Porous silica–laser dye composite: physical and optical properties

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The optical properties of rhodamine B dye molecules confined in porous silica are reported. Porous silica–laser dye composite is obtained by simple impregnation of porous silica (PS) in rhodamine B (RhB) solution. The FTIR spectroscopy shows penetration of rhodamine molecules in the matrix. A nonradiative excitation transfer due to dipolar interaction is evidenced from the effect of the RhB concentration on the PL emission and confirmed by FTIR spectroscopy. It was found that the formed composite displays an efficient and stable PL. An anti-Stokes emission is observed and its origin is attributed to chemical species interactions with one photon absorption.

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1 Introduction

Since 1980, the research in the field of the dye-laser has been oriented towards the possibility to realize solid state active media by means of the introduction of dye molecules in solid matrices of organic or hybrid nature [1, 2]. Studies on the feasibility of solid-state dye laser have recently generated increasing interest. Moreover, dye molecules embedded in solid matrices have emerged as potential non linear optical materials [1–4]. When developing a solid-state dye laser, one of the most important problems to face is dye photostability, which is mainly related to the photochemical degradation of organic molecules in their gain range [1, 5, 6]. However till now the desired dye photostability has not been achieved. Different methods to trap organic molecules within solid substrates have been developed, including direct soaking of the host with dye solutions [3, 7, 8] where the chemical bond between organic molecules and inorganic matrices is weak (hydrogen bonding, Van der Waals interactions …). This class of hybrids can be obtained through impregnation of solid hosts with solutions of the desired molecule [7, 8].

In the present work, the spectral properties and the excitation mechanisms of rhodamine B (RhB) molecules adsorbed in porous silica are investigated.

2 Experimental

Porous silica (PS) layers were obtained by electrochemical anodization of (100) oriented p^+ silicon substrates (10^{-3}–10^{-2} Ω cm) in an electrolyte solution composed of $HF:C_2H_5OH:H_2O = 2:1:1$. The porosity and the thickness of the layer are about 80% and 3 μm, respectively. Then the samples were pre-oxidized at 300 °C for half hour followed by oxidation at 1000 °C for two hours in order to obtain porous silica

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from total oxidation of the porous layer. Porous silica is impregnated in rhodamine B solution (with different concentrations) for one hour. The formed composite is then rinsed in ethanol in order to resolve all residual RhB molecules at the top surface of the sample.

Fourier Transformer Infrared (FTIR) spectra were recorded in transmission mode using a Bruker IFS 66 v/s FTIR spectrometer at 4 cm^{-1} resolution. The PL measurements were performed using a triple monochromator and a GaAs photomultiplier. The excitation sources are an argon laser and He$-$Ne laser (632.8 nm). All the measurements were performed at room temperature.

3 Results and discussion

Figure 1 shows FTIR spectra of PS impregnated in two RhB solutions with different concentrations. The relatively large and intense bands at 800 cm^{-1} and 1050 cm^{-1} are assigned to Si$-$O vibrations in the silica matrix. The presence of strong Si$-$O vibrations and the absence of signals from Si$-$H wagging modes between 600 and 700 cm^{-1} are in agreement with an oxidation of the porous silicon matrix and the formation of porous silica layer. The bands at 1340 cm^{-1}, 1468 cm^{-1} and 1590 cm^{-1} are characteristic of the stretching mode vibrations of the C$-$N$-$, $-$CH$_2-$ and C$=$C species of the RhB molecules, respectively. The results clearly indicate the penetration of rhodamine molecules into the pores of PS. The comparison of the two FTIR spectra, in the range 1300$-$1650 cm^{-1}, highlights the effect of the concentration on the amount of rhodamine molecules incorporated in the porous silica matrix. In fact, the increase of the peak intensity is directly related to the quantity of dye molecules penetrated in the silica layers.

Figure 2 exhibits the PL spectra of the PS layer, RhB solution and the nanocomposite RhB/PS. The PL spectrum of RhB/PS (Fig. 2c) is largely shifted towards high energies compared to that of both PS (Fig. 2a) and RhB solution (Fig. 2b). The PL intensity of RhB/PS is more intense than that of PS. Thus, the PL of the nanocomposite is not due to RhB alone or PS alone. This indicates that the RhB molecules penetrate inside the pores and throughout the PS matrix. The fact that the RhB molecules, in solid phase, present an efficient emission is a direct proof of their penetration and dispersion in the porous matrix, since it is known that dye molecules don't emit in solid phase. The PL band of RhB molecules in PS presents a relatively large blueshift, which can be attributed to the increase of molecule-molecule interactions in solid and purely molecular nature of dye when dispersed in liquid [9]. In fact, it has been reported that interactions between dye molecules and host material lead to an increase of the band gap of the excited states [10]. Consequently, the PL band of RhB in PS presents a blueshift compared to that observed for RhB in solution.
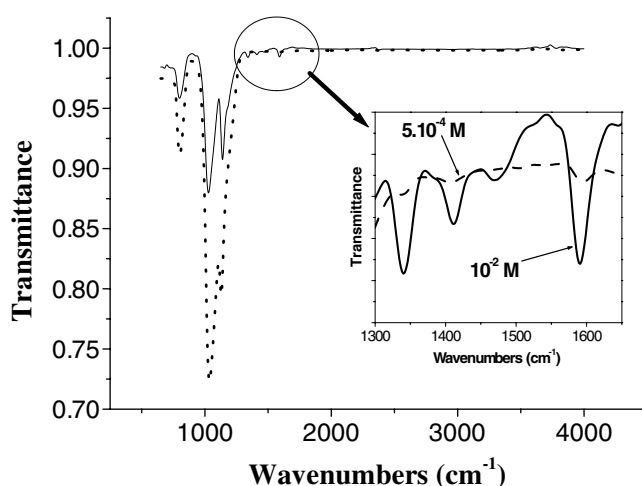

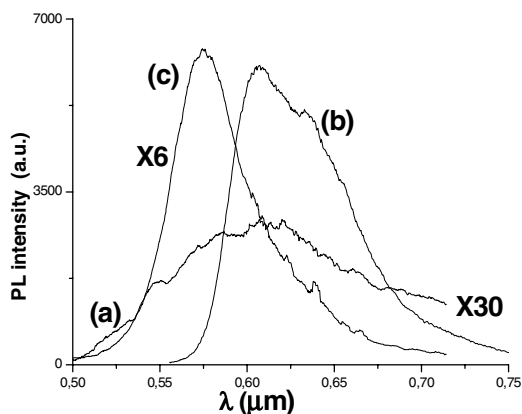**Fig. 1**   IR spectra of RhB/PS: $C = 5 \times 10^{-4}$ M (dashed line) and $C = 1 \times 10^{-2}$ M (solid line).

Fig. 2 PL spectrum of PS (a), RhB solution (b) and PS/RhB (c) (λ_{exc} = 488 nm).
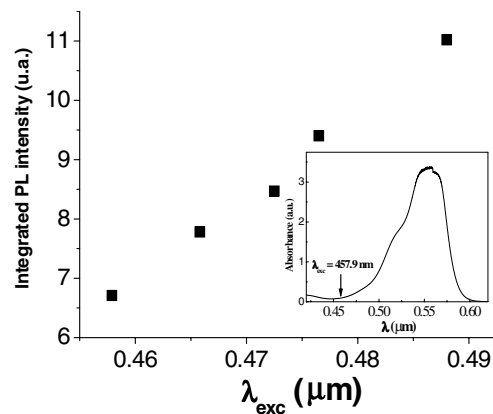

Fig. 3 Evolution of the integrated PL intensity of PS/RhB versus excitation wavelength.

The effect of the excitation wavelength beam shows efficient PL of the formed composite even for the line 457.9 nm where the RhB absorption is very weak (Fig. 3). The absorption spectrum of rhodamine in ethanol is shown in the inset of Fig. 3. The conditions of radiative excitation transfer in the composite are satisfied. In fact, the PS acts as donor and RhB acts as acceptor since the PL spectrum of PS overlaps with the spectral absorption range of RhB in solution. So, light emitted by PS can be absorbed by RhB molecules embedded in the pores. However, such process is weak compared to direct excitation of dye molecules or to non radiative excitation transfer since the emission of PS is feeble.

Figure 4 shows the PL spectra of the RhB in freshly porous silicon and in porous silica (PS). The PL band of freshly porous silicon appears in the PL spectrum. The initial PL intensities of the two substrates (porous silicon and porous silica) are in the same order. So, the difference of the PL intensities relatives to the formed nanocomposites is not due to a process of radiative excitation transfer from the hosts. The PL intensity of the RhB molecules in porous silicon was found to increase with the degree of oxidation of the substrate. We think that nonradiative excitation transfer assisted from species interaction can play a key role in the observed process. In fact, rhodamine is known to be cationic and interacts preferentially
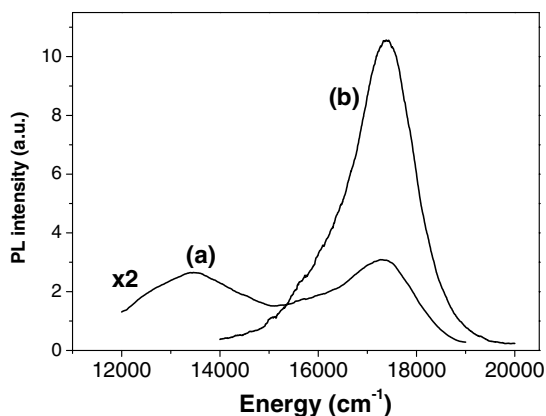

Fig. 4 PL spectra of RhB molecules in as prepared porous silicon (a) and in porous silica (b).
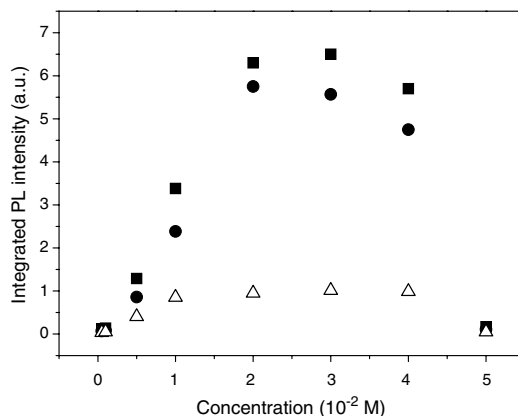

Fig. 5 Effect of RhB concentration on total integrated PL intensity (■), integrated Stokes PL (●) and integrated APL intensity (△) of RhB/PS nanocomposites.

with "O" sites, which dominate the PS surface after oxidation [11]. This raises the possibility of a charge transfer between Si surface and dye according to Dexter theory [12]. In addition, porous silica has an open sponge-like structure and its surface is naturally OH-terminated. Different OH species are found: silanol groups (SiOH) and adsorbed water molecules. Thus, hydroxyl groups play a major role on the physical and chemical adsorption of guest species. Moreover, the polar character of porous silica walls due to the presence of surface hydroxyl groups can be invoked to explain the blueshift of PL spectra with respect to those of dye in solution [13].

Figure 5 shows the evolution of the integrated PL intensity of the RhB/PS nanocomposite versus the concentration C of the RhB solution for the 632.8 nm excitation beam wavelength of a He−Ne laser. The PL intensity increases with the RhB concentration and reaches its maximum for $C = 3 \times 10^{-2}$ M, then it decreases quickly. The obtained results follow the expected trend based on the mechanism of light output of the dye. Indeed, the molecules of rhodamine emit only when they are dispersed.

For dye concentration $C \leq 2 \times 10^{-2}$ M, the behavior of PL intensity is linear with the increasing of concentration. For these concentrations the molecules of rhodamine are sufficiently dispersed and do not form any aggregates. When the dye concentration was between 2×10^{-2} M and 4×10^{-2} M, it was found that the integrated PL intensity was quasi constant and one can say that the aggregates start to form and the self-quenching prevents the linear increase. Since, for high dye concentrations one expects to have formation of aggregates and thus self-quenching of the photoluminescence [13]. Our results clearly show the existence of a critical concentration ($C > 3 \times 10^{-2}$ M) for aggregate formation.

The evolutions of the total integrated PL intensity, the integrated Stokes PL intensity and the integrated anti-Stokes PL (APL) intensity of PS/RhB versus concentration of RhB solution are quite similar.

When a He−Ne laser (632.8 nm) was used, only the dye molecules are excited since the absorption of PS is negligible at this wavelength, we found that the PL intensity of the PS/RhB composite was practically quasi-stable after ageing for 4 months in ambient (Fig. 6). It seems that the composite structure becomes stable with time. A possible explanation of the FWHM increase with ageing time is the existence of further dipolar interactions between RhB molecules and diffused H_2O molecules. As a result of these interactions, the APL intensity increases and the total PL spectrum is blueshifted.

The PL spectrum shows an anti-Stokes PL (APL) for RhB/PS whereas the RhB solution and the PS solely do not present any APL. The total PL band seems to be continuing at the excitation energy, which is in agreement with previous results [14] where the APL band was found to be independent of the excitation energy in the absorption range of RhB. Such APL can be attributed to RhB−RhB or to RhB-chemical species interactions. The APL intensity was found to present a nonlinear behaviour versus laser power: $I_{PLA} = P^{1.27}$ (Fig. 7). This result confirms the nonlinear optical properties of dye molecules.
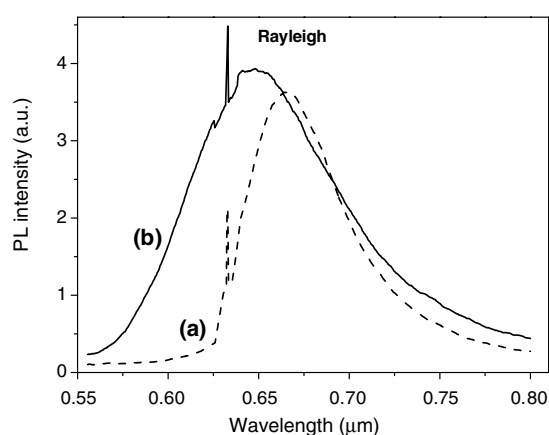

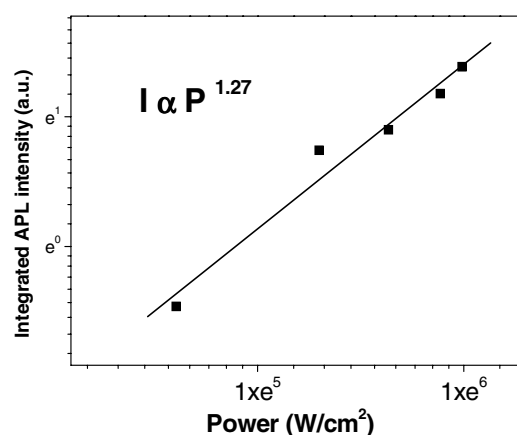**Fig. 6** PL spectra of the PS/RhB composite just after impregnation (a) and after ageing for 4 months (b).

Fig. 7 Integrated APL intensity of RhB/PS according to the excitation power ($\lambda_{exc} = 632.8$ nm) in ln−ln representation.

4 Conclusion

RhB/Porous Silica nanocomposites are prepared by simple impregnation of PS in RhB solution. FTIR spectroscopy analysis showed a penetration of the RhB molecules in the pores of the PS matrix. Apart from direct excitation, the results show the existence of excitation transfer between dye molecules and PS. A non radiative excitation transfer between the host and the RhB molecules is suggested from the effect of the oxidation degree of porous silicon on PL intensity. The study of the effect of the dye concentration on the PL intensity highlighted the existence of a critical concentration for the formation of aggregates of RhB molecules. It was demonstrated that porous silica layers can constitute a host for RhB molecules guests since the formed nanocomposite is stable in time and thus represents a potential candidate for solid state dye laser.

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