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Guangzhou *Tongcao* painting in late China Qing Dynasty (1840–1912 AD): technology revealed by analytical approaches

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Abstract

Guangzhou *Tongcao* paintings in Qing Dynasty of China witnessed the exchange of economy, culture, art and technology between China and foreign countries, which were an important export product in historical China. In this paper, by using Optical Stereo Microscope, Polarized Light Microscope, Scanning Electron Microscope attached Energy Dispersive Spectroscopy and micro confocal laser 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 which was easily observed in the *Tongcao* pith could contain more pigments and increase the stereo sense of painting, and the cell of historical *Tongcao* pith had started to degrade, which indicated an urgent requirement on conservation of *Tongcao* paintings; (2) alum was needed 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 (synthetic ultramarine, prussian blue and emerald green) were applied in this painting, which reflected the bi-directional communication of culture and technology between China and western world. Meanwhile, the existence of synthetic ultramarine, prussian blue and emerald green was helpful to further identify the production date of this painting was late Qing Dynasty, mainly the mid-late 19th century.

Keywords: *Tongcao* painting, Cell morphology, Alum, Pigment, Technology, Culture

Introduction

Tongcao (通草) paintings, which were painted directly on *Tongcao* pith (the stem of *Tetrapanax papyriferus* without any chemical treatment), were a kind of export watercolor painting. They were produced mainly in late Qing Dynasty of China (1840-1912AD) in Guangzhou, and yet specially sold to European. As *Tongcao* paintings imitated western painting style to some extent and vividly recorded nearly all aspects of local customs of Guangzhou at that time, they were favored by foreigners once they were created. Almost every foreigner would buy and bring them to his homeland to share with his friends and families what they saw in Guangzhou before the invention of camera, so they also had another name of Guangzhou Postcard. As a representative export painting from Guangzhou in the 19th century, *Tongcao* paintings were a vivid reflection on the integration of trade, culture and art between China and the West along the Maritime Silk Road. Therefore, for a long time they were focused by experts in different fields, including history, archaeology, art and so on.

As early as 1970s-1990s, American scholar Carl L. Crossman studied the creation and trade transmission of *Tongcao* paintings [1, 2]. 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

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study *Tongcao* paintings in the context of port history [3], 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* paintings in different periods [4], whose research became the first monographic study of *Tongcao* paintings in China. Meanwhile, some western scholars carried a series of researches to explore the reparation and conservation of *Tongcao* paintings from the usage of new reparation materials, treatment methods & specific operation, and the control of storing environment [5, 6]. In 2014, basing on the images of *Tongcao* paintings, Patrick Conner fully studied the style and feature of *Thirteen Hongs* commercial area along the *Pearl River* in Guangzhou [7]. In the same year, Ifan Williams and Cheng Meibao cooperatively published a book, where all the *Tongcao* paintings from 29 museums and galleries of the world were systemically sorted and classified according to their content and subjects [8]. Furthermore, *Guangzhou Thirteen Hongs Museum* (a museum collecting historical artifacts of *Thirteen Hongs*, which was the monopoly organization managing the foreign trade in Guangzhou appointed by Qing government) published a book to show abundant exquisite *Tongcao* paintings stored in its museum, which demonstrated a great deal of historical information of historical Guangzhou [9].

Overall, the study of *Tongcao* paintings was still in the early phase and principally relied on methods like Iconography and the analyses of historical documents, where scientific studies were very rare. As *Tongcao* paintings combined selection and cutting of *Tongcao* pith, treatment of alum, painting and other techniques, they partly reflected the technological complexity of folk painting in Guangzhou at that time. Given these considerations, the attempt to comprehensively analyzed representative *Tongcao* paintings samples from a technological perspective was required to disclose the materials and drawing procedure of such painting. Not only would these studies bring new insights into techniques that produced *Tongcao* paintings, but they were 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* paintings had more practical impact that provided the scientific foundation of preserving and restoring this kind of painting.

In this paper, we analyzed a historical *Tongcao* panting by using Optical Stereo Microscope (OM), Polarized Light Microscope (PLM), Micro Confocal Laser Raman Spectroscope (μ-RS), and Scanning Electron Microscope with Energy Dispersive X-ray Spectrometer (SEM–EDS). Basing on the analyses, we attempted to reveal, from a technological perspective, what kinds of materials and how they were prepared in the whole manufacturing process of *Tongcao* paintings. Meanwhile, we discussed the types of pigments (both domestically produced in China and the imported) used in this painting, which could throw a light on exploring the cultural and technological communication between China and Europe.

Materials and methods

Sampling

The historical Tongcao painting

The historical *Tongcao* Painting was kindly provided by the Anthropology Museum of Sun Yat-sen University. It depicted a scene that a senior official lady of imperial court was appreciating flowers accompanied by a maid (Fig. 1), and the painting was applied with different kinds of colors including blue, green, yellow, red, white and black. Not only this painting was rich in colors and of exquisite image, meaning the complexity of manufacturing technique, but such kind of subject was universal in *Tongcao* paintings and welcomed by foreigners at that time, so it was a representative piece at that time. However, it was a pity that the information about its

Fig. 1 Guangzhou *Tongcao* painting of late Qing Dynasty of China

production year appeared on the tag of the painting was absent, which brought difficulty for us to judge its specific production date. Therefore, it was generally identified to be an artwork of late Qing Dynasty (1840–1912AD) based on conventional view.

The detection points of number 1 to 16 were selected for Raman spectrum analysis nondestructively (Fig. 1), whose details could be seen in Table 1, including the areas and colors they referred to.

Tongcao pith of 2015

The *Tongcao* pith produced in Guizhou province 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* (芥子园画传) [10], 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 SEM–EDS analyses. Meanwhile, the unpainted piece (named as q_0) and coloring pieces (respectively named as q_1 and q_2) of the historical painting were served as compared samples.

Analytical facility

Microscopy

A RH-2000 optical stereo microscope (Japan) with multiple range of 35–2500 × was used to in situ and nondestructively 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.

A Polarized Light Microscope (ortholux11PPL-BK, Leitz, Germany) was used to check the purity, shape and size of blue particles which were separated from a fragment of the historical *Tongcao* painting, helping to identify the composition of blue pigment.

Table 1 Basic information of 16 detection points for Raman spectroscopy

Number	Detection area	Color
1	Maid's sleeve	Light blue
2	Maid's collar	Deep blue
3	Back of chair	Bright green
4	Maid's hair	Black
5	Table leg	Orange red
6	The horn of dragon pattern on hostess's gown	White
7	Decorative pattern of floor	Light yellow
8	Back of chair	Yellow
9	The edge of vase	Deep yellow
10	The center of vase	Light yellow
11	Leaves of flowers in vase	Dark green
12	The mouth of dragon pattern on hostess's gown	Red
13	Decorative pattern of floor	Blue
14	The lower hem of hostess's gown	Red
15	Decorative pattern of floor	Blue
16	Decorative pattern of floor	Yellow

Micro confocal 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 was 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 were obtained in ambient air. Raman spectra presented here were smoothed without baseline correction.

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.

Results and discussion

The Tongcao pith

As the carrier of *Tongcao* Paintings, *Tongcao* pith, with the yellowish white appearance, was cut from the stem of *Tetrapanax papyriferus*, which were usually planted in southern China like Guizhou, Fujian, and Taiwan. In Qing Dynasty, *Tongcao* was recorded to be used in painting by craftsmen in Guangzhou.

It was well kown that *Tongcao* pith had not been treated by any chemical process, and its hexagonal cell structure could be clearly seen under the microscopy (Fig. 2), which differentiated from that of Xuan paper with numerous and various sizes of fibers mixed together irregularity. Under the SEM–EDS, surface of *Tongcao* pith looked like the honey honeycomb, which was helpful

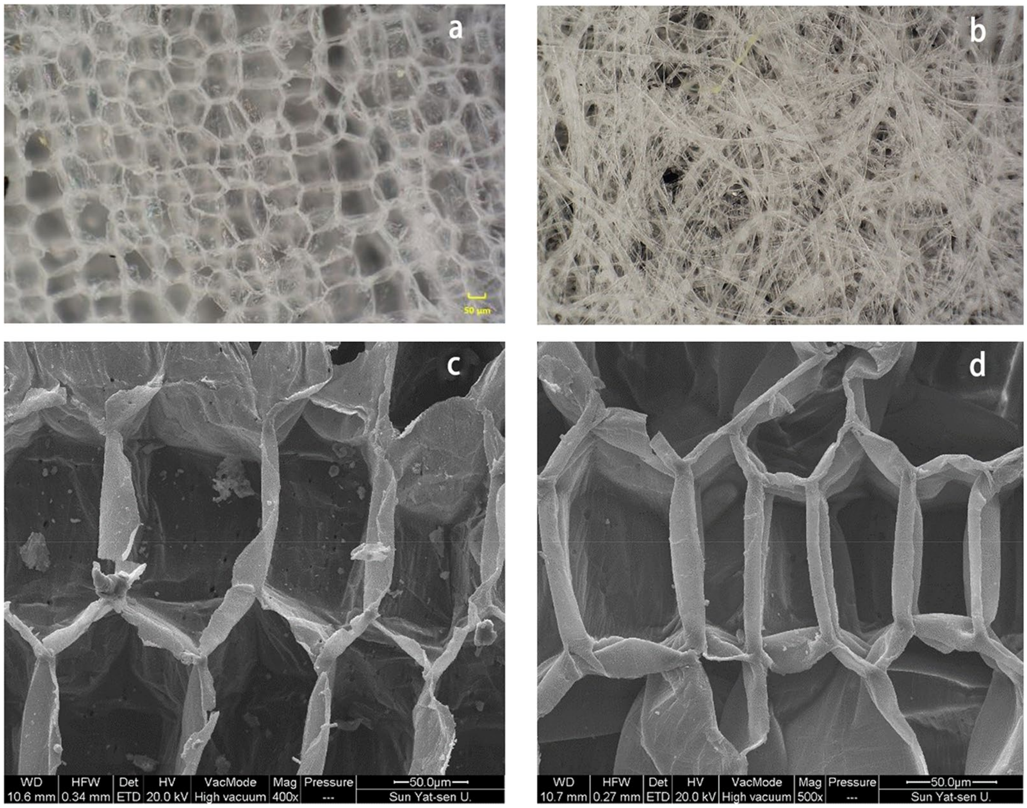

Fig. 2 Microscopic comparison between: **a** *Tongcao* pith and **b** Xuan paper under OM; **c** the unpigmented area of ancient *Tongcao* painting and **d** modern *Tongcao* pith under SEM–EDS

for the stack of pigments and formed an uneven surface for the distribution of pigments, so *Tongcao* paintings looked stereoscopic and colorful. Generally, the cell wall of plants mainly consisted of cellulose micro fibrils, lignin, hemicellulose and a few pectin as well as glycoprotein [11]. 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 historical 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 correlating conservation work of *Tongcao* paintings needed to be carried out emergently.

The usage of alum in Tongcao painting

The alum glue, a kind of solution which mixed the alum and gelatin, was chiefly used as an adhesive in the process of drawing, mounting and repairing of painting and calligraphy [12], which on one hand could enhance the binding force among plant fibers, and on the other hand, had the function of fixing pigments, keeping painting bright-colored, 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* paintings 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 colors. 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 [13].*

Since the drawing technique of *Tongcao* paintings had been lost, whether alum glue had been applied in the manufacture process of *Tongcao* paintings 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 historical painting.

The chemical formula of alum was $KAl\ (SO_4)_2 \cdot 12H_2O$. As shown in Table 2 and Fig. 3, the chemical difference among samples was mainly on the elements Al and S. It was easy to find that with the increase of coating times, content of Al and S were on an increasing tendency, indicating the higher concentration of alum. However, they 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 unpainted area and pigments area of the historical *Tongcao* painting. These findings were basically in accord with *Downing*'s record.

The pigments

In China, the archaeological evidence revealed that as early as the Shan dingdong Man archaeological site (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 historical 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 historical trade and technological transmission. Our studies disclosed the following pigments were applied in the historical *Tongcao* painting.

The black pigment

Figure 4a was the Raman spectrum of black pigment, where Raman peaks of 1324 and 1596 cm^{-1} were

Table 2 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

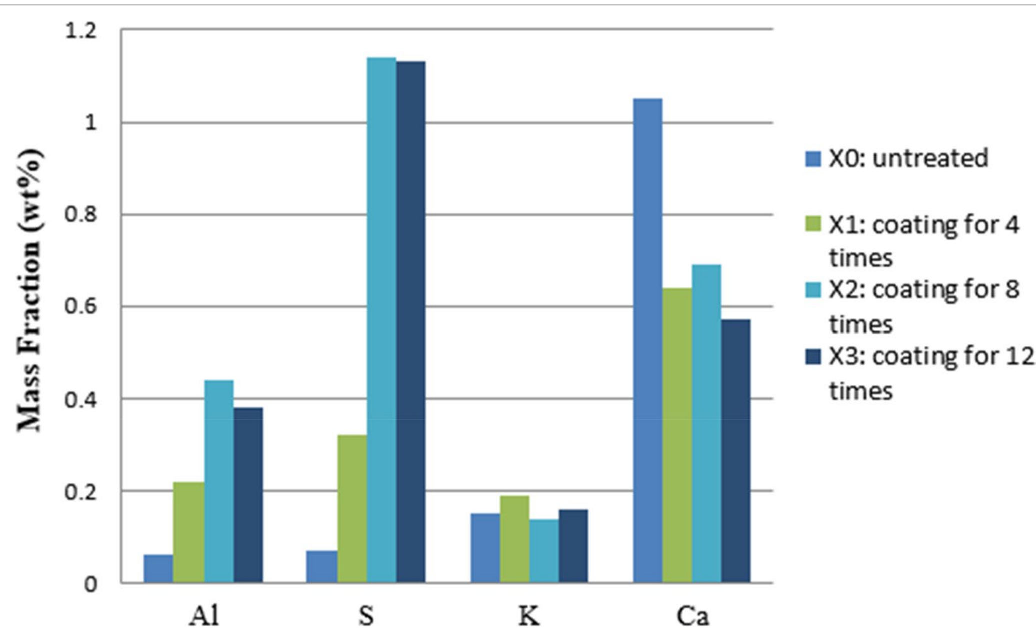

Fig. 3 The chart of elemental concentration in modern Tongcao pith with different treatment

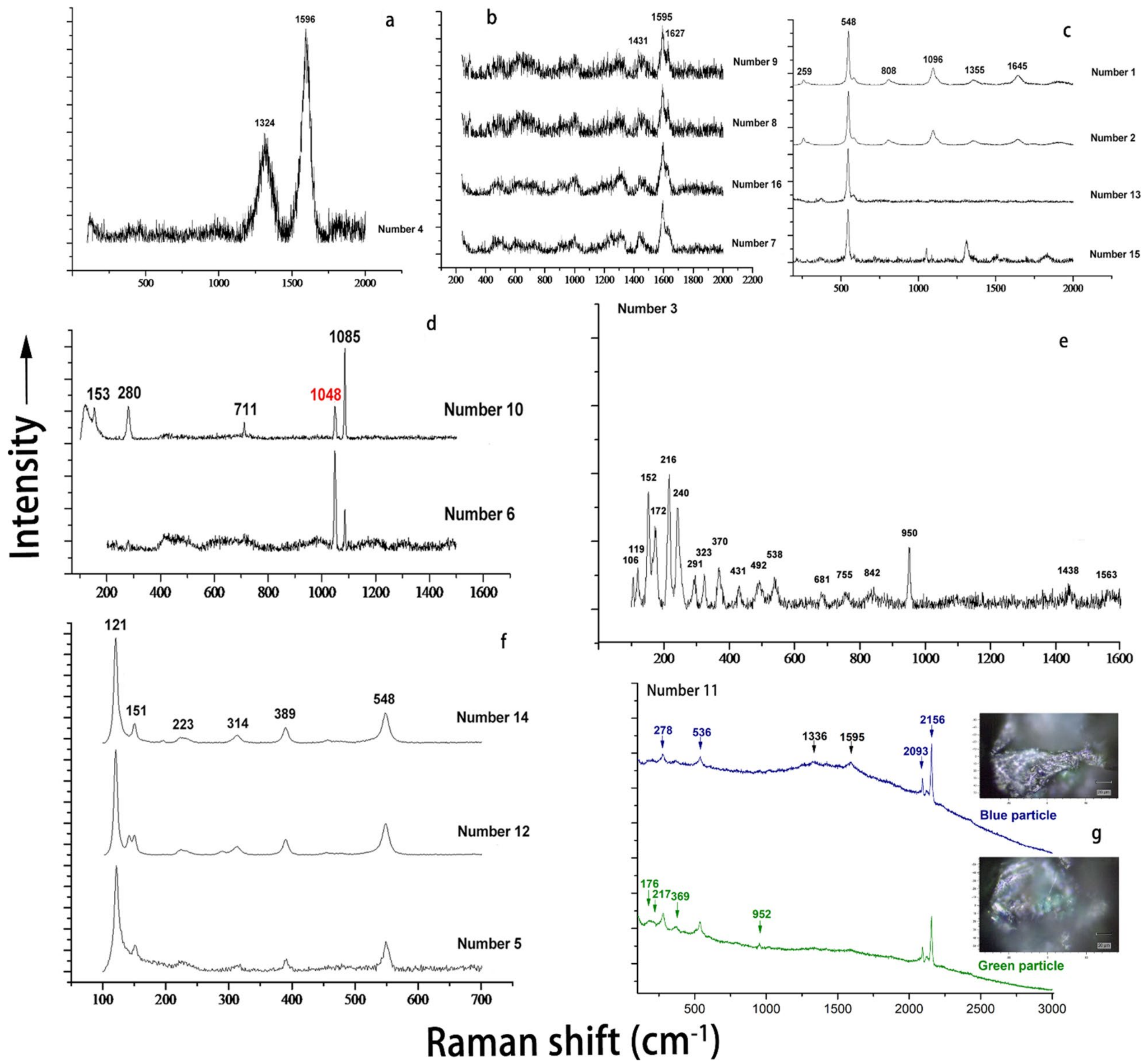

Fig. 4 Raman spectra of definite pigments applicated in the painting: **a** carbon black; **b** gamboge; **c** synthetic ultramarine; **d** calcite and lead white; **e** emerald green; **f** red lead; **g** the mixture of prussian blue, emerald green and carbon black

basically consistent with carbon black [14]. As we knew, 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 historical China.

The white pigment

As shown in Fig. 4d, the Raman peaks of 153, 280, 711 and 1085 cm^{-1} were consistent with calcite [15], while that of 1048 cm^{-1} was the characteristic peak of lead white [16]. Therefore, two white pigments (calcite and lead white) were used both in these areas. 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 knew, lead white had better whiteness and coverage, so when painting the area of white dragon pattern (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.

The yellow pigment

Serial Raman peaks of 1431, 1595 and 1627 cm^{-1} (Fig. 4b) demonstrated the existence of gamboge [16] in different tested areas of Number 7, 8, 9 and 16. Gamboge was a kind of gelatinous resin secreted by plant of gamboge, mainly planted in India, Vietnam and Thailand. The earliest archaeological case of gamboge as a yellow pigment in China was the wooden objects unearthed from the tomb of Astana in Xinjiang province, which could date back to Tang Dynasty [17].

The red pigment

Figure 4f showed that the spectra of three detection points (Number 5, 12 and 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, which was introduced from the West via the Silk Road [18]. Because there was extremely few red lead in natural minerals, red lead was generally produced by certain processes, no matter in historical times or modern times. It was a kind of pigment universally used in Chinese artworks, the color of which varied from orange to red depending on its purity [19].

The blue pigment

It was clearly seen in Fig. 4c 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 [20]. Nevertheless, there were two kinds of ultramarine blue: the natural form extracted from Lapis lazuli and the synthetic form first synthesized by Jean Baptiste Guimet in 1828, a French industrial chemist [21]. 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} belong to the calcite component in blue particles of natural ultramarine, which were absent in synthetic ultramarine [22]. To further support this, we separated some blue pigments from a fragment of this painting, treated them with absolute alcohol and filtered out the scattered blue particles on glass slides. Under the polarized light microscope, the majority of particles were round and homogeneous with diameter of 2–4 μm, and meanwhile, they were pure in deep blue color (Fig. 5), whose characteristic were closer to synthetic ultramarine [23].

Compared with natural ultramarine, the price of synthetic ultramarine was cheaper, so it was not surprising that the craftsmen would select such blue pigment for creating *Tongcao* paintings, as they belonged to the export paintings of assembly line production. Besides,

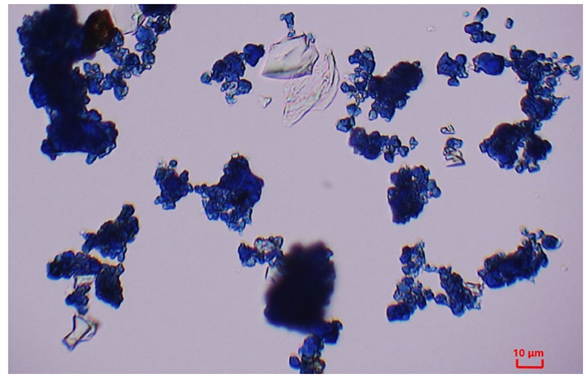

Fig. 5 The microscopic image of blue pigment (treated by absolute alcohol) under PLM

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 into China by sea in late Qing Dynasty, and until 1927 Chinese chemist in Nanjing university successfully synthesized ultramarine blue [24].

The green pigment

The painting showed two kinds of green pigment: one was the bright green chair (Number 3), and the other was the dark green leaves (Number 11).

In the spectrum of green chair (Fig. 4e), 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 [25] 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 [26].

Under microscopy, the dark green pigment was the mixture of blue particles, a few bright green particles and black particles. Figure 4g showed the Raman peaks of 278, 536, 2093 and 2156 cm^{-1} of blue particles were consistent with prussian blue (Fe_4 $[Fe$ $(CN)_6]_3$) [20], which could also explained the existence of high content Fe (2.39%) in dark green area by SED-EDS (Table 3), 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,

Table 3 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

369 and 952 cm^{-1} of green particles would be related to emerald green.

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 [27]. According to documentary records, British east India Company had been exporting prussian blue from Britain to Guangzhou since 1775 [28]. 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.

Results of Raman analyses of the above pigments could be summarized in Table 4:

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.

Since late Qing Dynasty, imported pigments began to be introduced into China at a large scale. At present, it was reported that synthetic ultramarine had been found in *Mogao Grottoes* of Gansu [29], *Cizhong Catholic Church* of Yunnan [22], *Wuhou Memorial Temple* of Chengdu [30] as a blue pigment of architectural painting, murals and painted sculpture. Emerald green, however, was mainly served as a decorative color of architectural painting in the process of construction and restoration. Besides the *Cizhong Catholic Church* mentioned above, archaeologists also found the use of emerald green in *Drum Tower* of Xi'an [31], *Zhendu Men* [32] and *Wuying Hall* [33] of the Imperial Palace in Beijing. Moreover, it was worth noting that a portrait painting of Taoism figure in late Qing Dynasty also used synthetic ultramarine and emerald green [34]. Compared with these pigments, the use cases of prussian blue seemed to focus on painting in China. It was reported that prussian blue was used in *Zhenhai Tower* [28], a Qing Dynasty oil painting for export, and glass paintings collected by *Palace Museum* [35] in Beijing.

These cases revealed that in late Qing Dynasty of China, craftsmen had consciously used imported synthetic pigments to partly replace traditional mineral pigments like azurite and malachite. As a kind of folk painting art at that time, pigments applied in *Tongcao* paintings also accorded with such development trend. The analytical result of pigments in our studies revealed both China's domestic mineral pigments and plant dyes, and western synthetic pigments, were applied in

Table 4 Raman spectroscopy characteristics of pigments in different colors

Color	Raman shift (cm^{-1})	Pigment identified	Detection points
Black	1324, 1596	Carbon black	Number 4
Yellow	1431, 1595, 1627	Gamboge	Number 7, 8, 9 and 16
Blue	259, 548, 808, 1096, 1355, 1645	Ultramarine blue	Number 1, 2, 13 &15
White	153, 280, 711, 1048, 1085	Calcite and lead white	Number 6 and 10
Green (Bright)	106, 119, 152, 172, 216, 240, 291, 323, 370, 431, 492, 538, 681, 755, 842, 950, 1438, 1563	Emerald green	Number 3
Green (Dark)	176, 217, 278, 369, 536, 952, 1336, 1595, 2093, 2156	The mixture of prussian blue, emerald green and carbon black	Number 11
Red	121, 151, 223, 314, 389, 548	Red lead	Number 5, 12 and 14

the making process of this *Tongcao* paintings. We also discovered that multi-pigments with different concentration were mixed together to paint different areas in pursuing visual effect, which not only demonstrated the complexity of manufacturing process of *Tongcao* paintings, but also witnessed the arrival and application of western pigments in Guangzhou.

Conclusion

Analytical studies were helpful to disclose the materials, pigments and manufacturing technique of *Tongcao* paintings: (1) Microscopic study showed the cells of *Tongcao* pith were hexagonal and hollow, which were connected together through cell walls to form a relatively stable honeycomb structure, ultimately contributing to the stack of pigments and forming an uneven surface for the distribution of pigments, which might be the direct reason for strong stereoscopic effect of *Tongcao* painting. Meanwhile, The cells of historical *Tongcao* pith had started to degrade, which indicated an urgent requirement on conservation of *Tongcao* paintings. (2) The simulation experiment and SEM–EDS analyses revealed this *Tongcao* painting was supposed to be treated by alum up to 8 layers in the painting process, which confirmed the truth of *Downing*'s travel notes. (3) Raman spectroscopy proved both China domestic pigments including red lead, calcite, lead white, carbon black and gamboge, and the synthetic pigments imported from Europe (synthetic ultramarine, prussian blue and emerald green) were applied in this painting, which not only witnessed the technical and commercial communication between China and the West, but was helpful to identify the production date of this painting was late Qing Dynasty, mainly the mid-late 19th century.

Our study highlighted the importance of *Tongcao* paintings in history and archaeology from a technological point of view, however, it was just a preliminary research to arouse the attention of academic community. As for the development process of materials, pigments and manufacturing technique of *Tongcao* paintings, more samples needed to be collected to conduct deeper and more systematically comparative studies.

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Authors' contributions

CZ responsible for experiments of Microscopy, Raman Spectroscopy and SEM–EDS; JBH collecting literature and writing the paper; TQZ making deep interpretation basing on experimental data and literature; RLZ Assisting in sorting literature and other documents. All authors read and approved the final manuscript.

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Availability of data and materials

The datasets acquired are available from the corresponding author.

Competing interests

The authors declare that they have no competing interests.

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