TiO$_2$ NANOPARTICLES INFLUENCE
ON RHODAMINE 6G DROPLET EMISSION

M. BONI[1,2], ANGELA STAICU[1], I.R. ANDREI[1], ADRIANA SMARANDACHE[1], V. NASTASA[1,3], Z. SAPONJIC[4], M.L. PASCU[1,2]

[1] National Institute for Laser, Plasma and Radiation Physics, P.O. Box MG-6, RO-077125 Bucharest-Magurele
E-mails: *mihai.boni@inflpr.ro, angela.staicu@inflpr.ro, ionut.andrei@inflpr.ro, adriana.smarandache@inflpr.ro, mihai.pascu@inflpr.ro*
[2] University of Bucharest, Faculty of Physics, Romania, P.O. Box MG-6, RO-077125 Bucharest-Magurele, Romania,
[3] "Horia Hulubei" Extreme Light Infrastructure, Nuclear Physics/National Institute for R&D in Physics and Nuclear Engineering, 30 Reactorului Street, 077125, Magurele, Ilfov, Romania
E-mail: *viorel.nastasa@eli-np.ro*
[4] Vinča Institute of Nuclear Sciences, Department of Radiation Chemistry and Physics, Serbia
E-mail: *saponjic@vinca.rs*

Abstract. This work aims to investigate the effect of TiO$_2$ nanoparticles addition on the fluorescence emission of solutions of Rhodamine 6G excited in micro-volumetric droplets. In this paper are presented the similarities and the differences of the emission spectra by modifying parameters such as TiO$_2$ concentration, solutions pH and laser fluence. The pumping laser source used was the second harmonic beam emitted by a pulsed ns Nd:YAG laser at 532 nm. Lasing emission is observed and it is favorised by the solution acidity and laser beam intensity.

Key words: TiO$_2$ nanoparticles, Rhodamine 6G, fluorescence, lasing, droplets.

1. INTRODUCTION

Techniques such as fluorescence or Raman spectroscopy have a significant versatility and are used in different fields such us biomedicine, material sciences and environment monitoring [1–8].

A recent evidenced trend in science and technology is the development of micro and nano devices for use in connection with spectroscopic techniques that define micro- and nano-spectroscopy.

The presence of scattering particles in the laser dye solutions can influence their optical emission. Several studies were reported on the effect of different nanoparticles such as TiO$_2$ [9–11], ZnO [12], silica [13] in the enhancement of fluorescence emitted by laser dyes doped with nanoparticles.

In such cases, the so-called random lasing [14–16] occurs when the feedback mechanism is not based on a conventional resonant cavity, but it is strongly influenced

by nano-scatters introduced in solutions as disordering factor. Depending on the properties of the nanostructures such as material type, dimensions of nanoparticles and distance between them, a coherent feedback is obtained that acts on the intensity or amplitude of emitted radiation [17]. Random laser emissions with very good properties were reported for a multitude of systems: colloidal systems with laser dyes [18], photonic crystals [19, 20], polymeric matrices [21], doped nanoparticles with rare earth elements [22], quantum dots [23–25], semiconductors [26, 27], biological tissues [28]. In all these cases, optical pumping produces the excitation.

It is a well-known fact from literature that by modifying the pH of the solution in which are kept the TiO_2 nanoparticles [29–31], the agglomeration number is changed. The modification of the acidity of the laser dye solution also implies changes in the emission spectra [32].

We recently reported several studies on the emission properties of microdroplets containing dye solutions [8, 33, 34], dye emulsions [35], drug solutions [36, 37] and dye solutions doped with TiO_2 nanoparticles at pH 5 [18].

Here we extend the report of the later study [18] including the effect of pH solutions on the emission of droplets that contain TiO_2 nanoparticles in Rhodamine 6G (Rh6G) water solutions.

A combined action of the droplet spherical cavity that acts by itself such as a resonant cavity and the presence of TiO_2 scatterers that can induce random laser effect, takes place. This effect is investigated here having as experimental parameters nanoparticles concentration, solutions' pH and energy of laser excitation beam.

2. MATERIALS AND METHODS

The studied samples consist of Rhodamine 6G (Rh6G) at 5×10^{-4} M in distilled water and doped with TiO_2 nanoparticles from stock colloidal solutions having concentration 0.24 M, pH 2.5, number of particles 1×10^{17} part./ml, agglomeration number (number of TiO_2 molecules in one particle) 1402.

These samples were investigated in droplets generated by a Microlab 500 dispenser procured from Hamilton (USA). Rh6G at concentration 5×10^{-4} M and pH 2.5 in water solutions containing TiO_2 nanoparticles at two concentrations (10^{11} part./cm^3 or 10^{12} part./cm^3). The pH of the solutions was adjusted using NaOH or HCl concentrated solutions and controled with a Lab860 (Scott Instruments) pH-meter equiped with BlueLine 16 pH electrode.

The experimental set-up used for Laser Induced Fluorescence (LIF) studies on pendant droplets was presented in detail in [33–35]. Laser source used to pump the dye doped micro-volumetric droplets was the second harmonic of a pulsed Nd: YAG laser (Minilite II, Excel technology), pulse duration at half-maximum 6 ns, frequency 10 Hz, energy varied between 2–8 mJ. The emission signal was sent *via* an

optical fiber (400 μm diameter) to the enter slit of a spectrograph Spectra Pro SP 2750 (Acton Research) coupled with an ICCD PIMAX 1024 RB (Princeton Instruments) for detection and analysis. In this case, the spectra were collected pulse by pulse for 10 successive laser pulses. The spectrograph grating had 150 lines/mm with a 0.8 nm spectral resolution.

Before LIF studies, the solutions absorption spectra UV-Vis and NIR were recorded by a Perkin Elmer Lambda 900 spectrophotometer (spectral range 200–800 nm, resolution 1 nm) and a FTIR spectrometer type Nicolet^{TM} iS50 (4000–400 cm^{-1}, resolution 4 cm^{-1}).

3. RESULTS AND DISCUSSIONS

3.1. ABSORBTION SPECTROSCOPY

The change of the absorption properties of studied samples with the variation of solutions' pH is shown by the spectra registered between 200-800 nm for TiO$_2$ colloidal suspensions with particle number density 10^{11} part/cm^3 and pH 2.5 and 5 (Fig. 1).
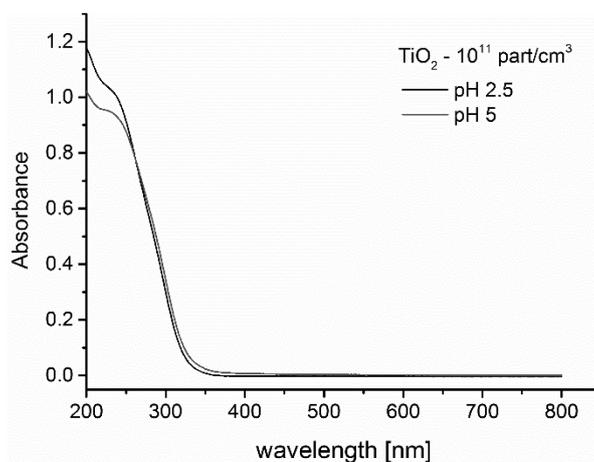

Fig. 1 – The absorption spectra of TiO$_2$ colloidal suspensions at 10^{11} part/cm^3 and pH 2.5 and 5.

It can be noticed that for lower pH, the absorption edge is shifted to shorter wavelength, which shows the decrease of agglomeration number of TiO$_2$ nanoparticles. Therefore, in the case of our dye solutions doped with TiO$_2$, it is expected an effect of nano-scatterers aggregate size on emission spectra collected from micro-droplets.

In Fig. 2, FTIR absorption spectra for the solutions of Rh6G doped with TiO$_2$ at the pH 2.5 and 5 are presented. Modifications of Rh6G molecular vibrations

are observed with the change of pH to 5, as follows: the absorption peak centered at 780 cm^{-1} is splitting into a doublet, which highlights the xanthene ring deformation; the allure change of the broad but weak band between 810-850 cm^{-1} along with rising of the peak at 842 cm^{-1} suggests out of plane CH bending of the external groups modes; between (1 280–1 300) cm^{-1} CN stretching vibrations of the aromatic secondary amine were assigned; between (1 445–1 460) cm^{-1} the methylene CH bend vibrations appear; on the broad band between (2 800 and 3 800) cm^{-1} assigned to the NH stretching modes of the Rh6G, the narrow and weaker bands arising between (3 000–3 100) cm^{-1} are due to CH stretching of the xanthene ring and the phenyl, ethyl and methyl external groups.

The changes in the IR spectra maybe due to possible agglomeration of the Rh6G molecules themselves with pH increase [32].
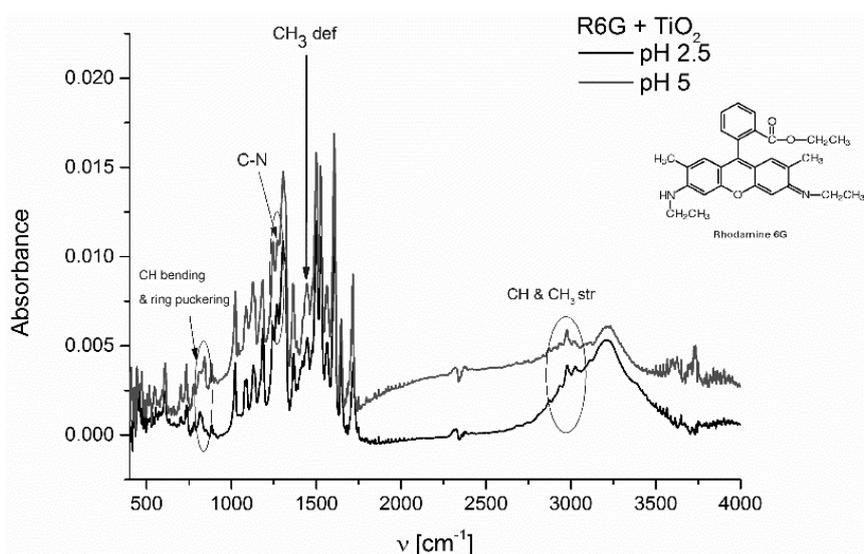

Fig. 2 – The FTIR spectra of Rh6G and TiO_2 at pH 2.5 and 5.

3.2. LIF

The influence of TiO_2 nanoparticles on the fluorescence emitted by microdroplets of Rh6G solutions excited with 532 nm laser light (energy/pulse 2 mJ) implies a walk-off of peaks' intensities to longer wavelength and a decrease of intensity at 0.17 mol/l concentration of TiO_2 added in the droplet (Fig. 3).

In this study, the experiments were carried out to investigate the influence of the solutions' pH on dye emission characteristics. Spectra measured on solutions with pH adjusted to 2.5 are shown and discussed in comparison with previous results.
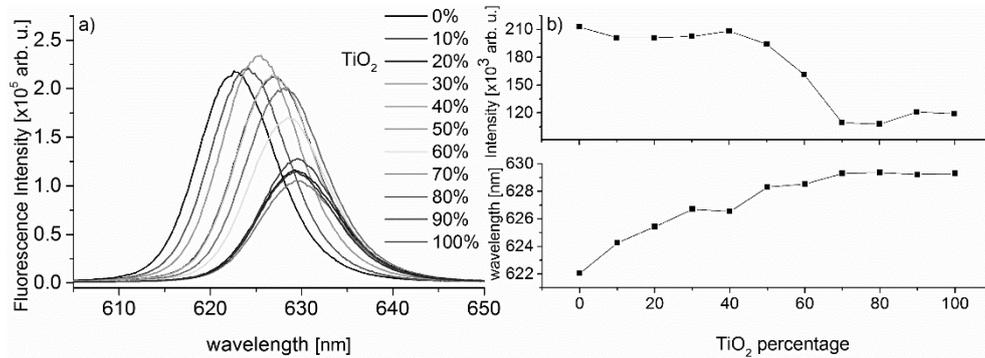
Fig. 3 – (a) LIF spectra measured for 1 µl droplets of Rh6G solutions in water (10^{-4} M) and TiO$_2$ at different percentages from a stock solution of 0.24 mol/l. (b) Fluorescence peak intensity and wavelength variation function of TiO$_2$ percentage.

In Fig. 4, are shown the emission spectra of solutions having only Rh6G at 5×10^{-4} M in distilled water (pH 2.5) or being doped with TiO$_2$ nanoparticles at 10^{11} part/cm^3 or 10^{12} part/cm^3 concentrations. The spectra are registered for a sequence of 10 pulses; each spectrum corresponds to a single laser pulse.
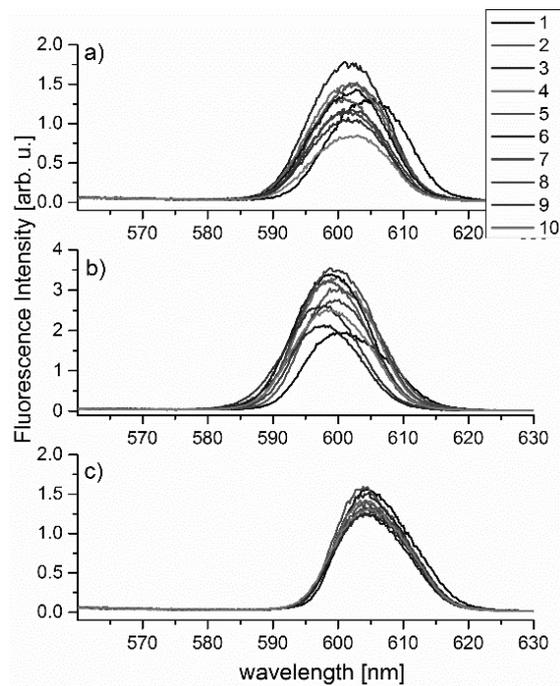

Fig. 4 – Emission spectra of 1 µl droplets containing Rh6G water solutions at 5×10^{-4} M, pH 2.5 (a) and doped with TiO$_2$ nanoparticles at two number densities: 10^{11} part/cm^3 (b) or 10^{12} part/cm^3 (c). Excitation at 532 nm, beam energy 6 mJ. Insertions in the figure indicate the laser pulses number.

For a pumping beam energy of 6 mJ, it can be notice only small influence of TiO$_2$ addition on the emission spectra for Rh6G solutions at pH 2.5. Only one band is present in the spectrum having FWHM about 15 nm and the maximum of emission is in the range 600.5 – 605.5 nm for droplets of pure dye solutions. At TiO$_2$ addition (10^{11} part/cm^3) the spectral range of the peak is shifted towards 597–601 nm. When the concentration of TiO$_2$ is one order of magnitude higher, the peak's wavelength is almost constant at 604.5 nm.

As for fluorescence intensity, addition of TiO$_2$ at 10^{11} part/cm^3 increases the peak intensity about two times when pH is 2.5, compared to five times when pH is 5. Higher concentrations of TiO$_2$ induces an about two times decrease of fluorescence intensity, either at pH 2.5 or at 5.

All these observations are summarized in Fig. 5 where the emission peak wavelength range (a) and the intensity of the fluorescence peak (b) are plotted *versus* laser pulse shot for all the samples excited with 6 mJ.
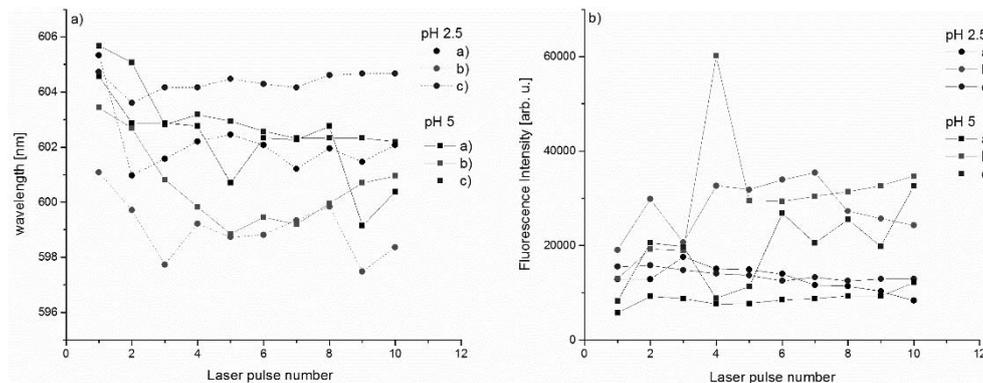

Fig. 5 – a) The emission peak wavelength *versus* laser shot; b) the intensity of the maximum plotted *versus* laser pulse shot. Excitation energy 6 mJ.

In Fig. 6, the emission spectra for excitation energy of 8 mJ are shown. The same characteristics as in the case of pH 5 for the emission spectra are observed when the TiO$_2$ number density is 10^{11} part/cm^3: the fluorescence band located at longer wavelength (the spectral range 594.6 – 598.2 nm at pH 2.5) is accompanied by two other bands placed at shorter wavelengths.

The intensity of these 2 new peaks is about two times stronger when solutions pH is 2.5 compared to 5 (spectra shown in previous study [18]) and it is shown in Fig. 7 for the third peak placed towards blue range. Moreover, it can be seen that this peak appears only for first laser shots at pH 5 compared to the case of samples with pH 2.5, for which the peak is present for every pulse.

The intensity of the three peaks of emission spectra varies from pulse to pulse and increases on the expense of the others shown in Fig. 6. This results from Fig. 8, where also average values were plotted for each laser pulse.
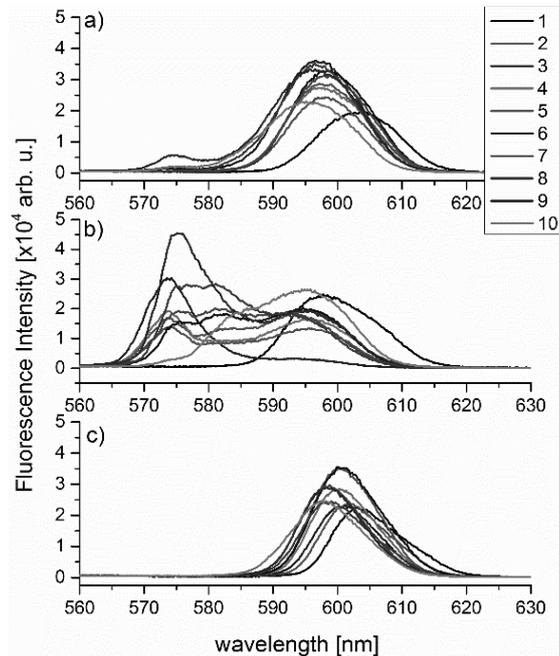
Fig. 6 – Emission spectra of 1 µl droplets containing Rh6G water solutions at 5×10^{-4} M, pH 2.5 (a) and doped with TiO$_2$ nanoparticles at two number densities: 10^{11} part/cm^3 (b) or 10^{12} part/cm^3 (c). Excitation at 532 nm, beam energy 8 mJ. Insertions in the figure indicate the laser pulses number.
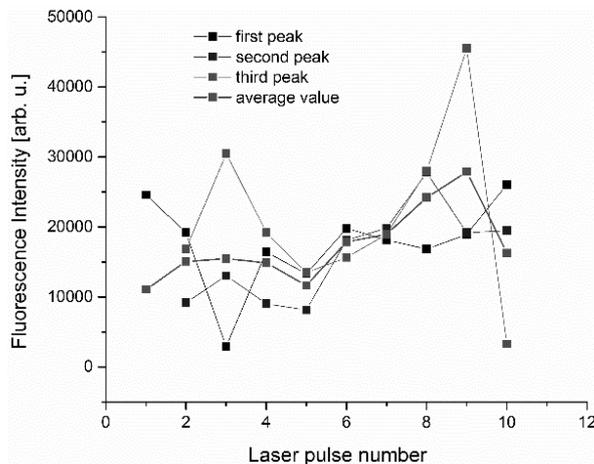

Fig. 7 – The third peak intensity and wavelength dependence on laser pulse number for pH 2.5. and 5.

At 8 mJ excitation energy, for the other 2 types of solution with no TiO$_2$ or TiO$_2$ at 10^{12} part/cm^3, the changes of the emission spectra are not as spectacular as in the previous case. Mainly, one emission band is observed and the fluorescence

peaks are placed at wavelengths in the following ranges 594.9 – 603.6 nm at pH 2.5 (for samples without nanoparticles) and respectively 597. 6 – 603.1 nm at pH 2.5 (for samples with TiO_2 at 10^{12} part/cm^3).
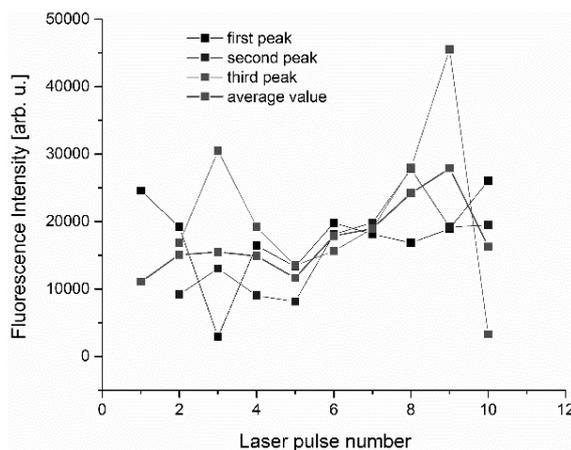

Fig. 8 – The intensity of the main emission peaks and the average value *versus* laser pulse number. Excitation energy 8mJ, pH 2.5, and $N_{TiO2} = 10^{11}$ part/cm^3.

Comparing these intervals, it can be concluded that the addition of TiO_2 at this density induces a shift to longer wavelengths of the maximum with respect to pure dye sample, regardless the solution's pH and in contrast to the case of TiO_2 number density of one order of magnitude lower where the shift is towards blue. This is shown in Fig. 9, where the wavelength for the first peak is shown for all the droplet samples excited at 8 mJ energy *versus* laser shot.
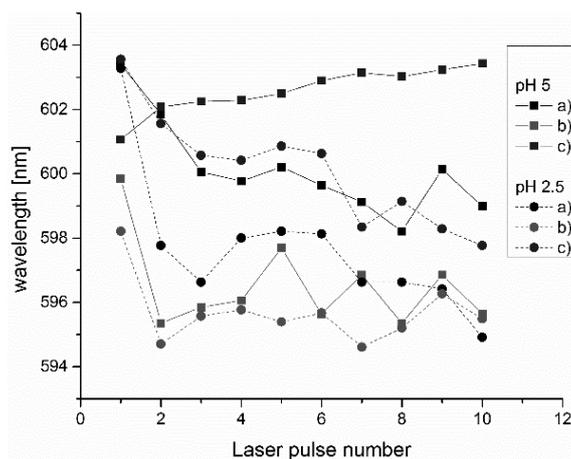

Fig. 9 – The emission peak wavelength variation with the laser pulse for studied samples.

All the shown data prove the TiO$_2$ nanoparticles suitability to be used in solutions of dye lasers to obtain laser radiation from pendant droplets. By changing the concentration, pH and laser excitation energy, a broader tunability of the laser radiation can be obtained.

4. CONCLUSION

The emission spectra of microdroplets containing solutions in water doped with TiO$_2$ nanoparticles were shown. It was observed that the presence, in the droplet that contain laser dye solution, of TiO2 nanoparticles induces emission spectra modifications depending on nanoparticles number density and laser beam pumping energy and solution's pH. A concentration of 10^{11} part/cm^3 nanoparticles favors the formation of two other emission bands that are shifted to the blue with respect to the main band. Comparison between the emission characteristics at two different pH (2.5 and 5) was made. While for the first peak of emission placed to longer wavelength, the increase of pH induces an increase of intensity, for the new peaks, which appear at the blue side, the acidity of the solution favorizes an enhancement of emission intensity.

These data suggest that TiO$_2$ nanoparticles addition to pure dye droplet solutions has an influence on the emission spectra, which can be modulated by varying nanoparticles concentration, pumping laser energy, and pH solutions.

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