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Characterization of a Mahamayuri Vidyarajni Sutra excavated in Lu'an, China

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Abstract

Historically, sutras played an important role in spreading Buddhist faith and doctrine, and today these remain important records of Buddhist thought and culture. A *Mahamayuri Vidyarajni Sutra* with polychrome paintings was found inside the cavity on top of the Nanmen Buddhist pagoda, built in the early Tang dynasty (618–627 CE) and located in Anhui Province, China. Textile was found on the preface which is strongly degraded and fragile. Unfortunately, the whole sutra is under severe degradation and is incomplete. Technical analysis based on scientific methods will benefits the conservation of the sutra. Optical microscopy (OM), micro-Raman spectroscopy combined with optical microscope (Raman), scanning electron microscopy in combination with energy dispersive X-ray analysis (SEM–EDS) and Fourier Transform Infrared Spectroscopy (FTIR) were used to characterize the pigment and gilded material, as well as the paper fiber and textile. Pigments such as cinnabar, minium, paratacamite, azurite, lead white were found. Gilded material was identified as gold. A five-heddle warp satin, made of silk, was found as the textile on the preface of the sutra. The sutra's preface and inner pages were made of paper comprised of bamboo and bark. As a magnificent yet recondite treasure of Buddhism, the sutra was analyzed for a better understanding of the material. A conservation project of the sutra will be scheduled accordingly.

Keywords: Sutra, Pigment, Micro-Raman spectroscopy, Conservation

Introduction

Nanmen Buddhist pagoda, located in Luan city, Anhui province, China, was built in 618–627 CE during the early Tang dynasty, with restoration carried out in Song dynasty (960–1279 CE) and again in the Qing dynasty (1636–1912 CE) [1]. In 2010, further restoration of the pagoda revealed a stone reliquary box in a cavity at its top. Writing in red pigment on the box lid records that the box was made in October, 1834 (during the Qing dynasty). The characters also state that a *Mahamayuri Vidyarajni Sutra* (36 cm*16 cm) was stored inside the box, for the purpose of fostering peace and safety. The *Mahamayuri Vidyarajni Sutra* was an early text translated from Sanskrit into Chinese, with a total of six different translated versions in Chinese language; it has also been translated from Sanskrit into Nepali and Japanese [2–4]. The cult of *Mahamayuri Vidyarajni* endured for more than 600 years, starting in the Tang dynasty. *Mahamayuri Vidyarajni* (Great Peacock Wisdom Queen), known in China as Kongque Mingwang, is a protective Buddhist female guardian with the special function to prevent or cure injuries caused by poison [5].

The sutra and statues of *Mahamayuri Vidyarajni* have been found in the Mogao Grottoes of Dunhuang and the Dazu Stone Carvings in Chongqing. Importantly, the sutra found in Nanmen pagoda, is the first example of a *Mahamayuri Vidyarajni Sutra* to be found in central China [6].

The sutra found in the box has both exquisite polychrome paintings and characters, but is suffering from severe degradation. Ash on some pages and absence of several parts indicate the sutra has experienced fire. Deformation and shrinkage are also apparent, causing the adhesion of some pages to each other. Degradation of the polymer chain of the paper has resulted in its loss of strength. All of damage mentioned above puts the sutra into a dangerous situation. Fortunately, a part of the

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sutra with paintings of Buddhist stories survived. Various colors such as blue, green, black and red were found in the paintings, giving them an exquisite and vivid appearance (Fig. 1a, c, d). Textile was found on the preface which is strongly degraded and fragile (Fig. 1b).

Technical studies of other sutras have been reported for the purpose of identification and conservation. SEM–EDS, XRD, Raman Spectroscopy and XRF were applied to the identification of pigment and paper fiber in ancient tripitaka, while enzyme-linked immunosorbent assay combined with FTIR was used in characterization of proteinaceous binders and organic coating of tripitaka [7, 8]. Accelerator mass spectrometry radiocarbon was applied in the dating of ancient Japanese sutras with the results corresponding to the historical ages recorded on the artefacts [9, 10]. Analysis by means of a minimally invasive, multi-analytical approach based on micro-Raman spectroscopy will inform the information of the sutra [11]. In this work, micro-Raman spectroscopy combined with several other techniques were applied to investigate the sutra, for a better understanding of the materials used in the sutra, as well as offering basic information for restoration.

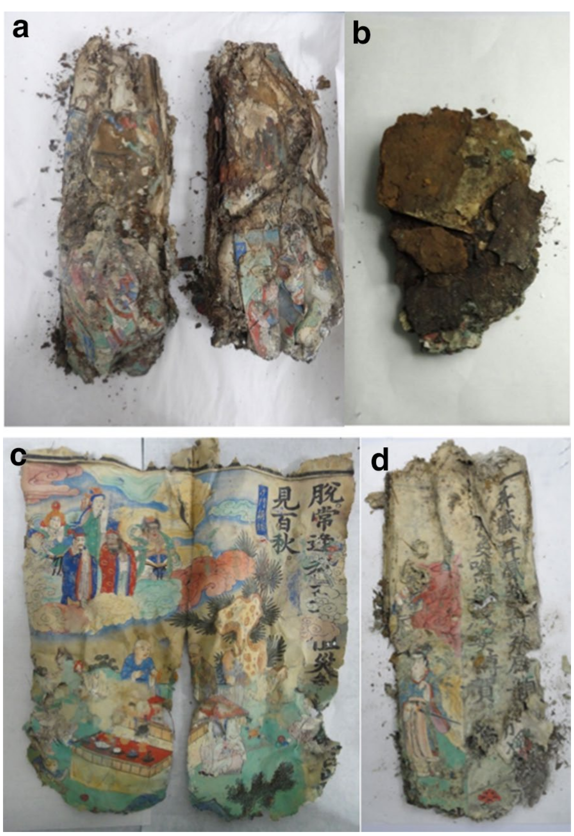


Fig. 1 Pages of the sutra (**a** total view of the sutra, **b** textile on the preface, **c**, **d** pages of the sutra)

Materials and methods

Materials

A non-invasive approach is preferred in the field of cultural heritage. Due to the lacking of portable equipment, five different fragment samples were carefully selected from the fallen part of the sutra for non (micro)-destructive analysis (Table 1). Pigments with different color (red, light red, green, blue, white) were found. Gilded material was also collected. Fiber from paper and textile were selected for analysis.

Methods

Optical microscopy

Microscopic studies of the pigment were based on a KEYENCE VHX-2000C microscope for micromorphology observation. Paper fiber was observed under a XWY-VI fiber analysis microscope. Sample preparation of paper fiber was by following steps: dispersing the paper fiber into water, putting the single fiber on a glass slide and dyeing the fiber with I_2–$ZnCl_2$ solution [12].

Micro Raman spectroscopy

Micro-Raman analysis of the pigment was performed by a LabRam spectrometer (purchased from Horiba Jobin–Yvon, France) coupled with a microscope. Point measurements were performed using an argon gas laser at 514.5 nm and a 50× working distance objective. The spectral resolution was 0.6 cm^{-1}. The laser power used was approximately 0.5 mW, which ensured that good-quality spectra was recorded. The system used a thermoelectrically cooled CCD detector, which operated at − 65 °C, and an 1800 groove/mm dispersive grating.

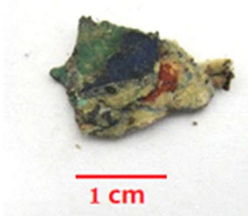
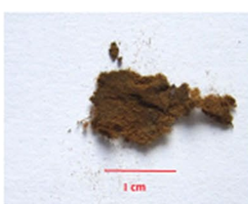
SEM–EDS

SEM–EDS was used for element characterization of pigment and morphological observation of textile fiber. Due to the limited choice of analysis equipment, a micro-destructive method SEM–EDS was chosen instead of XRF for element characterization. A small particle of pigment (less than 1 mm) was selected under microscope for analysis. The instrument used for SEM–EDS analysis was a Sirion 200 of the FEI Company, USA. Samples were analyzed with 20 kV acceleration voltage and 5 mm working distance. Fibers of the textile were cut by a fiber slicer to achieve the cross section for observation. A steamed gold process was carried out on pigment samples and textile sample due to their poor conductivity. The process was not used in the gilded sample.

FTIR

A non-destructive method by ATR-FTIR was used to classify the textile fiber with 64 scans over the range of 4000–700 cm^{-1} by a Nicolet-6700 instrument, the resolution is 4 cm^{-1}.

Table 1 Sample collection

Sample number	Sample Photo	Description	Pigment for Analysis
1		At least two pages are stuck together.	Red and green area, paper fiber of inner page
2		Gold is found on the surface in the patterned area.	Light red area and gold area
3		The whole sample is darkened.	Blue area
4		Fiber is adhered to the sample.	White area
5		Preface of the sutra.	Textile and paper fiber

Results and discussion

Microscopic observation of pigments

Plenty of colors were observed (Fig. 2). White particles (identified as SiO_2 and calcium salt later) and minerals were found on the surface of the samples. Cracks also appeared on the surface of the pigment (Fig. 2b, f), indicating that the samples are in poor condition. Pigments have dropped off from the fiber (Fig. 2a, c), possibly caused by the failure of binding materials. Loss of pigment makes the color inhomogeneous and therefore the illustrations within the sutra are incomplete. Gilding was frequently used in the illustrations, which is the indicative of the sutra's high value.

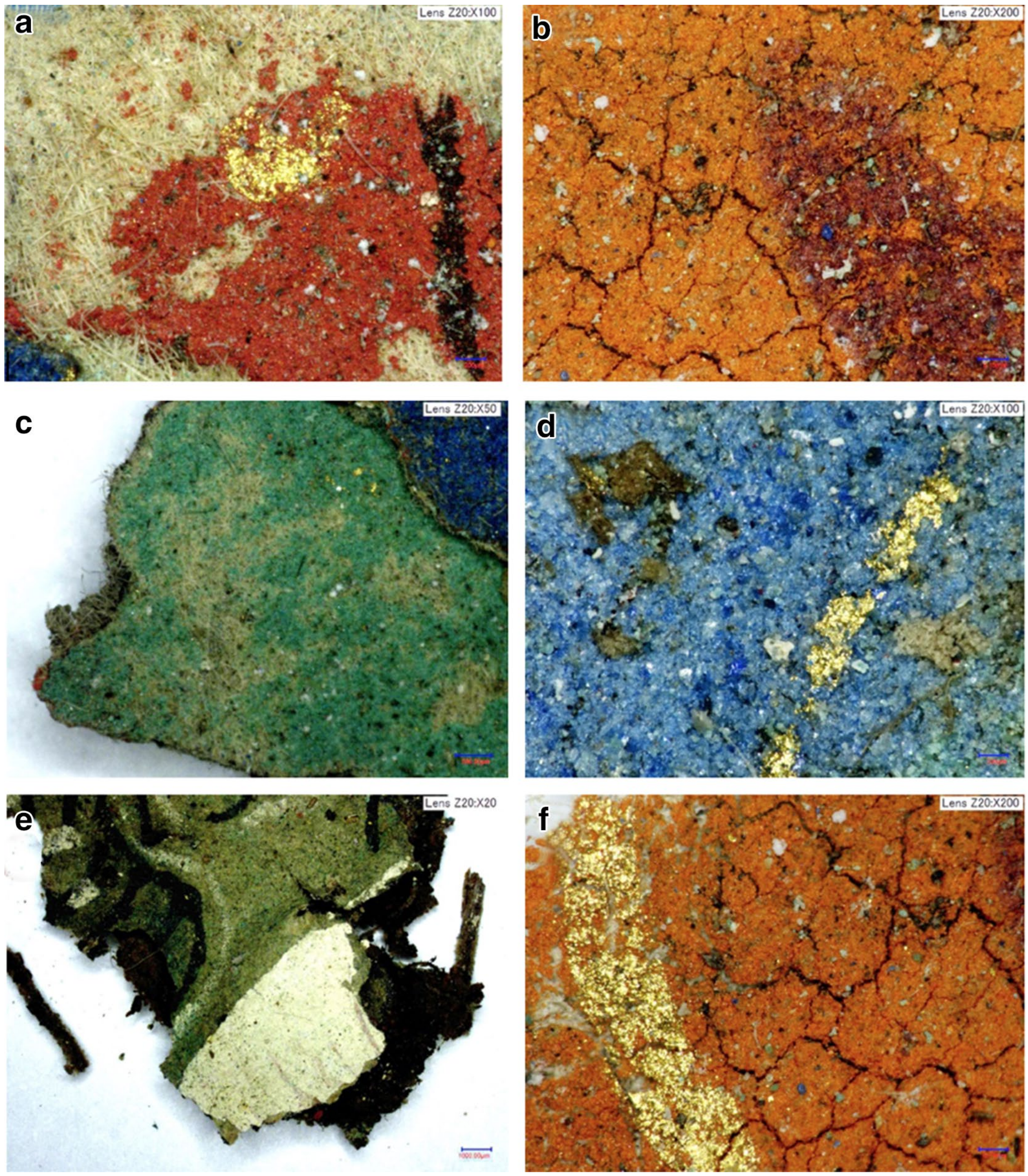


Fig. 2 Microscopic observation of pigments (**a** red pigment ×100, **b** light red pigment ×200, **c** green pigment ×50, **d** blue pigment ×100, **e** white pigment ×20, **f** gilded material ×200)

Chemical composition of the pigment

SEM–EDS and Micro-Raman spectroscopy were used to identify the chemical composition of the pigments. Table 2 shows an overview of the pigments that were identified. The different colored samples were analyzed by micro-Raman spectroscopy to reveal the molecular composition of pigments [13]. Element information of each pigment was acquired by SEM–EDS. As shown in Fig. 2, samples were covered by pollutant minerals (mainly from soil), which caused the detection of elements such as Si, Ca, K and Al in samples.

The elements Hg and S were found by SEM–EDS, indicating that the red pigment consists of cinnabar (vermilion). The existing of cinnabar was also showed by Raman spectra (Fig. 3-red). A very strong band at 253 cm^{-1}, arising from the stretching vibration of Hg–S bond was

Table 2 Chemical composition of the pigment

Color	Elements detected by SEM–EDS	Raman bands/cm^{-1}	Pigment
Red	*Hg*, *S*, Si, Ca, K, O, C	253, 347	Cinnabar
Light red	*Pb*, O	120, 161, 224, 307, 478, 546	Minium
Green	*Cu*, *Cl*, Ca, Si, K, Al, O, C	120, 151, 175, 251, 364, 402, 450, 510, 580, 901, 924, 976	Paratacamite
Blue	*Cu*, O, C	249, 400, 765, 836, 940, 1095, 1432, 1580	Azurite
White	*Pb*, Cu, Cl, O, C	1051	Lead white
Gilded material	*Au*, Ca, K, Fe, O, C	–	Gold

Major elements are denoted in italics

clearly identified [14, 15]. The use of cinnabar was known since Neolithic times [16, 17]. Cinnabar has been mined in both prehistoric and historic China [18]. As one of the most widely used pigments in ancient China, cinnabar has been identified as the red pigment in famous Buddhist sites such as the Mogao Grottoes, Jokhang Monastery and other Buddhist rock-cut temples [19–21].

Pb appeared in the element analysis. The spectral bands at 120,161, 224, 307, 478, and 546 cm^{-1} are assigned to minium (Pb_3O_4) (Fig. 3-light red). The strong absorption appearing at 540 cm^{-1} is attributed to the stretching of the Pb–O bond [22, 23]. Minium was usually used, besides cinnabar, as red pigment to achieve red colors, but it suffers easily from oxidation caused by environmental factors. The chemical reaction makes minium transform into plattnerite, and makes the color change from red to brown-black [24]. Fortunately, the sutra was kept inside the box, away from oxidizing agents, keeping the color stable.

Cu, Cl, Ca, Al, K were found as main elements in the green pigment sample, of which Cu and Cl came from the green pigment. Peaks at 120 cm^{-1}, 151 cm^{-1} and 175 cm^{-1} of green pigment can be assigned to O–Cu–O bending, while peak at 251 cm^{-1} is attributed to lattice mode. Peaks at 364 cm^{-1} and 402 cm^{-1} are attributed to the vibration of Cu-Cl stretching; peaks at 450 cm^{-1} and 510 cm^{-1} belong to Cu–O stretching. Peaks from 901 cm^{-1} to 976 cm^{-1} belong to hydroxyl deformation (Fig. 3-green). All the vibrations indicate that the pigment is paratacamite [25, 26]. Paratacamite has been used as green pigment in the Buddhist Grottoes along the silk road [27].

Cu was characterized as the main element in the blue pigment. Raman spectra of characteristic bands of azurite could be found in 249, 400, 765, 836, 940, 1095, 1432 and 1580 cm^{-1} [28–30] (Fig. 3-blue). Azurite was the most important blue pigment in European paintings throughout the Middle Ages and Renaissance because of its fine texture and surface quality [31]. Azurite was widely used as a pigment in China from Tang dynasty in mural paintings and sculptures to replace lapis lazuli which was more expensive [32].

Pb, as well as Cu and Cl were identified in the white pigment. Detection of Cu and Cl was caused by a coverage of small particles of green pigment. Vibration at 1051 cm^{-1} can be attribute to the absorption of lead white [33–35] (Fig. 3-white).

Gilded material was identified as gold. Gold was frequently used as gilding material in precious sutra in ancient China.

Analysis of the paper fiber and textile

Two different types of paper fiber were found. Observation by fiber analysis microscope (Fig. 4) shows that the fiber from the preface is straight. The fiber from the preface has an abundance of stone cells and smooth epidermal cells, indicating it is made from bamboo. Fiber from the inner page is thinner and longer, and it is covered by a gelatinous coating, which is characteristic of bark fiber [36].

The woven structure of the textile is five-heddle warp satin (Fig. 5) a typical structure for ancient silk fabric from the Tang dynasty, which was subsequently replaced by other weaving methods due to its complexity [37, 38]. SEM shows the shape of the cross section is a rectangle with round edge (Fig. 6), which is in accordance with silk (*Bombyx mori*) fiber [39, 40]. Several fibers were bonded together by the covering minerals, as a result, the surface was no longer smooth (Fig. 7). The typical vibration bands of silk are Amide I (stretching vibration of C=O), AmideII (bending vibration of N–H) and Amide III (stretching and bending vibration of C–N and N–H), the bands have been found in 1636 cm^{-1}, 1525 cm^{-1} and 1381 cm^{-1} [41–43] (Fig. 8). It should be noted that the absorption bands of contamination appear on the surface of textile, indicating the appearance of mineral.

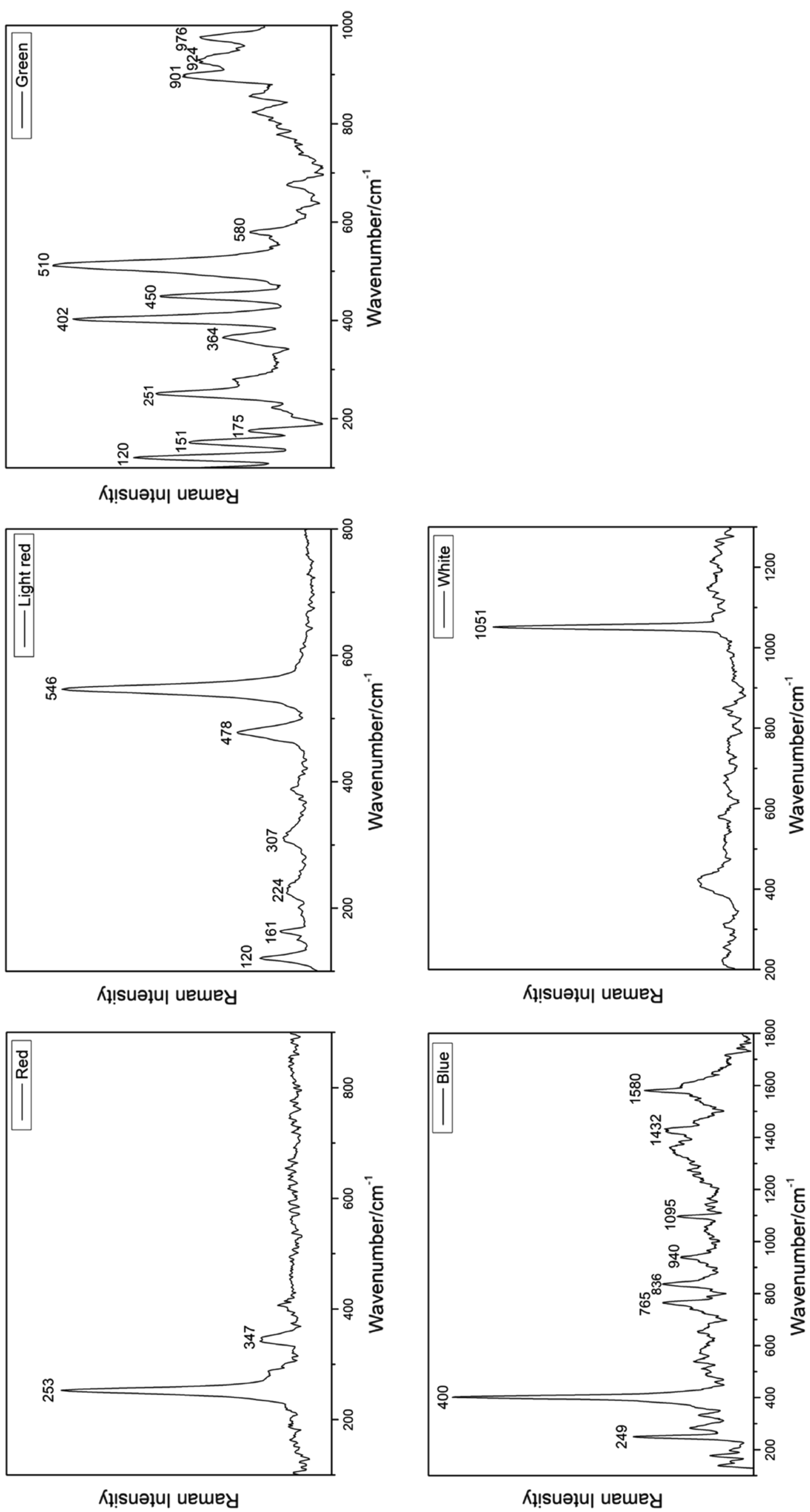


Fig. 3 Raman spectra of the pigments

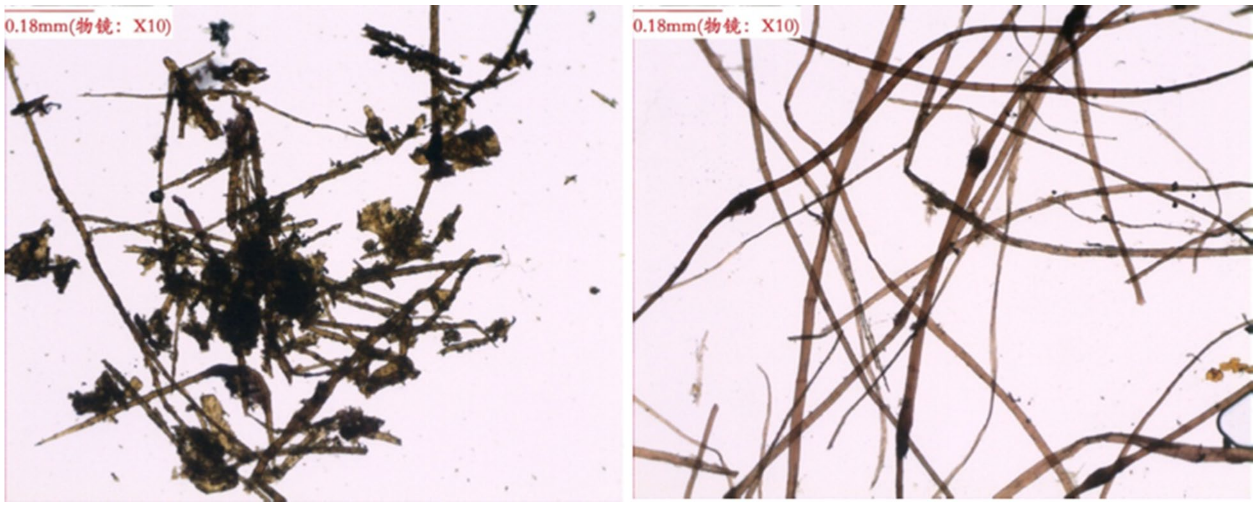


Fig. 4 **a** Left: paper fiber of the preface ×10. **b** Right: paper fiber of the inner page ×10

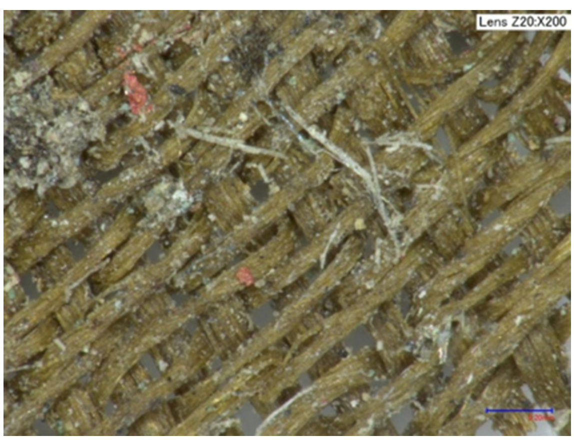


Fig. 5 Microscopic observation of the textile by OM ×200

Fig. 7 Surface of the textile fiber

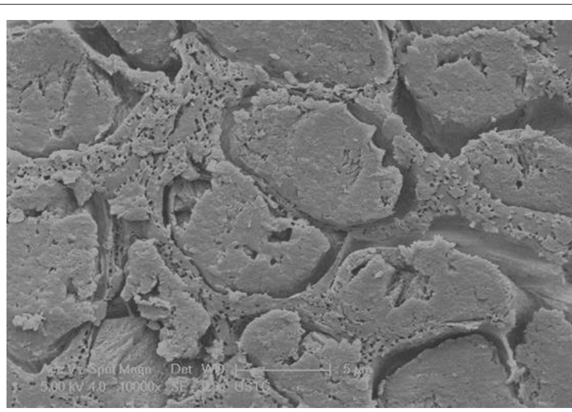


Fig. 6 Cross section of textile fiber

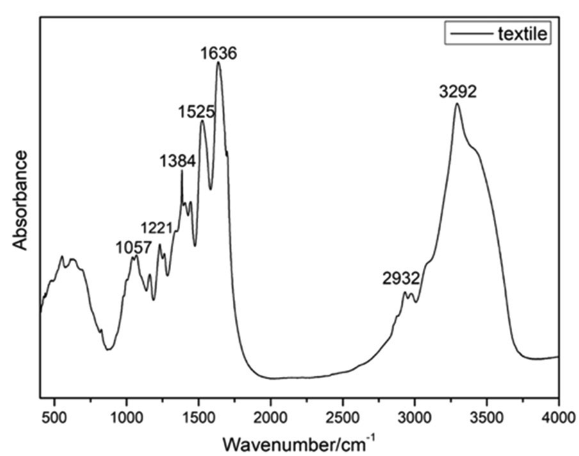


Fig. 8 FTIR spectra of the textile

Conclusions

The *Mahamayuri Vidyarajni Sutra*, is a magnificent recondite treasure of Buddhism, believed to have special functions in prevention and cure of injuries caused by poison in ancient times. Five samples, taken from the sutra, were studied by several scientific techniques to characterize the materials and assess the preservation situation.

Different materials, such as cinnabar, minium, paratacamite, azurite, lead white and gold were identified as red pigment, light red pigment, green pigment, blue pigment, white pigment and gilded material, respectively. Two different paper fibers were found in the preface and inner page. The textile from the preface is a five-heddle warp satin and is made of silk (*Bombyx mori*). This complicated type of woven silk fabric, reserved for important uses was not employed after the Tang dynasty. The whole sutra is in a state of severe degradation.

This study shares insights into the materials employed, as well as assessing the preservation situation of the sutra and providing support for scientific protection and restoration schemes. Furthermore, restoration based on the research will benefit the study of Buddhism in ancient China.

Abbreviations

OM: optical microscopy; Raman: micro-Raman spectroscopy combined with optical microscope; SEM–EDS: scanning electron microscopy in combination with energy dispersive X-ray analysis; FTIR: Fourier transform infrared spectroscopy.

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Authors' contributions

LL did data analysis and article written. DG did sample collection. ZY provided background, photos and samples. LX performed OM and SEM–EDS. ZZ performed analysis of FTIR, Raman. TE helped with the English language improvement. All authors read and approved the final manuscript.

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Availability of data and materials

All data generated or analyzed during this study are included in this published article.

Competing interests

The authors declare that they have no competing interests.

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