

Research Article

Nonlinear Optical Properties of a MMA-Silica Nanohybrid Material Doped with Rhodamine 6G

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A novel nanohybrid material based on MMA-Silica has been synthesized with an organic dye dopant (R6G) to tailor the optical properties. This novel material can be used on several devices such as active laser media for an organic solid state laser, OLEDs, or as a characterization media for new organic dye molecules. Thin films were deposited by dip-coating and characterized by absorption and reflection UV-VIS, photoluminescence, SEM, and Z-scan technique to verify their nonlinear behavior. R6G dye dopant has been used to verify that the nanohybrid matrix does not inhibit its optical properties.

1. Introduction

There is a need for developing new economical and simple materials suitable for different applications, in particular those related to nonlinear optical behavior, for applications ranging from nanomedicine to nanoelectronics. For instance, when a nonlinear material is doped with an organic dye it can be used as a laser medium for solid-state organic dye lasers. Nowadays solid-state polymeric dye lasers are of interest [1–3]; they can be used in medicine and cosmetology [4–6], optics [7, 8], electronics [9, 10], and other disciplines. New ways to generate laser light have been developed; tunable solid-state lasers can be obtained by the incorporation of guest dyes in solid host materials and this is one of the ideas that motivates this work. So far, several light-emitting solid systems based on the inclusion of laser dyes inside organic and inorganic solid matrix and hybrid and nanohybrid materials have been developed [11]. The use of

sol-gel technique [12] allows incorporating dyes in a solid material at the nanoscale; this technique is based on the hydrolysis of a precursor, forming a gel, and in this part of the process a dopant can be added. When solvents are volatilized a nanoporous glass with the inclusion of the dopant is obtained. So this technique is important because it can change optical, mechanical, thermal, and electrical properties of the matrix formed by the precursor by adding different kinds of dopants like powders, liquids, organic and inorganic materials, nanoparticles, and so forth. The dopants chosen depends on the required material properties and the changes on the amount of dopant inside the matrix. For example, it is possible to add an organic dye to have specific optical properties and some polymer to change its mechanical properties, like flexibility, or to protect the organic dye; PMMA (polymethylmethacrylate) decreases organic dyes degradation on solid-state dye lasers. OLEDs [13, 14] are another technology where organic dyes are used

and can be created with sol-gel technique adding dopants like R6G (rhodamine 6G), an element of a family of dye molecules used in a variety of applications. As a dye it can be used in staining materials or as a tracer in flow and speed determinations of water or other solvents. It possesses a characteristic absorbance spectrum which can be easily detected. In addition R6G fluoresces with high efficiency making it an invaluable component of a dye laser which can be pumped by the second harmonic of a Nd:YAG laser ($\lambda = 532$ nm); for this purpose its very important to study its photobleaching features in order to know how it degrades under the incident pump laser; this is achieved by doping PMMA with R6G [15]. The optical properties of a hybrid material can be tailored doping it with several dyes in order to obtain a variety of emission lines; this could be of interest in the manufacture of dye lasers [16].

2. Experimental

The sol-gel technique is characterized by many of its advantages such as simplicity of the synthesis, facility to be prepared at room temperature, and convenience to be doped with different materials like powders or liquids. This is important because dopant can change the optical or mechanical properties of the material, at the nanoscale, for example, by adding PMMA to a nanoporous silica matrix improving a more flexible material in comparison to a pure nanoporous silica matrix that is hard. We choose silica and PMMA as precursors because both are transparent materials at visible region so they do not change the optical properties of organic dyes and R6G was chosen for its well-known UV-Vis spectra, so R6G:ethanol spectrum can be compared with Hyb:R6G to check for changes. Deep-coating technique is used to grow thin films on glass substrates.

For the synthesis of this nanohybrid material [17], by sol-gel technique two steps are required; reaction was initiated with MMA and some pills of NaOH in a clean flask; the reaction was allowed to proceed for 15 min. In a second glass MMA, TEOS (tetraethyl orthosilicate), TMSPM, ethanol, and water are poured with molar ratio MMA:TEOS:TMSPM:ethanol:water of 3:1:1:15:15. Finally both containers are poured into one glass and drops of HCl are added to obtain a pH 4. It was stirred for 24 hours. All reactions occurred at room temperature. R6G was used as dopant with a molar ratio TEOS:R6G of 1:0.001; that is, the molar amount (ν) of R6G added to the hybrid matrix is given by $\nu = 0.001\nu_{\text{TEOS}}N$, where ν_{TEOS} are the moles of TEOS and N the concentration number of R6G which goes from $N = 0$ not dopant, $N = 1$ the first concentration of R6G, and so on until saturation.

Thin films were deposited using deep-coating technique on glass substrates previously cleaned in piranha solution, rinsed in ethanol, and dried at room temperature. Thin film thickness is controlled by fixing the substrate deposition extraction rate and speed.

A Spectronic Unicam UV 300 spectrometer was used to measure absorption and reflectance UV-Vis; photoluminescence was obtained using a B&W TEK 407 nm violet solid state laser 3.04 eV, 60 μ W, Sciencetech 9040 monochromator

of 0.5 m optical path. For the Z-scan technique was used a He:Ne laser as light source, $\lambda = 633$ nm of 10 mW of power; SEM micrographs were taken in a JEOL JSM-6610.

3. Results and Discussion

Figure 1 contains the IR-transmission spectrum of nanohybrid matrix and nanohybrid matrix doped with R6G; no mayor differences were found because R6G does not change the nanohybrid matrix. We can find bands representing the nanoporous silica matrix at 1194 and 939 cm^{-1} for Si-O-Si and Si-OH asymmetric stretching vibrations, respectively, also among those bands can find one related to Si-O-CH₃; and a peak at 787 cm^{-1} related to Si-O-Si symmetrical vibrations. Some other bands related to PMMA are found at 2351 cm^{-1} and 2912 cm^{-1} . This indicates that the nanoporous silica matrix and the polymeric matrix are independent of each other; they are related only by a bending vibration at 1457 cm^{-1} due to TMSPM. The aliphatic chain -CH- is revealed through a stretching band at 2959 cm^{-1} . Absorbed water band is at 3350 cm^{-1} . A weak C=C peak at 1700 cm^{-1} is due to unpolymerized MMA; CH₂ band is at 2926 cm^{-1} and an aliphatic chain -CH- at 2840 cm^{-1} .

Beer-Lambert law ($A = mct$, m molar absorbance coefficient) shows that absorbance A increases when dopant concentration c or sample thickness t is increased. That behavior is observed in Figure 2, where we plot thin films absorption spectra of the nanohybrid material at different concentrations of R6G, without R6G ($N = 0$), with a first concentration of R6G ($N = 1$), and so forth. When R6G concentration is increased the absorbance increases. Another way to change the absorbance is by changing the film thickness; however, in all the samples used here thickness remains constant because the speed of immersion and extraction of the substrates were fixed.

R6G is absorbed in the visible spectrum between 440 nm and 580 nm, corresponding to frequencies between the end of violet and half yellow having a maximum absorption for the green at 532 nm (Figure 2); a secondary maximum is shown at 490 nm, so R6G absorption spectrum profile is the convolution of two absorptions. The same profile is generated with ethanol:R6G. The authors Lu and Penzkofer [18] determine the optical properties of R6G dissolved in methanol and of a solid R6G film finding deviations from Beer's law due to the mutual interactions of neighbouring molecules and explain what the main and secondary peak are due for the generation of monomers and dimmers of R6G. R6G dissolved in methanol shows a peak at 530 nm, due to monomers and a secondary peak at 490 nm due to dimmers or multimers; monomers population is higher than dimmers. In the case of the hybrid material ethanol is part of the medium and during the hydrolysis reaction ethanol is produced so R6G immersed in the hybrid matrix has the same behavior as in methanol. This is the reason why the absorbance spectrum is maintained; on the other hand PMMA and SiO₂ are transparent at visible region of the spectrum so they do not have any optical contribution to the dye absorbance.

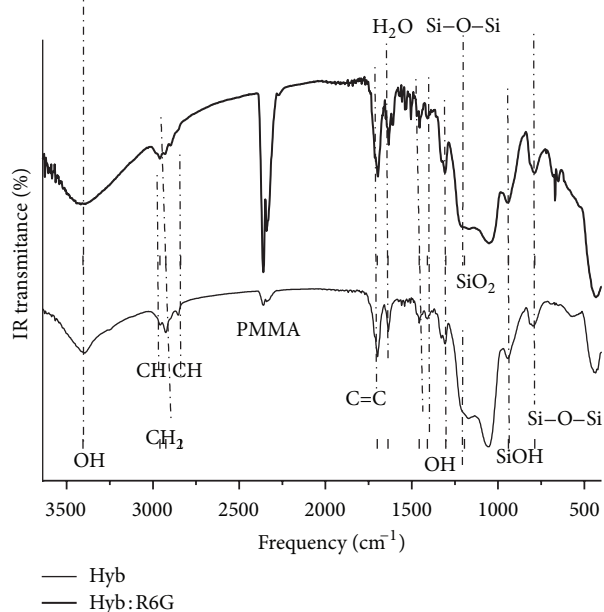


FIGURE 1: IR transmittance for hybrid material and Hybrid:R6G. Silica matrix is represented by Si-O-Si, SiO₂ bounds; polymeric matrix peak is at 2351 cm⁻¹ and 2912 cm⁻¹.

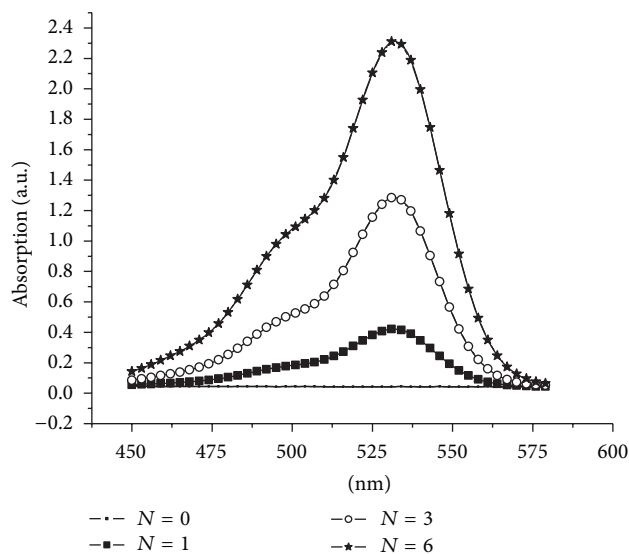


FIGURE 2: Hybrid material does not present absorption at visible spectra; when dopant of R6G is increased absorption response is increased according to Beer-Lambert law; this spectrum is characteristic for the R6G where the principal peak is around 532 nm.

Figure 3 shows the reflectance spectrum of thin films with different concentrations at 30°; when the R6G concentration increases the reflectance of the samples between 450 nm and 590 nm decreases and broadens; it is due to the absorbance at 532 nm; this behavior is useful for a device in which we need to have a filter for those frequencies; the control is generated through the concentration of R6G.

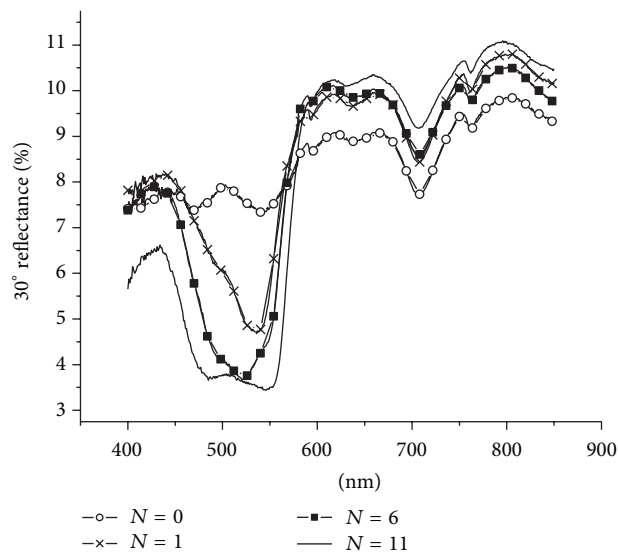


FIGURE 3: Reflectance spectra of the samples without dopant, first concentration of rhodamine 6G, and sixth and eleventh concentration measured at 30 degrees; the higher concentration decreases the reflectance between 450 nm and 590 nm.

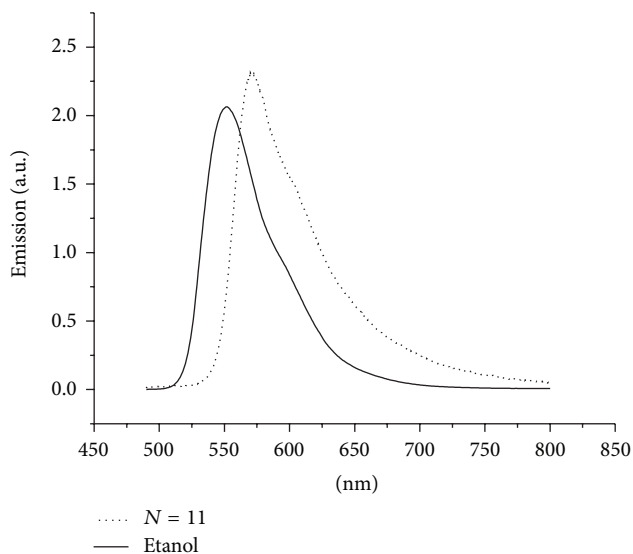


FIGURE 4: Photoluminescence spectra of Hyb:R6G for the eleventh concentration compared to the emission of R6G dissolved in ethanol; both spectra are similar.

Photoluminescence is the emission of light from a material if their atoms were excited by absorption of incident light; when they decay into lower energy states part of the absorbed energy is emitted as photons of less energy than the incidents. Luminescence can be emitted by organic or inorganic compounds. Figure 4 shows the photoluminescence spectrum of the hybrid material doped with R6G showing a maximum luminescence at 571.8 nm, and a secondary at 600 nm; these correspond to the emissions for the absorbed photons at 532 nm and 590 nm, respectively, which is very close to that reported when R6G is immersed in ethylene

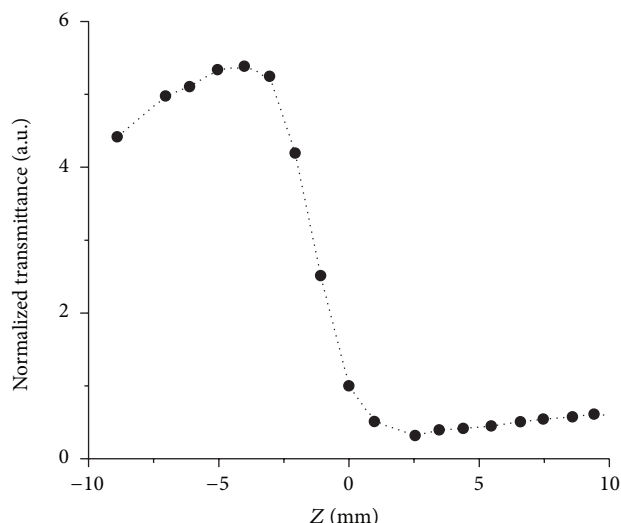


FIGURE 5: Z-scan curve of R6G dissolved in ethanol immersed in the nanohybrid material. Nonlinear behavior is due to the rhodamine 6G molecule. Hybrid material does not inhibit the nonlinear behavior.

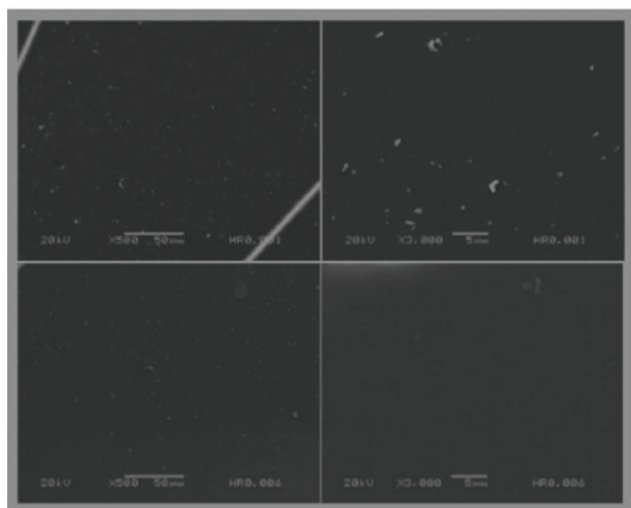


FIGURE 6: Micrographs of thin films with the first (first row) and sixth (second row) concentrations of R6G, at 500x (first column) and 3000x (second column); none of the films show fractures.

glycol [19], where a fluorescence peak is at 578.2 nm and when R6G is immersed in ethanol where the maximum photoluminescence is at 551 nm. So we can argue that the hybrid matrix does not radically change the wavelength of fluorescence of R6G; it is important to notice that hybrid matrix does not present photoluminescence so the observed spectrum is due solely to R6G photoluminescence spectra; the reason that the hybrid matrix does not show emission is because SiO_2 and MMA were not absorbed at visible region. To know photoluminescence spectra can be of interest to develop a solid-state dye laser [20]. A scintillator is a material used for detection and monitoring of accelerated particles like cosmic rays, among others; R6G is a dye used for scintillators due to its fluorescence emission properties [21].

Not only with R6G optical absorption and fluorescence properties are maintained but also with any organic dye dissolved in ethanol, so the same hybrid matrix can be doped with several organic dyes at the same time maintaining their optical properties. For many years it has been known that some kinds of organic materials exhibit extremely large nonlinear optical and electrooptical responses. The electronic nonlinearities in the most efficient organic materials are essentially based on molecular units containing highly delocalized π -electrons and additional electron-donor and electron-acceptor groups on opposite sides of the molecules. The highly active molecules tend to be highly polarized. The most polar molecules have a tendency to crystallize in a centrosymmetric structure which does not show nonlinear optical effects of second order. The choice of special molecules and the crystal growth methods used are of main importance for obtaining electrooptically active single crystals of good quality and large size. A main advantage of the organic materials is the possibility of altering the molecular structure for optimizing the electrooptical or nonlinear optical properties.

Figure 5 shows the Z-scan curve for a sample of R6G dissolved in ethanol immersed in the nanohybrid material, using as light source a He:Ne laser, with an intensity of 790 W/cm^2 in the material, $\lambda = 633 \text{ nm}$. The sample exhibits a negative nonlinear optical response. This nonlinear behavior is due to the presence of R6G in the hybrid material which does not show a nonlinear optical response so nonlinear curve shown in Figure 5 is only due to R6G dissolved in ethanol, hybrid matrix does not inhibit its nonlinear response which can be modified by increasing dopant quantity or adding different organic dyes.

Different samples were observed by SEM showing that during the drying process of thin films solvents are volatilized breaking the films, but these films do not have fractures (Figure 6) because the polymer matrix is flexible so that the fractures are reduced owing to the matrix by which is opened allowing the passage of solvents.

4. Conclusions

A simple and inexpensive optically nonlinear nanohybrid material, based on a TEOS:MMA nanoporous matrix, was developed. Optical response control depends on the thin film thickness or on the amount of dopant; these results can be seen using R6G as reference. The TEOS:MMA hybrid matrix does not change the absorbance and photoluminescence spectra of the organic dopant because TEOS and PMMA are transparent at visible spectra. Sol nanoparticles of the hybrid material doped with an organic dye show optical nonlinear response due to the dopant. Some potential applications for this material include lasers, photochromic coatings, and photoluminescent materials for organic devices and biomedical imaging.

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