**Supplementary Information**

**Strong enhancement of effective refractive index in structured colloids (TiO2@Silica)**

Jessica Dipold1, Niklaus U. Wetter1, Francisco C. Marques2, Aristide Dogariu3, Ernesto Jiménez-Villar2,3\*

*1Instituto de pesquisas Energéticas e Nucleares, CNEN\_IPEN, São Paulo, SP 05508-000, Brazil*

*2Instituto de Física “Gleb Wataghin”, Universidade Estadual de Campinas, Campinas SP 13083-859, Brazil*

*3CREOL, The College of Optics and Photonics, University of Central Florida, Orlando, FL 32816, USA*

\*Corresponding author: [Ernesto.jimenez@uv.es](mailto:Ernesto.jimenez@uv.es)

**Materials and Methods:**

Ethanol alcohol HPLC with spectroscopic grade purity was supplied by MERCK, tetra-ethyl-ortho-silicate (TEOS) was supplied by Sigma-Aldrich, and the ammonia P.A. was supplied by MERCK. The titanium dioxide (TiO2) with a rutile crystal structure was acquired from DuPont Inc. (R900). The TiO2 grains have an average particle diameter of 410nm with a polydispersity of 25%. TiO2 nanoparticles were coated with a silica shell of ~40 nm thickness via the Stöber method. In the first stage, 5 g of TiO2 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 (NH4OH 28%-30%) were added alternately in 100 portions of 100 μl and 220 μl, respectively. The synthesized TiO2@Silica nanoparticle suspension was centrifuged at 3000 g for 20 minutes and the pellet was dried in an oven at 70 °C for 12 h.

Long-range Coulomb interaction between scatterers

According to the classical theory of Derjaguin-Landau-Verwey-Overbeek (DLVO)1, the pair-wise particle interaction arises from the interplay of attractive van der Waals forces (Fattr) and repulsive Coulomb forces (Frep, double layer force) screened by the Debye-Hückel ions’ cloud. The modulus of both interaction potentials (electrostatic repulsion, Uelec, and the van der Waals attraction, Uvdw) increases when the separation between particles decreases. The total interaction potential between two particles (*U*TDLVO) can be expressed as the sum of the electrostatic repulsion (Uelec) and the van der Waals attraction (Uvdw): *U*TDLVO =Uelec(r)+Uvdw(r), where r is the distance (center-to-center) between two particles of radii a (r = h+2a, with h being the distance between the surfaces). Depending on the particle size and the thickness of the double layer, the electrostatic repulsion potential (Uelec) between two colloidal particles of radii a can be expressed as:

(A1)

Where εr is the permittivity of the medium, Ψ0 is the potential at the particle surface, which can be estimated from the ξ-potential measurements2, *κ* is the inverse Debye length (λDebye), which is the thickness of the double layer and Δ is the thickness of the Stern layer. For spherical particles with constant surface potential and the background ionic strength, the van der Waals attraction Uvdw between the two particles can be calculated as:

(A2)

where *A* is the Hamaker constant, which is for short-range and plays an important role in describing the attraction energy between particles. Note that the modulus of both potentials (Uelec and Uvdw) increases when the radii *a* of the particles increases, which induces a stronger and larger-range interaction between them. When the mean separation distance between particles (*rm*), which can be calculated from the concentration by assuming a uniform distribution, is much higher than the particle’s hydrodynamic diameter, a random distribution in the particles position is expected (like an ideal gas). Otherwise, for a *rm* similar or smaller than DHyd, strong particle interaction is expected, which could lead to a correlation in the particles’ position3. The mean electric potential between two neighboring particles is given by the overlap of the repulsive and attractive potentials of the two particles. When λDebye is of the order or larger than *hm/2*, where *hm* is the mean distance between the opposite particle surfaces, a sharp secondary minimum of the mean potential is expected. A more uniform distribution or crystallization starts when the colloidal particles fall into this secondary minimum of depth larger than the thermal energy. When silica NPs is added to the TiO2@Silica NPs suspension, an increase in particle-particle Coulomb interaction is expected. Silica NPs (20 nm diameter) should be localized at the intermediate positions between TiO2@Silica NPs (scatterers), due to their higher mobility and the strong Coulomb repulsion exerted on them by the larger TiO2@Silica NPs (500 nm diameter). Consequently, due to the high dielectric constant of silica NPs, a sharper (electrical) potential minimum is expected at the intermediate region between TiO2@Silica NPs (scatterers), favoring the order or correlation in the scatterers position. In this way, silica NPs act like pivots or bridges for the Coulomb interaction between TiO2@Silica NPs. DLVO theory is not fully effective in describing ordering processes such as the formation of colloidal crystals in suspension and additional interactions should be considered, particularly in water suspensions, where hydrogen bonding and the hydrophobic effect and hydration pressure can play an important role. A detailed work on this topic has been published elsewhere4,5.

**Raman measurements**

A Micro-Raman (LabRAM HR Evolution, Horiba Scientific) with a 532 nm CW laser as excitation source was used for Raman scattering measurements. Micro-Raman measurements were done using a Leica 50× objective with numerical aperture NA=0.55. Raman measurements were collected with three different set-ups, one without a cover slide and the other two using glass and Sapphire cover slides (see figure 1). For the of glass slide, Sapphire slide and air arrangements, the collection depths (*d*B) are 2.67 μm, 3.13 μm and 1.76 μm, respectively. For these glass and Sapphire slide and air arrangements, the pumping spot sizes are 1.2 μm, 1.4 μm and 0.8 μm, respectively. The latter represents pumping power densities of 4.4x1010 W/m2, 3.2x1010 W/m2 and 10x1010 W/m2 for the glass and Sapphire slide and air arrangements, respectively. For each arrangement and sample, a total of 4 spectra from different points were collected. The position of the focal plane of the objective relative to the sample surface was chosen such that the maximum Raman signal was obtained. Raman measurements were performed in samples with *FF*TiO2 of: 0.26%, 0.54%, 1.35%, 4.8%, 8.8% and 12.1% with both 0.75% and 1.5% *FF*SiO2. The samples are stirred before each measurement and the Raman collection is performed during a time shorter than 1 minute. After several minutes the Raman signal starts to decrease slowly, which could be a consequence of an effective *FF*TiO2 decrease close to the sample-cover slip interface, probably due to the gravity effect.

Figure S1 shows the collected Raman spectra of the TiO2@Silica suspension plus silica NPs at *FF*TiO2=4.8% and *FF*SiO2=0.75%, using the three set-ups shown in figure 1.

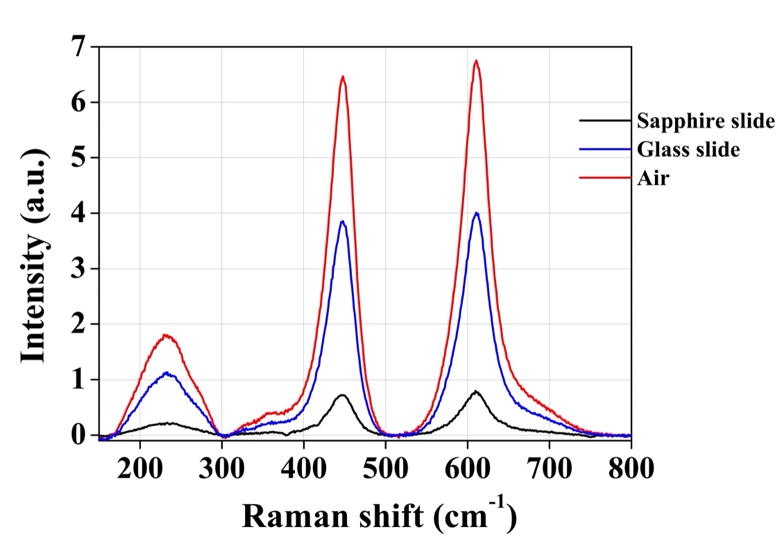


Figure S 1. *For FF*TiO2=4.8% and *FF*SiO2=0.75% *(TiO2@Silica suspension plus silica NPs), Raman spectra collected with the three arrangements (figure 1) show a higher Raman signal without using a cover slide (air). Raman spectra collected using: a sapphire slide (Black line); a glass slide (blue line) and without a cover slide, air (red line).*

**Correction by pumping and collection depth**

The effective pumping intensity (*I*PM) and collected Raman signal are both affected by the scattering strength (scattering length, *l*s) of each sample, which depends on the *FF*TiO2. For correcting the effective pumping intensity by the pumping depth (depth of focus or depth of pumping, *d*B), we have taken into account the scattering lengths *l*s for each sample. We considered that the mean pumping intensity (*I*PM(λ)) at depth of focus (*d*B(λ)) into the sample depends on *l*s(λ) as follows:

(A3)

Where *d*B(λ), *I*P(z) and *I*0 are the depth of focus and/or collection depth (that depends of the objective and pumping wavelength used), the ballistic pumping intensity at *z* depth into the sample and the incident pumping intensity at *z*=0, respectively. z=0 is at the sample input surface, i.e., at the sample-slide interface (glass). Clearly, when *l*s>>*d*B, *I*PM≈*I*0. *I*0 does not depend on the sample and neither on the pumping wavelength. The collected Raman signal is also the mean of the emitted Raman signal in the collection depth, which is the same as the pumping depth. Therefore, in order to correct the collected Raman intensity (ICR), the measured Raman signal is divided by for each sample and specific pumping wavelength, considering pumping and collection.

Additionally, we must include a correction for the reflected pumping light at the air-slide and slide-sample interfaces, and the reflection of the emitted light at the slide-air interface (by non-index matching). Therefore, the measured Raman signal must also be divided by <1-RefCM>, where RefCM is the average reflection coefficient between 0º and θCM at the above interfaces (see table S1). In this way, collected Raman intensity is scaled by the following expression:

|  |  |
| --- | --- |
|  | (A4) |

The table shows the values of θCM, *n*CS and <1-RefCM> for the Sapphire and glass slides and air, where *n*CS is the classical refractive index for each *FF*TiO2 (sample) calculated using the Maxwell-Garnett approximation.

Table S1: *Parameters used for calculations for each FFTiO2, showing the classic refractive index calculated with Maxwell-Garnett theory (nCS), the cone angle for each cover slide (θCM) and the average reflection coefficient (<1-RefCM>).*

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| *FF*TiO2;(*FF*SiO2= 0.75 & 1.5 %) | *n*CS |  | Sapphire | Glass | Air |
|  |  | θCM | 18º | 21.2º | 33.4º |
| 0,26% | 1.37 | <1-RefCM> | 0.825 | 0.908 | 0.976 |
| 0,54% | 1.38 | <1-RefCM> | 0.826 | 0.908 | 0.976 |
| 1,35% | 1.4 | <1-RefCM> | 0.828 | 0.909 | 0.973 |
| 4,8% | 1.44 | <1-RefCM> | 0.832 | 0.91 | 0.967 |
| 8,8% | 1.49 | <1-RefCM> | 0.835 | 0.908 | 0.96 |
| 12,1% | 1.54 | <1-RefCM> | 0.838 | 0.905 | 0.953 |

Figure S2 shows the effective refractive indexes of the Sapphireand glass slides at the sample-slide interface, extracted by the above method, as a function of *FF*TiO2. For comparison, the classical refractive indexes of the Sapphireand glass slides are also depicted. An increase of the effective refractive indexes is observed as *FF*TiO2 is increased. For all *FF*TiO2and samples with *FF*SiO2=1.5%, both effective refractive indexes of the Sapphireand glass slides at the sample-slide interface are higher than those of the samples with *FF*SiO2=0.75%. This is expected for *FF*TiO2<4.8%, since Raman enhancement for *FF*TiO2<4.8% is stronger in the samples with *FF*SiO2=1.5%, which would lead to a stronger interaction with the evanescent wave in comparison to the samples with *FF*SiO2=0.75%. However, for *FF*TiO2 ≥4.8%, range for which the enhanced Raman signal is larger for those samples with *FF*SiO2=0.75%, the above behavior is not intuitive. This latter may be the result of a higher residual absorption in the samples with *FF*SiO2=1.5% (larger quantity of SiO2 NPs surface), which for *FF*TiO2≥4.8% would begin to contribute appreciably on the deviation factors used to calculate the effective refractive index.

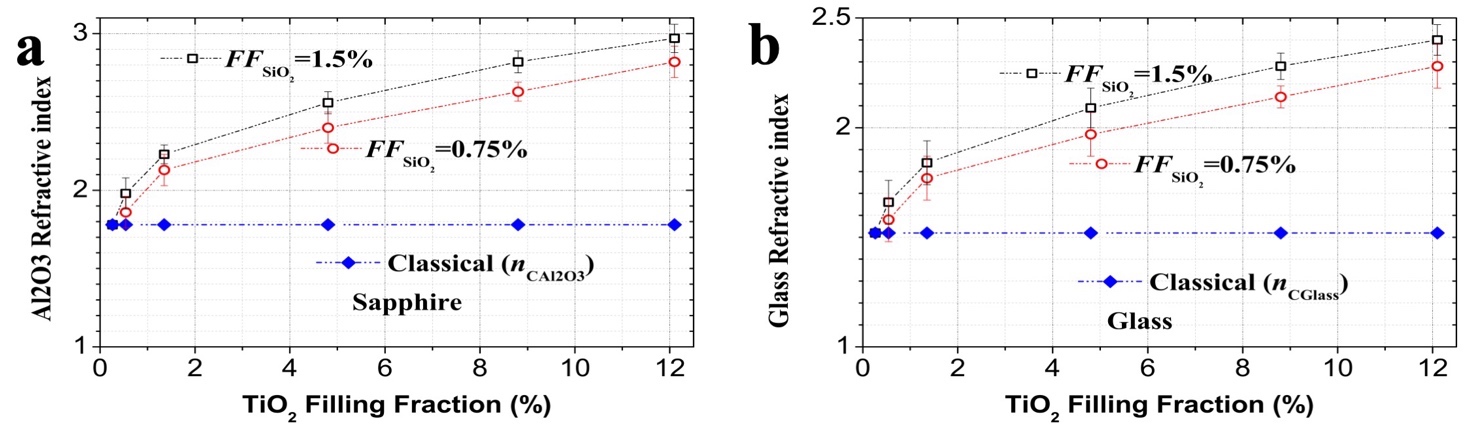


Figure S 2. *The effective refractive indexes of the Sapphire a)and glass b) slides at the sample-slide interface as a function of FFTiO2 with FFSiO2=1.5% in black squares and FFSiO2=0.75% in red circles.*

Figure S3 shows a schematic diagram of the flow of operations to determine the effective refractive indexes of the sample and slides (*n*S, *n*Al2O3 and *n*Glass) at the sample-slide interface.

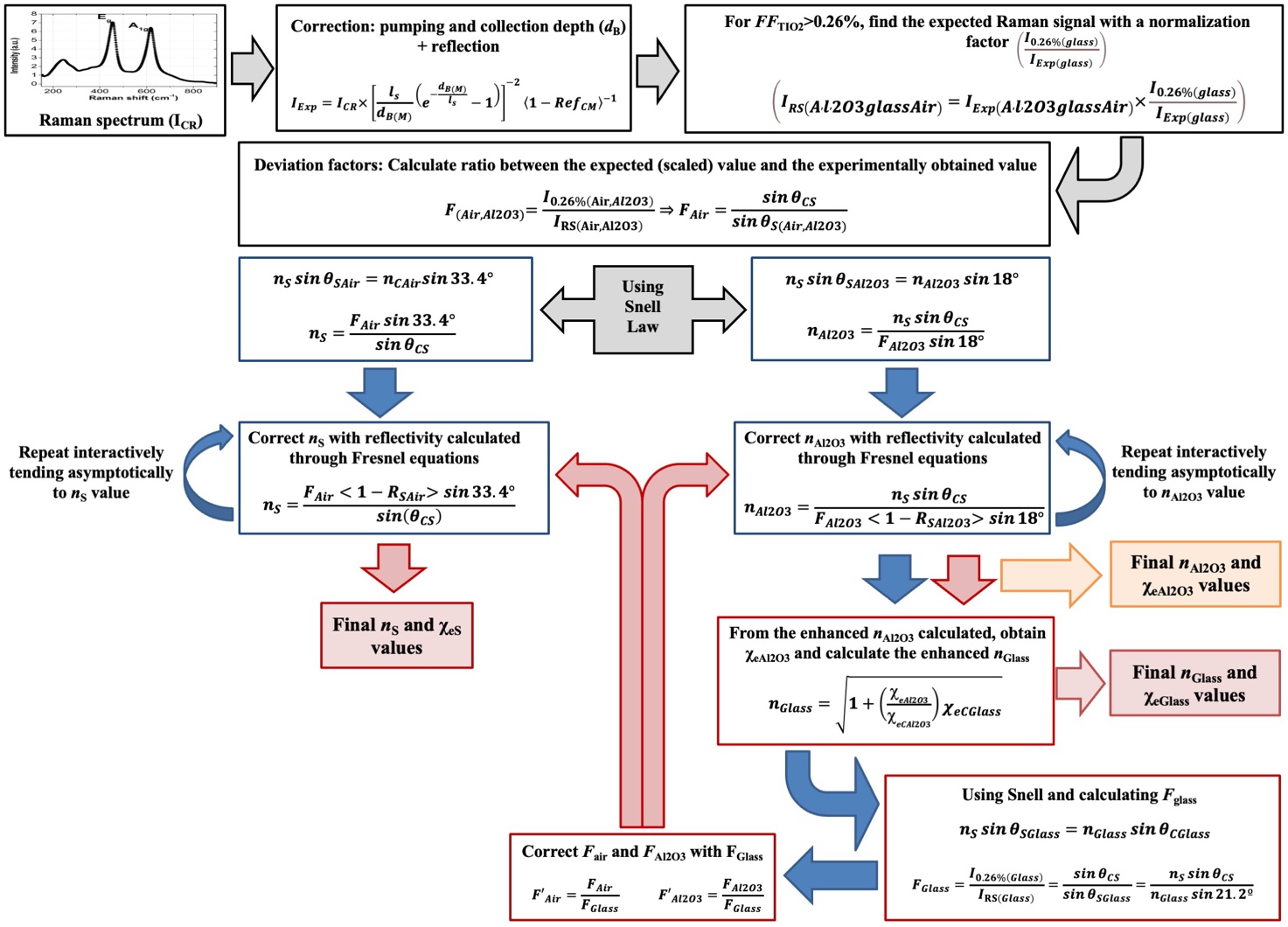


Figure S 3. *Represents the flow of operations executed to determine the effective refractive indexes (nS, nAl2O3, nGlass) of the sample and slides at the sample-slide interface.*

**References**

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