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Optical Investigation of Nanocomposite of Porous Silicon - Rhodamine 6G

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Abstract — **We have elaborated nanocomposites based Porous silicon (PS) and rhodamine 6G (Rh 6G) by simple impregnation. New luminescence properties were shown. This luminescence could occur by energy transfer from silicon nanocristallites to dye molecules. FTIR spectroscopy suggests the incorporation of rhodamine molecules into the pores of the matrices. An energy transfer was demonstrated from Si nanocrystallites to Rh6G molecules. We also study the effect of the concentration of Rh6G molecule on optical properties of nanocomposites PS/Rh6G**.

Keywords - Nanocomposite of porous Silicon - Rhodamine 6G, FTIR spectroscopy* Photo*luminescence.

INTRODUCTION

The incorporation of organics dyes into solid matrix is attracting wide interest because of such useful applications as lights concentrators in solar cells, optical waveguides, lasers materials, sensors and nonlinear materials [1,2].

Different methods to trap organic molecules within solid substrates have been developed, including the direct soaking of the host material with dye solutions [3,4].

The amount of matter which is introduced into the pores can vary to a very large extent. Canham [5] is the first who has tried the impregnation into the pores of different laser dyes.

Rhodamine dyes is widely used and have been studied in diverse areas of research and for commercial purposes due to their good fluorescence properties. Compared to other dyes, the Rh6G has a high photostability, high fluorescence quantum yield (0.95), a low cost, and its lasing range has close proximity to its absorption maximum [6,7]. In recent years, many efforts have been devoted to the elaboration of nanocomposites based porous silicon (PS). The objective could be the stabilisation of light emission of PS, or the formation of new luminescing properties, or to improve the electroluminescence efficiency [8,9,10]

A. *Experimentation*

Silicon substrates of around 10 Vcm were electrochemically etched in HF:C_2H_5OH:H_2O solution in order to obtain PS layers having 70% porosity with different thickness. The samples were impregnated for different times in a solution of rhodamine 6G with different concentration $C_1=5\ 10^{-4}M$, $C_2=10^{-3}M$, $C_3=5\ 10^{-3}M$ and $C_4=10^{-4}M$ and than dried at a temperature of 60°C. We note that the molecule of rhodamine 6G has a length smaller than 1 nm which makes its impregnation into the pores (3 nm for PS (p).

Fourier Transform Infrared (FTIR) spectra were recorded in absorption mode using a Bruker IFS 66 v/s FTIR spectrometer at 4 cm^{-1} resolutions. The PL measurements were performed with a triple monochromator using the ray 514.5 nm of an Ar-laser or the ray 632.8 nm of He–Ne laser as excitation sources.

B. *RESULT*

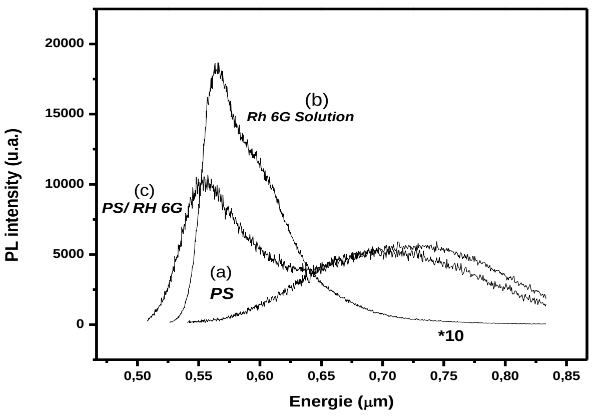

Fig. 1. PL spectra of PS layer (a) dye in solution (b) and PS/Rh6G after drying (c)

In Fig. 1, we present PL spectra of PS layer (a), dye in solution (b) and PS/Rh6G after drying (c). The nanocomposite PS/Rh6G luminance out of the spectral range of PS emission (blue shift to lower wavelength) and its PL is more efficient than that of the PS layer. This indicates that the PL of the nanocomposite Rh:PS does not originate only from PS. This may characterize the emergence of dye molecules into the pores up to saturation.

It is well known that the luminescence of a dye depends strongly on its concentration in solution. The PL intensity becomes weaker when the molecules become too concentrated and eventually can be totally quenched. This means that more the dye molecules are dispersed, more the luminescence is efficient. This can explain the origin of the strong luminescence of the nanocomposite PS/Rh6G since the molecules penetrate into the pores and are sufficiently dispersed in the porous matrix. Each process could be produced by excitation transfer from nanocristallites to dye molecules. In fact, the conditions of excitation transfer are satisfied for PS and rhodamine 6G: the Rh6G absorbs in the range 500–700 nm, which recovers with the range of PS emission.

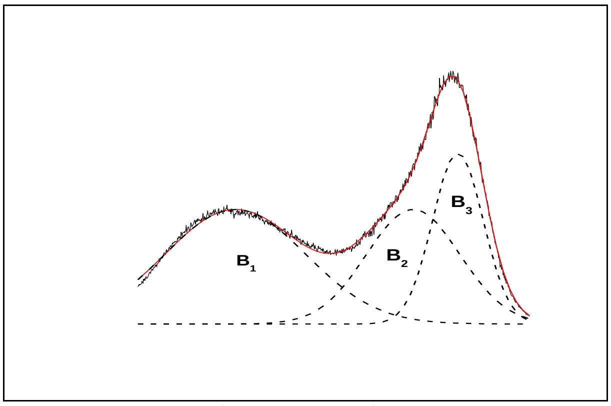

Fig 2. Decomposition of the PL spectra of nanocomposite PS/Rh6G

To explain these changes occurred we decompose the nanocomposite spectrum into three bands (Figure 2): the band B1 is identical to that of the SP, the B2 band whose maximum is centered at 550 nm is specific to the PL molecules Rh6G present on the surface of the SP and which do not undergo interactions. The offset of the third band B3 with respect to the Rh6G solution is probably due to interactions between the molecules of the chemical species Rh6G and the inner surface of PS.

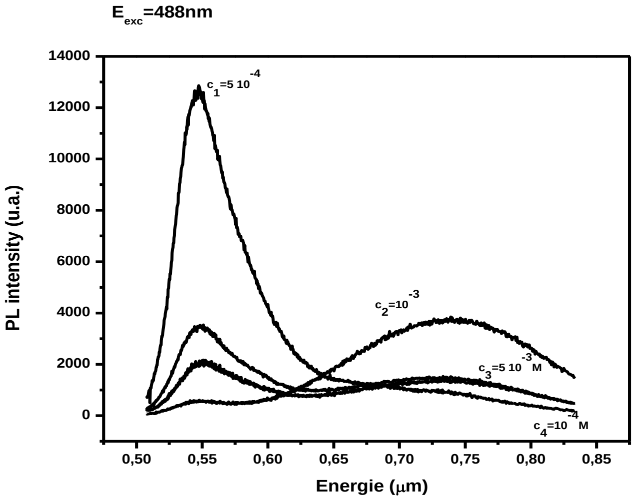

Fig 3. PL spectra of nanocomposites PS/Rh6G for different rhodamine concentration
C1 = 5 10^{-4}M, 10^{-3}M = C2, C3 and C4 = 5 10^{-3}M = 10^{-4}M

It is therefore important that the molecules are well dispersed. We had the idea of the SP impregnated by Rh6G solution of different concentration and mainly studied the energy transfer phenomenon in the matrix. Studied nanocomposites are obtained by impregnating PS samples for one hour and 15 minutes with solutions of Rh6G dissolved in ethanol concentration C1 = 5 10^{-4}M, 10^{-3}M = C2, C3 and C4 = 5 10^{-3}M = 10^{-4}M.

The variation of the integrated intensities of the PL nanocomposites PS / Rh6G in function of the concentration C is shown in Figure 6. The increase in the concentration of Rh 6G promotes an increase of the PL intensity nanocomposites SP / Rh6G, but decreases beyond
C = 5 10^{-4}M.

The PL is increased due to an increase in the rate of active molecules of rhodamine without a formation of aggregates of molecules. For concentrations bigger than C = 5$10^{-4}$M, the quantity of molecules contained in the pores increases, which leads to strong interaction between the molecules and consequently a reduction in radiative processes. This is accompanied by a decrease in PL intensity: It's the self-extinguishing phenomenon.

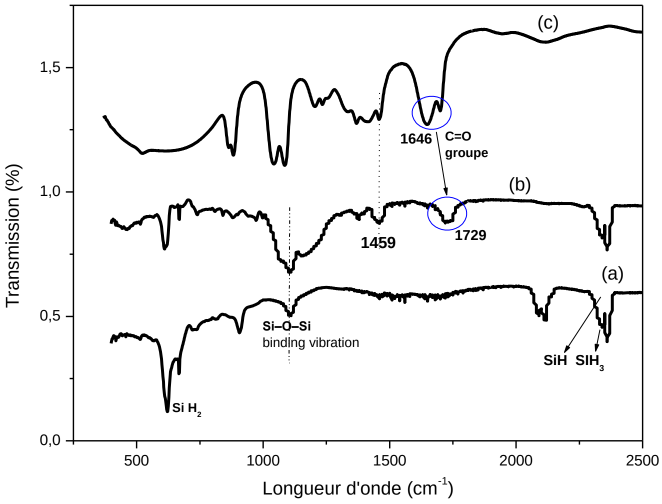

Fig 4. FTIR spectra of PS (a), PS/Rh6G (b) and Rh6G solution (c).

The principle of the study is based on the energy change of a system by absorption of an electromagnetic wave (infrared source). The resulting vibration phenomena are accompanied by a transfer of energy when the frequency of the wave is equal to the natural frequency of the atomic bonding (resonance condition). This analysis is useful for the qualitative determination of the species present in the nanocomposites SP / Rh6G. Having regard to the chemical formulas of Rh6G is expected to found the types of bonds C = C, C = N, C = O.

Bond	Absorption frequency (cm^{-1})
C=N	1640 - 1685
C=C	1575- 1650
C=O	1640 - 1730
N=O	1430 - 1500

Table 1. Absorption frequency

Analyses by FTIR spectroscopy prove the presence of the molecules of Rh6G in the pores of PS (Figure 4).

C. CONCLUSION

Porous silicon (PS)-laser dye composites were obtained by simply immersing PS in ethanolic solutions of rhodamine 6G (Rh6G). PSi was also used as a host matrix. Fourier transform infrared spectroscopy suggests that the dye molecules fully penetrate into the porous matrix.

The present results indicate that PS is useful not only as a luminescent material but also as an active host matrix for guest dye molecules.

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