

## Research Article

# Fluorescent Rosamine/TiO<sub>2</sub> Composite Films for the Optical Detection of NO<sub>2</sub>

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Two rosamine derivatives were used as fluorescent sensors for the detection of NO<sub>2</sub>, a toxic and oxidant gas whose presence in populated areas needs to be controlled. Both compounds shared the same molecular structure but had different peripheral substituents: a carboxylic acid and an amino group. Transparent nanocrystalline TiO<sub>2</sub> films were prepared by screen printing and used as substrates, where the rosamines were incorporated by simple immersion into their respective solutions to form composite films. According to the molecular structures of the rosamines, the anchoring to the substrates was proposed to be by either covalent bonding and electrostatic interaction, or only electrostatic interaction, and was determined by the different substituents in each rosamine. Upon their exposure to increasing concentrations of NO<sub>2</sub>, both types of composite films showed intense and fast spectral changes, and the speed of response was related to the concentration of the gas. The anchoring mode and the electrophilic effect of the substituents determined the better sensing capability and the faster response shown by the carboxylic derivative in all cases.

## 1. Introduction

Xanthene dyes are a family of compounds characterized by an intense absorption and fluorescence that has been widely employed for a variety of technological applications [1–5]. Some of these compounds, such as the well-known rhodamines, have been largely used for the fabrication of solar cells or sensing devices [6–8], and their intense fluorescence emission makes them appropriate to be used as efficient probes for a number of applications [9–12]. Dye-based sensors, either based on UV-Vis or fluorescence spectroscopies, have proved to be a valid alternative to traditional gas identification techniques, such as gas chromatography, because of their lower operational cost and simplicity. Among them, those based on fluorescence usually feature better sensitivity and robustness justifying its choice over absorption spectroscopy [13].

Although possible, the use of fluorescent sensors in solution is not a practical approach. Most applications require the dye molecules to be supported on a solid substrate, especially those focused on gas sensing. Techniques such as spin coating or Langmuir-Blodgett allow the deposition of molecular films onto a solid substrate. However, the stability of these films is not always satisfying given the little or null chemical interaction between the adsorbates and the substrate [14], and, in the latter case, the procedure is particularly time-consuming. An important challenge derived from the deposition of dyes onto solid substrates is their strong tendency to form aggregates, which are known to be detrimental for gas sensing purposes [14]. Aggregation of dye molecules results in important changes in their photophysical properties, such as the broadening of the absorption bands because of the coexistence of various species, resulting in less-defined peaks and poorer monitoring of the spectral

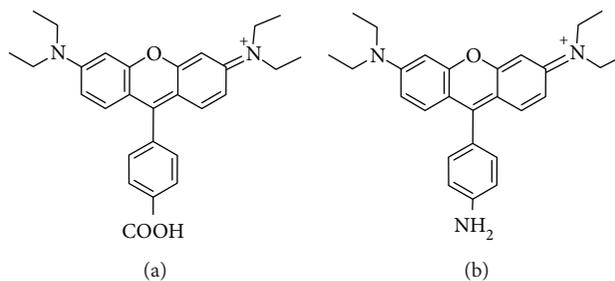


FIGURE 1: Molecular structures of (a) RosCOOH and (b) RosNH<sub>2</sub>.

changes induced by the sensed analyte and limiting their use as optical probes [15–17]. At the same time, high molecular aggregation hinders the access of gas analytes to the active recognition sites of the dyes, causing a delay in their spectral response [14]. Functionalized substrates with specific compositions and structures are among the preferred options to deal with these drawbacks [18–25]. Among them, the preparation of TiO<sub>2</sub> substrates following diverse methodologies has been used in the past for solar cell and gas sensing purposes, proving their suitability for the covalent anchoring of dyes with carboxylic groups [16, 26] or for the attachment by electrostatic interaction [27]. Specifically, nanocrystalline TiO<sub>2</sub> films prepared by screen printing have shown promising features in terms of transparency and porosity, besides their low cost and simplicity of fabrication.

Here, we use transparent nanocrystalline TiO<sub>2</sub> films prepared by screen printing as substrates for the incorporation of two rosamine derivatives featuring a carboxylic acid and an amino group, respectively. The anchoring of carboxylic rosamines to inorganic substrates prepared by physical vapor deposition has been previously studied with promising gas sensing results [28]. Our main objectives are to compare the film formation capabilities of both rosamines regarding their different molecular structures and to analyze the gas sensing properties of the rosamine/TiO<sub>2</sub> composites towards NO<sub>2</sub> gas. The detection of this toxic gas has attracted much attention given its elevated toxicity and participation in the formation of other pollutants. This is of particular concern in urban areas, where it can be found in dangerous concentrations as a result of the combustion of fossil fuels. We hypothesize that (i) the different substituents of both rosamines will be determinant in their respective anchoring to the substrates and (ii) it may result in different gas sensing responses.

## 2. Materials and Methods

**2.1. Chemicals.** The optimized synthesis of [9-(4-carboxyphenyl)-6-diethylamino-3-xanthenylidene]-diethylamine chloride (RosCOOH, Figure 1(a)) and [9-(4-aminophenyl)-6-diethylamino-3-xanthenylidene]-diethylamine chloride (RosNH<sub>2</sub>, Figure 1(b)) is described elsewhere [29]. Their molecular structures present strong similarities to the well-known rhodamine B, and hence their optical properties in dichloromethane solution are similar to those of this compound [29]. Dichloromethane was supplied by Sigma-Aldrich (Madrid, Spain) and was used as received.

**2.2. Fabrication of Rosamine/TiO<sub>2</sub> Composite Films.** Nanocrystalline TiO<sub>2</sub> films were prepared on glass substrates with Dyesol 18NR-T (Dyesol, Queanbeyan, Australia), a paste containing TiO<sub>2</sub> nanoparticles with an average size of 20 nm. We followed the screen printing procedure, which consisted in the application of one layer of the TiO<sub>2</sub> paste through a 43T mesh screen that led to the formation of a transparent TiO<sub>2</sub> film of 0.16 cm<sup>2</sup> active surface. Then, the substrates were sintered for 30 min at 500°C. The average thickness of these films was found to be about 1.8 μm according to scanning electron microscopy measurements (not shown). Incorporation of rosamines into the TiO<sub>2</sub> films was accomplished by simple immersion of the samples in 3.6 μM dichloromethane solution containing either RosCOOH or RosNH<sub>2</sub> for 24 h at room temperature. After this, the films were rinsed with dichloromethane for 10 min to remove any dye molecules that were not incorporated into the TiO<sub>2</sub> matrix and allowed to air-dry.

**2.3. Spectroscopy and NO<sub>2</sub> Exposure.** UV-visible absorption spectra were recorded using a Cary 100UV-Vis spectrophotometer (Agilent, Madrid, Spain). Photoluminescence spectra and sensing kinetics were recorded with a Hitachi F-7000 Fluorescence Spectrophotometer (Hitachi High Technologies, Krefeld, Germany). For the exposure to NO<sub>2</sub>, rosamine/TiO<sub>2</sub> composite films were inserted in a purpose-modified sealable fluorescence cuvette with a gas inlet and an outlet. The flow rates of gases were controlled using two Bronkhorst F-201FV mass flow controllers (Bronkhorst High-Tech BV, Ruurlo, The Netherlands). In order to remove any possible contaminating gases, dry N<sub>2</sub> was flushed into the cuvette before introducing the sample. After inserting the sample in the cuvette, a constant dry N<sub>2</sub> flow was kept to prevent contamination during thermal stabilization. A constant flow of NO<sub>2</sub> (5, 10, 20, 30, or 50 ppm) was obtained from a 50 ppm NO<sub>2</sub> cylinder from Abelló Linde (Cádiz, Spain) and its subsequent dilution with dry N<sub>2</sub> from the same supplier. In all cases, the gas flow rate entering the cuvette was 1 L/min. The gas mixture was introduced into the cuvette until complete saturation of the rosamine. All exposures were performed at room temperature.

## 3. Results and Discussion

**3.1. Spectroscopic Characterization of RosCOOH/TiO<sub>2</sub> and RosNH<sub>2</sub>/TiO<sub>2</sub> Composite Films.** UV-Vis absorption spectra

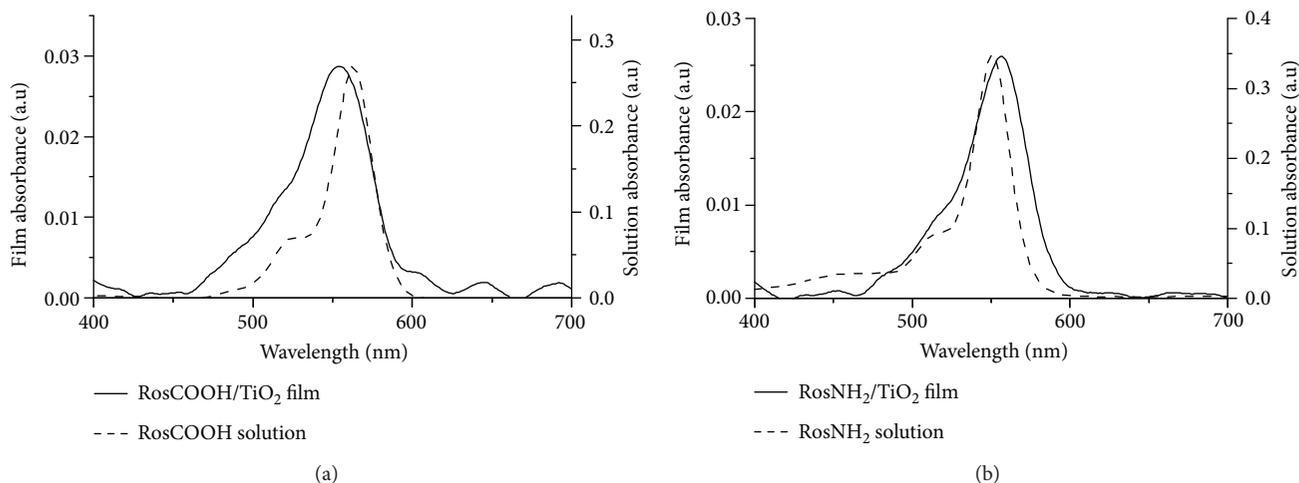


FIGURE 2: UV-Vis absorption spectra of (a) RosCOOH and (b) RosNH<sub>2</sub> in dichloromethane solution (dashed line) and anchored to nanocrystalline TiO<sub>2</sub>-based composite films (solid line).

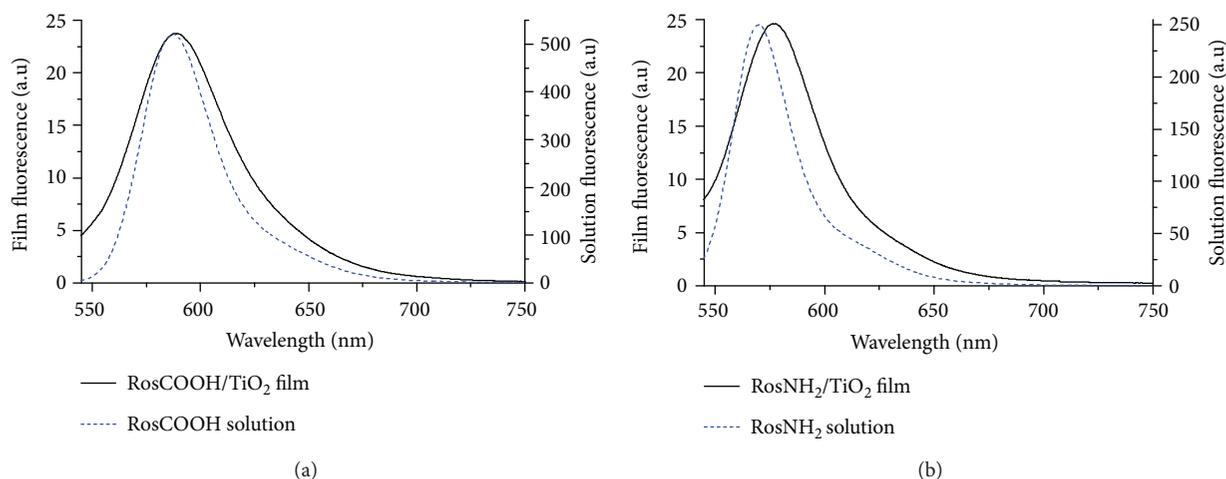


FIGURE 3: Photoluminescence spectra of (a) RosCOOH/TiO<sub>2</sub> film ( $\lambda_{\text{ex}} = 530$  nm) and RosCOOH dichloromethane solution ( $3.6 \mu\text{M}$ ) and (b) RosNH<sub>2</sub>/TiO<sub>2</sub> film ( $\lambda_{\text{ex}} = 525$  nm) and RosNH<sub>2</sub> dichloromethane solution ( $3.6 \mu\text{M}$ ).

of dichloromethane solutions of RosCOOH ( $3.6 \mu\text{M}$ ) and RosNH<sub>2</sub> ( $3.6 \mu\text{M}$ ) showed their monomer bands at 563 nm and 551 nm, respectively (Figure 2). A vibronic shoulder was located at 525 nm for RosCOOH and 514 nm for RosNH<sub>2</sub>. The highly diluted conditions ensured that the rosamine molecules were in their monomeric forms. Once anchored to TiO<sub>2</sub>, each rosamine experienced different spectral changes. The absorption bands in the RosCOOH/TiO<sub>2</sub> film appeared broadened (full width at half maximum [fwhm] for the film: 52 nm, fwhm for the solution: 29 nm) and blueshifted (9 nm) with respect to the solution spectrum (Figure 2). Such modifications in the rosamine spectrum indicate that *H*-aggregation, or face-to-face stacking [30, 31], would be occurring between RosCOOH molecules in the film as a result of  $\pi$ - $\pi$  interactions. The spectrum of RosNH<sub>2</sub>/TiO<sub>2</sub> showed less broadened absorption bands than those of the carboxylic rosamine (fwhm for the film: 43 nm, fwhm for the solution: 28 nm) and was

shifted towards higher wavelengths (5 nm). In this case, the spectral shifting would be caused by *J*-aggregation of RosNH<sub>2</sub> molecules [32].

To obtain more insight into the aggregation process occurring between rosamine molecules in the films, we compared the fluorescence spectrum of each of the rosamine films with their respective solution (Figure 3). When anchored to the TiO<sub>2</sub>, RosCOOH spectrum showed mainly its monomeric form, with a slight redshift (1 nm) with respect to its solution spectrum due to a minimal contribution of *J*-aggregates. The presence of *H*-aggregates already identified in the absorption spectrum would not induce shifts in fluorescence [28, 33, 34], hence the absence of further shifting in the fluorescence spectrum of this rosamine. On the other hand, RosNH<sub>2</sub>/TiO<sub>2</sub> film spectrum featured a redshift (7 nm) with respect to its solution spectrum, which was attributed to the presence of *J*-aggregates as they are characterized by a shifting towards higher wavelengths of

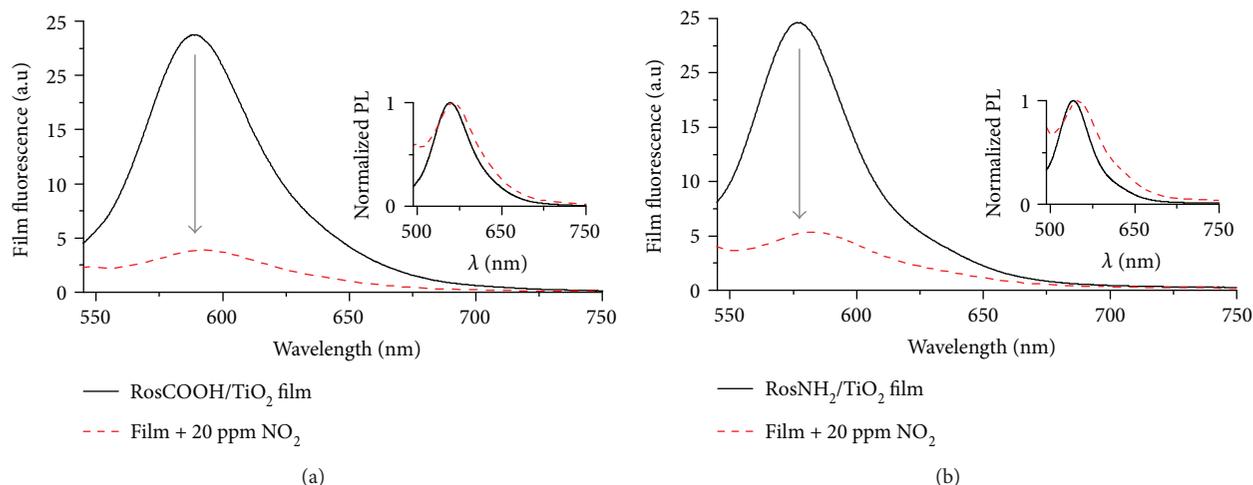


FIGURE 4: Photoluminescence spectra of (a) RosCOOH/TiO<sub>2</sub> ( $\lambda_{\text{ex}} = 530$  nm) and (b) RosNH<sub>2</sub>/TiO<sub>2</sub> ( $\lambda_{\text{ex}} = 525$  nm) composite films before and after their exposure to 20 ppm NO<sub>2</sub>. Insets: normalized photoluminescence (PL) spectra for each of the rosamines before and after their exposure to NO<sub>2</sub>.

the bands in the fluorescence spectrum [28, 33, 34]. This is in agreement with the information obtained from the analysis of the absorption spectrum of the film.

The different types of aggregation between rosamines once anchored to the TiO<sub>2</sub> molecules in the film and their implications on their respective spectra can be explained in terms of the type of interaction between rosamine and TiO<sub>2</sub>, taking into account that the transition dipole moments for both rosamines are located along the xanthene ring. The binding of RosCOOH to TiO<sub>2</sub> has been extensively discussed elsewhere [28]. Briefly, the molecular structure of RosCOOH allows its anchoring to TiO<sub>2</sub> by covalent bonding (through the carboxylic group) and by electrostatic interaction (through the ammonium group). With this arrangement, RosCOOH would be chemically anchored to the surface via its phenyl group, which would act as a lever that lifts up the xanthene ring due to the additional electrostatic interaction. This tilting would favor the  $\pi$ - $\pi$  stacking and therefore the formation of *H*-aggregates. On the other hand, the anchoring of RosNH<sub>2</sub> molecules would only be possible through electrostatic interaction with the film surface. This type of interaction between positively charged dye molecules and TiO<sub>2</sub> films has been studied in previous works [27]. In this case, RosNH<sub>2</sub> would be anchored by only one point to the substrate, allowing a wide variety of angles between rosamine and substrate and increasing the possibility of formation of *J*-aggregates. An excellent discussion about aggregation states in xanthene derivatives alongside an illustrative scheme of possible geometric dispositions can be found in Martínez et al. [35].

The presence of both *H*- and *J*-aggregation may have implications in the gas sensing capabilities of the composite films. The effects of molecular aggregation caused by  $\pi$ - $\pi$  interactions on gas sensing have been previously discussed in the literature [14]. Besides limiting the access of analyte molecules into the film, molecular aggregation results in broadened absorption bands with less defined peaks that leads to poor monitoring of the spectral changes induced

by the sensed analyte. The use of fluorophores allows the use of photoluminescence to monitor the changes induced by their exposure to analytes, with the advantage of being less sensitive to aggregation, yet more sensitive to the changes induced on the fluorophores. In our case, the presence of aggregates was not intense enough to avoid the interaction with gas molecules or to lead to the formation of large clusters that would prevent the use of UV-Vis spectroscopy. However, the analysis of the gas sensing capabilities of rosamine/TiO<sub>2</sub> composite films would benefit from the higher sensitivity and robustness of photoluminescence. Hence, we focused on the modifications produced on the emission spectra of our composite films by their exposure to different concentrations of NO<sub>2</sub>.

**3.2. Sensing Response to NO<sub>2</sub>.** Both RosCOOH/TiO<sub>2</sub> and RosNH<sub>2</sub>/TiO<sub>2</sub> composite films showed intense photoluminescence once excited at a wavelength ( $\lambda_{\text{ex}}$ ) of 530 nm and 525 nm, respectively (Figure 4), which is a common feature of rhodamine derivatives [13, 36]. It is proved that the binding to the substrate did not produce a substantial quenching of the typical emission of this kind of fluorophore. Upon their exposure to 20 ppm NO<sub>2</sub>, the emission spectra of both composite films experienced an intense decrease leading to the almost complete loss of their photoluminescence (Figure 4). The amount of quenching at saturation was similar in both cases, around 84% for RosCOOH and 78% for RosNH<sub>2</sub>. Such changes indicate that rosamines anchored to a solid matrix of TiO<sub>2</sub> represent a good choice for the detection of NO<sub>2</sub>.

A slight redshift was found in the fluorescence maxima of both RosCOOH/TiO<sub>2</sub> and RosNH<sub>2</sub>/TiO<sub>2</sub> after NO<sub>2</sub> exposure (Figure 4, inset). We attributed this shifting to the less responsiveness featured by *J*-aggregates. Assuming that films of both rosamines were partially composed by *J*-aggregates, as elucidated previously, they would not interact with NO<sub>2</sub> as fast and intensely as the rosamine monomers. After the quenching of the

fluorescence of the monomers, the fluorescence spectra of the rosamines would primarily be composed by the remaining emission of the *J*-aggregates, reshaping the spectra towards a redshifted one. This shifting was found to be more intense in RosNH<sub>2</sub>/TiO<sub>2</sub> films than in RosCOOH/TiO<sub>2</sub> films, which has been attributed to the higher proportion of *J*-aggregates in the former.

Given the strong electron-withdrawing nature of NO<sub>2</sub> and the electron-donating character of rosamines, the most plausible mechanism for the changes induced on the rosamines would be an oxidation through a charge transfer process from the electron-rich xanthene group to the oxidant gas. Ohyama et al. [37] reported that rhodamine B fluorescence is quenched after exposure to NO<sub>2</sub>, due to the aforementioned oxidative nature of this gas. The strong similarities between rhodamine B and the rosamines used in this work support the idea that the same process may be occurring in our sensor. Similar interactions have been found between NO<sub>2</sub> and other dyes with rich  $\pi$ -electron systems [38, 39].

The exposure of RosCOOH/TiO<sub>2</sub> and RosNH<sub>2</sub>/TiO<sub>2</sub> composite films to 20 ppm NO<sub>2</sub> also resulted in the decrease of the absorption bands in their UV-Vis spectra. The decrease was found to be 52% for RosCOOH/TiO<sub>2</sub> and 49% for RosNH<sub>2</sub>/TiO<sub>2</sub>, confirming the better sensitivity of photoluminescence and its choice over UV-Vis spectroscopy. After their exposure to NO<sub>2</sub>, the composite films were flushed with dry N<sub>2</sub> to attempt their recovery, but the changes induced on the rosamine spectra were found to be irreversible. Such behavior suggests the use of our composite films as single-use NO<sub>2</sub> sensors, which would be a plausible approach given their low cost and relative ease of fabrication. Other recovery strategies are currently a subject of further research.

In order to further analyze the sensing capabilities of RosCOOH/TiO<sub>2</sub> and RosNH<sub>2</sub>/TiO<sub>2</sub> composite films towards NO<sub>2</sub>, we analyzed the speed of response of their exposure to increasing concentrations of the toxic gas in the range 5–50 ppm by monitoring the emission at the wavelength of maximum change (577 nm for RosCOOH and 590 nm for RosNH<sub>2</sub>, Figure 5). Both rosamines showed a fast response towards NO<sub>2</sub>, as indicated by the slope of their kinetics. This can be attributed to the high responsiveness of our rosamines and to the elevated porosity of the TiO<sub>2</sub> substrates that would allow a fast diffusion of the gas molecules inside the film and their contact with the active sites of the rosamines. The slopes of the response of RosCOOH/TiO<sub>2</sub> to each of the NO<sub>2</sub> concentrations were higher than those corresponding to RosNH<sub>2</sub>/TiO<sub>2</sub>, indicating that the carboxylic rosamine responded significantly faster than the amine derivative in all cases, being the differences more remarkable for the exposures to lower concentrations of NO<sub>2</sub>. In both cases, the slopes of the response increased with NO<sub>2</sub> concentration, that is, the response times were concentration dependent. These results suggest that a calibration of the composite film response within the desired range of concentrations would allow its use for quantification purposes. After a time that varied according to the rosamine and NO<sub>2</sub> concentration, the signal stabilized with a horizontal slope,

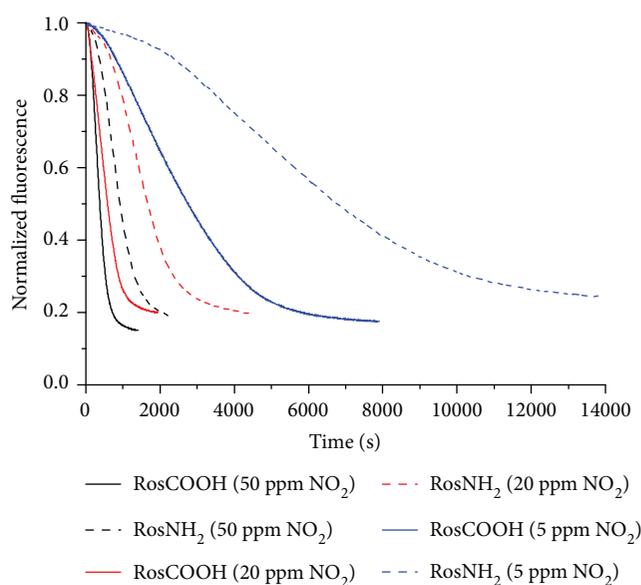


FIGURE 5: Kinetics of the exposure of RosCOOH/TiO<sub>2</sub> (monitored at 577 nm,  $\lambda_{ex} = 530$  nm) and RosNH<sub>2</sub>/TiO<sub>2</sub> (monitored at 590 nm,  $\lambda_{ex} = 525$  nm) composite films to 5, 20, and 50 ppm NO<sub>2</sub>.

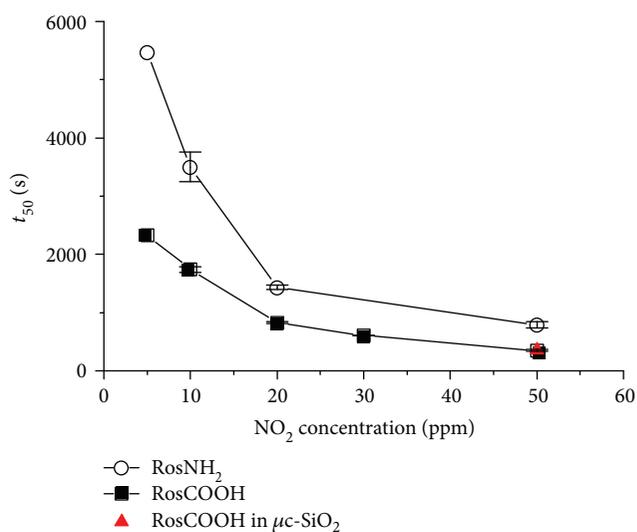


FIGURE 6: Response time ( $t_{50}$ ) corresponding to the exposure of RosCOOH/TiO<sub>2</sub> and RosNH<sub>2</sub>/TiO<sub>2</sub> composite films to NO<sub>2</sub>. Error bars indicate  $\pm\sigma$  (standard deviation). The response time of RosCOOH anchored to microcolumnar ( $\mu$ c-) SiO<sub>2</sub> once exposed to 50 ppm NO<sub>2</sub> is included for comparison.

indicating that there were no more available active sites for the gas molecules to interact with the dyes.

In light of the different responses observed for both composite films, we proceeded to quantify their speed of response towards different concentrations of NO<sub>2</sub>. We calculated  $t_{50}$ , which is the time taken for the signal to reach 50% of its maximum change, and found that it decreased with NO<sub>2</sub> concentration and that in all cases it was lower for RosCOOH/TiO<sub>2</sub> than for RosNH<sub>2</sub>/TiO<sub>2</sub> composite films (Figure 6). We attribute these differences in the sensing

properties to different charge densities in both rosamines. RosCOOH is linked to  $\text{TiO}_2$  forming a carboxylate allowing for the xanthene ring to preserve a higher negative charge density than its amino-derivatized counterpart. A higher negative charge density would mean higher availability of electro-deficient compounds as is the case of  $\text{NO}_2$ , to be attracted by the aromatic core. As a result, the changes induced on RosCOOH upon exposure to the oxidant gas would occur faster, hence improving its performance with respect to RosNH<sub>2</sub>.

In a previous work, RosCOOH was used to prepare composite films based on microcolumnar ( $\mu\text{c}$ -)  $\text{SiO}_2$  following the same infiltration procedure as the one shown here. Microcolumnar  $\text{TiO}_2$  was also studied but omitted here due to poor gas sensing results. RosCOOH/ $\mu\text{c}$ - $\text{SiO}_2$  films were exposed to 50 ppm  $\text{NO}_2$ , leading to spectral changes similar to those obtained in this work. However, the analysis of the  $t_{50}$  revealed a slightly slower speed of response than when using nanocrystalline  $\text{TiO}_2$  as substrates ( $t_{50} = 350$  s for RosCOOH/ $\text{TiO}_2$ ,  $t_{50} = 360$  s for RosCOOH/ $\mu\text{c}$ - $\text{SiO}_2$ ). It is worth mentioning at this point that both substrates differ highly in their preparation procedures. Microcolumnar  $\text{SiO}_2$  films were prepared by glancing angle physical vapor deposition while nanocrystalline  $\text{TiO}_2$  was made by the screen printing procedure, being the latter significantly faster and simpler and requiring less sophisticated laboratory equipment. Hence, the moderately faster response of nanocrystalline RosCOOH/ $\text{TiO}_2$  composite films alongside the higher simplicity of their preparation justifies its choice over microcolumnar RosCOOH/ $\text{SiO}_2$  composite films.

#### 4. Conclusions

Two rosamine derivatives, containing either a carboxylic acid or an amino group as peripheral substituent, were successfully incorporated into transparent nanocrystalline  $\text{TiO}_2$  films. The anchoring of the dyes to the substrates was found to be compatible with either chemical binding and electrostatic interaction, or only electrostatic interaction, according to the different substituents in each rosamine. The exposure of the composite films to  $\text{NO}_2$  resulted in intense and fast spectral changes, which were attributed to a charge transfer process from the electron-rich xanthene group to the oxidant gas. The speed of response, calculated through the  $t_{50}$  parameter, was related to the concentration of the gas. This indicated a concentration-dependent behavior and the possibility of quantification of the gas concentration by calibrating the response. The binding of the sensing molecules to the substrates was found to be determinant for the sensing capabilities of each of the composite films. The carboxylic-derivatized rosamine showed a faster response than the amino derivatized in all cases, and this behavior was attributed to a higher negative density of charge in the former that would enhance its spectral response to  $\text{NO}_2$  gas. These results are similar to those previously obtained using microcolumnar- $\text{SiO}_2$  composite films, with the main advantage of featuring an easier substrate fabrication.

#### Disclosure

This work is part of the PhD thesis of María G. Guillén entitled “Development of optical sensors based on thin films of fluorescent organic materials for the detection of toxic gases” (July 2017, University Pablo de Olavide, Sevilla, Spain).

#### Conflicts of Interest

The authors declare that there is no conflict of interest regarding the publication of this article.

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