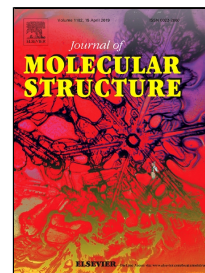# Accepted Manuscript

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Gold loaded textile fibres as substrates for SERS detection

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Abstract

Spectroscopic methods based on surface-enhanced Raman scattering (SERS) are among the analytical tools most exploited in recent years for the detection of vestigial amounts of compounds with environmental and health relevance. In the last decades, SERS methods have been largely improved with the unprecedented progress in instrumentation and materials development in the scope of nanoscale science. The current developments in Raman instruments, in particular for Raman imaging, brought a new look on composites and its applications. The use of confocal microscopes allows high resolution Raman mapping with short measurement times, creating strongly improved Raman images in two and three dimensions. In this manuscript, we will present an overview of our own research on the development of malleable and easy-handled SERS substrates based on textile fibres for analytical detection. The strategies employed for the coating of the textile fibres with gold nanoparticles (NPs) will be described in detail. A final section will focus on the combination of Raman imaging and SERS for the development of substrates based on textile fibres and their application on the detection of water pollutants and biomolecules. A case study on the development of cotton swab fibres coated with Au NPs for SERS detection of L-lactate will be illustrated in more detail.

1. Introduction

The application of conventional Raman spectroscopy for molecular trace detection of compounds of environmental and biological relevance, was constrained by the detection limits. The small Raman scattering cross-section implies that concentrated solutions of the analyte sample are required [1, 2]. The discover of Surface enhanced Raman scattering (SERS) allowed to overcome that limitation. The SERS effect consists in a large enhancement in the Raman signal intensity for molecules that are adsorbed in metal surfaces, typically of gold and silver [3, 4]. Among several factors that influence the Raman signal enhancement, the chemical nature and morphological features of the employed SERS substrates are of particular relevance. As such, great efforts have been made in order to fabricate sensitive SERS substrates with controlled features at the nanoscale level [5, 6]. Moreover, there has been interest that such substrates might be explored as handy and low-cost analytical platforms, using products such as paper and textiles as supports for the SERS active metal nanoparticles.

Textile products, such as fibres, yarns, and fabrics, are good candidates as supports in the design of wearable biosensors and electrical conductive devices with diverse functionalities [7-9]. The incorporation of inorganic nanoparticles (NPs) can confer additional functionalities namely antimicrobial properties, self-cleaning and UV-protection, or simply aesthetic effects for decoration [10-15]. Hence, Kelly and Johnston have demonstrated that Ag NPs attached onto merino wool fibres result in textiles with antimicrobial and antistatic properties [10]. Mao *et al*. have developed textile based devices using ZnO/Au/rGO-functionalized silk fabrics for human physiological monitoring, such as arterial pulse and breathing [12]. Elmaaty and co-workers have reported an approach for printing and finishing polyester and cotton fabrics using Au and Ag NPs [13].

The wearable devices should have specific properties such as biocompatibility, stability and functionality when applied to the human body. Hence, Au has been regarded as a good material for such devices due to its optical properties and electrical conductivity along with the well-known inertness and biocompatibility [16-18]. Table 1 presents several Au textile nanocomposites and respective applications. The integration of distinct applications in the same type of fabric is an endeavour to be explored.

Table 1: Applications of Au loaded textile nanocomposites.

	Textile fibres	Application
Synthetic fibres	Polyester	Electronics and circuits [19, 20]; Water repellence [21]; UV-protection [13]; Antimicrobial activity [13]; Electroluminescent wearable devices [22];
	Para-aramid	Electronics and circuits [23];
	Polyamide	Colouration [24]; SERS [25];
Natural fibres	Silk	Electronics and circuits [26]; UV-protection [11]; Antimicrobial activity [11, 27]; Colouration [11, 24]; Clinical diagnosis, daily healthcare monitoring and voice recognition [12];
	Cotton	Electronics and circuits [20, 28]; UV-protection [11, 13, 29]; Antimicrobial activity [11, 13, 27, 30]; Colouration [27, 31]; SERS [30, 32]; Water repellence [21];
	Wool	Colouration [24, 33]; Self-cleaning property [14]; Antimicrobial activity [14]
	Cellulose (filter paper)	SERS [34-36]; Catalysis [36];
	Leather	Antimicrobial activity [27]; Colouration [27];
	Viscose	UV-protection [29];

In comparison to paper products, which have been included in Table 1 for comparative purposes, Au loaded textile products have been less investigated as active SERS substrates [30, 32]. Hence, Tang *et al.* have reported the fabrication of multifunctional Au/cotton nanocomposites using the chemical reduction method [30]. They have demonstrated that Au NPs placed at the cotton's surface improved UV-blocking ability of the fabric, resulting in multifunctional materials that show antibacterial activity, exhibited catalytic activity and SERS sensitivity for the detection of dyes on fabrics.

This manuscript provides an overview of our research on several textile based nanocomposites that have been investigated aiming at the fabrication of active SERS substrates. The preparation strategies will be firstly mentioned as an important step to fabricate such nanocomposites [37]. Although the emphasis has been on materials development rather than on the implementation of analytical protocols, several analytes have already been tested in SERS detection. In particular, the focus has been on the SERS

detection of organic compounds that raise serious concerns due to adverse effects as water pollutants and negative health impact. Finally, a case study on Au loaded cotton swab fibres for the SERS detection of L-lactate will be described in more detail, thus illustrating an integrated approach from nanomaterials to practical SERS detection.

2. Strategies aiming at the preparation of textile fibres coated with gold NPs

The attachment of Au NPs onto textile fibres has been carried out by several procedures that include sputtering [19], electrostatic assembly via polyelectrolytes [28, 32], chemical reduction in solution [30, 38], dip-coating [11, 21, 22, 24, 33-36], electroless plating [20, 23], drop and dry [32], biosynthesis (e.g. using bacteria as reducing agent) [27] and printing paste method [13]. Figure 1 illustrates some of the strategies employed by our group in the preparation of Au based textile composites for SERS applications. The examples indicated in Figure 1 involved aqueous routes that rely on the use of previously prepared Au NPs or the *in situ* reduction in the presence of the fibres. These methods have been applied either to natural or synthetic fibres and are briefly discussed below.
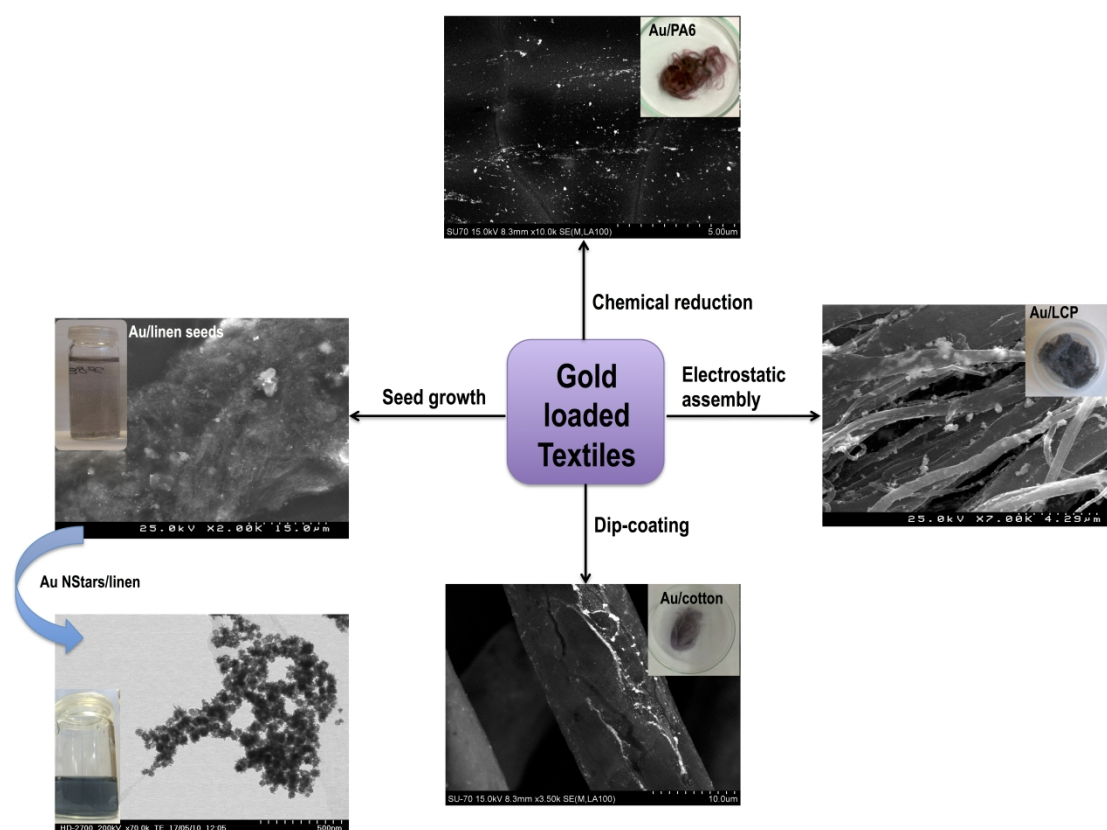

Figure 1: SEM images of materials obtained by distinct strategies for the preparation of Au based textiles nanocomposites.

2.1 *In situ* chemical reduction

The metal NPs can be generated *in situ* in the presence of the fibres by chemical reduction of a metal precursor using reducing agents such as sodium citrate or sodium borohydride. The Au/textile nanocomposites were obtained by chemical reduction of the metal cations loaded in natural fibres, such as cotton, linen and silk, or synthetic fibres namely polyamide 6 (PA6), poly(ethylene terephthalate) (PET), poly(butylene succinate) (PBS), poly(vinylidene fluoride)

(PVDF) and LCP (liquid polymer crystal - vectran). Figure 2 shows the optical spectra and the digital photographs of the respective composites.

Colloidal Au nanospheres prepared by the citrate reduction method have a single absorption band peaked at 520 nm ascribed to a localized surface plasmon resonance (LSPR) [39, 40]. The Au/textile composites presented in Figure 2 show the LSPR band of Au NPs, peaked at 540 nm, 544 nm, 561 nm and 545 nm for Au/cotton, Au/silk, Au/PBS and Au/PVDF, respectively. For comparative purposes, the visible spectra of the neat textile fibres, for all composites, are also presented. In Figure 2, the band broadening observed to longer wavelength for all composites can be attributed to the presence of Au aggregates, possibly due to the preparation method employed to fabricate such composites. In the *in situ* method, the Au NPs are prepared by the reduction of a Au(III) precursor in the presence of the textile fibres, thus the aggregation of the NPs might be facilitated at the surface of the polymeric matrix. We have observed a similar behaviour by recording the SPR band for composites based on linen and liquid polymer crystal (LCP) coated with Ag NPs [41, 42].
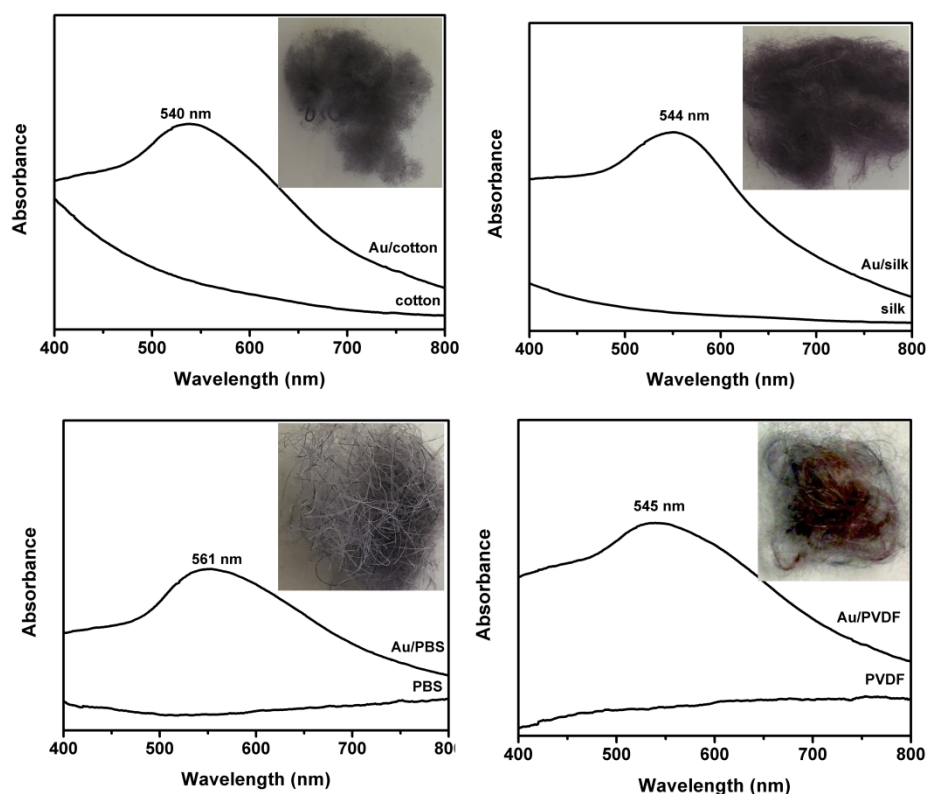

Figure 2: Optical spectra of Au loaded textile based composites and correspondent digital photograph using either natural (top) or synthetic fibres (down). The optical spectra of the raw textiles are also shown for comparative purposes.

2.2 Seed growth method

The shape of colloidal Au NPs influences their optical properties and can be exploited to induce the formation of hotspots for SERS applications. Hence, star shaped Au NPs show strong local electromagnetic fields at the apexes, inducing enhancement of the Raman bands of molecules that are in the vicinity of the metal tips [43]. Star shaped Au NPs, as well as other types of shapes, can be synthesised via a seed growth method in the presence of surfactants (e.g. cetyltrimethylammonium bromide, CTAB). This morphological dependent optical behaviour has also been observed when using Au containing solid substrates such as textile based SERS platforms [44, 45]. Thus, the seed growth method was used to prepare Au nanostars and nanoflowers supported on linen fibres by using an adaptation of the method applied to reduced graphene oxide as the substrate [46]. Briefly, the Au seeds were generated by citrate reduction of Au(III) species in micro textile linen fibres submitted to previous sonication treatment. The Au/linen seeds were then used as aqueous suspensions for growing Au nanostars (AuNSs) in acidic medium, or Au nanoflowers (AuNFs) when using an alkaline reacting medium, but in both cases without addition of surfactants. The Au based textile composites were tested as SERS substrates for the detection of antibiotics in aqueous solutions.

The method above can be extended to other solid substrates that might confer additional functionalities to the final nanocomposites. This can be illustrated by the use of Fe_3O_4 NPs as substrates for the heterogeneous nucleation of Au seeds that then will grow into Au NSs or Au NFs. A great advantage in using such multifunctional SERS substrates is the ability for magnetic separation from the liquid medium by applying an external magnetic field. This is a convenient strategy to develop magnetic nanosorbents that allow to uptake and pre-concentrate target analytes for subsequent SERS detection [47]. Figure 3 shows a transmission electron microscopy (TEM) image of cubic shaped Fe_3O_4 NPs decorated with Au NFs obtained by using the seed mediated growth method in alkaline conditions.
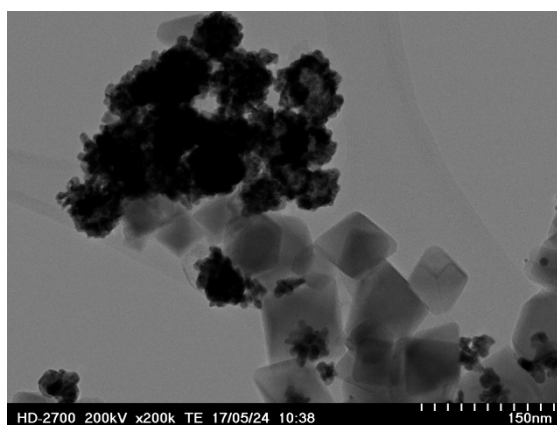

Figure 3: TEM image of AuNFs/magnetite hybrid particles as multifunctional nanosorbents.

2.3 Dip-coating and electrostatic assembly

The dip-coating methodology has been commonly used to fabricate metal loaded textile fibres. Advantages of this method include its simplicity, cost-effectiveness and easy scale-up. The preparation method involves the immersion of the textile fibres into metal sols over a certain period of time. In order to improve the surface coating of the fibres, the respective suspensions might be thermal treated under stirring. Also, the knowledge of the overall surface charge of both components, i.e. colloidal particles and textile fibres, is determinant to obtain a homogenous coating because electrostatic repulsion between those components should be avoided. Therefore, this procedure has been associated to electrostatic assembly methods that employ multilayers of polyelectrolytes and metallic NPs of opposite charges. For instance, Dong and Hinestroza have described cotton composites coated with Pd and Au after applying an electrostatic assembly method [38]. In this research, the cotton's surface was chemically modified by using (2,3-epoxypropyl)trimethylammonium chloride (EPTAC), thus providing a positive charge at the surface. This surface modification improved the affinity of the citrate coated metallic NPs for the cotton substrate due to coulombic interactions. This methodology is not limited to textile for fabrics and in fact other biopolymers have been investigated, such as SERS substrates based on cellulose products [41, 42,48].

Liquid crystal polymers (LCP) coated with Ag or Au NPs have been prepared using the dip-coating method or the electrostatic assembly method, that envisage the SERS detection of pesticides in contaminated waters [41]. In a first step, the LCP textile fibres were grinded and surface coated with colloidal metal NPs (Ag or Au), whose shape was also varied (nanospheres and nanorods). In a subsequent step, the composites were mechanically pressed into filter type membranes and then used in a syringe filter holder to load the sample solution. Figure 4 presents the optical spectra and respective digital photographs of Au based LCP composites loaded with Au spherical particles (AuNSpheres) with a diameter of 15 nm and Au nanorods (AuNRods) with an aspect ratio of 3.8. The materials were obtained by using either the dip-coating method or the electrostatic-assembly method and then submitted to pressure. The optical spectra indicate that both the AuNSpheres and AuNRods maintain the characteristic LSPR bands ascribed to particles having such morphologies in the colloidal state. On the other hand, band broadening and band shifts to longer wavelength occurred which might be associated to particle aggregation and the use of dispersing media having distinct dielectric constants. The nanocomposites were evaluated as active SERS substrates for the detection of pesticides such as sodium diethylditiocarbamate (NaDTC). The LCP fibres loaded with AuNRods have shown greater SERS sensitivity for the detection of NaDTC as compared to the composite containing Au nanospheres. It has been reported in the literature that in comparison to AuNSpheres, the AuNRods exhibit reduced plasmon damping and strongly enhance the local electromagnetic field at the particles' edges [49, 50]. Typically, the Au NRods {100} facets are less coated with the CTAB surfactant bilayer, thus allowing better chemisorption of the molecular probes at those facets [51, 52]. This is a plausible explanation

for the observation that among those substrates, the LCP textile fibres coated with AuNRods are more sensitive for NaDTC detection.
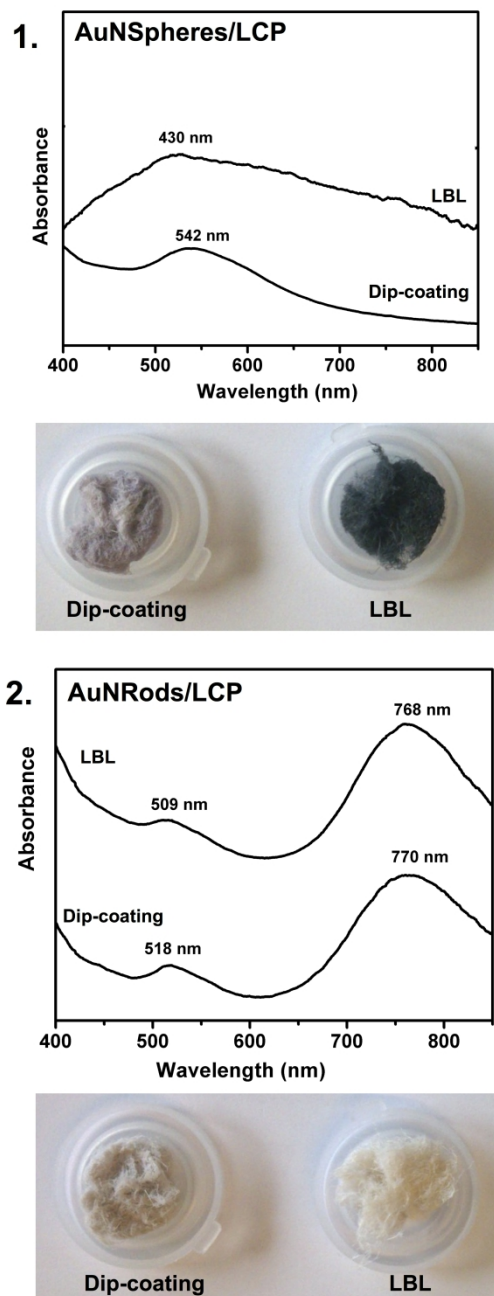

Figure 4: Optical spectra of AuNSpheres/LCP (1) and AuNRods/LCP (2) textile based composites and respective digital photographs.

3. SERS and Raman imaging methods applied to textile nanocomposites

Although the SERS effect was discovered in the early 70s, this spectroscopic method had seen unprecedented progress in the last few decades due to instrumentation and materials development specific to nanoscale science. SERS analysis using solid substrates show great dependency on the distribution of the molecular probe over the metal surface and on the orientation of molecules attached to the metal surface [2, 4]. The fabrication of sensitive SERS substrates at low-cost is a key aspect to expand the application of this technique to a wider analytical context, such as in environmental monitoring and trace chemical analysis [6, 37].

In this context, metal loaded textile fabrics are of interest because can be used as relatively cheap analytical platforms. Moreover textile based nanocomposites can be incorporated into clothing for *in situ* monitoring of biomarkers [25, 41, 42, 53-55]. Despite such technological potential only a few reports describe the use of textile fabrics coated with Au NPs as SERS substrates [30, 32, 56]. Ballerini *et al.* have reported cotton thread functionalized with Au NPs as disposable SERS substrates for low-cost-per-test diagnostics using Raman spectroscopy [32]. Wang and his team have reported Au silk nanocomposites for the SERS detection of several analytes such as *p*-aminothiophenol, 4-mercaptopyridine and crystal violet [56]. The authors have correlated the SERS activity of the substrates to the content and morphology of the Au NPs on the silk fabrics. Fateixa *et al.* have reported a method to prepare SERS-active filter membranes based on polyamide fibrils, decorated with Ag and Au NPs, following filtration under reduced pressure [25]. The ensuing textile based composites were investigated as substrates for SERS imaging studies envisaging the spectroscopic detection of vestigial organic pollutants dissolved in water.

Figure 5 shows examples of Au loaded textile substrates employed as SERS substrates for the detection of different molecular compounds. For example, Au NPs with 35 nm of diameter attached to LCP textile fibres have been successfully used as active platforms for the SERS detection of pesticides, such as thiram and sodium diethyldithiocarbamate (NaDTC). The Raman spectrum of thiram solution (1 mM) obtained by using those composites as substrates (Figure 5-1) suggests a perpendicular orientation of the C-N bond in relation to the metal surface, possibly due to bidentate coordination of dithiocarbamate to Au sites. The absence of the band at 1452 cm^{-1} assigned to the $\delta_{assym}(CH_3)$ is an evidence for such bidentate adsorption mode. Moreover, the band at 1498 cm^{-1} which is assigned to the ν(C-N), is enhanced in the SERS spectrum in comparison to the conventional Raman spectrum of thiram and the S-S vibrational band at 559 cm^{-1} decreases because it is easily cleaved (see grew shadows in the spectrum) [41, 57].

Natural fabrics such as cotton and linen have been evaluated as SERS substrates to monitor the dying process on textile fibres and for biomolecular detection. Adenine is a bioanalyte with special relevance in deoxyribonucleic acid (DNA) studies because its vestigial detection might elucidate about a number of vital processes that depend on the biochemistry of this nucleobase [58, 59]. This has implications on clinical diagnosis and also in fundamental knowledge associated to DNA biochemistry [60]. The SERS spectrum of adenine solutions with concentration of 10 µM, by using the Au/cotton composites as substrate (Figure 5-2), shows a strong band at 731 cm^{-1} attributed to the in-plane ring breathing mode. This study revealed that these easy-handle cotton composites have potential for the development of smart sensors for DNA fragment detection.

The SERS detection of antibiotics, such as tetracycline and sulfamethoxazole, was performed by using Au nanostars (AuNSs) and Au nanoflowers (Au NFs) that were grown on the surface of linen micro fibres (Figure 5-3). In this work, the gold morphology and laser excitation wavelength have been adjusted in order to optimise the substrate performance, thereby to enhance the Raman signal of the antibiotic. The use of these materials as SERS platforms led to detection limits in the order of 10 µM, however in changing the linen substrates by magnetic NPs as supports for the growth of the AuNSs and AuNFs, lower detection limits were achieved. This is because such magnetic substrates allowed the pre-concentration of the target analyte by sequential extraction from aqueous solution via magnetic separation.
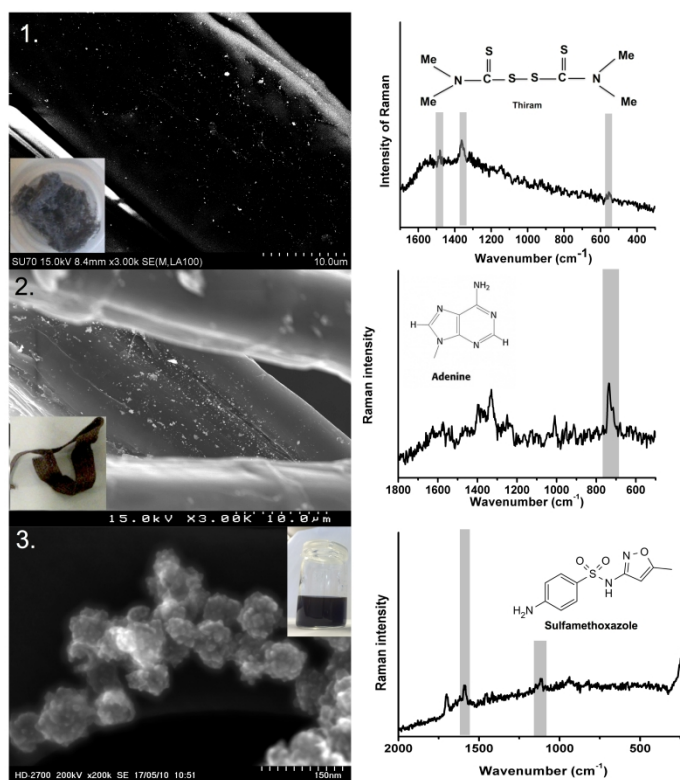

Figure 5: SERS analysis using Au loaded textile based composites as substrates. 1. Detection of thiram using LCP textile fibres coated with Au NPs (d~35nm); 2. Au/linen composites for detection of adenine 3. AuNFs/linen microfibres for detection of sulfamethoxazole.

The current developments of techniques such as Raman imaging, through high resolution Raman mapping with short measurement times, have brought a new look on composites and their applications in the context of Raman analytical methods [61-63]. The combination of Raman imaging and SERS is almost unexploited but that show strong potential for the textile industry, namely in monitoring products quality and processes [25, 41, 42, 64, 65]. For example, SERS and Raman imaging were used with advantage in the monitoring of textile fibres dyeing [42, 64]. It was demonstrated that by using Raman imaging associated to the presence of Ag NPs, it was possible to distinguish the local distribution of the organic dye (methylene blue) over textile surfaces enriched in Ag. Raman imaging provided insights about the distribution of Ag NPs over the textile fibres and knowledge about the adsorption modes of the dye molecules on the metal surfaces. It should be noted that textiles incorporating Ag NPs have been produced and commercialized as antimicrobial products, which makes this type of study particularly relevant from a technological point of view.

Similarly, Au loaded textile substrates, such as linen, cotton and silk, have been prepared and dyed with common colorants. Hence, the use of methylene blue (MB) and rhodamine 6G (R6G) as textile dyes also allowed their use as molecular probes to map the distribution of the Au NPs on the textile fibres by SERS imaging (Figure 6-1). The dependence of the SERS sensitivity for dyes detection was evaluated under different experimental conditions, namely by varying the laser excitation wavelength (633 and 532 nm) and also by using different preparative methods for SERS substrates based on textile fibres (cotton, silk or linen). The better SERS performance was observed by using nanocomposites prepared by a dip-coating method with the laser source set at 633 nm for Raman mapping.

Commercial polyamide (PA) filter membranes have demonstrated to be useful platforms for the deposition of metallic NPs and consequently to be explored as SERS substrates [25, 53]. For example, citrate coated Au NPs (15 nm and 35 nm average diameter) and polyvinylpyrrolidone (PVP) capped Au NSs have been loaded on PA filter membranes by filtering under reduced pressure the respective colloids. The sensitivity of the SERS substrates was investigated in the extraction and detection of crystal violet (CV) by varying the size, morphology and amount of Au NPs retained in the filter membranes, and using SERS spectroscopy coupled with Raman imaging. These substrates led to good SERS response in the analysis of CV with detection limits of 100nM or even lower. Following this study, Au/LCP/PA filter membranes were fabricated for the extraction and SERS detection of a pesticide (thiram) present in water samples that have been passed through such membranes. The Au NPs were previously prepared *in situ* in the presence of LCP using the citrate reduction method and then the composite was pressed upon a PA filter membrane. The distribution of the pesticide and the Au NPs on the filter surface was probed by SERS imaging as shown in Figure 6-c.
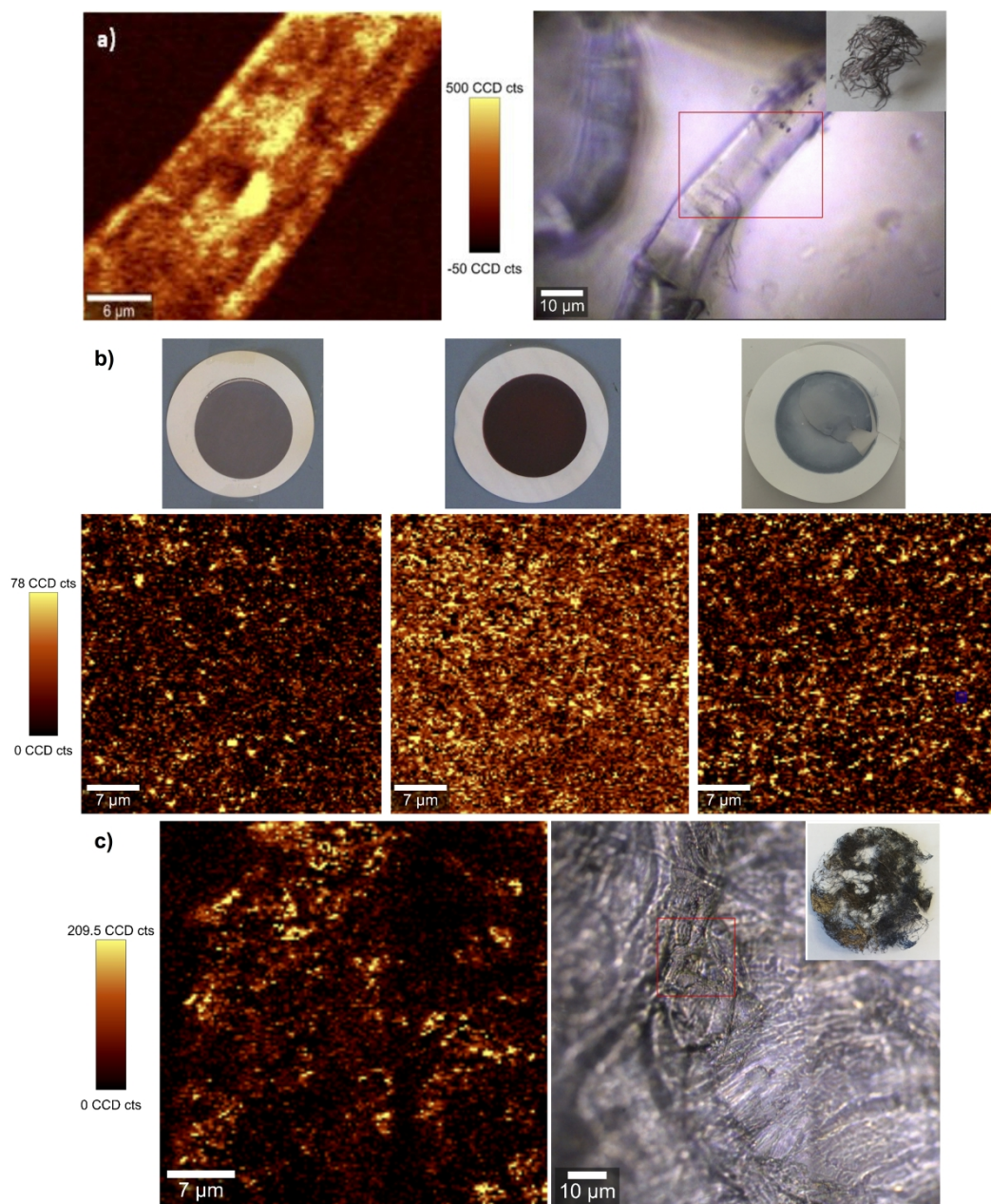
Figure 6: a) Optical /digital photographs (right) and Raman image (left) of MB 10 mM using Au/linen composite prepared by a dip-coating method. The integrated intensity of the band at 1620 cm^{-1} in the SERS spectrum (excitation at 633nm) was used for the Raman map; b) Digital photographs of Au/PA filter membranes having distinct Au NPs (15 nm NSpheres, 35 nm NSpheres, NStars) (up) and respective Raman images (down) obtained using the integrated intensity of the band at 1371 cm^{-1} in the SERS spectrum of CV (excitation at 532nm); c) Optical/digital photographs (right) and Raman image (left) of thiram using Au/LCP/PA substrates (excitation at 633 nm); the integrated intensity of the band at 1376 cm^{-1} in the SERS spectrum was used to obtain the Raman maps.

4. SERS and Raman imaging methods applied to lactic acid detection

As a last example of development of SERS substrates based on Au NPs and textile fibres, we have selected the preparation of Au loaded cotton swabs envisaging point of use technologies. These SERS substrates might find use in several contexts but we have focused our efforts on the development of robust and handy platforms to monitor lactic acid, a biomarker of great importance to monitor routine performance levels, fatigue and hydration in anaerobic-sports. The SERS detection of lactic acid has been very challenging still requiring further developments but can be regarded here as an illustrative example of a general strategy to develop textile based SERS substrates. L-lactate was selected as the analyte probe, because its concentration increases during physical exercise, making it a valuable parameter in sports medicine to monitor wellness, physical fitness and the effects of physical activity.[66] Lactic acid is mainly produced in muscle and red blood cells by an anaerobic glycolysis process, when our body needs to break down carbohydrates, to produce energy during periods of low oxygen levels. The detection of L-lactate is usually performed in blood via electrochemical methods [66, 67], however L-lactate can be found also in sweat, offering a less invasive way of measuring lactate if an adequate detection method is developed [66]. The lack of reports describing the SERS detection of L-lactate demonstrates that this has not been trivial and a possible reason is the absence of highly sensitive SERS substrates [68, 69].

Au loaded cotton net (swab) nanocomposites were prepared by an *in situ* method using the citrate reduction method in the presence of the cotton fibres. Then the substrates were evaluated as SERS substrates for the detection of L-lactate dissolved in water and using the 633 nm laser source. Figure 7-1 shows the optical spectrum of the Au/cotton swab composite and the corresponding digital photograph of the sample. The cotton fibres in the swab exhibit a purple coloration due to the presence of Au NPs, probably aggregated in some extent, in agreement with the red shift of the SPR band of Au NPs observed in the visible spectrum of the nanocomposite. For the SERS experiments, an aqueous solution of L-lactate (100mM) was prepared and a drop of 10 μL of the molecular probe was added to the surface of the Au/Cotton swab. After drying at room temperature, the nanocomposites were evaluated as active SERS substrates for the detection of L-lactate.

Figure 7-2(a) shows that the conventional Raman spectrum of an aqueous solution of L-lactate (2M). The assignment of the vibrational modes of L-lactate was made according to literature reports as follows [68, 70, 71]: 540 cm^{-1}, $\omega(CO_2)$; 866 cm^{-1}, $v(C-CO^-)$; 920 cm^{-1}, $\delta_{in-plane}(CH_3)$; 1046 cm^{-1}, $v(C-CH_3)$; 1084 cm^{-1}, $v(CO)$ from alcohol ; 1420 cm^{-1}, $v_{sym}(CO_2)$; 1457 cm^{-1}, $\delta_{assym}(CH_3)$. The Raman spectrum of L-lactate (100 mM) using the nanocomposite substrate is presented in Figure 7-2(b) and it is distinct from that of neat Au/cotton swab (Figure 7-2(c)). Raman bands of the analyte appear clearly using the composite swab as

SERS substrate and the detection limit found in these conditions was 10 mM. The bands observed at 1118 and 1091 cm^{-1} are assigned to the vibrational bands of cellulose, one of the main components of cotton. Raw cotton swabs, i.e. without Au NPs, were also used in control experiments for the detection of the analyte but the Raman signal of L-lactate was not observed in such cases. Therefore, the vibrational features observed in Fig. 7-2(b) are ascribed to SERS of L-lactate molecules in the vicinity of Au NPs present in the cotton textile fibres surface.
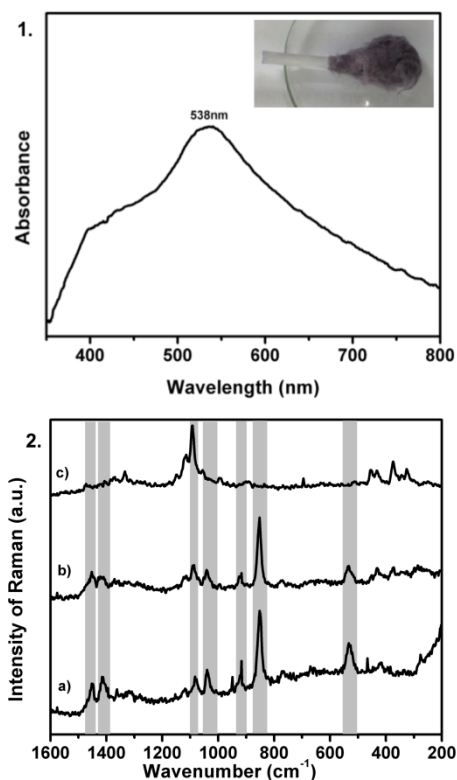

Figure 7: 1) Visible spectrum and digital photograph of Au/cotton swab composite prepared by *in situ* method; 2. a) Conventional Raman spectrum of an aqueous solution of l-lactate (2M); b) SERS spectrum of l-lactate (100 mM) dropped in Au/cotton swab; c) Raman spectrum of Au/cotton swab composite (grey bars to guide the eye).

In order to obtain Raman images of L-lactate on Au loaded cotton swab, the spatial distribution of the analyte over the surface was evaluated for selected SERS recording conditions. Figure 8 shows the optical micrographs together with the respective 2D Raman images of L-lactate, using the Au/cotton swab composite as SERS substrate. Raman imaging was performed by raster-scanning the laser beam over the composite's surface area around 235 x 210 μm^2 and accumulating a full Raman spectrum at each pixel. The Raman image was constructed by integrating the area of the band at 866 cm^{-1} assigned to the C-CO stretching mode of the L-lactate molecule. The brighter areas in the Raman map indicates strong signal from L-lactate molecules located in such regions. It also indicates the presence of Au particles in the fibres considering that the SERS signal can only be obtained for L-lactate close to the Au surfaces. The Raman images show that the analyte molecules and the

respective Au particles are evenly dispersed over the textile fibres. Future work envisages the use of these swab composites for fast collection of sweat samples and subsequent SERS detection of L-lactate.
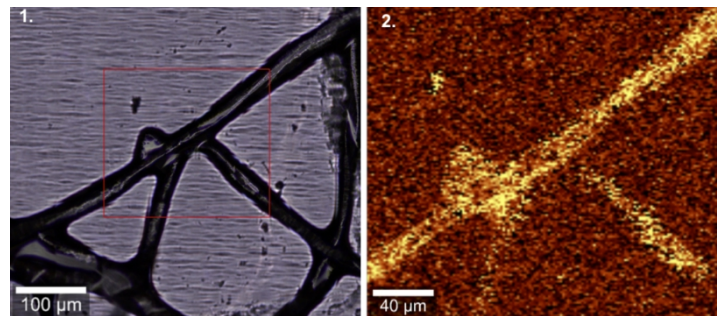

Figure 8: Optical image of Au/cotton swab showing the scanned area inside the red square (1) and Raman image (2) obtained after integrating the intensity of the Raman band at 860 cm^{-1} in the SERS spectrum of l-lactate 100 mM using such nanocomposite (excitation at 633 nm, 3 mW laser power).

5. Conclusion

This article provided an overview of our research in the development of SERS substrates based on gold loaded textiles fibres. Vestigial detection using SERS is very promising in a number of areas but still dependent on the optimization of nanostructured substrates. As such, this review focused mainly on the development of textile nanocomposites and, in particular, on aspects related to surface chemistry in order to optimize the SERS detection. Textile products containing Au nanoparticles also offer the possibility of being integrated into clothing in order to monitor biomarkers associated with various human activities. It is a field that is still underdeveloped but is anticipated as very promising, especially considering late developments on Raman instrumentation, such as Raman confocal microscopy and portable equipment.

Abbreviations

(2,3-epoxypropyl)trimethylammonium chloride – EPTAC
Crystal violet – CV
Cetyltrimethylammonium bromide – CTAB
Deoxyribonucleic acid – DNA
Gold nanorods – AuNRods
Gold nanospheres - AuNSpheres
Liquid-crystal polymer– LCP
Localized surface plasmon resonance – LSPR
Methylene blue – MB
Nanoflowers – NFs
Nanoparticles – NPs
Nanostars – NSs
Polyamide - PA
Poly(butylene succinate) – PBS
Poly(ethylene terephthalate) – PET
Poly(vinylidene fluoride) – PVDF
Poly(vinylpyrrolidone) - PVP
rGO – reduced graphene oxide
Rhodamine 6G - R6G
Sodium diethyldithiocarbamate – NaDTC
Surface-enhanced Raman scattering – SERS
Transmission electron microscopy – TEM
Ultraviolet – UV

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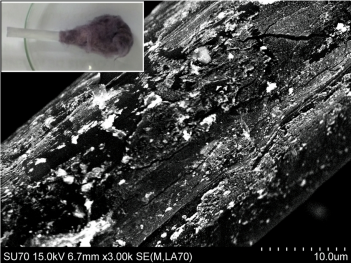
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Highlights

- Development of handy SERS substrates based on gold nanoparticles and textile fibres.

- Critical assessment of distinct strategies to prepare textile based nanocomposites loaded with gold nanoparticles.

- Application of Raman imaging coupled with SERS methods for characterization of fabrics.

- Cotton swabs coated with Au NPs as SERS substrates for the detection of L-lactate.

SERS imaging

L-lactate

H_3C O

O^-

OH