Supplementary Information

Novel core-shell (TiO$_2$@Silica) nanoparticles for scattering medium in a random laser: higher efficiency, lower laser threshold and lower photodegradation.

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Materials

R6G laser dye (C$_{28}$H$_{31}$N$_{2}$O$_{3}$Cl), with molecular weight 479.02 g/mol, supplied by Fluka: Ethanol alcohol (C$_2$H$_5$OH) with spectroscopic grade purity, supplied by Alphatec: Tetra-ethyl-ortho-silicate (TEOS), supplied by Sigma-Aldrich. The titanium dioxide (TiO$_2$, nanoparticles 410 nm) of rutile crystal structure was acquired from DuPont Inc (R900).

Chemical synthesis of silica-coating on TiO$_2$ nanoparticles

In the first stage, 2 g of TiO$_2$ Np were diluted in 250 ml of absolute ethanol. The solution of TiO$_2$ nanoparticles was then divided into two equal portions of 125 ml. One of the parts was placed in a bath at 5 °C and 1.1 ml of TEOS, previously diluted in 11 ml of ethanol, was added. The 10% diluted solution of TEOS was added in 110 portions of 100 μl during the course of 1 hour.

The solution was stirred during the TEOS addition. The other portion was stored and used as a reference in every experiment. Previously, before adding the TEOS, the solution of TiO$_2$ Np was placed in an ultrasound bath for 20 minutes to disperse the particles.

The TEOS hydrolysis and subsequent condensation of silica on the TiO$_2$ surface was provoked, taking advantage of the catalytic effect in the near surroundings of TiO$_2$ Np. In addition, the possible accumulation of water molecules around the nanoparticles would favor TEOS hydrolysis. Probably, the electric potential associated with the surface of the nanoparticles themselves, in conjunction with the higher dielectric permittivity of the water, should promote the accumulation and polarization of water molecules in the vicinity of TiO$_2$ Np. Self superficial hydrolysis of TiO$_2$ nanoparticles would also favor the TEOS hydrolysis. The superficial irregularities of the TiO$_2$ nanoparticles must cause intensification of superficial electric potential in the regions with a smaller curvature radius. This phenomenon should increase the medium polarization, water accumulation and catalytic effects in these regions, leading to silica coating irregularities.

Characterization and sample preparation:

Transmission electron microscopy (TEM) was used on a 100kV JEOL, model 1200EX, microscope. The commercial carbon-coated Cu TEM grid was immersed in the solution of TiO$_2$@Silica nanoparticles that had previously been diluted 50-fold and then left to dry, before being introduced into the microscope. The stoichiometric ratio (Ti/Si) was determined by Energy Dispersive X-Ray fluorescence (ED-XRF) using an X-ray spectrometer SIEMENS D5000. The sample was prepared in three steps: precipitation, washing and drying. The nanoparticle powder (TiO$_2$@Silica) was pressed into a tablet form with a 12 mm diameter.

Experimental setup of random laser measurement

Supplementary Figure 1S shows a schematic diagram of the random laser (RL) experimental setup. The pumping source of the random laser was the second harmonic of a Q-switched Nd:YAG Continuum Minilite II (25 mJ, λ = 532 nm, with a pulse width of ~6 ns, repetition rate up to 15 Hz and spot size of 3 mm). The pump laser beam was incident upon the sample at 15 degrees. The laser power was regulated through neutral density filters (NDF), a polarizer and a half wave plate.

Supplementary Figure 1S. Schematic diagram of the RL experimental setup; NDF neutral density filter.

The samples were accommodated in a 2 mm path length quartz cuvette. The emission spectra were collected through a multimode optical fiber (200 μm), coupled to a spectrometer HR4000 UV-VIS (Ocean Optics) with a 0.36 nm spectral resolution (FWHM). The collection angle was ~60 degrees with respect to the sample surface, that is, 45 degrees with respect to the incident pumping beam. The liquid samples were placed in an ultrasound bath for about 10 minutes before recording the spectrum, in order to obtain the same dispersion of nanoparticles (initial conditions) in all measurements.
Random laser action

The pumping energy fluence varied between 0.12 and 120 mJ/cm² for the study of random laser action. This range of fluences is below those used to study the photodegradation process (180 J/cm²). Each value of emission intensity and bandwidth represented in the graphs (fig. 1c and d) was taken by integrating 10 laser pulses, which allowed us to rule out any photodegradation effects during the measurement.

Supplementary Figure 2S (a and b) shows two typical emission spectral curves for the dye solution for two kinds of nanoparticles (TiO₂, TiO₂@Silica) at 5.6x10⁻¹⁰ Np/ml; the broad spectrum was obtained for excitation well below the laser threshold (0.24 mJ/cm²), while the narrow spectrum was recorded for 120 mJ/cm². The peak intensities of the narrow and broad peaks were normalized to show the narrowing effect more clearly. For the TiO₂ and TiO₂@Silica systems, the peak intensity decreases for higher fluencies from 0.6 mJ/cm² up to 4.8 mJ/cm².

For suspensions of two different concentrations (5.6x10⁻¹⁰ Np/ml and [1x10⁻⁴ M] for R6G, nanoparticle concentration was 5.6x10⁻¹⁰ Np/ml and [1x10⁻⁴ M] for R6G) for 120 mJ/cm². The peak intensities of the narrow and broad bands were normalized to show the narrowing effect more clearly. For the TiO₂ and TiO₂@Silica systems, the peak intensity relationship (narrow/broad) is 3.6 and >4 orders of magnitude larger, respectively. Note that the RL spectrum is redshifted, with respect to the center of the luminescence spectrum at low pump intensity of >3nm for the TiO₂ system. This shift was previously explained by a model considering absorption and stimulated emission at the transition between the ground and the first excited singlet of the dye molecule. The redshift of the RL spectrum is close to unit [R6G][R6Gstimulated]≤1 at 120 mJ/cm², which is evidenced in a higher efficiency of the RL (TiO₂@Silica). The peak position of the emission spectrum was measured as a function of the pumping energy fluence (between 0.12 and 120 mJ/cm²).

Supplementary Figure 2S (c) shows a comparison of these peak positions with fluence for the TiO₂@Silica and TiO₂ systems. The emission spectrum shows a redshift for the TiO₂ system, which undergoes a large increase in fluorescence between 0.12 and 12 mJ/cm² (0 to 2.8 nm). This redshift increases slightly (between 3 and 3.6 nm) for fluencies >12 mJ/cm². Instead, the emission spectrum peak for TiO₂@Silica system shows a blueshift for fluences ≤12 mJ/cm². For fluences between 12 mJ/cm² and 120 mJ/cm², the redshift increases in the same fashion, from 0 up to ~0.5 nm.

Figure 2Sd shows the fraction of absorbed pumping (FAP) as a function of energy fluence for the two systems (TiO₂@Silica, TiO₂). The parameters I₀ and Iₐ are the average photon path length and ballistics absorption length, respectively. The FAP values at fluences well below (FAPₐT) and above the (FAPₜT) RL threshold are constants for either system (TiO₂, TiO₂@Silica). The FAP value decreases for fluencies from 0.24 mJ/cm² up to 2.4 mJ/cm² (TiO₂@Silica). For the TiO₂ system, the FAP value decreases for higher fluences from 0.6 mJ/cm² up to 4.8 mJ/cm².

This effect should be associated with a decrease in R6G molecules in the ground state S₀ and/or the population increment at S₁ excited singlet states, which requires higher fluences for the TiO₂ system. The fast process of vibrational relaxation of R6G molecules (~2ps) prevents a greater drop in FAP values (FAPₗT/FAPₜT). The ratio between photon residence time (τₑₒ) and the vibrational relaxation times (τₗ₆G) of R6G molecules (τₑₒ/τₗ₆G) should determine the relationship between FAP values, before and above the RL threshold (FAPₗT/FAPₜT).

Colloidal stability and scattering mean free path measurements

The above results of RL action could be associated with a more colloidal stability of TiO₂@Silica nanoparticles, which would represent a higher effective scattering surface. It is known that silica nanoparticles have a higher colloidal stability than those of TiO₂. The issue related to the colloidal stability of the scattering medium has not been discussed much in regards to the treatment of RLs. The authors of these papers do not take into account the effects of agglomeration of the particles that compose the scattering media, which would significantly change the scattering mean free path (lₛ), a crucial parameter in the operation of RLs. Additionally, the electrical interaction between rhodamine molecules and nanoparticle components of the scattering medium should increase local concentration of rhodamine around the nanoparticles, affecting the colloidal stability. The fact that the counterion of the rhodamine is much heavier than Cl⁻, would cause a decrease of the zeta potential associated with the TiO₂ nanoparticles (negative), approaching zero.

Experimental setup for scattering mean free path measurements

For suspensions of two different concentrations (5.6x10⁻¹⁰ Np/ml and 8.9x10⁻¹¹ Np/ml) of TiO₂ and TiO₂@Silica, we determined the scattering mean free path from the transmission experiment. Figure 3Sb shows a schematic diagram of the scattering mean free path measurement. The transmitted intensity Iₜ was determined as a function of slab thickness: the laser beam (second harmonic of Q-switched Nd:YAG Continuum Minilite II, λ = 532 nm)
nm, 1 μJ (1mJ attenuated 10⁵ times by neutral density filters), with a pulse width of ~6 ns, repetition rate 10 Hz) was passed through a positive lens L₁ (200 mm focal length) so as to obtain the focus with its waist near the pinhole PH₁ (600μm diameter). The cell consisted of two optical flat F in wedge form, in this way; the slab thickness depends on the incidence point of the cell. Another pinhole, PH₂ (1200μm diameter), was positioned 80 mm away to PH₁ in order to reduce the diffuse light. Yet another lens, L₂ (50 mm focal length), allowed focalization of the coherent light on the optical fiber (200μm). Figure 3b and c shows typical curves of TiO₂@Silica samples (concentrations 5.6x10¹⁰ Np/ml and 8.9x10¹¹ Np/ml) versus slab thickness.

Supplementary Table 1S. Iₜ values determined by transmission experiment for the TiO₂@Silica and TiO₂ systems at two nanoparticle concentrations (5.6x10¹⁰ Np/ml and 8.9x10¹¹ Np/ml).

<table>
<thead>
<tr>
<th>Concentrations (Np/ml)</th>
<th>TiO₂@Silica</th>
<th>TiO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.6x10¹⁰</td>
<td>8.9x10¹¹</td>
<td>8.9x10¹¹</td>
</tr>
<tr>
<td>Iₜ values (μm)</td>
<td>20.6±0.2</td>
<td>2.1±0.04</td>
</tr>
<tr>
<td></td>
<td>52±4</td>
<td>15±1</td>
</tr>
</tbody>
</table>

Supplementary Figure 3S. a) Schematic diagram of the experimental setup for the determination of transmitted intensity as a function of slab thickness. L₁ and L₂, lens; F+F, cell consisting in two optical flat mounted on a translation stage; PH₁ and PH₂, pinholes; OP, optical fiber to collect the light in the spectrometer. b-c) typical curves of transmission light versus slab thickness for the TiO₂@Silica system: b) for [5.6x10¹⁰ Np/ml], Iₜ determined was 20.6±0.2 μm, c) for [8.9x10¹¹ Np/ml], Iₜ determined was 2.1±0.04 μm. The red solid lines correspond to the fitted exponential functions.

FAPₚ values allow us to determine the average photon path length (pumping light) \( \bar{\ell}_p = \ell_p \times \ln[FAPₚ] \). In this way, the average number of scattering events undergone by each \( N_t \) incident channel before being reflected could be determined from \( \ell_p \) values. Each \( N_t \) channel of a pumping beam would be scattered an average of \( N_d \) times in volume \( V_p \approx \ell_p^2 \), where \( N_d \approx \ell_p^2/N_t \) and \( V_p \) is a cube with sides equal to \( \ell_p \). The channel numbers that propagate \( N_p \) through area \( A_0 \) at λ=532nm (TiO₂@Silica), could be estimated by:

\[
N_p = \frac{(20.6μm)^2}{(0.532μm)^2} \approx 1500 \text{ channels.}
\]

For the TiO₂@Silica system and [5.6x10¹⁰ Np/ml] (FAPₚ=4.7):

\[
\ell_p = \frac{885μm \times \ln(4.7)}{1370μm} \text{ and } N_p = \frac{1370μm/20.6μm \approx 66 \times 1500}. \]

Therefore, if \( N_p \ll N_p \), it would mean that differential events are highly unlikely. For the sample containing TiO₂ nanoparticles at [5.6x10¹⁰ Np/ml] (FAPₚ=2.5):

\[
\ell_p = \frac{885μm \times \ln(2.5)}{810μm}, \quad \quad N_p = \frac{(52.4μm)^2}{(0.532μm)^2} = 9700 \text{ channels and } N_p = \frac{810μm/52.4μm \approx 15 \times 9700}. \]

However, the concentration and refractive index of the samples are similar. The specular reflections are similar for both systems (TiO₂ and TiO₂@Silica), so the coupling of pumping radiation to the samples is the same. Notice that, at this concentration, the particle volume represents < 1% of the samples. Therefore, from these facts it can be inferred that we are in the presence of two colloidal systems with different stabilities (TiO₂@Silica>TiO₂). This means that the effective concentration of TiO₂ nanoparticles is lower, suggesting the formation of agglomerates. In other words, the effective scattering surface is lower in the TiO₂ system. Even when the TiO₂@Silica nanoparticles agglomerate, the effective scattering surface would be preserved, unlike with TiO₂ nanoparticles.

**Photodegradation studies**

The photocatalytic pathway involves a reaction on the TiO₂ surface following several steps: 1) photogeneration of electron–hole pairs by exciting the semiconductor with >3.2 eV light, 2) separation of electrons and holes by traps existing on the TiO₂ surface and 3) a redox process induced by the separated electrons and holes with the adsorbates present on the surface.

The exponential decrease of the RL intensity, for the system TiO₂, indicates that the photodegradation is proportional to its derivative, as to the photodegradation rate. This means that the charge transfer, and therefore the redox reaction, will cause a greater charge transfer in the next laser shot. Thus, one might think that the high concentrations of charges created by the TiO₂ nanoparticles at high pumping fluencies must react with the proper surface of the nanoparticles, reducing Ti⁴⁺ and oxidizing O₂⁻. This process results in oxygen vacancies, which act as traps for photoelectrons. These electrons, trapped near the surface, act as a source of electron transfer coming from these superficial traps, increasing the efficiency of the redox process. Additionally, the creation of oxygen vacancies in TiO₂ causes a progressive decreasing of gap on the nanoparticle surfaces (TiO₂), which is reflected in the progressive increase in the creation of electron-hole pairs. This photo-darkening effect is observed in films of TiO₂ exposed to successive irradiation of laser pulses.

The photodegradation process for the TiO₂@Silica system presents a linear behavior. However, the modulus of the slope increases slightly after the emission intensity decreases to 50%. This fact indicates that the photodegradation rate of R6G remains constant until the emission intensity decreases to 50%. Subsequently, the photodegradation rate experiences a slight increase, but remains constant. This phenomenon could be due to the decreased absorption of R6G, provoking an increase of the effective pumping fluence inside the scattering medium.
(TiO2@Silica), which would increase the photodegradation rate of R6G.

Photodegradation as a function of pumping fluence

In the sample containing TiO2 nanoparticles, the photodegradation has an exponential-linear dependence with pumping fluence. The linear part corresponds to the region with low fluencies (<140 mJ/cm²) and the exponential component to that with high fluencies (>160 mJ/cm²). This exponential behavior must be the result of a progressive increase in the degradation rate of the TiO2 nanoparticle surfaces with fluence. This effect has been previously observed in films composed of TiO2 nanostructures. The linear behavior shows a photodegradation rate of -4.9 ± 0.5 x 10⁻³ mJ cm⁻²/shot, which is 3 times higher than that observed for the TiO2@Silica system, however the FAP values for both systems are ~2.1 times smaller and ~2.5 times greater, respectively. Thus, one might think that the mechanisms of the RL photodegradation are different in the TiO2 and TiO2@Silica systems. The FAP values (TiO2 and TiO2@Silica) decrease with increasing number of shots. For a very large number of shots, values tend to hover around 0.9 and 1 for TiO2 and TiO2@Silica systems, respectively. The FAP values should tend to 1 for the two systems; however, for the TiO2 system, it tends to be at around 0.9. This is most likely because the effective pumping intensity is higher inside the sample and TiO2@Silica system, it tends to be at around 0.9. This is most likely because the effective pumping intensity is higher inside the sample without R6G. Therefore, the photodegradation rate of TiO2 Np should be higher for the sample without R6G. Thus, after the R6G is degraded, the pumping intensity reflected by the TiO2 scattering medium without R6G is lower than the one with R6G. This effect does not occur for the TiO2@Silica system, because these nanoparticles do not undergo photodegradation. The photodegradation rate of R6G in the TiO2@Silica system remains constant with the pumping fluence (~1.55 ±0.05 x 10⁻³ mJ cm⁻²/shot), which is similar to the one reported by Yamashita M. and Kashiwagi H.

Higher particle concentration

For the TiO2@Silica system, at this high Np concentration, the values obtained for the narrower bandwidth and laser threshold were 4.2 nm and 1.65 mJ/cm², respectively (Figure 3b). The laser threshold is lower than the obtained at lower nanoparticles concentration (1.81 mJ/cm²), however, the bandwidth increases. Notice that the measure obtained with our experimental setup averaged over the irradiation (3mm diameter) and coherent emission areas at this high concentration should be around three orders lower. Moreover, it should be noted that the FAP value starts to decrease to fluencies >0.036 mJ/cm², which is less than those for lower Np concentrations (>0.24 mJ/cm²). This could mean that, for higher particle concentrations, the population inversion could be achieved for lower fluences (Figure 3c). RL action studies from micrometer-sized areas are in development, which could bring more clarity.

For the TiO2 system at high fluences (≥48 mJ/cm²), the RL efficiency increases (Figure 3a) and the redshift of the RL emission peak decreases (Figure 3d). These effects could be associated with decreasing lᵣ, which would mean that the pumping energy is confined in a smaller volume. It is known that potent laser pulses induce disaggregation of particles, which would result in an effective increase in the Np density. For the lowest TiO2 Np concentration, the fluencies per unit volume achieved within the sample should be insufficient to cause particle disaggregation. The ABS values ratio for [10⁻⁴M] of R6G (ABS(TiO2@Silica)/ABS(TiO2)) = 0.48/0.19 = 2.53 is higher than the one for a lower Np concentration, but it does not correspond to the RL ratio (~2.5 ±0.2). The inequality (ABS(TiO2@Silica)/ABS(TiO2)) ≫ (RL(TiO2@Silica)/RL(TiO2)) could be caused by the decrease of fluorescence lifetime and the quantum efficiency of R6G molecules closer to the TiO2 surface. For higher Np concentrations (8.9x10¹¹Np/ml), the R6G molecules must be a good deal closer to the TiO2 surface, which favors the fast electron transfer into the conduction band of the TiO2. An insulating silica shell (1-10nm) on the surface of the TiO2 shields the R6G molecules from the semiconductor surface.

FAP values could determine the average number of scattering events, Nₛₐ, undergone by each Np incident channel before being reflected. Thus, for the TiO2@Silica system at [8.9x10¹¹Np/ml]:

Nₛₐ = 885µm*ln(2.0)/2.1µm ≈ 292 and;
Nₛ = (2.1µm)²/(0.532µm)² ≈ 16 < 292

Therefore, if Nₛ ≫ Nₛₐ, it would mean that the probability of interferential events can be increased. Despite that, at lower concentrations (5.6x10¹⁰ Np/ml), Nₛ ≈ 66 < Nₛₐ ≈ 9700, which means that interferential events are highly unlikely. For the TiO2 system and high Np concentrations (8.9x10¹¹Np/ml):

Nₛₐ = 885µm*ln(1.36)/15µm ≈ 18 and;
Nₛ = (15µm)²/(0.532µm)² ≈ 795 > 18

On the other hand, the great redshift (5.4 nm) of the RL emission peak, together with saturated absorption and emission, could mean that the few R6G molecules in the ground state, S₀, exhibit an absorption band equivalent to that of a higher concentration. This phenomenon could be associated to interferential events, which could provoke an increase in the transition probability per unit time from ground state S₀ to S₁ excited singlet states.

We should note that all measures, random laser action and FAP were repeated three times yielding the same results. Therefore, we can rule out any possible effect of photodegradation in the samples during measurement.

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