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## Chapter

# Theoretical and Experimental Study on the Functionalization Effect on the SERS Enhancement Factor of SiO<sub>2</sub>-Ag Composite Films

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## Abstract

Herein we addressed a study to determine the enhancement factor (EF) of the Raman signal reached by composite films with two main components, Ag nanoparticles and SiO<sub>2</sub> spheres. The study involves the synthesis, structural composition and optical response by using experimental techniques and theoretical-numerical modeling. A colloid with single NPs and agglomerates of them, with a tannic acid layer on its surface, was produced. Separately, porous SiO<sub>2</sub> spheres were obtained. A mixture of both, Ag NPs and SiO<sub>2</sub> particles was used to produce the films by solvent evaporation method. It is shown that single or agglomerated Ag NPs are preferentially located at the interstices of the SiO<sub>2</sub> spheres. Using discrete dipole approximation, the SERS EF has been estimated considering the agglomeration and tannic acid layer. Both, the dielectric spheres and tannic acid layer diminish the electric field intensity and therefore the SERS EF. When a Ag NP with/without a dielectric shell is touching a SiO<sub>2</sub> sphere, the EF is as high as  $1 \times 10^3$ , the zones where this value is reached are smaller when the dielectric layer is present. With a cluster of 3 nude Ag NPs surrounded by SiO<sub>2</sub> spheres an EF of  $2.4 \times 10^3$  is obtained.

**Keywords:** SiO<sub>2</sub> spheres, silver nanoparticles, composite film, tannic acid, functionalization, near field intensity, discrete dipole approximation

### 1. Introduction

Research around the optical properties of Ag nanoparticles (NPs) has been a topic of high importance for diverse applications as coating, plasmonic antennas, for drug delivery, as components of molecular detectors, among others [1–6]. The convenience of using Ag NPs lies in their intense plasmonic response with a surface plasmon resonance (SPR) in the visible optical range. The SPR is a phenomenon that occurs when a metal NP is excited by an electromagnetic wave, the conduction electrons respond to the electromagnetic field in such a way that oscillations of the electron charge distribution occur in the vicinity or on the surface of the particle. Ag NPs have their SPR in the range from 350 to 600 nm, depending on their size and morphology [7, 8].

To improve the colloidal stability and surface properties of Ag NPs the functionalization is a feasible option. This chemical process modifies the NP's surface charge using a specific chemical compound that successfully encapsulates the NP, attributing the surface with a neutral, negative or positive character [9]. Once NPs are functionalized can be used for different purposes, for example, to selectively adsorb drugs to later release them in a controlled way [3], to inhibit the growth of bacteria [5], to prevent agglomeration in a colloid [10], among others.

Tannic acid is commonly used in synthesis methods as a stabilizer, it is a typical hydrolyzable tannin derived from plants with various biological properties such as antioxidant, antitumor, antimutagenic, antimicrobial and anti-inflammatory, besides its ability to interact with proteins [11]. The structure of tannic acid is made up of tannins that contain digalloyl ester groups connected to a central glucose nucleus. These groups can interact ionically with others, also can interact through hydrogen bonding with alike or different molecules, and moreover bond to a metal [12].

Silicon dioxide, SiO<sub>2</sub>, is considered a useful material for coating because of its physical and chemical properties such as chemical stability, optical transparency, biocompatibility, inert-material character and reactivity with various coupling agents [13, 14]. Specifically, amorphous SiO<sub>2</sub> substrates have the advantage of a very high specific surface area. In addition, they promote the dispersion and homogeneous distribution of metallic NPs on it [14]. The last, seems promising for Surface Enhanced Raman Scattering (SERS) based-metal substrates purposes. The SERS enhancement factor (EF) that can be reached is directly related to the SPR of the used NPs through the  $|\mathbf{E}|^4$  approximation.

To determine the electric field intensity on the NP's surface and away from it, exist various options, some of the most common are based on finite elements methods, finite difference time domain or volume integral equations. In particular, Discrete Dipole Approximation (DDA) is a flexible integral equation method that allows to study the optical response of targets with a size smaller or similar to that of the incident wavelength. With this method is possible to study isolated or periodic targets with arbitrary shapes [15, 16]. On the other hand, this method has been widely used to study the absorbed and scattered light by several systems as nanoparticles, bacteria, films, red blood cells, among others [17, 18].

Along this chapter we present a study of films composed by Ag NPs and SiO<sub>2</sub> spheres. The films are proposed as SERS substrates with the characteristic of Ag NPs very well located at the interstices of the silica spheres. It is worth mentioning that the NPs have a tannic acid layer on its surface. Through a combination of experimental techniques and theoretical-numerical modeling a study of structural and optical properties has been realized, in addition the SERS EF has been estimated. The content of the chapter is as follows. In section 2 the methodology followed for the synthesis of Ag NPs, SiO<sub>2</sub> spheres and composite films is addressed. In sections 3 and 4, the determination of size and morphology of Ag NPs is presented, and the presence of a layer of tannic acid on its surface is also shown. Subsequently, in section 5 and 6 the structural composition of the SiO<sub>2</sub> spheres and composite films is shown, respectively. Section 7 contains the details of the methodology followed to estimate the SERS EF of systems made of Ag NPs and SiO<sub>2</sub> spheres. Finally, the conclusions are stated.

#### 2. Synthesis methodology

#### 2.1 Ag NPs synthesis

Ag NPs were synthesized using the seed growth method reported by Bastús et al. [19], they reported an experimental methodology para obtainer Ag NP de 4 a

200 nm de diameter. The methodology describes different conditions to obtain a specific size. In essence, the required size is achieved from the number of growth steps. Here, Ag seeds of approximately 35 nm in diameter were obtained as follows. 50 ml of 0.1 mM tannic acid (Sigma Aldrich, 98%) and 50 ml of 5 mM sodium citrate (J. T. Baker, 96%) were mixed and then the solution was heated up to 90 ° C. Subsequently, 1 ml of 25 mM silver nitrate (Riedel-de Haën, 98%) was added and the solution was kept stirring for 30 minutes. At this point, to eliminate secondary products, the solution was centrifuged at 20,000 rpm, for 15 minutes. The supernatant solution was separated and subsequently the Ag seeds were redispersed in 20 ml of deionized water. The elimination of secondary products was repeated 3 times. The final solution is named the seed solution.

In order to obtain Ag NPs of 100 nm of diameter, a 4-stage growth procedure was followed. The first stage consisted of diluting 20 ml of the seed solution (0.21 M) with 16 ml of deionized water and then heated up at 90 °C. Subsequently, 500 µl of 25 mM sodium citrate, 1.5 ml of 2.5 mM tannic acid and 1 ml of 25 mM silver nitrate were added. This stage ends after 30 minutes of reaction maintaining the temperature at 90 °C. As a second stage, the same amounts of sodium citrate, tannic acid and silver nitrate were added keeping the same reaction conditions. Third and fourth stages were alike than the second one. The elimination process of secondary products was carried out according to the one indicated above, with the difference that a centrifugation velocity of 18,000 rpm was used.

#### 2.2 SiO<sub>2</sub> spheres synthesis

A common method to synthesize SiO<sub>2</sub> spheres is the Stöber method [20], which consists of the hydrolysis of tetraethylorthosilicate (TEOS) with an alcohol as solvent, and an hydrolysis catalyst. With this method polydisperse SiO<sub>2</sub> colloids are obtained. On the other hand, Razo and collaborators [21] obtained monodispersed SiO<sub>2</sub> microspheres with characteristic sizes between 150 and 600 nm in diameter. In their work they reported the relation between the sphere diameter of SiO<sub>2</sub> as a function of the moles of TEOS. During all the study the number of moles of NH<sub>3</sub>/  $H_2O/C_2H_5OH$  was fixed. Using 0.46 moles of NH<sub>3</sub>, 2.89 moles of H<sub>2</sub>O and 2.15 moles of C<sub>2</sub>H<sub>5</sub>OH (relation A) they obtained microspheres with size from 150 nm to 600 nm in diameter. Whereas using 0.41 moles of NH<sub>3</sub>, 2.20 moles of H<sub>2</sub>O and 2.15 moles of C<sub>2</sub>H<sub>5</sub>OH (relation B) microspheres from 350 nm to 600 nm were produce.

Herein we synthesize SiO<sub>2</sub> spheres of 300 nm based on relation A. Separately, two solutions were prepared: the first one consisted of 9 ml of TEOS (Sigma Aldrich, 98%) and 125 ml of ethanol (Sigma Aldrich, 80%). The second solution was formed from 52 ml of deionized water and 30 ml of ammonium hydroxide (J. T. Baker, 64%). Later, both solutions were mixed and the reaction was maintained for 3 hours, under constant stirring at room temperature. For the purification of the SiO<sub>2</sub> spheres, the same washing procedure (elimination of the secondary products) used for the Ag NPs was followed.

#### 2.3 SiO<sub>2</sub>-Ag composite film deposition

To obtain the films of the  $SiO_2$ -Ag composites, the solvent evaporation method was used. For this, 25 ml of solution of  $SiO_2$  spheres (5 mM) dispersed in ethanol were mixed with 5 ml of Ag NPs solution (3 mM) dispersed in water.

On the other hand, the glass substrate was cleaned with neutral soap in a sonic bath, dried with pressurized air and immersed for 1 hour in 100 ml of piranha solution (3: 1 of sulfuric acid and hydrogen peroxide). After this time, the substrate was rinsed with deionized water and dried with compressed air. The substrate was introduced into the colloid formed by microspheres of  $SiO_2$  and Ag NPs. Subsequently, it was heated in a muffle at 70 °C for 24 hours.

#### 3. Determination of the size and shape of Ag NPs

**Figure 1** shows the Absorbance of the Ag NPs colloidal solution measured from the ultraviolet to the visible region. The maximum of the spectrum is located at 421 nm and the shape-line is asymmetrical, with a shoulder covering from 480 nm to 550 nm. To have an insight about the origin of the maximum and the shoulder we proceed to calculate the optical extinction efficiency ( $Q_{ext}$ ) of a spherical Ag NP of various diameters. The Absorbance and extinction efficiency are directly related through the next expression:

$$A(\lambda) = CQ_{ext}(\lambda)\pi r^2 L/\ln(10), \qquad (1)$$

where *C* is the concentration of Ag NPs (in particles/cm<sup>3</sup>), *L* is the length of the sample (1 cm), *r* the radius of the NP and ln is the natural logarithm function. The linear relation between *A* and  $Q_{ext}$  indicates that both of them have the same spectral shape-line but different intensities. The  $Q_{ext}$  was calculated using the well-known Mie theory [22].

As we can see in the **Figure 1**, the  $Q_{ext}$  spectra that better fit to the Absorbance are those of a Ag NP with a diameter of 63 nm and other of 100 nm. This indicates that in the colloidal solution predominates the presence of Ag NPs of 63 nm and 100 nm. According to the intensity of the spectrum one can expect that the number of NPs with a size of 63 nm is larger than that with a size of 100 nm.

Apart, the size distribution was also determined using Dynamic Light Scattering (DLS), a technique that provides information of the hydrodynamic diameter of the entities in the solution. Under optimal particle concentration, that is, sufficiently low to disesteem particle-particle interaction and sufficiently high to have a strong signal, the hydrodynamic diameter of spherical particles matches to the physical diameter. From the size distribution a main value around 66 nm is observed, also



#### Figure 1.

Measured and calculated optical response of the Ag colloid. The calculated spectra were obtained using Mie theory for a spherical NP with a diameter D = 63 nm and other with a D = 100 nm.



**Figure 2.** *Size distribution of the Ag NPs in solution, measured with DLS technique.* 



the presence of NPs with a diameter of 100 nm is detected, see **Figure 2**. Therefore, there is a good agreement with the predicted calculations obtained with Mie theory and shown in **Figure 1**.

Small and big Ag NPs were also observed by using an Atomic Force Microscope (AFM), see **Figure 3**. However, the "big NPs" are actually quasi spherical agglomerates of Ag NPs with an average size of  $96\pm9$  nm, the statistic was done over 166 particles. This fact clarifies the deductions made from DLS and spectroscopy techniques, and Mie theory, the solution contains single Ag NPs and agglomerates of them.

#### 4. Functionalization of Ag NPs

In **Figure 4** the zeta potential profile of the Ag NPs is shown, there a negative superficial charge of -52.5 mV is detected. To expose the origin of the negative



**Figure 4.** Zeta potential of the Ag NPs in solution.



Figure 5.

Measured absorbance of the Ag NPs (black line), tannic acid (red line) and sodium citrate (blue line). To the right a scheme of the adsorption of tannic acid molecules on the NP surface is depicted.

superficial charge, a comparison among the optical spectrum of the Ag NPs, the tannic acid and the sodium citrate is presented in **Figure 5**. The last two were used as reducing and stabilizing agents during the synthesis procedure of the NPs. The band of the sodium citrate is out of the measured interval, whereas the optical response of the tannic acid is characterized by one band located at 214 and other at 268 nm. These two bands are well superimposed to the shape line of the Ag NPs spectrum in the interval of ultraviolet light. Therefore, the tannic acid is present in the colloid even after the several washing times. The negative charge of the NPs is explained as follows. Assuming the tannic acid molecules are adsorbed on the surface of the NPs, the negative charge detected is probably because of a partial deprotonation of the OH groups bonded to aromatic ring (see scheme in **Figure 5**). It is worth mentioning the fact that the electronic interband transitions of Ag take place at wavelengths lower than 320 nm, therefore they also contribute to the Absorbance in the UV range [23].

#### 5. Determination of size and shape of SiO<sub>2</sub> particles

A transmission electron microscopy (TEM) image of the  $SiO_2$  spheres is shown in **Figure 6A**. It is observed that the spheres are amorphous because of their porosity. In the inset of **Figure 6A** we illustrate the structure of one pore. The formation of the pores takes place when some periodic chains of Si-O were not carried out during the polymerization reaction, in addition, some OH groups may stay on the surface [13].

The optical UV–Vis spectrum is shown in **Figure 6B**. An absorption edge starting at approximately 300 nm and a maximum in 290 nm are observed. The width of absorbance spectrum corresponds to the band gap (Eg) energy of amorphous SiO<sub>2</sub>. The Eg was estimated by extrapolating the absorption edge to the photon energy axis through a linear fit, then the Eg value in the direct transition of SiO<sub>2</sub> turned out to be 3.98 eV. This value is in agreement with the reported Eg of 3.8 eV in the case of SiO<sub>2</sub> nanostructures [13, 24]. This value is lower than that reported for crystalline SiO<sub>2</sub> (quartz), which is approximately 9 eV [25] and is a consequence of the defects mentioned above.

The zeta potential of the  $SiO_2$  colloid is shown in **Figure 7**, a negative surface charge of -44.1 mV is detected. The minus sign is attributed to the oxygens of the OH groups located on the surface or in the pores.

The spherical shape of the  $SiO_2$  particles is corroborated by the AFM images in **Figure 8**. A large concentration of  $SiO_2$  spheres covering a glass substrate is



#### Figure 6.

(A) a TEM image of SiO<sub>2</sub> spheres. (B) UV-vis spectrum of the colloidal solution of SiO<sub>2</sub> particles.



**Figure 7.** Zeta potential of the  $SiO_2$  particles in solution.



observed. The main feature is a short-range order with spheres forming hexagonal arrays and multilayers. From a statistical analysis over 120 particles, an average size is estimated in  $289 \pm 55$  nm.

# 6. Structural composition of the SiO<sub>2</sub>-Ag composite films

AFM technique was also used to analyze the structure of the SiO<sub>2</sub>-Ag composite films, the micrographs are shown in **Figure 9**. In different areas of the film it is observed that the spheres are arranged in a short-range hexagonal packing, a similar spatial distribution than the observed in the SiO<sub>2</sub> films. Because of the absence of SiO<sub>2</sub> and Ag NPs some voids are created. The single or agglomerates of Ag NPs are located in the interstices among SiO<sub>2</sub> spheres. The fact that the Ag NPs do not surround the SiO<sub>2</sub> spheres is because of the surface charge, of both Ag NPs and SiO<sub>2</sub> spheres, is negative (-52.5 mV and -44.1 mV, respectively).



Figure 9.

AFM micrographs of the  $SiO_2$ -Ag composite films at different amplifications. The right panel shows that Ag NPs are found in the interstices.

# 7. Estimation of the SERS enhancement factor

As Raman signal of molecules is very weak for detecting them at very low concentrations various proposals for different condition are required. One way to enhance the signal is with the use of metallic surfaces, because of their excitation of the surface plasmon. The magnitude of the Raman signal enhancement is influenced by some factors:



- Laser excitation: wavelength, angle of incidence, power, interval of time.
- Plasmonic Surface: chemical composition, refractive index, shape, surface roughness.
- Analyte: Intrinsic properties such as polarizability tensor or optical cross section, concentration, compatibility to be adsorbed to the metal surface.

To quantify the enhancement of the Raman signal factor (EF) the Single-Molecule SERS EF or the Average SERS EF are defined. The first one quantifies the amplification of the Raman signal of one molecule at a particular position, whereas the second one is the average of the intensity when considering random positions along an area of the substrate. Here we are focused on the Single-Molecule SERS EF (SMEF) expressed as

$$SMEF \approx \frac{|E_{loc}(\omega_{exc})|^2}{|E_{inc}(\omega)|^2} \frac{|E_{loc}(\omega_{Raman})|^2}{|E_{inc}(\omega)|^2},$$
(2)

where  $E_{inc}(\omega)$  is the incident field,  $E_{loc}(\omega_{exc})$  and  $E_{loc}(\omega_{Raman})$  are the local electric field at the excitation frequency and Raman frequency, respectively. When the excitation frequency is similar to the Raman frequency then

$$SMEF \approx \frac{|E_{loc}(\omega_{exc})|^4}{|E_{inc}(\omega)|^4},$$
 (3)

this expression is called the  $|E|^4$  approximation.

To calculate the local field, the DDA and its numerical implementation DDSCAT code have been used [26]. The fundamentals of DDA are widely detailed elsewhere [27]. The basic idea is the representation of the target by a discrete array of N point dipoles. Each dipole is at the site of a cubic lattice with a lattice parameter  $d_0$ , being this smaller than the wavelength of the incident electric field. The chosen N value determines the convergence and numerical error in the calculations, in **Figure 10** a particle with a spherical shape is represented by N = 462,758 and N = 3,775,

DDA assumes that the target is illuminated by an external source of monochromatic radiation represented by a plane wave,  $\vec{E}_{inc}(\omega) = \vec{E}_0 e^{i\left(\vec{k}\cdot\vec{r}-\omega t\right)}$ . In **Figure 11** a plane wave with a) y-polarization and b) z-polarization state is depicted. The electric plane wave induces a dipole moment on each dipole (see **Figure 11**). Because of the dipole–dipole interaction an induced electric field is originated given by: Silver Micro-Nanoparticles - Properties, Synthesis, Characterization, and Applications

$$\vec{E}_{ind,i} = -\sum_{j}^{\prime} \mathbb{A}_{ij} \cdot \vec{p}_{j} \mathbf{i} = 1, \dots, \mathbf{N}, \qquad (4)$$

where  $\mathbb{A}_{ij}$  represents the dipole–dipole interaction and depends on the relative position between the dipole *i* and *j* ( $\vec{r}_{ij} = \vec{r}_j - \vec{r}_i$ ),  $\sum_j$ ' indicates that  $i \neq j$ ,  $\vec{p}_j$  is the dipole moment of the *j* dipole. Conventionally  $\mathbb{A}_{jj} = 0$ . Considering that  $\vec{p}_i = \alpha_i \vec{E}_{T,i}$ , being  $\alpha_i$  the polarizability tensor and  $\vec{E}_{T,i}$  the total field at  $\vec{r}_i$  and that

$$\vec{E}_{T,i} = \vec{E}_{inc,i} + \vec{E}_{ind,i},$$
(5)

is possible to get a system of 3 N complex equations that in matrix notation is expressed as:

$$\hat{\mathbb{B}}\vec{\mathrm{P}}=\vec{E}_{inc},\tag{6}$$

with  $\vec{P} = (\vec{p}_1, \vec{p}_{2,...}, \vec{p}_N)$ ,  $\vec{E}_{inc} = (\vec{E}_{inc,1}, ..., \vec{E}_{inc,N})$  and  $\hat{\mathbb{B}}$  a  $N \times N$  symmetric matrix [27].

Once the Eq. (6) is solved, that is,  $\vec{p}_1, \vec{p}_{2,...,} \vec{p}_N$  are known, then the electric field in, on and outside the target can be calculated. To solve Eq. (6) we used the software DDSCAT, which is a numerical implementation of DDA. Because we are interested in the SERS EF, we focused on the electric field on and outside the particle. DDSCAT code allows to calculate the electric field on a point with coordinates (x, y, z):

$$\vec{E}(x,y,z) = \vec{E}_{inc}(x,y,z) + \vec{E}_{scat}(x,y,z),$$
(7)

where an incident field of magnitude 1 is specified, that is,  $\left| \vec{E}_{inc} \right| = E_{inc} = 1$ , and

 $E_{scat}$  is the scattered field of the N radiating dipoles representing the target [28]. In addition, we used the Lattice Dispersion Relation (an option in the DDSCAT code) to describe the polarizability of each dipole [29].



Figure 11.

Scheme of an incident plane wave on a spherical target with (a) y-polarization and (b) z-polarization. The electric field induces a dipole moment on each dipole (tiny spheres).

$$\alpha_i = \frac{\alpha_i^{nr}}{1 - 2i \, k^3 \alpha_i^{nr} / 3} \, i = 1, 2, ..N,$$
(8)

where  $\alpha_i^{nr} = \frac{\alpha^{CM}}{1 + \alpha^{CM} k^2 [b_1 + m^2 b_2 + m^2 b_3 S]/d}$ , being *k* the wavenumber of the incident plane wave,  $\alpha^{CM}$  the well-known Clausius- Mossotti polarizability, *m* the refractive index of the material, *S* contains information of the polarization state and direction of propagation,  $b_1, b_2$  and  $b_3$  are constants, and *d* is the separation distance between two adjacent dipoles.

The polarizability depends on the dielectric function through the refractive index and the Clausius- Mossotti polarizability. To describe properly the polarizability an analysis of the size-dependent dielectric function was carried out.

A size correction in the bulk dielectric function of a material was firstly proposed by Kreigib [30]. He proposed whether the dimensions of the material are smaller than a critical diameter  $D_c$ , then quantum effects should be considered. As the diameter of the particle becomes of the order or greater than  $D_c$  then the electronic levels become a finite set of energy levels forming the conduction band, as it occurs in a bulk material.

Finite size correction (FSC) theory is based in the assumption that the free electrons have instant collisions with the lattice ions and also with the surface of the particle, the last acts as a scatterer of the electrons reflecting them diffusely. Then, the damping constant is expressed as

$$\Gamma = \Gamma_{bulk} + \frac{V_F}{l},\tag{9}$$

where  $\Gamma_{bulk}$  is the bulk damping constant,  $V_F$  is the Fermi velocity and l is the mean free path.

On the other hand, the bulk dielectric function is expressed as

$$\epsilon_{bulk}(\omega) = \epsilon_{inter}(\omega) + \epsilon_{intra}(\omega), \tag{10}$$

where the intraband contribution is because of free electron transitions in the conduction band, whereas the interband contribution is because of band-to-band transitions of the core electrons. The interband transitions become important at smaller wavelengths than 320 nm for Ag [23]. Because interband electrons are not notably affected by the surface,  $\epsilon_{inter}(\omega)$  can be assumed size independent. Therefore, considering that intraband electrons behave as Drude electrons with a damping constant as Eq. (9), the dielectric function of a particle with radius *a* is [31].

$$\epsilon(\omega, a) = \epsilon_{bulk}(\omega) - \epsilon_{intra} + \left\{ 1 - \frac{\omega_p^2}{\omega[\omega + i\Gamma_{bulk} + iV_F/a]} \right\},\tag{11}$$

 $\Gamma_{bulk} = 1/\tau$ , with  $\tau$  the relaxation time and  $\omega_p$  the plasma frequency.  $\tau$  is also related to the mean free path of the electrons, *l*. For Ag  $\hbar\omega_p = 9.6$  eV,  $1/\omega_p\tau = 0.00188$ ,  $V_F = 1.39 \times 10^6$  m/s and l = 52 nm [32].

We explore the FSC in the dielectric function in an interval of diameters between 20 nm and 100 nm. In **Figure 12** we present the real and imaginary part of the dielectric function for only the extreme values of the studied interval, the curves of other diameters are in between. The optical response when the size of the material is 100 nm matches with that of the bulk Ag.

The SPR of a Ag NP in water and with a diameter (D) in the interval between 20 nm and 100 nm is shown in **Figure 13** a). For this interval, as the size increases,



Real and imaginary part of the dielectric function of silver in bulk (blue line) and taking into account FSC with a diameter of 20 nm (yellow line) and 100 nm (dashed blue line).



The SPR vs diameter (D) of a spherical Ag NP is shown in panel (a). The magnitude of the electric field of a Ag NP with a D = 20 nm and D = 100 nm is shown in panel (b) and (c), respectively, the incident plane wave has a wavelength of 632 nm. In panel (d) |E| at a point in the zenith of the NP vs D is presented. The NP is in water (refractive index of 1.33).

the SRP is red shifted. In addition, the magnitude of the complex electric field vector on a plane crossing the center of the NP is shown in panel b) and c) for a D = 20 nm and D = 100 nm, respectively. The plane wave has a wave vector  $\vec{k}$  in x-direction, a linear polarization state in y-direction and a wavelength of 632 nm. Along the xy plane the small NP has the characteristic field intensity distribution of a dipole plasmon. Whereas, for the large NP the intensity distribution is slightly distorted from that of a dipole surface plasmon. To visualize the relation  $\left|\vec{E}\right| vs D$  a specific hot spot in the zenith of the sphere was chosen, its electric field magnitude

|E| (not the intensity or irradiance) *vs* D is shown in panel d). For the sizes studied here the magnitude of the electric field varies from 4 to 6, therefore the SERS EF of a molecule located at the zenith of the sphere is SERS EF =  $|\vec{E}|^4 = 1.3x10^3$  for a Ag NP with a D = 100 nm.

Because a common laser to study SERS signal is that with a 632 nm wavelength, and based on the results shown in **Figure 13**, the Ag NP with a SPR wavelength close to the laser has a diameter of 100 nm. Therefore, in the following sections we have considered a Ag NP with that size and an excitation wavelength of 632 nm.

#### 7.1 Electric field magnitude of the composite thin film

From the experimental techniques we observed that the Ag NPs have a preferred location at the interstices of the  $SiO_2$  spheres when in substrate, particularly creating clusters or agglomerates. Moreover, the Ag NPs are covered by a layer of tannic acid.

To estimate the SERS EF of the composite material the layer of the tannic acid was taken into account and a study of the agglomerated NPs was carried out. Figure 14 shows the electric field magnitude of a single SiO<sub>2</sub> sphere with a D = 290 nm (see panel a)), of a single Ag NP with a D = 100 nm (see panel b)), same NP as in b) with a shell of 1 nm of tannic acid (see panel c)), a  $SiO_2$  sphere and a Ag NP touching (see panel d)), and same array as in d) with the tannic acid shell of the NP (see panel e)). For all the cases mentioned, the plane wave with the same characteristics as in **Figure 13** were considered. The refractive index is 1.46 for SiO<sub>2</sub> [33], 1.704 for tannic acid [34], and 1.0003 for the surrounding medium (the composites are in air). Clearly, the electric field on and away from the surface of the dielectric SiO<sub>2</sub> sphere is less intense than that of the Ag NP. The presence of the dielectric tannic acid layer affects the plasmonic response of the NP and the result is a less intense electric field with a spatially symmetric distribution. There is a "screening" effect because of the presence of the dielectric shell, this is observed in the presence and absence of the SiO<sub>2</sub> sphere. When a Ag NP with/without a tannic acid shell is touching a SiO<sub>2</sub> sphere a SERS EF can be as high as  $1 \times 10^3$ , the zones where this value can be reached are smaller when the dielectric layer is present.



#### Figure 14.

Local electric field of (a) a single SiO<sub>2</sub> sphere, (b) a single nude Ag NP, (c) a single Ag NP with a tannic acid shell of 1 nm thick, (d) nude Ag NP touching a SiO<sub>2</sub> sphere, and (e) Ag NP-tannic acid shell touching a SiO<sub>2</sub> sphere.



Magnitude of the electric field along a center-to-center path, see red line in the inset of panel (B). When the sphere and NP are touching d = 0 and a point on the surface of SiO<sub>2</sub> sphere is at a position of 145 nm (D = 290 nm of a SiO<sub>2</sub> sphere). Panel (A) shows |E| values as d increases and the Ag NP is nude, whereas in panel (B) the tannic acid shell has been considered.

Because SiO<sub>2</sub> spheres and Ag NPs have a negative superficial charge, -44.1 mV and -52.5 mV, respectively, we deduce there is not surface-to-surface contact. We explore surface-to-surface separation distances (*d*) between 0.5 nm and 3.5 nm and how this modifies the electric field.

In **Figure 15** is shown the magnitude of the electric field along a straight path starting at the center of the SiO<sub>2</sub> sphere and ending at the center of the Ag NP, this is illustrated as the red line shown in the inset of panel B). The size of the SiO<sub>2</sub> sphere is D = 290 nm and of the Ag NP D = 100 nm, therefore when d = 0, that is, the sphere and Ag NP are in contact, the contact point is at a position of 145 nm. Panel (A) and (B) shows |E| values as d increases when the Ag NP is nude and with



#### Figure 16.

Dipoles array and |E| values along the yz-plane of an array of 3 SiO<sub>2</sub> spheres with (a) one Ag NP, and (b) 3 Ag NPs with no coplanar centers, at the interstice. For both cases, the incident field has a wave vector along x, y-polarization and a wavelength of 632 nm.

the tannic acid shell, respectively. For both cases, the magnitude of the electric field presents inappreciable changes.

To inquire about the electric field intensities in the composite material, we explore the case with one and three Ag NPs at the interstice of three SiO<sub>2</sub> spheres. Again, the size of the SiO<sub>2</sub> sphere is D = 290 nm and of the Ag NP D = 100 nm. The refractive index of the medium is air and the incident electromagnetic field travels in the positive x-direction with a y-polarization, its wavelength is 632 nm. It is worth mentioning that in these cases the tannic acid layer was not considered. To illustrate the systems under study, their respective array of dipoles is shown in **Figure 16**. Because of the complexity of the 3D arrays we chose only the yz-plane to exemplify the field magnitude. As expected, the electric field of the Ag NP in presence of three SiO<sub>2</sub> spheres is weak because of the screening effect promoted by the dielectric material, whereas, in the array of three Ag NPs, relative hot spots are present in the space among them. The hot spots may provide a SERS EF of the order of  $2.4 \times 10^3$ .

#### 8. Conclusions

In this chapter we present the synthesis, structural composition and optical response of composite films with two main components, Ag nanoparticles and SiO<sub>2</sub> spheres. The independent production of Ag NP and SiO<sub>2</sub> sphere colloids were the basis to fabricate the composite films by evaporation solvent method. According to the analysis made to Atomic Force microscopy images, measurements of Absorbance and Dynamic light scattering, and numerical calculations supported on Mie theory, we conclude that single NPs and also agglomerates of Ag NPs were produced with a NP mean diameter of 96  $\pm$  9 nm. In addition, the presence of a tannic acid layer covering the surface of the NP is deduced. With the synthesis method followed to produce the SiO<sub>2</sub> particles it was possible to obtain porous spherical particles with a mean diameter about 289  $\pm$  55 nm.

The composite films are characterized by a short-range order with local hexagonal arrays of SiO<sub>2</sub> spheres with Ag NPs, single or agglomerated, located at the interstices. Some voids are also observed, that is spaces without the presence of NPs and/or spheres. We attribute the preferred location of the NPs to the negative surface charge of both, Ag NPs and SiO<sub>2</sub> spheres. Another aspect deduced from the same sign of the surface charge is that the NP and sphere are not touching, that is, there is no surface-to-surface contact. To have an insight about how this affects the magnitude of the electric field  $|\vec{E}|$ , and therefore, the SERS EF, DDA calculations were carried out.

When the separation distance between the surface of a NP and that of a SiO<sub>2</sub> sphere is varied from 0 to 3.5 nm the intensity of the field is practically the same. The last was observed with a nude NP and with a NP covered by the tannic acid shell. Furthermore, the dielectric tannic acid layer generates a screening effect on the field intensity, besides, a different intensity distribution is observed when compared to that of a nude NP. With both a nude or covered Ag NP when in presence of the SiO<sub>2</sub> sphere, a maximum SERS EF estimated is of the order of  $1 \times 10^3$ . The difference is that this EF can be reached in smaller regions when the NP is covered compared to that when the NP is nude. Finally, the SERS EF of an agglomerate of three Ag NPs surrounded by three SiO<sub>2</sub> spheres was estimated. Even with the presence of the dielectric SiO<sub>2</sub> spheres that screens the electric field intensity, relative hot spots are observed in the regions where the nude NPs are very close one each other, giving place to a maximum SERS EF of the order of  $2.4 \times 10^3$ .

Despite this order of magnitude is not as large to the usually reported with plasmonic NPs, this composite films have the advantage of being prepared by inexpensive methods, moreover, the NPs are located at specific positions, a fact that can be taken advantage of for SERS applications, as proposed here, or many others.

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# **Conflict of interest**

The authors declare no conflict of interest.

# Appendices and nomenclature

SERS	Surface Enhanced Raman Scattering
NPs	Nanoparticles
DDA	Discrete Dipole Approximation
SPR	Surface Plasmon Resonance
DLS	Dynamic Light Scattering
AFM	Atomic Force Microscope
TEM	Transmission Electron Microscopy
EF	Enhancement Factor
SMEF	Single-Molecule SERS Enhancement Factor
FSC	Finite Size Correction

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# References

[1] Li WR, Xie XB, Shi QS, Zeng HY, Ou-Yang YS, Chen YB. Antibacterial activity and mechanism of silver nanoparticles on Escherichia coli.
Applied Microbial and Cell Physiology.
2010; 85; 1115–1122. DOI: 10.1007/ s00253-009-2159-5

[2] Hoang TB, Akselrod GM,
Argyropoulos C. Ultrafast spontaneous emission source using plasmonic nanoantennas. Nature Communications.
2015; 6; 1–7. DOI: 10.1038/ncomms8788

[3] Ivanova N, Gugleva V, Dobreva M, Pehlivanov I, Stefanov S, Andonova V. Silver Nanoparticles as Multi-Functional Drug Delivery Systems. In: Muhammad Akhyar F, editor. Nanomedicines IntechOpen, p. 71–92. DOI: 10.5772/ intechopen.80238.

[4] Beckett R, Jue Z, Giddings JC. 1987
Determination of molecular weight distribution of fulvic and humic acids using flow field-flow fractionation.
Environmental Science & Technology.
1987; 21; 289–295. DOI:10.1021/es00157

[5] Keziban A, Münteha Ö, Mahmut Ö. Investigation of antibacterial properties of novel papain immobilized on tannic acid modified Ag/CuFe2O4 magnetic nanoparticles. International Journal of Biological Macromolecules. 2017;109; 720–731. DOI: 10.1016/j. ijbiomac.2017.12.066

[6] Shafer-Peltier K, Haynes CL, Van Duyne RP. Toward a Glucose Biosensor Based on Surface-Enhanced Raman Scattering. 2003; 125; 588–593. DOI: 10.1021/ja028255v

[7] Sijo F, Siby J, Ebey K, Beena M. Microwave assisted green synthesis of silver nanoparticles using leaf extract of elephantopus scaber and its environmental and biological applications. Artificial Cells, Nanomedicine, and Biotechnology. 2017; 46 ;795–804. DOI:10.1080/ 21691401.2017.1345921

[8] Alesenkov A, Pilipavicius J,
Beganskiene A. Nonlinear properties of silver nanoparticles explored by a femtosecond z-scan technique.
Lithuanian Journal of Physics. 2015; 55; 100–109. DOI: 10.3952/physics.
v55i2.3100

[9] Le Trequesser Q, Seznec H,
Delville MH. Functionalized
nanomaterials: their use as contrast
agents in bioimaging: mono- and
multimodal approaches.
Nanotechnology Reviews. 2013; 2(2); 1–
44. DOI:10.1515/ntrev-2012-0080

[10] Liu Y, Li Y, Li XM, He T. Kinetics of
(3-Aminopropyl) triethoxylsilane
(APTES) Silanization of
Superparamagnetic Iron Oxide
Nanoparticles. Langmuir. 2013; 29;
15275–15282. DOI: 10.1021/la403269u

[11] Kumari MM, Aromal SA, Philip D. Synthesis of monodispersed palladium nanoparticles using tannic acid and its optical non-linearity. Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy. 2013; 103; 130–133. DOI: 10.1016/j.saa.2012.11.020

[12] Opes L, Brito LM., Bezerra TT, Gomes KN, Carvalho FA. Silver and gold nanoparticles from tannic acid: synthesis, characterization and evaluation of antileishmanial and cytotoxic activities. Anais da Academia Brasileira de Ciências, 2018; 90(3); 2679–2689. DOI: 10.1590/ 0001-3765201820170598

[13] Carmona-Carmona AJ,
Palomino MA, Hernández O, Sánchez E,
Toledo M. Synthesis and
characterization of magnetic opal/
Fe3O4 colloidal crystal. Journal of
Crystal Growth. 2017; 462; 6–11. DOI:
10.1016/j.jcrysgro.2016.12.105

[14] Munnik P, de Jongh PE, de Jong KP.
Recent Developments in the Synthesis of Supported Catalysts. Chemical
Reviews. 2015; 115(14); 6687–6718.
DOI: 10.1021/cr500486u

[15] González AL, Santos A, Toledo M.
Metallo-Dielectric Colloidal Films as SERS Substrate. In: Morteza Sasani Ghamsari, Soumen Dhara, editors.
Nanorods and Nanocomposites.
IntechOpen 90313. 2019. 1-17 p. DOI: 10.5772/intechopen.90313

[16] Santos A, González AL. Far Field Optical Proprieties of a Monolayer of SiO<sub>2</sub> Spheres and Small Au Nanoparticles. Material Research Society Advances. 2018; 3; 3917–3923. DOI: 10.1557/adv.2019.128

[17] Santos A, González AL. Far field optical properties of a monolayer of  $SiO_2$ spheres and small Au nanoparticles. MRS Advances. 2018;3(64):3917–3923. DOI: 10.1557/adv.2019.128

[18] Méndez PA, Soto L, Sánchez E, González AL, Romo JM, Gervacio JJ, Martínez LJ. Damage on Escherichia coli and Staphylococcus aureus using White light photoactivation of Au and Ag nanoparticles. Journal of Applied Physics. 2019; 125; 213102. DOI: 10.1063/1.5090273

[19] Bastús G, Merkoçi F, Piella J. Synthesis of Highly Monodisperse Citrate-Stabilized Silver Nanoparticles of up to 200 nm: Kinetic Control and Catalytic Properties. Chemistry of Materials. 2014; 26; 2836–2846. DOI: 10.1021/cm500316k

[20] Stöber W, Bohn FA. Controlled growth of monodisperse silica spheres in the micron size range. Journal Colloid Interface Science. 1968; 26; 62–69. DOI: 10.1016/0021-9797(68)90272-5

[21] Razo D, Pallavidino L, Garrone E, Geobaldo F. A version of Stöber synthesis enabling the facile prediction of silica nanospheres size for the fabrication of opal photonic crystals. Journal of Nanoparticle Research. 2008; 10; 1225–1229. DOI: 10.1007 / s11051– 008–9373-4

[22] Mei KK. MEI Method. In: K. Chang, editor. Encyclopedia of RF and Microwave Engineering. 1st ed. Chichester: Wiley; 2005. DOI: 10.1002/ 0471654507.eme570

[23] González AL, Reyes-Esqueda JA, Noguez C. Optical Properties of Elongated Noble Metal Nanoparticles. Journal Physical Chemistry C. 2008; 112; 7356–7362. DOI: 10.1021/jp800432q

[24] Bachan N, Asha A, Jeyarani WJ, Kumar DA, Shyla JM. A Comparative Investigation on the Structural, Optical and Electrical Properties of SiO<sub>2</sub>–Fe3O4 Core–Shell Nanostructures with Their Single Components. Acta Metallurgica Sinica. 2015; 28; 1317–1325. DOI: 10.1007/s40195-015-0328-3

[25] Weinberg ZA, Rubloff GW,
Bassous E. Transmission,
photoconductivity, and the
experimental band gap of thermally
grown SiO<sub>2</sub> films. Physical Review B.
1979; 19 (3107); 3107–3117. DOI:
10.1021/la403269u

[26] Draine BT. The discrete-dipole approximation and its application to interstellar graphite grains.
Astrophysical Journal. 1988; 333; 848– 872. DOI: 10.1086/166795

[27] Purcell EM, Pennypacker CR.
Scattering and absorption of light by nonspherical dielectric grains.
Astrophysical Journal. 1973; 186; 705– 714. DOI:10.1086/152538

[28] Jackson JD. Classical Electrodynamics. 3rd ed. New York: John Wiley and Sons Inc; 1999. 832 p.

[29] Draine BT, Goodman J. Beyond Clausius-Mossotti: Wave propagation on

a polarizable point lattice and the discrete dipole approximation. Astrophysical Journal. 1993; 405; 685– 697. DOI: 10.1086/172396

[30] Kreibig U. Electronic properties of small silver particles: the optical constants and their temperature dependence. Journal of Physics F: Metal Physics. 1974; 4; 999–1014. DOI: 10.1088/0305-4608/4/7/007

[31] González AL, Noguez C, Ortiz GP, Rodríguez -Gattorno G. Optical Absorbance of Colloidal Suspensions of Silver Polyhedral Nanoparticles. Journal Physical Chemistry B. 2005; 109; 17512– 17517. DOI: 10.1021/jp0533832

[32] Ashcroft NW, Mermin ND. Solid State Physics. 7th ed. Philadelphia: Saunders college; 1976. 826 p.

[33] Gao L, Lemarchand F, Lequime M. Refractive index determination of SiO<sub>2</sub> layer in the UV/Vis/NIR range: spectrophotometric reverse engineering on single and bi-layer designs. Journal of European Optical Society Rapid Publications. 2013; 8; 13010. DOI: 10.2971 / jeos.2013.13010

[34] CAS. Refractive index Tannic Acid [Internet]. Available from: http://www. chemnet.com/cas/en/1401-55-4/tannicacid.html [Accessed: 2019-05-20]