Research article

Journal of RAMAN SPECTROSCOPY

Received: 29 November 2013 Revised: 26 May 2014 Accepted: 2 June 2014 Published online in Wiley Online Library

(wileyonlinelibrary.com) DOI 10.1002/jrs.4533

Surface-enhanced Raman spectroscopy (SERS) analysis of organic colourants utilising a new UV-photoreduced substrate†

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In the present work, a new substrate is proposed for the surface-enhanced Raman spectroscopy (SERS) analysis of samples, which are of cultural heritage importance. A new and simple procedure is presented for the preparation of a stable SERS-active substrate. It is based on the photoreduction of silver nitrate by ultraviolet light utilising hydroxypropyl cellulose as stabilising agent. The substrate's characteristics were tested and compared with a known substrate: a citrate-reduced silver colloid, with alizarin as a reference material. Using the new substrate, it was possible to positively detect the organic dye alizarin red S, and two organic pigments: madder lake and alizarin crimson dark, as well as organic colourants prepared in paint layers with different organic binders without an interfering signal arising from the media, and without sample pre-treatment. Furthermore, the investigated substrate also shows promising characteristics for the analysis of the cross sections of the samples because of its viscosity and the possibility of maintaining better control of the application of the substrate to the layer of interest. Copyright © 2014 John Wiley & Sons, Ltd.

Keywords: Raman spectroscopy; SERS; silver nanoparticles; organic colourants; cultural heritage

Introduction

In the field of the cultural heritage, the identification and characterisation of materials for the accurate design of conservation and restoration treatments are a complex task. A great variety of inorganic and organic components can be found in works that have relevance for cultural heritage. For this reason, several advanced analytical approaches have been successfully employed for such investigations, including spectroscopic,[1–3] immunological[4] and chromatographic[5,6] techniques. Since ancient times, organic pigments and dyes have formed an essential part of a wide selection of artists' materials that have been extensively used for colouring textiles and on paintings mainly for glazing purposes. Glaze layers are almost translucent layers with low proportions of colourants in the organic matrix (i.e. the binder). Originally, dyes were extracted from plants (e.g. indigo dye and madder), insects (e.g. lac, kermes and cochineal) and shellfish (e.g. tyrian) and bound to metal cations to form mordant dyes or lake pigments. Organic colourants can be categorised, based on their chemical structure, into anthraquinones, flavonols, phenoxazines, carotenoids, indigoids and so on.[3,7–10]

Complete analysis of lake pigments and organic dyes is still an on-going challenge as they are usually present in low concentrations because of their high tinting potential and are mixed with other organic and/or inorganic compounds. Although conventional Raman spectroscopy has already assumed an important place in the analysis of materials of cultural heritage importance, particularly in the case of inorganic pigments, minerals and various synthetic pigments,[11–14] the technique faces great limitations when analysing natural organic lake pigments and dyes. The signal of these weakly Raman active compounds is often obscured by a large interfering background generated by luminescence, which arises from the dye itself and/or also from the organic binding medium. Surface-enhanced Raman spectroscopy (SERS) has helped to overcome this problem, because it offers signal enhancement by several orders of magnitude. SERS outranges many advanced analytical techniques for the detection of organic colourants with regard to selectivity, sensitivity and sample requirements.

Surface-enhanced Raman spectroscopy was first reported in the mid-1970s by Fleischman and his co-workers,[15] but it took more than two decades for the method to be recognised as a powerful vibrational spectroscopic technique that allows ultrasensitive analysis.[16–18] It is based on the enhancement of the Raman scattering signal of certain molecules when they are adsorbed or placed in the proximity of appropriate metallic nanostructures, usually noble metals such as silver, gold or copper.[19,20] The molecules included in the SERS effect are predominately those adsorbed onto aggregates, which are favourable for surface plasmon resonances. The rate of enhancement strongly depends on the properties and quality of the substrate.[21,22] The SERS method allows investigation of organic samples that do not usually produce a sufficient signal for the use of conventional Raman spectroscopy. Thus, it is, from many aspects,

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† *This article is part of the special issue of the Journal of Raman Spectroscopy entitled "Raman in Art and Archaeology 2013" edited by Polonca Ropret and Juan Manuel Madariaga.*

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a suitable and recommended method for the study of highly fluorescent organic colourants with weak Raman scattering activity, which can, because of their chemical nature, interact with the surface of metallic nanostructures.

Over the past decade, conservation science has benefited from the integration of SERS. The extensive study of the Raman scattering properties of the anthraquinone pigment alizarin published by Cañamares *et al.*[23] was a great contribution, followed by several studies devoted to the analysis of many different materials of cultural relevance, demonstrating the effectiveness of the SERS technique.[24–27] A variety of real samples have been already subjected to SERS studies, e.g. paintings,[26] polychrome works of art,[27] archaeological samples[28] and textile fibres.[29,30] A great number of studies are still dedicated to several red colourants,[31–33] with less focusing on the yellow[34,35] or blue[36] counterparts; however, understandings of theoretical implications and continually evolving SERS procedures are permitting valuable contributions in this field. The majority of SERS investigations rely on the use of silver or gold colloids as substrates, which are prepared by simple chemical reduction, but also other successful techniques of substrate preparation, including island films,[31] *in situ* photoreduced nanoparticles,[29,37] nanocomposite hydrogels[30,38] and colloidal pastes[39] have been introduced in this field. Several researchers have focused their attention on the development of an appropriate and efficient pre-treatment method of the investigated material. It has been shown that the gel extraction of dyes prior to SERS analysis can be used for non-destructive studies.[40] Moreover, acid hydrolysis of metal–dye complexes can lead to more intense discriminant bands in the obtained spectra depending on the release of the dye.[24,35] Even though the pre-treatment step results in an increase in sensitivity because of dye adsorption on the nanostructures, it can interfere with the integrity of the sample, and as has been shown by Pozzi *et al.*[41] it can cause degradation of the proteins in dyed silk fibres. SERS can also be successfully coupled and correlated with other analytical techniques,[42,43] often leading to even more detailed information about the structure of the pigments and dyes. Overall, development and advances in the application of the SERS method to the field of the cultural heritage are now, whenever possible, focussed on the application of the method in a minimally destructive,[44] non-hydrolysis and extractionless,[25,29,39] and minimally invasive manner.[38]

In this work, we demonstrate the use of a new (UV)-photoreduced SERS substrate, which could contribute for a better characterisation of organic colourants relevant for cultural heritage. The described facile synthesis is focussed on the preparation of SERS-active and stable silver nanoparticles using hydroxypropyl cellulose (HPC) as the stabiliser. HPC is a green reagent and a widely spread polymer, which is used in the food and pharmaceutical industry, as well as for the preparation of nanogels, which serve as precursors for novel hybrid nanomaterials[45] and in conservation science.[46] The addition of the polymer hydroxyproply cellulose to the colloidal dispersion increases the durability of the SERS substrate as well as its viscosity. The goal of this research was to investigate organic colourants as powders, in paint layers without sample pre-treatment, and to test the ability of the substrate for use on the cross sections of the samples.

Experimental

Materials

Chemicals were purchased at the following sources: silver nitrate (99.9% $AgNO_3$, Sigma-Aldrich 209139), sodium citrate dihydrate ($C_6H_5O_7Na_3 \cdot 2H_2O$, Sigma-Aldrich W302600), magnesium sulfate ($MgSO_4 \cdot 7H_2O$, Sigma-Aldrich M2773), hydroxypropyl cellulose (Aldrich 191906), alizarin ($C_{14}H_8O_4$, Sigma-Aldrich 122777), alizarin carmine (alizarin red S, Kremer Pigmente 94150), madder lake violet (Kremer Pigmente 37218) and alizarin crimson dark (Kremer Pigmente 23610). All the solutions were prepared in ultra-pure water (miliQ) using clean glassware.

Sample preparation

Model panels were prepared according to the Baroque technology.[47,48] For this purpose, organic dye (M1 – alizarin red S) and two organic pigments (M2 – madder lake, M3 – alizarin crimson dark) were dispersed in four different binders [non-fatty egg yolk (B1), fatty egg yolk (B2), linseed oil (B3) and linseed oil with mastic (B4)] and were applied as glaze paint layers on model panels and also on glass slides, which served as reference material. For the preparation of cross sections, a small amount of the sample was taken from the model panel and then embedded in the polyester resin and polished. Investigations were carried out on dye and pigments powders (without a binder), glaze layers (organic colourants in paint layers with organic binders) and on the cross sections of the samples.

Substrate preparation

Three different SERS substrates were prepared: two UV-photoreduced colloids and a citrate-reduced colloid (Lee–Meisel colloid).

The UV-photoreduced silver colloids were prepared using hydroxypropyl cellulose (HPC) as the stabilising agent. Silver nitrate and HPC were dissolved in miliQ water to achieve a weight ratio between $AgNO_3$ and HPC of either 1 : 0.6 (AgHPC1) or 5 : 0.6 (AgHPC5). The solutions were stirred for 2 days at room temperature so that the HPC was completely dissolved and swelled. The selected ratio between the silver nitrate and the HPC was chosen in order to achieve complete water solubility of the HPC in correlation to the time of preparation, whilst achieving satisfactory viscosity and preventing rapid sedimentation of formed nanoparticles under the chosen conditions. Reduction was carried out in a UV illuminator.

The citrate-reduced silver colloid was prepared following the procedure described by Lee and Meisel.[49] Of $AgNO_3$, 18 mg was dissolved in 100 ml of miliQ water and heated to its boiling point. Whilst stirring, 2 ml of the reducing solution, which consisted of 1 wt.% sodium citrate, was added. The solution was kept at boiling point for another hour. Prior to the SERS analysis, aggregation of silver colloid was induced by 0.1 M $MgSO_4$ (2.5 ml of colloid and 0.5 ml of the aggregating agent). Then, individual drops of the aggregated colloid were deposited on the investigated samples.

Methods

Optical microscopy

The cross sections of the samples were examined with an Olympus BX 60 microscope, which was connected to a JVC 3-CCD video camera using visible light.

Raman spectroscopy

The spectra of the samples and substrates were recorded using a 514.5 nm laser excitation line with a Horiba Jobin Yvon LabRAM HR800 Raman spectrometer coupled to an Olympus BXFM optical microscope. The spectra were recorded using a x100 objective lens and/or a x50 long working distance objective lens, and a 600 grooves/mm grating, which gave a spectral resolution of ~1 cm^{-1}/pixel. The power at the samples was set to between

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0.02 and 2 mW using neutral density filters. A multi-channel, air-cooled CCD detector was used, with integration times of between 20 and 50 s, and the spectral range was set between 50 and 2500 cm^{-1}. The wavenumber calibration was performed using a silicon wafer. For the SERS analysis, a drop of the substrate was deposited on a small amount of powder samples or on the surface of the prepared paint layers, which partially dissolved in the SERS substrate. The SERS spectra were collected from the drop or at the interface of the sample and the drop. When analysing the cross sections of the samples, a capillary (application under the microscope, drop diameter approximately 200 μm) was used to precisely apply the substrate above a specific layer (the area of interest), and the spectra were recorded from the interface between the substrate drop and the paint layer of interest.

UV–vis absorption spectroscopy

The UV–vis spectroscopy measurements of colloid solutions were performed within the spectral range of 200–800 nm, using a Perkin Elmer Lambda 750 spectrophotometer.

Field emission scanning electron microscopy

The size and shape of the silver nanoparticles were determined by field emission scanning electron microscopy (FE-SEM, Zeiss ULTRA plus, Germany). Micrographs were obtained using secondary electron detectors (InLens and SE2). The measurements were performed in the low-voltage mode ($V = 1–3$ kV).

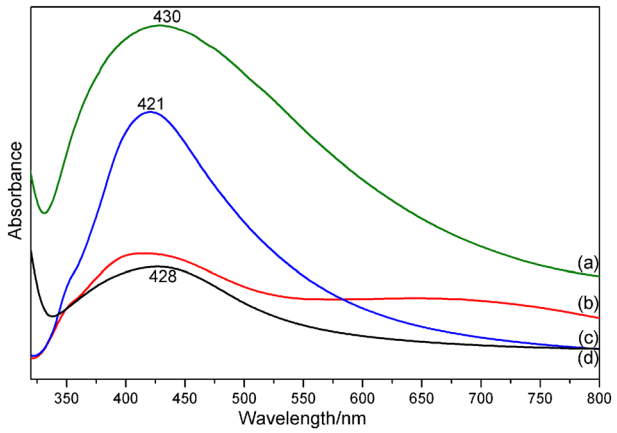

Figure 1. UV–vis absorption spectra of (a) the UV-photoreduced substrate AgHPC5, (b) the aggregated Lee–Meisel colloid, (c) the Lee–Meisel colloid and (d) the UV-photoreduced substrate AgHPC1.

Results and discussion

Characterisation of the SERS substrates

UV–vis absorption spectroscopy and electron microscopy

The substrates were examined by means of UV–vis absorption spectroscopy in order to determine the position of the surface plasmon resonance of the prepared nanoparticles (Fig. 1). The solution of the Lee–Meisel colloid showed a grey–greenish colour with a maximum in the UV–vis absorption spectrum centred at 421 nm [Fig. 1(c)], which corresponds to the localised surface plasmon resonance of the silver nanoparticles. The UV-photoreduced colloids (AgHPC1 and AgHPC5) have a yellowish tint. Maxima of the localised surface plasmon resonances were detected at 428 and 430 nm, respectively [Fig. 1(a) and (d)]. Both bands are broadened, implying that the particles are rather polydispersed. The diameter of the UV-photoreduced nanoparticles varies between 20 and 60 nm in the AgHPC1 colloid, and 20 and 80 nm in the AgHPC5 colloid. The band positions are consistent with the average size of Ag nanoparticles, suggesting a higher average size in the case of the AgHPC5 colloid. This assumption is supported by the observation that the position and bandwidth of the plasmon absorption of colloidal nanoparticles are size dependent, as has been reported by Link and El-Sayed.[50] The nanoparticles in the Lee–Meisel colloid are isolated and occur in a variety of shapes, such as spheres, rods and needles (the SEM images not shown). The UV-photoreduced silver nanoparticles yield mainly spherical particles, which are also formed in segregated aggregates of the nanoparticles as revealed by electron microscopy (Fig. 2). The presence of aggregates can also arise in the case of solvent evaporation and volume reduction of the substrate, which can result in the particles coming close to one another, as also explained by Aldeanueva-Potel *et al.*[51] On the contrary, the formation of aggregates in the Lee–Meisel colloid is induced after the addition of the $MgSO_4$ solution, which is also confirmed by the differences in the absorption spectrum, with band broadening and increased absorbance in the region between 600 and 800 nm [Fig. 1(b)]. The UV-photoreduced nanoparticles remained stable in the suspension for several months. Their stability is attributed to the stabilisation provided by the hydroxypropyl cellulose because of the structure of the polymer with its long chains of a high molecular weight. It is most likely that the silver nanoparticles are loaded and trapped inside the structure. For this reason, the rapid sedimentation and precipitation of silver and eventual loss of performance of the SERS substrate were avoided. The structure of the HPC is very complex, so it seems that more than one mechanism (e.g. the possible formation of different reducing active sites formed under UV exposure) is

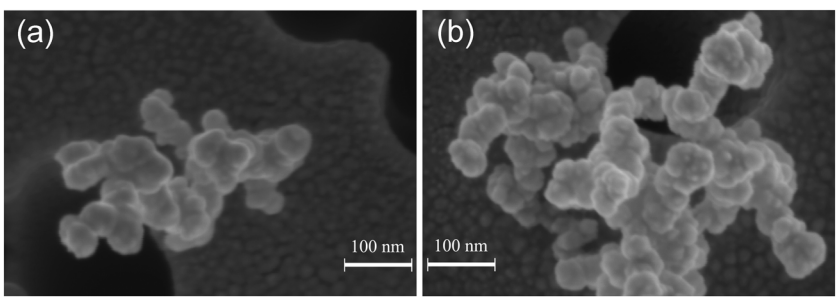

Figure 2. FE-SEM images of (a) AgHPC1 and (b) AgHPC5.

involved in the formation of silver nanoparticles and in their stabilisation, which is all still under investigation.

Raman spectroscopy

The excitation line of 514.5 nm was chosen to increase sensitivity, as high SERS intensities occur when the excitation line overlaps the plasmon resonance. The UV-photoreduced substrates (AgHPC1 and AgHPC5) alone showed only weak Raman activity because there are no specifically strong Raman bands in the spectra [Fig. 3(c) and (d)]. The most pronounced band is located at 1050 cm^{-1} and most likely indicates the presence of a nitrate group [$\nu(NO_3^-)$] in the solution, which is also consistent with the assumed reaction reduction path. UV light initiates and accelerates the reduction of silver(I) ions to silver in a zero oxidation state (nanoparticles), and the nitrate ions remain in the solution. The band positions between the substrates and the silver nitrate solution are in good agreement [Fig. 3(b)–(d)]. Contrastingly, the Lee–Meisel colloids exhibit a typical background signal because of the different vibration modes of the citrate ions and/or of the reduction by-products.[52] The bands assigned as citrate bands are even more enhanced in the case of the aggregated colloid [Fig. 3(a)]. The addition of aggregating agents is, in the case of photoreduced substrates, not necessary as the aggregates are already present. Comparing the SERS spectra of the Lee–Meisel colloid and of the UV-photoreduced colloids [Fig. 3(a), (c) and (d)], it can be concluded that UV-photoreduced substrate showed less spectral interference for the further analysis of target molecules.

Testing of SERS activity using alizarin as a probe molecule

The SERS activity of newly prepared UV-photoreduced silver colloid was tested with alizarin as a probe molecule and compared with the well-known SERS-active colloid, known as the Lee–Meisel colloid. Alizarin was chosen as it is one of the most common chromophores in organic dyes and pigments used as artists' materials. The SERS bands of alizarin using UV-photoreduced substrates [Fig. 4(a) and (b)] are observed at 345, 399, 473 and 636 (skeletal vibrations), 664 γ(C═O)/δ(CCC), 684 γ(C═O)/γ(C–O), 766 γ(C–H)/γ(C═O)/τ(CCCC), 820 ν(CC), 903 γ(C–H), 1018 ν(CC)/δ(CCC), 1052 δ(CCC), 1162 ν(CC)/δ(CH), 1189 ν(CC)/δ(CH)/δ(CCC), 1211 δ(CH)/δ(CCC), 1262 ν(CO)/ν(CC), 1290 ν(CO)/ν(CC)/δ(CCC), 1324 ν(CC), 1427 ν(CC)/δ(COH), 1480 ν(CO)/ν(CC)/δ(CH), 1561 ν(CC), 1590 ν(CC) and 1609 cm^{-1} ν(CC).[23] The band positions are consistent with those typical of alizarin, also obtained using the aggregated Lee–Meisel colloid [Fig. 4(c)] and published in the literature.[23] However, in comparison with the spectrum of alizarin obtained with the aggregated Lee–Meisel colloid, some differences in the band intensities can be observed. The observed variations of the relative intensities in the region above 1400 cm^{-1} can be attributed to the different adsorption modes of the alizarin molecules on the surface of the nanoparticles. In the case of the photoreduced substrates, the relative intensity of the band at 1427 cm^{-1} is increased in comparison with the intensity of the band obtained with the aggregated Lee–Meisel colloid, which could be the consequence of a strong contribution of the dianionic form with two deprotonations. On the other hand, the observed variations in the band intensities also depend on the selected excitation wavelength and on the concentration of the alizarin.[23] In such cases, it is important to consider a number of parameters that can affect the spectral response, i.e. the acid–base properties of the investigated molecule and the pH value of the colloidal solution, the concentration of the alizarin and the energy of the incident light. Further collected results were obtained by using the UV-photoreduced substrate with a lesser initial amount of silver nitrate, which made it possible to obtain better results.

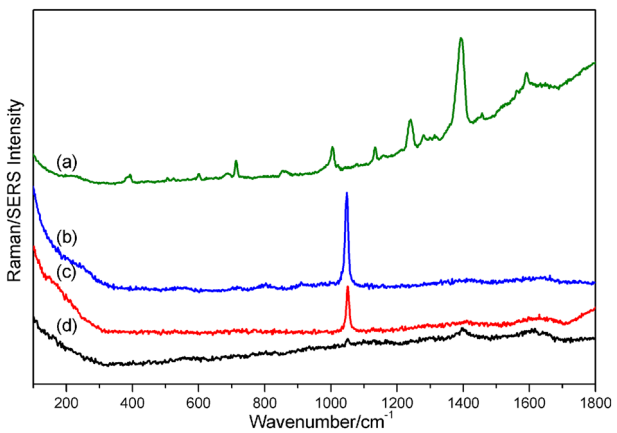

Figure 3. Spectra of (a) the aggregated Lee–Meisel colloid, (b) the silver nitrate solution, (c) the UV-photoreduced substrate AgHPC5 and (d) the UV-photoreduced substrate AgHPC1.

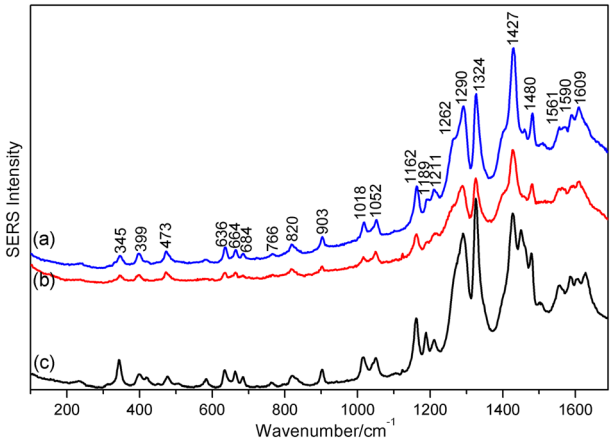

Figure 4. SERS spectra of alizarin using (a) the UV-photoreduced substrate AgHPC1, (b) the UV-photoreduced substrate AgHPC5 and (c) the aggregated Lee–Meisel colloid.

SERS of organic colourants using UV-photoreduced colloids

Dye and pigments powders

Alizarin red S is a hydroxyanthraquinone derivative with a sulfonate group bonded to an aromatic ring. Figure 5(a) shows the SERS spectrum of the dye powder obtained using the UV-photoreduced substrate AgHPC1. Typical bands can be observed at 326, 370, 412, 455, 483, 595, 795, 876, 929, 1036, 1060 $\nu(SO_3)$, 1166 $\nu(SO_3)$, 1182 ν(CC)/δ(CH)/δ(CCC), 1248 ν(C═O), 1328 ν(CC), 1427 ν(CC)/δ(COH), 1450, 1467 ν(CC)/δ(COH)/δ(CH), 1483 ν(C═O)/ν(CC)/δ(CH), 1540, 1566, 1635 cm^{-1} ν(C═O).[53] Often, some variations in the relative intensities, especially of the bands located at ~1427, 1450 and 1467 cm^{-1}, can be observed, which can be explained by the chemical interaction between the dye and colloid surface and the changes in the spectra as a function of the time of application of the substrate and the measurement.[53]

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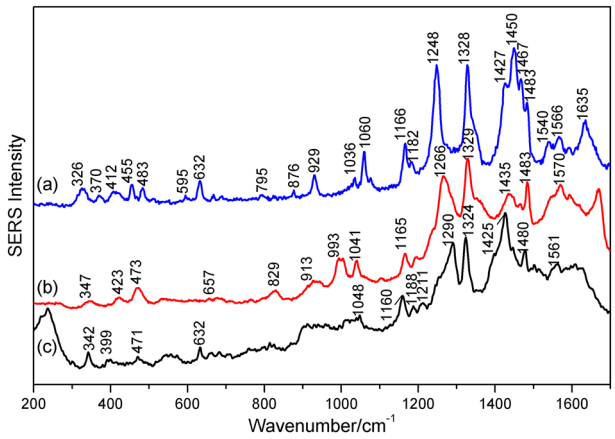

Figure 5. SERS spectra of (a) alizarin red S, (b) madder lake and (c) alizarin crimson dark, using the UV-photoreduced substrate AgHPC1.

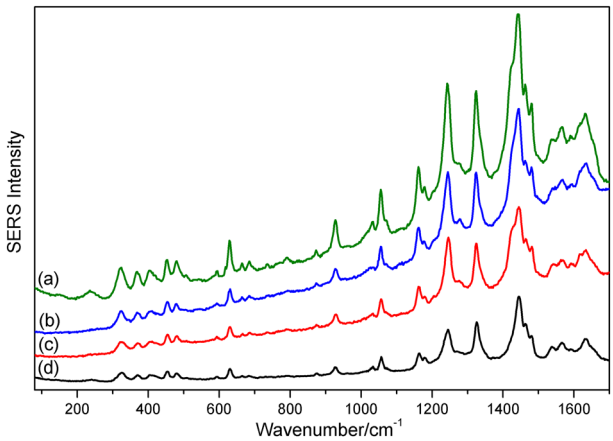

Figure 6. SERS spectra of alizarin red S dispersed in four different organic binders; (a) fatty egg tempera, (b) linseed oil with mastic, (c) linseed oil and (d) non-fatty egg tempera.

Figure 5(b) shows the SERS spectrum of madder lake. The selected pigment was prepared according to a historic recipe from the extract of a madder plant's root as indicated by the supplier. According to a study of alizarin and purpurin lakes, which was performed by Van Elslande *et al.*[28] it seems that both lake pigments were detected in our sample. The stronger contribution of purpurin lake can be suggested, based on the high intensities of the bands located at 913, 993, 1165, 1266, 1329 and 1483 cm^{-1}. Usually, alizarin or its lake is easier to detect because of its lower detection limit in comparison with purpurin, and differentiation between them can be accomplished on the basis of the presence of the band located at 993 cm^{-1}, which belongs only to the purpurin lake.[28]

Alizarin crimson dark is an organic pigment, based on the dyestuff alizarin, which was also unambiguously identified [Fig. 5(c)]. The presence of alizarin as the main colouring matter was confirmed based on the observed bands at 342, 399, 632, 1048, 1160, 1290, 1324, 1425, 1480 and 1561 cm^{-1}.[23]

Organic colourants in the paint layers

In order to examine the effect of different organic binders on the accurate characterisation of organic dyes and pigments, a number of samples were prepared by mixing the colourants with binders having different chemical structures. Two major limitations that can cause incomplete and/or incorrect interpretation exist: luminescence arising from the media obscuring the spectra of the colourant or an enhanced signal of the binder overlapping the signal of the colourants. When analysing the organic dye alizarin red S, dispersed in four different organic binders (non-fatty and fatty egg yolk, linseed oil and linseed oil with mastic), a perfect similarity in the spectral features (Fig. 6) was observed with regard to the position and intensity of the bands. A comparison with the SERS spectrum of the dye powder [Fig. 5(a)] clearly showed that it was exclusively this organic colourant, which exhibited higher signal enhancements. Identification of alizarin red S was successful without sample pre-treatment, and no interfering signal of the binder was present. Similarly, purpurin lake was also confirmed in the paint layers prepared from madder lake in two different organic binders (non-fatty egg tempera, and linseed oil and mastic) (Fig. 7). In both cases, positive detection was confirmed according to the bands that were located at 331, 416, 461, 610, 655, 825, 925, 988, 1034, 1160, 1197, 1267, 1285, 1325, 1430, 1481, 1538, 1572 and 1595 cm^{-1}.

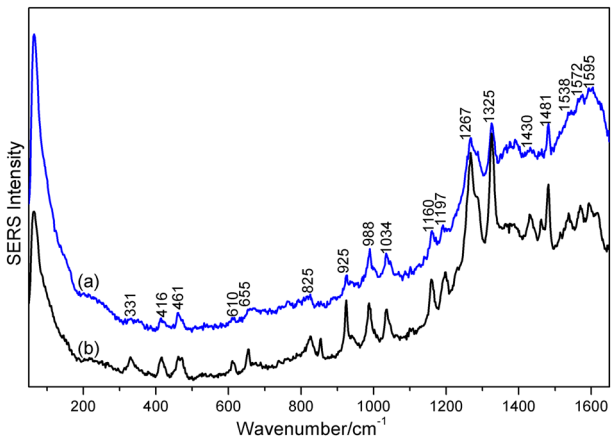

Figure 7. SERS spectra of madder lake paint layers prepared in two different organic binders; (a) linseed oil with mastic and (b) non-fatty egg tempera.

SERS performed on the cross sections of the samples

The SERS research also included examination of the glaze on the cross section of the sample (Fig. 8) taken from a mock panel. Based on the higher viscosity of the substrate, improved control of the application was achieved, compared with the other tested substrate that had a lower viscosity (i.e. the Lee–Meisel colloid). Precipitation of silver onto the larger part of the sample was thus avoided. Despite the small thickness (below 10 μm) of the investigated layer and the low concentration of the organic dye, positive detection of alizarin red S (Fig. 9) utilising the substrate AgHPC1 was confirmed by the bands that were located at 324, 372, 406, 455, 484, 632, 666, 687, 929, 1057, 1165, 1246, 1326, 1427, 1443, 1464, 1483, 1544, 1564 and 1620 cm^{-1}. The UV-photoreduced substrate allowed selective identification of the investigated dye present in the glaze layer without interfering signal from the organic media or the components making up the layers below the glaze. These were the first tests of the new SERS substrate's performance on the cross sections of the samples. To achieve an even smaller area of application and thus better control of the deposition of the substrate onto the desired paint layer within the cross sections of the samples, further improvements of the substrate in terms of optimised viscosity, and improvements in application method are needed.

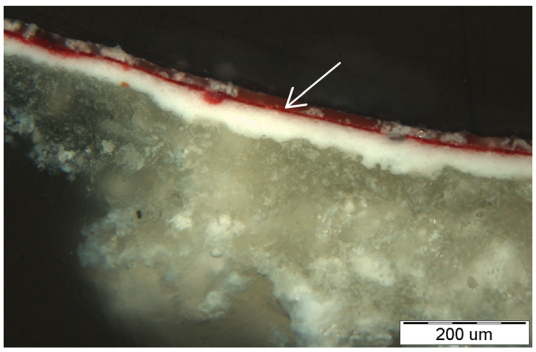

Figure 8. Photomicrograph of the cross section of a sample. The investigated layer is marked with an arrow.

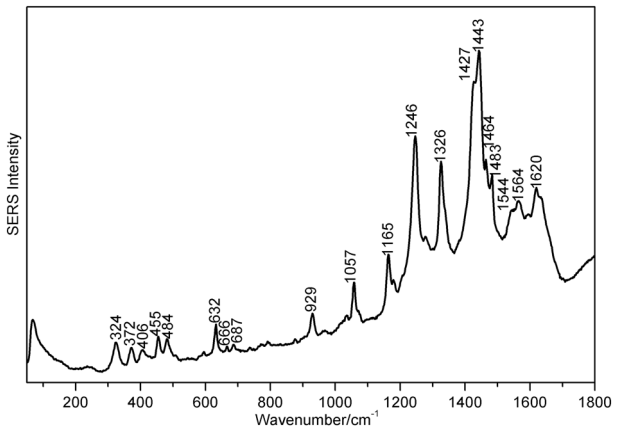

Figure 9. SERS spectrum obtained on the glaze layer, identifying organic dye alizarin red S.

Conclusions

The presented research focussed on the synthesis of a stable and reproducible substrate of high viscosity. The UV-photoreduced substrate showed great potential for use in the characterisation of paint layers in works of art as it gave promising results for the detection of organic dyes and pigments. In general, Ag colloids must be aggregated in order to obtain better enhancement. The aggregation induced by external agents and, consequently, enhancement of the Raman signal are difficult to reproduce, and therefore, it is paramount that these processes are carefully controlled. In the case of the presented substrate, aggregates are formed already in the colloidal suspension and stabilised sufficiently to avoid rapid precipitation of silver out of the solution. Consequently, there was no need for the additional formation of silver aggregates, which can be a step in the SERS procedure that gives rise to undesirable effects on the obtained vibrational information. The complete reduction and nanoparticle formation mechanisms are as yet still under investigation. With regard to this study, the investigated substrate also provided selectivity in the case of the identification of organic dyes and pigments prepared in paint layers using different organic binders, without interfering signal, and without sample pre-treatment. Owing to the high viscosity of the substrate, it was possible to exert better control of the application of the substrate, when examining the thin glaze made of organic dye on the cross section of the sample taken from a mock panel. Thus, the precipitation of silver onto the larger part of the sample was avoided. On the basis of this study, the advantages of the new UV-photoreduced substrate can be attributed especially to SERS activity, stability and viscosity. With further optimisation of the substrate's properties, a complete analysis of the stratigraphy of the samples on cross sections in the presence of organic pigments or dyes could be performed with minimal intervention and contamination. Our further work will focus on optimisation of the substrate's preparation, as well as of its characteristics, and on the expansion of the range of application of the substrate to the study of other and more complex chemical substances.

Acknowledgements

The financial support of the Slovenian Research Agency (grant L6-4217) is much appreciated. This article is also a result of doctoral research, in part financed by the European Union, European Social Fund and the Republic of Slovenia, the Ministry for Education, Science and Sport within the framework of the Operational programme for human resources development for the period 2007–2013 (operation No. 3330-13-500221). Furthermore, the authors would also like to thank Barbka Gosar Hirci, academic painter, Head of the Easel Paintings Department (Institute for the Protection of Cultural Heritage of Slovenia, Conservation Centre, Restoration Centre) for the help with the preparation of the model paintings.

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