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journal homepage: www.elsevier.com/locate/snbA transparent TMPyP/TiO₂ composite thin film as an HCl sensitive optochemical gas sensorManuel Cano^{a,b,*}, Pedro Castellero^{a,c}, Javier Roales^a, José M. Pedrosa^{a,*}, Stuart Brittle^b, Tim Richardson^b, Agustín R. González-Elipe^c, Angel Barranco^c^a Departamento de Sistemas Físicos, Químicos y Naturales. Universidad Pablo de Olavide, Ctra. Utrera Km. 1, 41013 Sevilla, Spain^b Physics and Astronomy Department, University of Sheffield, Hicks Building, Hounsfield Road, Sheffield S3 7RH, United Kingdom^c Instituto de Ciencia de Materiales de Sevilla, Universidad de Sevilla-CSIC, Américo Vespucio 49, E-41092, Sevilla, Spain

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ABSTRACT

Tetracationic porphyrin (TMPyP) molecules were incorporated into an optically transparent TiO₂ thin film, prepared by Glancing Angle Physical Vapour Deposition (GAPVD), by simple infiltration (at pH 6.4). The preparation of optically transparent TMPyP/TiO₂ composite thin films provides a method for the integration of the porphyrin molecules into photonic devices for direct monitoring of gases. Previously, UV-visible and fluorescence spectral techniques have been used to study the reversible protonation of TMPyP in aqueous solution. The optical spectrum of TMPyP shows an intense Soret band at 423 nm with a 22 nm red shift upon protonation by HCl. The experimental conditions for monitoring the concentration of HCl gas by absorption spectroscopy have been optimized. The maximum absorbance change was observed at the Soret band wavelength. A selected temperature of 80 °C and a 300 s recovery period were found to be the optimum operating parameters (response time $t_{50} = 16.8 \pm 0.7$ s). The composite with smaller surface concentration of TMPyP ($\Gamma = 0.3 \times 10^{-9} \text{ mol cm}^{-2}$) presented the best detection limit (0.1 ppm). The response of the composite sensor was highly stable for several months.

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1. Introduction

The need to control the emission of acidic gases in the atmosphere has increased in recent years, mainly because these compounds are hazardous to the human body and a source of acid rain. One of those acids is hydrogen chloride (HCl) gas, which now is strictly regulated in the workplaces of many countries. HCl gas is primarily produced by burning fuels that contain chloride and incinerating waste that contains plastics [1]. For this reason, HCl sensors with high sensitivity and reliability are in great demand [2–6]. Optochemical sensing of HCl gas using organic dyes is an attractive technique because it functions at room temperature to detect gas concentrations at the ppm level or less. The use of porphyrin dyes has been recently examined for the detection of HCl gas [2–4]. Different porphyrins and methods to prepare sensitive thin films were used in these studies. For example, Supriyatno et al. [2] examined a tetraphenylporphyrin dispersed in copolymers, Itagaki et al. [3] used a tetra(4-hydroxyphenyl)-porphyrin dispersed on sol-gel composite films, and Kalimuthu and John [4] studied a

meso-tetramesitylporphyrin deposited by direct coating onto glass. In the first two investigations, it was demonstrated that the sensitivity of the composite sensors was strongly affected by the nature of the matrices that determines the interaction between porphyrins and the analyte gases. Moreover, the third study showed a structural change from a planar to saddle conformation of the porphyrin ring upon protonation, which can result in a change in the aggregation state and may be detrimental for the interaction between the porphyrin molecule and the substrate. In turn, this effect may result in a loss of porphyrin during each exposure event, highlighting the necessity of using improved host materials to contain the sensing molecules.

In the present investigation, a new composite system is presented for HCl gas detection. The composite is based on meso-tetra(4-methylpyridinium)-porphyrin (TMPyP) as the sensing molecule and columnar optically transparent TiO₂ films, prepared by glancing angle physical vapour deposition (GAPVD) [7,8], as the host material. The incorporation of the porphyrin into the open microstructure of these TiO₂ thin films is performed by simple immersion into the dye solution and has been characterized previously [7]. The main advantages of the TMPyP/TiO₂ composite thin film are its high porosity, which allows an easy diffusion of the toxic gas; a low refraction index, necessary for its use as optical sensor; a good stability with temperature, facilitating the heating process to induce a fast recovery; and an efficient adsorption of

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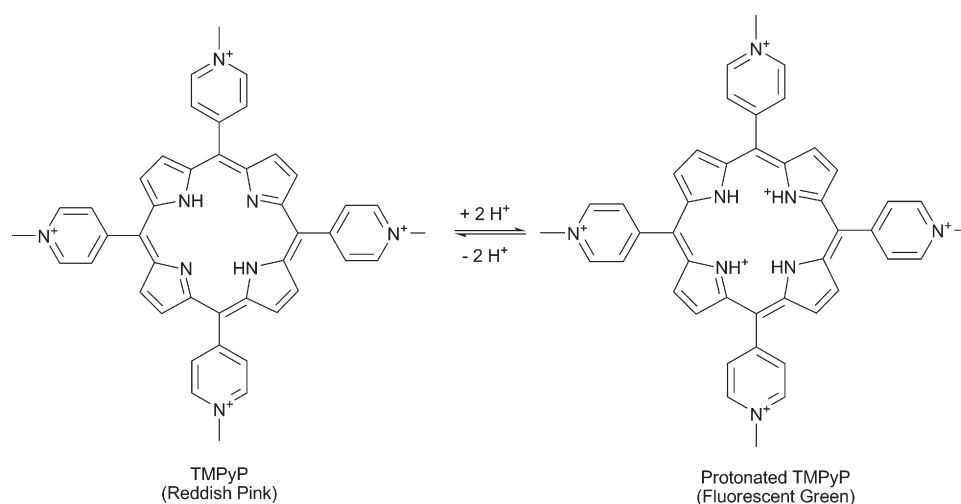


Fig. 1. Chemical structure of 5,10,15,20-Tetrakis(1-methyl-4-pyridyl)-21H,23H-porphyrin (TMPyP) and its protonated form.

the TMPyP by electrostatic interaction with the host medium. The exposure of the TMPyP/TiO₂ composite to HCl vapour leads to protonation of TMPyP as shown in Fig. 1. The protonation of TMPyP in water solution has been studied using UV-visible and fluorescence spectroscopies. The absorbance changes at the Soret band were used to monitor the presence of HCl in gaseous phase.

2. Material and methods

5,10,15,20-Tetrakis(1-methyl-4-pyridyl)-21H,23H-porphyrin (TMPyP, Aldrich) was used without further purification. All other reagents were Merck A.G. and used as supplied. Ultrapure water from a Millipore Direct-Q system (>18 MΩ cm) was used throughout. A scheme of the reversible process with the structure of the TMPyP molecule and its protonated form is presented in Fig. 1.

The TMPyP/TiO₂ composites were prepared using porous TiO₂ thin films as host materials. For this purpose, transparent and amorphous TiO₂ films were prepared by GAPVD at room temperature on glass substrates [7,8]. A characteristic of these films is that they are very porous and possess a tilted columnar microstructure [8,9]. For the present work the substrates were placed at an angle of 70° with respect to the evaporator source. The film thickness was approximately 350 nm.

Two solutions with different concentrations of TMPyP (5 and 100 μM) in water at the original pH (6.4) were used for the preparation of the TMPyP/TiO₂ composites. The infiltration time was 24 h in both preparations. The corresponding surface concentration Γ , was calculated by using UV-visible spectroscopy [7]. The TMPyP/TiO₂ composite was obtained by simple immersion of the TiO₂ thin films into water porphyrin solutions. The TiO₂ matrix prepared by GAPVD shows a high robustness and stability in water solution [7] as compared to other hosting materials such as polymers [2] or direct coating onto glass [4]. A sample with a $\Gamma = 0.3 \times 10^{-9} \text{ mol cm}^{-2}$ was obtained with a 5 μM TMPyP solution, whereas a $\Gamma = 1.9 \times 10^{-9} \text{ mol cm}^{-2}$ was produced for a 100 μM TMPyP solution [7]. After this, the samples were taken out from the solution and washed with water at the same pH. During this washing cycle, any dye molecule which is not incorporated into the host matrix is removed from the surface. The films were then dried in a two-step process: firstly by blowing nitrogen onto their surfaces for 5 min and then by a heating at 80 °C for 1 h. After these treatments, the composite thin films presented the characteristic yellowish colour of porphyrin thin films. The intensity of the colour was different between the two preparations with different TMPyP surface concentrations.

UV-visible spectra of the TMPyP water solutions were recorded on a Cary 100 Conc UV-visible spectrophotometer. Fluorescence spectra of both the TMPyP in dichloromethane-ethanol mixture and the composite TMPyP/TiO₂ films were recorded in a Jobin-Yvon Fluorolog3 spectrofluorometer. The TMPyP-TiO₂ composite films were exposed to HCl gas using a specially designed gas testing chamber comprising two Tylan FC-260 mass flow controllers, which deliver a mixture of pure N₂ and standard dry HCl gas (5 ppm) for the exposure stage, followed by pure N₂ for the recovery stage. The delivery of these gases was controlled and automated using a program developed using Labview software. For the exposure of the composite sensor films to higher concentrations of the acid, pure N₂ was pumped through a closed bottle containing HCl solution (see design [10]). The temperature of the HCl solution was maintained at 0 °C by submerging the bottle in iced water, therefore mixing the N₂ gas with the analyte at a known vapour pressure. The resultant mixture was then mixed again with a second supply of N₂ controlled with another Tylan FC-260 mass flow controller and then fed into the test chamber. The effect of the humidity was also controlled. To minimize the slight contribution of the water vapour to the composite sensor signal, a similar level of humidity was incorporated into the pure N₂ (recovery) as the HCl vapour (exposure). Before starting the measurement, the %RH level of the HCl vapour was evaluated and this information was used to regulate the pure N₂ humidity to this level.

The TMPyP-TiO₂ composite films to be tested were introduced in a test chamber [10] onto a Peltier heating stage capable of controlling the film temperature in the range 20–80 °C. The Peltier heating device contains an aperture in its centre to allow in situ UV-visible spectroscopy. The composite film spectra over the range of 350–850 nm (tungsten light source) were continually monitored during exposure and recovery using a World Precision Instruments "Spectromate" spectrometer. The spectra of the composite are presented in absorbance after subtracting the spectrum of the TiO₂ substrate.

All the experiments were carried out at least four times.

3. Results and discussion

3.1. Study of the TMPyP protonation in solution

UV-visible and fluorescence spectroscopic techniques were used to study the reversible protonation of the TMPyP. Fig. 2 shows the absorption spectra of the TMPyP in water during the exposure to different concentrations of HCl. The Soret band at 423 nm (Fig. 2a)

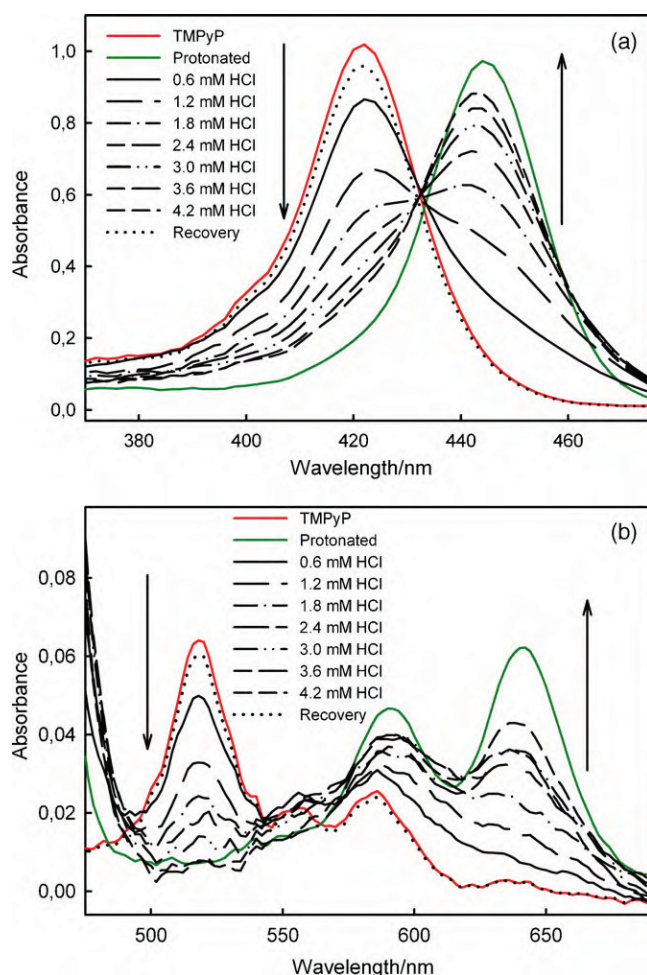


Fig. 2. Absorbance spectra of $1.5 \mu\text{M}$ TMPyP in water containing of 0, 0.6, 1.2, 1.8, 2.4, 3, 3.6, 4.2 mM of HCl, completely protonated with excess of HCl, and the recovered spectrum after addition of excess of ammonia to the sample with 4.2 mM of HCl. (a) In the Soret band region and (b) in the Q band region.

and the four Q bands at 518, 555, 584 and 634 nm (Fig. 2b) showed the expected intensities [11]. With this original D_{2h} molecular symmetry, the $Q_y(0,0)$ band at 518 nm appears as the most intense band and the $Q_x(0,0)$ band at 634 nm is the least intense one in the TMPyP molecule. The ability of the TMPyP molecule to become protonated in acid solutions is a well known property of this molecule (the pK of TMPyP is around 1.5 [11]) and it leads to a protonation of tertiary nitrogen resulting in changes in the Soret and Q bands [3]. In this case the Soret band featured a red shift of 22 nm, from 423 to 445 nm. This shift is bigger than that obtained for meso-tetramesitylporphyrin by Kalimuthu and John [4], indicating that TMPyP shows a more sensitive behaviour for HCl detection than the previous porphyrin. Moreover, the Q band region featured an important change since the original four bands turned into two bands due to the higher molecular symmetry (D_{4h}) and the degeneration of the excited state of the protonated porphyrin. All these changes in the spectrum resulted in the modification of the colour of the solution. After the protonation of TMPyP, the $Q_x(0,0)$ band at 634 nm became the most intense band with a 7 nm red shift (Fig. 3b) and the $Q_y(0,0)$ band at 518 nm became the least intense one. The $Q_x(0,0)$ band at 634 nm has been attributed to the formation of a dication [12]. The appearance of an isosbestic point at 432 nm in Fig. 3a clearly confirms the protonation of TMPyP. Addition of ammonia to the protonated TMPyP solution results in deprotonation, and therefore the change of the colour of the solution from fluorescent green to reddish pink.

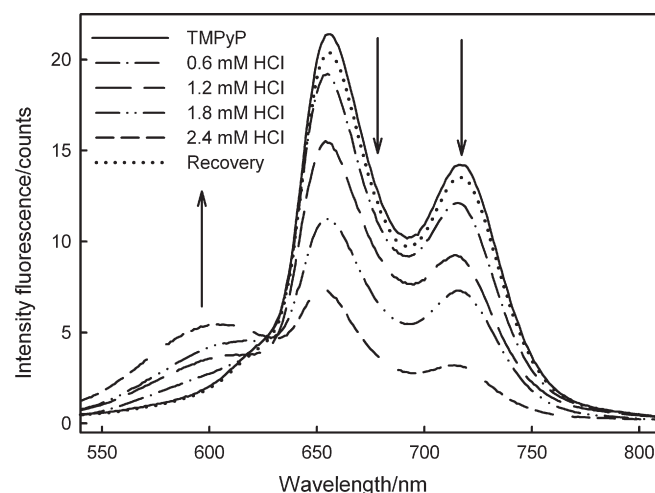


Fig. 3. Fluorescence spectra of $1.5 \mu\text{M}$ TMPyP in dichloromethane-ethanol mixture (excitation wavelength = 423 nm) containing of 0, 0.6, 1.2, 1.8, 2.4 mM of HCl, and addition of excess ammonia to the sample with 2.4 mM of HCl (Recovery).

Fig. 3 shows a representation of the fluorescence spectra recorded for the TMPyP in dichloromethane-ethanol mixture solution against addition of HCl aqueous solution. The excitation of TMPyP at 423 nm results in two well differentiated bands corresponding to the degeneracy of the lowest singlet configuration of the TMPyP [13]. These two bands, $Q(0,0)$ and $Q(0,1)$, are centred approximately at 654 and 716 nm respectively. In water solution, the bands appear at 666 and 704 nm and are less resolved than in dichloromethane-ethanol mixture whose emission spectrum is more similar to that obtained in the solid composite films (see Fig. 9). This difference has been attributed to a change in the resonance interaction between the pyridinium group and the π system of the porphyrin macrocycle due to the polarity of the media [14]. For aqueous solution, this resonance interaction increases and results in an overlapping between the two bands [11,14]. The exposure to HCl changes the shape of the whole emission spectrum with a drastic decrease in the intensity of the fluorescence spectrum. Similar results have been obtained by Kalimuthu and John [4]. This is mainly due to the loss of planarity of the porphyrin ring thereby increasing conjugation with the methyl pyridinium groups in solution.

The use of the TMPyP to develop a composite film as optical sensor is further justified by the fact that, according to Figs. 2 and 3, the absorption and fluorescence spectra almost recover fully their initial intensity and shape by addition of excess ammonia. This recovery of the shape of the spectra indicates that the process is reversible.

3.2. Detection of HCl gas by the composite TMPyP/TiO₂

The TMPyP molecules were infiltrated into the host TiO₂ thin films by their immersion in water solutions at controlled pH values. The TMPyP/TiO₂ composite film has been characterized in a previous work [7]. In order to address the interaction process within the composite films, the UV-visible spectrum has been recorded and the corresponding response in the presence of ~ 250 ppm HCl gas is shown in Fig. 4. The inset pictures show the colour difference between the composite film in the absence and presence of HCl gas. The wavelength of the Soret band (437 nm) appears red-shifted with respect to that in water solution [7] and was selected to monitor the absorbance change with respect to the concentration of the toxic gas.

Several parameters were tested in the gas testing chamber during the cycles of exposure and recovery in order to improve the

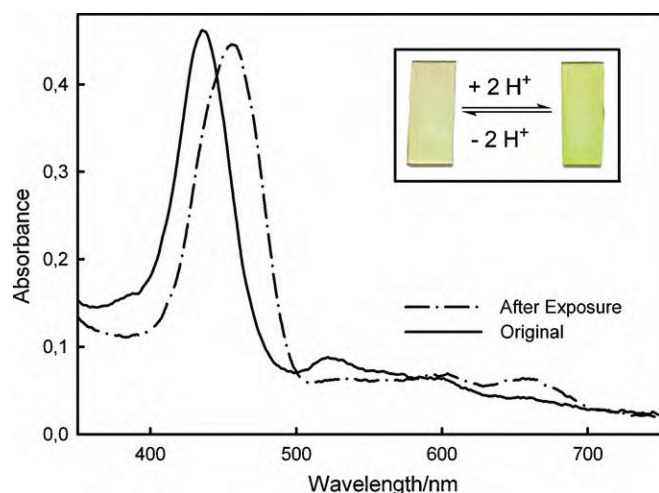


Fig. 4. (Top) Absorbance spectra for the TMPyP/TiO₂ composite thin film in the absence and presence of ~250 ppm HCl vapour. $\Gamma = 0.3 \times 10^{-9} \text{ mol cm}^{-2}$. (Inset) Images taken for the film at each stage.

behaviour of the HCl sensor. An important parameter is the temperature of the sensor. In this case, a Peltier heater was used to heat the films during the recovery phase. A high temperature produces a very fast recovery but it can also be detrimental for the stability of the porphyrins. Therefore, the selected temperature for the recovery phase was 80 °C. Other parameters to be optimized are both the exposure and the recovery time. Fig. 5 shows the variation time (at 25, 50, 100, 200 and 300 s) of the absorption spectra of the TMPyP/TiO₂ composite during the exposure to ~250 ppm HCl gas at 20 °C (Fig. 5a), and the recovery time when exposed to N₂ (g) at 80 °C (Fig. 5b). An exposure time of 300 s was found to be sufficient when the HCl gas concentration is lower than 1000 ppm.

Typical sensor responses of the TMPyP/TiO₂ composite at 437 nm for three different concentrations of HCl gas are shown in Fig. 6. The composite film shows a fast decrease in the absorbance after exposure to 1, 3 and 5 ppm HCl gas which implies the good sensing capability of our sensor towards HCl gas. The t_{50} parameter, defined as the response time at 50% of the maximum absorbance change during the gas exposure, was used and the value obtained was 16.8 ± 0.7 s. When the N₂ gas stream was directed to the film at 80 °C after reaching the equilibrium state, the absorbance increased until the original intensity was reached, suggesting the deprotonation of the TMPyP. This heating ensures a complete and faster recovery compared to other similar sensors [4]. A set of three successive exposures to HCl of the TMPyP/TiO₂ composite sensor is shown in Fig. 7. The sensor shows good response at a concentration of 3 ppm, with good reversibility and reproducibility.

The absorbance variation (ΔA) was obtained from the differences between the absorbance intensities of the composite film at 437 nm before and after the exposure to different HCl concentrations [12]. To obtain the calibration curve, the concentrations of HCl against the ΔA have been plotted. Table 1 shows the summarized analytical characteristics of two preparations with different concentration of TMPyP into the composite film. The limits of detection (LOD) were calculated according to the three signal/noise (s/n) criterion. As expected, comparing the calibration slope values obtained, the highest sensitivity was achieved for the composite film with more surface concentration of TMPyP ($\Gamma = 1.9 \times 10^{-9} \text{ mol cm}^{-2}$). However, the best LOD was obtained for the composite film with less surface concentration of TMPyP ($\Gamma = 0.3 \times 10^{-9} \text{ mol cm}^{-2}$). A slight improvement in the regression coefficient was found in case of the less concentrated preparation.

The fact that the highest slope value is obtained for the most concentrated preparation, suggests an enhancement of the sensor

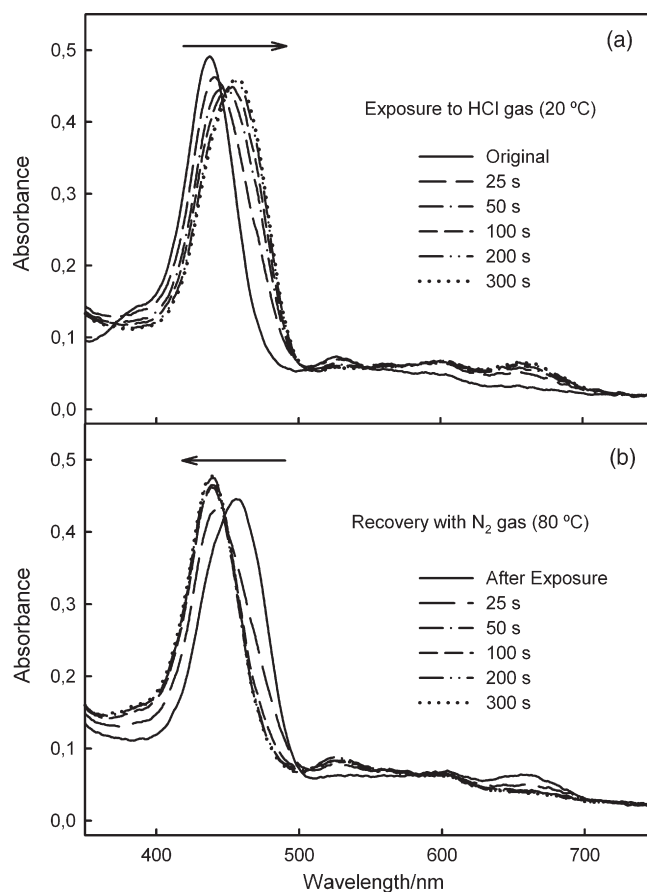


Fig. 5. (a) Temporal evolution of the absorbance spectrum of a TMPyP/TiO₂ composite film (25, 50, 100, 200 and 300 s) during the exposure to ~250 ppm HCl vapour at 20 °C. (b) Absorbance spectra of the TMPyP/TiO₂ composite during the recovery phase (25, 50, 100, 200 and 300 s), exposed to N₂ (g) at 80 °C. $\Gamma = 0.3 \times 10^{-9} \text{ mol cm}^{-2}$.

response with the increment of TMPyP molecules in the composite film. Nevertheless, an increment of the TMPyP yields a possible increase of the noise, and consequently a worse LOD and regression coefficient.

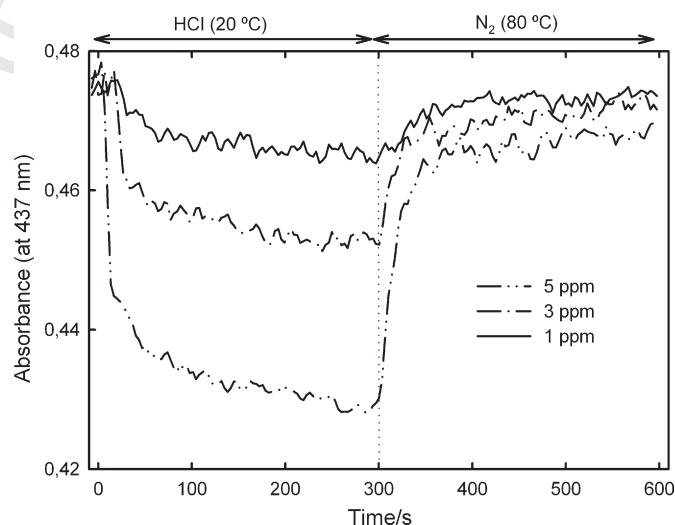


Fig. 6. Comparison of the absorbance changes at a wavelength of 437 nm during three exposure (5, 3 and 1 ppm HCl vapour for 300 s) and recovery (N₂ for 300 s) cycles for the TMPyP/TiO₂ composite film. $\Gamma = 0.3 \times 10^{-9} \text{ mol cm}^{-2}$.

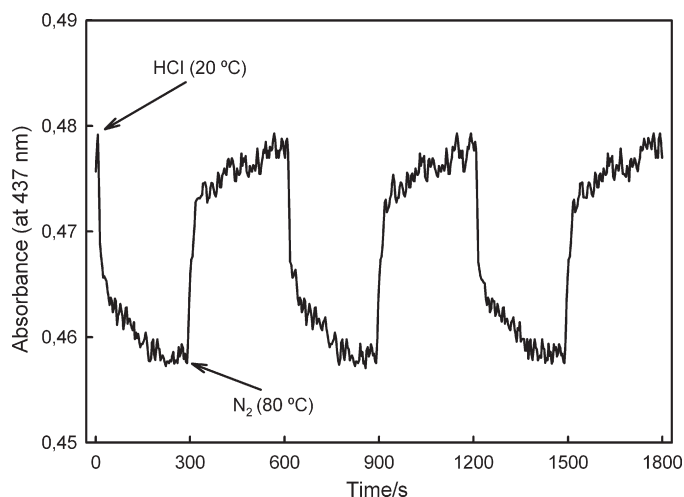


Fig. 7. Reversibility and reproducibility of the absorbance change of 437 nm during three cycles of exposure to 3 ppm HCl for the TMPyP/TiO₂ composite film. $\Gamma = 0.3 \times 10^{-9} \text{ mol cm}^{-2}$.

The reproducibility of the response of each composite was estimated from the response to 3 ppm HCl gas. We obtained a relative standard deviation (R.S.D.) of 3.7% for five successive determinations using the same TMPyP/TiO₂ composite. The obtained values show remarkable reproducibility (Table 1).

The stability of the sensor has been investigated by recording a weekly calibration curve for one month. After this period of time, ΔA_{max} becomes 84% of its initial value, although its decrease is not significant during the first 14 days. This demonstrates that the use of the columnar TiO₂ as host material allows a good stability of the porphyrin response with the time.

The TMPyP/TiO₂ composite presents two main advantages comparing the results with the obtained for other authors [2–4]. The first one is a faster response and recovery because of the high porosity and stability of the TiO₂ as host material, and the second one is the extremely low concentration of TMPyP necessary to obtain a sensing film with a good response to the analyte. These two features lead to a very little aggregation of the porphyrin in the solid film which is of great importance when designing dye-based optical gas sensors [15].

3.3. A future HCl gas detection by a fluorescence sensor

In order to further improve the sensing capability of the TMPyP/TiO₂ composite thin film an alternative technology based on emission fluorescence is now being tested. As shown in Fig. 8, the protonation of the TMPyP molecules into the TiO₂ thin film

Table 1

Analytical characteristics obtained from the calibration plots in the determination of HCl gas with two different TMPyP/TiO₂ composites films.

	$\Gamma = 1.9 \times 10^{-9} \text{ mol cm}^{-2}$	$\Gamma = 0.3 \times 10^{-9} \text{ mol cm}^{-2}$
Intercept (nm)	$(8.4 \pm 2.9) \times 10^{-4}$	$(8.0 \pm 0.3) \times 10^{-4}$
Slope (nm/M)	60.67 ± 3.23	35.65 ± 0.37
Regression coefficient (r)	0.9916	0.9997
Standard deviation of residuals ($S_{y/x}$)	2.8×10^{-4}	3.3×10^{-5}
LOD ^a (ppm)	0.52	0.10
R.S.D. (%)	4.4	3.7
Measurement wavelength (nm)	437	437

^a Criterion of signal/noise = 3.

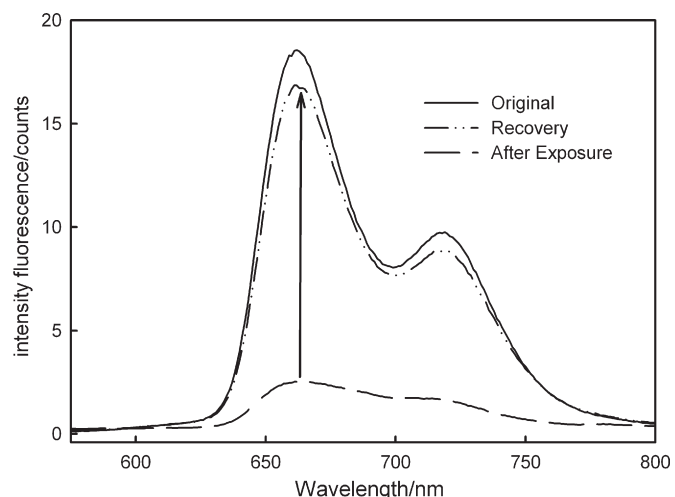


Fig. 8. Fluorescence spectra of the change and recovery under HCl exposure, recorded for the TMPyP/TiO₂ composite.

produces a drastic decrease in the fluorescence intensity. This spectrum is more similar to that in dichloromethane-ethanol solution as compared to the corresponding spectrum in water solution [7]. The higher change in the fluorescence intensity can improve the sensor performance in terms of sensibility, selectivity and LOD. Technical and analytical parameters such as response and recovery time, sensibility and analyte concentration dependence are being optimized and will be presented in a future publication.

4. Conclusions

The sensitivity of TMPyP to HCl vapour has been demonstrated through UV-visible spectroscopy. A new TMPyP/TiO₂ composite film has been developed for HCl gas detection. TMPyP can be used both in solution and within a composite thin film. The inclusion of the TMPyP in the composite entails a remarkable improvement in the solid state sensor, such as fast response, long-term stability and a low surface concentration of the used porphyrin compared to other previously researched systems

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