Surface-Enhanced Raman Spectroscopy: A Direct Method to Identify Colorants in Various Artist Media

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Surface-enhanced Raman spectroscopy (SERS) has been developed as a direct, extractionless, nonhydrolysis tool to detect lake pigments and colorants of various classes used in a variety of artist materials. Presented first is the SERS analysis of the natural colorant turmeric (Curcuma longa L.), main component curcumin, as present in dry pigment. This experiment demonstrated that it is possible to detect in organic matrixes of increasing complexity, allowing its unambiguous identification in a wide range of artists' materials, even at very low concentration and in the presence of binders such as glue. In addition, removal of the colorant from the complex with the inorganic substrate or mordanted yarn was not necessary for identification. This proof-of-concept study was then extended to include analysis of several pastel sticks from a historical pastel box and two samples from a pastel artwork, both attributed to American painter Mary Cassatt (1844–1926). This study represents the first extractionless, nonhydrolysis direct SERS study of multiple artist materials, including identification of natural and synthetic colorants and organic pigments contained in historic artists' pastels spanning a broad range of chemical classes: polyphenols, rhodamines, azo pigments, and anthraquinones. Successful identification is demonstrated on samples as small as a single grain of pigment.

Identification of pigments and colorants contained in artworks and historical textiles is of fundamental importance for the study of their manufacturing technology and to their conservation and long-term preservation. Conventional methods for the identification of natural and synthetic organic dyes include high-performance liquid chromatography (HPLC) and UV–vis spectroscopy. The former method is destructive and requires relatively large amounts of sample (low microgram) not always available from priceless works of art, even if chromatographic separations followed by online identifications of separated components may sometimes be necessary to identify the biological source of the colorant down to the species level. The latter method has poor specificity and suffers greatly from matrix interferences. The ideal analytical tool for the identification of artist dyestuffs would be minimally destructive, highly diagnostic, sensitive and would be capable of probing a broad range of samples in a variety of matrixes. Among the vibrational spectroscopic techniques that have been applied to the analysis of organic colorants (i.e., Fourier transform infrared (FT-IR) and near-IR (NIR) spectroscopy), normal Raman spectroscopy in theory provides the most promise for identification of colorants in minute amounts of sample. However, normal Raman spectroscopy suffers from inherently weak signals and interference from fluorescence. As a result, this tool is not easily applied to the identification of natural organic dyes and pigments especially when the latter are embedded in biomaterial matrixes such as traditional artists’ paints or historic textiles. However, the use of surface-enhanced Raman spectroscopy (SERS) allows for both an enhanced Raman signal and substantial quenching of fluorescence through use of noble metal substrates. Recently a number of papers have reported success in using SERS to identify organic, highly fluorescent dyes commonly found in works of art. One of the most commonly followed approaches involves samples (mainly textile yarns) where the dye was extracted from the host material. A handful of studies have reported on analysis done directly on the samples without extraction; however, these studies were limited to dyed reference textiles or paint mock-ups and did not include analysis...

(11) Leona, M.; Stenger, J.; Ferloni, E. J. Raman Spectrosc. 2006, 37, 911.

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on actual historic works of art. Indeed, one of the main limitations of SERS up to the present day, seriously hampering its use in art conservation applications, has been that while it has proven greatly successful with model reference materials, translation to actual works of art has been difficult. This is because real artworks present the challenge of incorporating the target dye molecule(s) in a complex host matrix, and both dye and host matrix will have generated byproducts as a consequence of aging. The first direct SERS study of an actual archeological pigment containing purpurin was reported by Van Eslande et al. in 2008.14

The present study used nonextractive, nonhydrolysis, direct SERS for the identification of organic chromophores contained in a variety of artist materials in a proof-of-concept fashion, using reference materials containing the yellow organic dye turmeric (Curcuma longa L) main component curcumin (a polyphenol), and this methodology was then used to analyze actual historic pastel samples contained in a pastel box once belonging to American painter Mary Cassatt (1844–1926), now part of the collection of the Museum of Fine Arts, Boston, and samples from a pastel artwork attributed to Cassatt in the collection of the Art Institute of Chicago.

EXPERIMENTAL SECTION

Materials. Silver nitrate (99+%), and sodium citrate were purchased from Sigma-Aldrich (St. Louis, MO). Dyed yarn samples of turmeric, as well as turmeric pigment precipitated on alumina and turmeric pigment bound in animal glue and painted on glass, were prepared by the Getty Conservation Institute as part of the Institute’s Asian organic colorants project (details of manufactory are given elsewhere).15 Curcumin was obtained from Sigma-Aldrich (St. Louis, MO, 99%), while madder root was obtained from Kremer pigments (New York, NY). Samples from the pastel box of Mary Cassatt were provided by the Boston Museum of Fine Arts. Two minute samples were taken using a tungsten needle from the pastel artwork “Sketch of Margaret Sloane, Looking Right” attributed to Mary Cassatt and part of the collection of the Art Institute of Chicago (pastel on tan wove paper; 410 mm × 330 mm; gift of Laura May Ripley, AIC 1992.158).

Preparation of Citrate-Reduced Colloids. Citrate-reduced silver colloids were prepared using the standard Lee and Meisel preparation,16 having a peak absorption wavelength of ~500 nm and a full width at half-maximum (fwhm) of ~100 nm. After being cooled, they were centrifuged 10 times (relative centrifugal force = 36 000g, 15 min per cycle) to concentrate the colloid. The colloids prepared this way were stable at room temperature (stored in the dark) for up to 3 weeks.

Surface-Enhanced Raman Spectroscopy. All SER spectra were collected on a custom-built macro setup. The 632.8 nm excitation was obtained using a HeNe laser (12 mW output power, 9 mW at the sample, 0.8 mm beam diameter) (Research Electro-Optics, Boulder, CO). The SERS measurements employ 1 in. interference and notch filters (Semrock, Rochester, NY), a single-grating monochromator with the entrance slit set to 100 μm (model VM-505, Acton Research Corporation, Acton, MA), a liquid N2 cooled charge-coupled device (CCD) detector (model Spec10:400B, Roper Scientific, Trenton, NJ), and a data acquisition system (Photometrics, Tucson, AZ). The spectral positions of the CCD pixels were calibrated using a neon lamp. The spectral resolution was 4 cm−1. Although excitations of 532 and 785 nm were also evaluated for SERS of these dyes, 633 nm excitation was found to give the most intense SERS signal, with a minimum of interfering fluorescence.

Sample Preparation. For all of the samples in this study, 5 μL of the centrifuged, citrate-reduced colloids was added directly to the sample and mixed with a clean gold wire. The sample mixed with the colloids was then applied to a clean glass microscope slide (if not already present on a microscope slide), and the SER spectra were recorded after the colloid paste had dried onto the sample. Excellent SER spectra could be obtained from the same sample after several months of storage.

RESULTS AND DISCUSSION

Proof-of-Concept Study on Curcumin-Containing Reference Materials. As proof-of-concept for the application of nonextractive, nonhydrolysis SERS for the direct detection and identification of natural organic dyes in a variety of artists’ materials and media, turmeric, used as a dye or precipitated on alumina to form a lake pigment, was studied. This colorant was chosen because it was available in several different matrices that could be studied and also because, although several studies of anthraquinones have been published,12,17–19 far fewer SERS studies on yellow lake pigments are available.20 Parts a–c of Figure 1 show the SER spectra for a painting layer containing turmeric lake bound in animal glue (as could be suggested, for example, in traditional Asian wall paintings)15 and painted on glass, a curcumin-dyed silk yarn, and for turmeric precipitated out on alumina, respectively. When compared to the SER spectrum for the free dye (curcumin) (Figure 1d), the data show that all three spectra are distinctive for curcumin, having bands arising at 1587, 1525, 1489, 1293, 1250, 1158, and 1125 cm−1.20 These results indicate that SER spectra can be obtained without the need for extraction/hydrolysis of the pigment from the host material. In fact, although slight laser photodegradation of the mordanted dye was observed, evidenced by the appearance of large, broad background features at ~1250 and ~1550 cm−1 (due to amorphous carbon),20 its extent is less significant compared to the free dye, indicating enhanced photostability of the complex. This experiment represents a fundamental step forward in the ability to use SERS as an additional tool for the identification of colorants in works of art especially when only minute amounts of material are available, down to a single particle of pigment. To extend this on-the-specimen SERS analysis of artist materials further, analysis was preformed on actual samples of historical pastel grains.

SER Spectra for Pastels from the Pastel Box of Mary Cassatt. A few grains of colored powder were sampled from pastel (14) Van Eslande, E.; Lecomte, S.; Le Hô, A-S. J. Raman Spectrosc. 2008, 39, 1001.
sticks contained in the pastel box of Mary Cassatt (Figure 2a). The colors of the pastels chosen for this study ranged from bright red to pale pink and from dark purple to mauve, reflecting increasing dilution of the coloring agent with inorganic fillers (such as calcium carbonate and kaolin clay or, occasionally, barium sulfate and gypsum) and mixing with other pigments to achieve the purple hues (Figure 2b). Figures 3–5 show the SER spectra for the six pastels. The red pigment in pastel sticks nos. 9 (lilac), 10 (bright red), and 17 (light pink) was identified as carmine lake\(^2\)\(^1\)\(^,\)\(^2\)\(^2\) (Figure 3), mixed with ultramarine blue to achieve a purple hue in the case of pastel no. 9. The fuchsia pigment in the pink pastel stick no. 14 was identified as a mixture of rhodamine B\(^2\)\(^3\)\(^,\)\(^2\)\(^4\) and rhodamine 6G,\(^2\)\(^4\) indicated in Figure 4 as the gray and black labeled peaks, respectively. In addition, the strong band at \(\sim 1070\) cm\(^{-1}\) indicates the presence of hydro-magnesite, a mineral binder, in the pastel sample. The purple pastel sticks nos. 1 and 7 were found to give strong SER spectra (Figure 5), confirming that they contain the same dyestuff. The bands at 1603, 1537, 1350, and 1160 cm\(^{-1}\) are characteristic for nitrobenzene,\(^2\)\(^5\)\(^,\)\(^2\)\(^6\) whereas the band at 1487 cm\(^{-1}\) indicates an azo ring vibration.\(^2\)\(^7\) The band at 1389 cm\(^{-1}\) indicates the presence of an N\(\equiv\)N azo moiety, and bands at 484 and 716 cm\(^{-1}\) indicate the presence of a naphthol moiety.\(^2\)\(^8\) This spectroscopic evidence seems to point toward the identification of this early synthetic organic pigment as belonging to a \(\beta\)-naphthol and/or monoazo class of dyes. Although attempts have been made to more precisely identify this dye by visual comparison with available databases and direct SERS compar-
son with reference samples of PR3 (1-{(4-methyl-2-nitrophenyl)azo}-2-naphthalenol), PR4 (1-{(2-chloro-4-nitrophenyl)azo}-2-naphthalenol), PO5 (1-{(2,4-dinitrophenyl)azo}-2-naphthol), and PR23 (3-hydroxy-4-{(2-methoxy-5-nitrophenyl)azo}-N-(3-nitrophenyl)-2-naphthalene carboxamide), all of which contain the functional groups described above, a perfect match has remained elusive. This observation underscores the necessity for the development of more extensive SER spectral databases of dyes and colorants, including these early synthetic dyes. Highly specific identification of a dye is especially relevant for synthetic organic dyes developed in the late 19th and early 20th century, as the finding of a specific dye may have important dating implications for the work of art on which it is used or for timing of an intervention such as an overpaint. For example, many different monoazo red pigments have been used as artists’ pigments, but while the \( \beta \)-naphthol and naphthol reds were introduced in the early 1900s, benzimidazolones were first patented in the 1960s\(^{29}\) and would be anachronistic materials for a Cassatt pastel, leading to questions about authenticity.

SER Spectra of Samples Taken from the Mary Cassatt Pastel “Sketch of Margaret Sloane, Looking Right”. Two minute samples were taken for analysis from the pastel artwork by Mary Cassatt, shown in Figure 6. The first sample was taken

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from the fleshtone color used in the face of the sitter in the sketch, and the second sample was taken from mauve-colored strokes in her white ruff. Figures 7 and 8 show the SER spectra for these samples, respectively. When compared with the pastel sticks sampled in this study, it is apparent that the fleshtone color used for the face was achieved using the same pigment found in pastel sticks nos. 1 and/or 7, exemplified by bands at 1537, 1350, and 1487 cm\(^{-1}\). In addition, the presence of bands at \(\sim 1050\) and \(\sim 825\) cm\(^{-1}\) indicate the presence of lead white and chrome yellow-orange, respectively.\(^{30}\) The mauve color sampled from the artwork contains a pink colorant that provides a SER spectrum which is similar to madder with bands at 452, 807, 1158, 1398, 1468 cm\(^{-1}\) and a second component with bands at 998, 1112, 1248, 1340, 1635 cm\(^{-1}\), for which a good match could not be found. Since the colors used in the artwork were achieved by mixing multiple pastel sticks and were layered on the silica-coated paper used as support, it is not surprising that these spectra contain more than one component. The spectra for this second artwork sample in particular contain a number of peaks of unknown origin, underscoring the necessity to develop comprehensive databases of SER spectra of modern synthetic organic pigments for positive identification of the materials.

**CONCLUSIONS**

This work demonstrates nonextractive, nonhydrolysis, direct SERS applied for the first time to the identification of both synthetic and natural organic dyes present in a wide variety of artist materials in various media, including a pastel study attributed to the American artist Mary Cassatt. Positive identification was possible on a sample as small as a single grain of pigment (particle size 1–6 \(\mu m\)). The fact that multiple samples coming from different sources could be analyzed, and the chromophores could be detected directly on a minute sample taken from a precious artwork, highlights the usefulness and versatility of this technique for art conservation studies. In the majority of cases, the pigment could be readily identified. In some cases it was not possible to unambiguously identify the colorant, and this exemplifies the need for the collection and dissemination of more extensive SERS reference libraries of pigments and the need for a closer collaboration with theoreticians who would be able to construct libraries of theoretical SERS spectra for chromophores of interest.

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**Figure 8.** SER spectra of (a) madder root (\textit{Rubia tinctorum} L.) and (b) sample no. 12 “mauve” from Mary Cassatt’s “Sketch of Margaret Sloane, Looking Right”. Dashed lines indicate peaks that are consistent with madder root dye. Solid lines indicate unidentified bands due to a second component in the sample. In the inset is a photomicrograph of sample no. 12.