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Raman spectroscopy of organic dyes adsorbed on pulsed laser deposited silver thin films

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ABSTRACT

The results of a surface-enhanced Raman scattering (SERS) study performed on representative organic and inorganic dyes adsorbed on silver nanostructured thin films are presented and discussed. Silver thin films were deposited on glass slides by focusing the beam from a KrF excimer laser (wavelength 248 nm, pulse duration 25 ns) on a silver target and performing the deposition in a controlled Ar atmosphere. Clear Raman spectra were acquired for dyes such as carmine lake, garanza lake and brazilwood overcoming their fluorescence and weak Raman scattering drawbacks. UV–visible absorption spectroscopy measurements were not able to discriminate among the different chromophores usually referred as carmine lake (carminic, kermesic and laccaic acid), as brazilwood (brazilin and brazilein) and as garanza lake (alizarin and purpurin). SERS measurements showed that the analyzed samples are composed of a mixture of different chromophores: brazilin and brazilein in brazilwood, kermesic and carminic acid in carmine lake, alizarin and purpurin in garanza lake. Detection at concentration level as low as 10^{-7} M in aqueous solutions was achieved. Higher Raman intensities were observed using the excitation line of 632.8 nm wavelength with respect to the 785 nm, probably due to a pre-resonant effect with the molecular electronic transitions of the dyes.

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1. Introduction

Identification of dyes is of central interest in the cultural heritage field from the historical, conservation and restoration view points. Although several analytical techniques can be used to identify such dyes, most of them show limitations when they are applied to organic dyes, or to exiguous sampled quantities, as is required in artwork analysis [1,2]. In particular elemental signature is missing in X-ray fluorescence [3], Fourier transform infrared spectroscopy suffers from the presence of binders and extenders, UV–visible absorption spectroscopy is scarcely specific [4]. In this respect micro-Raman spectroscopy is a non-destructive technique able to detect dyes and to provide a precise molecular fingerprint. The technique finds application with a variety of substances, but presents two main problems: analytes such as natural and synthetic dyes found in textiles, inks, and paints have very low Raman scattering cross sections and a fluorescent background, that put severe limits to the quality of the spectra [5,6]; such problems are

expected whenever the Raman activity is associated to the presence of C–H and O–H groups [7].

Surface-enhanced Raman scattering (SERS), using noble metal surfaces appropriately corrugated at the nanometer scale, exploits the giant field enhancement at the metal surface to increase the Raman signal, thus making possible the detection of analytes even at very low concentrations [8].

Several varieties of dyes can be produced following different extraction procedures: this way each dye is characterized by various chromophores, still being identified by the same general name. Carmine lake for example, has different origins depending on the insect specie from which the dyes were extracted: namely *Dactylopius coccus*, *Kermes vermilio* and *Kerria lacca*. The corresponding chromophores are carminic, kermesic and laccaic acid. Kermes and cochineal are obtained by water or alcohol extraction of the dried wingless female scale insects of two different species: *K. vermilio* Planch (kermes) and *D. coccus* L. Costa (cochineal) either cultivated or wild. In the case of brazilwood, the chromophores are brazilin and its oxidized form brazilein; they are obtained from the West Indies and South America, and belong to the genera *Caesalpinia* and *Peltophorum* of the natural order Leguminosae [9]. The colouring-matter of brazilwood is extracted for use by simple infusion or decoction of the coarsely-powdered wood. When freshly prepared

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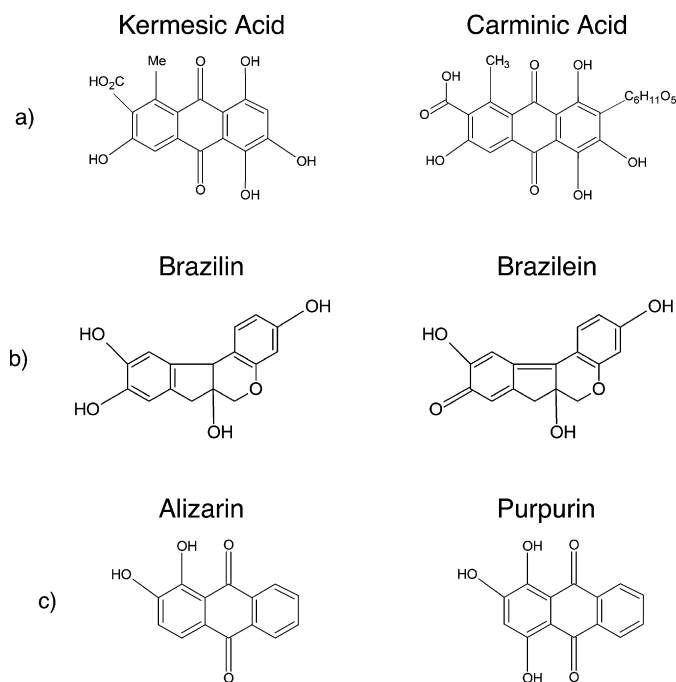


Fig. 1. Structural formulae of (a) kermesic and carminic acid, (b) brazilin and brazilein, (c) alizarin and purpurin.

the extract is yellowish; by contact with the air, or by addition of an alkaline solution, it develops a brick-red colour. As to garanza lake, it has vegetal origins, being extracted from the root of *Rubia tinctorum* plant. It usually refers to two different chromophores: alizarin and purpurin. The structural formulae of the above mentioned chromophores are reported in Fig. 1.

In this frame a non destructive analytical identification of key molecular signatures for the main components of dyes is fundamental in the cultural heritage field. In a previous paper [10] the SERS activity of substrates covered with gold and silver nanostructures grown by pulsed laser ablation was found to depend both on the substrate preparation method (pulsed laser ablation PLD, or pulsed laser ablation in liquid, PLAL) and on the nature of the metal (gold, or silver). With PLD synthesized films, made of self-assembled silver nanoparticles, the Raman features of *all* the investigated dyes were identified, while with gold substrates only brazilwood and dragon blood showed a clear Raman activity. With colloidal solutions, either using silver, or gold, Raman activity was detected only in the case of brazilwood.

In this paper we aim at testing the lowest detection limit. Aqueous solutions of the investigated dyes were prepared at different molar concentrations down to 5×10^{-7} M. We used glass substrates covered with silver nanoparticles deposited by PLD, due to their superior SERS activity. For all investigated dyes clear Raman spectra were acquired that allowed for the identification of the constituent chromophores.

2. Experiment

Silver nanoparticles were deposited onto glass slides, with typical dimensions of 1 cm^2 , by pulsed laser ablation. A detailed description of the deposition can be found in previous works [11–14]. The relevant process parameters used in this study are: Ar pressure 70 Pa, number of laser shots 30,000, laser fluence 2.0 J cm^{-2} , target to substrate distance 35 mm. The surface morphology was studied by Scanning electron microscopy (SEM) using a Zeiss Supra 40 field ion microscope. Before carrying out the measurements, the SERS activity of the substrates was tested using a

Rhodamine 6G (R6G) aqueous solution at the concentration level of 1×10^{-4} M. Aqueous solutions of the investigated dyes were prepared at the molar concentrations of 5×10^{-3} M, 5×10^{-4} M, 5×10^{-5} M, 5×10^{-6} M and 5×10^{-7} M by a dilution procedure. The metallic substrate, together with an uncovered glass slide, were soaked into the solutions for 1 h, then rinsed with deionized water and dried in air. SERS measurements were performed thereafter. Raman spectra were excited with both the 632.8 nm and the 785 nm laser lines. The Raman signal was collected with a Jobin Yvon HR 800 spectrometer equipped with a Peltier-cooled charge-coupled device (CCD) sensor as the detector; the elastically scattered radiation was rejected by a RazoEdge filter. The laser power at the sample surface was kept as low as possible using a long working distance $50\times$ microscope objective and a neutral optical filter to avoid sample degradation; representative laser power values at the sample surface ranged between 0.45 and 0.04 mW. Accumulation times were varied, depending on the signal-to-noise ratio, between 2 and 240 s; all spectra reported here are normalized to their own integration times. UV–visible absorption spectra were obtained using an UV/VIS/NIR Lambda 750 spectrometer (PerkinElmer) in the 190–1100 nm range. Dyes were used as received from Zecchi (Florence).

3. Results and discussion

3.1. Silver thin films morphology

In Fig. 2a the SEM image of the surface of a silver substrate deposited by pulsed laser ablation is shown. The growth mechanism of nanostructured silver thin films was studied in previous papers [11–13]. It was found that fixing the other deposition parameters, *i. e.* laser wavelength, fluence and target to substrate distance at 248 nm, 2.0 J cm^{-2} and 35 mm respectively, changing laser pulse number and Ar pressure it is possible to control the morphology of the silver thin films. It was found that sample surface morphology can be controlled using these two parameters, ranging from percolated structures, to silver islands, to nearly spherical, isolated nanoparticles. The SERS activity of the resulting films is strictly related to their surface morphology. The samples used as SERS substrates in this study, which were grown at 70 Pa of Ar, using 30,000 laser pulses, were the most SERS sensitive substrates [13]. The surface morphology is characterized by a dense network of isolated nanoparticles. The surface plasmon peak shown in Fig. 2b lies at about 680 nm: the large red shift of the plasmon position, besides its broadening with respect to the one measured for isolated nanoparticles around 400 nm [15], can be attributed to the strong electronic coupling between closely spaced Ag nanoparticles.

3.2. UV–visible absorption spectroscopy

The materials presented herein were chosen because they are the most commonly found in artistic production from the antiquity to the 19th century. UV–visible absorption spectra of carmine lake, brazilwood and garanza lake water solutions are displayed in Fig. 3. Garanza lake shows weak absorption: indeed the spectrum in Fig. 3, that is magnified by a factor of two for clarity, refers to the solution of highest concentration (5×10^{-3} M). UV–visible spectra of carmine lake and brazilwood refer to the 5×10^{-5} M concentration. The main features are a band located at 280 nm and a weak and broad band between 500 and 600 nm. Concerning carmine lake spectrum, two absorption bands are located at 280 and 330 nm, while a structured band is observed between 400 and 600 nm. These bands are attributed to the different acid–base forms of carminic acid when it is dispersed in water: CA, CA⁻, CA²⁻, CA³⁻ and CA⁴⁻, with the associated bands at 473, 493, 530 and 565 nm,

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