Micro-Raman Spectroscopy Study of Colloidal Crystal Films of Polystyrene–Gold Composites


INTRODUCTION

Colloidal crystals are well-ordered structures formed by spontaneous ordering of monodisperse spheres of dielectric materials such as silica or polymers. These materials have been the subject of study for several decades because of their unique properties in terms of light propagation and are expected to have applications as functional components for diffractive devices such as filters and switches, optical sensors, and photonic band gap crystals.1–4 For all of the applications, it is important to have control over the quality and, in particular, the thickness of the film.

A variety of methods of self-assembly of spherical colloids into crystalline lattices have been explored and improved over the past years. They include methods such as gravitational sedimentation of colloids from dispersions, dip-coating, spin-coating, vertical deposition, and the Langmuir–Blodgett (LB) method (see Refs. 5–8 and references therein). As for gold composites, they are generally prepared either by infiltrating a polystyrene (PS) or silica template with gold or by the simultaneous convective assembly of PS microspheres and gold nanoparticles.9,10

Monolayers and multilayers of polystyrene (PS)–gold composite films prepared by two different deposition methods have been investigated by atomic force microscopy (AFM), scanning electron microscopy (SEM), X-ray diffraction (XRD), and confocal Raman microspectroscopy. The intensity of the 1001 cm$^{-1}$ ring breathing mode of PS is used to evaluate the degree of ordering of monolayers and multilayers within a colloidal crystal. The depth profiling capability of confocal Raman microscopy is used to probe the regions inside the fractures in multilayered films. The intensity profile of the 1001 cm$^{-1}$ peak revealed the presence of fractures of different shapes. This enhancement is attributed to the surface plasmons generated by the periodic structure of the gold nanoparticles.

Our group has prepared and characterized high-quality PS and silica colloidal crystals as well as titania inverted opals by a vertical deposition technique.11–14 Recently, we have used a similar method to prepare in one step composite films from the aqueous suspension of gold colloids and PS microspheres.15 A new and effective method for the self-assembly of colloidal spheres in ordered monolayers has been developed by our group.16 The technique, based on the Langmuir–Blodgett method, is simple. It does not require any special apparatus and it brings together the advantages of previous techniques such as dip-coating and self-assembly under a small inclination angle. Optical microscopy and atomic force microscopy (AFM) measurements have shown that by using this method the quality of the film (the degree of ordering and the coverage) is controlled by both the liquid surface dropping velocity and the volume fraction of PS in the suspension. When the liquid surface dropping velocity was kept lower than 20 $\mu$m/s, a crystalline film covering an area of 0.5 cm$^2$ can be formed. When a vertical deposition method is used, an area as large as 1 cm$^2$ can be formed, large enough for the fabrication of optical devices. Preliminary micro-Raman spectroscopy results demonstrated that the Au aggregates act as “hot spots” and enhance the Raman signal of the polystyrene microspheres adsorbed on them.

In the past, PS microspheres have been successfully used as surface-enhanced Raman scattering (SERS)-active supports.17–21 To produce surfaces that have reproducible structures, the nanospheres are drop- or spin-coated on a solid support. The nanostructured support is subsequently covered with a layer of silver (or gold), usually by thermal evaporation. The effect of the sphere size and metal layer thickness upon the SERS intensity has been thoroughly investigated.22 The silver-coated nanospheres were found to be among the most robust, strongly enhancing substrates investigated, with enhancement factors comparable to or greater than those found for electrochemically roughened surfaces. This technique, called nanosphere lithography, is a powerful fabrication technique that inexpensively produces nanoparticle arrays with controlled shape, size, and interparticle spacing.23

The advent of micro-Raman techniques has enabled the spatially localized study of chemical species with a high spectral resolution. This technique has been found to be well suited to the study of layered thin films of polymers, semiconductors, and...
porous solids.\textsuperscript{24,25} However, this new attribute of micro-Raman spectroscopy has been only scarcely exploited for the study of photonic materials. Arsenault et al.\textsuperscript{26} have used this technique to probe the design defects created in an inverse silicon colloidal crystal. Also, due to the high sensitivity of the Si Raman modes for local mechanical stress, many studies\textsuperscript{27,28} in the past focused on the micro-scale characterization of stresses in microelectromechanical systems (MEMS).

Confocal Raman micro-spectroscopy is particularly well suited to investigate composite materials that contain gold aggregates within ordered polymer microspheres. The characteristics of these aggregates, their shape and spatial distribution in the film, as well as the interactions between the aggregates and PS microspheres, are investigated in this work. The excitation of surface plasmons in Au–PS nanostructures attests to their potential use as active surfaces in SERS and optical biosensing. The depth profiling capability of confocal Raman microscopy is exploited here to identify and study fractures in films prepared by vertical deposition and the mechanism of their formation. This is of crucial importance for improving the quality of photonic crystal optical devices. Finally, Raman data on Au–PS composite monolayers prepared by our flow-controlled inclined deposition (FCID) method are compared to those on multilayer films produced by vertical deposition.

\section{EXPERIMENTAL}

Aqueous suspensions of a mixture of 510 nm carboxylate-stabilized polystyrene and 20 or 5 nm gold colloids have been used in all the experiments. Commercial Au nanoparticles (for the 5 nm gold) or gold colloids prepared by reduction of tetrachlorauric acid with trisodium citrate dihydrate according to Turkevich's method\textsuperscript{29} have been used. For a better wetting of the aqueous suspension onto the surface of the glass substrate, the clean substrate was immersed in a solution of (3-aminopropyl) tris [2-(2methoxyethoxy] silane in acetone substrate, the clean substrate was immersed in a solution of the aqueous suspension onto the surface of the glass substrate, the clean substrate was immersed in a solution of the aqueous suspension onto the surface of the glass substrate, the clean substrate was immersed in a solution of the aqueous suspension onto the surface of the glass substrate, the clean substrate was immersed in a solution of the aqueous suspension onto the surface of the glass substrate, the clean substrate was immersed in a solution of the aqueous suspension onto the surface of the glass substrate, the clean substrate was immersed in a solution of the aqueous suspension onto the surface of the glass substrate.

To increase the distance between the aggregates, various flow rates were used. The % relative standard deviation (RSD) in the intensity was calculated as 27.3 (± 0.5) cts/s. The % relative standard deviation (RSD) in the intensity was calculated as 27.3 (± 0.5) cts/s.

\section{RESULTS AND DISCUSSION}

The AFM images of Au–PS composite mono- and multilayer films are given in Figs. 1A and 1B, respectively. The monolayer was deposited by the FCID method at an inclination angle of 45° and a rate of approximately 40 μm/s. We have shown that when using the FCID method, the uniformity as well as the degree of coverage of the substrate depends strongly on the liquid surface dropping velocity. The film appears opalescent. Figure 1A-i represents the autocorrelation analyses of the AFM image presented in Fig. 1A. This is the correlation product of the image data obtained by shifting the image on itself. This autocorrelation image was used here to provide a qualitative description of the ordering of the PS spheres on the treated glass substrate. The autocorrelation image brings out the well-defined neighborhood distance. This image of a hexagonal pattern of dots highlights the inherent hexagonal periodic self-assembly of the PS spheres and indicates that the average size and separation of the surface features is 433 ± 17 nm. Figure 1B shows the top view of a Au–PS composite film on a surface-treated glass substrate. Both, the AFM and scanning electron microscope (SEM) images (Figs. 1 and 5) of the strongly opalescent film have shown that the sample is a polycrystalline multilayer (around 20 layers) with a number of domains with different crystalline arrangements and orientations with respect to the substrate. For example, autocorrelation analysis of the AFM images shows two types of crystalline domains. The insets in Fig. 1B-i and 1B-ii show the autocorrelation analyses of two parts of the AFM image. The pattern seen in the autocorrelation image Fig. 1B-i indicates the hexagonal ordering of PS spheres located in the region indicated by the light colored box.

Figure 2 compares the Raman spectra and the white light optical microscopic images (60 × 70 μm) of the Au–PS composite films prepared by the FCID method (Figs. 2A and
2B, respectively) and the vertical deposition method (Figs. 2C and 2D, respectively). Raman spectra were recorded in the range of 70–4000 cm\(^{-1}\) at the center of the cross indicated in the white light optical microscopic images. Figure 2A shows the Raman spectrum of the monolayer Au–PS film deposited on a glass substrate by the FCID method. The intensity of the spectrum is given in counts/second to avoid the ambiguity in the data acquisition time. The Raman intensity of the ring breathing mode of PS microspheres at 1001 cm\(^{-1}\) is very low (2 counts/s) and the spectrum is dominated by the fluorescence of the glass substrate. The CH\(_2\) and CH\(_3\) symmetrical and asymmetrical vibrations of the PS microspheres are very weak and not discernable. Figure 2C shows the Raman spectrum of the multilayered Au–PS film prepared by the vertical deposition method. It can be seen from Fig. 2C that the Raman spectrum of PS microspheres is very clear and the Raman bands are very well defined and their intensity is higher when compared with the film prepared by the FCID method. The band at 1001 cm\(^{-1}\) corresponding to the ring breathing mode is the most intense peak and has been selected to compare the intensities between the two films.\(^{30}\) The area under the curves for this peak has been calculated by the integration of the spectroscopic data after a baseline correction. When compared to the Au–PS monolayer film produced by the FCID method, the intensity of the 1001 cm\(^{-1}\) peak is 123 times higher in the Au–PS multilayer film deposited by the vertical method. This result indicates that the intensity increases non-linearly with the thickness (the number of layers) of the sample. In addition, the mapping over a large sample area with a 0.2 \(\mu\)m step shows a uniform intensity of the 1001.9 cm\(^{-1}\) Raman peak over the whole area, with a % RSD of 1.8%. In terms of the structure of the colloidal crystal, the uniform Raman intensity reflects the ordered distribution of the PS microspheres over the mapped area as it can be seen in the AFM image (Fig. 1) and in the SEM image of the corresponding inverse opal (as given in Fig. 3), respectively. This is an important result as it points to the possibility of using, under certain circumstances, the Raman mapping as a tool for the evaluation of the quality of the colloidal crystal.

Wide-angle X-ray diffraction patterns of multilayer samples, prepared by vertical deposition with two different gold–polystyrene ratios (Figs. 4a and 4b, respectively) are shown at the top of Fig. 4. Broad peaks at low angles, marked by dashed vertical lines, are typical of bulk atactic polystyrene.\(^{31}\)
In Fig. 4b, the (111) and (200) diffraction lines of the fcc colloidal gold particles can be distinguished. Their line widths indicate particle sizes of about 9 and 6 nm for the <111> and <200> directions, respectively. Only a weak (111) gold peak is present in Fig. 4a. X-ray scattering of a monolayer sample produced by FCID, Fig. 4c, does not differ significantly from the scattering of an empty glass slide.

The line mapping of the intensity of the 1001 cm$^{-1}$ peak in

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the Raman spectra led to another interesting result concerning the fractures present in the samples obtained by the vertical deposition method. Fractures, sometimes called "dissipative structures" or "growth imperfections," are structural patterns of different morphologies that are the result of fractures caused by the volume shrinkage of wet films during the drying process. Due to post-growth fractures, films obtained by vertical deposition are not continuous; they are separated in many individual "grains" by longitudinal and transversal fractures. Figure 5 shows the SEM image of a large (6–7 μm) fracture in a highly ordered PS film. It can be seen that the crystalline order is preserved across the fracture, indicating that the different “grains” are not the result of independent nucleation. It is clear that, from the perspective of device fabrication, the presence of fractures in colloidal crystals is not desirable. Therefore, the detailed study of the mechanism of their formation is of crucial importance for obtaining high-quality photonic crystal optical devices.

In this work, Raman spectroscopy with imaging capability has been used to identify the fissures formed in the vertically deposited films. It is to be noted that the Raman imaging has been used primarily as a qualitative tool for locating the fissures. The lateral spatial resolution is limited by the laser spot size, which is about 1 μm for the objective of 100× with a numerical aperture of 0.9. The depth resolution (vertical spatial resolution) depends on the absorption coefficients of the Au–PS composite film. As in the composite, the PS spheres have a large volume ratio in comparison with the Au nanoparticles; we have assumed that the optical properties are determined by the polystyrene spheres. Inagaki et al.\textsuperscript{37} have reported that the polystyrene has a negligible absorption coefficient (\(k \approx 0\)) value for the incident light of wavelength 632.8 nm. Hence, we can consider that Au–PS composite films are absorption free, except for the absorption of Au nanoparticles. In a confocal setup the vertical spatial resolution is determined by the confocal hole. For an absorption-free film, with the dimension of the laser spot of 1 micrometer, and with a confocal hole of 300 micrometers, the sampling volume is approximately 10 micrometers. In our case, approximately 20 layers of PS are involved in the Au–PS composite film, with a sphere size of 4.3 \(\pm 0.2\) \(\times 10^{-2}\) nm, which results in a thickness of \(\sim 9\) micrometers. Hence, when Raman spectra are recorded using the confocal microprobe arrangement, the laser will sample the entire thickness of the Au–PS composite film.

Moreover, it would be hard to quantify the thickness of the PS layers inside the fissures (structural deformation). This is because the arrangement and the abundance of PS spheres inside the fissure would be determined by the mechanisms involved in the creation of dissipative structures. In order to highlight the dimensions of such structures and the relative abundance of the PS spheres inside the fissures, scanning electron microscope images of the Au–PS composite film are

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**Fig. 4.** XRD pattern of Au–PS composites prepared by the FCID method and the vertical deposition method. (a) 80 μg/mL Au:1 mL aqueous suspension of PS (5% wt/v), and (b) 200 μg/mL Au:1 mL aqueous suspension of PS (5% wt/v).
presented in Fig. 5. Figure 5A shows the multilayers involved in the construction of the composite films. It also shows that the dimensions of the fissures can vary. Figure 5B is the magnified SEM image and it shows that the film has many layers of ordered polystyrene spheres and that on the bottom of the fissure there is a reduction in the amount of polystyrene. The Raman spectra have been recorded in some of those fissures randomly. Because the amount of polystyrene is low inside the fissure, the intensity is reduced proportionally to the abundance of PS inside the fissures. As the thickness of the film is ~9 micrometers, it is safe to assume that the entire volume of the composite within a 1 μm diameter is sampled, and any reduction in the thickness would lead to reduction in the Raman intensity of the PS. Based on this fact, Raman line mapping studies were performed to study the fissures.

Indeed, the capability of the Raman mapping technique to probe the regions inside the fissure provided valuable information on the profile of the fracture. The white light optical microscopic image, the Raman line intensity profile of the ring breathing mode (1001 cm\(^{-1}\)) across a fissure, and the micrometric line scanning in the range 900 to 1800 cm\(^{-1}\) across the fissure (0.2 μm step size) are shown in Figs. 6A, 6B, and 6C, respectively. It is emphasized from Fig. 6C that all the other Raman modes show a consistent intensity profile across the fissure, similar to the profile shown by the Raman mode at 1001 cm\(^{-1}\). The intensity profile as well as the micrometric line scanning indicate the presence of a small amount of PS microspheres on the bottom of the fissure. Similar results have been obtained by mapping a different fissure (see Fig. 7) showing a well-defined step inside of the fissures. All the mapping results, no matter the shape, showed the presence of some PS microspheres inside the fissures. This result may be of some consequence in establishing the mechanism of formation of the fissures in the film. Indeed, the results prove without any ambiguity that the fissures are formed after the ordering of the spheres (after film formation) due to capillary stresses, and that they further fissure on drying and sintering at 60 °C for 24 h. This observation is further evidenced by AFM images. Thus, the Raman and the AFM experimental observation on the hexagonal symmetry of the structure extending over the fissures confirms the envisaged mechanism.

Figure 8 shows a comparison of the Raman spectra of the Au–PS film deposited by the FCID method on glass (Fig. 8A) and on Ag coated glass (Fig. 8B). The white light optical
microscopic image of the film on Ag is shown in Fig. 8C. It can be seen from Fig. 8 that the Raman signal from the Au–PS film on Ag (Fig 8B) shows a larger signal-to-noise ratio, without any background fluorescence. All the Raman bands of PS microspheres are present and their intensity is high, compared to those corresponding to the film on glass (Fig 8A). In order to evaluate the enhancement factor, the intensity of the ring breathing mode at 1001 cm$^{-1}$ was chosen. The intensity ratio of the 1001 cm$^{-1}$ mode from the two spectra was obtained by integration of the spectroscopic data after a baseline correction. This analysis shows that the intensity of the Raman mode at 1001.9 cm$^{-1}$ recorded from the PS microspheres is 95 times greater on Ag than on the glass substrate. The enhancement of the Raman spectrum is accounted for mostly by the presence of an important amount of light reflected by the silver that may enhance the Raman scattering. The thickness of the sputtered silver in this experiment was 100 nm, and, as this is much more than the optimum thickness for SERS to occur, which is 7–10 nm (below its percolation threshold), the sputter-deposited Ag film would probably not have a significant influence on the surface plasmon.$^{38}$ Also, it should be noted that the enhancement is relatively low because of the size of Au nanoparticles. According to Moskovits,$^{39}$ the optimal range for the Au nanoparticles to produce a very high enhancement is between 10 and 100 nm. The dependence of the plasmon frequency on both the excitation wavelength and the Au nanoparticle size has been reported. Baia et al.$^{40}$ have shown that the localized plasmons on gold nanoparticles of 50 nm size (lateral dimension) can strongly absorb the 633 nm radiation. The resonant wavelength was found to increase from 600 to 740 nm when the Au nanoparticle size was increased from 70 to 104 nm (Su et al.$^{41}$) In this work, 5 nm Au nanoparticles have been used, which are too small for the plasmon resonance to occur with laser excitation of 633 nm and to produce a significant enhancement.

The white light optical microscopic image of a region of the Au–PS film produced on Ag coated glass substrate (Fig. 9I) has evidenced the presence of several gold aggregates. Figure 9II-A shows the Raman spectrum of PS microspheres recorded in a location where Au aggregates are present, whereas Fig. 9II-B shows the spectrum of PS microspheres in a location where no aggregates are seen. For comparison purposes, the spectrum of PS microspheres of the Au–PS film on a glass substrate is also shown in Fig. 9II-C. The spectrum of PS microspheres on the glass has been enlarged so as to make it visible, and the intensity (counts/s) is shown in the right-hand y axis. It is evident from Fig. 9II-A that the intensity of the Raman spectrum of PS...
microspheres recorded in the proximity of the Au aggregates is strongly enhanced. In order to evaluate the enhancement factor of the Raman signal due to Au aggregates, the mode located at 1603 cm\(^{-1}\) was chosen. This mode (1603 cm\(^{-1}\)) is emerging because of the C=C vibrations from the PS microspheres. The peak position of the C=C mode at 1603 cm\(^{-1}\) is blue shifted to 1616 cm\(^{-1}\) in the Raman spectrum recorded from the Au aggregate. The intensity of this mode was calculated, and it was found to be 1272 times (three orders of magnitude) higher than that emerging from the film on a glass substrate. A similar analysis was performed to compare the intensities of the C=C band emerging from Au nanoparticles and from the Ag coated surface. In this case, it was found to be 21 times higher than that emerging from the Ag coated surface. Again, the weak enhancement can be accounted for by the thickness of the Ag layer (100 nm), which is beyond the percolation thickness able to generate surface plasmons. This enhancement can be attributed to the surface plasmon modes generated by the Au nanoparticle aggregates. The reflectance spectrum of this Au–PS composite film (not shown here) shows two surface plasmon resonances in the wavelength range below 900 nm. The first band is located in the range between 520 and 530 nm, which is due to isolated spherical

![Graph](image1)

**Fig. 8.** Comparison of Au–PS films deposited on Ag coated glass substrate and on a bare glass substrate by the FCID method: (A) Raman spectrum of the Au–PS film deposited on the glass surface. (B) Raman spectrum of the Au–PS film deposited on a sputtered Ag surface. (C) The white light optical image of the surface of the Au–PS film deposited on a Ag surface.

![Graph](image2)

![Image](image3)

![Image](image4)

**Fig. 9.** (I) White light optical microscopic image of the Au–PS film on the Ag coated glass substrate (deposited by the FCID method), where Au aggregates are seen. (II) Comparison of Raman spectra of PS microspheres from the Au–PS film deposited by the FCID method: (A) on a Ag coated glass substrate at a location with Au aggregates, (B) on a Ag coated glass substrate at a location without Au aggregates, and (C) on a glass surface alone.
particles, and the second band, a broad one at 690–736 nm, is attributed to the closely aggregated Au nanoparticles. As mentioned in the Experimental section, the Raman experiments were performed with a laser excitation of 632.8 nm. Hence, the surface plasmons between 690 nm ($\Delta \nu_{632.8-690} = 1310$ cm$^{-1}$) and 736 nm ($\Delta \nu_{632.8-736} = 2215$ cm$^{-1}$) excited by the incident electromagnetic wave (laser source) create a large local field and, consequently, the Raman signal intensity is enhanced. The enhancement was significantly larger for the bands appearing between 1300 and 2215 cm$^{-1}$. This result demonstrates that the Au nanoparticle aggregates enhance the Raman spectra due to the surface plasmon resonance. The enhancement of only three orders of magnitude—relatively low when compared to the much higher enhancements produced by surface plasmon resonance (six orders of magnitude)—can be accounted for by the size of the Au nanoparticles. For SERS to occur, the metal particles or aggregates must be small with respect to the wavelength of the exciting light but not smaller than the electronic mean free path of the conduction electrons. As we have already mentioned, the optimal range for the Au particles spans approximately 10–100 nm. In our case, as we have used 5 nm Au nanoparticles, the enhancement is limited to three orders of magnitude.

CONCLUSION

Confocal Raman micro-spectroscopy was used to investigate the characteristics of Au–PS composite opal films prepared by the two deposition techniques flow-controlled inclined deposition (monolayer film) and vertical deposition (multilayer film). It has been found that in a sample deposited vertically, the intensity of the 1001 cm$^{-1}$ PS breathing mode is 100 times larger than that in the monolayer. Mapping over a large sample area of the multilayer sample, the intensity of this band was found to be very uniform, in agreement with the highly ordered structure shown by the AFM and SEM images. Probing the regions inside the fractures normally present in multilayer samples, valuable information has been collected on the shape of the fractures and on the presence of PS microspheres inside the fractures. Indeed, the data prove that, due to the stresses developed in the film, the fractures are formed after the film formation. Thus, micro-Raman mapping has been successfully utilized to study the quality (degree of ordering) of the colloidal crystal, as well as to study the fractures and their characteristics in multilayered colloidal crystal films.

Hence, our results have proved that micro-Raman spectroscopy may become a valuable tool for the study of photonic materials. A strong enhancement of the intensity of the 1001 cm$^{-1}$ band in monolayer films deposited on a sputtered silver surface has been evidenced. By scanning a larger area of the sample, gold aggregates of different shapes have been identified. The Raman spectrum of PS microspheres on the aggregates appears enhanced by three orders of magnitude compared to that of the PS spheres on the “normal” silver surface. XRD data have shown the presence of atactic polystyrene and of fcc Au nanoparticles having a size around 8 nm.

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