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DEVELOPMENT OF HIGH EMITTING ROSAMINE-TIO_2/SIO_2 COMPOSITE THIN FILMS

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Summary: *In this work we have studied the incorporation of Rosamines, rhodamine derivatives without 2'-carboxilic group, into transparent and microstructured columnar TiO_2 and SiO_2 (MO_2) thin films prepared by evaporation at glancing angles (GAPVD). The anchoring process of the emitting dye has been described by a Langmuir type adsorption isotherm and an Elovich-like kinetics. The state of anchoring and aggregation of the absorbed molecules, the infiltration efficiency and the adsorption kinetics were studied by UV-Vis adsorption and fluorescence spectroscopies. Moreover, it has been investigated the influence of pre-ilumination and the pH of the infiltrating solution on the emission properties. Finally, the anchoring mechanism of the rosamine to the MO_2 matrix has been revealed by specular reflectance FTIR.*

1 INTRODUCTION

The rapid advance of emerging technologies leads to the development of new materials whose properties enable the creation of novel applications in industry and hybrid materials are one of them. Commonly consisted of organic- inorganic material, the unusual features of hybrids make these materials useful in areas as diverse as optics, environment, medicine, or electronics. In all of these areas, fluorescence-based techniques have a wide range of applications due to its inherently sensitivity, selectivity, diversity and non-destructive, potentially applicable in real time and in situ measurements. In most of these techniques, the dye molecules must be hosted in a solid support which poses new challenges in the development of solid-state platforms.

Incorporation of dye molecules into thin films has been recently studied [1] [2] and its application as gas sensors has been very satisfactory. [3] [4] Rhodamine derivatives are particularly attractive as dye molecules because of their excellent photophysical properties, [5] [6] [7] being used as chemosensor, [8] thermometer [9] or laser dyes. [10] Although for some of these applications the dye is used in solution, for most of them the fluorescent probe must be anchored to a solid surface.

Although several rhodamine derivatives are commercially available, they are quite expensive and most of the compounds commonly used for further derivatization are only

accessible as a mixture of 4'- and 5'-regioisomers. Rosamines, rhodamine derivates without 2'-carboxilic group, have been recently synthetized in an easy way. [11]

The similarities between rhodamines and rosamines make them suitable for similar applications. For instance, their intense fluorescence emission allows their use as fluorescent probes, but they are also used as laser dyes, pigments and fluorescent standards. This molecules are also widely used in biotechnology, for example in the study of the fluidity of membranes, the structure and dynamics of micelles, imaging in cells, and also in sensors used for the detection of mercury, copper, iron and chromium in cells. [12] [13] [14]

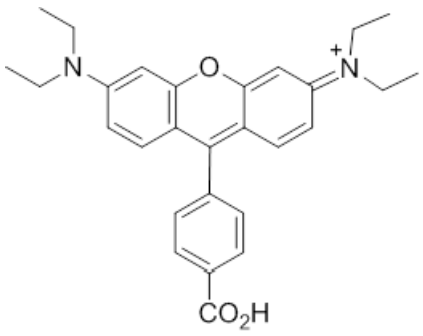

Figure 1: Molecular structure of rosamine 1

An innovative aspect of the present work is the incorporation of rosamine 1 (R1), shown in the Figure 1, into thin films of a metal oxide semiconductor, in particular, we have used non dispersive thin films of both TiO_2 and SiO_2 as hosting matrices. They are formed by a columnar microstructure with wide open voids which make them transparent with a low refractive index, high porosity and controlled thickness, constituting a perfect substrate for the design of new devices. The anchoring process of the emitting dye has been described by a Langmuir type adsorption isotherm and an Elovich-like kinetics, what implies that these columnar microstructures not only exhibit a very good infiltration capacity, but also an excellent accessibility of the incoming rosamine molecules to the active adsorption sites. Hybrid composites were prepared by simple immersion of the MO_2 films into dicholomethane solutions of the rosamine at different concentrations. The state of anchoring and aggregation of the absorbed molecules, the infiltration efficiency and the adsorption kinetics were studied by UV-Vis adsorption and fluorescence spectroscopies.

2 RESULTS

2.1. Composite Rosamine/MO_2 films characterization

The luminescent behavior and quantum efficiency of rhodamine derivates in solution or in solid matrices is very dependent of the aggregation state of the molecules which, in turn, depends on the hosting medium and other factors like concentration or pH. UV-vis solution spectra of different solutions of R1 with a maximum around 565 nanometers as previously reported for this compound, [11] showed that apparently there was no aggregation between the molecules in the solution.

However, attending to the Stokes shift, the difference (in wavelength) between the positions of the band maxima of the absorption and emission spectra, we observed an increment due to a bathochromic shift in the fluorescent band with the dye concentration, suggesting the presence of *J*-aggregates of the dye in the solution. An analysis of the

fluorescence efficiency, defined as the ratio between the fluorescence intensity and the absorbance at the excitation wavelength (I_{fl}/A_{exc}), showed a decrease with the dye concentration, a result according to the possible presence of aggregates that quench the monomers emission.

Once normalized for a better comparison, the absorbance spectrum and the excitation one shown in Figure 1, are almost coincident which indicates that existence of reabsorption of light can be discarded.

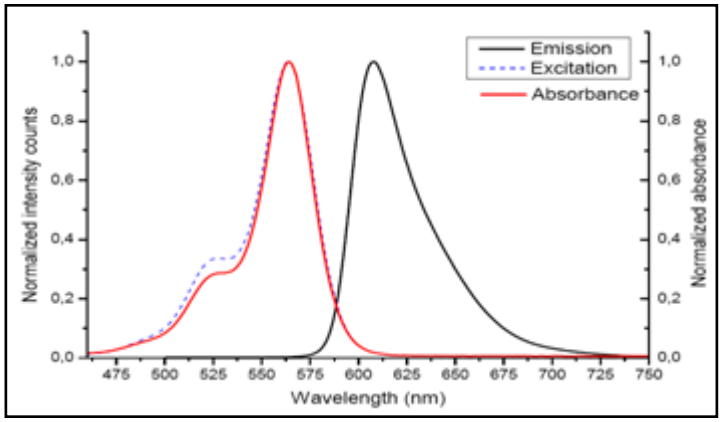

Figure 1. Emission, excitation and absorbance spectra of a 3,58 x10^{-5} M dicloromethane solution of R1.

Hybrid composites were prepared by using porous MO_2 thin films as a hosting matrix. For this purpose, transparent and amorphous films of this material, with a thickness around 350 nm, were prepared by GAPVD at room temperature at an angle of 60º with respect to the evaporation source. The glancing geometry produces films with a tilted columnar microstructure [15, 16]. A characteristic of these films is that they are very porous and, therefore, are characterized by relatively low refractive index values. Different solutions of the dye in dichloromethane were used for the infiltration experiments. After infiltration time of 24 hours under darkness conditions, thin films samples were washed and dried at room temperature. UV-visible absorption spectra shown in Figure 2 were analyzed, founding a clear dependence of the peak area (amount of infiltrated molecules) with the concentration of the solution. Compared with spectra in solution, changes in the shape were observed when anchoring to MO_2 films, according to the presence of new species in the columns, such as dimers, or higher aggregates.

A small shoulder on the left appeared when the concentration of dye molecules is increased, indicating the formation of H-type aggregates. This phenomenon of aggregation is much more evident when anchoring to TiO_2 than to SiO_2.

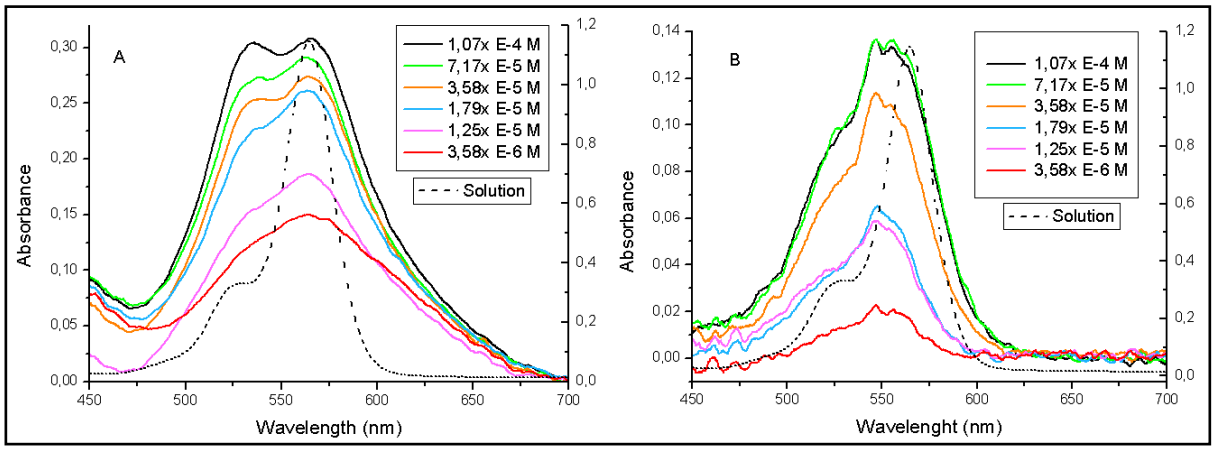

Figure 2. Absorption spectra for composite R1/MO_2 thin films (M_A: TiO_2; M_B: SiO_2) prepared by infiltration from dichloromethane solutions at different concentrations

Figure 3 represents the emission counts of composite thin films prepared by infiltration during 24 hours from dichloromethane solutions at different concentrations of the dye. It could be observed how the emission of these R1-MO_2 composite films decreases when the concentration of the rosamine molecules in the infiltrating solution increases, something which is directly related to the aggregation of the dye. [1]

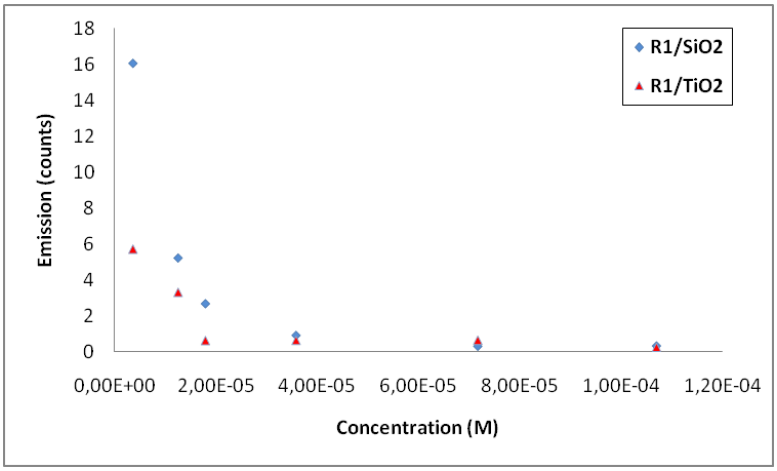

Figure 3. Evolution of Emission intensity for composite R1/MO_2 thin films prepared by infiltration from dichloromethane solutions at different concentrations

The emission using porous SiO_2 thin films is higher than in the case of TiO_2, probably due to the less aggregation of the molecules in this material.

In order to describe the anchoring process of the rosamine molecules to the MO_2 films a Langmuir adsorption isotherm could be a helpful tool. This isotherm can be expressed by:

$$\frac{n_{ads}}{N_S} = \frac{\lambda c}{1+\lambda c} \quad (1)$$

where n_{ads} is the number of the adsorbed molecules (proportional to the peak area), N_S is the number of adsorption sites available on the MO_2 surface, λ is a constant relating to the adsorption capacity of Rosamine 1 and c is the concentration of the dye in solution.

Rearrangement of Equation 1 leads to the linear form of the Langmuir adsorption isotherm, where a plot of c/n_{ads} (or *c/peak area*) versus *c*, should yield a straight line if the conditions of the Langmuir isotherm are fulfilled. In Figure 4 is shown the plot of *c/peak area* vs. *c* that fitted a straight line, indicating that the conditions for the Langmuir adsorption model are satisfied.

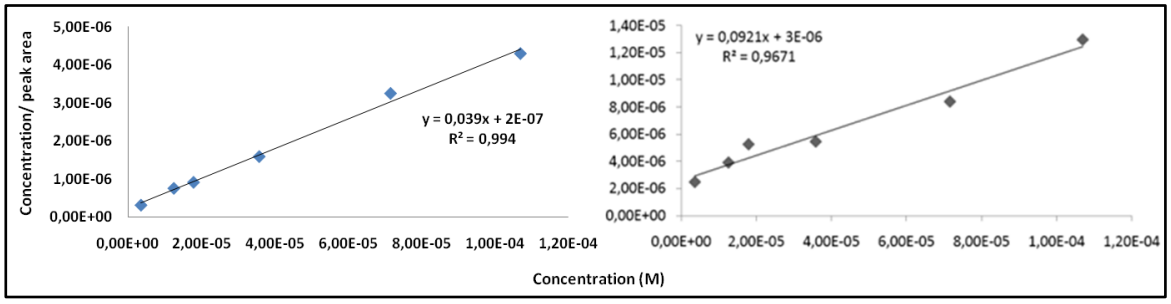

Figure 4. Langmuir adsorption plot for R1 in TiO_2 (blue) and SiO_2 (grey) composite films

Therefore, and according to the assumptions of this model, it can be concluded that the activation energy of adsorption is the same for all binding sites in the MO_2 films, that there are a fixed number of localized surface sites present on the surface and that rosamine molecules striking a surface site that is already occupied do not adsorb onto that particular site.

The infiltration of the dye molecules into the columnar MO_2 films is a time dependent process. Kinetic studies were made considering the time evolution of the rosamine surface concentration Γ as it becomes incorporated into MO_2 thin films at a solution concentration of 3,58 x 10^{-5} M. The defined curve can be divided in two parts, a first one characterized by a fast growth of the amount of infiltrated molecules followed by a much slower process where the film is approaching saturation. This growth pattern can be adjusted with the Elovich adsorption kinetics model where the evolution of the surface coverage Θ as a function of time, t, is given by:

$$\Theta = \left(\frac{1}{\beta}\right)\ln(t) + K \tag{2}$$

Where β and K are constants. Eq 2 indicates that there is an exponential decrease of the rate of the surface adsorption as the coverage of the surface increases. Defining the peak area as an equivalent magnitude to Θ we have found a good fitting to the model as shown in Figure 5, which is indicative of an exponential decrease of the probability of adsorption of dye molecules with the number of occupied adsorption sites on the surface of the columnar MO_2 structure. [17] Moreover, the good fitting with the Elovich equation reveals that the MO_2 columnar microstructure not only exhibits a very good infiltration capacity, but also an excellent accessibility of the incoming rosamine molecules to the active adsorption sites.

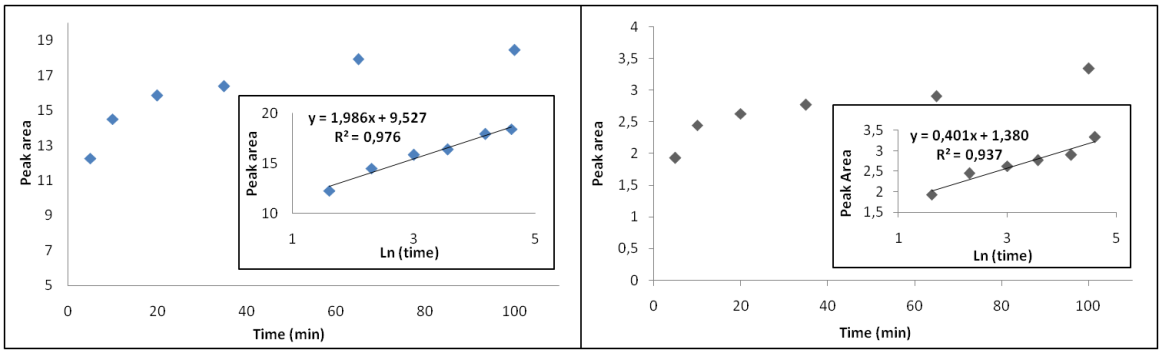

Figure 5: Elovich plot for R1 in TiO_2 (blue) and SiO_2 (grey) composite films

The emitting capacity of the composites remains stable over time and has been directly correlated with the concentration and time of infiltration. Figure 6 shows the fluorescence spectra of R1/ SiO_2 composite films prepared by infiltration from dichloromethane solutions at two different concentrations of the dye plotted at different times of infiltration.

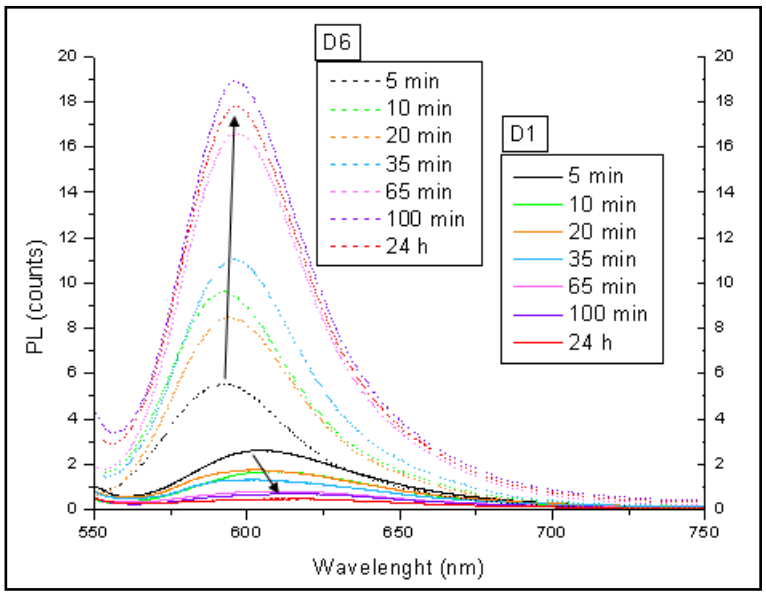

Figure 6: Evolution of Emission Spectra of R1 anchoraged to SiO_2 from solution concentration of 1,07 x 10^{-4} M (D1) and 3,58x 10^{-6} M (D6) with the time of infiltration

As we can see, infiltration using very diluted solutions of rosamine lead to a significant increment of the emission when the time of infiltration increases. On the contrary, when the infiltration occurs from a concentrated solution of the dye, the emission decreases with time because of molecular aggregation.

9 CONCLUSIONS

An innovative aspect of the present work is the incorporation of rosamines, into transparent and microstructured columnar TiO_2 and SiO_2 (MO_2) thin films prepared by evaporation at glancing angles (GAPVD) resulting in new transparent materials with low refractive index, high porosity and controlled thickness.

The anchoring process of the emitting dye has been described by a Langmuir type

adsorption isotherm and an Elovich-like kinetics, what implies that these columnar microstructures not only exhibit a very good infiltration capacity, but also an excellent accessibility of the incoming rosamine molecules to the active adsorption sites.

The emitting capacity of these composite films remains stable over time and has been directly correlated with the concentration of the dye in the infiltrating solution and the time of infiltration. When concentration of rosamine molecules increases, the phenomenon of aggregation is much more evident and this results in a decrease in the fluorescence of the films. Increased time of infiltration also generally increases the aggregation of the dye molecules, except in the case of the less concentrated solution, which shows that increasing the infiltration time also causes an increase in fluorescence.

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