Light diffraction in ordered photonics colloidal suspensions

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Abstract: Light diffraction measurements show order in photonic colloidal suspensions of scatterers. Strong and long-range Coulomb interaction explains the order and correlation in the scatterers' (TiO$_2$@Silica) position, which favors significantly the localization (interference) of light.

1. Introduction: A comparative study of light diffraction is performed in colloidal suspensions containing core-shell TiO$_2$@Silica NPs suspended in either ethanol or water solution. The silica shell on TiO$_2$ core (rutile, 410 nm mean diameter) induces an electrostatic field (ζ–potential) on the TiO$_2$@Silica surface provoking strong interaction between the TiO$_2$@Silica NPs and, consequently, a good optical colloidal stability [1–4]. The theoretical framework employed in colloid science to study particle–particle interactions has been the classical theory of Derjaguin-Laudau-Verwey-Overbeck (DLVO). This theory 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 [5,6]. 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 (center-to-center) between two particles of radii a. The electrostatic repulsion potential (U_{elec}) between two colloidal particles of radii a can be expressed as: $U_{elec}(r) = 2\pi\varepsilon_0\varepsilon_r(a + \Delta)\psi_0^2 e^{[-\kappa(r-2\Delta-2a)]}$, where ε_r is the permittivity of the medium, Ψ_0 is the potential at the particle surface, which can be estimated from the ξ-potential measurements [7], κ is the inverse Debye length (λ_{Debye}), which is the thickness of the double layer and Δ is the thickness of the Stern layer. For spherical particles and constant surface potential and the background ionic strength, the van der Waals attraction U_{vdw} between the two particles can be calculated as: $U_{vdw}(r) = -\frac{A}{6}\left[\frac{2a^2}{r^2-4a^2} + \frac{2a^2}{r^2} + \ln\frac{r^2-4a^2}{r^2}\right]$, where A is the Hamaker constant, which is for short-range and plays an important role in describing the attraction energy between particles. The thickness of the double layer (λ_{Debye}) can be determined by the measurement of D_{Hyd} $\left(\lambda_{Debye} \approx D_{Hyd}/2 - a\right)$. D_{Hyd} of the TiO$_2$@Silica NPs, measured by dynamic light scattering (DLS) at very low [TiO$_2$@Silica], shows a larger D_{Hyd}~890 nm for the ethanol suspension when compared to water D_{Hyd}~570 nm. The latter must be because the water dielectric constant is considerably higher than the ethanol (~3 times). For both systems, the ξ-potential is practically the same ~(-75 mV). When λ_{Debye} is of the order or larger than $h_m/2$, where h_m is the mean distance between the opposite particle surfaces, a sharp secondary minimum is expected, which should lead to a correlation in the particles' position (order) [8]. In the particular case of a photonic colloid, the correlation in the particles' (scatterers) position can give rise to correlated long-range hopping for scattered photons, which favors interferential phenomena (light localization) [9–12]. Localization induced by correlation has been addressed recently by Kravtsov and co-workers in higher dimensional systems, showing the universality of this phenomenon [13]. Here, we studied the diffraction pattern originated by TiO$_2$@Silica suspensions (ethanol and water) when collecting the backscattered light perpendicular to the sample surface. The diffraction pattern, coming from the first scattering event, can reveal the distribution of the scatterer positions. For TiO$_2$ filling fraction (FF_{TiO2}) of: FF_{TiO2}=0.26%, FF_{TiO2}=1.06% and FF_{TiO2}=4.8%, diffraction patterns were obtained for TiO$_2$@Silica suspensions in ethanol and water. A linearly polarized laser beam (He–Ne) was used to measure diffracted light. The laser beam was focused through a lens of +50 mm focal length in order to obtain a parallel beam at the focus with its waist (~4.4 µm diameter) located on the sample's input surface. For detailed description of the experimental setup, see ref. [11]. In order to obtain a meaningful statistic and average the speckle pattern, a total of 400 images were recorded for each sample. The collection time for each image was 50 µs. The Fourier transform (FT) was determined separately for each of the 400 images, and then a mean FT was extracted. Afterward, the diffraction pattern is obtained by the FT of this mean FT.

2. Results: Figure 1a and 1b show the diffraction patterns obtained for TiO$_2$@Silica suspensions at FF=4.8% in ethanol and water, respectively. For both suspensions, a diffraction pattern with an approximately hexagonal structure at the center can be observed, being clearly stronger and containing higher diffraction orders for the ethanol suspension than in water. The latter indicates a stronger correlation in the scatterers position for the ethanol suspension. This diffraction pattern (hexagonal structure) seems to be proper of a cubic structure oriented in the (111) direction. The above result could be due to the isotropy of the interaction between scatterers (which are approximately spheres), whose repulsive

and attractive electrostatic forces present spherical symmetry. This colloidal system has similarity to the gold and silver crystalline structures, that arise from the electrostatic attractive force between conduction electrons and positively charged metal ions. In this colloidal system, the TiO_2@Silica NPs strongly interact with each other (repel and attract) within an "incompressible" liquid (ethanol or water) that tends to keep the colloidal volume constant. Consequently, the particles tend to become distributed at similar equilibrium distances giving rise to a correlation in the scatterers' position. For both suspensions (ethanol and water) at FF_{TiO2}=1.06%, the diffraction pattern is less defined (Fig. 1c and 1d), containing fewer diffraction orders than for FF_{TiO2}=4.8%. For the ethanol suspension with FF_{TiO2}=1.06%, the definition of the diffraction pattern and the amount of diffraction orders is still better defined than for FF_{TiO2}=1.06% in water. No diffraction pattern is observed for FF_{TiO2}=0.26% (fig. 1e and 1f), which indicates a homogeneous random medium.
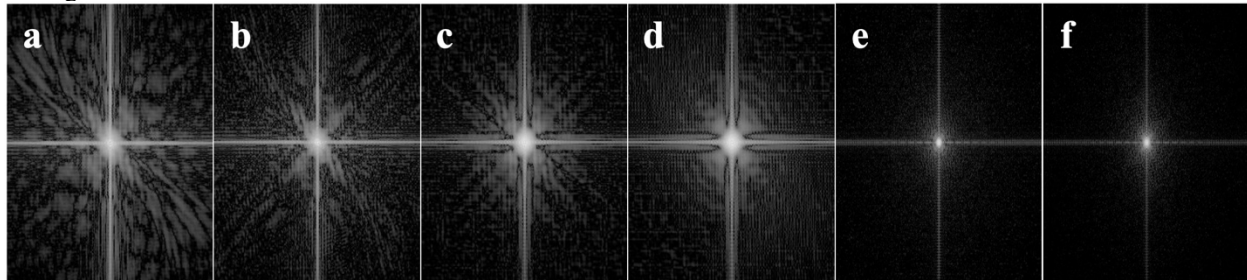

Figure 1. For FF_{TiO2}=4.8% in ethanol suspension, a) diffraction pattern (hexagonal structure) is clearly stronger and contains higher diffraction orders than in water b). For FF_{TiO2}=1.06%, c) and d), diffraction patterns are less defined than for FF_{TiO2}=4.8%, however, they are still better defined and containing higher diffraction orders for the ethanol c) than for the water suspension d). No diffraction pattern can be distinguished for FF_{TiO2}=0.26% in ethanol e) and water f) suspensions.

3. Conclusion: Light diffraction measurement demonstrates the correlation in the scatterers' (TiO_2@Silica) positions (order) in this photonics colloidal suspension. Particularly for FF_{TiO2}=4.8% a seemingly cubic structure oriented in the (111) direction is observed (patterns hexagonal structure). We attributed the correlation of the scatterers' positions to the strong and long-range Coulomb interaction between TiO_2@Silica NPs, revealing to be of stronger and longer range in the case of TiO_2@Silica suspensions in ethanol when compared to water. This latter can be understood from the Debye length of TiO_2@Silica NPs (measured by DLS), which is larger in ethanol (lower dielectrics constant) than in water. A decrease of TiO_2@Silica NPs concentration (h_m increase) can provoke that λ_{Debye} becomes shorter than $h_m/2a$ weaking the particles interaction (Coulomb) and the correlation of the scatterers' positions.

References

1. E. Jimenez-Villar, V. Mestre, P. C. de Oliveira, and G. F. de Sá, "Novel core–shell (TiO2@Silica) nanoparticles for scattering medium in a random laser: higher efficiency, lower laser threshold and lower photodegradation," Nanoscale **5**(24), 12512 (2013).
2. E. Jimenez-Villar, V. Mestre, P. C. de Oliveira, W. M. Faustino, D. S. Silva, and G. F. de Sá, "TiO 2 @Silica nanoparticles in a random laser: Strong relationship of silica shell thickness on scattering medium properties and random laser performance," Appl. Phys. Lett. **104**(8), 081909 (2014).
3. E. Jimenez-Villar, V. Mestre, N. U. Wetter, and G. F de Sá, "Core-shell (TiO2@Silica) nanoparticles for random lasers," in *Complex Light and Optical Forces XII*, E. J. Galvez, D. L. Andrews, and J. Glückstad, eds. (2018), **10549**, pp. 105490D--10549--10.
4. E. Jimenez-Villar, I. F. da Silva, V. Mestre, P. C. de Oliveira, W. M. Faustino, and G. F. de Sá, "Anderson localization of light in a colloidal suspension (TiO 2 @silica)," Nanoscale **8**(21), 10938–10946 (2016).
5. R. J. Hunter, *Foundations of Colloid Science*, 2nd ED. (Oxfort University press, 2001).
6. O. L. Sánchez-Muñoz, J. Salgado, J. Martínez-Pastor, and E. Jiménez-Villar, "Synthesis and Physical Stability of Novel Au-Ag@SiO2 Alloy Nanoparticles," Nanosci. Nanotechnol. **2**(1), 1–7 (2012).
7. D. Bastos and F. J. de las Nieves, "Colloidal stability of sulfonated polystyrene model colloids. Correlation with electrokinetic data," Colloid Polym. Sci. **272**(5), 592–597 (1994).
8. L. Bressel, R. Hass, and O. Reich, "Particle sizing in highly turbid dispersions by Photon Density Wave spectroscopy," J. Quant. Spectrosc. Radiat. Transf. **126**, 122–129 (2013).
9. E. Jimenez Villar, M. C. S. Xavier, J. G. G. S. Ramos, N. U. Wetter, V. Mestre, W. S. Martins, G. F. Basso, V. A. Ermakov, F. C. Marques, and G. F. de Sá, "Localization of light: beginning of a new optics," in *Complex Light and Optical Forces XII*, D. L. Andrews, E. J. Galvez, and J. Glückstad, eds. (Proceeding SPIE 10549, 2018), p. 1054905.
10. E. Jimenez-Villar, M. C. S. Xavier, N. U. Wetter, V. Mestre, W. S. Martins, G. F. Basso, V. A. Ermakov, F. C. Marques, and G. F. de Sá, "Anomalous transport of light at the phase transition to localization: strong dependence with incident angle," Photonics Res. **6**(10), 929 (2018).
11. V. A. Ermakov, W. S. Martins, N. U. Wetter, F. C. Marques, and E. Jiménez-Villar, "Localization of light induced in ordered colloidal suspensions: powerful sensing tools," Nanoscale **13**(13), 6417–6425 (2021).
12. C. T. Dominguez, A. A. V. Gomes, N. U. Wetter, J. Dipold, V. Mestre, W. S. Martins, and E. Jiménez-Villar, "Random lasing at localization induced in correlated colloidal system," Opt. Mater. (Amst). **120**, 111428 (2021).
13. P. A. Nosov, I. M. Khaymovich, and V. E. Kravtsov, "Correlation-induced localization," Phys. Rev. B **99**(10), 104203 (2019).