Guangzhou Tongcao painting in late China Qing Dynasty（1840—1912 AD): technology revealed by Analytical Approaches

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Abstract

Guangzhou *Tongcao* painting of China late Qing Dynasty witnessed the exchange of economy, culture, art and technology between China and foreign countries, which was an important exported product in the ancient China. In this paper, by using stereo microscope, Scanning Electron Microscope attached Energy Dispersive Spectroscopy and micro Raman Spectroscope, a Qing Dynasty Tongcao painting with the subject of family life of an official's female relative was analyzed. Our study revealed that: 1) the hexagonal cell morphology could be easily observed in the Tongcao pith which could contain much more pigment and increase the stereo sense of painting, and the cell of the ancient Tongcao pith had started to degrade, which indicated an urgent requirement on conservation of the tongcao painting; 2) alum was applied as the fixing agent in the preparation of pigments and the painting process; 3) both the China domestic pigments including red lead, calcite, lead white, carbon black and gamboge, and the synthetic pigments imported from Europe (artificial ultramarine, Prussian blue and emerald green) was applied in the painting, which reflected the bi-directional communication of culture and technology between China and the western world.

1. Introduction

Tongcao(▯▯) painting, which was painted directly on the Tongcao pith (the stem of *Tetrapanax papyriferus* without any chemical treatment), was a kind of exported painting in late Qing Dynasty of China (1840-1912AD), and it was produced in Guangzhou and yet specially sold to the European. As *Tongcao* painting had the similar stereoscopic effect as Oil painting and meanwhile, it recorded nearly all aspects of city landscape and the local customs of Guangzhou at that time, it was favored by the foreigners once it was created. Almost every foreigner would buy and bring it to homeland to share with his friends and families what they saw in Guangzhou before the invention of camera, so it also had another name of Guangzhou Postcard. As a representative exported painting from Guangzhou in the 19th century, *Tongcao* painting was a vivid reflection on the integration of trade, culture and art between China and the western world along the Maritime Silk Road. Therefore, for a long time it was focused by experts in different fields, including history, archaeology, art and so on.

As early as in 1970s, American scholar Carl L. Crossman studied the creation and trade transmission of *Tongcao* painting [–]. Since that time, more and more attention had been paid to this special kind of painting. In 2007, professor Jiang of Sun Yat-sen University tried to study *Tongcao* painting in the context of port history [▯], which aroused a tremendous interest on such painting among Chinese scholars. Later in 2008, professor Cheng focused on the manufacture technique of *Tongcao* pith and development of *Tongcao* painting in different periods [▯], whose research became the first monographic study of *Tongcao* painting in China. Meanwhile, some western scholars carried a series of researches to explore the reparation and conservation of *Tongcao* painting from the usage of the new reparation material, treatment methods & specific operation, and the control of the storing environment [–]. In 2014, Based on the images of *Tongcao* painting, Patrick Conner fully studied the style and features of *Thirteen Hongs* commercial area along the *Pearl River* in Guangzhou[▯]. In the same year, Ifan Williams and Cheng Meibao cooperatively published a book, where all the *Tongcao* Paintings in different 29 museums of the world were systemically sorted and classified according to their content and subjects[]. Furthermore, Guangzhou Thirteen Hongs Museum published a book to show the abundant exquisite *Tongcao* paintings stored in its museum, which demonstrated a great deal of historical information of ancient Guangzhou [].

Overall, the study of *Tongcao* painting is still in the early phase and principally relies on methods like the Iconography and the analysis of historical documents, where scientific studies are very rare. As *Tongcao* painting combined selection and cutting of Tongcao pith, treatment of alum, painting and other techniques, it partly reflected the technological complexity of folk painting in Guangzhou at that time. Given these considerations, the attempt to comprehensively analyze representative *Tongcao* painting samples from a technological perspective is required to disclose the materials and drawing procedure of such painting. Not only will these studies bring new insights into techniques that produce *Tongcao* painting, but they are also helpful to understand the technical decisions made by craftsmen basing on the background of economy, culture and art in late Qing Dynasty. Technical analyses on *Tongcao* painting have more practical impact that provides the scientific foundation of preserving and restoring this kind of painting.

In this paper, we analyzed the ancient *Tongcao* panting by using optic stereo microscope (OM), micro confocal laser Raman spectroscope (μ-RS), and scanning electron microscope with Energy Dispersive X-ray Spectrometer (SEM-EDS). Based on the analysis, we attempted to reveal, from a technological perspective, what kinds of materials and how they were prepared in the whole manufacture process of *Tongcao* painting. Meanwhile, we discussed the types of pigments (both China domestically produced and the imported) used in the painting, which could throw a light on exploring the cultural and technological communication between China and Europe.

2. Materials And Methods

2.1. Sampling

2.1.1. The ancient Tongcao painting

The ancient *Tongcao* Painting, which was identified to be an artwork of Late Qing Dynasty (1840-1912AD), was kindly provided by the Anthropology Museum of Sun Yat-sen University. It depicted a scene of an official lady appreciating flowers accompanied by a maid (Fig. 1), with different kinds of colors including blue, green, yellow, red, white and black.

The different areas of number 1 to 16 were selected for Raman spectrum analysis nondestructively, which respectively referred to maid's sleeve (light blue), maid's collar (deep blue), chair (green), maid's hair (black), table leg (orange red), the horn of dragon pattern on hostess's gown (white), floor (light yellow), chair (yellow), vase (deep yellow), vase (light yellow), leaves (green), the mouth of dragon pattern on hostess's gown (red), floor (blue), the lower hem of hostess's gown (red), floor (blue) and floor (yellow).

2.1.2. Tongcao pith of 2015

The *Tongcao* pith produced in Guizhou in 2015 was collected and cut into several pieces (respectively named as x_0, x_1, x_2, x_3) for simulative experiments.

According to the records of *The Painting Manual of the Mustard Seed Garden* (□□□□□)□, we prepared the solution of gelatin and alum in ratio of 7:3, which was then coated on x_0 for 0 times, x_1 for 4 times, x_2 for 8 times and x_3 for 12 times for the chemical analysis. Meanwhile, q_0 (unpigmented areas), q_1 (yellow areas) and q_2 (pink areas) of the painting were served as compared sample.

2.2. Analytical facility

2.2.1. Stereoscopic microscopy

A RH-2000 stereo microscope (Japan) with multiple range of 35-2500x was used to in situ and non-destructively observe the microscopic state of cells and pigments of samples. As configured with Hirox software system, not only could this microscope capture the high-definition image in real time, but it was able to synthesize the image in 3D.

2.2.2. Laser Raman Spectroscopy

The Renishaw Invia laser Raman spectroscope (Gloucestershire, UK) was chiefly employed to analyze phase structure of different pigments on the painting, which used argon ion laser as light source, with an excitation wavelength of 785 nm, an objective lens of 50x, a spot size of 1 μm and a spectral resolution of 1 cm^{-1}. Raman spectra were recorded in wavenumber mainly between 100 and 3000 cm^{-1}, with spectral accuracy of about 1 cm^{-1}. An optical microscope was used to focus the laser on samples, at × 50, throughout the analysis. Calibration is carried out on the Raman spectrometer on a daily basis using the Raman signal of silicon at 520 cm^{-1}. Background spectra of water and carbon dioxide are obtained in ambient air. Raman spectra presented here were smoothed without baseline correction.

2.2.3. Scanning Electron Microscope with Energy Dispersive X-ray Spectrometer

Equipped with INCA X-ray spectrometer (EDX, Oxford, UK)), The Quanta-400F thermal field environment scanning electron microscope (ESEM, Philips, the Netherlands) was used to analyze the micro structure and composition of samples, with the experimental voltage of 20kv and the mode of low vacuum, under which the pressure of sample chamber was 60 Pa. By using this machine, the very small pieces fell down from the painting, as well as the Tongcao pith of 2015 were collected and analyzed.

3. Results And Discussion

3.1. The Tongcao pith

As the carrier of *Tongcao* Painting, Tongcao pith, with the yellowish white appearance, was cut from stem of *Tetrapanax papyriferus* which was usually planted in southern China like Guizhou, Fujian, and other areas.

As we know, *Tongcao* pith had not been treated chemically, and its hexagonal cell structure could be clearly seen under the microscopy, which differentiated from that of Xuan paper with numerous and various sizes of fibers mixed together unregularly(Fig. 2). Under the SEM-EDS, surface of *Tongcao* pith looked like the honey honeycomb, which provided an ideal space for the stay of much more pigments with the small size of 5–10 μm, so the *Tongcao* painting looked more colorful and had the similar stereoscopic sense as oil painting. Generally, the cell wall of plants mainly consisted of cellulose microfibrils, lignin, hemicellulose, pectin and glycoprotein . There were special cross-linked substance among these components, which enabled the cell wall to own enough mechanical strength in all directions, providing source for the structural support of *Tongcao* pith. However, compared with microstructure of *Tongcao* pith produced in 2015, cells of the ancient painting had changed in their shape, which suggested the start of degradation of secondary cell wall. Meanwhile, the connection among cell walls seemed very loose in the painting, which directly led to the strength reduction of its mechanical support and eventually resulted in the rupture and smash of *Tongcao* pith. Therefore, the related conservation work of Tongcao painting needed to be carried out emergently.

3.2. The usage of alum in Tongcao painting

Alum glue, a kind of solution which mixes the alum and gelatin, is chiefly used as an adhesive in the process of drawing, mounting and repairing of painting and calligraphy , which on one hand can enhance the binding force among plant fibers, and on the other hand, has the function of fixing color, enhancing water resistance of paper and inhibiting growth of microorganism. In the mid-19th century, British traveler *Downing* once recorded in his travel notes the making and drawing procedure of Tongcao painting in detail as followed:

The paper being ready, it is washed over with a weak solution of alum, as they consider it is thus rendered more fit to receive the colours. This wash is frequently repeated during the progress of the work, so that before it is finished, it has received seven or eight coats. It is difficult at first to conceive the utility of the alum, but upon reflection it appears to me, that it is this mineral which gives such a degree of permanence to the coloring of the Chinese .

Since the drawing technique of Tongcao painting had been lost, whether alum glue had been applied in the manufacture process of Tongcao painting was a controversial question. In order to solve this question, we compared the chemical difference among *Tongcao* pith with and without alum glue treated, and both pigments area and unpigmented area of the ancient painting.

Table.1 Semi quantitative analysis results of SEM-EDS(wt%)

Samples	x_0	x_1	x_2	x_3	q_0	q_1	q_2
Al	0.06	0.22	0.44	0.38	0.17	0.12	1.43
S	0.07	0.32	1.14	1.13	0.10	0.26	0.85
K	0.15	0.19	0.14	0.16	0.17	0.11	0.18
Pb	/	/	/	/	/	/	32.1
Ca	1.05	0.64	0.69	0.57	2.32	1.14	2.84

The chemical formula of alum is $KAl(SO_4)_2 \cdot 12H_2O$. As shown in Table.1 and Fig. 3, the chemical difference among samples was on the elements Al and S. It was easy to find that with the increase of coating times, content of Al and S was on an increasing tendency, indicating the higher concentration of alum. However, it basically stopped increasing when the number of coating times was over 8, revealing the adsorption capacity of cells tended to be saturated. On the other hand, content of Al and S remained in q_0, q_1 and q_2 apparently exceeded than that of x_0, relatively close to x_1 or x_2, which proved alum was applied both in the unpigmented area and pigments area of the ancient Tongcao painting.

3.3. the pigments

In China, the archaeological evidence revealed that as early as the *Shandingdong* Man period (30,000–40,000 years ago), hematite was ever used as the red pigment in burial area of this archaeological site. Subsequently, more and more types of pigments were used to paint the life of ancient human being. The pigment itself not only recorded ancestor's knowledge of natural pigments including all kinds of mineral powder and plant dyes, but also memorized the new invention of artificial synthesis pigments. In addition, pigment also witnessed ancient trade and technological transmission. Our study disclosed the following pigments were applied in the ancient *Tongcao* painting.

3.3.1. The black pigment

Figure 4-a was the Raman spectrum of black pigment, where Raman peaks of 1324 and 1596 cm^{-1} were basically consistent with carbon black []. As we know, Carbon black was black outside appearance with particle size of 30–40 μm, and was a kind of amorphous graphite, which was usually applied as black pigment in ancient China.

3.3.2. The white pigment

As shown in Fig. 4-d, the Raman peaks of 153, 280, 711 and 1085 cm^{-1} was consistent with calcite [], while that of 1048 cm^{-1} was the characteristic peak of lead white []. Therefore, white pigment was the mixture of calcite and lead white. Surprisingly, judging from the intensity of Raman shifts at 1048 cm^{-1} and 1085 cm^{-1}, it was easily to conclude that the proportion of calcite and lead white used as the white pigments in different areas were different. As we know, lead white had better whiteness and coverage, so when painting the area of white dragon (Number 6), the artist specially selected the higher proportion of lead carbonate as the white pigment to protrude the dragon and meanwhile, more lead carbonate could reduce the interference effect of blue pigment under it.

3.3.3. The yellow pigment

Serial Raman peaks of 1431, 1595 and 1627 cm^{-1} (Fig. 4-b) demonstrated the existence of gamboge [16] in different tested areas of Number 7, 8, 9&16. Gamboge was a kind of gelatinous resin secreted by plant of gamboge, mainly planted in India, Vietnam and Thailand. As a kind of yellow pigment, gamboge was used to paint the wooden objects unearthed from the tomb of Astana in Xinjiang province, which could date back to Tang Dynasty of China(618-907A.D) ▯.

3.3.4. The red pigment

Figure 4-f showed that the spectra of three detection points (Number 5, 12 & 14) were basically the same. Serial Raman peaks of 121, 151, 223, 314, 389 and 548 cm^{-1} referred to red lead [16], whose main component was lead tetroxide (Pb_3O_4). The used of red lead could date back to Eastern Han Dynasty of China(25-220A.D), which was introduced from the West via the Silk Road ▯. Because there was extremely few red lead in natural minerals, red lead was generally produced by certain processes, no matter in ancient times or modern times. It was a kind of pigment often used in Chinese works of art, the color of which varied from orange to red depending on its purity ▯.

3.3.5. The blue pigment

Under microscopy, particles of blue pigment were bright and blue with the size of 5–10 μm. It was clearly seen in Fig. 4-c that Raman spectra of four detection points numbered 1, 2, 13 and 15 were basically the same, where Raman peaks of 259, 548, 808, 1096, 1355 and 1645 cm^{-1} referred to ultramarine blue ▯. Nevertheless, there were two kinds of ultramarine blue: the natural form extracted from Lapis lazuli and the synthetic form firstly synthesized by Jean Baptiste Guimet in 1828, a French industrial chemist▯. In recent years, researchers had used SEM-EDS, FITR, μ-Raman and other methods to find out there were some characteristic peaks of 156, 283, 713 and 1086 cm^{-1} belonging to that of the calcite component in blue particles of natural ultramarine, which were absent in synthetic ultramarine▯. Therefore, blue pigment of this painting was synthetic ultramarine.

Compared with natural ultramarine, the price of synthetic ultramarine was cheaper, so it was not surprising that the craftsmen would select such pigment in *Tongcao* painting, as they belonged to the export paintings of assembly line production. Besides, as its color was more gorgeous than azurite(a traditional Chinese precious mineral pigment), craftsmen in Guangzhou hence added it to their palette without hesitation. It originated in France and might be introduced to China by sea in later Qing dynasty, and in 1927 Chinese chemist in Nanjing university successfully synthesized ultramarine blue ▯.

3.3.6. The green pigment

The painting showed two kinds of green pigment: one was the bright green chair, and the other was the dark green leaves.

In the spectrum of green chair (Number 3, Fig. 4-e), serial Raman peaks of 106, 119, 152, 172, 216, 240, 291, 323, 370, 431, 492, 538, 681, 755, 842, 950, 1438, and 1563 cm^{-1} were consistent with emerald green[20]. As a kind of artificial pigment, emerald green consisted of fine particle with high purities, which was first synthesized in 1814[] and was brighter and durable than copper carbonate used at that time. However, it tended to fade and blacken when exposed to an atmosphere containing hydrogen sulfide, and meanwhile, the arsenic inside emerald green ($Cu(C_2H_3O_2)_2{\cdot}3Cu(AsO_2)_2$) would be easily separated out in the wet air ,which made it extremely poisonous, so it was stopped to produce in 1950[].

Under microscopy, the darker green pigment was the mixture of blue pigment, a few green pigment and black pigment. Figure 4-g showed the Raman peaks of 278, 536, 2093 and 2156 cm^{-1} of the blue particle were consistent with Prussian blue ($Fe_4 [Fe (CN)_6]_3$) [20], which could also explained why the existence of high content Fe (2.39%) in darker green area by SED-EDS (Table.2), while two broad Raman peaks of 1336 and 1595 cm^{-1} referred to carbon black. In addition, the SEM-EDS analysis revealed that this area contained a small amount of Cu (0.49%) and As (0.26%), so Raman peaks of 176, 217, 369 and 952 cm^{-1} of the green particle would be related to emerald green.

Table.2 Semi quantitative analysis results of Number 11 by SEM-EDS

Weight%	C	O	Al	Si	S	Cl	K	Ca	Fe	Cu	As	Pb
Area	50.6	41.89	0.17	0.32	0.13	0.31	0.49	1.82	2.39	0.49	0.26	1.14

Prussian blue was a kind of synthetic blue pigment which had similar color with azurite. As early as 1704, Ghislain Diesbach revealed the manufacturing process of Prussian blue, which was later introduced to painters as a blue pigment. Until the mid-18th century, it had been widely used in European oil painting []. According to documentary records, British east India Company had been exporting Prussian blue from Britain to Guangzhou since 1775 []. Apparently, the clever craftsmen that time mixed the Prussian blue, a few emerald green and a little carbon black to paint green leaves, which looked somewhat dark green and formed a different visual effect from green chair.

As early as Nanyue Kingdom period (204–112 BCE), the connection had been established between Guangzhou and the world through the sea road, which could be reflected in the silver box of Persian style and the blue glasses from Western Asia that were excavated from the Western Han Nanyue kingdom mausoleum. Since Tang dynasty, Guangzhou had been regarded as one of the biggest harbor cities, which played an important role in promoting the cultural communication between China and western world. When it came to Ming & Qing Dynasty, more and more European arrived and carried out all kinds of business activity in Guangzhou, which could be recorded by lots of historical documents. In this process, Chinese goods including ceramic, tea and silk were numerously shipped and sold to European Countries, and on the other hand, many goods such as oil painting, glass and pigments were imported into Guangzhou and other cities in China.

The analytical result of pigments discovered both China's domestic mineral pigments and plant dyes, and western synthetic pigments, were applied in the making process of this Tongcao paintings. Our study also revealed that multi- pigments with different concentration were mixed together to paint different areas in pursuing a certain kind of visual effect, which not only demonstrated the complexity of manufacturing process of Tongcao painting, but also witnessed the arrival and application of western pigments in Guangzhou.

4. Conclusion

There are several significant points to be concluded:

1) The cells of *Tongcao* pith was hexagonal and hollow, which was connected together through cell walls to form a relatively stable honeycomb structure. This special structure thus provided a good space for the distribution of pigments, which might be the direct reason for strong stereoscopic effect of *Tongcao* painting. Meanwhile, the cell of ancient *Tongcao* pith has started to degrade, which indicated an urgent requirement on conservation of *Tongcao* painting.

2) This *Tongcao* painting was supposed to be treated by the solution of gelatin and alum, which confirmed the truth of Downing's travel notes.

3) Both China's domestic mineral pigments and plant dyes, and western synthetic pigments, were applied in the making process of this Tongcao paintings. In addition, multi-pigments with different concentration were mixed together to paint different areas in pursuing a certain kind of visual effect, which not only demonstrated the complexity of manufacturing process of Tongcao painting, but also witnessed the arrival and application of western pigments in Guangzhou.

Declarations

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Declarations of interest

None

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Figures

Figure 1

Guangzhou Tongcao painting of Late Qing Dynasty of China

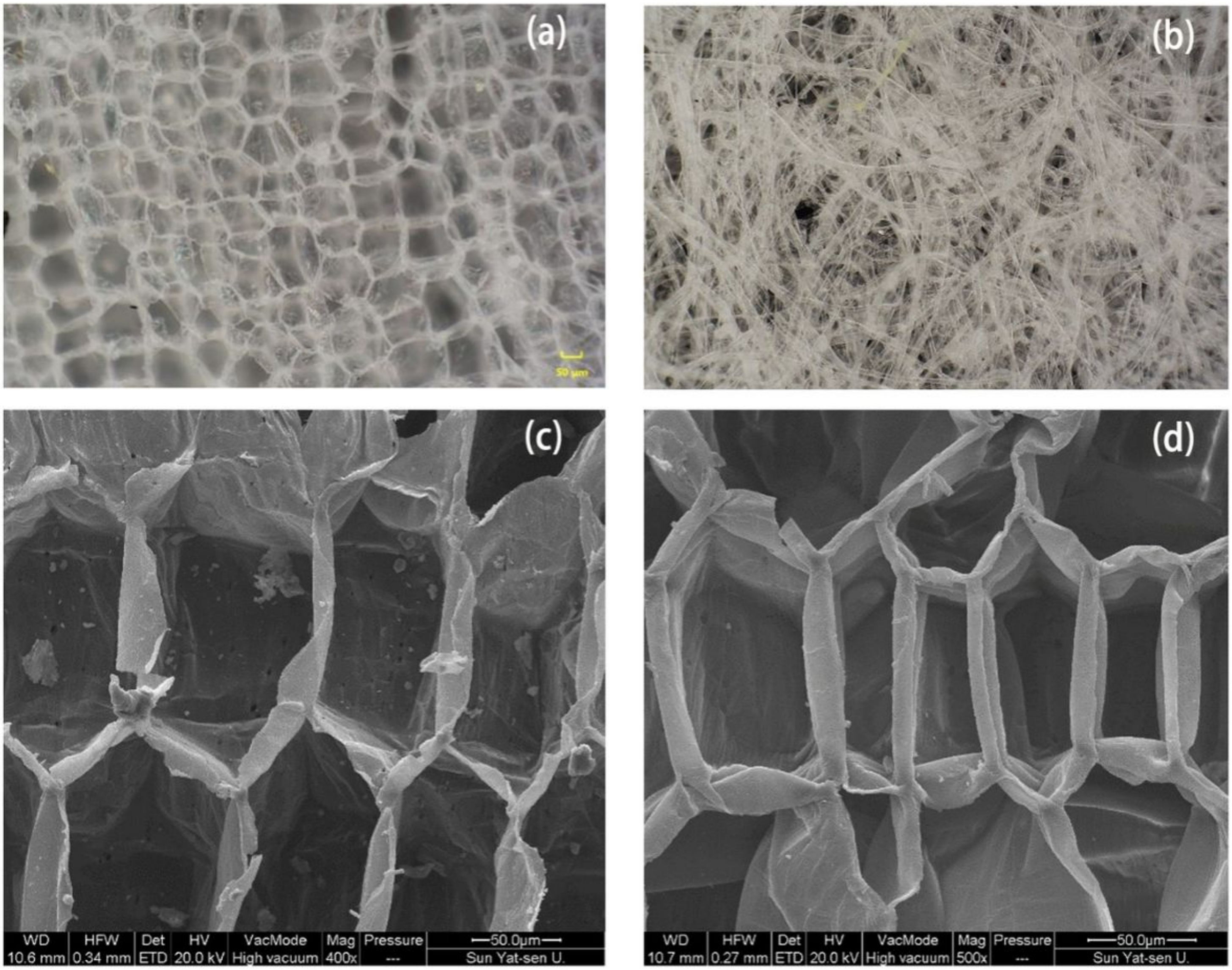

Figure 2

Microscopic comparison between: (a) Tongcao pith and (b) Xuan paper under OM; (c) the unpigmented area of ancient Tongcao painting and (d) modern Tongcao pith under SEM-EDS.

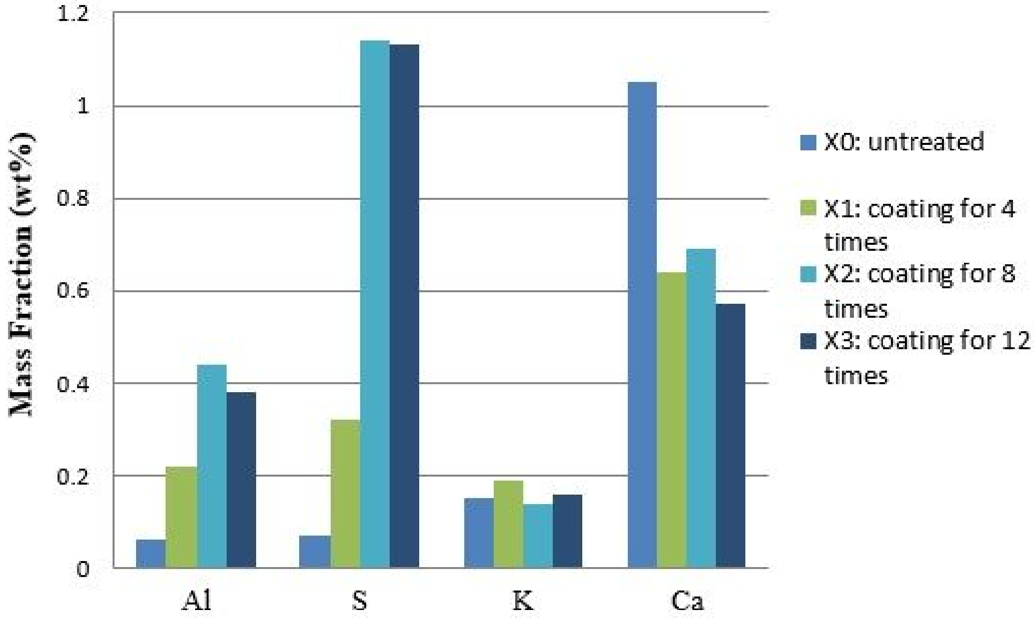

Figure 3

the chart of elemental concentration in modern Tongcao pith with different treatments

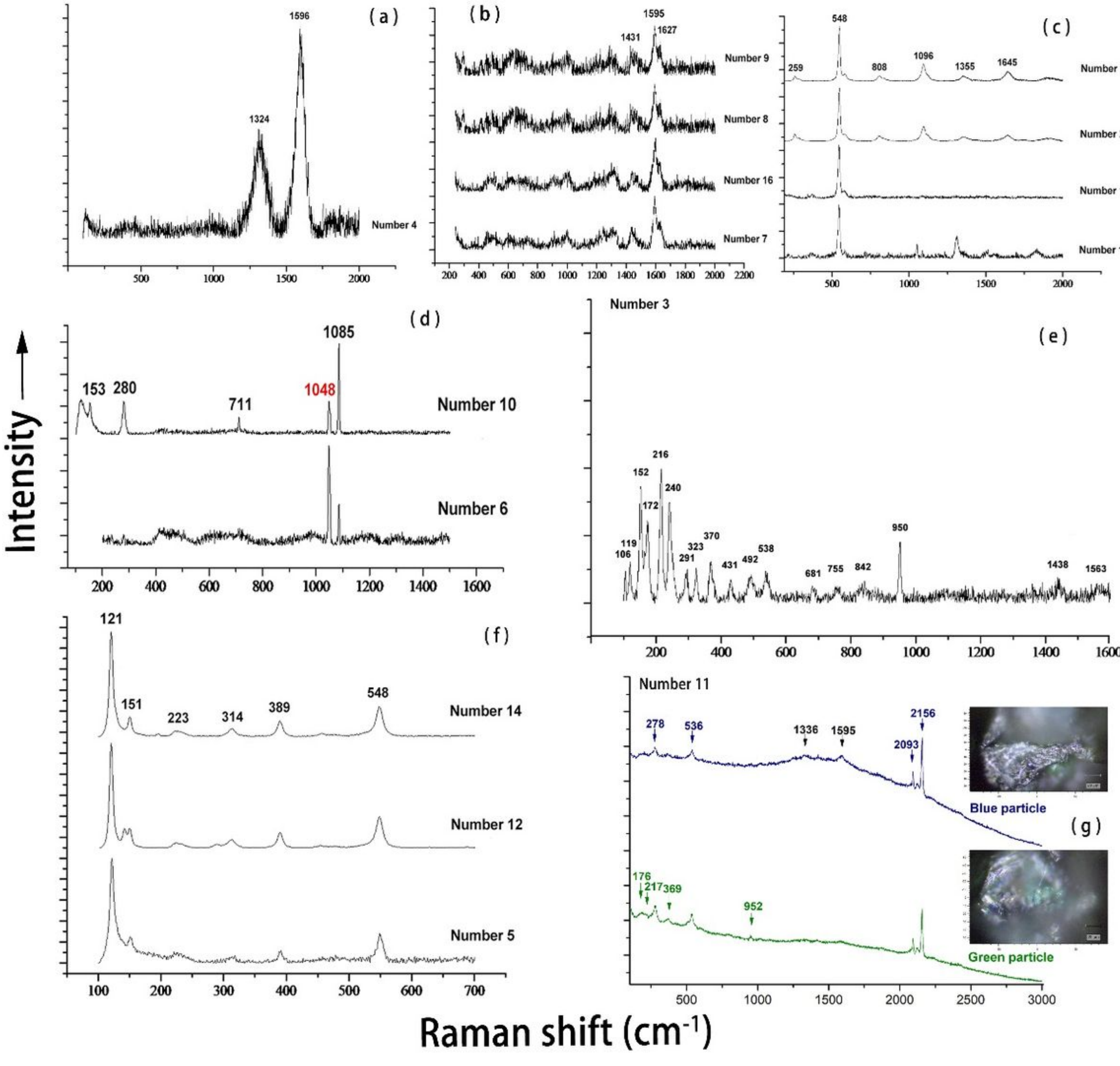

Figure 4

Raman spectra of definite pigments applicated in the painting: (a) carbon black; (b) gamboge; (c) synthetic ultramarine; (d) the mixture of calcite and lead white; (e) emerald green; (f) red lead; (g) the mixture of prussian blue, emerald green and carbon black.