Vibrational Spectroscopy 85 (2016) 181–184

Contents lists available at ScienceDirect

Vibrational Spectroscopy

journal homepage: www.elsevier.com/locate/vibspec

Raman spectroscopy of the pigments on Korean traditional paintings☆

Ji-Yeon Nam[a], Kiok Han[a], Jeong-Eun Ji[a], Seung Kim[a], Hanhyoung Lee[b], Daiill Kang[b], Minsu Han[c], In-Sang Yang[a,*]

[a] Department of Physics and Division of Nano-Sciences, Ewha Womans University, Seoul 120-750, South Korea
[b] Department of Conservation Science, Korea National University of Cultural Heritage, Buyeo 323-812, South Korea
[c] Conservation Science Division, National Research Institute of Cultural Heritage, Daejeon 341-22, South Korea

ARTICLE INFO

Article history:
Received 13 October 2015
Received in revised form 23 February 2016
Accepted 20 April 2016
Available online 23 April 2016

Keywords:
Traditional pigments
Mineral pigments
Raman spectroscopy
Traditional painting
Nondestructive measurements
Vibrational spectroscopy

ABSTRACT

Raman spectroscopy is now a well-established tool in characterizing archaeological materials, such as traditional paintings. In this report, we applied Raman spectroscopy to investigate the pigments used in Korean traditional paintings. Korean traditional colors are often represented by the five basic colors; blue, red, yellow, white, and black. In real paintings, the colors are more diverse including orange and green. We report a Raman spectroscopy of the various pigments found in Korean traditional paintings. Raman spectra are used to identify the minerals in the pigments by comparing the spectra with those of known minerals. Our work would provide a useful scientific basis for the conservation and restoration of aged and damaged Korean traditional heritages.

1. Introduction

Raman spectroscopy is widely used in characterizing archaeological materials, such as traditional paintings and building decorations. Non-destructive *in-situ* analysis of pigments in large paintings by mounting the Raman microscope on a scanning gantry is presented by Ernst [1]. With the recent advent of hand-held Raman instruments with relatively good resolution, applicability of the Raman spectroscopy in art and archaeology is even greater [2].

Raman spectroscopic library of pigments of various origins from prehistoric ages are already available [3]. However, Raman measurements on pigments found on Korean heritage are not readily seen. Korean traditional colors are often represented by five basic colors ("Obang" colors); blue, red, yellow, white, and black, meaning east, south, center, west, and north, respectively (Fig. 1). The "Obang" colors are abundantly found in traditional Korean food, costumes, ornaments, paintings, and building decorations. In real paintings and decorations, more diverse colors including orange and green are readily found.

In this article, we report a Raman spectroscopic analysis of several kinds of pigments, especially the mineral pigments found in traditional paintings. We have identified the pigments and dye on a 18th -century Buddha painting of the Tongdosa temple, Korea. Our Raman analyses of the pigments and dyes on a Korean traditional painting would be a starting point of similar scientific work on Korean traditional arts, which would eventually be useful in preserving and restoring the valuable Korean cultural heritage.

2. Experimental

Raman spectra of the pigment samples were measured using Horiba Jobin Yvon LabRam Aramis with 532 nm excitation source, ×10 lens of microscope, 1800 gr/mm-reflective grating with focal length of 450 mm, and Peltier-cooled CCD of 1024 × 256 arrays. The diameter of the focused beam on the sample surface was 2.6 μm. The spectral resolution was found to be about 2.5 cm^{-1} at 532 nm excitation when the entrance slit was set to 100 μm. For pigments which are photo-degradable, we used high throughput capability of NANOBASE XperRam200 with 1800 lpmm holographic transmissive grating. The spectral resolution of NANOBASE XperRam200 was about 3.0 cm^{-1} at 532 nm excitation line.

The pigments from the Buddha painting of Tongdosa temple were obtained from the National Research Institute of Cultural Heritage of Korea during the restoration process of the Korean heritage. Fig. 1 shows the Buddha painting of Tongdosa temple with several indications of the location of the pigment sampling. The colors of the pigment or dye samples are denoted in the figure. Even one kind of color is sampled from several locations, and all the seven colors are measured in our Raman measurements.

☆ Selected paper from 8th International Conference on Advanced Vibrational Spectroscopy, 12-17 July 2015, Vienna, Austria.

* Corresponding author.
E-mail addresses: yang@ewha.ac.kr, yang2059@hanmail.net (I.-S. Yang).

http://dx.doi.org/10.1016/j.vibspec.2016.04.011
0924-2031/

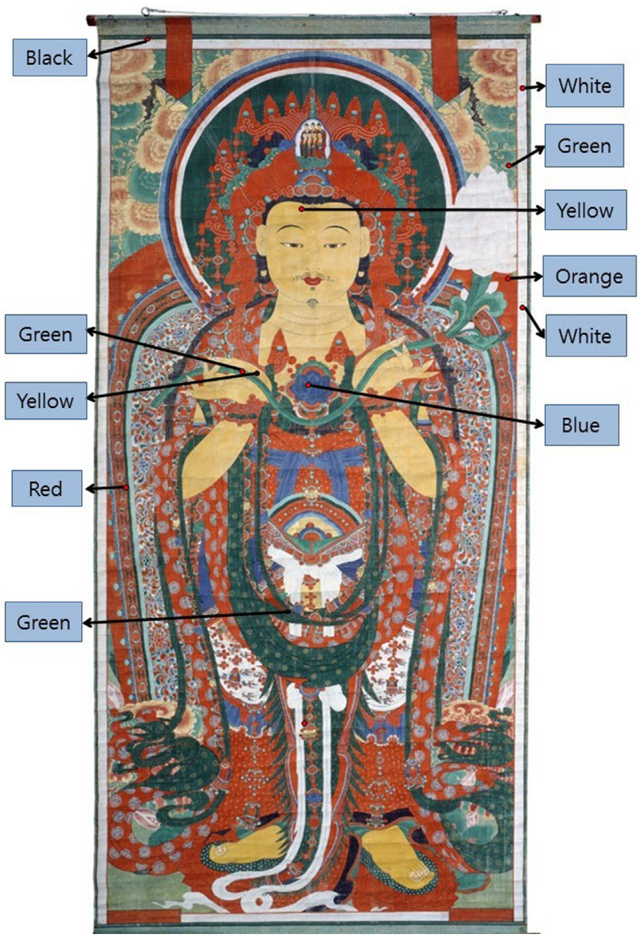

Fig. 1. The Buddha painting of Tongdosa temple with several indications of the location of the pigment sampling. The colors of the pigment or dye samples are denoted. (For interpretation of the references to colour in the text, the reader is referred to the web version of this article.)

The Tongdosa Buddha painting measured in this study was first completed in 1792 during Yi dynasty by at least 23 artists, and all the information is recorded in the bottom of the painting. The painting was done on silk with several layers of back sheets. The size of the painting is $11.01 \times 5.21\ m^2$. The record shows that the back sheets were replaced during the preservation process in 1994, and no other record of previous conservation activity is known. The painting was registered as the Korea treasure No. 1351 in 2002.

Raman spectroscopy is non-destructive when the incident laser power is low enough. However, excessive laser power could not only damage the valuable heritage but also alter the phase or physical and chemical state of the mineral pigments on the paintings during the measurements. For example, strong laser power can blacken the azurite by altering it into the copper oxide (tenorite). Mattei et al. [4] studied the laser-induced degradation of azurite as a function of the particle size. They found that the temperature of the particles decreases as the size increases, and azurite degrades into tenorite only below the critical value of 25 μm. The typical particle sizes of pigments on the paintings are smaller than 25 μm. Therefore extreme care was paid in measuring the Raman spectra of all the pigment samples. NANOBASE XperRam200 was highly effective in throughput so that high signal-to-noise ratio could be achieved even at low laser power. All Raman measurements were done with laser power less than $\sim$0.1 mW/μm^2 and excitation time of 10 s with multiple averaging.

3. Results and discussion

Fig. 2 shows Raman spectra of the pigments and dyes obtained from the Tongdosa Buddha painting. The colors measured are blue, red, yellow, white, black, orange, and green. The pigment for blue color is easily identified to be azurite, not smalt, as clearly seen in top part of Fig. 3. The reference Raman spectra of azurite and smalt are taken from RRUFF project website [5]. The RRUFF Project website contains an integrated database of Raman spectra for various minerals, as well as x-ray diffraction and chemistry data for the minerals. The Raman spectra of azurite have been studied extensively by Frost et al. [6]. Azurite is monoclinic in crystal structure, and it is $Cu_3(CO_3)_2(OH)_2$ in chemical formula. The characteristic mode at $\sim$400 cm^{-1} is Cu—O stretching mode, and most of the Raman modes above $\sim$700 cm^{-1} are from the hydroxyl group and carbonate group in the azurite crystal structure. It has been used as a pigment for blue color from ancient time, as found in cave paintings at Dunhuang in Western China and wall paintings in Central China from the Tang and Song dynasties. It was also the most important blue pigment in European painting throughout the middle ages and Renaissance.

On the other hand, smalt is an artificial blue pigment, potassium glass containing small amounts of cobalt oxide, and it was widely used in Europe as early as 16th century because of its low cost in manufacturing. It has been often used as a blue pigment in 11th–13th century Chinese wall painting and became widespread in the 16th–17th-centuries [7].

In the bottom of Fig. 3, the Raman spectrum for the yellow color of the Tongdosa Buddha is shown along with those of gamboge and

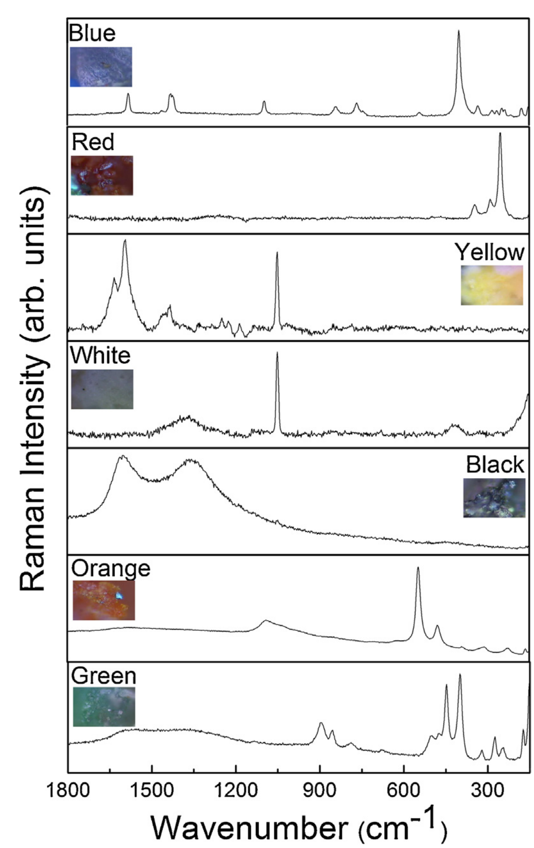

Fig. 2. Raman spectra of the pigments from the Tongdosa Buddha painting. (For interpretation of the references to colour in the text, the reader is referred to the web version of this article.)