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Title: Anderson Localization of light in a colloidal suspension (TiO$_2$@Silica)

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Abstract: In recent years, there has been dramatic progress in the photonics field in disordered media, ranging from applications in solar collectors, photocatalyzers, random lasing, and other novel photonic functions, to investigations into fundamental topics, such as light confinement and other phenomena involving photon interactions. This paper reports several experimental evidences of localization transition in a strongly disordered scattering medium composed of a colloidal suspension of core-shell nanoparticles (TiO$_2$@Silica) in ethanol solution. We demonstrate the crossover from a diffusive transport to a localization transition regime as nanoparticles concentration is increased, and that an enhanced absorption effect arises at localization transition.

Introduction

Scattering media have attracted much attention in recent years, due to potential applications in solar energy, [1, 2] photocatalyzers, [3] random lasers [4], and novel optical devices. [5, 6] The coherent superposition of input fields could give rise to fundamental effects, such as light confinement (localization), [7, 8, 9, 10, 11] enhanced backscattering, [12] much further transmission than the mean free path through the sample, [13] and coherently enhanced absorption.
Localization of light and a wide variety of associated phenomena have greatly attracted the attention of researchers in the past decades. Localization in a three-dimensional (3D) system could only take place in extremely strongly scattering medium. The requirement is known as the Ioffe–Regel criterion \((kl_s \leq 1)\),[15] where \(k = 2\pi/\lambda\) and \(l_s\) are the wave number and scattering mean free path, respectively. However, critical regime in the approaching to localization (localization transition) has been reported to not so high scattering strengths \((kl_s \leq 5)\).[9] In the localization regime, the transmission decreases exponentially instead of linearly with the thickness of a sample \((d)\). At the transition, the transmission must have a quadratic dependence on the inverse thickness.[16, 17] This quadratic decay can be interpreted as the onset of localization. However, the residual absorption can provoke a similar decay, which has lead to an important debate.[18, 19, 20] In fact, various evidences of Anderson localization have been reported, but questioned. Additionally, according to the theoretical prediction of Sajeev John, an enhanced absorption must arise when the system approaches to mobility edge.[7] Recently, Sperling et al. provided evidence for the transition from diffusive light propagation to localization.[10] Significantly, they employed approaches that are intrinsically independent of residual absorption. The localization or localization transition regimes are extremely difficult to be obtained, especially in a colloidal suspension. Particles in a suspension tend to agglomerate and/or precipitate, which causes a decrease in scattering strength. Indeed, to our knowledge, the localization or localization transition regimes have not yet been reported in a colloidal suspension. A scattering medium in liquid suspension, among others advantages, facilitates the dissolution of molecules, harvesting of products resulting from a photochemical reaction and allows a better study of the Anderson localization itself and associated phenomena. In previous works,[21, 22] we introduced a scattering medium for a random laser composed of a colloidal suspension of core-shell TiO\(_2@\)Silica nanoparticles (Nps), whose silica shell showed an irregular morphology. The silica shell provides a better optical colloidal stability (OCS) and light-coupling enhancement (LCE) with TiO\(_2\) scatter
cores. Moreover, the silica coatings provide inertness\textsuperscript{[23,24]} and high dispersibility of Nps,\textsuperscript{[25, 26, 27]} which has enabled their use in numerous applications.\textsuperscript{[28, 29, 30]} The effects of OCS and LCE were proposed as likely causes of the increased scattering strength.\textsuperscript{[21, 22]} Experimentally determined can be several times lower than $l_c$ calculated by Mie-scattering calculation.\textsuperscript{[22]} This fact was explained through a possible light coupling enhancement effect with the TiO$_2$ cores, due to light refraction at ethanol-silica interface. Here, by using an improved Stöber method,\textsuperscript{[31, 32]} TiO$_2$ nanoparticles were coated with a homogenous silica shell of ~40 nm thickness. A homogeneous silica shell must improve the LCE effect, leading to a significant scattering strength, higher than the reported in our previous works.\textsuperscript{[21, 22]} Here, localization transition was demonstrated by several approaches, among others-measurement of the relative fluctuations of the inverse participation ratio (propagating experiment), inversely proportional to dimensionless conductance, which reflects the extent of localization, even in the presence of absorption.\textsuperscript{[19]} Additionally, an enhanced absorption phenomenon is reported at the localization transition. Localization of light in a colloidal suspension could open new avenues for the designing and manufacture of novel photochemical reactors, powerful sensing tools and others photonic devices based on highly disordered scattering media.

Material and Methods:

\textit{Synthesis and characterization of Silica shell:}
In the first stage, 5 g of TiO$_2$ Nps were dispersed in 500 ml of spectroscopic ethanol. The suspension of TiO$_2$ nanoparticles was placed in an ultrasound bath 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 and dried in an oven at 70 °C for 2 h. In order to prepare the scattering medium with different [Nps], the TiO$_2$@Silica powder is re-dispersed in the appropriate ethanol volume. The silica coating on the TiO$_2$ nanoparticles
was examined by transmission electron microscopy (TEM) and electron-energy-loss spectroscopy (EELS), using a Carl Zeiss Libra 120 kV transmission electron microscope. The stoichiometric ratio (Ti/Si) of nanoparticles (TiO$_2$@Silica) was determined by Energy Dispersive X-Ray fluorescence (ED-XRF). The mass percentage ratio (Ti/Si), determined by ED-XRF, was Ti$_{72}$/Si$_{28}$. Considering the typical density of the silica obtained by the TEOS hydrolysis around 2 g cm$^{-3}$,[33] we determined an average silica shell thickness of $\sim$42 nm. The sample preparation details for these characterizations and additional TEM images can be found in the supplementary information.

Transport experiments:

For transport experiments, the second harmonic of a $Q$-switched Nd: YAG Continuum Minilite II (25 mJ, 532 nm, pulse width of $\sim$4ns, repetition rate up to 15 Hz, multimode, linearly polarized and spot size of 3 mm) was used and attenuated $10^3$ times by neutral density filters (1µJ)(see supplementary information, Figure S2a and S2b, for experimental setups).

For transmission coefficient measurements, a CW He-Ne laser, model Uniphase 1125P (10 mW, 633 nm) was also used. The transmission coefficient ($T(d)$) is defined as the ratio between total transmitted flux and the incident flux. The total transmission is measured with an integrating sphere placed in contact with the back of the sample (fused silica cuvette). For the propagation experiments and coherent backscattering, the same CW He-Ne laser was used (experimental setups, Figure S4 and S5a, supplementary information).

Result and discussion

Silica shell study

Figure 1 shows the TEM image and mapping EELS (Si) of the core-shell TiO$_2$@Silica NPs.

In the TEM image (Figure 1a), the silica coating on the TiO$_2$ particles shows a regular morphology, with a thickness around 40 nm. Figure 1b shows the Si mapping EELS (orange) of TiO$_2$@Silica Nps. As it is observed, the silica coating presents great homogeneity. A homogeneous silica shell is expected to improve the LCE effect, leading to increased
scattering strength. A better definition of the ethanol-silica interface should increase the light refracted toward the TiO₂ scatter core.

Scattering Medium Study

In order to study the scattering medium composed of these core-shell nanoparticles (TiO₂@Silica) in ethanol solution, a set of transport experiments were performed. The transmitted coherent intensity (I_T) and the transmission coefficient (T(d)) were determined as a function of slab thickness (d) for [Nps] of 280, 140, 70, 47, and 14; x10^10 Nps ml⁻¹. I_T should show an exponential decay (linear in log scale). The lₚ values can be determined from slopes. Figure 2a shows the coherent transmission curve (normalized) versus slab thickness for [140x10^10 Nps ml⁻¹], using the Nd:Yag laser. Three different parts can be distinguished (I, II, and III). In part I, the transmitted intensity decreases more quickly than an exponential.

The green line represents the exponential decay (I_T = e⁻^d/lₚ) determined by fitting with the first experimental points. From the derivative, an initial (d near to zero) scattering mean free path (lₚ₀) is obtained, lₚ₀ = 1.15μm. The red line represents the decay behavior of experimental points. As can be observed, the slope is not constant; it progressively decreases as slab thickness is increased (part I). For slab thickness greater than ~6 μm (near point A), the transmitted intensity starts to decay more slowly. This should be because the diffuse intensity (I_dif) starts to overweigh the coherent intensity. Near point B, the inelastic scattering should start to play a role, and in part III, the decay is exponential (e⁻^d/l_MA, blue line). From the inverse slope, we can obtain the macroscopic “absorption” length (l_MA), where “absorption” represents the losses by inelastic scattering processes. l_MA can be expressed as l_MA = (l_T × l_in)¹/², where l_T and l_in are the transport and inelastic mean free path, respectively. l_T for d near to zero (l_T₀), can be determined from the lₚ₀ values by l_T₀ = lₚ₀ / (1 - (cos θ)) equation, where (cos θ) is the average cosine of the scattering angle (see sup. Information). l_in near to zero (
$l_{In0}$, determined through above equation ($l_{In0} \approx 2680 \mu m$), is more than three orders larger than $l_{s0} = 1.15 \mu m$ and more than 10 times larger than the average photon path length ($l_{0(\text{Micro})}$) inside the scattering medium before being reflected ($l_{0(\text{Micro})} \approx 240 \mu m$). \(^{[34]}\) At localization transition, $l_{0(\text{Micro})}$ must be approximately equal or lightly higher than the optical path length of localized photons inside the scattering medium (microscopic coherence length, $\xi_{\text{coh}}$), since the overall path length of non localized photons must vanish when $l_T$ decreases approaching to localization.

Figure 2b shows the coherent transmission curves (part I) for [Nps] of 140, 70, 47 and 14 $x10^{10}$ Nps ml$^{-1}$. The transmitted intensity decreases more quickly than an exponential for [Nps] $\geq 47x10^{10}$ Nps ml$^{-1}$. This effect is pronounced as [Nps] is increased (from 47 to 140; $x10^{10}$ Nps ml$^{-1}$). This fact represents an anomalous behavior. The green lines represent the exponential decay, determined by fitting with the first experimental points, and red lines represent the experimental behavior. For $280x10^{10}$ Np ml$^{-1}$, the intensity in part I decays extremely quickly, which prevented a reliable measurement. For $14x10^{10}$ Nps ml$^{-1}$, $I_{TC}$ decay exponentially. $l_{s0}$ values extracted from the derivative of the green lines are plotted as a function of [Nps] (Figure 2c), revealing that $l_{s0}$ decrease linearly as [Nps] is increased ($l_{s0} \propto 1/\text{[Nps]}$).

Part III of the coherent transmission curves are shown in the supporting information (fig. S2 c-g). $l_{MA}$ determined from the inverse slopes (parts III) shows an anomalous behavior as [Nps] is increased. $(l_{MA})^{-1}$ increases more quickly than the expected linear increase (fig. S2h supp. information). Notice that, if $l_{T0}$ and $l_{In0}$ would be inversely proportional to [Nps], a $(l_{MA})^{-1} \propto [\text{Nps}]$ dependence must be expected. Therefore, in order to study in depth this anomalous “absorption” behavior, $l_{In0}$ values were determined through $l_{MA} = (l_{T0} \times l_{In0})^{1/2}$ equation (table SI supp. information). $(l_{In0})^{-1}$ per filling fraction ($\alpha_{FF0}$) is plotted (fig. 2d left) as a function of the filling fraction ([FF]). For each [FF], $\alpha_{FF0}$ values (“absorption” coefficient) are
determined from $\alpha_{FF0} = (l_{l_{x0}} \times [FF])^{-1}$. In order to determine $l_{l_{x0}}$ for $[280\times10^{10}$ Np ml$^{-1}$], $l_{l_{x0}}$ was extrapolated following the $l_{T0} \propto 1/[N_{ps}]$ criterion. Contrary to expectations, $\alpha_{FF0}$ is not constant; it increases quickly in [FF] as a function $\alpha_{FF0} = \alpha_0 + C([FF] - [FF_0])^2$, where $C$ is a constant, and $\alpha_0$ and $[FF_0]$ are $\alpha_{FF0}$ at the limit of diffusive regime and the critical filling fraction which starts the $\alpha_{FF0}$ anomalous increase, respectively. This anomalous increase of “absorption” coefficient at $d$ near to zero represents a very interesting result, which could be strong evidence of the existence of the photon mobility edge.$^{[7,35,36]}$ According to the theoretical prediction of Sajeev John, a signature of the electromagnetic mobility edge in a disordered medium is an anomalous rise in energy absorption.$^{[7]}$ Fig. 2d (right) shows the enhanced “absorption” factor for $d$ near to zero ($\gamma_0$) determined by the ratio between effective and classical “absorption” ($\gamma_0 = \alpha_{FF0}/\alpha_0$). This $\gamma_0$ parameter could be interpreted such that one photon travels an average of $\gamma_0$ times around a closed loop path at $d$ near to zero, i.e. each photon would interact an average of $\gamma_0$ times with the same particles, atoms or molecules within the closed loop paths. This idea could be extrapolated to the elastic polarization of valence electrons to virtual states, which would imply an increase also in the effective refractive index at $d$ near to zero ($n_{eff0}$). This supposed increase of the effective refractive index by localization effect finds a parallel in the dynamic barrier proposed by Campagnano and Nazarov$^{[37]}$ in the border of a disordered electronic medium at localization.

Figure 2e shows the transmission coefficients, measured using two laser sources: one pulsed (Nd:Yag, 532nm) and the other CW (He-Ne, 633nm), for $[Nps]$ of 280, 140, 70, 47 and 14; x$10^{10}$Nps ml$^{-1}$. The fluence of the Nd:Yag laser was $\sim 10^7$ times higher than of He-Ne laser. For $[Nps] \geq 47\times10^{10}$Nps ml$^{-1}$, the transmission coefficient shows a similar quadratic decay $T(d) \propto \beta(d_0 + d)^{-2}$ for the two laser sources, which suggests a quadratic decay seemingly insensitive to wavelength and fluence (in this range). This is exactly the behavior of the scaling theory of localization at the localization transition, predicted by Anderson and
co-workers. [16, 17] For 14x10^{10}\,\text{Nps}\,\text{ml}^{-1}, the transmission coefficient shows a classical behavior \((d_0 + d)^{-1}\). The green and red solid lines (Figure 2e) are the fitting with experimental points for Nd:Yag and He-Ne lasers, respectively. Notice that for \([\text{Nps}] \leq 140x10^{10}\,\text{Nps}\,\text{ml}^{-1}\), the transmission coefficients tend to \(\sim(0.47)\) instead of 1. This effect is explained by the total internal reflection at the output interface air-silica of cuvette (see supporting information for an expanded discussion). For \([280x10^{10}\,\text{Nps}\,\text{ml}^{-1}]\), the transmission coefficient tends to \(\sim0.3\) instead of expected value \((\sim0.42)\), which must be a result of an appreciable increase of the losses due to enhanced “absorption”. Notice that, appreciable losses in the light transport must lead to a transmission coefficient lower than expected, especially at \(d=0\). From the quadratic decay of the total transmission, it is difficult to demonstrate being so close to the localization transition, since the losses by the inelastic scattering processes could lead to a similar decay. [18] However, a detailed treatment of the data and an expanded discussion about “absorption” contribution can be found in the supporting information.

From the above results it could be inferred that an anomalous light transport is reached for \([\text{Nps}] \geq 47x10^{10}\,\text{Nps}\,\text{ml}^{-1}\). However, \(I_{T0}\) values seem too high, corresponding to \(kI_{T0} > 5\). In order to resolve this mismatch, \(I_T\) values were also determined by backscattering method (supp. Information, fig. S5). \(I_T\) values, extracted from the angle of backscattering cones for \([47, 70, 140\,\text{and}\,280; x10^{10}\,\text{Nps}\,\text{ml}^{-1}]\), correspond to 0.93, 0.7, 0.64 and 0.47\,\mu m, respectively. A simple model for internal reflection was taken into account for correction of \(I_T\) values. [38] \(I_T\) determined through backscattering method does not decay inversely proportional with \([\text{Nps}]\) and these \(I_T\) values are several times lower than \(I_{T0}\) values. This is an anomalous and seemingly contradictory result. Therefore, other \(I_T\) alternative values \((I_{T*})\) were also determined considering an increase in the effective refractive index \((d\,\text{near to zero})\) by localization effect. Let us introduce the following conjecture: if the \(\alpha_{FF0}\) increases \(\gamma_0\) times at \(d\)
near to zero because each photon interacts an average of $\gamma_0$ times with the same particles, atoms
or molecules (within the closed loop path), then $n_{\text{eff0}}$ must also increase as $n_{\text{eff0}} = 1 +$
$\gamma_0(n_{\text{eff}} - 1)$ (see sup. Information). Thereby, in order to estimate the internal reflection, the
effective refractive indexes for each [Nps] were scaled through the enhanced “absorption”
factor $\left(n_{\text{eff0}} = 1 + \gamma_0(n_{\text{eff}} - 1)\right)$ (table SI supp. Information). $l_{T^*}$ values for [47, 70, 140
and 280; $10^{10}$Nps ml$^{-1}$], determined through the $n_{\text{eff0}}$ correction, correspond to 0.86, 0.6, 0.49
and 0.24$\mu$m, respectively. As can be appreciated, both $l_T$ and $l_{T^*}$, determined by backscattering
method (fig.S6, supp. Information), are several times lower than $l_{T0}$, which represents another
interesting result that could be explained by an $l_T$ decrease in depth ($d$). Consequently, the
coherent backscattering cone yields an $l_T$ value averaged by depth. Of course, the calculus of
$n_{\text{eff0}}$ and the subsequently determined $l_{T^*}$ values may not be strictly correct because just at $d=0$
an additional increase in the effective refractive index would be expected. Notice that, the $l_{00}, l_{T0}$
and $\alpha_{FF0}$ are average values determined in a region near to $d=0$, not at $d=0$ (interface silica-
sample), where these values should increase even more. Additionally, the enhanced factor of
coherent backscattering is lower than expected (1.8) for [Nps] $\geq 140\times 10^{10}$Nps ml$^{-1}$, which
could introduce an error in estimating the backscattering cone angle. The $l_T$ decrease in depth
could be an additional evidence of localization transition. Various authors have theoretically
suggested the $l_T$ decrease in depth$^{[16, 39]}$ at the critical regime of approaching to localization.
This fact can be understood by internal reflection of the coherently backscattered photons in
the sample input border, which forces the photons path to be longer. Consequently, the
likelihood of closed loop path must also be increased. Furthermore, an increase in the closed
loop paths must also induce an increase in the effective refractive index at $d$ near to zero ($n_{\text{eff0}}$),
which in turn should lead to the internal reflection increasing. The $l_T$ increase for $d$ near to
zero would not mean an increase in the physical distance between two successive scattering
events; this could be interpreted as an increase in the effective optical pathlength between two
successive scatterings, because the effective refractive index must increase for \(d\) near to zero. Of course this effect would be appreciable when the coherently backscattered light (closed loop paths) starts to have an appreciable contribution. Obviously, the influence of internal reflection decreases with depth; however, it should increase as angle of incidence is increased. The above effects can be understood such that the density of localized states must increase in the vicinity of the boundary, which was theoretically predicted by Mirlinin disordered electronic media.\[39, 40\] Other perspective about this issue was provided by Ramos and co-workers,\[41\] who demonstrated that the presence of a finite barrier in the input border provokes an increase of the quantum interference (localization) in a disordered electronic medium. The slope decrease with depth in the coherent transmission curves (part I) for \([\text{Nps}] \geq 47 \times 10^{10}\text{Np ml}^{-1}\) could be a consequence of a decrease in depth. The last has an important physical connotation because it would mean that for large \(d\), the effective “absorption” coefficient \(\alpha_{\text{eff}}\) could be even lower than the classical “absorption” coefficient \(\alpha_0\). This would imply that the photon cloud propagation does not fill completely all the sample volume, which means that for large \(d\), the photons are propagated by specific paths, i.e. like a much further transmission than the mean free path through the sample\[^{13}\] and/or a subwavelength light localization.\[^{42}\] This means that, only those photons with very specific entry phase (\(\phi\)) into the scattering medium (position \((x,y,d=0)\)) could reach large \(d\), and that at position \((x,y,d)\) such photons would be strongly correlated. However, at different positions \((x,y,d)-(x',y',d)\) in the \(d\) plane the photons would be completely uncorrelated (localization). Therefore, for a large enough \(d\), the photon paths would cease to be equally probable. This statistical problem at the mobility edge in a 3D system was addressed for the first time by Altshuler et al.,\[^{43}\] who proposed a Poisson law because the paths would be completely uncorrelated.

*Propagating experiment*
In order to corroborate localization transition, another experiment has been performed. The intensity structure of a probe beam (He-Ne laser) was measured after propagating a distance $d=1.8\text{mm}$ through the scattering medium. A CCD camera collected the image of intensity profile $I(x,y)$ at the sample output face (figure S4 supp. information). The input probe beam is $<100\ \mu\text{m}$ full-width at half-maximum (FWHM) and is perpendicular to the sample surface. For the five [Nps], the normalized intensity profiles at samples output are displayed in figure 3. As can be observed, the beam intensity structure narrows as the [Nps] is increased. For $14 \times 10^{10} \text{Nps ml}^{-1}$, a Gaussian beam profile $e^{-2(\frac{r}{\sigma})^2}$ is observed, where $r$ is the radial distance of the beam center. However, for $[\text{Nps}] \geq 47 \times 10^{10} \text{Nps ml}^{-1}$, the beam profile ceases to be Gaussian, it could be fitted with a $e^{-2(\frac{r}{\sigma})^{1+\nu}}$ function, where $0 < \nu < 1$. For each [FF], the confinement of the beam at the output plane is quantified by the inverse participation ratio $P \equiv \frac{\int I(x,y)^2 \, dx \, dy}{\left[ \int I(x,y) \, dx \, dy \right]^2} = \frac{1}{\pi} \frac{\int I(r)^2 \, dr}{\left[ \int I(r) \, dr \right]^2}$, which has units of inverse area, and an effective width $\omega_{\text{eff}} = (P)^{-1/2}$. If absorption is negligible, $\sigma$ in the fitting function $e^{-2(\frac{r}{\sigma})^{1+\nu}}$ must be proportional to $\omega_{\text{eff}} (\sigma \propto \omega_{\text{eff}})$.

Figure 3f shows the effective width at the samples output and $\nu$ value (extracted from fitting), as a function of filling fraction, revealing that $\omega_{\text{eff}}$ and $\nu$ decrease monotonically as the filling fraction is increased. Notice that for $[280 \times 10^{10} \text{Nps ml}^{-1}]$ (fig.3e), the intensity profile shows a rounding at $r$ near to zero, and for larger $r$, it decreases more quickly than the $e^{-2(\frac{r}{\sigma})^{1+\nu}}$ fitting function (red solid line). This effect can be associated to an increase in the losses by enhanced “absorption”. In this fitting, $\nu$ was fixed and its value was taken by extrapolation ($\sim 0.28$). $\sigma$ value was also fixed following the same ($\sigma \propto \omega_{\text{eff}}$) criterion. Figure 3g shows the corresponding value of the inverse participation ratio ($P$) as a function of the filling fraction, along with its statistical standard deviation (marked by error bars). The
statistical standard deviation \((\Delta P)\) is determined by
\[
\left( \frac{1}{\pi} \sqrt{\frac{d[P(r)]}{dr}} \right)^2 \times \text{unitdistance}
\]
evaluated in \(r \approx 0\). Figure 3h presents the relative fluctuations of the inverse
participation ratio, \(\Delta P/p\), as a function of filling fraction. As can be observed, \(\Delta P/p\) value
increases with the filling fraction. For a filling fraction of 3.5 \%, equivalent to \(47 \times 10^{10}\) Np ml\(^{-1}\),
\(\Delta P/p = 0.67 \approx 2/3\), which corresponds to the onset of localization suggested by Genack and
coworkers.\(^{[19]}\) The \(\Delta P/p\) increase agrees with the prediction\(^{[16,39]}\) that the relative fluctuations
in \(P\) are inversely proportional to the dimensionless diffusion coefficient, which must tend to
unity (“absorption” negligible) when the system approaches to localization (Poisson law). For
\(280 \times 10^{10}\) Nps ml\(^{-1}\), \(\Delta P/p\) is lightly above unity, which must be a consequence of
“absorption”.\(^{[19]}\) The above result represents an additional evidence of localization transition.
However, the “absorption” could also have influence over the beam propagation. But, there is
not an easy analytical expression for the dependence of “absorption” with angle at the
localization transition regime. One can think that the “absorbed” light would increase with \(r\)
because the effective photon pathlength increases with \(r\). However, the “absorbed” light could
increase even more with \(r\) at localization transition because the enhanced “absorption” factor
can increase with the incidence angle. Notice that, the incidence angle should influence over
the photons transport at localization transition because the internal reflection must increase as
incidence angle is increased regarding to normal incidence. This fact might increase the
likelihood of closed loop paths, leading to a conductance decrease. Therefore, an additional
experiment was performed in order to confirm localization transition. The probe beam was
introduced in the scattering medium at 30\(^{\circ}\), 45\(^{\circ}\) and 60\(^{\circ}\) regarding to normal incidence. The
intensity profiles \(I(x,y)\) at the sample output face were collected for [Nps] of: 14 and 140;
\(x10^{10}\) Nps ml\(^{-1}\). If \(\omega_{\text{eff}}\) decrease in [Nps] would be caused by the “absorption”, \(\omega_{\text{eff}}\) must be
independent to incident angle for the two [Nps]. Instead, if \( \omega_{\text{eff}} \) decrease is basically a consequence of the approaching to localization, the profile width should decrease as incidence angle is increased, i.e. a narrowing of the intensity profile must be observed. Notice that an increase in the incidence angle must provoke an increase in the internal reflection of the coherently backscattered photons, i.e. an increase in the effective barrier at the input border. Consequently, an increase in localization must be expected.\(^{[41]}\) This would mean a decrease of diffusion coefficient with incidence angle. This effect would be strong evidence of the approaching to localization, since incidence angle should not be an influence on the “absorption” or in the light transport at diffusive regime. Figures 4a-b show a comparison of the normalized intensity profiles for [14 and 140; \( x10^{10} \) Nps ml\(^{-1} \)] and incidence angles of 0\(^{\circ} \) and 60\(^{\circ} \). As can be clearly observed for [14x10\(^{10} \) Np ml\(^{-1} \)] (diffusive regime), the incidence angle has no influence on the intensity profile. However, a narrowing of the intensity profile is observed for [140x10\(^{10} \) Np ml\(^{-1} \)] (localization transition) as incidence angle is increased, revealing a linear \( \omega_{\text{eff}} \) decrease (fig. 4c). This is strong evidence of an anomalous transport. Note that for the incidence angle of 60\(^{\circ} \) and [140x10\(^{10} \) Nps ml\(^{-1} \)] (fig. 4b), the intensity profile is sharpened at \( r \) near to zero. This could be caused by a decrease of diffusion coefficient. Additionally, the intensity profile decreases more quickly than the fitting function \( e^{-2(\left| r \right| / \sigma)^{1+y}} \) at large \( r \) (red solid line). The last could be a consequence of the increase of enhanced “absorption” factor (\( \gamma_0 \)) with incidence angle, which must be caused by an increase in the likelihood of closed loop paths by the internal reflection. On the other hand, the narrowing of the intensity profile, as angle of incidence is increased, would be further evidence that the “absorption” effect is negligible for [Nps] \( \leq 140x10^{10} \) Np ml\(^{-1} \), such as was inferred from the propagation experiments and total transmission. An expanded study of propagation and “absorption” as a function of incidence angle and [Nps] is called for, in order to understand in depth the photons transport at localization and the associated phenomena to
it. From the above results, a clear transition is observed for \([\text{Nps}] \geq 47 \times 10^{10} \text{Nps ml}^{-1}\), which corresponds with a \(k_lT_s \approx 8.6\). This critical value is higher than that reported by Sperling et al. \((k_lT \approx 4.5)\). \(^{[10]}\) Note that for \([47 \times 10^{10} \text{Nps ml}^{-1}]\), the filling fraction is only 3.5%. In turn, the critical regime is reached for a filling fraction \(\sim 10\) times lower than that reported by Sperling et al. The higher filling fraction in their samples combined with the high powers used in their experiments must lead to an increase in the inelastic scattering processes. \(^{[11]}\).

Probably for this reason, they did not observe an appreciable change in the statistical distribution of the photon cloud. The losses by inelastic scattering must provoke a smoothing in the maximum of intensity profile, appearing like a Gaussian distribution. Additionally, a high filling fraction combined with very high power should also give rise to a significant increase in the nonlinear refractive index, leading to an increasing of the photon-photon interaction. \(^{[45]}\) The latter must lead to a decrease in the coherence length, \(\xi_{\text{coh}}\).

Consequently, a higher scattering strength would be required in order to get the critical regimen of localization transition.

**Conclusion**

Core-shell TiO\(_2@\)Silica nanoparticles with an appropriate silica shell (thickness and homogeneity) allowed us to obtain a liquid suspension with a significantly high scattering strength. We report several evidences of the critical regime of localization transition in a colloidal suspension, which is achieved at \([\text{Nps}] \geq 47 \times 10^{10} \text{Nps ml}^{-1}\). For \([\text{Nps}] \geq 47 \times 10^{10} \text{Nps ml}^{-1}\): The transmitted ballistic intensity starts to decay more quickly than an exponential, the “absorption” coefficient (near to zero) shows an quadratic increase in \([\text{Nps}]\) (instead a constant value), from which an increase of refractive index also close to zero is proposed; the transmission coefficient starts to show a quadratic decay and a Gaussian probe beam that is propagated through the samples showed a \(e^{-2(|r|/\sigma) ^ {1+v}}\) \((0 < v < 1)\) intensity profile at sample output, instead a Gaussian profile. We also must highlight that for a probe beam inclined
regarding to normal incidence, the intensity profiles are similar for $\left[14 \times 10^{10} \text{Np ml}^{-1}\right]$ (diffusive regime). However, for $\left[140 \times 10^{10} \text{Np ml}^{-1}\right]$, a narrowing of the intensity profile is observed as incidence angle is increased. Additionally, an $l_T$ decrease in depth for $\left[Nps\right] \geq 47 \times 10^{16} \text{Nps ml}^{-1}$ is inferred from the measurements of coherent backscattering and ballistic transmission (part I).

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Author Contributions

All authors conceived, designed, performed and analyzed the experiments; E.J-V, P.C.O, W.M.F. and G.F. de S. contributed materials/analysis tools; E.J-V guided the research and wrote the manuscript.

Additional Information

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Figure 1. Characterization of TiO$_2$@Silica nanoparticles via transmission electron microscope. a) TEM image and b) EELS-TEM (Si) chemical mapping of core-shell TiO$_2$@Silica Nps demonstrates the presence of silicon (orange) onto the TiO$_2$ surface. The dotted green line (a) indicates the outer surface of the silica coating. The scale bar corresponds to 200 nm.
Figure 2. Transport experiments. a) Transmitted coherent intensity ($I_{TC}$) versus slab thickness $[140 \times 10^{10}\text{Nps/ml}]$ (blue line, fitting at part III), and b) $I_{TC}$ for [Nps]: 14, 47, 70, and 140; $x10^{10}\text{Nps ml}^{-1}$. The red and green lines represent the decay behavior of experimental points and the exponential fitting with the first experimental points, respectively. c) $I_{00}$ versus [Nps], d) anomalous increase of: $\alpha_{FF0}$ (left) and the $\gamma_0$ (right) as [FF] is increased, red dotted line represents $\alpha_0$ value, error bars correspond to fitting errors. e) Transmission coefficient for the lasers: pulsed Nd:Yag and CW He-Ne and [Nps] of: 14, 47, 70, 140 and 280; $x10^{10}\text{Nps ml}^{-1}$. Open and filled symbols correspond to experimental points for Nd:Yag and He-Ne (lasers), respectively. The green and red solid lines represent the fitting with experimental points for Nd:Yag and He-Ne (lasers), respectively.
Figure 3. Experimentally measured intensity distributions at the samples output for [Nps]: a) 14, b) 47, c) 70, d) 140 and e) 280 × 10^10 Nps ml^-1. The propagation length of probe beam was 1.8 mm and scale bar represents 5 mm. For [14×10^10 Np ml^-1], the intensity profile fits very well with a gaussian profile $e^{-2(r/\sigma)^2}$. In b), c), d) and e) ([Nps] ≥ 47×10¹⁰ Np ml⁻¹), the intensity profiles could be fitted to $e^{-2(|r|/\sigma)^{1+\nu}}$, where $0 < \nu < 1$. f) $\omega_{eff}$ (left) and $\nu$ (right, red) versus [FF]. g) Inverse participation ratio $P$ as function of [FF]. The error bars are the statistical standard deviations of $P$ around $r = 0$. h) Relative fluctuations of the inverse participation ratio, $\langle \Delta P/P \rangle$, as a function of [FF]. The increase monotonically of $\langle \Delta P/P \rangle > 2/3$, and the transition from the gaussian curve of a) to the $e^{-2(|r|/\sigma)^{1+\nu}}$ decaying curves of b), c), d) and e) display the crossover from diffusive transport a) to the localization transition regime.
Figure 4. Propagating experiment as a function of incidence angle for: a) \([14 \times 10^{10} \text{Np ml}^{-1}]\), the output intensity profiles independent to incidence angle, equal Gaussian profiles \(e^{-2(\theta/\sigma)^2}\) are observed; b) \([140 \times 10^{10} \text{Np ml}^{-1}]\), the intensity profile narrows as incidence angle is increased, showing a decrease in the photon conductance. c) \(\omega_{\text{eff}}\) monotonically decreases with incidence angle for \([140 \times 10^{10} \text{Np ml}^{-1}]\), showing that photon transport is determined by localization phenomenon, not by “absorption”, as already was previously inferred.
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