Random laser in ordered colloidal suspensions

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Abstract: Random lasing is achieved in an ordered photonic colloidal (TiO_2@Silica) suspension. Stronger correlation in the scatterers' (TiO_2@Silica) position, induced by stronger and longer-range Coulomb interaction improves light localization and random laser performance.

1. Introduction: A comparative study of random lasing is performed in colloidal suspensions containing core-shell TiO_2@Silica NPs, with two different silica shell thicknesses (SST) (40 nm and 70 nm), suspended in a R6G ethanol solution. The silica surface on TiO_2 core (rutile, 410 nm mean diameter) induces an electrostatic field (ζ–potential) on the TiO_2@Silica surface, providing optical colloidal stability [1–3], which can give rise to strong Coulomb interaction between NPs when [TiO_2@Silica] is increased. The particle-particle interaction is based on the idea that pair-wise interactions arise from the interplay of attractive van der Waals forces (F_{attr}) and repulsive Coulomb forces (F_{rep}, double layer force) screened by the Debye-Hückel ions' cloud [4]. The total interaction potential between two particles (U_T) can be expressed as the sum of electrostatic repulsion (U_{elec}) and the van der Waals attraction (U_{vdw}): $U_T=U_{elec}(r)+U_{vdw}(r)$ where r is the distance between two particles. The modulus of both potentials (U_{elec} and U_{vdw}) increases when the radii a of the particles and/or the hydrodynamic diameter (D_{hyd}) and ξ-potential increases [4]. When the mean separation distance between particles (r_m) is similar or smaller than D_{hyd}, strong particle interaction is expected, which leads to a correlation in the particles' position [5,6]. In recent works [6,7], we showed a correlation in the scatterers' (TiO_2@Silica) position, which was associated to the strong and long-range Coulomb interaction. The correlation in the scatterers' position favors interferential phenomena (Localization of light). Localization induced by correlation has been addressed recently by Kravtsov and co-workers in higher dimensional systems, showing the universality of this phenomenon [8]. We remark that localization of light is an interferential phenomenon with additional complexities associated to scale factor [9]. In the present work, two random laser samples were prepared by dispersing in ethanol a solution of the TiO_2@SiO_2 NPs, with SST of 40 nm and 70 nm, at TiO_2 filling fractions (FF_{TiO2}) of 4.8%, equivalent to [$140x10^{10}$ NPs mL^{-1}]. R6G at [10^{-4}M] was added to both suspensions. D_{Hyd} of the TiO_2@Silica NPs, measured by dynamic light scattering at very low [TiO_2@Silica], shows a larger D_{Hyd}~1450 nm for the thicker silica shell (TiO_2@SiO_2+SiO_2) when compared to D_{Hyd}~890 nm for the thinner silica shell (TiO_2@SiO_2). For both systems, the ξ-potential of -70 mV is the same. In previous works [6,10–13], at this FF_{TiO2}=4.8%, we showed several pieces of experimental evidence of localization of light. An enhancement of the light-matter coupling (enhanced absorption and Raman signal) arises when the system approached localization. Localization gives rise to other associated phenomena, such as a photon-molecule bound state [14,15], which in turn, leads to the suppression of vibrational relaxation and spontaneous emission [16]. This latter is a consequence of the strong correlation of trapped photons in localized states [9,15].

2. Results: The samples were pumped by a Q-switched Nd:YAG (Continuum Minilite II, 25 mJ, 532 nm, pulse width of ~4 ns). The emission spectra were collected through a multimode optical fiber (200 μm), coupled to a spectrometer HR4000 UV−VIS (Ocean Optics). For additional details of the experimental setup see ref. [7]. Figure 1a shows the behavior of the emitted intensity as a function of the pump energy fluence. RL efficiencies (RL_{eff}) for both systems are not constant. For the TiO_2@SiO_2 system, RL_{eff} decreases for pumping fluencies (P_F) >15 mJ cm^{-2} and for P_F>75 mJ cm^{-2}, a complete saturation of the emission is observed. For the TiO_2@SiO_2+SiO_2 system, RL_{eff} decreases for P_F>20 mJ cm^{-2} and a complete saturation of the emission is observed above ~110 mJ cm^{-2}. For the TiO_2@SiO_2+SiO_2 system, RL_{eff} (P_F<15 mJ cm^{-2}) is ~25% higher than for the TiO_2@SiO_2, and the saturated RL emission intensity is also around 25% higher than for the TiO_2@SiO_2 system. The above results can be explained by higher density of localized states (stronger localization) for the TiO_2@SiO_2+SiO_2 system. For P_F>75 mJ cm^{-2} (TiO_2@SiO_2 system) and P_F>110 mJ cm^{-2} (TiO_2@SiO_2+SiO_2 system), (saturated RL emission) a cavitation effect (bubbles emerging) starts to be observed. This latter result could indicate that the pressure exerted by trapped light inside localized states does not provoke an appreciable cavitation effect, which could be due to the "rigid" structure formed by the scatterers (their positions being strongly correlated) as a consequence of the strong bond between them. For an expanded explanation about this phenomenon, see ref. [7]. For both RL systems, the RL emission peak

(Figure 2b) shows a redshift that increases rapidly for P_F from ~0.08 up to ~8 mJ cm^{-2} and the maximum redshift value (~7.6 nm) is large when compared with the customary maximum redshift for a TiO_2 NP system (3-4 nm). For both RL systems, the wavelengths of the RL emission peak below the RL threshold (fluorescence) is considerably lower (~558 nm) than for the TiO_2 NPs system and TiO_2@SiO_2 system in the diffusive regime (~564 nm) [1]. This fact can be explained in the following way: The redshift was previously explained by a model considering absorption and emission at the transition between the ground state and the first excited singlet state of the dye molecule [17]. Polarization of R6G molecules below the population inversion threshold, induced by pump photons trapped within the localized states, should give rise to a photon-molecule bound state, due to the strong correlation of such photons [9,15]. After some time (residence time of the pump photons), the quantum state of the localized states changes due to thermal and/or nonlinear effects [18,19] giving rise to the emission of strongly correlated photons (fluorescence), which would propagate being poorly absorbed.

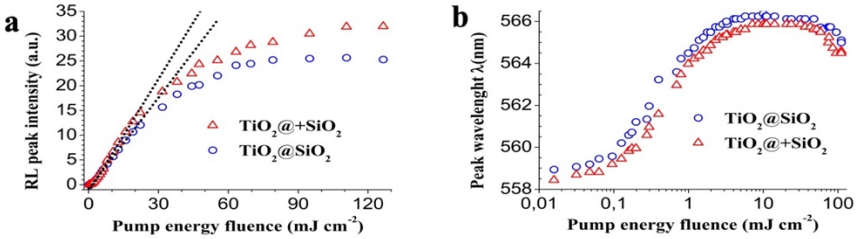

Figure 1. For TiO_2@+SiO_2 and TiO_2@SiO_2, influence of P_F on a) the RL emitted peak intensity, RL_{eff}, for P_F<15 mJ cm^{-2} (black dotted lines) and b) the peak position of the emission spectrum.

3. Conclusion: The TiO_2@SiO_2+SiO_2 system presented an RL_{eff} (P_F<15 mJ cm^{-2}) and a saturated RL emission intensity 25% higher than the TiO_2@SiO_2 system. This latter is attributed to a stronger localization as consequence of a stronger correlation in the scatterers' position, due to stronger and longer-range Coulomb interaction.

This work was supported by FAPESP grant 2017/10765-5.

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