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Raman mapping and time-resolved photoluminescence imaging for the analysis of a cross-section from a modern gypsum sculpture

S. Mosca^{a,*}, A. Artesani^a, D. Gulotta^b, A. Nevin^c, S. Goidanich^b, G. Valentini^a, D. Comelli^a

^a Physics Department, Politecnico di Milano, Piazza Leonardo da Vinci 32, Milano 20133, Italy

^b Chemistry, Materials and Chemical Engineering "Giulio Natta" Department, Politecnico di Milano, Piazza Leonardo da Vinci 32, Milano 20133, Italy

^c Istituto di Fotonica e Nanotecnologie - Consiglio Nazionale delle Ricerche (IFN-CNR), Piazza Leonardo da Vinci 32, Milano 20133, Italy

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ABSTRACT

This work proposes a non-destructive multi-analytical approach, based on Raman and photoluminescence mapping to characterize the constituent materials and the stratigraphy of a multi-layer sample from a 19th century sculpture by Pompeo Marchesi. The study exploits a macro-Raman device, capable of mapping heterogeneities on a scale from sub mm² to cm² without the need for refocusing. The combination of the macro-Raman probe with a more conventional micro-probe improves the quality of Raman spectra and allows the material identification with a high level of confidence. Time-resolved photoluminescence microscopy allows the mapping of photoluminescent centres in the micro-sample, ascribed to crystal defects in inorganic materials. The proposed combination of optical analytical techniques provides an in-depth characterization of the constituent materials of the sample, yielding insights on its conservation history. The protocol could be potentially extended to the analysis of cross-sections of paintings.

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1. Introduction

The investigation of artefacts of the cultural heritage is generally aimed at the characterization of the constituent materials and the evaluation of their state of conservation. Research may shed light on the artistic and technical features of the artwork and on potential deterioration mechanisms, but also on the unique history of conservation treatments applied to the artwork. Such objectives are consistently pursued by means of a wide range of in-situ and laboratory techniques, but, given the very high value of the objects under investigation, non-destructive and micro-invasive multi-analytical approaches are desirable [1,2,3]. In the case of works of art showing complex or multi-layered finishing, the precise identification of the stratigraphic structure requires the analysis of polished cross-sections by means of different microscopic techniques. Well-established and integrated methodologies are extensively used to fulfill these tasks. Nevertheless, innovative instrumentation and improved characterization set-ups are continually developed and can provide new insights into the nature of complex layers and possibly reduce the need for extensive sampling [4,5].

In this context, the study of stone and gypsum sculptures provides a series of challenges due to their sensitivity to atmospheric interaction, especially in case of highly porous materials. In fact, such substrates can undergo serious surface alterations as discoloration, loss of material,

the formation of inorganic patinas, the development of black crusts and widespread biological attacks [6,7,8,9,10]. Moreover, sculpted surfaces of the cultural heritage can also be altered as a result of the intentional application of protective treatments or additional painted layers. It is hence clear that sculptures can have a complex stratigraphy, whose understanding in terms of both material composition and layer thickness is fundamental for the proper management of the overall conservation activity and, in particular, of the cleaning operations. For the purpose micro-samples, taken from altered surfaces, are commonly analyzed with conventional microscopy techniques, which include optical microscopy and scanning electron microscopy (SEM).

In this context, we exploit the capabilities of the combined use of Raman mapping and spectroscopy and Time-Resolved Photoluminescence (TRPL) microscopy to achieve the chemical identification of the different layers of a stratigraphic sample taken from a 19th century gypsum sculpture.

Raman spectroscopy is a widely employed technique for the study of the chemical composition of pigments and materials thanks to its high chemical sensitivity and its non-invasive nature [11,12,13]. In the framework of studies of works on stone, Raman has been used for the identification of pigments in complex polychrome sculptures [14,15] and, more interestingly, for the detection of surface decay compounds, which include hydrated sulfate and nitrate minerals on the surface of a 15th century limestone sculpture [16,17].

Photoluminescence (PL) spectroscopy has long been used to probe the peculiar luminescence emission of minerals [18], and more recently

* Corresponding author.

E-mail address: sara.mosca@polimi.it (S. Mosca).

for the in-depth study of modern semiconductor pigments [19][20][21][22] and organic and inorganic artists' materials [23]. Here, TRPL with multispectral detection is proposed in a microscopy configuration for the study of micro-samples [36]. With respect to standard epi-fluorescence microscopy, the use of a time-resolved and spectrally-resolved approach adds chemical sensitivity to standard PL observations [24]. Furthermore, the use of pulsed laser excitation and gated detection allows the elimination of the intense nanosecond emission from organic materials and the detection of the faint but significant long-lived emission from inorganic materials, which may be ascribed to specific crystal defects in semiconductors or inorganic compounds [25].

2. Material and methods

2.1. Sample

The proposed multi-analytical protocol has been tested on one stratigraphic micro-sample taken from the surface of the “Maddalena” statue (19th C.). The gypsum sculpture from the Galleria d'Arte Moderna of Milan (GAM) belongs to the artistic production of the Italian sculptor Pompeo Marchesi and depicts a female figure partially seated on a decorated cushion, with her lower body covered by drapery (Fig. S1, SI). In the past the statue was repeatedly moved through different exhibit locations, both indoors and outdoors, before being transferred to the Gallery deposit. Moreover, several maintenance activities were performed, which have altered the appearance of the artwork due to the application of additional finishing layers. Micro-samples were collected from different locations (Fig. S1, SI) in order to determine the stratigraphy of the surface and to discriminate between the historic substrate and the materials introduced in later treatments. Fragments were collected using a stainless steel scalpel and prepared in polished cross-sections using a bi-component epoxy resin (Mecaprex MA2 +®, Presi). In this work, that is aimed at validating a novel multi-analytical approach for the characterization of heterogeneous multi-layer samples, we present results of the analysis on a single sample, taken from the knee of the statue. It is worth noting that the stratigraphy identified in the selected sample is pretty representative of the finishing layers applied over the gypsum substrate of the whole statue. In fact a similar composition was detected in all the other analyzed samples. More detailed information on the results of analysis performed on all samples are provided in SI.

2.2. Raman spectroscopy

The Raman device is a flexible homemade system [16]. The system, based on a 785-nm CW laser source and a spectrometer coupled to a cooled Si-based CCD camera, allows the detection of Raman peaks in the spectral range 130–3000 cm^{-1} with a spectral resolution close to 10 cm^{-1} . The excitation and detection units are connected through optical fibers to two different optical probes (a macro- and a micro-probe), which can be alternatively used depending on the desired spatial resolution and size of the field of view. In a previous work, the performances of the two Raman probes have been studied and discussed in details [26]. Hereafter only the main features of the two probes are summarized.

2.2.1. Macro-probe

The macro-probe (MA-) Raman provides mapping capabilities [27]. The optical system, working in backscattering mode, delivers the excitation light to a point of interest of 500 μm in diameter at a working distance of 30 cm. The mapping capabilities of the device, achieved through a pair of galvanometric mirrors, allow the raster scanning of an area of interest within a field of view $65 \times 65 \text{ mm}^2$. In this work, a Raman map ($6 \times 1.5 \text{ mm}$ in size with a step of 0.25 mm) of the sample has been collected in 25 min. For each scanning point, Raman spectra have been collected in a spectral range from 130 to 1200 cm^{-1} with an acquisition time of 7 s and an irradiance of 77 W/cm^2 . Following spectral calibration of the dataset, it is possible to reconstruct one or

more Raman maps in a selected spectral window centered at the relative frequency ν . The reconstruction is performed by calculating the correlation of a triangular template (centered at the frequency ν with a base width $\Delta\nu$ of 20 cm^{-1}) with the Raman spectrum detected in each analysis point in the spectral band $\Delta\nu$. It has been reported that this post-processing method, in the following quoted as TC descriptor, is more selective than other mapping methods [28,29].

2.2.2. Micro-probe

The micro-probe allows the detection of Raman spectra at high signal-to-noise-ratio on selected spots of 50 μm in diameter at a working distance of $\sim 3 \text{ mm}$ [26]. Raman measurements have been carried out with an acquisition time between 5 and 15 s and an irradiance on sample between 700 and 3500 W cm^{-2} . In this study, the micro-probe has been used for point analysis and for line-scanning analysis along the sample. In the latter case, the micro-probe head has been coupled to a micrometric linear translation stage.

On the basis of the collected and post-processed Raman spectra, material identification is achieved through comparison with reference Raman data from a free online published database [<http://www.geologie-lyon.fr/Raman/>] or with reference Raman spectra of standard samples purchased from Kremer pigmente and Sigma Aldrich.

2.3. Optical microscopy and environmental scanning electron microscopy

A Leica M250C stereomicroscope integrated with a Leica DFC290 digital camera has been used for the preliminary observation of the cross-section.

A commercial optical microscope (Leica DM RE), equipped with a color digital camera (NIKON D750), has been employed for the observation of the sample in dark-field mode.

The polished cross-section has been analyzed in terms of Energy Dispersive X-ray (EDX) spectra, using a Zeiss EVO 50 EP Environmental Scanning Electron Microscopy (ESEM), equipped with an Oxford INCA 200 - Pentafet LZ4 spectrometer.

2.4. Time-resolved photoluminescence microscopy

The system is based on a Q-switching laser source, emitting sub-ns pulses at 355 nm, and on an intensified camera, capable of gated detection with a temporal width adjustable from few ns to the continuous mode. In conservation science this imaging device has been used to capture the emission decay kinetic of a variety of materials and works of art [25][30]. In this work both the laser and the image detector have been coupled to a microscopy stage [24], equipped with a $15\times$ reflective objective, to analyze the optical emission from the selected micro-sample [36]. The microscope has been used in epi-fluorescence mode with an excitation filter (FL355-10 Thorlabs Inc.) and a dichroic filter (LPD01-355RU, Semrock). Further, multispectral detection is achieved through a set of 10 band pass filters (FKB-VIS-40, Thorlabs Inc.) mounted on a filter wheel in front of the gated camera. The filters allow the detection of the emission in selected spectral bands (40 nm FWHM) within the spectral range between 400 and 850 nm.

In this work TRPL microscopy has been mainly employed for the detection of long-lived emissions (on the microsecond timescale) ascribed to crystal defects in minerals. Indeed, the use of a gated camera, triggered at a proper microsecond delay with respect to laser pulses, allows the detection of long-lived photons only, and is not compromised by nanosecond short-lived photons associated with fast recombination paths. The desired spectral and lifetime characterization of the long-lived optical emission is then achieved with the following measurement protocols:

- A sequence of PL gated images at a fixed delay (delay $D = 0.2 \mu\text{s}$, gate temporal width $W = 100 \mu\text{s}$) is recorded at different spectral bands. Following correction for the detector efficiency, it is possible to

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