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Direct identification of alizarin and lac dye on painting fragments using surface-enhanced Raman scattering

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Abstract

A surface-enhanced Raman scattering (SERS) based procedure was investigated for potential applications in the direct identification of selected anthraquinone dyes on works of art objects. The simplicity and effectiveness of this procedure was demonstrated in a proof-of-concept experiment. A microscopic fragment containing alizarin or lac dye was removed from a painting. A layer of silver nanoparticles was thermally evaporated directly on the fragment to induce SERS effect. SERS spectra were collected directly from the Ag-nanoparticle-coated sample fragments with a Raman microscope. Based on their characteristic SERS spectra, the presence of alizarin or lac dye in the sample fragments can be detected. The applicability of this procedure for potential applications in minimally invasive analysis of color layer from artwork objects is discussed. Finally, the thickness of the Ag nanoparticle layer was optimized.
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1. Introduction

Anthraquinone dyes are among the oldest and the most important dyestuffs used in works of art such as paintings, archaeological textiles, and drawings. For example, alizarin (1,2-dihydroxyanthraquinone), a major component in the extract of the madder root (*Rubia Tinctorum* L.), was extensively used in Asia and Egypt since ancient time to obtain pink to red pigments in textile materials and paintings [1]. Identification of these dyes is essential for dating, restoring, conserving artworks, and studying art history in general. Various analytical techniques have been employed for the analysis of dyes in cultural artifacts [2–7]. Among these techniques, gas chromatography (GC) and high-performance liquid chromatography (HPLC) are the most commonly used [4–7]. They are highly specific and very sensitive. However, most of them require laborious sample digestion and dye extraction procedures. Relatively large amount of sample is required in some cases due to the instability of some

anthraquinone dyes when digested in acidic conditions [8,9]. Optical techniques capable of non-invasive solid sample analysis, such as infrared spectroscopy and visible spectroscopy, have also been investigated [10]. Both methods can indirectly indicate the presence of some anthraquinone dyes when they are associated with protein. But they lack the sensitivity of HPLC and the degree of detail necessary for fingerprinting unknown materials. By and large, direct identification of dyes in heterogeneous matrices of artifacts with little or no sampling remains a challenging analytical task.

Raman spectroscopy has been a valuable technique for the analysis of dye [11]. The technique can be applied in situ, has high spatial and spectral resolution, is non-destructive, and requires only microscopic samples if a Raman microscope is used. However, weak Raman signal and strong fluorescence background have limited the application of Raman spectroscopy for the identification of highly fluorescent anthraquinone dyes. To address these issues, surface-enhanced Raman scattering (SERS) can be utilized by adsorbing dye molecules on atomically rough metal surface to induce SERS effect. By doing so, the intensity of the normally weak Raman scattering could be enhanced up to seven orders of magnitude when the Raman electromagnetic field is intensified by resonance with the metal

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plasmon. At the same time, dye fluorescence could be effectively quenched through electron transfer from the excited molecule to the metal. In several recent studies, SERS has been used to obtain the spectra of some anthraquinone dyes using Ag colloid or by incorporating the dyes into SERS-active Zr-Osmosil polymers [12–15]. However, both methods were used to characterize the dyes in aqueous media and extensive sample preparation is necessary in both cases. In this study, we explored the possibility of eliminating the tedious sample preparation steps by developing a simple SERS procedure for direct dye identification on sample fragments without solvent extraction.

2. Experimental

2.1. Materials

Alizarin was purchased at the highest purity from Sigma–Aldrich and lac dye (a mixture of four laccaic acids) was obtained from Tokyo Kasei Co., Japan. They were mixed in water/ethanol to prepare the painting. Silver beads (99.9 + %) used for the preparation of Ag nanoparticles was purchased from Aldrich.

2.2. Instrumentation

Raman and SERS spectra of alizarin were recorded using a 50× objective on a Renishaw InVia Raman microscope equipped with an ultra-low noise charge-coupled device (CCD) detector. The 632.7 nm line of a Helium–Neon (HeNe) laser was used for excitation with a bandpass filter to reject the unwanted stray light. The maximum laser power available is 50 mW and

the laser power at the sample can be adjusted by opening or closing an iris shutter. The laser beam was focused down to a diameter of ~100 μm at the sample, and the Raman radiation was collected at 180° with respect to the excitation beam. A holographic notch filter was employed to reject Rayleigh scattering. The spectrograph was equipped with an 1800-groove/mm grating, which offers a wavelength accuracy of $0.2\,cm^{-1}$ with 632.7 nm excitation. All data acquisition and processing were carried out using the WiRE 2.0 software package supplied by Renishaw.

2.3. Procedures

The sample for SERS measurements were prepared as follows: a small sample fragment containing alizarin or lac dye was removed from a painting (Fig. 1). The fragment was attached to a sample holder inside the deposition chamber of a vacuum evaporation system (CVE-301, Cooke Vacuum Products). A layer of silver nanoparticles was deposited directly on top of the sample fragment under a pressure of 2×10^{-6} Torr at a deposition rate of 0.1 Å/s. The holder was rotated during the evaporation process at a rate of approximately 30 rpm in order to ensure a uniform coating. Silver film thickness and deposition rate were monitored with a gold-plated sensing crystal (Sycon Instruments). The deposition rate was controlled by varying the electrical current passed through a heating boat. The coated sample fragment was left in the evaporation chamber after deposition to cool down for ~15 min and the SERS spectra were collected immediately following the evaporation process. An image of the Ag-nanoparticle-coated sample fragment under a 10× objective
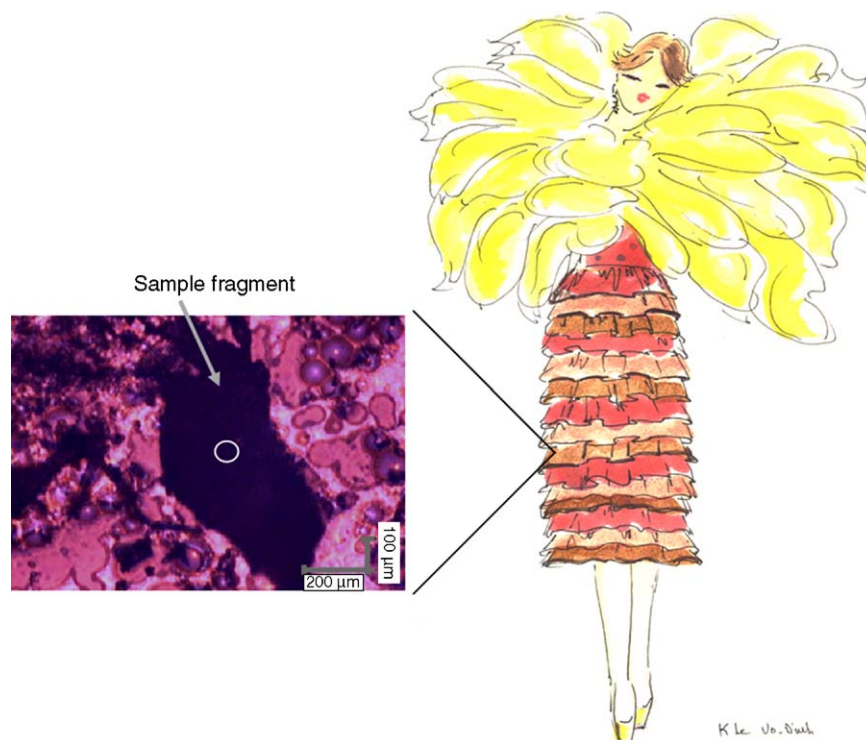

Fig. 1. A microscopic sample fragment is removed from a painting to be examined with the SERS procedure. The inset shows the image of the fragment under a 10× microscope objective. A white circle on the fragment indicates the typical size of the area needed to acquire a spectrum.