Supplementary Information

Random lasing at localization transition in a colloidal suspension (TiO$_2$@Silica)

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Materials and Methods:

R6G laser dye (C$_{28}$H$_{31}$N$_2$O$_3$Cl), with a molecular weight of 479.02 g mol$^{-1}$ was supplied by Fluka; ethanol alcohol HPLC with spectroscopic grade purity was supplied by TEDIA; tetra-ethyl-ortho-silicate (TEOS) was supplied by Sigma-Aldrich, and the ammonia P.A. was supplied by VETEC. The titanium dioxide (TiO$_2$) nanoparticles (NPs) of 410 nm with a rutile crystal structure was acquired from DuPont Inc. (R900). The nanoparticles were coated with a silica shell of ~40 nm thickness via the Stöber method. In the first stage, 5 g of TiO$_2$ Nps were dispersed in 500 ml of absolute ethanol. This suspension was placed in an ultrasound bath for 20 minutes to disperse the particles and 6.67 mL of ammonia and 10 mL of TEOS were added. The TEOS and commercial ammonia (NH$_4$OH 28%-30%) were added alternately in 100 portions of 100 µl and 220 µl, respectively. The synthesized TiO$_2$@Silica nanoparticle suspension was rota-evaporated, dried in an oven at 70 ºC for 2 h, and re-dispersed in ethanol. For the random laser, dye (Rhodamine 6 G, (R6G)) at [1x10$^{-4}$ M] was added to the TiO$_2$@Silica suspension with [140x10$^{10}$ Nps ml$^{-1}$].

Experimental setup for RL study:
Figure S1 shows two schematic diagrams of the experimental setup used for the random laser (RL) study and FAP (fraction of absorbed pumping) measurements. The pumping source of the random laser was the second harmonic of a $Q$-switched Nd:Yag (Continuum Minilite II; 25 mJ, $\lambda = 532$ nm, with a pulse width of $\sim 4$ns, repetition rate up to 15 Hz and spot size of 3 mm). The pump laser’s beam was incident upon the sample at $\sim 15$ degrees. The laser’s output power was regulated through neutral density filters (NDF), a polarizer and a half wave plate.

Figure S1a corresponds to the experimental setup used for the RL action study and FAP measurements (shown is the frontal collection). The sample was accommodated in a 2 mm path length quartz cuvette. The emission spectra were collected through a multimode optical fiber (200 $\mu$m), coupled to a spectrometer HR4000 UV-VIS (Ocean Optics) with a 0.17 nm spectral resolution (FWHM). The collection angle was $\sim 35$ degrees with respect to the sample surface; that is, $\sim 20$ degrees with respect to the incident pumping beam.

The sample was placed in an ultrasound bath for about 10 minutes before recording the spectrum, in order to disperse the nanoparticles (TiO$_2$@Silica). Figure S1b shows the
experimental setup used for the measurements of RL action and FAP measurements in a small micrometric volume ($FAP_{(\mu m)}$) near the input-pumping surface (<4 $\mu$m depth). This optical system is composed for one $F_1$ lens (19 mm focal length), another $F_2$ (250 mm focal length), and an optical fiber (50 $\mu$m) coupled to an HR4000 UV-VIS spectrometer (Ocean Optics). Notice that this detection system performs like a confocal microscope. The detection area was estimated at a diameter of ~3.8 $\mu$m. The depth of focus ($r_{axial}$) can be estimated by $r_{axial} \approx \frac{\lambda}{NA^2} \leq 4 \mu m$ equation, where $\lambda$ and NA are wavelength (532nm) and numerical aperture (>0.4), respectively. The collection angle was ~45 degrees with respect to the incident pumping beam, that is, ~0 degrees with respect to normal of the sample surface.

The $FAP$ can be expressed as $FAP = \left( \frac{I_{RNps}}{I_{RNp+R6G}} \right) = \frac{1}{e^{\left(\frac{l_eO}{l_a^*}\right)}}$, where $I_{RNps}$, $I_{RNp+R6G}$, $l_eO$ and $l_a^*$ are the light reflected by the samples without R6G, the light reflected by the samples with R6G, the average photon path length inside the scattering medium and the effective microscopic absorption length (R6G), respectively. $l_a^*$ can be expressed as $l_a^* = \frac{l_a}{\left(1 + \gamma_0\right)}$, where $l_a$ and $\gamma_0$ are the microscopic absorption length, which must be a constant that depends of the [R6G] (passive regime), and the enhanced absorption factor near the input-pumping surface, respectively. The term $\left(\frac{1+\gamma_0\gamma_0}{2}\right)$ represents an estimate of the mean value of the enhanced absorption factor in the region where absorption is enhanced, i.e. between 1 and $\gamma_0$. Thus, $l_eO$ at passive regime can be determined as follows: $l_eO = \frac{l_a}{\left(1 + \gamma_0\gamma_0\right)} \times \ln(FAP_{bT})$. $FAP_{bT}$ is the $FAP$ value at fluencies well below the RL threshold (passive regime), where $l_a$ only depends of the [R6G]. The effective refractive index is determined as follows: $n_{eff0} = 1 + (n_{eff} - 1) \left(\frac{1+\gamma_0\gamma_0}{2}\right)$. 

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The calculated concentration of scattering nanoparticles was $140 \times 10^{10}$ Nps/ml. For this calculation, the nanoparticles were considered to be completely dispersed, and free of any kind of agglomerates. For the study of random laser action, the pumping energy fluence varied between 0.003 and 72 mJ/cm$^2$. Typical emission spectra of the RL below (0.1 mJ/cm$^2$), close (1.2 mJ/cm$^2$), and well above (60 mJ/cm$^2$) the RL’s threshold are shown in Figure S2a, S2b and S2c, respectively. The RL emission spectra show the intensity increase and the bandwidth narrowing when the pumping energy fluence is increased. The emission intensity increases around 3 orders for pumping fluencies from 0.1 mJ/cm$^2$ to 60 mJ/cm$^2$ (below and well above the RL threshold, respectively). Figure S2d shows the behavior of the spectral width (FWHM), as a function of the pumping energy fluence. A typical bandwidth narrowing is observed when the pumping fluence increases (from ~50 nm up to ~5 nm).

**Figure S2.** Typical emission spectra of the RL for three pumping energy fluencies: (a) below (0.1 mJ/cm$^2$), (b) around (1.2 mJ/cm$^2$), (c) above (12 mJ/cm$^2$) and (d) well above (60 mJ/cm$^2$) the RL threshold. (e) Influence of the pump energy fluence on RL spectral width (FWHM). (f) detail of figure 1a, showing the RL threshold.

The peak position of the emission spectrum was measured as a function of the pumping energy fluence (between 0.012 and 72 mJ cm$^2$). The maximum redshift value (7.6 nm) was
truly large (fig.1d), especially when considering that the absorption and emission are both saturated. This shift was previously observed and explained by a model considering absorption and emission at the transition between the ground and the first excited singlet of the dye molecule.\textsuperscript{1} The saturated absorption means a very low percentage of R6G molecules in the ground state, $S_{0i}$, and/or a high population in the $S_{1i}$ excited singlet states (see fig. S3). Saturated emission means very low population of the first $S_{1i}$ excited singlet or/and a high population of $S_{0i}$ sublevels of ground states.

**Figure S3.** Potential curves of the $S_{0i}$ and $S_{1i}$ electronic states (R6G); q is the normal coordinate of a vibrational normal mode of the rhodamine molecule. $\lambda_{\text{Abs}}$ (532nm) is the pumping wavelength and $\lambda_{\text{Emi}}$ are the emission wavelengths.

The possible curves of these states as a function of the normal coordinate of an optical vibrational mode are shown in Figure S3. The last would mean a high percentage of R6G molecules in the $S_{1i}$ excited singlet states and/or $S_{0i}$ sublevels of the ground state. Thereby, the transition rates from $S_{0i}$ up to $S_{1i}$ (absorption) and from $S_{1i}$ to $S_{0i}$ (stimulated emission) should be higher than the vibrational relaxation in the $S_{1i}$ excited singlet states and in the $S_{0i}$ sublevels of the ground state. This phenomenon could be a consequence of the enhancement of absorption and stimulated emission by localization. On the other hand, the polarization of

\textsuperscript{1} M.A. Noginov, H.J. Caulfield, N.E. Noginova, P. Venkateswarlu, *Optics Communications* **1995**, *118*, 430-437.
R6G molecules by pumping photons trapped within the closed loop paths should give rise to a photon-molecule bound state, which in turn would lead to the suppression of vibrational relaxation and spontaneous emission. Thereby, the transition of R6G molecules from excited state $S_{1i}$ up to the $S_{0i}$ sublevels of the ground state, within the closed loop paths (localized state), could happen without losses by spontaneous emission or vibrational relaxation.

**RL study in a small micrometric volume**

The optical detection system (Figure S1b) is composed of one $F_1$ lens (19 mm focal length), another $F_2$ (250 mm focal length), and an optical fiber (50 µm) coupled to a HR4000 UV-VIS spectrometer (Ocean Optics). The detection region was estimated to be ~3.8 µm in diameter and with a depth of focus <4µm (near the input-pumping surface, <4µm depth). The pumping spot is ~3 mm of diameter. From $FAP_{(µm)}$ measurement the $l_a$ of R6G can be calculated above the RL threshold ($l_a^{*(µm)}$) in a small micrometric volume near the input-pumping surface.

$$l_{a^{*(µm)}} = \frac{l_e^{0(Micro)}}{\ln(FAP_{aT(µm)})} \approx \frac{104µm}{\ln(1.24)} \approx 483µm,$$

where $FAP_{aT(µm)}$ is $FAP_{(µm)}$ above the RL threshold. Additionally, if the sharp peaks are the result of localization then these peaks should be mainly emitted in the region where absorption is enhanced (closed loop paths). From our previous work, the enhanced absorption factor, $γ_0$, can be interpreted as the average number of turns executed by the photons around the closed loop paths, which must decrease as a function of depth. Therefore, an enhanced absorption factor averaged between 1 and $γ_0=1.84$ could be a good approximation, i.e. $\frac{(1+γ_0)}{2} = \frac{(1+1.84)}{2} = 1.42$.

Furthermore, the value of the transport mean free paths for $d$ near to zero ($l_{T0}$), determined

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2 Sajeev, J., Wang, J. Quantum electrodynamics near a photonic band gap: Photon bound states and dressed atoms. *Phys. Rev. Lett.* **64**, 2418 (1990).
3 Sajeev, J. Localization of light. *Physics Today* **44**, 32 (1991).
4 Yablonovitch, E. Inhibited Spontaneous Emission in Solid-State Physics and Electronics. *Phys. Rev. Lett.* **58**, 2059 (1987).
5 Jimenez-Villar, E. et al. Anderson localization of light in a colloidal suspension (TiO$_2$@Silica). *Nanoscale*, (2016), **8**, 10938–10946.
experimentally in our previous work, corresponds to $L_0 = 1.3 \mu m$. Thereby, the macroscopic absorption length ($L_{MA}$) of this system above the RL threshold can be expressed as:

$$L_{MA} = \left( \frac{L_0 \times L_T}{3} \right)^{1/2} = \left( \frac{483 \mu m \times 1.3 \mu m}{3} \right)^{1/2} \approx 14.5 \mu m.$$  Consequently, the pumping depth into the sample at fluencies above the RL threshold is estimated around 15\(\mu m\).

The emission spectra were acquired by integrating 21 laser shots. For an appropriate signal-to-noise ratio, an integrating time of 1.4 s at a repetition rate of 15 Hz was required. At the pumping fluence of 9.6 mJ cm\(^2\), the emission spectra integrated from 6 laser shots were also recorded for comparison, obtaining a good signal-to-noise ratio. However, for higher pumping intensity, the amount of narrow peaks did increase and their intensity did saturate, provoking a decrease in definition of these peaks.

**Figure S4.** Emission spectra collected from a small micrometric volume (<4\(\mu m\) diameter) near the input interface (<4\(\mu m\) depth) for pumping fluences of: 9.6 mJ cm\(^2\), integrating a) 21 and b) 6 laser shots; c-f) 6 mJ cm\(^2\), integrating 21 laser shots, and collected with a delay of ~(10-20s) between each spectrum. The solid red lines represent the respective noise signals.

Figure S4a and S4b show the RL emission spectra for a pumping intensity of 9.6 mJ cm\(^2\), integrating 21 and 6 laser shots, respectively. Figure S4 c-f show the RL emission spectra for a pumping fluence of 6 mJ cm\(^2\), integrating 21 laser shots and collecting them with a delay of
~(10-20) seconds between each. The frequency of these sharp peaks changes little in a few 
seconds, it only changes completely after tens of seconds or by stirring the sample. The RL is 
a liquid suspension, which means a continuous change in the particle configuration. In this 
way, if peaks of the emission spectrum are depending on particle configuration, these peaks 
should change after some time or by stirring the sample, like it was observed.

We note that the intensity of these narrow peaks, relative to the fluorescence band, is lower 
than that reported by Cao and co-workers, which could be a consequence of the extremely 
reduced (effective) size of their random laser. ZnO nanoparticles of 50 nm clustered in 
micrometric structures (diameter of several micrometers) compose their random laser. In turn, 
it is known that the density of strongly localized modes (anomalous localized modes, long 
lifetime) increases in the vicinity of the boundary, which was theoretically predicted by Mirlin 
in disordered electronic media. The anomalous localized modes are those where the 
boundary is part of the closed loop path (localized state). Thereby, the density of anomalous 
localized modes (long lifetime) must increase and the total amount of localized modes 
decrease as system size is decreased below localization length. The latter can be interpreted as 
an increase in the extent of localization (modes of long lifetime, decrease of the effective 
localization length) for a reduced number of anomalous localized modes (decrease of the total 
amount of localized modes) within these micrometric clusters. Additionally, an increase of 
the effective refractive index is expected near the boundaries (localization). Consequently, 
owing to the fact that surface-volume ratio is considerably higher in these clusters; the 
interference (localization) must be increased, since the photon pathlength is forced to be

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6 Cao H. et al. Spatial confinement of laser light in active random media. *Phys. Rev. Lett.* **84**, 5584 (2000).
7 Mirlin, A.D. Spatial structure of anomalously localized states in disordered conductors. *J. Math. Phys.* **38**, 1888 (1997).
8 Mirlin, A. D. Statistics of energy levels and eigenfunctions in disordered systems. *Phys. Rep.* **326**, 259–382 (2000).
9 Campagnano, G., Nazarov Yu. V. *G_0* corrections in the circuit theory of quantum transport. *Phys. Rev. B* **74**, 125307 (2006).
longer due to the internal reflection. The latter can be understood such that the presence of a finite barrier in the border provokes an increase of the quantum interference (localization), which was theoretically demonstrated by Ramos and co-workers in disordered electronic media.\textsuperscript{10} Therefore, lasing emission in their sample (clusters) must be confined to fewer lasing modes (anomalous localized modes) with higher intensity (high quality factor, long lifetime). However, our sample is a three-dimensional (3D) semi-infinite system with just one effective border, the input interface (silica-sample). On the other hand, contrary to our sample, where an R6G quantum efficiency near unity is expected, the fluorescence in their sample must be greatly quenched due to the superficial defects and dangling bonds of ZnO nanoparticles. Nevertheless, the excitation of ZnO or R6G molecules within the closed loop paths (excitation within localized state) would be free of quenching, since such molecules would be strongly correlated.\textsuperscript{2,3} Therefore, the intensity ratio (peaks/fluorescence) reported by Cao and co-workers (clusters)\textsuperscript{6} must be necessarily greater than that observed in our sample. In this way, the system studied by Cao and co-workers (very small size)\textsuperscript{6} should be addressed as a particular case of random lasing at localization or localization transition in 3D (reduced size). Indeed, in a subsequent study conducted by the same group,\textsuperscript{11} ZnO spheres of 85-617 nm diameters were cold pressed to form pellets. In this case, the relative intensity of the sharp peaks was considerably lower and for the sample of 85 nm spheres, lasing was not observed, which was attributed to a drastic increase of the random laser’s cavity size brought about by an increase in transport mean free path. The latter indicates that the clustered structure (composed by 50 nm Nps) with very small dimensions (micrometric)\textsuperscript{6} must play a crucial role in the localized lasing phenomenon. The above perspective represents another approach

\textsuperscript{10}Barbosa, A.L.R., Bazeia, D., Ramos J.G.G.S. Universal Braess paradox in open quantum dots. \textit{Phys. Rev. E} \textbf{90}, 042915 (2014).

\textsuperscript{11}Wu, X. \textit{et al.} Random lasing in closely packed resonant scatterers. \textit{J. Opt. Soc. Am. B} \textbf{21}, 159–167 (2004).
to addressing the random lasing at localization, since the shape and size of a random laser should have strong influence on localization and consequently on random lasing.

**Back collected measurements**

A schematic diagram of the experimental setup for the studies of RL back-collected emission is shown in Figure S5a. An optical fiber of 200 µm was placed near to the back surface of a quartz cuvette, in order to collect the RL emission after it traversed the sample.

The collected spectra consist of a broad emission band (~50 nm bandwidth) with an overlapped single emission band, whose intensity and bandwidth are dependent of the pumping energy (Fig. Sb-e). In order to determine the RL emission band, two methods were used: 1) the previously rescaled fluorescence spectrum at a fluence <0.5 mJ cm$^{-2}$ was reduced to the collected spectra, 2) the emission spectrum was deconvoluted with several Gaussians, extracting a baseline that allows also to determine the superimposed emission band of the random laser. The results of both methods are similar.

**Figure S5.** a) Schematic diagram of the experimental setup for back collection of RL emission. RL emission spectra by this back collection method for pumping fluencies of: b) 1.2 mJ cm$^{-2}$, c) 12 mJ cm$^{-2}$, d) 36 mJ cm$^{-2}$, and e) 60 mJ cm$^{-2}$. The arrows denote the RL emission and R6G fluorescence band, respectively. f) Bandwidth of the emission spectrum, extracted from the front and back collection, as a function of the pumping energy fluence.
The intensity of the emission spectrum was plotted as a function of the pumping energy fluence. The experimental points were rescaled; such that, $RL_{\text{eff-back}}$ was equal to the saturated $RL_{\text{eff}}$ obtained for frontal collection (Figure 1a, fluencies > 36 mJ cm$^{-2}$, blue line). The RL emitted light should traverse through the sample and, as a result, will suffer attenuation. If we consider that the saturated $RL_{\text{eff}}$ (Figure 1a, fluencies >36 mJ cm$^{-2}$, blue line) corresponds to the $RL_{\text{eff}}$ of the band mode (ASE; $RL_{\text{eff-B}}$), because the RL peaks mode is saturated, we can rescale the experimental points by a mathematic factor such that the $RL_{\text{eff-back}} = RL_{\text{eff-B}}$. Figure S5b, S5c, S5d and S5e show the spectra collected at the back of the cuvette. The $RL_{\text{eff-back}}$ was constant without depletion (Figure 3). The $RL_{\text{eff-B}}$ for fluencies <12 mJ cm$^{-2}$ was 1.8 times lower than the $RL_{\text{eff-P}}$, and $RL_{\text{eff-P}}$≈0 for fluencies ≥36 mJ cm$^{-2}$. The latter means that the contribution of localized modes progressively decreases as fluence is increased above 36 mJ cm$^{-2}$. In turn, the redshift starts to decrease progressively for fluencies ≥36 mJ cm$^{-2}$. In this way, one can infer that the large redshift (∼7.6 nm) observed in RL emission must be associated to the emission of localized modes.

Figure S6. RL emission spectra by frontal and back collection for pumping fluencies of: a) 12 mJ cm$^{-2}$, b) 36 mJ cm$^{-2}$ and c) 60 mJ cm$^{-2}$. The back-collected spectra were rescaled, such that the intensity ratio (frontal/back collection) for each fluence would be the same found in figure 3a. The red solid lines represent the resulting spectra from the subtraction between frontal and back spectra (front-Back).

Figure S5f shows the bandwidth of the emission spectrum, extracted from the frontal and back collection, as a function of the pumping energy fluence. As can be observed, the bandwidths
of the frontal-spectra are larger than the back-spectra. Additionally, the frontal spectra are slightly asymmetrical, showing a widening towards longer wavelength (figure S6). Figure S6 shows the emission spectra from the frontal collection, the back collection and the subtraction between both spectra (front-back), for fluencies of 12 mJ cm\(^{-2}\), 36 mJ cm\(^{-2}\) and 60 mJ cm\(^{-2}\). The resulting spectrum from the subtraction between both spectra, which must correspond with the peaks emission spectrum integrated over the whole emission volume, shows a plateau in intensity (~2-3nm). This indicates suppression of interaction between the peaks, which is a signature of random lasing at localization. Figure S7 shows a representative picture of this phenomenon of suppression of the interaction between localized modes. Pump photons from different localized modes that spatially overlap (region magnified and framed with white circle) only interact with the specific R6G molecule (called \(\alpha\) and \(\beta\)). Although, the \(\alpha\) and \(\beta\) pumping photons are spatially overlapped and both have the same frequency, each photon can only interact with its respective molecule, \(\alpha\) or \(\beta\), since the \(\alpha\) and \(\beta\) photons would be strongly uncorrelated.

Collections: frontal (micrometric) and back.

Figure 3e shows the RL emission spectra at 6 mJ cm\(^{-2}\) for both collections, frontal (small micrometric volume, less than 4 µm depth) and back. The resulting spectrum from the difference between both spectra (figure 3f), which corresponds to the emission spectrum of the peaks mode, shows narrow peaks with similar intensities in a large frequency range (~7-8 nm). The similarity in intensity of the narrow peaks must be because the interaction between the peaks is suppressed by localization.\(^{12}\) Additionally, the stimulated emission rate must be higher than the vibrational relaxation rate, which results in a gain of the peaks that is approximately equal over the whole bandwidth. Notice that, the spontaneous emission and vibrational relaxation must be inhibited by localization. Therefore, the gain of the peaks mode

\(^{12}\) Stano, R. & Jacquod, P. Suppression of interactions in multimode random lasers in the Anderson localized regime. *Nature Photon.* 7, 66–71 (2013).
(in this frequency range) would be mainly dominated by the quality factor (Q) of the passive resonators (scattering medium). Because the extent of localization hardly varies in this RL frequency range, the RL peaks intensity should be similar. The plateau in intensity observed in the peaks mode spectrum (∼7-8nm; figure 3f) of the small micrometric volume is broader than that observed in the spectrum of the integrated peaks mode (∼2-3nm) extracted through the integrated collection (figure 3d and figure S6). This is probably because the acquisition depth for the micrometric collection (<4 µm depth) is shallower than that for the integrated collection (∼15 µm depth). Therefore, the peaks mode spectrum integrated over the whole emission volume represents passives modes with a range of quality factors broader than that from the small micrometric collection volume near to the input interface. Notice that, the quality factor of the passive modes of a scattering medium at localization must present strong dependence with depth, since localization decreases in depth.

**Figure S7.** Representative picture of the phenomenon of suppression of the interaction between localized modes of a random laser at critical regime of localization. The white spheres and red points represent the TiO$_2$@Silica Nps and R6G molecules, respectively. The β pumping photon can only excite the β R6G molecule and the α R6G molecule is only excited by the α pumping photon (region magnified, framed with the white circle). The green lines represent the flux of pumping photons. The red lines represent the flux of the emitted photons from localized lasing. The outgoing red cone represents the localized lasing emission.