Porphyrin and Zn-Phtalocyanine as Optical-Sensor

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Contributor: Marco Zannotti

In the detection of molecular species, optical sensing methods are very attractive. Planar Optical Waveguide (POWG) sensor represents an interesting system that consists of a waveguide layer, that usually is a potassium-ion-exchange glass substrate, and a sensor layer; the response of this sensor depends on the evanescent wave principle of laser light. The detection of the molecule is based on two important factors: the absorbance of the film, that is affected by the interaction with the analyte molecules and the change of the reflected light intensity from the POWG thin film that is related to the absorbance changes.

Keywords: metal-free porphyrin ; zinc phthalocyanine ; spin-coated thin film ; planar optical waveguide sensor ; HCl vapor ; xylene-styrene vapors

1. Overview

The sensing behavior of a thin film composed of metal-free 5, 10, 15, 20-tetrakis (p-hydroxy phenyl) porphyrin and zinc phthalocyanine complex towards m-xylene, styrene, and HCl vapors in a homemade planar optical waveguide (POWG), was studied at room temperature. The thin film was deposited on the surface of potassium ion-exchanged glass substrate, using vacuum spin-coating method, and a semiconductor laser light (532 nm) as the guiding light. Opto-chemical changes of the film exposing with hydrochloric gas, m-xylene, and styrene vapor, were analyzed firstly with UV-Vis spectroscopy. The fabricated POWG shows good correlation between gas exposure response and absorbance change within the gas concentration range 10–1500 ppm. The limit of detection calculated from the logarithmic calibration curve was proved to be 11.47, 21.08, and 14.07 ppm, for HCl gas, m-xylene, and styrene vapors, respectively. It is interesting to find that the film can be recovered to the initial state with trimethylamine vapors after m-xylene, styrene exposures as well as HCl exposure. The gas-film interaction mechanism was discussed considering protonation and π-π stacking with planar aromatic analyte molecules.

2. Optical Sensing

Aromatic organic solvents such as m-xylene, styrene are common chemicals in almost every chemistry laboratory, while exposure to these solvents or their vapors causes health issues such as insomnia, damage to the neurological system, respiratory system, liver, and kidney. Instrumental methods such as high-performance liquid chromatography (HPLC) and high-performance capillary electrophoresis (HPCE), quantum resistive sensors (QRS) are generally used for vapor detection [1][2]. However, methods with low-cost and facile processing are needed to study and advance this field. Different materials are reported in the literature for the detection of aromatic compounds and HCl, for example, V_2O_5 doped $ZnFe_2O_4$ composited thin film was used to detect xylene and styrene at room temperature using optical waveguide [3], pentacene-based organic field-effect transistor (FET) was applied to detect HCl [4], terbium-based metal-organic frameworks (MOF) to detect styrene through fluorescence mechanism [5]. In addition, composite sensors of poly(styrene-acrylic acid) with TiO_2 nanoparticles [6] and MOF/polymer-based photonic crystal [7] were applied for the detection of volatile aromatic hydrocarbon vapors.

In the detection of molecular species, optical sensing methods are very attractive. Planar Optical Waveguide (POWG) sensor represents an interesting system that consists of a waveguide layer, that usually is a potassium-ion-exchange glass substrate, and a sensor layer; the response of this sensor depends on the evanescent wave principle of laser light [8][9] The detection of the molecule is based on two important factors: the absorbance of the film, that is affected by the interaction with the analyte molecules and the change of the reflected light intensity from the POWG thin film that is related to the absorbance changes[10]. The analyte detection by POWG sensors has several advantages with respect to other sensor materials: high potential sensitivity, fast response and recovery times, ability to work at room temperature, anti-electromagnetic interference, remote monitoring, safe detection, simple structure with easy manufacturing, and particularly important, low production costs [11][12].

In this contest, optical waveguides composed of metal-oxides, organic dyes, or carbon nanomaterials are promising methods for gas exposure detection due to the optical and chemical changes within the sensing layer[9]. Hence, thin films deposited on a transparent glass substrate with large refractive index difference and low loss, display intense responses toward surface condition transformations [13].

Nonlinear optical organic compounds such as porphyrins (P) and phthalocyanines (Pc) are promising chemicals in optical waveguides to limit the laser radiation due to their large nonlinearities, inherently fast response, broadband spectral response, and ease of processing [14]. Ps are composed of four pyrrole subunits interconnected at α carbon position via methine bridges, while Pc has nitrogen instead of CH at the meso-position of the porphyrin, and the pyrroles are conjugate with four benzene rings. Therefore, porphyrins and phthalocyanines exhibit outstanding chemical and optical character due to their macrocyclic structure with 18 delocalized π electrons. Ps exhibit large excited-state absorption cross-sections, and long triplet excited state lifetimes, which enables porphyrins to serve as an effective optical limiter [14]; Pcs are similar to P and are also attracting extensive attention thanks to their nonlinear optical characteristics, strong light absorption properties in the visible region, and small dielectric constants[15]. Ps show a strong Soret band between 400–500 nm and less intense Q bands in the range between 550–650 nm; Pcs usually show a deep-blue color with a strong Q-band in the visible region and a weak Soret band in the UV-spectral region[16] [17].

Because of the inner center of the macrocycle and high electron density, these dyes can coordinate with almost all metals and numerous volatile organic compounds through strong chemical bonds and weak non-covalent bonds such as hydrogen bonding, π-π interactions, or Van der Waals forces.

Due to their high molar absorption coefficient, high refractive index, and absorption/emission properties in violet and visible region, P and Pc are applied as solar cells[16], opto-chemical and electrochemical sensors [17]. The tendency of Pc to self-assemble on a substrate is higher than that of porphyrin, and Pc has been widely applied as light-harvesting/donor molecules in solar cells owing to high absorption extinction coefficients in the visible region, and p-type semiconducting behavior [18]. Refractive index (n) and extinction coefficient (k) of Pc film at visible spectra region were rather steady compared to ultra-violet region with a value as $n = 1.6–1.9$, $k = 5 \times 10^8$ M^{-1} cm^{-1} with optical energy gap equals to 1.97 eV [19].

P and Pc derivatives have been studied in the thin-film state for different optical chemical detection with various instrumental methods. In the application of ZnPc films, visible light absorption [20], the transition temperature of crystalline form, surface morphology, and the molecular alignment of Pc films grown on different substrates [21][22][23], were studied. Besides, P and metallo-Pc derivatives were fabricated on different substrates and used as opto-chemical detectors of HCl [17], alcohol vapors [24], amines, ketones, alkanes, and pyridine vapors [25]. All of these researches indicate that thin-film fabricated with the blend of derivatives of P and Pc can be considered as one of the promising candidates for gas sensors.

3. Conclusions

Opto-chemical sensing behavior of metal-free porphyrin and zinc phthalocyanine thin film, with the exposure of HCl, m-xylene, and styrene gases in planar optical waveguide system, was studied. The PWOG response behavior of the film presents sufficient linear correlation with the spectral absorbance changes; the LOD and LOQ values are calculated from the calibration curve, within the range 25–1500 ppm, that is linearized by using the logarithm of the concentration of the gases. Film-gas interaction mechanism is discussed in terms of protonation, π-π stacking between macrocyclic molecules in the sensing film and the analyte aromatic molecules.

This system will be studied in the future with real samples in the presence of multiple components, to improve the application of this device in analysis.

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