm × 20 mm × 1 mm were coated by a thin homogeneous layer of gold on a glass prism that allowed measurement in liquid or air. A low power laser diode (630 to 670 nm) source was aligned on the gold surface to achieve resonance with the plasmons on the surface at a characteristic resonance angle θ_{SPR} and total internal reflection of light at the surface was obtained. At a specific angle of incidence, called the resonance angle, polarized light coupled in the surface plasmon mode where reflectance from the surface was a minimum. The resonance angle is strongly dependent on the dielectric constant of the metal film (ε_M) and the dielectric constant of the glass prism (ε_P) as shown in EQ1 (Knoll 1998):

$$\theta_{SPR} = \sin^{-1}\left(\frac{\varepsilon_M}{\varepsilon_P(\varepsilon_M + 1)}\right)^{1/2} \tag{1}$$

The dependence of the reflected light intensity as a function of the angular change is called a surface plasmon resonance curve. The angular sensitivity of this instrument was 0.003°. Moreover, a shift in the resonance angle $\Delta\theta$ occurs when a thin film with a

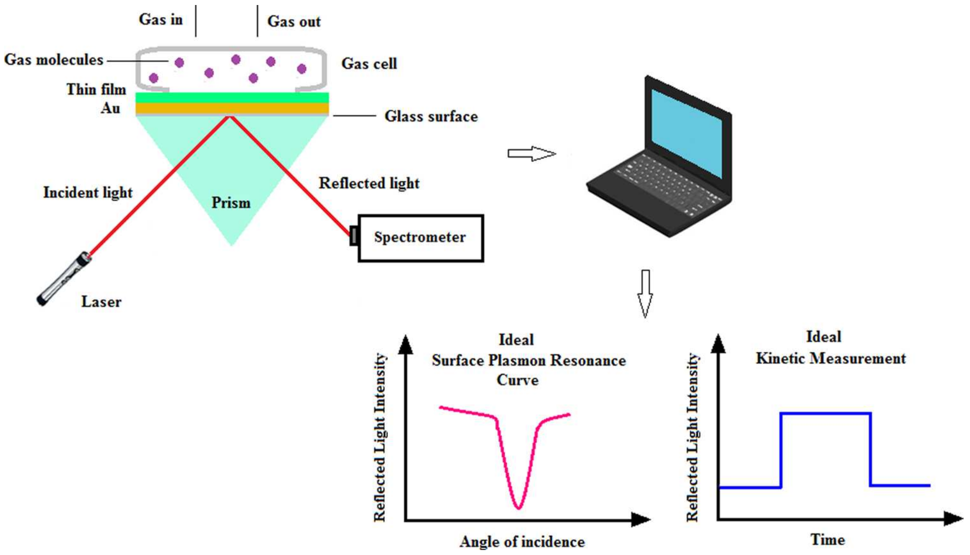

Figure 2. Schematic of the surface plasmon resonance instrument including an ideal curve and the kinetic response.

thickness of d and dielectric constant of ε is fabricated on the metal film. This shift of Δθ is described by Hassan, Goy, and Nabok (2008):

$$\Delta\theta = \frac{(2\pi/\lambda)(|\varepsilon_M|)^{3/2} d}{\sqrt{\varepsilon_P}\cos\theta(|\varepsilon_M - 1|)^2 \varepsilon}(\varepsilon - 1) \tag{2}$$

where $|\varepsilon_M|$ is the modulus of the real part of the dielectric constant of the metal film.

For kinetic measurements, a compatible transparent plastic flow cell with an inlet and outlet connected to silicon tubes was employed for sensing of volatiles. The volume of the cell was 20 µl (Biosuplar, Germany). The saturated concentrations of the volatile organic compounds were introduced into the cell to perform measurements and the shift in resonance angle was monitored. For the time dependent kinetic gas sensing measurements, the angle of incidence was fixed around the value of resonance angle and the change in the reflected light intensity following exposure to gases was monitored. All measurements were performed at room temperature.

Results and discussion

Ultraviolet-visible spectra of the porphyrin thin films were employed to evaluate their quality. Figure 3 shows that the thin films were fabricated on the glass substrates. The electronic transition for the octaethyl porphyrins are predominantly from the highest occupied molecular orbital to the lowest unoccupied molecular orbital. Ultraviolet-visible spectra of porphyrins include a strong Soret band between 400 and 500 nm involving n-π* transitions and Q-bands between 500 and 700 nm due to π—π* transitions. The strong band at 415 nm (S band (0–0) transition) with shoulders at 525 nm, 603 nm, and 651 nm was consistent with the literature (Tsuboi and Tanigawa 2003; Mensing et al. 2013) and observed for the metal-free octaethyl porphyrin thin film. The strong Soret band at 400 nm (S band (0–0) transition) and a Q band (0–0) transition) at 570 nm were obtained for the octaethyl zinc porphyrin thin film (Stampor 2004; Musselman, Larsen, and Hoffman 2013). The blue

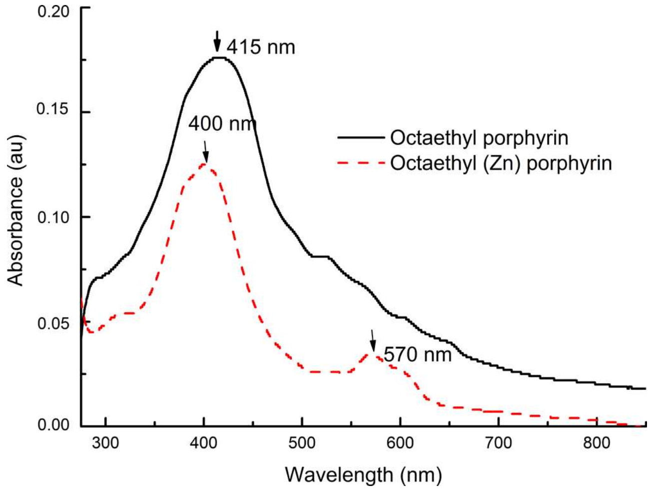

Figure 3. Ultraviolet-visible absorption spectra of the octaethyl porphyrin and octaethyl zinc porphyrin thin films.

shift of the Soret band for the metallated thin film is generally attributed to H-aggregation of the molecules during formation (Okada and Segawa 2003).

Surface plasmon resonance curves of the octaethyl porphyrin thin film, exposure to saturated acetone vapor, and recovery with dry air is presented in Figure 4. A resonance angle of 45.7° for the octaethyl porphyrin thin film was obtained that demonstrates fabrication on the substrate because the value of a classical 50 nm thick gold substrate is approximately 44.2° (Gwon and Lee 2010). The resonance angle may shift due to differences in the thickness and the dielectric constants of the thin films as shown in Equation 2. The surface plasmon resonance curve of the octaethyl zinc porphyrin thin film, its exposure to saturated acetone vapor, and recovery with dry air is presented in Figure 5. The fabrication of the thin film on the gold coated substrate resulted in a resonance angle of 46.6° for the octaethyl zinc porphyrin thin film.

The interaction of the thin film with the gas molecules is believed to occur on the surface followed by diffusion into the bulk of the thin film. This interaction causes a change in the thickness or the dielectric constant of the thin film that induces a shift in the resonance angle. Figure 4 shows that the recovery of the octaethyl porphyrin thin film is incomplete. A shift in the resonance angle of 0.12° was observed for the octaethyl porphyrin thin film in the presence of acetone. No shift was observed for the octaethyl zinc porphyrin thin film that demonstrates poor interaction between the thin film and acetone. Similar results were obtained for chloroform.

The kinetic response of the octaethyl porphyrin thin film due to interaction with acetone and chloroform is shown in Figure 6. The inset shows the response in dry air at atmospheric pressure. The response is provided as the normalized response as:

$$\text{Normalized response}\,(\%) = \frac{\Delta I}{I} = \frac{I_{gas} - I_{air}}{I_{air}} \times 100 \qquad (3)$$

where I_{gas} and I_{air} are the measured reflectance of octaethyl porphyrin thin films during exposure to the analyte vapor and dry air, respectively. Figure 6 shows that chloroform and acetone interact with the octaethyl porphyrin thin film. The normalized response values, recoveries, and response times are provided in Table 1 for the octaethyl porphyrin

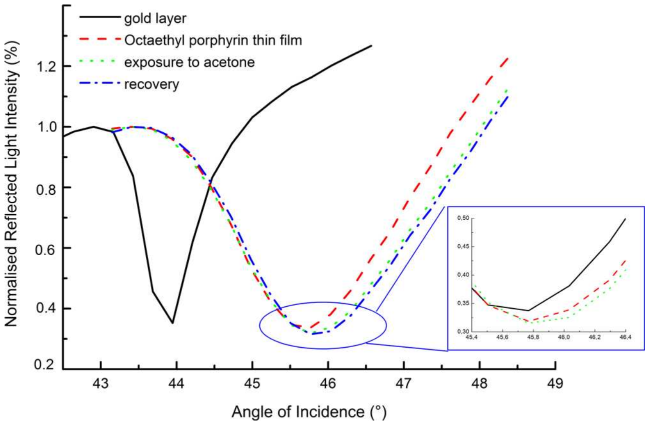

Figure 4. Surface plasmon resonance curves of the octaethyl porphyrin thin film, its exposure to saturated acetone vapor, and recovery in dry air.

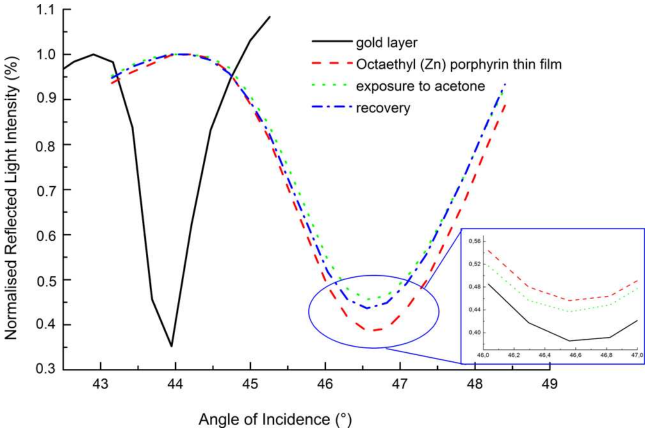

Figure 5. Surface plasmon resonance curves of the octaethyl zinc porphyrin thin film, its exposure to saturated acetone vapor, and recovery in dry air.

thin film. The kinetic values for the octaethyl zinc porphyrin thin film are also listed in Table 1. The kinetic measurements for the octaethyl porphyrin thin film were in good agreement with the results obtained using surface plasmon resonance curves. Figure 4 shows that the interaction of the gas molecules with the octaethyl porphyrin thin film was significant with weak recovery values. For the octaethyl zinc porphyrin thin film, a sudden interaction between the thin film and the gas molecules was observed. Figure 5 shows that the interaction of the octaethyl zinc porphyrin film was weak with acetone. The surface plasmon resonance and the kinetic measurements were in good agreement.

The interaction of the porphyrin thin films with the gas molecules has previously been characterized by the conjugated π electron system causing charge transfer between the molecules, condensation of gas molecules on the thin film that changes the optical properties, and physical absorption by dipole-dipole forces or hydrogen bonding between the thin film and the gas molecules (Giancane and Valli 2012). The sizes of the gas molecules are also

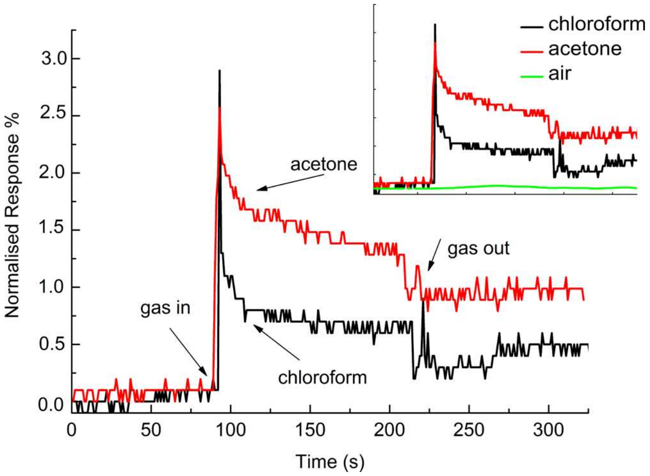

Figure 6. Kinetic response graphs of the octaethyl porphyrin thin film to saturated chloroform and acetone vapor. Inset: kinetic response at atmospheric pressure.

Table 1. Normalized response, response time, and recovery of the thin films.

	Normalized response (%)		Response time (s)		Recovery (%)	
	Chloroform	Acetone	Chloroform	Acetone	Chloroform	Acetone
Octaethyl porphyrin	1.5	2.5	5	2	80	50
Octaethyl zinc porphyrin	1.0	1.3	3	2	–	–

important due to diffusion in the thin film. The central metal of the metalloporphyrin also affects gas sensing in terms of their electron affinity, ionization energy, and metallic character. These processes were considered in developing an interaction mechanism in this work.

Although the octaethyl porphyrin thin film responded to saturated chloroform and acetone, the sensitivity was higher for the latter. This phenomenon may be due to the trigonal planar shape of the acetone compared to the tetrahedral shape of chloroform. The planar structure of acetone may lead to enhanced interactions with the porphyrin, as reported previously (Umar, Saleh, and Yahaya 2008). Another interaction between the thin film and the gas molecules may involve physical absorption through dipole-dipole forces. The higher interaction of acetone with the thin film may be explained by its higher dipole moment (2.91 D) compared to chloroform (1.15 D). The dominant interaction of the gas molecules with the thin film may be physical absorption as previously reported (Ichinohe, Tanaka, and Kanno 2007; Ceyhan et al. 2007). Figure 6 shows that the recovery of the thin film following interaction with chloroform is higher than the recovery with acetone, probably due to the larger size of acetone that may prevent the removal of the molecules from the thin film.

Table 1 shows that the interaction of chloroform and acetone with the octaethyl zinc porphyrin thin film is poor, probably due to a more uniform film with fewer π-stacked aggregates as previously reported (García-Berríos et al. 2013). This aggregation of the metallated porphyrin was also present in the ultraviolet-visible spectra (Figure 3). The blue shift of the Soret Band in the thin films was attributed to the H-aggregation of the molecules during thin film formation. In this study, poor interaction of the Zn octaethyl porphyrins were observed compared with the other metalleted octaethyl porphyrins due to reduced π-stacked aggregates.

Conclusions

The gas sensing measurements of the thin films of metal-free octaethyl porphyrin showed its potential application for the determination of chloroform and acetone. The interaction mechanism was described on the basis of molecular shape, size, and dipole moment. The zinc octaethyl porphyrins poorly interacted with the gas molecules due to reduced π-stacked aggregation of the molecules on the surface compared with the metal-free thin films. For further characterization of surface interaction of the molecules, scanning probe techniques are required. Future work will concentrate on these surface investigations of these thin films.

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