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Production and Characterization of Thin Film Materials for Indoor Optical Gas Sensing Applications

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Abstract. Pure and Nile-Red-doped polyimide and porphyrin films have been deposited and their optical response to different organic vapours has been tested. Polyimide films were obtained by spin coating a solution containing 4,4'-4,4'-(hexafluoroisopropylidene) diphthalic anhydride and 2,3,5,6-tetramethyl-1,4-phenylenediamine. Free, cobalt and iron chloride 5,10,15,20 *meso*-tetraphenyl porphyrin films were deposited by spin coating and by high vacuum evaporation. Exposure to water, ethanol and isopropanol vapours produce reversible changes of the fluorescence features of both pure and doped polyimide films. Exposure to methanol, ethanol and isopropanol vapours gives rise to changes of the optical absorption of porphyrin films. The results of the optical measurements point out that the synthesized films can be used for the detection of volatile organic compounds.

1. Introduction

In the search for new and more efficient optical sensors for gases and vapors a large number of phenomena and a wide range of materials have been explored by the scientific community [1,2]. Growing attention has been paid to the indoor vapor detection and monitoring in order to prevent fatal accidents and to improve the air quality in confined spaces such as factories and laboratories. Several types of optical responses to vapors have been investigated, involving changes of fluorescence, optical absorption, refractive index and surface plasma resonance features [3].

Organic matrices are currently attracting a great deal of interest because of the wide range of physical and chemical properties which can be tailored by varying their composition. Among the different classes of organic materials, aromatic polyimides and porphyrins are promising materials owing to their peculiar thermal, optical and chemical properties.

In this work polyimide films have been deposited by spin coating a solution of polyimide powder derived from 4,4'-4,4'-(hexafluoroisopropylidene) diphthalic anhydride (6FDA) and 2,3,5,6-tetramethyl-1,4-phenylenediamine (DAD). This polyimide exhibits high permeability, optical transparency and fluorescence emission. The changes of the fluorescence features of pure 6FDA-DAD films and of 6FDA-DAD films doped with the solvatochromic dye Nile Red (NR) have been monitored under exposure to different organic vapors, namely water, isopropanol and ethanol.

Free (H_2 TPP), cobalt (CoTPP) and iron chloride (FeTPPCL) 5,10,15,20 *meso*-tetraphenyl porphyrin films have been deposited by spin coating and by high vacuum evaporation. The changes of the optical absorption of TPPs' films have been measured during exposure to methanol, ethanol and isopropanol.

2. Experimental

The 6FDA-DAD polyimide precursor monomers were poly-condensed in a NMP solution and the resulting poly-amic acid was chemically imidized. The polyimide powders were precipitated in water and redissolved. The solution was spin-coated on quartz substrates and thermally treated in vacuum at 200 °C. Nile Red doping was performed by adding the dye to the solution (1.0 % weight of solid).

Thin films of free, cobalt and iron chloride tetra-phenyl porphyrin (H_2 TPP, CoTPP and FeTPPCL) were deposited onto quartz substrates by vacuum evaporation (VE) (crucible temperature of 300°C, working pressure of 5×10^{-4} Pa). Thin films were also obtained by spin coating (SPIN) by solving the compounds in C_6H_{10} , spinning the solution for 30 sec at 800 rpm and curing in air at 60 °C for 10 h.

For the optical testing under vapour exposure, the samples were put into a chamber connected to a Jasco 770 spectrofluorimeter (fluorescence measurements) and to a Jasco V-570 spectrophotometer (absorption measurements). Two mass flow controllers were used to adjust the flow rate of pure N_2 and of N_2 -diluted vapour to the chamber. All the samples underwent a thorough conditioning procedure with the vapours of the various analytes. Complete fluorescence or absorption spectra and intensity changes at fixed wavelength were taken at different analyte concentrations in N_2 . All the measurements were performed at room temperature.

3. Results and discussion

3.1. Optical response of polyimide films

Pure 6FDA-DAD films exhibit a fluorescence emission band peaked at about 500 nm, whose excitation feature is placed in the UV range with the maximum at about 290 nm. In presence of the different vapours the band intensity lowers and the maximum shifts to longer wavelengths as can be observed in figure 1. The change of the fluorescence band depends on different parameters: the hydrogen bond strength between analyte and polyimide, the analyte molecule sterical hindrance and the polyimide intrinsic permeability to the different molecules. The hydrogen bond strength affects both the fluorescence intensity and the peak position.

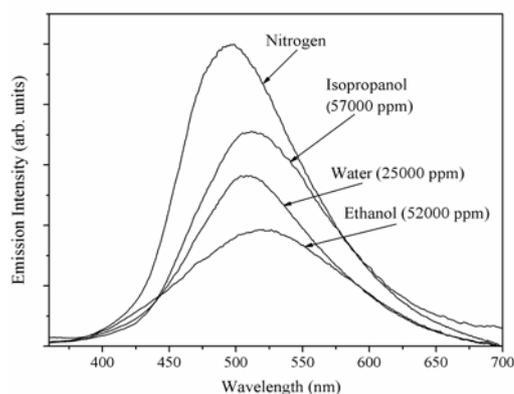


Figure 1. Intrinsic emission band (λ_{ex} 290 nm) of 6FDA-DAD during exposure to nitrogen, isopropanol, water and ethanol.

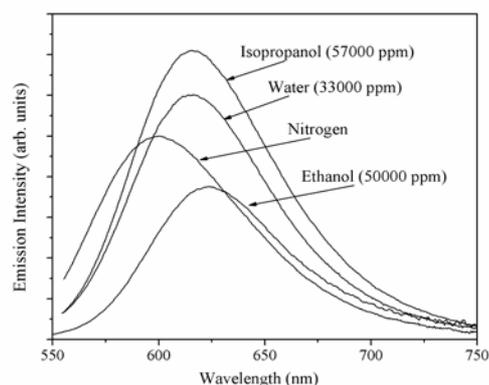


Figure 2. Emission band (λ_{ex} 545 nm) of NR-doped 6FDA-DAD during exposure to nitrogen, isopropanol, water and ethanol.

NR-doped 6FDA-DAD films exhibit an emission band peaked at 600 nm, which shifts to longer wavelengths in presence of the different analytes and whose intensity decreases with ethanol and increases with water and isopropanol (see figure 2). The intensity change is related to different parameters: the formation of hydrogen bonds with the analyte and the change of the polymer structure

around Nile Red. The former effect results in a lower fluorescence emission, while the latter increases the band intensity when the polymeric chains are less tightly packed around the dye. The resulting fluorescence features depend on the combined contribution of the described mechanisms.

Dynamic measurements of pure 6FDA-DAD films were made by exciting at 290 nm and measuring the emission at 465 nm at different vapor concentrations and as a function of time. In figure 3 both the dynamic response to ethanol and the absolute value of the relative optical response (ROS) for the three vapors at different concentrations are shown. The response times are tens of seconds for water and ethanol and a hundred of seconds for isopropanol. The detection threshold is about 500 ppm for ethanol and 1000 ppm for water and isopropanol. The response is related to the vapor species and concentration: 6FDA-DAD films exhibit a higher sensitivity toward ethanol at low concentration with respect to water and isopropanol; at higher concentrations the sensitivity to the two alcohols is low and that to water is higher, owing to the smaller size of water molecule.

Dynamic response of Nile-Red-doped polyimide films were made by exciting at 510 nm and measuring the emission at 585 nm. For these samples the response times are in the order of tens of seconds for each analyte. Detection threshold is about 500 ppm for each analyte. NR-doped polyimide films exhibit a stronger response to water and ethanol with respect to isopropanol (figure 4).

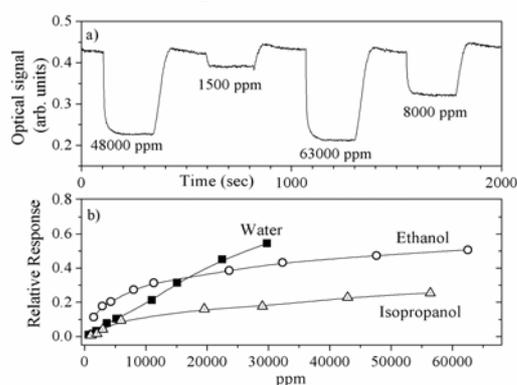


Figure 3. a) Dynamic response to ethanol of 6FDA-DAD films. b) Relative response of 6FDA-DAD intrinsic fluorescence, as a function of the analyte concentration, for water, ethanol and isopropanol.

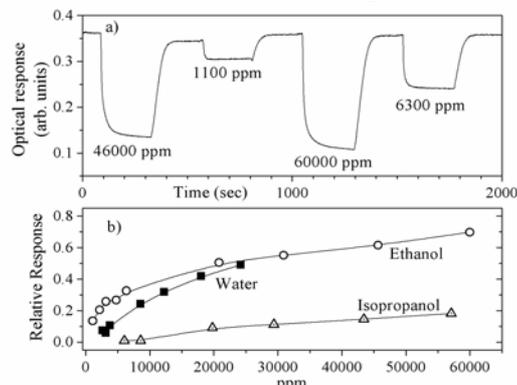


Figure 4. a) Dynamic response to ethanol of NR-doped 6FDA-DAD films. b) Relative response of NR-doped 6FDA-DAD films as a function of the analyte concentration.

3.2. Optical response of porphyrins films

Optical absorption spectra of the porphyrins films before exposure (A_0) and after exposure to the analytes (A_1) were acquired in the 350-750 nm range. The percentage absorbance change was then calculated as: $\Delta A\% = 100 \times (A_1 - A_0) / A_0$. Figure 5 shows absorption spectra and $\Delta A\%$ graphs of VE and SPIN samples of H_2TPP exposed to ethanol. VE samples show higher optical absorbance changes in comparison with the SPIN ones with all the organic tested vapors, pointing out stronger interactions with the analyte molecules: this is due to the solvent retention in the SPIN samples which hinders the adsorption process of analyte molecules.

The dynamic response of the samples has been tested by measuring the absorbance change at a fixed wavelength: the evolution of the Soret band (410 nm) intensity of the SPIN and VE samples of FeTPPCL as a function of time upon exposure to 3000 ppm of ethanol is shown in figure 7. The VE response exhibits a fast increase after ethanol input (at 100 s) followed by a slow increase until saturation is reached. After ethanol output (at 700 s) the signal rapidly decreases and, by 950 s, the original value is recovered. It is noteworthy that the behavior of the SPIN sample is characterized by a smaller absorbance change (about a third) and by a slower response.

4. Conclusions

This work showed that 6FDA-DAD fluorinated polyimide films, both pure and doped with Nile-Red dye, and porphyrins films deposited by vacuum evaporation and spin coating are suitable for optical sensing of volatile organic compounds owing to fluorescence and absorption changes, respectively, as induced by the permeation of the different analyte molecules. The response is related to the analyte species and depends on both the different permeability into the film and the different strength of the hydrogen bond developed by the vapor molecules.

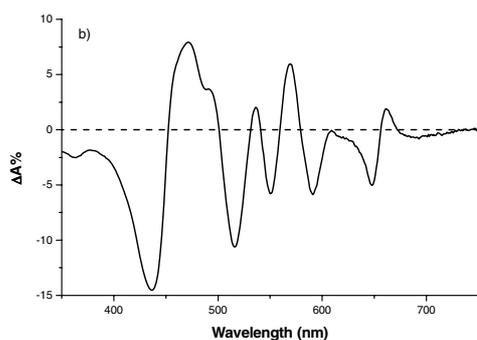
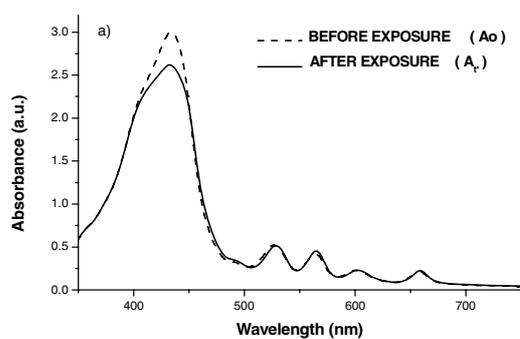


Figure 5. a) Absorbance spectra of VE H₂TPP sample before (dashed line) and after exposure (solid line) to ethanol; b) the corresponding $\Delta A\%$ graph.

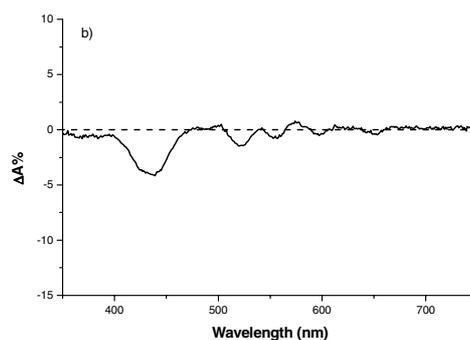
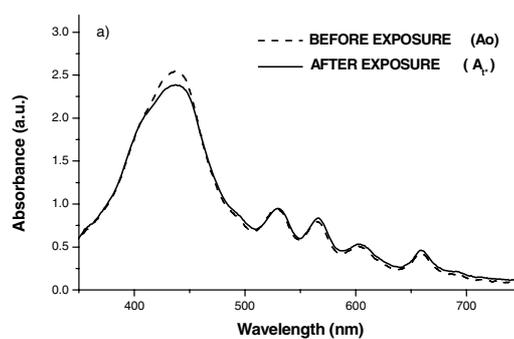


Figure 6. a) Absorbance spectra of SPIN H₂TPP sample before (dashed line) and after exposure (solid line) to ethanol; b) the corresponding $\Delta A\%$ graph.

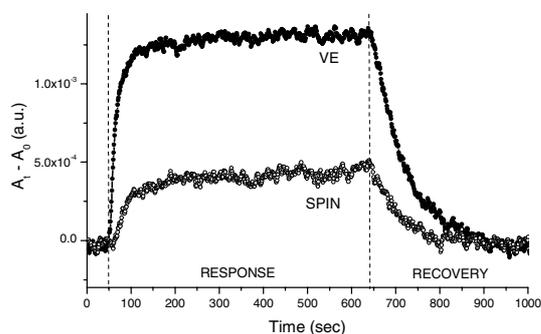


Figure 7. Absorbance variation of the Soret band (410 nm) of VE (●) and SPIN (○) films of FeTPPCL as a function of time during exposure to 3000 ppm of ethanol.

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