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Nature Inspired Plasmonic Structures: Influence of Structural Characteristics on Sensing Capability

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Featured Application: The Plasmonic structures presented can be integrated in optical sensors applicable to complex biological mixtures.

Abstract: Surface enhanced Raman scattering (SERS) is a powerful analytical technique that allows the enhancement of a Raman signal in a molecule or molecular assemblies placed in the proximity of nanostructured metallic surfaces, due to plasmonic effects. However, laboratory methods to obtain of these prototypes are time-consuming, expensive and they do not always lead to the desired result. In this work, we analyse structures existing in nature that show, on a nanoscale, characteristic conformations of photonic crystals. We demonstrate that these structures, if covered with gold, change into plasmonic nanostructures and are able to sustain the SERS effect. We study three different structures with this property: opal, a hydrated amorphous form of silica (SiO₂·nH₂O); diatoms, a kind of unicellular alga; and peacock tail feather. Rhodamine 6G (down to 10^{-12} M) is used to evaluate their capability to increase the Raman signal. These results allow us to define an alternative way to obtain a high sensitivity in Raman spectroscopy, currently achieved by a long and expensive technique, and to fabricate inexpensive nanoplasmonic structures which could be integrated into optical sensors.

Keywords: optical sensors; plasmonics; nanostructures

1. Introduction

Raman spectroscopy is a powerful vibrational spectroscopy technique that has many advantages. It is an analytical technique with high specificity for the identification of various chemical compounds [1–3]. In addition, it is a non-invasive approach that allows measurements to be performed without any sample preparation, and the measurement time is generally very short. However, the Raman signal is very low and difficult to detect. Statistically, for every 1–10 million photons bombarding a sample, only one will result in Raman scattering [4,5]. For this reason, Raman spectroscopy is often coupled to substrates integrating metal plasmonic nanostructures that reproduce an SERS (surface enhanced Raman scattering) effect [6–8]. The molecules, which need to be analysed,



are deposited on these substrates and are excited by an electromagnetic (EM) field, which is enhanced by the proximal metal nanostructures. The amplified EM field interacts with molecules and produces Raman scattering which is again amplified by the metal nanostructures [9–11]. In greater detail, the incident EM waves excite plasmon resonances within the metal nanostructures. Due to resonance effects, the local electric field is enhanced in the proximity of metal nanoparticles. The molecules at the metal surface then experience an enhanced local EM wave, and produce higher Raman signals than those molecules far from the metal surface. Moreover, since Raman signals are a type of EM wave, the same route through plasmon resonances will further enhance the outgoing Raman field. In the end, plasmon resonances are responsible for the double amplification Raman signals of molecules close to metal nanostructures, thus producing a surface-enhanced Raman effect. A detailed review of plasmon-enhanced spectroscopies can be found in [12]. The Raman signal enhancement strongly depends on the size and shape of the metal particles [13–15], and different methods to fabricate them exist in the literature [16–18]. The combination of a top down method, that is, electron beam lithography, with a bottom up technique, that is, chemical electroless deposition, allows a SERS substrate of a self-similar chain of silver nanospheres to be obtained [19]. Plasmonic nanoholes can be made with a template-stripping technique that involves the fabrication of a Si template obtained with electron beam lithography [20]. The Ag-decorated nanotip array, obtained with Electron Beam Induced Deposition and Silver Electroless Deposition, is another efficient 3D plasmonic device, that can be used to obtain a SERS effect [21]. The prototypes described above, although very efficient, are difficult, expensive and time-consuming to fabricate. Other techniques allow the fabrication of nanoplasmonic structures using faster and inexpensive processes. In this regard, metallic colloids [22–24], metallic films [25,26], sensors fabricated by nanosphere lithography [27], and plasmonic systems exploiting nanoparticle self-assembly properties [28,29] have been developed. However, some of the processes to achieve these kinds of low-cost SERS substrates lack reliability in regard to obtaining large sensing surfaces [30,31]. These disadvantages in contrast to the benefits of Raman spectroscopy, which allows information to be obtained easily and without any particular sample preparation [32,33]. Consequently, research involving alternative ways to maintain the SERS effect [34], is of crucial importance. Some structures existing in nature show, on the nanoscale, a conformation called photonic crystal. Photonic crystal, a periodic structure in an optical medium, creates unusual optical dispersion properties, which cause the iridescent colours in some butterfly wings and beetle armours and other structures present in nature [35,36]. These structures, if metallized, can be assimilated to the SERS devices and used as optical sensors [37-39]. Here, we focus on the peacock feather, opal and diatoms, because they are easy to find in nature. We cover their surfaces with gold to change the photonic nanostructure in a plasmonic nanostructure, and we characterize them by detecting Rhodamine, using Raman spectroscopy. Each element shows a different behaviour due to structural characteristics (which we discuss in the following sections). The best response is obtained with opal, allowing the analysis of molecules at very low concentrations and thus confirming their potential application for biosensing devices.

2. Materials and Methods

Metallic nanoparticle aggregates are able to maintain high enhancement of the SERS signal (in the order of 10¹¹) [40]. Experimental evidence shows that by placing two spherical nanoparticles at a distance of less than 5 nm, there is an amplification of the local electric field of several orders of magnitude greater than when the nanoparticles are isolated, at the midpoint between the two. This enhancement of the electric field results from the constructive interference of the surface plasmonic resonances of the two particles. The antiparticle regions with field amplification are called hot spots [41,42]. By metallizing the surface (e.g., with gold), it is possible to assimilate natural nanophotonic structures to metal nanoparticle aggregates, producing plasmonic nanostructures, which can cause high amplification of the SERS signal [43,44].

2.1. Natural Nanophotonic Structures

We used the following natural components:

2.1.1. Peacock Feather

The peacock livery is a typical example of sexual dimorphism. Indeed, the male peacock tail consists of very lengthy feathers that extend to form a 'palette' with the typical eyespot and iridescent colours. This feature is supposed to attract mates and to disorient predators. To investigate the structural properties of the peacock feather, we collected a feather from a male peafowl (*Pavo cristatus*) and focused on its eyespot. At the nanoscale, it is characterized by the presence of cellular organelles, called melanosomes, which are arranged to form a typical two-dimensional crystalline lattice. This arrangement causes the characteristic iridescent colours. The size of the melanosome and another is about 105 nm long, and the distance between the centre of a melanosome and another is about 175 nm. There is a correlation between the diameter of a melanosome and the brightness of cells—brightness increases as the melanosome diameter increases [45].

2.1.2. Opal

Opal is a mineral made of silica, formed by the slow geological deposition of a colloidal gel at a low temperature. Various types of opal exist in nature; the kind of opal we analysed is called *Ethiopian Welo Opal*. It is characterized by its transparency and its vibrant reflections which show all the colours of the rainbow, in particular, yellow, orange, red and green. On the nano-cale, it can be considered a typical example of colloidal crystal, due to its orderly aggregate of particles similar to standard crystal, with subunits of atoms or molecules. The arrangement of amorphous silicon dioxide spheres and their sizes give the structure its optical properties. In fact, the internal colours are determined by the interference and diffraction of light passing through the microstructure of the opal. The spheres are about 10 nm in diameter, while the space between one sphere and another is of a smaller order of magnitude.

2.1.3. Diatoms

Diatoms are unicellular and eukaryotic algae, which can live in isolation or form colonies either in freshwater or marine environments. Diatoms are hundreds of μ m in size [46], with a distinctive shell wall consisting of two hydrated silica valves, interconnected in a structure called a frustule. Frustules present patterns of regular arrays of holes, the areolae, which are characterized by sub-micrometric dimensions. There are about 10⁵ species of diatoms, whose frustules differ in shape, morphology and size. The dimensions of the frustule pores, typically hundreds of nanometres, provide diatom frustules with peculiar optical properties. In the present work, we considered C. wailesii diatoms, in which organic matter was removed by means of strong acid solutions [47]. The diameter of the valves ranged from 100 to 200 μ m, while the average thickness of the wall was about 1 μ m. Every single valve is formed by two co-joined plates. The external plate comprises a complex hexagonal arrangement of hollow pores with a diameter (\cong 200 nm) below the visible wavelength. On the other side, the internal plate of the valve is characterized by hexagonally-spaced pores with diameters in the range of 50 nm and by a lattice constant of about 50 nm.

2.2. Theoretical Simulations

Theoretical simulations of different natural SERS substrates (peafowl, diatoms and opal) were performed using the finite difference time domain method [48]. The designs of these structures were constructed to mimic the actual structures of the devices. The electric field distribution over the nanostructures was calculated using Lumerical, a commercial software package. The mesh size was fixed to 1 nm in the *X*, *Y* and *Z* directions for all calculations. Regarding peafowl, a gold bar (side length = 370 nm, material dispersion from Johnson and Christy [49]) with many overriding functions

of dielectric materials (refractive index = 1, side length = 50 nm) was designed in such a manner that the refractive index of the metal area where dielectric bars were inserted became equal to the dielectric one. The gap between the adjacent dielectric materials wais 35 nm. Periodic boundary conditions in the X and Y directions were chosen to calculate the distribution of the electric field (EF). A plane wave with polarization along the horizontal axis at 633 nm was employed to illuminate the peafowl device from the top. Regarding the opal's structure, many gold spheres (radius = 40 nm, material dispersion from Johnson and Christy [49]) were immersed in the dielectric material to resemble the design of an opal. The gap between two gold nanosphere was fixed to 5 nm. Periodic boundary conditions in the X and Y directions were adopted to calculate the distribution of the EF. An incident wavelength of 633 nm was chosen to illuminate the device, and polarization was fixed to an angle of 45°. Regarding the diatoms, we first constructed four circular toroid structures with inner radii of 905 nm and ring widths of 100 nm. The height of the gold ring structures was 92 nm. Within this toroid, many small, circular toroid structures of 105 nm radius (height of gold ring = 10 nm, ring width = 10 nm) were placed randomly. These structures were placed over a dielectric surface (refractive index = 1) deposited over a gold bar. The calculations were made by illuminating the device with an incident wavelength of 633 nm. The incident field considered was 1 V/m.

2.3. SEM Characterization

Several scanning electron microscope (SEM) images of the samples were captured to investigate the sub-micrometre features of the feathers, opals and diatoms, utilizing a Dual Beam scanning electron microscope-focused ion beam (SEM-FIB) Nova 600 NanoLab system (FEI Company, Eindhoven, Netherlands). During the acquisitions, beam energies of 5 and 15 keV, and 45 corresponding electron currents of 0.98 pA and 0.14 nA, were used. Optical images were taken on a Nikon Ti-E, on which a colour camera Nikon DS-Fi2 was mounted (Nikon Instruments SpA, Firenze, Italy).

2.4. Raman Spectroscopy Characterization of the Natural Plasmonic Nanostructures

To determine the effect of SERS on the natural structures, we metallized their surfaces. An apparatus for deposition by sputtering was used to deposit a thin layer of gold (Au) onto the structures. The opal, 10×14.5 mm in size, a sample of a few centimetres cut out from the feather eyespot and diatoms were processed for 30 s, using a current of 50 mA at a voltage of 230 Volts (50 Hz) and a pressure of 100 mbar, to deposit around 10 nm of gold on the samples' surfaces. An Au thickness of 10 nm was chosen to avoid excessive filling of the nanohole structures (this is especially visible in Figure 1C,D). Obviously, the Au thickness was kept constant for all samples to allow a comparison between them. An inVia confocal Raman microscope was used for the optical characterization of the natural plasmonic nanostructures. We set used a wavelength of 633 nm for the laser, a $50 \times$ objective and an integration time of 10 s, while the power was set to 2.5 mW for each sample. Spectra were recorded by raster scanning the samples' surfaces, collecting at least 100 spectra, so that for each sample, the point-to-point variation could be estimated. The SERS capabilities of the natural structures were probed using Rhodamine-6G, a fluorescent organic molecule purchased from Sigma Aldrich. A drop of 200 μ L of Rhodamine-6G at a concentration of 10^{-5} M was deposited on the opal and feather samples. Meanwhile, 5 mg of diatoms were dissolved in 100 μ L of Rhodamine-6G at a concentration of 10^{-5} M and placed on a calcium fluoride slide. Each sample was analysed by recording the Raman signal after the samples had been completely dried in air. Because the opal showed the highest amplification effect (as will be seen in the next sections), 200 μL of Rhodamine-6G at concentrations of 10^{-7} M and 10^{-12} M were deposited on these samples and measurements were recorded. To demonstrate the amplification effect of the mentioned natural structures on Raman spectroscopy, we compared the response of the signal coming from Rhodamine-6G deposited on a flat silicon substrate, covered with gold.

The SERS spectra shown in this work represent the average spectrum of ten spectra recorded at different positions on the samples. Before the comparison between the SERS spectra, a background

subtraction was carried out using the spectra recorded on the same samples without R6G (under the same experimental conditions).



Figure 1. SEM image of the peacock feather (**A**); scanning electron microscope (SEM) images of an opal fragment (**B**); the outer (**C**) and inner (**D**) plates of a single valve of C. wailesii.

3. Results and Discussion

3.1. Optical and SEM Images of the Characterized Samples

Regarding the diatoms, on a micrometric scale it is possible to highlight the sub-micrometric structures randomly placed in the space from regular and repeated perforations in the thickness of the frustules. The diameters of the pores vary, and their dimensions range from 50 nm to 0.5 μ m (Figure 1C,D). The opal, on the scanning electron microscope, as shown in Figure 1B, appeared as a homogenous agglomerate of nanospheres with a diameter of tens of nanometres. Taking a SEM image of the peacock feather was very difficult (Figure 1A). In fact, on the micrometre scale, it showed a complex three-dimensional structure. This did not allow us to deposit a thin homogenous layer of gold on it; therefore, SEM imaging was not always clear. However, the SEM image in Figure 1 clearly shows the sub-micrometric structures of the feather.

3.2. Simulated Enhanced Fields

Three different calculations were made for different structures to resemble their associated SERS structures using the FDTD (Finite-Domain Time-Domain) method. The design of the peacock feather

is shown in Figure 2A, representing the perspective view of the structure. The calculation shows the confinement of the electric field at the corners of the peafowl structure. The maximum electric field was reached at close to 7 V/m, as shown in Figure 2B. In the case of the opal structure, the localization of electric field in the gap can be observed clearly (Figure 2D). The maximum electric field was 18 V/m. Regarding the diatom structure, non-homogeneous confinement was observed at the edge of the toroid structure and the maximum amplitude was found to be 7 V/m (Figure 2F). The above findings indicate the superior performance of the opal structure as a SERS substrate exited at a wavelength of 633 nm.



Figure 2. From top left: perspective view of the peacock feather (A); opal (B) and diatom (C) nanostructures. From top right: simulated enhanced electric field of the peacock feather (D); opal (E) and diatom (F) nanostructures.

3.3. Raman Analysis

The preparation of the natural nano structures to be applied in the Raman analysis did not require any particular technique as explained in the Section 2.4. These were used as substrates to perform Raman measurements on samples of Rhodamine 6G. Under the action of the laser excitation, Rhodamine 6G showed peaks at 614, 774, 1182, 1362, 1507 and 1648 cm⁻¹. The 614 cm⁻¹ peak corresponds to the C–C–C ring in-plane bending mode. The C–H out-of-plane bending mode for R6G was observed at 774 cm⁻¹ while the C–O–C stretching frequency appeared at 1182 cm⁻¹. Peaks centred at 1362, 1507, 1571 and 1648 cm⁻¹ were attributed to the aromatic C–C stretch of the R6G molecule [50]. As is evident from the spectra images (Figure 3), typical characteristic peaks from Rhodamine-6G are observed our measurements.

The spectra obtained from each natural structure were processed with the aim of highlighting the qualitative aspects of the results and comparing the measurements. Each sample showed a different behaviour, mainly due to structural reasons. The best response came from the opal (marked in red in the image above). This was due to the small size of its nanospheres, whose diameters are a few dozens of nm, as well as its regular and flat conformation, which allowed, in addition to complete gold coverage, direct interaction between the source laser and the molecule. The spectrum obtained using the peacock feather as support for the Raman analysis, showed visible, but low intensity, peaks (marked in green in the image above). In fact, the irregular structure of the peacock feather does not allow complete gold coverage, and consequently part of the sample was not able to produce the SERS effect. Moreover, since the surface of the feather, at the microscale, was not flat, the deposited solution containing Rhodamine did not stand in position, falling out of the sample in a few minutes. Another limitation was the usable power intensity as high powers can damage the feather. The detected peaks concerning the diatoms (marked in blue in the image above) were indistinguishable from baseline and did not allow the characterization of the molecule. This happened because, while in the peacock feather and the opal, the nanostructures were in direct contact with the analyte and largely exposed to the laser beam, the diatoms 3D tubular structures were casually arranged in the space. In addition, the 3D structure caused the absorption of a portion of the molecule; thus, most of the signal came from diatoms and not from Rhodamine, and that is why the silicon pattern (marked in black in the image above), even without nanostructures, showed peaks higher than those of the diatoms. Furthermore, the irregularity of the diatoms does not allow total gold coverage; the size of the diatom nanostructure is bigger than the nanostructure of the other samples, causing a decrease in the enhancement obtainable. Improvements in the SERS signals were computed as intensity ratios between the natural nanostructures and flat Si–Au samples for the peak at 1358 cm⁻¹. We found that the SERS improvement for opal was approximately 13.88, peafowl had a much lower value of 1.88, while for diatom, the value of 0.63 indicated that the Si–Au substrate behaved much better as SERS substrate. Considering that SERS intensities scale like the fourth power of the electric field, the just-mentioned ratios correspond to the following improvements in the enhancing factors: 1.93 for opal, 1.17 for peafowl, and 0.89 for diatom. It is worth remarking that these values are not the absolute enhancing factors of the electric field, but only the relative values with reference to Si-Au SERS enhancing factor. As already reported the literature (see as an example [51]), the overall SERS intensity in plasmonic nanostructures is strongly dominated by only few positions where the highest electric field enhancement is achieved (hot spots). By comparing the signal intensities at 1361 cm⁻¹, we observed a SERS ratio of approximately 3 between the opal and the peacock feather samples. On the other hand, by comparing the maximum enhancement factors of the electric fields obtained with the FDTD simulations, the same SERS ratio was approximately 36 between the opal and peacock samples (taking into account that SERS signal scale up like the fourth power of the electric field). However, it should be considered that the spatial pitch (1D) of the opal structures was double that of the pitch of the peacock feather, and consequently the opal sample had a number of hot spots per surface unit that were four times smaller than those of the peacock feather. As a conclusion, the FDTD simulations provided an SERS ratio of approximately 9 between the opal and peacock samples. The further disagreement between the FDTD and experimental values was likely due to the structural variations intrinsically expected in natural nanostructures. Finally, even though the maximum enhancement factor of the electric field in the diatom hot spots was similar to that of peacock feather, the number of hot spots per unit surface was much smaller in diatoms, thus explaining the low SERS intensity observed in the experiments. In conclusion, the positive performance shown by the opal allowed a greater decrease in the Rhodamine-6G concentration. Using this sample, Rhodamine-6G was detected at a value of 10^{-12} M (Figure 4).



Figure 3. Raman spectra of Rhodamine-6G dispersed in a solution at a concentration of 10^{-5} M measured on opal fragments (opal), peacock feathers (peafowl), diatoms (diatom) and flat silicon surface (Si–Au). It is possible to note the characteristic peaks of the Rhodamine at 1182, 1361, 1508 and 1647 cm⁻¹. The gray shadow of each curve displays the standard deviations of the SERS spectra.



Figure 4. Raman spectra of Rhodamine-6G measured at a different concentration on opal fragments. The grayshadow of each curve displays the standard deviations of the SERS spectra. In the inset, the 1361 cm⁻¹ peak intensity is reported as a function of the R6G concentration, in a log–log plot.

4. Conclusions

Nowadays, the fabrication of prototypes able to sustain the SERS effect requires high costs and time-consuming procedures, which do not always allow the expected result to be achieved. In this work, we exploited samples existing in nature to obtain SERS devices capable of increasing the Raman signal. The integration of natural structures into Raman analysis is linked to a lower cost, speed and greater ease of use. Each analysed sample showed a different response due to structural reasons. The diatoms were not suitable for the experiment, the peacock feather could be suitable with some modifications and improvements, and the opal was an efficient medium that was able to determine a positive response even at very low concentrations. This result could become a relevant device for the Raman spectroscopy community.

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