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Sensing Characteristics to Acid Vapors of a TPPS Coated Fiber Optic: a Preliminary Analysis

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***Abstract*—**In this work we report on preliminary analysis of a novel optoelectronic gas sensor based on an optical fiber integrated with a tetrakis(4-sulfonatophenyl)porphyrin (TPPS) thin film. The sensitive materials are selectively deposited on the core region of a fiber tip by UV light induced deposition technique. A simple and cheap process which can be easily extended to different porphyrin derivatives. When the TPPS film on the fiber tip is exposed to acid and/or base vapors, dramatic changes occur in the aggregation structure of the dye molecules in the film, from J- to H-type, resulting in a profound modification of their corresponding reflectance spectra. From the achieved experimental results it is evident that the presence of intense and narrow band peaks in the reflected spectra could be monitored to detect hazardous vapors.

***Keywords*—**Optical fiber sensor, Porphyrins, Thin films UV-induced deposition, TPPS.

I. Introduction

ENVIROMENTAL monitoring of air, water, and terrestrial zones for compounds that may pose a risk to human or ecosystems health is a critical part of efforts directed toward pollution prevention, industrial and agricultural waste regulation, and cleanup of hazardous waste sites by the environmentalists [1]. Due to the scope and enormous expense associated with this task, there exists a clear need for field-portable, real-time, and cost-effective environmental monitoring technologies.

In recent years, great efforts have been dedicated to realizing chemical sensors based on the integration of proper sensitive layers and suitable high-sensitivity in-fiber transducing mechanisms [2]-[3]. The sensitive element is the interface between the transducer and the external environment so that the nature, the selectivity, and sensitivity of a chemical sensor depend upon these interactive materials. These materials should optimize specific interactions with a target analyte, or a narrow class of analytes, to provide a fast and reversible diffusion of the penetrants and small recovery times, and should maintain the physical state as well as the geometry over several cycles of use, in order to avoid hysteresis effects, thus ensuring the reproducibility [2]. The natural step following the selective recognition of an analyte from the sensitive layer is the signal transduction, and thus the choice of the opportune technique to read the physical or chemical changes occurring at the sensing part. Optical transduction techniques are very attractive in chemical sensing applications as compared with electronic counterparts. They offer numerous advantages due to some unique characteristics such as immunity to electromagnetic interference, small size, light weight, low cost, and the possibility to use them in a harsh environment [3]-[6].

In this respect porphyrins and their metal derivatives have been large investigated as sensitive layer of novel sensors for their ability to interact with many different chemical species with consequent changes in their photophysical properties [7]. The simplicity in synthetic protocols leading to porphyrin molecules as well as their linear and non-linear optical properties characteristics for this class of molecules [8]-[10] coupled with simple deposition techniques such as layer-by-layer electrostatic absorption [11], self-assembling monolayer [12] and the more recent UV-light induce deposition [13], make this class of materials very attractive to develop new sensing configurations. The idea to integrate a porphyrin layer with optical fiber technology to realize novel optoelectronic sensors attracted a lot of interest in past years. Various porphyrins have been employed in combination with complicated bifurcated optical probes to detect chemical species like berberine, mercury ions and picric acid [14]-[15]. Recently, alternative fiber optic configurations have been also investigated [16], [17]. First, an acid-sensor based on protonation of a porphyrin solution within a single-hole structured optical fiber has been reported in the literature [16]. In this latter case, the critical issue remains the geometrical complexity of the experimental setup: two different fibers need to be perfectly aligned to measure transmitted spectra, while a gap in between is requested to allow the diffusion of acid. As well, a gas sensor able to detect ammonia emitted from human skin has been obtained through coating an unclad fiber with a multilayered porphyrin film [17]. However, while cladding removal permits light interaction with the active multilayer, the final device would exhibit poor mechanical robustness.

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This paper presents preliminary results of a novel optoelectronic sensor capable to detect the presence of acid vapors based on an optical fiber tip coated with tetrakis (4-sulfonatophenyl) porphyrin thin film. When the TPPS film on the fiber tip is exposed to acid and/or base vapors, dramatic changes occur in the aggregation structure of the dye molecules inside the film, from J- to H-type. This results in a profound modification of the reflected spectral features appearing in the signal. In particular the reflected spectrums of J-aggregates, which form in the presence of acid vapors, exhibit an intense and narrow band around 490 nm, which completely disappear in presence of basic vapor. In this work, we will initially focus our attention on the deposition approach, based on UV-light induced chemical process, capable to selectively deposit TPPS thin film on the core region of the fiber tip. Successively, the sensing properties of TPPS-coated fibers are investigated towards the presence of acid/basic vapors.

II. Deposition of Thin Film

This section deals with the deposition of TPPS film on fiber optic tip. Methods for the deposition of porphyrin layers have been investigated in past years [12], [18]. Recently an efficient approach consisting in a UV-induced deposition of these molecules has been demonstrated on various planar surfaces, leading to the growth of discrete crystals or uniform thin films [5], [14]. Here, this technique has been coupled to fiber optics technology to take advantage of the versatility of the optical device, which can act both as a waveguide for the UV-light triggering the deposition processes, and as a substrate for the film growth.

To this aim a multimode optical fiber with 200 μm core and 240 μm outer diameter (from Ocean Optics) was selected for its capabilities to propagate in the UV-VIS range.

Fiber optic terminal is first carefully cleaved by a precise cleaver in order to achieve a flat silica surface, as schematically reported in Fig 1(a). The successive step consists into the dipping of the cleaved tip of a multimodal optical fiber in a TPPS solution in dichloromethane (CH_2Cl_2) while the UV-light is coupled with optical fiber, Fig 1(b). As previously reported [19], the UV-induced TPPS deposition occurs by the following steps: (i) the slow decomposition of the halogenated solvent by UV photons, with the localized formation of hydrochloric acid (HCl) near the fiber end; (ii) the consequent protonation of the dye molecules by the tip with a reduction in their solubility; (iii) the deposition of the protonated dyes as self-assembled thin film right at the surface of the fiber tip [8], [13].

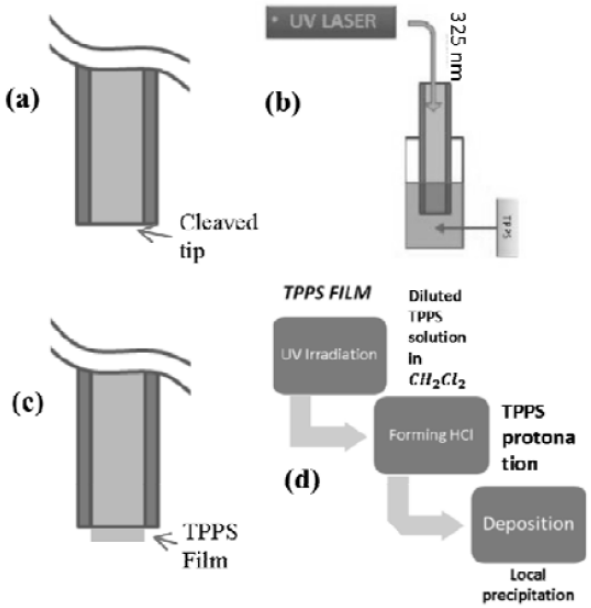

Fig. 1 scheme of (a) cleaved optical fiber, (b) deposition setup, (c) the deposited fiber, and (d) The deposition process

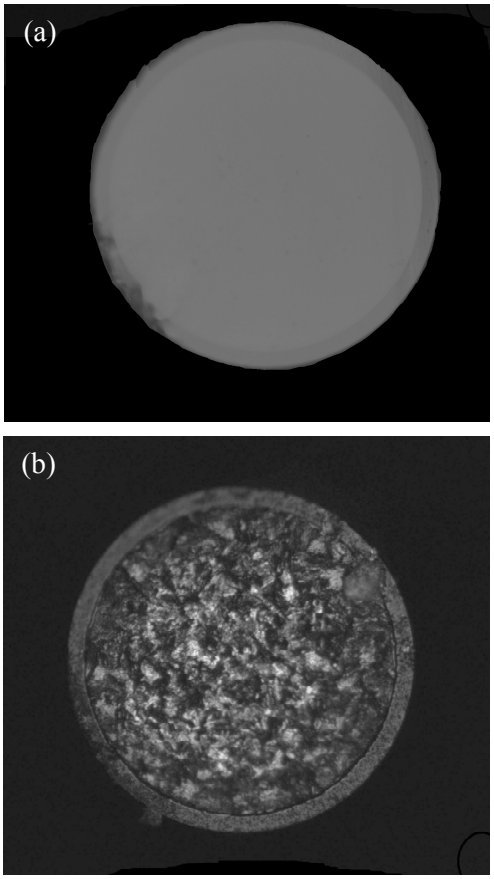

Fig. 2 Microscope images of (a) pristine and (b) TPPS deposited fiber tips

Here a He-Cd laser (325 nm; 9.5 mW power) was employed as UV source to irradiate dilute TPPS solution in CH_2Cl_2 (~10^{-5} mol L^{-1}).

It is worth noting that during the UV radiation the localized formation of HCl at the fiber end occurs principally near the core region (since the UV is guided in the fiber core). This results in a self-confinement of the deposition process on the core as schematically plotted in Fig. 1(c). The deposition process is resumed in the Fig. 1(d).

Fig. 2(a) and 2(b) compare microscope images of pristine and deposited fiber tips, respectively, in the former being clearly distinguishable core and cladding regions, and the crack at the bottom right being a cleaving defect. TPPS deposition is achieved after 150 minutes of irradiation and it is clearly evident that the deposition principally occurs on the core region due to self-alignment of the deposition process.

It is worth noting that simplicity of deposition process of TPPS film and its successful results could be easily extended to different porphyrin derivatives possibly leading to a simple multi-detection of various chemical species in future works.

III. Spectral Analysis

This section reports the spectral analysis of the TPPS deposited fiber highlighting relevant spectral features dependent on the acid/basic vapor exposure. In particular here the attention is focused on the spectral analysis in visible range of the light signal reflected from the fiber tip with TPPS coating. The optoelectronic setup for the spectral characterization is schematically plotted in Fig. 3. It includes an optical spectrometer in visible range (Avantes AvaSpec mod. 2048) and a 2×1 coupler (50% power splitting in both arms) which allows to separate the incident light emitted by a broadband light source in visible range, from the reflected light which has interacted with thin film (chemical interface).

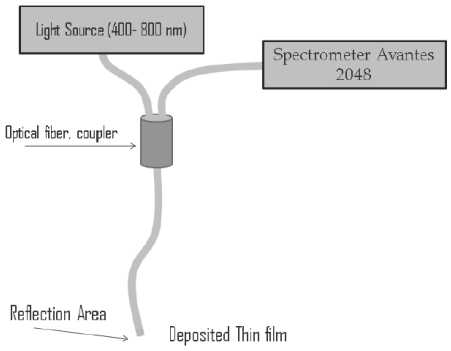

Fig. 3 Optoelectronic setup for reflected spectra analysis

The reflected spectra have been normalized with the spectra reflected from the bare fiber to remove the effect of non-flat source and detector sensitivity.

The reflectance spectra of the pristine and TPPS coated fiber tips are presented in Fig. 4. Obviously, the former consists in a constant line at 100% (due to the self-normalization), while the self-assembled TPPS thin film induces a quasi-constant attenuation of about 40% in the reflectance spectrum (see solid line in Fig. 4). From this consideration it seems that there are not significant spectral features attributable to the TPPS film deposition except for an uniform decreasing of the reflected light intensity in the entire investigated spectral range.

A dependence of the signal attenuation from the time of UV exposure, which can be probably ascribed to a dependence on the film thickness, has been observed measuring weaker reflected signals in the presence of longer exposures. This phenomenon is still under investigation.

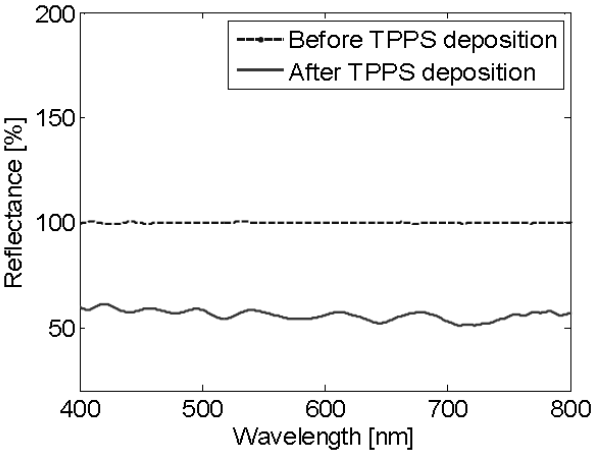

Fig. 4 Reflectance spectra before (blue line) and after (red line) deposition, showing an approximate 40% attenuation of the reflected light

To investigate the sensing capabilities in the detection of acid and basic vapors the fiber tip covered by the functional organic layer was cyclically exposed to different vapors as ammonia (NH_3) and hydrochloric acid (HCl) at room temperature and pressure. The fiber tip is put in contact first with ammonia vapors, given that the as-deposited film is acidic in nature (due to deposition mechanism). The reflected spectrum is plotted in fig. 5 (dashed red). As a consequence of the NH_3 exposure the reflected signal changes consistently: in particular a modulation of the quasi-flat signal is now evident, due to the absorption spectrum of TPPS H-aggregates, where the monomers adopt a face-to-face arrangement. As the coated fiber was exposed to hydrochloric acid vapor (for the first time) the reflected spectrum assumes a quasi-flat behavior very close to the solid line of fig. 4 (just after deposition) except for the presence of a small peak at 490nm (slightly higher than the baseline value).After a few cycles switching between exposure to acid and basic vapors the spectral response of the fiber tip coated by the functional organic layer significantly changes In the presence of acid, the spectrum is now characterized by the presence of narrow and intense peak close to 490 nm (solid line in fig. 5) [8]. This peak, which is due to resonant scattering of the incident light [20], is typical for TPPS J-aggregates, and it achieves reflectance values

which are almost twice as intense as the reference signal. J-aggregate formation is favored by water which forms in situ after cyclic between NH_3 and HCl vapors.

Further exposures to acid and basic vapors permit to cycle between J- and H- type aggregates, respectively while the spectral response switch from solid to dashed line with good repeatability. This switching process presents a good reproducibility over at least 10 cycles, and response times in the order of few seconds.

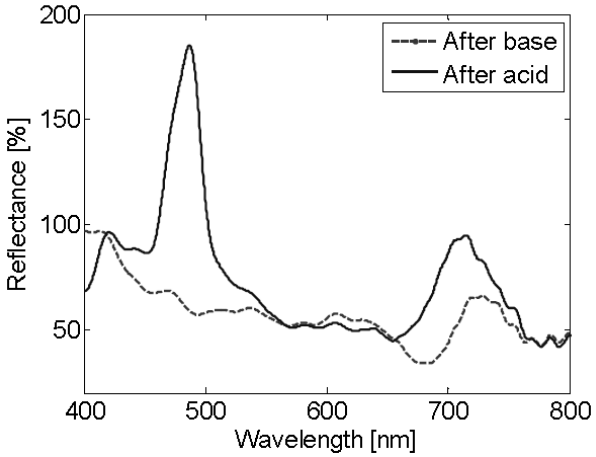

Fig. 5 The spectrum of acid exposed (blue) compared with base exposed (red) thin film

From these results it is reasonable to believe that the proposed device can act as technological platform to develop novel fiber optic sensors for the detection of acid and basic vapors. Further works aimed to complete characterize such structure in terms of response time, repeatability and aging are currently in progress.

IV. Conclusion

In the current study, the working principle of a novel sensing configuration consisting of TPPS thin films deposited on fiber optic interfaces is reported. The simplicity of the proposed configuration combined with the narrow spectral features sensitive to acid and base vapors encourage us to propose such configuration to realize novel sensing device. The obtained results are a promising starting point for further investigations aiming to assess the dose/response behavior of the device, as well as the effects of humidity and pressure on its sensing properties.

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