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Spotting aged dyes on paper with SERS

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Surface enhanced Raman spectroscopy (SERS) is a highly sensitive technique for non- or minimally invasive identification of molecules at very low concentrations. In this work, SERS is exploited using naked laser-ablated gold nanoparticles (AuNPs) for the detection of dyes on artificially aged paper inked with a ballpoint pen. Although several studies on inks with SERS are present in literature, most of them concern investigations on freshly prepared products, and less information is present on the detection of aged dyes and inks using SERS. Ballpoint inks are commonly used in daily activities, but have been also employed by several contemporary artists. These inks are very sensitive to light, and they discolor rapidly, making demanding their detection. In the present work, SERS spectra of a ballpoint pen ink on two types of paper were analyzed after light-induced ageing, and the importance of the dyes-AuNP interaction is discussed. The results show that the interpretation of SERS spectra of aged samples, such as those of interest in the Cultural Heritage field, is a tricky and delicate operation and that the diffusion of dyes to the hot spot regions of the plasmonic nanoparticles plays a pivotal role in the detection of degraded ink components. Therefore, a proper evaluation of the factors affecting the molecule-plasmonic nanoparticle interactions and of the history of the artwork to be analyzed is fundamental to avoid the misinterpretation of the spectra and, consequently, of the original composition of the analyzed artwork.

Introduction

Surface enhanced Raman scattering (SERS) is a powerful, versatile and highly sensitive vibrational spectroscopic technique. It allows detection of molecules at very low concentrations through a huge intensification of Raman signals. Since the discovery of the SERS effect in the mid-1970s[1,2] the interest in the technique has exponentially grown and SERS has been applied to a very wide variety of research fields (materials science, biochemistry, electrochemistry, catalysis, biosensing, imaging etc.).[3-5] SERS exploits the presence of molecules at nanometer distance from plasmonic nanostructures. This determines enhancements of the Raman signals also larger than 10^9, when the localized plasmon resonance is excited.

Among innovative applications, SERS recently emerged also in the Cultural Heritage (C.H.) field.[6] Raman scattering is among the most applied techniques in the analysis of artifacts for the wide range of advantages it offers.[7] However, Raman signals display very low intensities and fluorescence sometimes prevents the recording of Raman signals for several materials.

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SERS allows overcoming these limits, with huge amplification of the Raman signals and quenching of fluorescent emissions. It is, therefore, an ultrasensitive tool for the characterization of molecules in composite artifacts.[8-14] In this regard, we have recently addressed the detection of dyes in new and historical felt-tip pens.[15-17]

Here we exploit SERS with laser-ablated gold nanoparticles (AuNPs) for the identification of dyes included in a ballpoint pen ink which was deposited on paper and then artificially aged. SERS plays an important role in the identification of inks, especially in forensic science.[18-23] However, to the best of our knowledge, detailed studies of aged inks on papers have not yet been reported. Gold nanoparticles were chosen as a plasmonic substrate for their chemical stability and inertness, compared to other metallic nanoparticles, making them very promising for applications in Cultural Heritage, where metallic species can promote chemical degradation of the supports.[19] It was also shown that gold nanoinks, when excited in the red or infrared spectral regions, are efficient as the most commonly used AgNPs.[23]
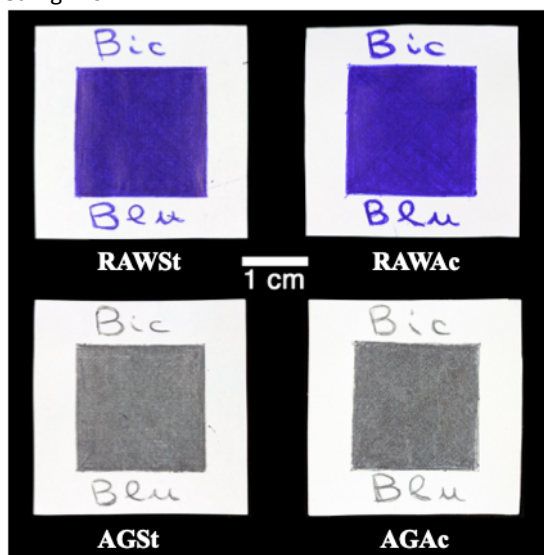
Figure 1. Samples prepared on standard (St) and acidic (Ac) paper using Bic Crystal Blue ballpoint pen. On the top row, untreated samples, namely Raw standard paper (RAWSt) and Raw acidic paper (RAWAc). On the bottom row, artificially aged samples, namely Aged standard paper (AGSt) and Aged acidic paper (AGAc).

Recently, the role of hot spots for the SERS enhancement with aggregated spherical nanoparticles, where hot spots are the contact regions among particles, was highlighted through detailed model calculations. It was shown that these SERS substrates are very efficient and that most of the SERS enhancement derives from a tiny fraction of molecules (less than 0.05 %) which are present in the hot spot regions.[24] These results demonstrate that the role of hot spots is a fundamental aspect of plasmonic substrates and the availability of these regions, to the molecules to be revealed, was not always evidenced in Cultural Heritage literature.

In this work, the importance of the interaction of dyes with aggregated gold nanoparticles is discussed with specific reference to the role of the hot spots regions. The effect on SERS of paper composition, pH and solvent polarity of the colloidal solutions is evaluated to show the factors affecting the enhancement of signals, which are particularly relevant for aged samples, such as those of interest in the Cultural Heritage field.

Experimental

Materials

Commercial standard (St) paper (Navigator Universal), acidic (Ac) paper (see next section for more information about the composition) and a Bic Crystal Blue ballpoint pen were used for samples preparation. Crystal Violet and Solvent Blue 38 were purchased from Sigma-Aldrich and used as standards of the dyes present in the Bic Crystal Blue ballpoint pen ink.[22]

A 1 M HCl solution was prepared from concentrated HCl (37%, Sigma-Aldrich, ACS reagent) and bi-distilled water. The water:acetone mixture for SERS analysis was prepared using acetone HPLC Plus (≥99.9%, Sigma-Aldrich, reagent grade) and bi-distilled water.

Samples preparation

Commercial acid-free standard (St) paper (grammage 80 g/cm^2) and the acidic (Ac) paper (paper grammage 90 g/cm^2, produced during the EU Papertreat project)[25] are the two types of paper used for preparing the samples. The exact composition of St paper is not known, except for the presence of calcium carbonate as a filler. Ac paper is composed of 70% hardwood bleached pulp, 30% softwood bleached pulp and 20% pulp-filling agent kaolin OT80. Acidity is due to the presence of an acidic resinous sizing (Sacocell 309 aluminum sulfate). Two squared pieces (approx. 10 cm^2) were cut out from the St paper and two from the Ac paper. 4 cm^2 of each sample were inked with the Bic Crystal Blue ballpoint pen by drawing a grid of thick lines to completely cover the paper. One St sample and one Ac sample were not further treated and were labeled as "Raw standard paper" (RAWSt) and "Raw acidic paper" (RAWAc). The other two St and Ac samples were artificially aged in a home-made ageing chamber equipped with three Neon Light Colour 765 BASIC Daylight Beghelli lamps. The emission spectrum of the lamps is provided in the Electronic Supplementary Information (Figure S1). The average illuminance was 11000 lx, RH was 40% and temperature was 36°C. The ageing lasted 70 days. Aged samples were labeled as "Aged standard paper" (AGSt) and "Aged acidic paper" (AGAc). In Figure 1 the two reference samples (RAWSt and RAWAc) and the two artificially aged systems (AGSt and AGAc) are shown. The comparison shows the ink fading after ageing in AGSt and AGAc.

Raman Spectroscopy

A *Renishaw inVia* μ-Raman spectrometer equipped with a *Leica DM-LM* microscope was used to register all the Raman spectra. Measurements were performed with the exciting line at λ = 632.8 nm of a He-Ne laser. 0.15 mW were used on a

spot of 10 μm of diameter with a 20x objective and exposure time of 10 s. The Raman spectra were recorded over the range 150-2000 cm^{-1} and the baseline was corrected with the instrument software. Although the paper is not spatially homogeneous, due to the discontinuity of the fiber network, no spatial averaging of Raman signal was used, because the Raman spot size is larger than the expected paper inhomogeneity. Direct comparisons of data were possible since all spectra were recorded with the same instrumental parameters and in the same conditions, thus no further data-processing was required.
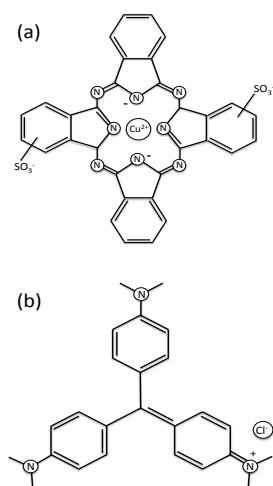
AuNP synthesis

Gold nanoparticles, prepared via LASiS technique (Laser Ablation Synthesis in Solution), were used as SERS-active substrate.[26] The nanoparticle synthesis was conducted with 9 ns pulses at 1064 nm of a Nd:YAG laser focused on a solid gold bulk target immersed in a 10 μM NaCl water solution. The synthesized nanoparticles have an average diameter of about 25 ± 5 nm and a naked surface,[27] which is very useful for SERS measurements since enhancements decrease with the

(a)

(b)

distance from the surface. The AuNP colloidal dispersion is stable without using stabilizing molecules, due to the native charges of the nanoparticles. The colloidal solutions are characterized by an absorption maximum at 520 nm and have typical concentrations of about 10 nM.[27] Nanoparticles show a ζ-potential of -30 mV, which gives stability to the colloidal solutions.[28]

SERS analysis

SERS measurements were carried out by depositing a microdrop of 2 μL of AuNP colloid on the sample surface. Once the solvent dried up, SERS spectra were recorded using the same instrumental procedure used for the Raman measurements. To observe the effect of pH on SERS measurements, a microdrop of 2 μL of 1 M HCl solution was deposited on the sample surface and once dried up, a

microdrop of 2 μL of AuNP colloidal solution was deposited on the same spot. After the second microdrop dried up the SERS spectrum was collected using the standard conditions. To observe the effect of the polarity of the solvent in which the AuNPs were dispersed, some measurements were carried out with a colloidal dispersion of AuNPs in a water:acetone mixture (90:10 vol%). Measurements were carried out following the procedure reported above.

Paper samples characterization upon ageing

Reflectance spectra were acquired in the 400–700 nm range using a Cary 100 Scan UV-VIS spectrophotometer equipped with an integrating sphere with a circular sampling spot of 1.5 cm. Colorimetric coordinates (L*, a* and b*) were extracted from reflectance spectra using standard illuminant D65 and a standard observer at 10° (CIE 1964).[29] More detailed information on the colorimetric coordinates can be found in the Electronic Supplementary information.
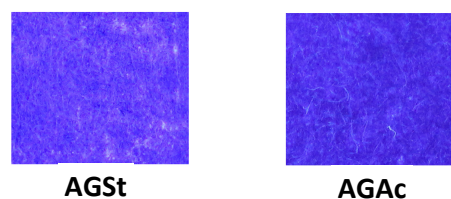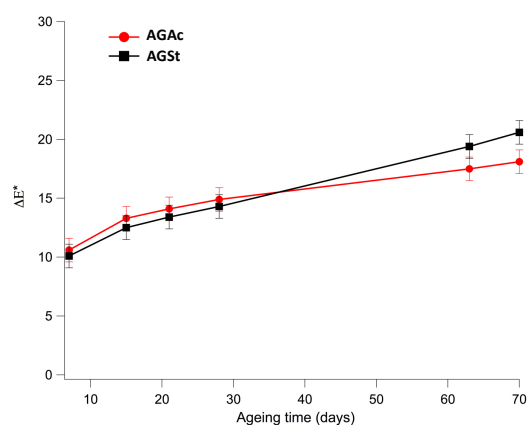

Figure 3. Top: ΔE^* as a function of ageing time for AGAc and AGSt. Bottom: UV-induced fluorescence pictures (area 0.2 cm^2 approx.) of the same samples at the end of ageing time. The blue hue of the samples is due to the use of an UV light to illuminate the samples. The real color of the ink in the aged samples is gray, as shown in Figure 1.

Results and discussion

Ageing strongly affects the visual aspect and the color of many artworks and SERS, due to its sensitiveness, is expected to be an appropriate technique to enhance the signals of degraded dyes and pigments. Since light-induced fading of organic dyes is one of the most important causes of dye degradation, here a commercial ballpoint pen ink was deposited on two types of paper and then artificially irradiated under neon light (see experimental section). As it can be clearly seen in Figure 1, the chromaticity of samples is significantly altered by the artificial ageing. The ΔE* parameter, reported in Figure 3, allows one to

(SERRS)). However, the most intense bands are related to the vibrational modes of the two dyes present in the BIC ink, namely Crystal Violet (CV) and Solvent Blue 38 (B38) (chemical structures in Figure 2). Figure S3 and Table S1 (Electronic Supplementary Information) allow assigning the bands at 1617, 1377, 1178 cm^{-1} to CV (marked by arrows in figure 4) and those at 1540, 1449, 1338 cm^{-1} to B38 (marked by asterisks). The CV bands at 1617 and 1377 cm^{-1} are mainly related to ring modes, while the band at 1178 is mainly due to (C-C$_{center}$-C) stretching. The B38 bands are dominated by C-N stretching
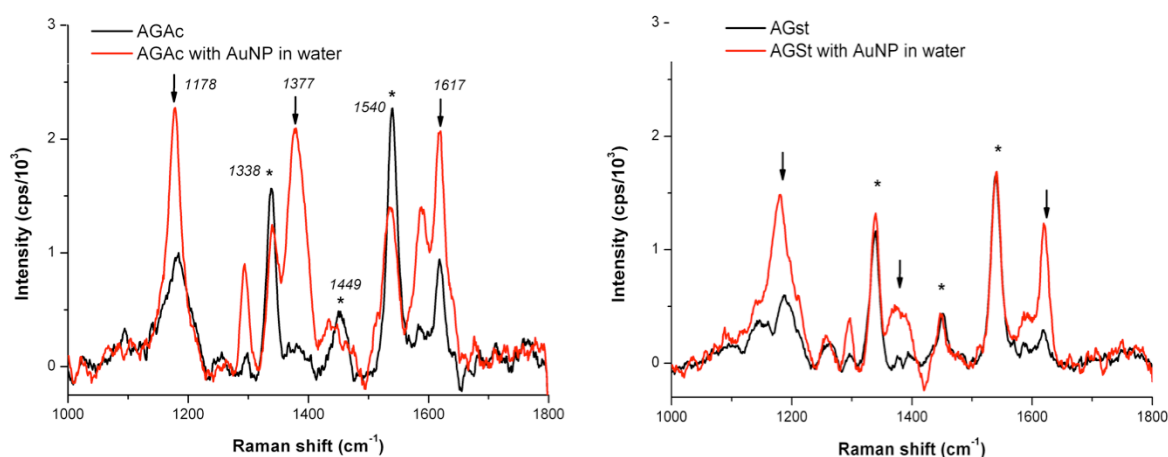
Figure 4. Comparison between the Raman (black lines) and SERS (red lines) spectra of the inked area in the aged samples AGAc (a) and AGSt (b). The arrows mark the position of the main CV bands, while the asterisks mark the position of the main B38 bands.

evaluate in a standard quantitative way the overall color change in samples AGAc (Aged acidic paper) and AGSt (Aged standard paper) at different ageing time (see Experimental Section). It is worth noting that a ΔE* above 1 is the smallest color difference an expert human eye can see through close observation, while ΔE* of 15-20, such as those measured on inked samples at the end of the ageing, are typical of a significant color change, perceptible at a glance. During the first 30 days of ageing, the color change in the two samples was very similar. A small difference, slightly above the experimental error and small if compared to the overall change in color, was observed after 70 days. This might be related to the appearance of brighter spots on sample AGSt, which can be seen in the UV-induced fluorescence pictures (Figure 3). These spots are probably due to the paper, which is highly fluorescent, and become visible due to a pronounced ink fading in AGSt.

SERS spectra (red lines) of the aged inked samples (AGAc and AGSt) and the comparison with the corresponding Raman spectra (black lines) are reported in Figure 4.

The SERS spectra were obtained by depositing 2 μL of the colloidal solution of the AuNP on a small area of the papers (see experimental section). One can see that the relative intensities of the bands are not the same in the Raman and SERS spectrum and the SERS spectra do not show a strong enhancement of the bands, although the dyes are in resonance with the laser excitation (see Figure S2) and further enhancement should be observed (usually this situation is named surface enhanced resonance Raman scattering

modes. [30,31] The comparison between Raman spectra of Figure 4 and those recorded before the ageing (see Figure S3) clearly shows a larger intensity reduction of the CV bands with respect to those of B38, which can be ascribed to the larger degradation of CV with respect to B38. The CV vibrational modes affected by photodegradation involve mainly aromatic rings, like the stretchings (C-C)$_{ring}$ and phenil-N, occurring respectively at 1617 and 1377 cm^{-1}.[30,31] The analysis indicates, therefore, a break of the aromatic system of the chromophore. This is not unexpected, since it is well known that triarylmethane dyes like crystal violet are characterized by low photostability,[32] particularly when applied on paper.[33]

The small SERS enhancement observed in Figure 4 is particularly evident comparing the SERS spectra of this figure with those obtained for the samples before ageing (RAW samples, see Figure S4 and Intensity scale) where, in particular for the CV bands, enhancements of about seven times can be observed. In Figure S4 different enhancement of different peaks can be observed, mainly due to the orientation of the dye molecule within the hot spots.[34,35]

SERS enhancement, as recalled before, derives from the presence of the molecules within the hot spot regions, that, for aggregated spherical particles, are the small regions between nanoparticles. Therefore, one can deduce that ageing makes more difficult the extraction of the dyes from the paper and their migration toward the hot spots. This can be understood because the phototransformation of the dyes is more pronounced on the surface, but also because changes of the structure of the paper surface could make less probable

the solubilization and migration of the dyes toward the hot spots of the aggregated nanoparticles.
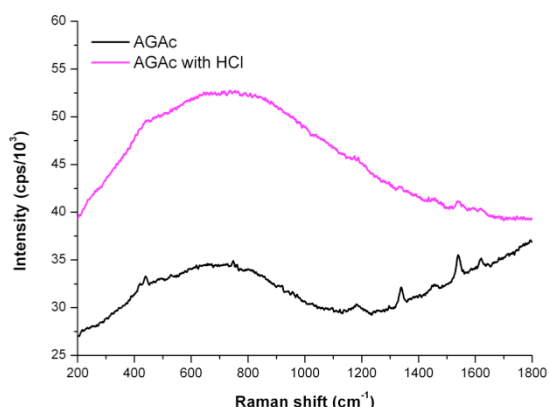
Figure 5. Raman spectra of the inked area of AGAc before (black line) and after (magenta line) dropping 2 µL of 1 M HCl solution on the surface. In the present case, the spectra are not baseline-corrected in order to show the contribution of the fluorescence. Uncertainties in the intensities, when a strong background is present, are of the order of 100 cps.

This explanation allows also understanding the smaller enhancement observed for B38 than for CV. In fact, one has to remember that AuNP are dispersed in water and that different solubility of CV and B38 in water suggests a different migration of the molecules toward the hot spots.

Following the above results, we exploited the chemical properties of CV and, in particular, its response to an acid environment, which, by the protonation of the amine group present in the molecule, increases its water solubility and therefore its extraction from the paper matrix. Therefore, a

fluorescence emission of the dye. A different situation occurs when the molecules are solubilized, and are, therefore, more isolated. In this case a stronger fluorescence can be predicted and in Figure 5 this can be observed for the acid-treated AGAc sample where the Raman spectrum (magenta line) is barely visible. These spectra also show that the presence of a strong fluorescence background makes difficult the detection of the Raman bands.

The solubilization of the molecules, however, favors the diffusion of the dyes within the hot spots of the AuNP aggregates and one expects an increase of the SERS signals and a decreasing of the fluorescent background when the AuNP particles are deposited.

The effect of the deposition of AuNP after the acid treatment can be seen in Figure 6a for AGAc, where the SERS enhancement (>20 times) is clearly evident, in particular for the signals of CV.

The effect of acidification can be observed also for AGSt in Figure 6b although in this case calcium carbonate (used as a filler in standard paper) partially neutralizes the acidity and the SERS signals are therefore less enhanced than in the case of the acidic paper.

Another consequence of a lower pH is the aggregation of AuNPs produced by LASiS.[37] This allows increasing the presence of hot spots and therefore the SERS signals. However, one can see in Figure 6 that the peaks due to B38 are almost not enhanced. This allows concluding that the diffusion of the molecules toward the hot spots is the driving process for the enhancement of signal intensities, whereas the number of hot spots seems not pivotal.

Following these considerations, we also explored the role of
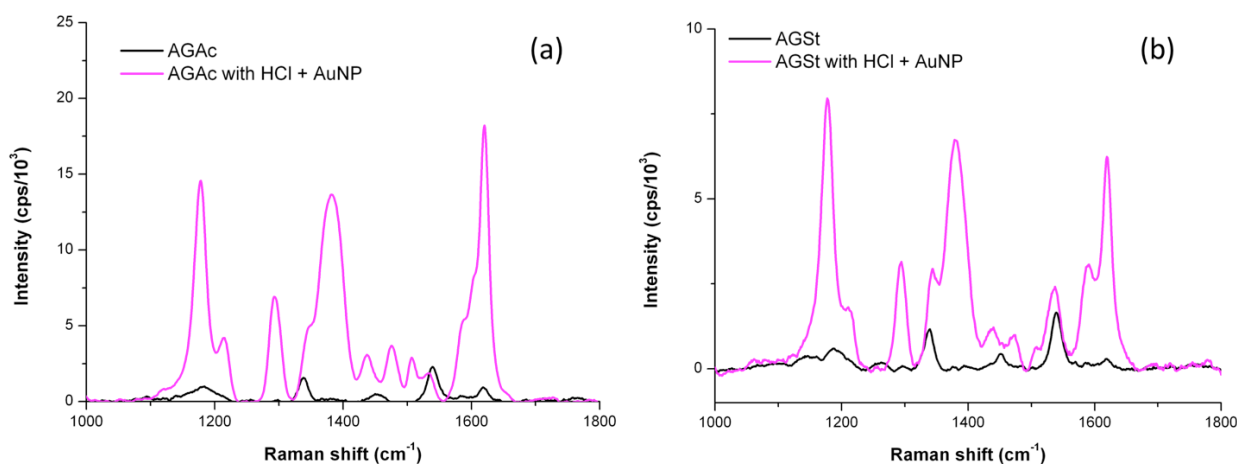
Figure 6. Raman (black line) and SERS (magenta) spectra of aged AGAc (a) and AGSt (b). Different intensity scales between (a) and (b) and with respect to Figure 4 are to be noted.

microdrop of 2 µL of 1 M HCl solution was deposited on the samples before applying the colloidal microdrop and the registration of the SERS spectrum (see experimental section).

CV is a well-known fluorescent molecule, but its emission is usually self-quenched when the molecules interact with each other, as commonly observed for aggregation of dye molecules.[36] For this reason, a Raman spectrum of an ink deposited on paper does not show a strong interference of the

the solvent polarity on the observed SERS signals by using a water: acetone mixture (90 % in volume of the original colloidal water solution and 10 % in volume of acetone, which results in a dilution of 11% of the nanoparticles) as the dispersing medium for nanoparticles. Being acetone a better solvent than water to B38, one expects that the spectrum of Solvent Blue 38 can be enhanced.

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Figure 7 reports the SERS spectrum of the AGSt obtained with the water:acetone AuNP colloids. As expected, the peaks due to B38 are now enhanced, whereas those of CV show a very small increase.

These results are a clear indication that in aged samples the SERS effect must be enhanced with the appropriate environment because the dyes must be able to diffuse to the hot spot regions for observing a SERS spectrum. This aspect of the SERS enhancement seems to be often overlooked.

The concept of hot spot accessibility is, therefore, of central importance in designing suitable protocols for SERS investigation of Cultural Heritage items, where dye-support degradation is often present and can be an obstacle to the dyes diffusion and therefore to their SERS identification.
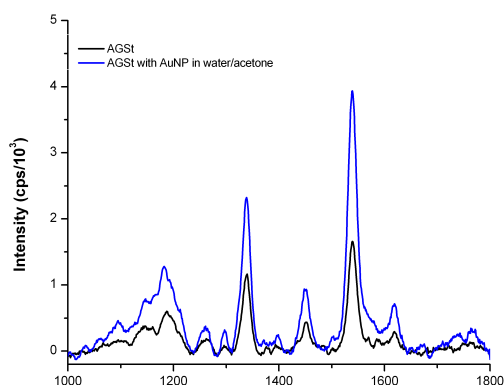
Figure 7. Comparison between the Raman spectrum (black line) and the SERS spectrum of AGSt with the water: acetone AuNP colloid (blue line).

Conclusions

SERS is a powerful, and highly sensitive technique and its use in Cultural Heritage is emerging. In this work, Raman/SERS is exploited using naked laser-ablated gold nanoparticles (AuNPs) for the detection of ballpoint pen inks on two different types of paper after light-induced ageing. These inks are very sensitive to light and discolor rapidly, making their detection a good test for understanding what occurs to the SERS spectrum.

Ageing of the samples produced a strong change in the color of the commercial ballpoint pen ink on paper, which moves from blue to gray. SERS spectra of the aged samples were found to be poorly enhanced, due to an ineffective diffusion of the dye molecules toward the hot spot regions of the aggregated AuNP. Two strategies were explored to obtain an enhancement of SERS signals on aged samples. In the first, an acid solution was used to promote the solubilization of the dyes. This approach led to a significant enhancement of the CV SERS signals. The second strategy was based on the use of a water:acetone mixture as dispersing medium for the AuNP colloid. The presence of acetone in the AuNP colloid allowed the solubilization of B38 and, therefore, the enhancement of its peaks in the SERS spectrum. These results clearly show that ink components must be able to diffuse to the hot spot regions

to be detected and that, depending on the chemical nature of each dye, different strategies must be used to reveal the exact composition of degraded inks.

Overall, we showed that the exploitation of SERS spectra of aged samples, such as those of interest in the Cultural Heritage field, is not a straightforward operation, because altered or degraded components might not be easily detected, leading to a misinterpretation of the acquired data and, consequently, of the composition of the original artwork. In that sense, a proper evaluation of the factors affecting the molecule-plasmonic nanoparticle interactions and of the history of the artwork to be analyzed is fundamental for the exploitation of these spectra.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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