

Characterization and Identification of Lacquer Films from the Qin and Han Dynasties

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A comprehensive investigation was undertaken of red-black lacquer films excavated from a tomb in the Qin and Han Dynasty period (221 BC to AD 8). Cross-sectional observation was conducted *via* metallomicroscopy and field-emission scanning electron microscopy (FE-SEM). Morphological characteristics were investigated *via* FE-SEM with energy dispersive X-ray spectrometry (EDX). X-ray diffraction (XRD) and Fourier transform infrared (FTIR) spectroscopy were also conducted. The results of the cross-sectional analysis showed that the finished lacquer films on the wood body included a ground layer with coarse materials and a lacquer layer with delicate materials. Both SEM and EDX indicated that carbon black was used as the main black pigment, and cinnabar was used as the main red pigment. Compared with the standard card test, the XRD patterns of the Chinese lacquer were similar to that of quartz (SiO₂), indicating that SiO₂ was used as a putty powder during lacquer finishing. Compared with the FTIR spectrum of the fresh lacquer film, only a small amount of free carbonyl was found in the degraded lacquer, and some organosilicates were likely generated during degradation spanning thousands of years.

Keywords: *Qin–Han dynasties; Lacquerware; SEM; XRD; FTIR*

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INTRODUCTION

Lacquering has been part of the most important traditional cultures in Chinese history, and its roots can be traced back to the Neolithic Age (Lu *et al.* 2006; Liu *et al.* 2014; Sung *et al.* 2016). Fossils of lacquer tree leaves excavated from Shanwang Village, Shandong Province show that the Chinese lacquer tree has existed for 18 million years (Zhang 2010). A red lacquer wooden bowl from the Hemudu site in Zhejiang Province suggests that Chinese lacquer has been used as a coating for more than 7,000 years (Chiavari and Mazzeo 1999, 2003; Wei *et al.* 2011; Liu *et al.* 2016). The long history of Chinese lacquer may be roughly divided into six stages of development (Lu and Miyakoshi 2015): incubation (in the Neolithic Age), germination (in the Bronze Age), growth period, (in the Iron Age), lacquer era (in the Qin and Han dynasties), recession (in the Buddhist era), and flourishing period (in the porcelain era). Lacquer ware in the Qin and Han dynasties significantly influenced the history of lacquer. Moreover, the Chinese lacquer technology and process considerably developed during this period. Thus, the Qin and Han dynasties are considered the lacquer era in Chinese cultural history (Zhang 2010), with black and red being the most predominant colors for decorating lacquerware (red painting on the black background or black painting on the red background).

To elucidate the processing and decoration technology of lacquerware in the Qin and Han dynasties, the Chinese lacquer film has to be characterized and identified. The Qin and Han dynasties marked the beginning of China's feudal society, and the handicraft industry developed further on this basis during the Zhou dynasty. The processing of lacquerware was mainly divided into designing the structure, setting the base layer, Chinese lacquer finishing, and decorating. According to the literature (Lu and Miyakoshi 2015; Zhang *et al.* 2019) in the Qin and Han dynasties, the main materials used for the lacquerware structure were wood (wooden body), bamboo (bamboo body), and cloth (“Jiazhu” body). The base layer, also called the ground layer, is located below the lacquer film (Research Institute of Chinese Cultural Heritage 2009; Wei *et al.* 2011; Liu *et al.* 2016; Zhang *et al.* 2019). Important ingredients in the ground layer of the lacquerware included the tile powder, lacquer, and pig's blood (Research Institute of Chinese Cultural Heritage 2009; Jiang 2016). During the Qin and Han dynasties, lacquerware was decorated by painting, needle carving, and inlaying (gold, silver, and shells), among other techniques (Research Institute of Chinese Cultural Heritage 2009). The painting patterns included mythical creatures (*e.g.*, dragon and phoenix), animals (*e.g.*, fish, bird, and tiger), geometric patterns (such as parallel lines on the bottom or top of lacquerware, as shown in Fig. 1), and cloud patterns (curl lines that look like clouds), among others (Zhang 2010; Ebert and Schilling 2016).



Fig. 1. A set of dressing lacquered boxes from a Han dynasty tomb collection in Nanjing (Nanjing Museum 2019)

Scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDX), X-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FT-IR), and other analytical techniques are commonly used to characterize and identify the materials used in excavated Chinese and Japanese lacquerwares (Wei *et al.* 2011; Liu *et al.* 2016). In this study, several Chinese lacquer films excavated from a Qin–Han dynasty tomb were analyzed. Cross-sectional analysis, scanning electron microscopy (SEM), X-ray diffraction (XRD), and Fourier transform infrared (FTIR) spectroscopy were performed. The results are described in detail. The findings are expected to provide relevant scientific information for the conservation of historic lacquerware.

EXPERIMENTAL

Materials

This study used Chinese lacquer films (Fig. 2) flaked off from a wooden object that was unearthed from a tomb called “Big Cloud Mountain” in the Qin–Han dynasty period in the Yangtze River Basin (Xuyi, Jiangsu, China). This tomb was shown to have belonged to a prince in the Han dynasty when daily necessities were made of gold, silver copper, iron, pottery, jade, and lacquered wood, *etc.* The object was more than 2000 years old and could not be restored. Only some fragments of the Chinese lacquer films remained. Wood fragments on the back of these layers were examined by microscopy and then identified as basswood (*Tilia platyphyllos*). The painted decoration of these lacquer films, which belong to the Nanjing Museum, closely resembles the boxes from the Palace Museum (Nanjing Museum 2019). Some studies (Zhang 2010; Wei *et al.* 2011) suggest that these designs feature cloud patterns, which, owing to their propitious meaning, were most widely used in the Han dynasty. As discussed previously and as shown in Fig. 1, geometric patterns of two parallel lines usually decorated the bottom or top of lacquerware. Thus, the two parallel lines in Fig. 2b reveal that the lacquer layer might have been peeled off the bottom or top of the lacquerware. The curve lines were identified as cloud patterns, which symbolize energy (Research Institute of Chinese Cultural Heritage 2009).

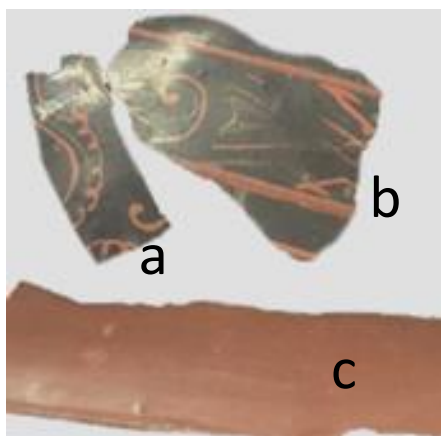


Fig. 2. Photo of Chinese lacquer films: a) Chinese lacquer with cloud patterns, b) Chinese lacquer with cloud patterns two parallel lines, and c) red Chinese lacquer film

Methods

Cross-sectional analysis

Due to their thinness and fragility, the lacquer films were immersed in a transparent epoxy resin (Guangzhou Pearl River Chemical Group Co., Ltd., Guangzhou, China) and then cut with a microtome to achieve a flat and smooth cross-section. Then, the structure of the cross-section was investigated with a metallomicroscope (HOMA-2000; Seepack Optical Instrument Co., Ltd., Shenzhen, China) and a SEM (JCM-7000; JEOLLtd., Tokyo, Japan).

Morphological characteristics

The surface shapes of these lacquer films were assessed based on morphological analysis by field-emission scanning electron microscopy with energy dispersive X-ray

spectroscopy (FE-SEM–EDX) using aJSM-7600F with a Genesis 4000 spectrometer (JEOL Ltd., Tokyo, Japan). To completely analyze and identify the material used, the black and red areas were examined. Increase in electrical conductivity of a sample is the single most common requirement for SEM. In this study, a sputter gold coating (2 nm) was applied on the Chinese lacquer film using a Gold Palladium SEM Annular Sputtering target 2" ID × 3" OD × 0.1 mm Anatech (SC502-314; Quorum Technologies, Ltd., Watford, UK).

X-ray diffraction

Several pieces of lacquer layers measuring 15*15 mm and with a flat surface were prepared for X-ray diffraction tests. The XRD spectra of these lacquer layers were obtained by *in situ* XRD using the X'Pert Pro Multipurpose Diffractometer (PANalytical, Almelo, Netherlands) equipped with a Rigaku Smart Lab 9kW XRD system (Shimadzu Corporation, Kyoto, Japan); the spectra were captured over the 10° to 90° diffraction range.

Fourier transform infrared spectroscopy

The FTIR analysis was conducted using an Alpha FTIR spectrometer (Bruker Vertex 70; Bruker Optik GmbH, Ettlingen, Germany) to analyze the chemical structure of the lacquer film surface. Spectra with a resolution of 4 cm⁻¹ and consisting of 24 scans were collected over the 4000 to 400 cm⁻¹ range.

RESULTS AND DISCUSSION

Cross-section Analysis

Figure 3a presents a micrograph of the cross-section of the lacquer layer with a thickness of 25 to 35 µm, while the remaining wood has a thickness of 70 to 90 µm. Figure 3b shows the micrograph recorded with a scanning electron microscope. The top layer with a thickness of approximately 12.8 µm is the lacquer layer finished with delicate materials; similarly, the bottom layer with a rough material is the ground layer with a thickness of 14.3 µm. Generally, the function of the ground layer is to improve the stability of the lacquer film on the body structure.

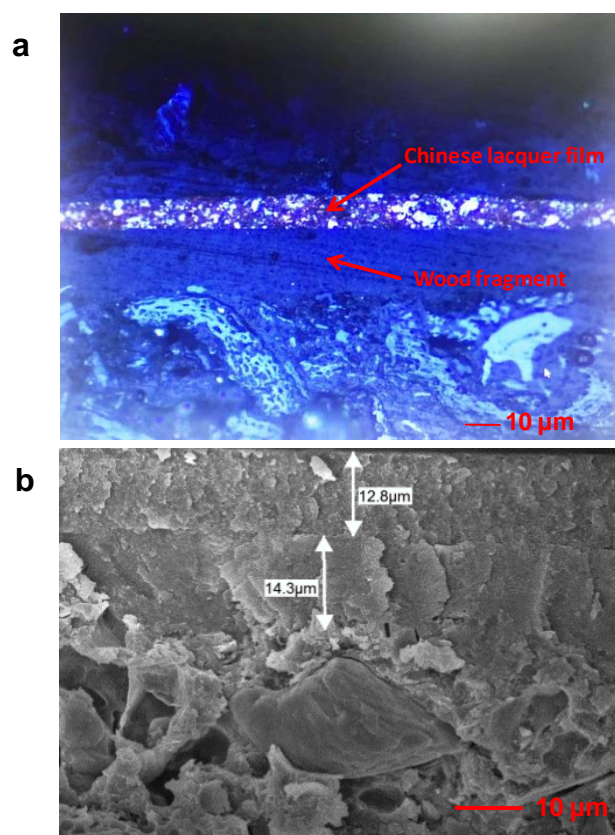


Fig. 3. Micrographs of cross-sections of the lacquer film: a) recorded with a microscope (500 \times); b) recorded with a scanning electron microscope (1000 \times)

Morphological Characteristics

The SEM micrographs of these Chinese lacquer films are illustrated in Fig. 4. The results demonstrate that the black area presents considerably smooth particles with hairlines (0.3 μm), and the red area presents square particles. The EDX analysis indicated that the black area consisted of 65.07% C, 23.21% O, 0.34% Na, 0.07% Mg, 0.20% Al, 0.13% Si, 1.66% Ca, 0.56% Fe, and 1.51% Mo. The red area consisted of 34.83% C, 19.46% O, 37.12% Hg, 5.47% S, 2.77% Ca, and 0.35% Al. These results led to the conclusion that the materials used in the black area were carbon, SiO_2 , CaCO_3 , and other mineral materials with Na, Mg, Al, Fe, and Mo. The main materials used in the red area were Chinese lacquer with cinnabar (HgS), which was consistent with the results in previous studies (Chiavari and Mazzeo 1999; Wei *et al.* 2011; Wang *et al.* 2014; Körber and Schilling 2016; Schilling *et al.* 2016).

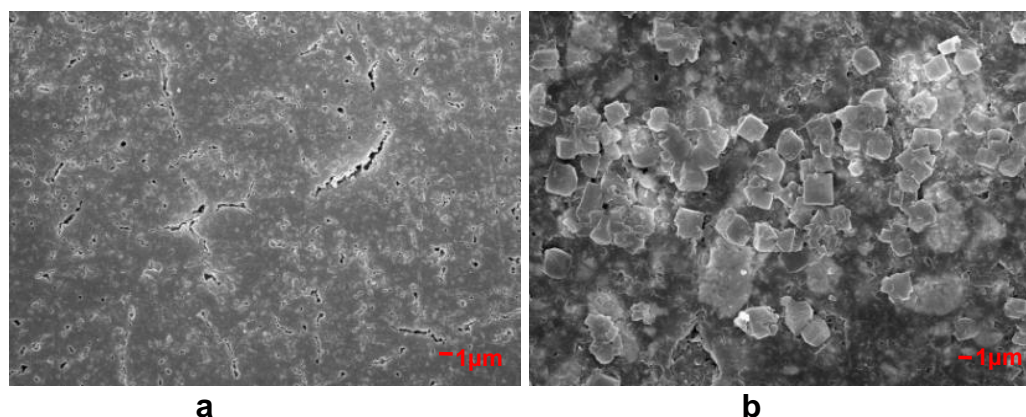


Fig. 4. Micrographs of the lacquer film surface: a) the black area (3000 \times) and b) the red area (3000 \times)

XRD Analysis

Figure 5 presents the XRD patterns of the Chinese lacquer layer, compared with the standard diffraction XRD card. A set of diffraction peaks at the position of 20.94, 26.66, 36.52, 39.50, 40.29, 50.60, 59.5, and 67.64° appeared to be attributable to quartz (SiO_2), exhibiting good coincidence. In addition, quartz was found in the particles. This conclusion was consistent with the EDX results for the black area.

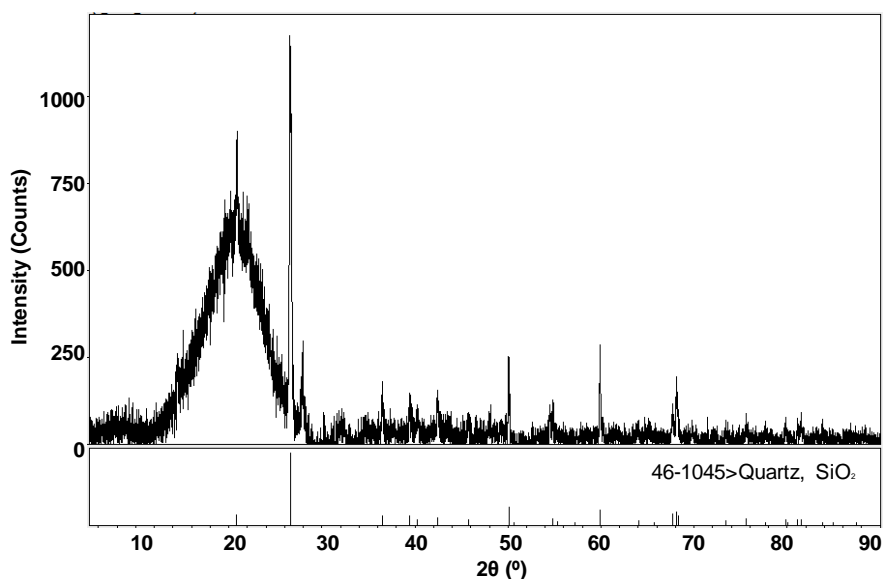


Fig. 5. X-ray diffraction pattern of the lacquer film sample

FTIR Investigation

Figure 6 presents the spectra of the ancient lacquer film in the red area and the black area. Fresh Chinese lacquer (*Toxicodendron vernicifluum* sap provided by the Xi 'an Institute of China lacquer, Xi'an, China) was used to investigate the chemical structure of the surface. The FTIR spectra reflect the chemical structural features of fresh Chinese lacquer and the changes after degradation spanning 2000 years. The main absorption bands in the fresh Chinese lacquer spectrum are those attributed to hydroxyl (3391 and 1366 cm^{-1}), methylene (2924 and 2854 cm^{-1}), and the aromatic ring (1600 and 1455 cm^{-1}). They

indicate a phenolic structure with a long aliphatic side chain. The presence of the out-of-plane oscillation vibration of C-H bond is highlighted by absorptions at 722 cm^{-1} , while carbonyl groups are denoted by the absorption band at 1737 cm^{-1} . The absorption bands at 1276 and 1153 cm^{-1} represent the O-H bending and C-O stretching of aliphatic carboxyl and hydroxyl groups overlapping with the C-O stretching of $-\text{COOR}$ (Liu *et al.* 2014).

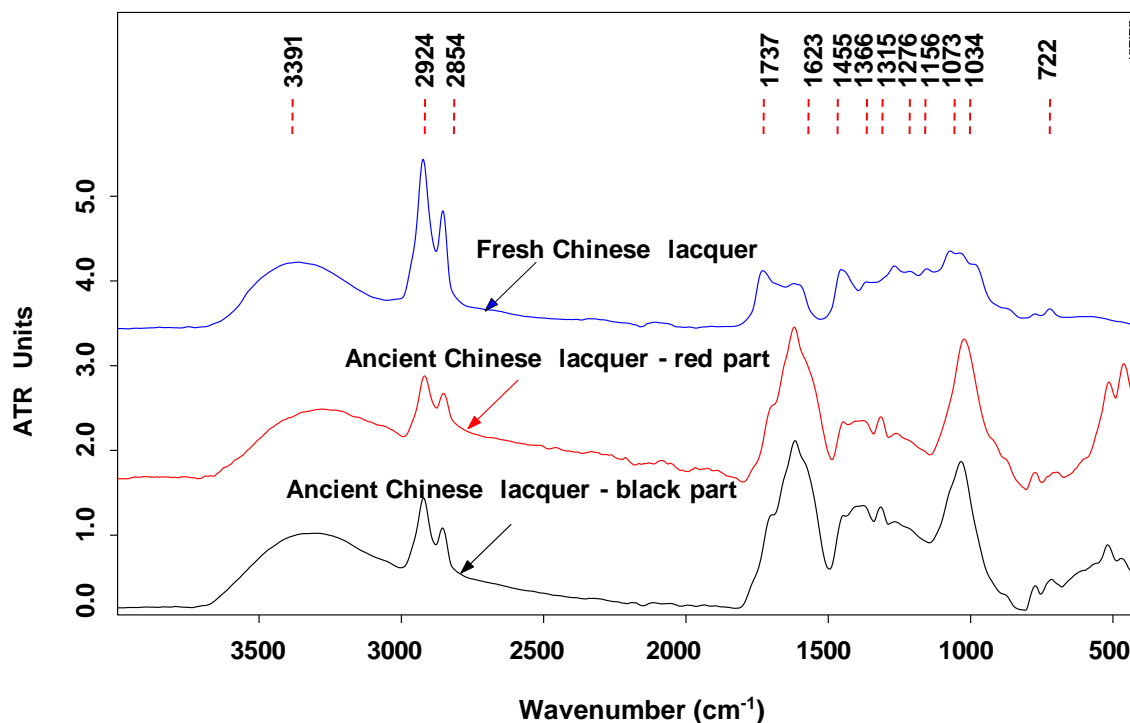


Fig. 6. Spectra of old Chinese lacquer film surface and fresh Chinese lacquer

Compared with the fresh lacquer film, the old lacquer films are complicated because the real artwork may contain unknown compounds, which may interfere with the lacquer components. The main absorption bands in the fresh Chinese lacquer spectrum are those attributed to hydroxyl (3391 cm^{-1}), methylene (2924 and 2854 cm^{-1}), and the aromatic ring (1623 cm^{-1}). A shoulder peak that was found at 1737 cm^{-1} can be attributed to carbonyl stretching, which indicates that only a small amount of free carbonyl was present in the degraded lacquer films. According to previous reports (Frade *et al.* 2010; Honda *et al.* 2015; Ma *et al.* 2017; Hao *et al.* 2019), during degradation spanning thousands of years, some organosilicates were generated because of the reaction of lacquer and partly silicon dioxide. This assumption is supported by the absorption bands at 773 , 519 , and 463 cm^{-1} .

CONCLUSIONS

1. Cross-sectional analysis of Chinese lacquer films from the Qin and Han Dynasty period indicates that the lacquer finish on the wooden body contained a ground layer and lacquer. The red patterns on the black lacquer were confirmed to be cloud patterns, which were widely known during the Qin and Han dynasties.

2. The EDX results indicate that carbon black was used as the black pigment, and cinnabar (HgS) was used as the red pigment. CaCO_3 and other mineral materials with Na, Mg, Al, Fe, and Mo might have also been applied during Chinese lacquer finishing. The SEM investigation of the cinnabar presented small square particles.
3. The XRD pattern showed that the quartz SiO_2 was used as putty powder during finishing. The spectra of these old lacquer films indicate that organosilicates were generated during degradation spanning thousands of years.

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