DEVELOPMENT OF DRY-STATE SERS SUBSTRATES FOR THE NON-INVASIVE DETECTION OF ARTISTIC DYES IN TEXTILES.

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ABSTRACT

Surface Enhanced Raman Spectroscopy (SERS) is a powerful technique for the detection of natural dyes, allowing one to overcome the limitations of conventional Raman spectroscopy, i.e. the weakness of the signals and the intense fluorescence background. Whereas in the artistic field a non-invasive approach is recommended, SERS is still an inherently invasive method, requiring the extraction of the analyte or a close contact with the object and a wet substrate. In this work, inexpensive and easy-to-produce substrates allowing dry-state measurements were fabricated, exploiting only the electromagnetic interaction between a nanostructured substrate and the dye molecules absorbed onto a textile. To this aim, different substrates were developed starting from two colloids (silver nanospheres and nanostars) immobilized onto a functionalized microscope glass slide, and some parameters connected to their synthesis were optimized to get a great enhancement of the signal in dry conditions. Finally, dry-state SERS spectra of four different dyes were successfully obtained from reference dyed wool threads.

KEY-WORDS

SERS spectroscopy, dry-state, SERS substrates, silver colloids, natural dyes, ancient textiles, non-invasive analysis.

1. INTRODUCTION

Surface-Enhanced Raman Spectroscopy (SERS) is a powerful analytical technique for the identification at trace level of organic compounds, allowing one to overcome the drawbacks of traditional Raman spectroscopy. As Fleischmann first observed in 1974 [1], a great enhancement of the Raman signal occurs when a molecule is absorbed on, or in the proximity of, a metal nanostructured surface. Indeed, thanks to this close contact, Raman scattering excited by visible light experiences an enhancement up to a factor of 10^8[2]. In addition, the metallic substrate absorbs most of the fluorescence photons emitted by the molecules, acting as quencher of the fluorescence emission often associated with organic substances.

For its potentiality, SERS has largely been exploited in the field of diagnostics of cultural heritage to study natural and synthetic dyes from several artistic and archaeological manufacts [3, 4]. Indeed, these compounds, most of all fluorescent, are not detectable by conventional Raman spectroscopy, whereas SERS, thanks to the strong enhancement of the signal and to the quenching of the fluorescence, is the ideal technique for their univocal identification. Traditionally, SERS experiments are performed with the use of colloidal (more commonly silver) solutions. This method is inherently invasive: it cannot be used directly on the artistic object as wetting is required, if not the use of extraction methods in order to separate by hydrolysis the colorant from its matrix (i.e the textile fiber for fabrics or the inorganic substrates for lakes) [3].

In the last years, many attempts have concentrated on the development of non-invasive SERS strategies using different approaches, i.e. hydrogels based on solid phase micro-extraction techniques which extract trace amounts of dyes and are then treated with silver colloid for SERS measurements [5 - 7] or laser ablation followed by the "in-situ" analysis of the ablated substances [8, 9]. A further step towards totally non-destructive SERS analysis is the implementation of "dry-state" measurements. The possibility to obtain a SERS response starting from a solid nanometric substrate in contact with dyes on textile has already been successfully experimented in the artistic field [10]. In this respect, it is worth noticing that the enhancement of the Raman scattering in SERS is due to two different mechanisms, an electromagnetic and a chemical one. The former is a long-range effect, based on the intensification of the electric field of the electromagnetic radiation in proximity of a nanostructured metallic surface, thanks to the excitation of surface plasmons of the metal. The latter needs instead a chemical interaction between the molecules and the SERS substrate to promote charge-transfer transitions. These two phenomena do not contribute at the same extent to the SERS intensification of the Raman scattering: indeed, the electromagnetic one contributes in an order of magnitude of 10^{10}, while the chemical one of 10^2. Thus, although the interactions are obviously more challenging to establish than those occurring between a solution of the target dye and the same substrate, a dry-state analysis leading to a completely non-invasive approach is, in principle, possible.

In this context, we developed a simple protocol to produce thin films obtained from deposition of silver colloids on an optically transparent support, such as a glass slide. The final aim is, in fact, to create simple, accessible and easy-to-produce SERS substrates suitable for *in-situ* analysis by means of portable Raman instrumentation, with no need of complex procedures as those already reported in the literature and cited above [10, 11]. To this aim, different experiments were carried out to improve the reproducibility of the substrates, both from the point of view of the colloid synthesis and of the conditions of deposition.

In this work, SERS-active silver films were prepared by drop-casting small volumes of concentrated Ag colloid on a microscope glass slide. In order to promote the adherence of the nanoparticles to the support and to prevent the so-called "coffee ring" effect, i.e. the accumulation of nanoparticles along the

perimeter of the film, a functionalization procedure of the glass slides with (3-aminopropyl)trimethoxysilane was developed combining different methods reported in the literature [12 - 15]. Two different silver colloids were experimented: Ag nanospheres synthesized according to the procedure reported by Lee-Meisel [16] and Ag-nanostars obtained following the Garcia-Leis method [17]. The morphology of the SERS substrates was characterized by scanning electron microscopy (SEM) in order to verify the presence of nanoparticle aggregates, which represent the so-called "hot-spots", highly localized regions of intense local field enhancement. UV-visible spectroscopy allowed us to check the plasmonic properties and the average thickness was estimated by profilometry. Dry-state SERS analyses were finally performed by means of a portable spectrometer on mock-up samples of wool yarn dyed with three anthraquinone dyes (alizarin, purpurin and lac dye) and indigo.

2. MATERIALS AND METHODS

2.1 Materials

Trisodium citrate dihydrate, silver nitrate, hydroxylamine 50% w/w in water, sodium chloride, sodium perchlorate, magnesium sulphate heptahydrate, sodium hydroxide, methanol, 3-(aminopropyl)trimethoxysilane, hydrochloric acid (37 %), sulfuric acid (95-97 %), indigo and alizarin were purchased from Sigma-Aldrich; purpurin were from Fluka and lac dye from Zecchi. All solutions were prepared in Milli-Q water.

2.2 Synthesis of silver colloids

2.2.1 Lee-Meisel nanospheres

The colloid was synthesized according to the procedure reported by Lee and Meisel [16]. Briefly, 150 mL of a 10^{-3} M $AgNO_3$ solution were prepared, using water previously degassed under a gentle N_2 flow. This solution was heated to boiling under constant magnetic stirring and then 3 mL of a 1% trisodium citrate aqueous solution were slowly dropped into the flask. After 60 minutes at the boiling point, the colloid becomes of a light green-grey opalescent color and it is stored in the refrigerator overnight before using. The diameter of these nanoparticles ranges from 60 to 150 nm [18] and the repeatability of the colloid after each synthesis was verified by UV-visibile spectroscopy: the sol should show an absorption band centered around 420 nm (data not shown).

2.2.2 Garcia-Leis nanostars

The starry-shaped colloid was produced following the procedure reported by Garcia-Leis [17]. Briefly, 500 μL of a 0.05 M NaOH solution were mixed for 1 minute with 500 μL of $6x10^{-2}$ hydroxylamine solution, then 9 mL of a 10^{-3} M $AgNO_3$ solution were added and the mixture was stirred at 670 rpm for 5 minutes. Finally, 100 μL of a 1% trisodium citrate solution were dropped and the stirring was continued for 15 minutes. The resulting colloid, having a dark green-black color, was stored overnight in the dark

101 before using, in order to allow nanostars to develop their final branched shape. The final diameter of the

102 nanoparticles ranges from 300 to 400 nm [17] and the repeatability of the syntheses in the subsequent

103 batches was verified by UV-visible absorption spectra, which for this star-shaped nanoparticles are

104 charachterized by a maximum around 380 nm and an ascent after 600 nm

105 2.3 Preparation of the SERS substrates

106 2.3.1 Functionalization of the glass supports

107 The functionalization process consists of two phases: washing and immobilization. The former allows to

108 make the hydroxyl groups of the glass slide free for the latter, that consists in the reaction between the

109 glass substrate and the immobilizing agent. In particular, 3-(aminopropyl)trimethoxysilane (APTMS) was

110 chosen as it binds the Ag nanoparticles to the surface of the silanized substrate through the amine groups.

111 For washing, the glass slide was dipped in a 1:1 methanol:hydrochloric acid solution for 30 minutes,

112 washed copiously with distilled water until a neutral pH is reached and then dried under a N_2 flux. Then,

113 it is immersed into concentrated sulfuric acid for 30 minutes and washing and drying were repeated as

114 described above.

115 For the immobilization, the glass slide was dipped in a solution containing 45 mL of methanol, 2.5 mL

116 of deionized water and 2.5 mL of APTMS. After 15 minutes it was carefully washed by immersion in

117 methanol and subsequently in water in order to eliminate all the residual traces of APTMS and finally put

118 into an oven at 90º C for 30 minutes. The functionalized glass slide must be used the same day.

119 2.3.2 Drop deposition of the colloid

120 Before drop casting, the colloid was centrifuged (15 minutes at 6000 rpm for nanospheres, 30 minutes at

121 3000 rpm for nanostars) and re-dispersed in water to obtain the right concentration factor (between 1:50

122 and 1:100). In this respect, after removing the supernatant, a suitable volume of water was added to the

123 nanoparticles paste deposited at the bottom of the centrifuge tube and the suspension was homogenized

124 by quick magnetic stirring. Moreover, Lee-Meisel nanospheres were aggregated by adding a suitable

125 electrolyte agent; for spherical particles, in fact, the aggregation step is crucial in order to induce the

126 formation of the hot-spots and to increase the magnitude of the SERS effect [19, 20] Different salts

127 ($NaClO_4$, $NaCl$, $MgSO_4$) were tested aiming at choosing the most effective one (see Discussion section).

128 On the other hand, silver nanostars were deposited without the addition of aggregating agents: the star

129 shape of these nanoparticles, in fact, allows a large intensification of the electromagnetic field, taking

130 place directly on the tips or in the spaces between the arms [21].

131 Finally, a micro-drop (10 μL) of the treated colloid was deposited by a micropipette on the functionalized

132 glass slide and put into oven at 50°C for around 2 hours, inducing a slow evaporation of the solvent to

133 obtain a homogeneous film.

134 2.4 Preparation of reference mock-up samples

135 To prepare reference samples, firstly wool threads were washed and mordanted with alum,

136 (KAl(SO$_4$)2·12H$_2$O) for a lasting and stable adhesion of the colorants to the fiber. Then wool threads

137 were dyed following the ancient recipes, as described elsewhere [22]. Before analysis, a small piece of the

138 dyed thread was washed in 1 mL of pure methanol in order to remove the not-mordanted dye possibly

139 remaining on the fiber. In the present work wool was dyed with the red anthraquinone dyes alizarin,

140 purpurin, lac dye and the blue dye indigo.

141 2.5 Instrumentation

142 2.5.1 Raman spectroscopy

143 SERS spectra were collected with a portable micro-Raman instrument (Jasco), equipped with a 1800

144 lines/mm grating, a notch filter, an Olympus 50× microscope objective and a Peltier-cooled CCD

145 detector (operating temperature -60º C); a Nd : YAG laser provided the exciting radiation at 532 nm,

146 with an output laser power of about 100 mW. Alternatively, the Raman probe can be coupled with a

147 near-infrared diode laser, emitting at 785 nm All SERS spectra were recorded between 2000 and 200 cm^{-1}

148 by collecting 30 scans with an exposure time of 2 s.

149 As the contact between the SERS-active substrate and the sample is fundamental for having a good SERS

150 response (the surface-enhanced electromagnetic field is a short range one [23], the wool tread is fixed in

151 close contact with the SERS substrate. The measurements were then performed by focusing the laser

152 beam on an area of the film where both an aggregate of nanoparticles and the dyed wool thread below

153 were visible through the SERS substrate thanks to the use of a visualization system coupled with the

154 Raman probe. The analytical set-up is presented in Fig. 1:
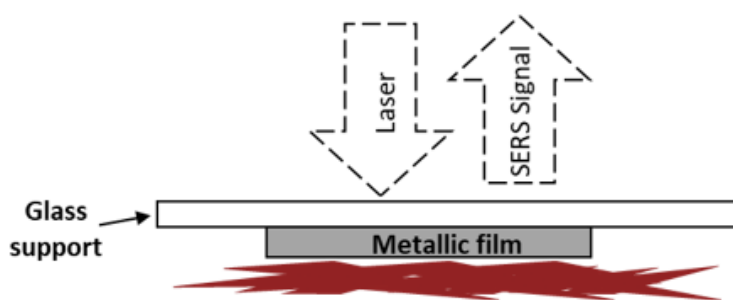
155

156 Figure 1. Schematic set-up for dry-state SERS analysis on dyed wool thread samples.

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203 2.5.2 UV-Visible spectroscopy

204 UV-visible spectra were acquired in the spectral range 400 – 800 nm using a JASCO UV/VIS/NIR V-

205 570 spectrometer, allowing measurements both in transmission and, when equipped with an integrating

206 sphere, in reflection mode.

207 2.5.3 Scanning Electron Microscopy (SEM-EDX)

208 SEM images were obtained using a Hitachi TM 1000 microscope, having a resolution of 1 nm and

209 equipped with an energy dispersion X-ray (EDX) spectrometer. The accelerating voltage was 15 kV.

210 2.5.4 Profilometry

211 The average thickness of the SERS substrates was evaluated by means of a Bruker DektakXT contact

212 profilometer, having a repeatability of 4 Å and capable of measuring <10 nm step heights.

3. Results and discussion

214 The detection of natural dyes on dyed wool by dry-state SERS is challenging, as the interactions between

215 the molecules of the colorants and the SERS substrate are obviously more difficult to establish than those

216 occurring between a solution of the analyte and the nano-structured film. Indeed, it should be considered

217 that in the former case only the electromagnetic mechanism contributes to the SERS enhancement, while

218 in the latter also the chemical one takes place. Moreover, to reach the detector the scattered Raman signal

219 has to pass through the nanoparticle film and the glassy support, undergoing invariably a loss of intensity.

220 To evaluate the applicability of the dry-state methodology, different substrates were tested as already

221 mentioned and the experimental conditions for the analysis were optimized. In particular, two different

222 laser sources were experimented for excitation: a near-infrared one, emitting at 785 nm, and a green one,

223 whose emission wavelength was 532 nm. In both cases the best results were obtained using the green

224 laser. In fact, its emission wavelength satisfies resonance conditions both with the absorption band of

225 the red dyes and the localized surface plasmon of the substrates.

226 The performance of the method was finally confirmed by comparing the SERS signals of the reference

227 dyed wool samples with conventional Raman analysis (no detectable signals, unless a fluorescence

228 background) and with the SERS spectra recorded on the substrates from the corresponding dyes in

229 methanolic solution (10^{-3} M). In this respect, a μ-drop (5μL) of the target dye solution was deposited on

230 the silver film and the measurements were executed on it. We also performed Raman measurements of

231 blank substrates as controls: they display signals due to citrate and hydroxylamine in the spectral range

232 between 1100-700 and 1700-1300 cm^{-1}. [24]

233 For both substrates, we experimented different concentrations of the re-dispersed colloid in order to

234 obtain a strong SERS response, while creating a substrate at the same time transparent enough to transmit

235 the laser and the scattered radiation.

236 In the sections below, the optimization of the procedures and the analytical results for Lee-Meisel

237 nanospheres and Garcia-Leis nanostars will be detailed.

238 3.1 Lee-Meisel substrates

239   For this colloid the best concentration to obtain the SERS substrates proved to be 1:100. In fact, it results

240   in obtaining a substrate rich in nanoparticles, but also having the required transparency.

241   Moreover, different electrolytes were tested in order to aggregate the pre-concentrated silver

242   nanoparticles: NaCl, NaClO$_4$ and MgSO$_4$. All solutions had a concentration of 10 mM and were added

243   to the pre-aggregated nanoparticles in a ratio water:electrolyte of 9:1. Their aggregation effect was studied

244   by UV-visible spectroscopy and SEM microscopy. As shown in Fig. 2a and 2b, the UV- vis spectra of

245   the colloid aggregated by NaCl and NaClO$_4$ do not differ significantly from those of the non- aggregated

246   pre-concentrated colloid; on the other hand, when MgSO$_4$ is added, the band shifted towards longer

247   wavelength indicating the formation of aggregates (Fig. 2c). This is due to the fact that Mg^{2+}ions, thanks

248   to their higher charge, induce stronger aggregation than singly charged cations [25]. The better

249   aggregation properties of Mg salts, in comparison with alkaline metal ones, are reflected also in the SEM

250   images of the SERS substrates obtained with the different aggregating agents, where larger ensembles of

251   nanoparticles are observed when MgSO$_4$ is used (Fig. 2c).
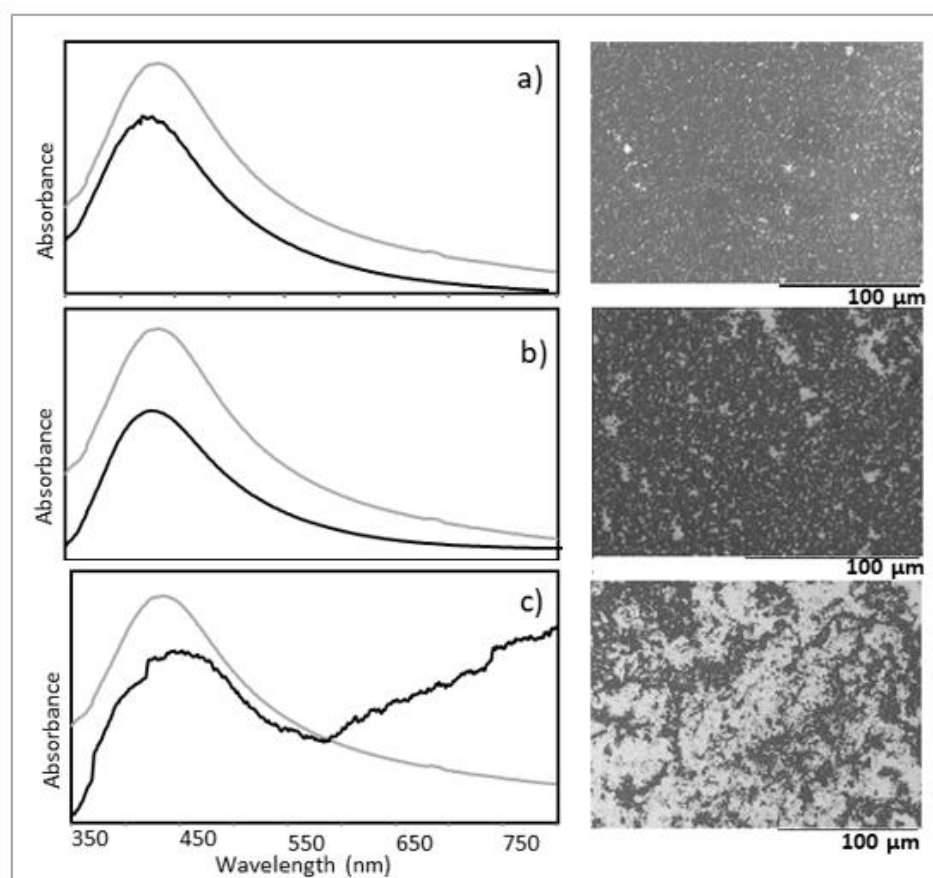
252

253   Figure 2. UV-vis absorption spectra of the reference Lee-Meisel colloid (grey line) compared with the same colloid
254   aggregated with a) NaCl, b) NaClO$_4$, c) MgSO$_4$. On the right, SEM images of the substrates obtained from the
255   corresponding aggregated colloid.

256

The latter electrolyte was therefore chosen and a further study was carried out to find the best water:electrolyte ratio for the re-dispersion of the concentrated colloid. 9:1, 8:2 and 7:3 ratios were experimented and 9:1 resulted to be best one.

The SERS substrates obtained by deposition of the concentrated and aggregated colloid were then characterized by UV-vis spectroscopy and profilometry. The average thickness of the film is 200 μm and the UV-vis spectrum shows a broad absorption band centered around 625 nm (Fig. 2a). The position of the plasmonic band is in accordance with the fact that better results are obtained by using the 532 nm excitation wavelength rather than the 785 nm one. SEM images revealed that the films exhibit little coffee ring effect, even if they are not really homogeneous as the aggregates are not uniformly distributed in the film area (Fig. 2 c, right column).
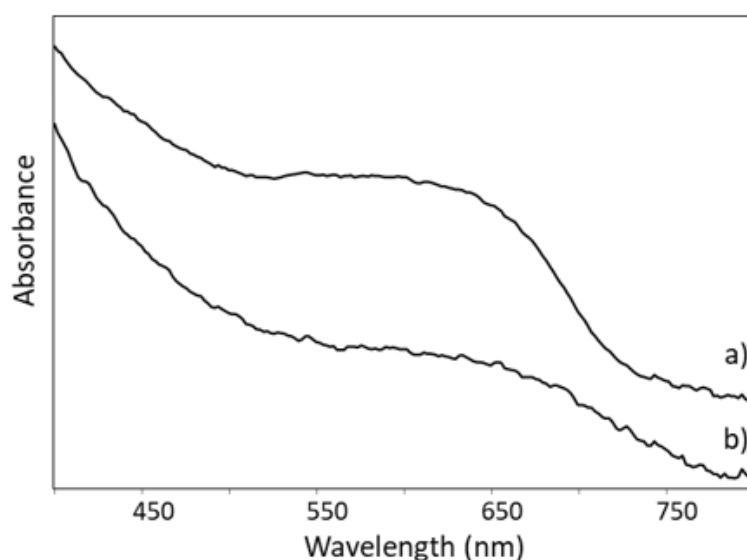

Figure 3. UV-visible reflectance spectra of the SERS substrate synthesized with a) Garcia-Leis and b) Lee-Meisel colloid.

The films were then successfully used for the detection of two anthraquinone dyes, alizarin and purpurin, absorbed onto a mordanted wool thread. The acquired SERS spectra (Fig. 4) show intense signals due to the two analytes and a low fluorescence background, allowing their certain identification. This is demonstrated by comparison with the spectra of the same compounds analyzed in solution on the same substrate, corresponding to those reported in the literature for the corresponding dye [26]. A strong dependence on the examined area was found: intense spectra with low fluorescence background are obtained when the laser beam is focalized onto an area of the substrates where a large aggregate of nanoparticles and, as a consequence, a hot-spot are located. For this reason, the inhomogeneity of the substrates obtained from the Lee-Meisel colloid represents a strong limitation.
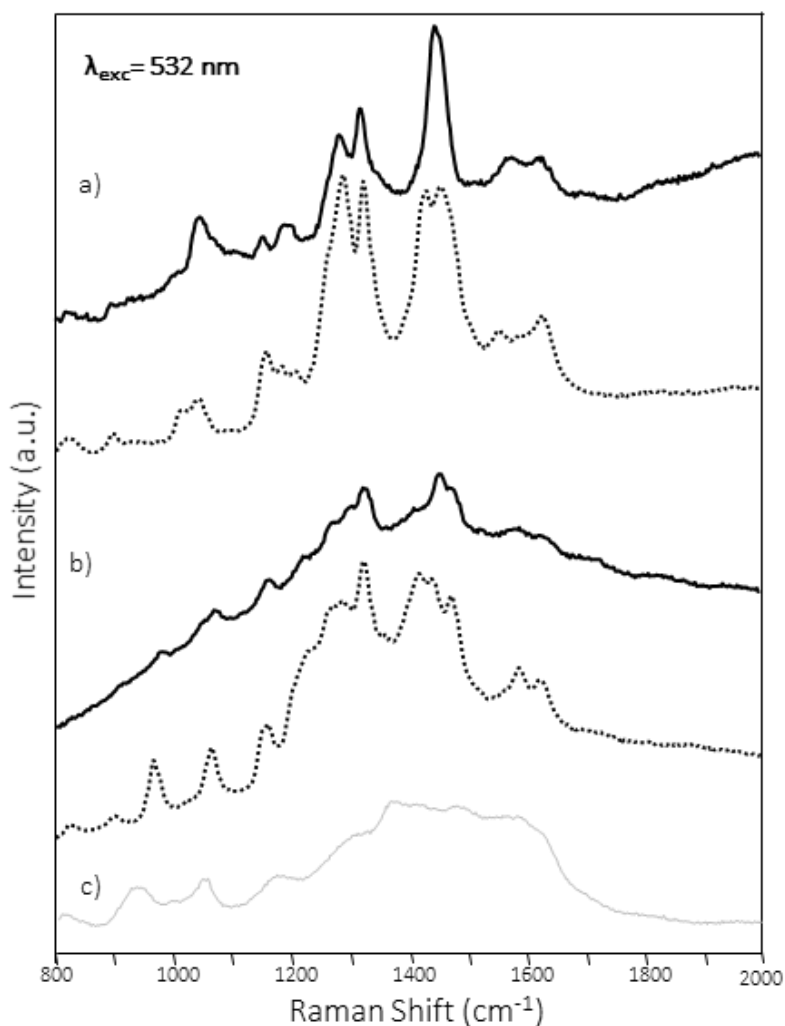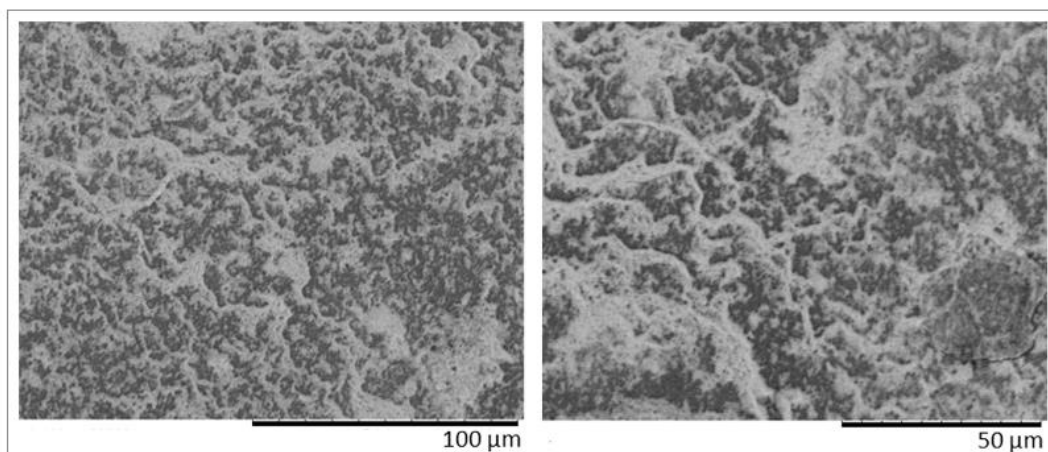
Figure 4. Dry-state SERS spectra acquired on Lee-Meisel substrates from wool samples (black line) dyed with a) alizarin and b) purpurin in comparison with those recorded on the same substrate from a 10^{-3} methanolic solution of the same dye (dotted line); c) background SERS spectrum of the Lee.-Meisel substrate.

3.2 Garcia-Leis substrates

Silver nanostars, because of the presence of long tips, are able to interact forming directly hot-spots. They were therefore tested to produce the SERS substrates avoiding the aggregation step and the consequent inhomogeneity of the surface.

Different concentration factors of the colloid (1:10, 1:20, 1:30, 1:50, 1:75 and 1:100) were tested to have also in this case a substrate dense in nanoparticles, but transparent enough to the laser radiation and to the scattered signal. The best results were obtained for the 1:50 concentration factor. The SEM images reveal a considerable presence of aggregates and a homogeneous distribution of the nanoparticles (Fig. 5). Profilometric analyses evaluated an average thickness of 200µm and the UV-vis spectrum is characterized by a broad absorption band centered around 608 nm (Fig. 2b). Again, this result is consistent with the greater enhancement obtained by the 532 nm excitation wavelength, in comparison with the 785 nm one.

9

Figure 5. SEM images of the substrates obtained from silver nanostars (concentration factor 1:50).

The nanostar substrates were finally successfully tested for dry-state SERS analysis of wool dyed with the anthraquinone dyes alizarin, purpurin and lac dye and also with the blue dye indigo. In Fig. 6, the acquired spectra are shown in comparison with the reference ones obtained from a solution of the same analyte on the same substrate. Again, the SERS signals correspond to those reported in literature [26, 27].
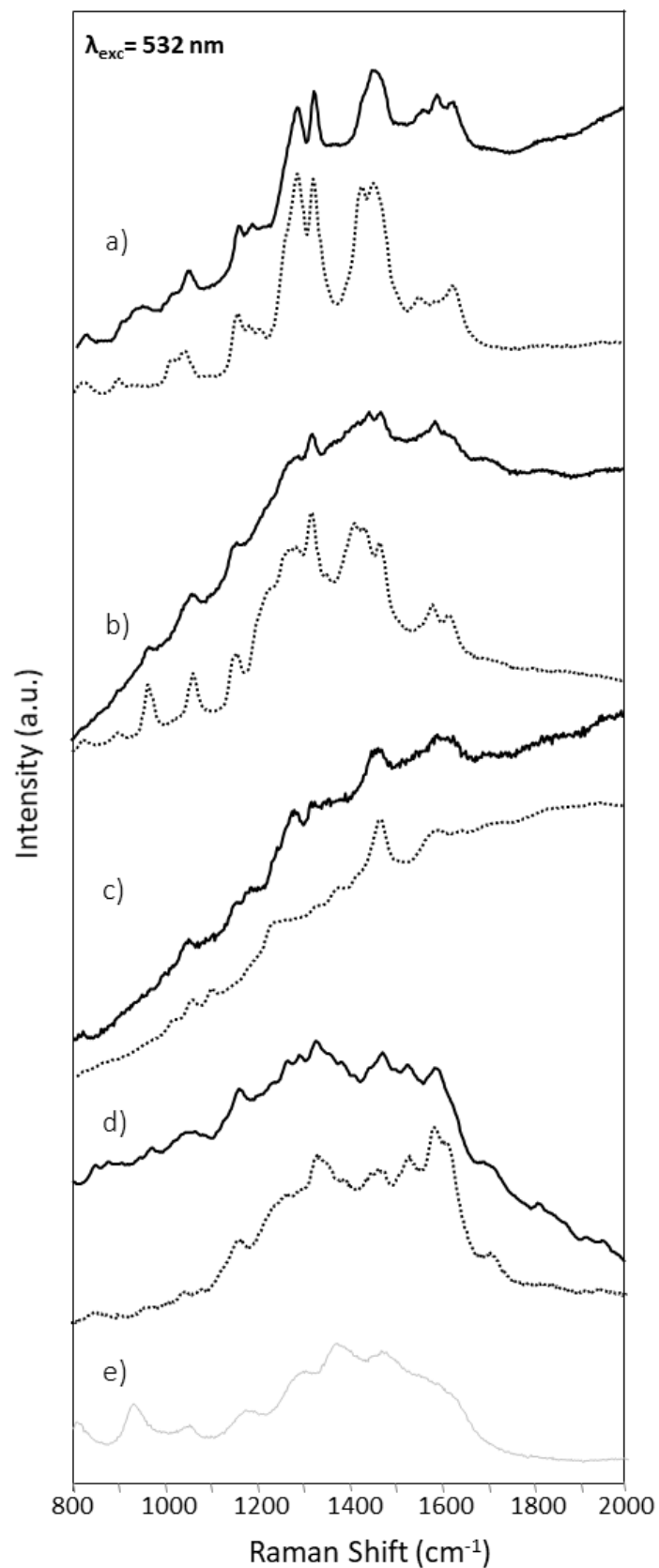
Figure 6. Dry-state SERS spectra acquired on Garcia-Leis substrates from wool samples (black line) dyed with a) alizarin, b) purpurin, c) lac dye and d) indigo in comparison with those recorded on the same substrate from a 10^{-3} methanolic solution of the same dye (dotted line); e) background SERS spectrum of the Garcia-Leis substrate.

Conclusions

The proof of concept of performing SERS analyses in dry-state condition by means of easy to realize and low expensive substrates for the identification of four natural dyes directly on wool yarns was given. This is possible by exploiting only the electromagnetic component of the SERS effect, which takes place when the analyte is in proximity of the substrate, not chemisorbed to it. This goal was reached by producing SERS substrates through the immobilization of silver nanoparticles synthesized (nanospheres and silver nanostars) on commercial microscopes glass slides, previously functionalized by ATPMS to promote the adhesion and a homogeneous distribution of the nanoparticles themselves. The best conditions to obtain reproducible films leading to a good enhancement of the Raman signal in dry state were individuated and the spectra of alizarin, purpurin, lac dye and indigo were successfully acquired by means of a portable Raman instrument, suitable for non-invasive, *in-situ* analysis directly on artefacts.

Acknowledges

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