Unveil the gold – Revealing metal threads and decorative materials of early 20th century traditional Chinese children's hats

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Abstract

This paper presents the study of metal threads and other decorative materials on eleven traditional Chinese children's hats dated to the early 20th century. The lavishly decorated hats are presented to children to protect them from evil and bless them for good health and fortune. Those hats were selected for display in the 2015 exhibition *Wearable Blessings: Traditional Chinese Children's Clothing* at the Hong Kong Heritage Museum (HKHM).

In addition to the conservation work, the hats were fully studied to encompass analysis of the materials and understand the craftsmanship of the exquisitely decorated hats. In particular, various forms of metal threads were identified. The majority of the threads were revealed to be "membrane threads", mostly gold or silver lamellae on leather substrates and are used in the hats as flat strips or foils. Among the eleven hats, nine are also decorated with metal-wrapped threads with fibrous cores (silk, linen or cotton). The base substrate of the membrane thread was identified as either sheep or goat skin by means of proteomics in eleven samples tested from six hats. These findings coincide with the information recorded in an ancient Chinese encyclopaedia "*Chinese Technology in the Seventeenth Century*". Using proteomics, we also found a collagen signal matching to a fish species, *Larimichthys crocea* or large yellow croaker that is suspected to come from the glue binding the metal onto the base substrate. Other than the metal threads, feathers were also identified by microscopic examination on one of the hats. In terms of craftsmanship, leather gold embroideries and the hidden framework of a three-dimensional lotus ornament were examined and revealed by X-radiography respectively. This study demonstrates that the integration of scientific analysis with conservation is valuable in the investigation of material cultures and intricate craftsmanship of the historical objects.

Introduction

The study of eleven traditional Chinese children's hats was initiated in 2015 to understand more about the materials and craftsmanship used in their production as, to the best of our knowledge, few studies have been published on this topic (Luo 2018). Those hats are richly decorated with metal threads and were showcased in an exhibition "*Wearable Blessings: Traditional Chinese Children's Clothing"* held in the Hong Kong Heritage Museum (HKHM).

The exhibition displayed the beauty and exquisiteness of Chinese children's clothing dated from the 19th to early 20th century. The clothing included hats, clothes, *dudou* (an undergarment halter covering the chest and belly), waistcoats, shoes and boots, earmuffs, locks, etc. The decorative symbolic motifs on the clothing are not only visually appealing but also shed light on the traditional Chinese culture that embraces blessings for children. The motifs present blessings for longevity, happiness, success, abundant offspring, etc.

The incorporation of precious metals to textiles dates back several thousand years. The earliest reference may probably be the Bible's Old Testament, Exodus 39:2-3, which describes the making of Aaron's vestment for service during the 12th -13th centuries BC (Járó 1990). Membrane thread made of metal coated leather, animal gut or paper in strip or wound around a fibrous core appeared in the 11th century (Járó 1990; Karatzani 2012). The gold membrane threads, the so called "Cyprus gold threads" or "gold saving" threads, began to spread to Europe from Byzantium or possibly from the Western Asian regions. They were lighter and more flexible than solid metal threads. This reduced the weight of the clothing and the production cost (Hacke et al. 2004; Járó 1990).

The use of precious metals on textiles in China also has a long history. The application of metal threads, in particular the gold-wrapped threads, could be traced back to the earliest archaeological fragments dated to the 3rd-4th centuries, which were excavated in Xinjiang (Dang et al. 2014; Hu and Yu 2016; Lu et al. 2017). The production of a gold brocade robe was mentioned in a historical text, *Suishu* "*The book of Sui dynasty* (AD 581-618)", the biographic chapter of *He Chou*. *He Chou* was an imperial officer and was requested by the emperor to make a gold brocade robe of exquisitely elaborate design with reference to the one presented by Persia (Zhao 2005).

A unique textile collection embellished with a vast amount of metal threads of the later Tang dynasty (AD 618-907) was unearthed in 1987. The archaeological textiles were excavated at the Famensi (Famen temple), a Buddhist pagoda dating back to the 6th century at Fufeng, a county in Shaanxi Province. The excavated textiles comprised a lot of metal threads, most of them were solid gold strips wound around a fibrous core (Karatzani et al. 2009; Yang et al. 2013). One silver-wrapped thread in a piece of cloth was reported to likely be made with an organic paper support (Lu 2015). Another important group of Tang dynasty's textiles illustrating the presence of metal threads are the textiles from Dunhuang. Gold strips backed with papers were thought to be used on silk tapestries (*kesi)* found at the library cave of *Qian Fo Dong*. (Zhao 2005; British Museum 2020 a). Moreover, one piece of embroidered fragment was reported to have the outlines of motifs originally made in gold strips. Most of these strips have disappeared, revealing a black substrate, probably from an animal tissue (Wang and Zhao 2012; British Museum 2020 b). Animal skin was notable as the backing of gold threads used in Nashishi (also known as Nachisi), the most famous gold woven brocade in the Yuan dynasty (AD 1271-1368). Nachisi is the transliteration of Nasich, the Persian word for gold-wefted brocade which comes from the Arabic language (Zhao 2005 and 2012). It was described in a historical text "*Dao yuan xue gu lu*", written by *Yu Ji* who served at the Yuan imperial court, as woven with gold threads attached onto leathers (Mao 2020; Zhao 2005).

Additionally, the making of metal coated skin strip (or generally-speaking membrane thread), also known as "leather gold", was recorded as early as 1637 (Ming dynasty) in an encyclopaedia "*Chinese Technology in the Seventeenth Century*": *"In Shensi (Shaanxi province) the people make "leather gold" by affixing gold leaves to sheep skin curved to an extreme thinness, so that it can be cut and made into articles of clothing or ornament, all of which gleam with gold splendor"* (Sung 1966). In China, a single Chinese character "羊" (*yang*) is the collective description for all breeds of Caprinae family which includes both "sheep" and "goat". It was noted in the encyclopaedia that there are two kinds of sheep: *"One is known as woolly sheep…… The other kind of sheep is called yu-tiao sheep (this is a foreign term)….. the Shensi people called this animal [cashmere] goat* (Sung 1966)."

In connection to the analysis and characterisation of metal threads, a large literature has been published. Optical microscopy is frequently used as a preliminary examination tool to investigate the type of metal threads, the deterioration of the surfaces, nature of core fibres, substrate materials, etc (Járó and Tóth 1991). Scanning electron microscopy (SEM) can be used in conjunction for the surface morphology investigation. Moreover, elemental compositions can be deduced using SEM coupled with X-ray energy dispersive spectroscopy (EDX) i.e. SEM/EDX (Kohara et al. 1998; Nord and Tronner 2000; Járó et al. 2000; Hacke et al. 2004; Muros et al. 2007, Rezić et al. 2010; Oraltay and Karadag 2020). Recently, various electron microscope techniques and micro-Raman spectroscopy have been used to study the production technologies of medieval metal threads. (Weiszburg et al. 2017). Imaging analytical techniques including micro-X-ray fluorescence (XRF) scanning and micro-X-ray radiography have been used on archaeological metal threads as no samples are required for the investigation. (Hložek et al. 2019).

In this study, decorative elements were firstly examined by visual examination such as optical microscopy and scanning electron microscopy (SEM) to obtain the surface morphologies, followed by SEM/EDX analysis. This initial examination found that nine hats were decorated with metal-wrapped threads. All had decorations of flat metal strips or foils. Close examination of the metal strips and foils revealed that the metal likely adhered to a substrate made of animal skin. While the analytical studies on metal threads are well established for the metal composition and fabrication techniques, less work has been reported on the identification of organic substrates of membrane metal threads

(Indicator et al. 1989). Yet, the identification of leather is commonly conducted by microscopy (Haines 2006) and infrared spectroscopy for the morphological comparison of the grain structures and possible differentiation of the natural and synthetic leathers respectively (Shao 2005; Luo et al. 2011). Nevertheless, the identification may pose difficulties as the characteristic appearances of animal skin leathers may be obliterated by tanning, leather treatment and finishing, or deterioration. DNA analysis from leather may be an option but DNA may be damaged during the manufacturing process such as tanning (Merheb et al. 2014 ; Matar and Merheb 2016).

Proteomics has been increasingly used in cultural heritage studies since early 2000 to identify protein based materials such as protein based binders (Tokarski et al. 2006; Leo et al. 2009; Ma et al. 2017), adhesives (Dallongeville et al. 2011; Dallongeville et al. 2013; Zhu et al. 2019) in artworks and polychromies as well as archaeological objects (Kumazawa et al. 2016; Vinciguerra et al. 2016; Solazzo et al. 2016). Proteomics is the study of the protein composition of tissues or other biological systems using an array of techniques based on mass spectrometric analysis. In relation to its application to historical textiles and clothing, including metal threads, the characterisation of ancient proteins can increase our knowledge of techniques of fabrication, and material availability, variety, or trade (Solazzo et al. 2013; Solazzo 2019). In the study of metal threads made with an organic support layer, proteomics is used for multiple purposes:

1. To characterise the type of support tissue. Although microscopy analysis should be sufficient to differentiate metal threads made with an animal membrane (usually intestinal tissues) or leather (made from skin), the thickness (e.g. thin skin from a young animal) or deterioration of the support layer might raise uncertainty in some cases. While leather is dominated by collagen, intestinal membranes have, in addition to collagen, an array of other proteins such as actin and myosin (Popowich et al. 2018). These proteins can be used to differentiate the two types of collagenous tissues.
2. To identify the source species of the support layer. In recent proteomics studies, the source is often from a bovidae species (sheep, goat, cow) (Popowich et al. 2018; Solazzo et al. 2019; Scibè et al. 2020).
3. To determine the presence, nature and source species of the adhesive used to bind the metal to the organic substrate. This adhesive can be, for example, collagen glue or egg-based (Solazzo et al. 2019; Scibè et al. 2020).

Proteomic was thus conducted further on eleven samples from six hats to identify the animal source of the skin. It is a state-of-the-art tool to study membrane threads and only minute samples (less than 0.1 mg) are required. Species identification of animal skins and the binding adhesive of the membrane threads can provide insight about the materials and craftsmanship of the decorative elements. The scientific findings may possibly link up the material knowledge of the membrane threads with the traditional production techniques which are rarely documented. The overall study offers added-value benefits to the long term preservation of the traditional Chinese children's hats of the early 20th century.

Traditional Chinese children's hats

Blessing

The birth of a child, especially a baby boy, is a great event for Chinese families. In rural China, the mortality rate of children was high before the mid-20th century due to inadequate hygiene and less favourable medical condition. (Leung 2010; Sun and Zhang 2008). Mothers or relatives conveyed their blessings to the children by hand-stitching the hats that were embellished with symbolic and auspicious motifs. Apart from protecting the children from cold, hats worn by children denoted wealth, luck and longevity. There was a wide variety of children's headwear, some were designed to be worn on festivals and special occasions. Children wore different types of hats from infancy to early teens; those hats intended to ward off evil spirits when the wearers were young and transitioned to bring future success to them when they grew older (Garrett 2008; Sezto and Garrett 1990). Some hats were especially designed for boys such as animal hats or scholar hats. Ferocious animal hats such as a lion's head or tiger's head (Figures 1a-e) were frequently depicted for protection. A back flap was added to cover the back of the neck in cold weather (Figure 1aii). Scholar hats were imbued with good fortune for future official examinations. Shaped like the ones worn by scholar officials, they were intended to give boys a head start on a future career as high-ranking officials. In addition, there were hats in the shape of a melon or pomegranate or lotus which symbolised endless descendants. (HKHM 2015; Leung 2010). A brief description of the hats in this study is presented in Table 1 and their images are shown in Figures 1a-k.

Children hats are heavily decorated with a variety of decorative motifs such as animals, plants, flowers, Chinese calligraphy, legends, etc (Garrett 2008; Lu and Cui 2016). These motifs have their implied auspicious meanings. The "meaning" is presented indirectly through three main forms of representation: symbolism (usually of the object's form, colour and nature), homophones and abstract motifs (Leung 2010). Animals are understood to bestow unique abilities such as strength and power, and the children are protected by virtue of these same qualities. Ferocious animals like tigers and lions are believed to protect them from harm.

The powerful tiger is a divine creature in Chinese folklore. Parents, especially in North China, believe that tigers frighten away the evil spirits and ensure a prospective future for their children (Leung 2010; Sezto and Garrett 1990). Wearing a tiger hat can ward off evil spirits or fool them into thinking that the child is a fearsome animal (Sezto and Garrett 1990). If the tiger hat was worn on birthdays or special occasions, it also brought luck and peace. The colour of a tiger hat might indicate its place of origin. Hats in natural yellow colour of the tiger are common in Shanxi, Shaanxi, Hebei, and Shandong (Cao 2010), while black tiger hats might originate from the northeast provinces of Heilongjiang, Jilin, and Liaoning, where the costumes were more unconstrained in style (HKHM 2015).

A typical feature of tiger hats is the presence of the Chinese character "王" (pronounced as "wang"), literally meaning "King" on its forehead between the eyes. The eyes and ears on a tiger hat are believed to spot danger and hear the approach of evil. Its mouth displays a full set of bared teeth, and the wavy embroidered stitches denote the tiger's stripes. A second animal's face on top of the tiger is believed to provide even greater protection (Figure 1f) (Garrett 2008).

In the Chinese language there are more written characters than spoken words. Therefore, many Chinese characters share the same pronunciations, i.e. homonyms with embedded symbolic meanings (Sung 1979). Two examples of homonyms are fish and bat. The Chinese character for fish (*yu* 魚) is pronounced the same as the Chinese character for "abundance" or "surplus" (*yu* 餘). Therefore, fish is a symbol for "more" in the sense of "more" good luck and good fortune. The Chinese character for bat (*fu* 蝠) is a pun on "fortune" (*fu* 福). If the bat is shown flying upside down i.e. "inverted fu" (*fu dao* 蝠倒), bat and fortune together form the rebus of "fortune arriving" (*fu dao* 福到) (Sezto and Garrett 1990; Sung 1979).

Flowers are common motifs on the hats, and depict wealth, honour, and good fortune (Sezto and Garrett 1990). Lotus, in particular, is a common motif on those children's hats under study. Lotus is pronounced as "*he hua"* (荷花) or "*lian hua"* (蓮花) in Chinese, the Chinese character "*lian*" (蓮/連) has the same meaning as to bind or connect (in marriage) and *"he"* (和) is a homophone for harmony. Lotus seeds are called "*lian zi*" (蓮子), the Chinese character and pronunciation for "*zi*" (子) is same as child or son. While plants usually produce flowers before bearing seeds, the lotus produces flowers and ripened seeds at the same time; as such the lotus is interpreted as the symbol of "soon giving birth to a noble son" (Sung 1979; HKHM 2015). One of the lotus hats is decorated with a large lotus seedpod in the centre (Figure 1k). The crown of the hat features a three-dimensional lotus with a figurine boy emerging from it. The boy is holding a seedpod studded with lotus seeds. These motifs convey the wishes for a son to be born every year and for the family to be succeeded with sons and grandsons. Another type of fruit, longan is also noted on one of the tiger hat (Figure 1 aii). Longan is also called *guiyuan*(桂圓) (the dried form). "*Gui"* (桂/貴) *is* a pun on "plucking the osmanthus", which alludes to "obtaining high honours at the imperial examination", *"yuan"* (圓 /元) is a pun on "supreme ultimate", suggesting "achieving the highest scores in three consecutive examinations" (HKHM 2015).

Table 1. Description and decorative features of children's hats (dated 1900 -1930) under analysis

Item no	Object	Features	Ground fabrics	Figure(s)
1	Orange tiger-head hat	-embroidered with the fruit *longan (guiyuan)* and the	Orange colour-silk	1ai & 1aii

		mythical Chinese unicorn *qilin* motifs on neck flap -decorated with metal-wrapped threads as the eyebrows - embroidered with gold foils on neck flap		
2	Yellow tiger-head hat	-embroidered with floral motifs on metal foils - decorated with metal-wrapped threads as the eyebrows -decorated with metal-wrapped threads on neck flap	Yellow colour-cotton	1b
3	Black tiger-head hat	-embroidered with floral and lotus motifs - decorated with metal-wrapped threads as the eyebrows -decorated with brown strips	Black colour-silk	1c
4	Black tiger-head hat	-embroidered with the Chinese mythical bird *phoenixes*, flowers , red and blue women and lotus -decorated with metal-wrapped threads as the eyebrows -decorated with embroidered gold foils	Black colour - silk	1d
5	Double-faced tiger-head hat	-superimposed by a yellow tiger's head -decorated with gold longevity roundels and *fu* 福 (fortune), *lu* 祿(emoluments), *shou* 壽 (longevity) Chinese characters	Orange colour – cotton Black colour - silk	1e
6	Dragon-head hat	-embroidered with floral motifs -decorated with gold strips	Green colour - silk	1f
7	Hat with double-fish and lotus motifs	-decorated with lotus motifs and gold strips on the goldfish -decorated with green feathers in the mouths of goldfish as waterweeds -decorated with metal-wrapped threads	Blue colour - silk	1g

8	Hat with double-fish and lotus motifs	-decorated with gold strips on a pair of catfish on the two sides and the lotus motifs at the front -decorated with metal-wrapped threads	Black colour- silk	1h
9	Hat with auspicious motifs	- shaped like a scholar hat -embroidered with numerous auspicious motifs such as inverted bats - decorated with gold strips and metal-wrapped threads	Black colour - silk	1i
10	Hat with bat, peach and *ruyi* motifs	-decorated with metal-wrapped threads -embroidered with motifs such as *ruyi* (wishes fulfilled), bats, etc -decorated with a few small brown strips around the eyes, nose and mouth of a bat	Black colour - silk	1j
11	Hat with boy and lotus motifs	-embroidered with lotus motifs -decorated with a three-dimensional (3D) lotus ornament with a boy figurine inside the lotus -decorated with metal-wrapped threads on the 3D lotus petals -decorated with brown strips	Black colour - silk	1k

Figures 1a-k. Images of the children's hats under study. Photos ©Hong Kong Heritage Museum

Elements of decoration and craftsmanship

The children's hats under study are elaborately decorated with appliqué, embroideries, metal threads, embroidered metal foils and other decorative items such as feathers. The feathers represent waterweeds in the mouths of two facing goldfish of a hat (object no 7, Figure 1g). The most commonly used techniques for decorating children's hats are embroidery and appliqué (Figures 2a and b). Stitches include chain stitch, satin stitch, couching (a way to anchor gold and silver thread), and *dazi* (knot stitch or "forbidden" stitch) (Lin 2007). The stitches and threads are the deepest expressions of a mother's affection to her child. The auspicious motifs include longan (*guiyuan)*, lotus blossoms and seedpods, phoenixes, peaches, ceremonial scepter *ruyi,* etc.

Figure 2. Embroideries on the children's hats (a: object no. 6, b: object no. 7). Microscope photos ©Hong Kong Heritage Museum

In addition to embroideries, metal threads are extensively used on the children's hats. The metal-wrapped threads are frequently found as the eyebrows of the tiger hats. They are also adopted as the outlines (Figure 2b) or decorative components of the embroideries. Apart from the metal-wrapped threads, the abundant metallic decorative elements on the children's hats are in the form of gold or brown strips (foils) and they are flexible in nature. Some golden colour foils combine with embroideries to form an array of motifs. Nevertheless, there is limited information about the manufacture techniques of the embroidered "gold" motifs that are stitched on the children's hats.

The constructing technique of embroidered golden foils is hence an area of interest to be explored. X-radiography is a non-destructive and non-invasive imaging technique. The X-radiography of textile objects can reveal construction, manufacturing techniques, use, patterns and repair details which are invisible to the naked eye (Brooks and O'Connor 2007; Hackett 2011). Some embroidery threads of two women figures of a tiger hat (object no. 4) were lost and the papers underneath were exposed i.e. the embroideries were stitched on top of paper supports. A tiny piece of gold emerged at an area where a small area of paper was lost. Gold foils may possibly be the underlining layers of the papers that were not only decorated along the borders of the embroideries. Therefore, the torn areas of two embroidered women figures with gold foils were X-rayed to seek for the layering information.

Conservation

The major conservation problem of the Chinese children's hats was deformation. Those hats might not have been properly stored before they entered the museum collection. The hats were seriously deformed or disfigured. For instance, a three-dimensional (3D) lotus ornament with a boy figurine featuring at the top of a hat (object no. 11) suffered deformation (Figure 3a) which was possibly caused by crushing. The boy figurine is surrounded with the flattened petals of the lotus and fastened to the petals by stitching. Some metal wires are exposed on the underside of the hat where the linings were damaged. X-radiography was conducted to study the possible unseen affixing mechanism of the lotus ornament and the boy figurine to aid in the treatment decision for realignment. Finally, the respective lotus and the boy figurine were straightened back to upright positions by manipulating the internal wirework mechanically and re-shaping the lotus petals by humidification (Figure 3b).

Generally, basic surface cleaning was done with fine brushes using vacuum cleaner with adjustable suction to the children's hats. Afterwards, they were reshaped by humidification and the internal shapes were maintained with the support of tailor-made cushioning materials, made from polyethylene foams or Fosshape®. Fosshape® is a non-woven polyester felt-like materials which can be activated by dry or steam heat to mould in the desired shape and regularly used in textile conservation. Due to the presence of metal threads and leather substrates, localised controlled humidification by using ultrasonic humidifier or moisture permeable material Gore-tex® was performed. Lastly, some tiny metal membrane strips were flaked slightly and Lascaux was used for consolidation.

Figure 3. (a) Deformed 3D lotus ornament with a boy figurine featuring at the top of a hat (object no. 11); (b) The 3D lotus ornament with a boy figurine on top of the hat was re-positioned. Photos ©Hong Kong Heritage Museum

Experimental

Sampling

Most of the samples were taken from the loose or partially detached pieces from the children's hats for SEM/EDX and proteomic analysis. A small portion of the samples were taken from the tiny torn or unobtrusive areas. As such, only selective metal threads on the children's hats were analysed.

Microscopic and SEM/EDX examination

Optical microscopy, a Leica M80 stereomicroscope was firstly used to investigate the types of metal threads on eleven hats. Samples were taken for subsequent examinations with a Leica MZ60 stereomicroscope to reveal the morphologies and a FEI Quanta 200 SEM/EDX to obtain highly magnified images as well as elemental compositions. Nine hats display the presence of metal-wrapped threads i.e. metal wound around a fibrous core. Samples of metal-wrapped threads from six hats were taken for SEM/EDX analysis (Tables 1 and 2: Object no. 1, 2, 4, 7, 10 and 11). Separately, metal strips or foils (gold or brown foils) from ten hats (Tables 1 and 3: Object no. 1 to 9 and 11) were taken for SEM/EDX analysis. Cross section of metal strips or foils were also examined using a FEI Quanta 200 SEM/EDX and an Olympus BX60 polarizing microscope. A green feather-like material representing the waterweeds in the mouths of two goldfish of a hat (object no. 7; Figure 1g) was also examined.

X-radiography

Embroidered golden foils on object no. 4:
X-radiography was used to reveal if the golden foil embroideries were supported wholly with "leather gold" beneath or just decorated along the borders of the embroidered motifs. Two areas of slightly torn embroidered women figures with gold foils (object no. 4) were X-rayed by a Faxitron®, X-ray System model 43855C, at an accelerating voltage of 20 kV and exposure time of 2 sec. The penetration of X-ray radiation is dependent on its energy, the type, and thickness of the object to be analysed. Organic materials such as textiles and papers are of low atomic numbers, the use of low energy or soft X-ray is known to be effective in producing detailed radiographic images (Brooks and O'Connor 2007). Low X-ray energy at 20kV was selected to obtain high contrast images.

A three-dimensional (3D) lotus ornament with a boy figurine on object no. 11:
X-radiography was conducted to study the possible affixing mechanism of a deformed lotus ornament (object no. 11) to aid in conservation treatment. The image was taken by Faxitron®, X-ray System model 43855C, at an accelerating voltage of 120 kV and exposure time of 30 sec. High energy X-ray was used to obtain a contrast image of the hidden metal wire structure inside layers of fabrics.

Proteomics

Eleven samples from six hats were analysed: Object no. 9, 8, 11, 7, 2, 6. The experimental protocol was adapted from previous studies (Solazzo et al. 2013):

Extraction:
Proteins were extracted from samples of about 0.1 mg or less by solubilization of the leather strips in 100 µL of a solution of 8M urea, 50 mM Tris and 50 mM tris(2-carboxyethyl)phosphine (TCEP) at pH 8.0, left overnight in shaker at maximum speed. The whole supernatant was alkylated for 45 min in the dark with 10 µL of 400 mM of iodoacetamide for a final concentration of 40 mM. Samples were dialyzed for 6h in dialysis units at 3500 Da (Thermo Scientific™ Slide-A-Lyzer™ 3.5K MWCO MINI Dialysis) with 100 mM Ambic (ammonium bicarbonate) at pH 8.0 (two changes).

Enzymatic digestion and purification:
The whole dialyzed sample was digested overnight with 1µg of trypsin at 37°C. After about 16h, the samples were acidified with 1% formic acid (FA) and the proteins extracted and purified by solid phase extraction with Empore SPE Extraction Disk (3M). The disks (Ø 0.1 cm) were washed with acetonitrile (1 min), conditioned with methanol (1 min) and washed with 0.1% FA solution (1 min) before being added to the samples and mixed for three hours to allow protein loading on the disk. Following a brief wash of the disk in 0.1% FA solution (1 min), the peptide mixtures were then eluted in 100 µL of 75:25 (v/v) acetonitrile:0.1% FA. All samples were then dried down on speedvac and resuspended in 10 µL of 0.1% FA.

Protein analysis by nano flow liquid chromatography tandem mass spectrometry (nanoLC-Orbitrap MS/MS) :
The samples were injected without further dilution; the injection volume was 1 µL. Samples were run in duplicates. The peptides were first loaded onto an in-house packed Thermo BioBasic C18 precolumn (30 mm x 75 µm i.d.) after which they were separated on an in-house packed analytical column (210 mm x 75 µm i.d.) made of the same stationary phase, using a Thermo Scientific Dionex Ultimate 3000 UHPLC system with the following gradient: 2% B 0-8 min, 55% B 98 min, 90% B 100-103 min, 2% B 104-120 min, where buffer A was 0.1% FA in H_2O and buffer B was 0.1% FA in acetonitrile (CAN). The UHPLC was directly coupled to a Thermo Scientific LTQ Velos Dual Pressure Linear Ion Trap mass spectrometer which analyzed the peptides in positive mode using the following parameters: MS1 60,000 resolution, 100 ms acquisition time, 1×106 automatic gain control (AGC), MS2 15,000 resolution, 250 ms acquisition time, 5×105 AGC, top 8, 30 normalized collision energy (NCE) higher-energy collisional dissociation (HCD).

Bioinformatics analysis:
For each sample, the two fractions were combined into one search to create one output file. PEAKS 8.5 (Bioinformatics Solutions Inc.) was used to search the RAW data for matches against publicly available sequences in imported UniProt (www.uniprot.org) and NCBI (https://www.ncbi.nlm.nih.gov/protein) databases. PEAKS PTM was enabled to identify unspecific PTMs.
A search was conducted against a large Uniprot database containing all mammalian and bird entries (Uniprot mammalia + aves, imported June 18th, 2018) to identify the source of the leather and possible adhesive such as egg white or yolk. Searches were carried out using trypsin as enzyme, one allowed non-trypsin cleavage at any end, one missed

cleavage, peptide mass tolerance (PMS) of 10 ppm, fragment mass error tolerance (MS/MS) of 0.02 Da, carbamidomethylation as a fixed modification, and deamidated (NQ), hydroxylation (RYFPNKD), and oxidation (M) as variable modifications. A maximum of five PTMs (Post-Translational Modification) were allowed.
In addition, NCBI was used to search specifically for collagen sequences as it contains additional entries for recently-sequenced species such as Capra hircus (whose collagen proteins are incompletely populated in Uniprot). Because NCBI is not curated as Uniprot, the database was limited in size to collagen sequences for all mammals as well as fish: NCBI Collagen mammalia + fish (last imported January 06th, 2020). Searches were carried out using trypsin as enzyme, one allowed non-trypsin cleavage at any end, three missed cleavage, peptide mass tolerance (PMS) of 10 ppm, fragment mass error tolerance (MS/MS) of 0.02 Da, carbamidomethylation as a fixed modification, and deamidated (NQ), hydroxylation (P), and oxidation (M) as variable modifications. A maximum of six PTMs (Post-Translational Modification) were allowed.

Results

Microscopic and SEM/EDX examination

Metal threads:
SEM-EDX analysis detected gold, silver or copper on the metal-wrapped threads (Table 2). Details of the metal-wrapped threads of object no.1 are shown in Figure 4a and the SEM image and EDX data are illustrated in Figures 4b & 4c respectively. Among the six samples, three of them are solid metal strips wound around a fibrous core, while the remaining three are strips made of metal-coated paper wound around a fibrous core.

Table 2. The elemental compositions and characteristics of metal-wrapped threads

Object no.	Type of metal threads	Area on hats	SEM-EDX results	Core thread	Substrate
1	Gold-wrapped threads	Eyebrows	Gold, Silver	Not tested	Paper
2	Metal-wrapped threads	Decorative motifs	Copper	Cotton	No substrate
4	Metal-wrapped threads	Eyebrows	Copper	Linen	No substrate
7	Gold-wrapped threads	Decorative motifs	Gold, Silver	Silk	Paper
10	Metal-wrapped threads	Decorative motifs	Silver	Cotton	Paper
11	Metal-wrapped threads	Lotus at the top	Silver	Silk	No substrate

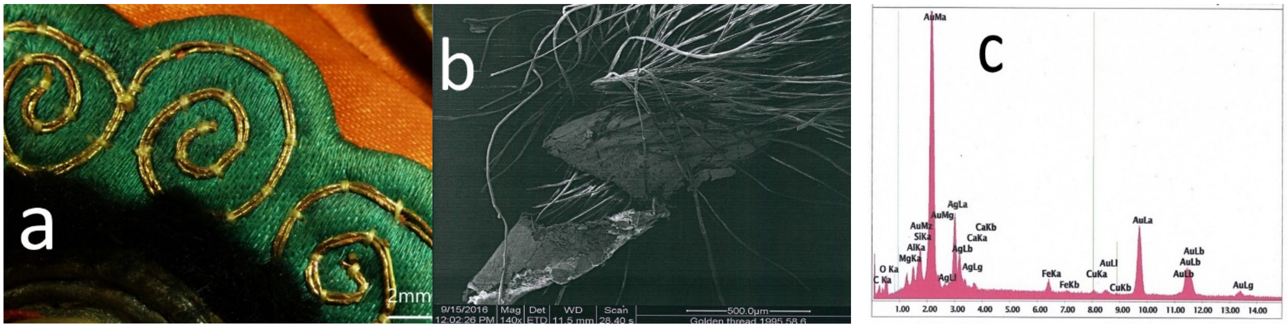


Figure 4. Gold-wrapped threads on the eyebrows of a tiger hat (object no. 1). (a) Details. Microscope photo ©Conservation Office; (b) SEM image of the gold-wrapped thread, at a magnification of 140X, 11.5 mm working distance and 30 kV accelerating voltage ©Conservation Office and; (c) EDX result of the gold layer of the gold-wrapped thread showing the presence of gold , at 30 kV accelerating voltage ©Conservation Office

Under microscopy, the surface morphologies of the gold (Figure 5a) or brown strips (foils) (Figure 5b) showed the presence of follicles like holes on the grain sides (Figures 6a & 7a) with fibrous structures on the undersides (Figures 6b & 7b) (Haines 2006; Haines and Barlow 1975).

The cross sections of the metal strips or foils (Figure 8) showed the presence of three layers (Figure 8b); a very thin layer of metal is seen on top of a dark brown layer while the bulk of the thread is composed of the thick skin base where collagen bundles are apparent. The thickness of the samples ranged from 50 μm to 200 μm. The brown layer can possibly be an adhesive layer for binding the metal and base substrate. As shown in Figure 9, an adhesive like layer is noticeable on the base substrate of a gold strip (object no. 8) where gold is missing.

SEM-EDX indicated that the major elements on the gold and brown strips or foils were gold and silver respectively (Table 3). Sulphur was also detected on the brown strips and foils, indicating that the silver was tarnished and accounted for the colour. The metal lamellae are thus composed of gold or silver which are coated on leather-like substrates. Calcium and potassium were detected on the undersides of the strips and foils and those elements likely result from the processing of leather (Florian 2006).

Table 3. SEM results of metal strips or foils samples

Object no.	Sample	Grain side composition	Underside composition
1	Gold foil	Gold, Silver,	Sulphur
2	Brown foil	Silver	Calcium, Sulphur
3	Brown strip	Silver, Sulphur	Not tested
4	Gold foil	Gold, Silver	Sulphur

5	Gold foil	Gold, Silver	Calcium, Sulphur, Silicon
6	Gold strip	Gold, Silver	Calcium, Sulphur, Potassium, Silicon
7	Gold strip	Gold	Sulphur
8	Gold strip	Gold, Silver	Calcium, Sulphur, Potassium
9	Gold strip	Gold, Silver	Calcium, Silicon, Sulphur
11	Brown strip	Silver, Sulphur	Calcium, Potassium, Silicon, Sulphur

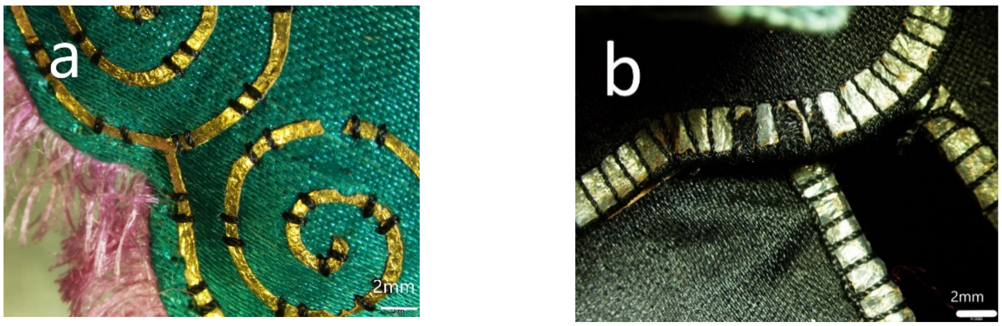


Figure 5. (a) Gold metal lamellae (object no. 6) and; (b) brown metal lamellae (object no. 11). Microscope photos ©Conservation Office

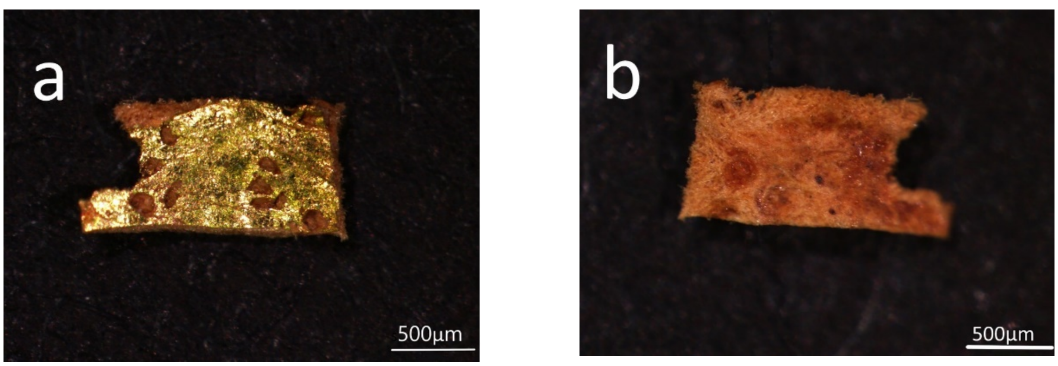


Figure 6. Microscope photos of gold lamellae (object no. 6, samples from ear) showing the presence of follicles (a) on the grain side and; (b) fibrous structure on the underside ©Conservation Office

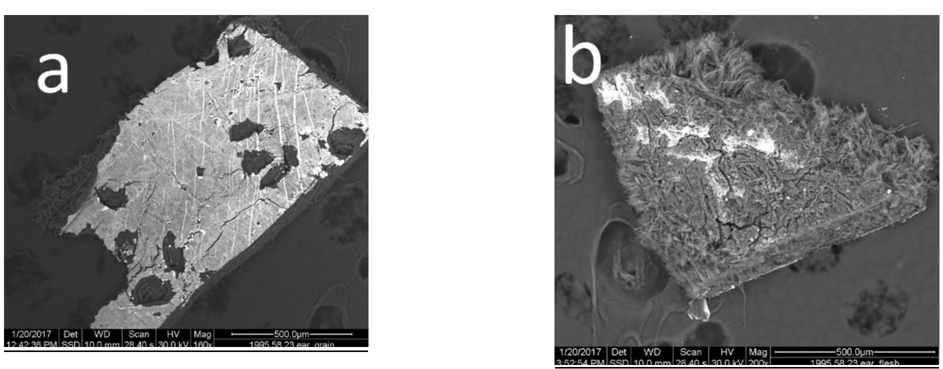
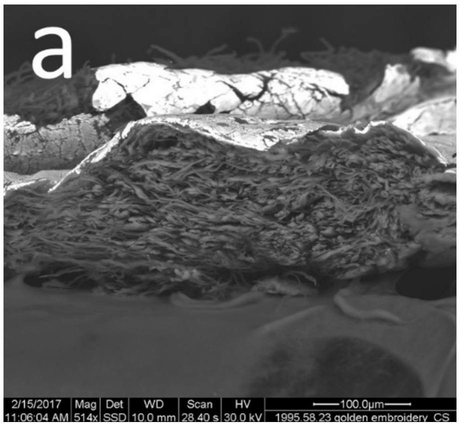


Figure 7. SEM images of gold metal lamellae (object no. 6, samples from ear) (a) grain side, at a magnification of 160X, 10 mm working distance and 30 kV accelerating voltage ©Conservation Office and; (b) underside, at a magnification of 200X, 10 mm working distance and 30 kV accelerating voltage ©Conservation Office



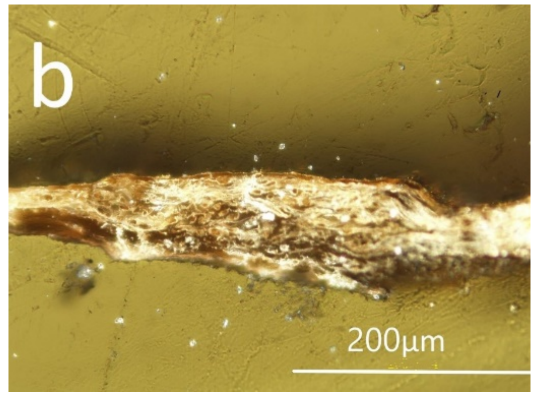


Figure 8. Cross section images of gold lamellae (object no. 6, samples from embroidery) under (a) SEM, at a magnification of 514X, 10 mm working distance and 30 kV accelerating voltage ©Conservation Office and; (b) optical microscope ©Conservation Office

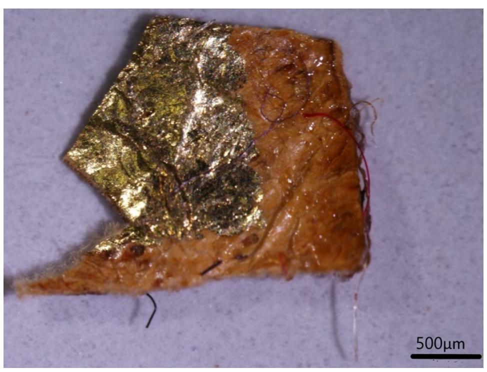


Figure 9. Microscope photo showing the presence of an adhesive like layer for binding the gold layer to the base substrate of a gold foil (object no. 8, sample S4 for proteomic analysis) ©Conservation Office

Feathers:
EDX analysis on the waterweeds in the mouths of two goldfish of a hat (object no. 7, Figure 1g) showed the presence of sulphur. Further examination indicates the features of barbules are consistent with ostrich feathers (Dove and Koch 2011). The barbules are uniform with distal prongs, without expanded nodes or pigment patterned (Figure 10). Bird feathers are made of proteins commonly known as β-keratins, a type of fibrous protein like the α-keratins that compose hair, horn, wool, and nails. Keratins have high content of cysteine, an amino acid containing sulphur (Hudon 2005; Staroń et al. 2011). The waterweeds of the fish hat are thus deduced to be feathers.

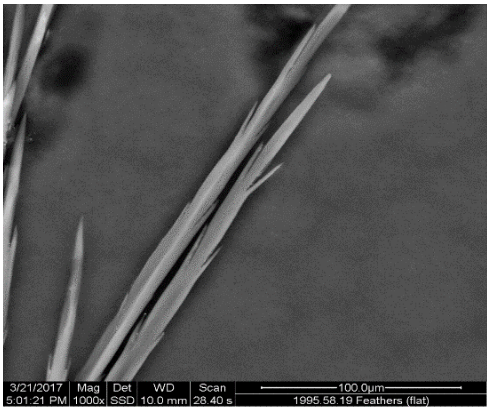


Figure 10. SEM image of the feathers representing waterweeds in the mouths of two goldfish of a hat (object no. 7) showing the presence of barbules, at a magnification of 1000X, 10 mm working distance and 30 kV accelerating voltage ©Conservation Office

X-radiography

Two embroidered women figures on a tiger hat (object no. 4) (Figures 11a & 12a):
The regions decorated only with "leather gold" were darker in intensities than those with embroideries, which appeared whiter. The intensities of the regions with embroidery threads or without threads (i.e. paper) were largely the same (Figures 11b & 12b). There was no distinct boundary between the "leather gold" and the embroidered motifs which indicated that "leather gold" was a continuous film across the underside of the embroideries (with paper). This shows that the base layer of the embroideries is a gold layer on leather substrate, it was covered with a layer of paper and then surface embroideries. The embroidered figures were thus made with layers of gold coated on leather, paper and embroideries and sewn onto the surface of a black fabric of the hat.

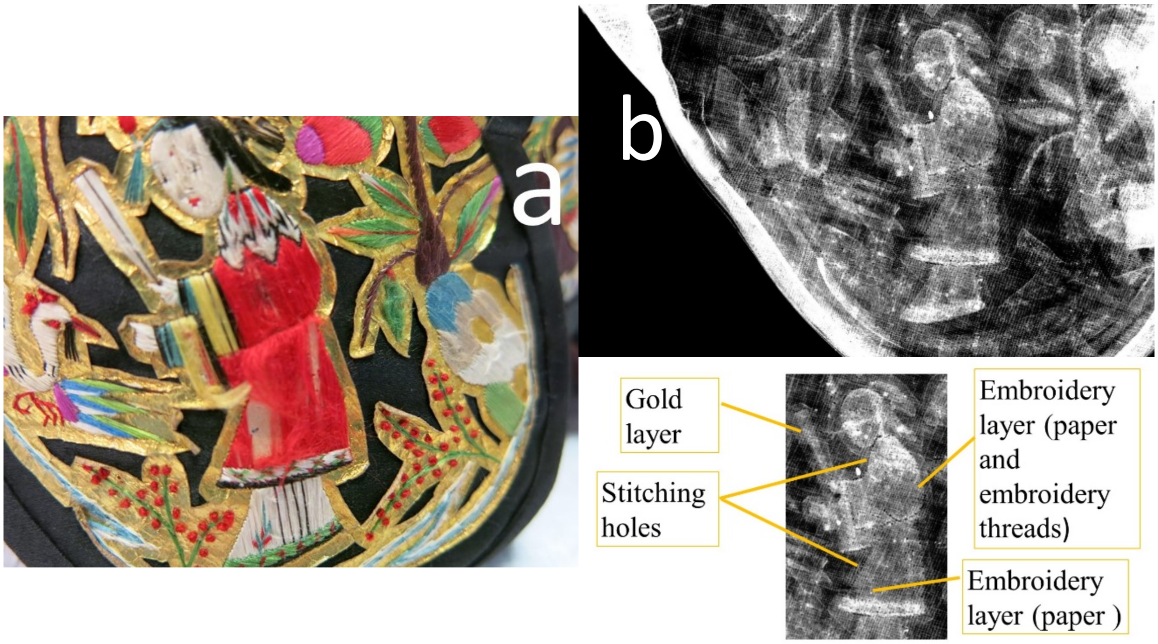


Figure 11. (a) Details of a red woman motif decorated with leather gold on a tiger hat (object no. 4). photo ©Hong Kong Heritage Museum and; (b) X-ray image of the red woman motif ©Conservation Office

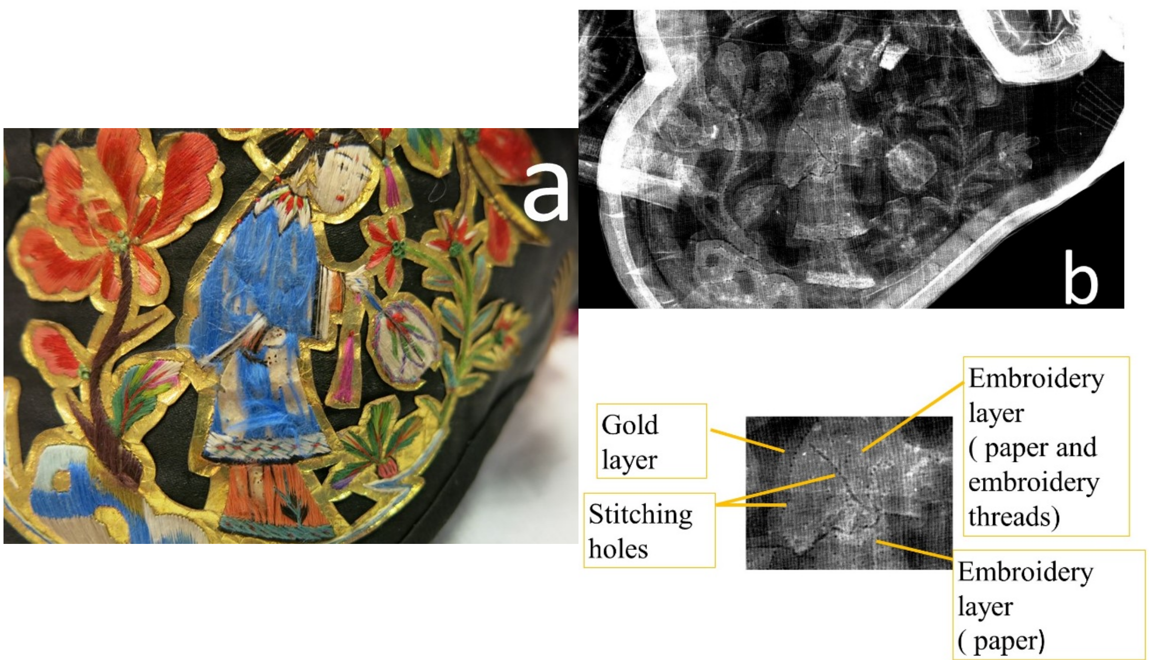


Figure 12. (a) Details of a blue woman motif decorated with leather gold on a tiger hat (object no. 4), photo ©Hong Kong Heritage Museum and; (b) X-ray image of the blue woman motif ©Conservation Office

A three-dimensional (3D) lotus ornament with a boy figurine on object no. 11 (Figure 13a):

X-ray image (Figure 13b) shows that U-shaped cross wires run inside the linings at the crown of the hat to maintain the hat's shape, a bundle of wires are located inside the 3D lotus ornament. The inner wires became visible when the lotus petals were opened up gently after humidification. Those wires are largely used to reinforce the positions of the petals though the petals themselves are stiff enough to stand alone. The boy figurine is stood on top of those wire clusters but not fixed to them.

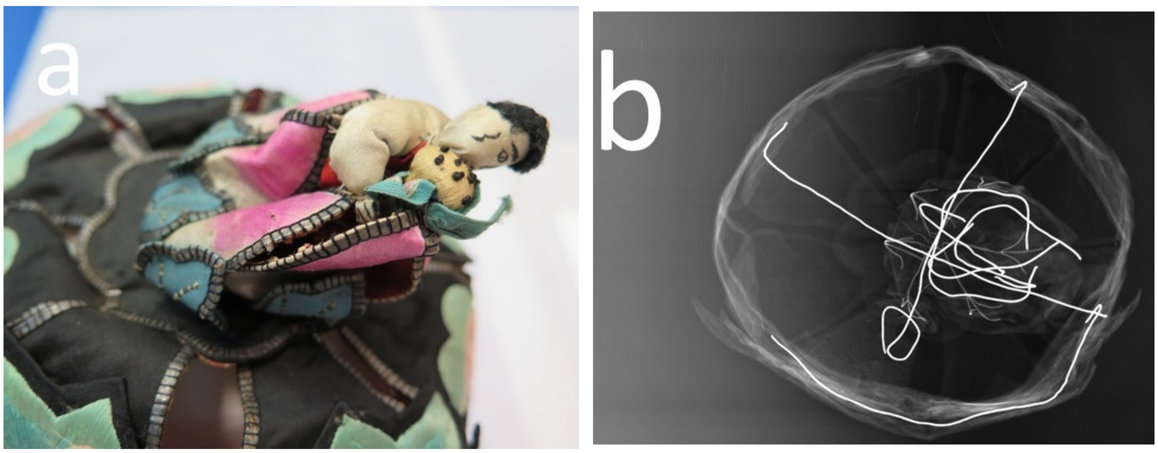


Figure 13. (a) Deformed 3D lotus ornament with a boy figurine featuring at the top of a hat (object no. 11), photo ©Hong Kong Heritage Museum ; (b) X-ray image showing the internal wiring framework of the lotus ornament with a boy figurine ©Conservation Office

Proteomics

A general search was conducted against a large Uniprot database containing all mammalian and bird entries to identify the source of the leather and possible adhesive, such as egg white or yolk.

Substrate identification:

The main hits were invariably Type I alpha-1 and alpha-2 collagen chains from *Ovis aries* (domestic sheep). However, because Uniprot had incomplete representation of the *Capra hircus* species compared to NCBI, a complementary search was conducted using a smaller NCBI database containing collagen proteins for all bovidae as well as fish species. Species markers that discriminate sheep from goat were searched to corroborate the database identification. Collagen Type I alpha-1 (collagen alpha-1(I)) and alpha-2 (collagen alpha-2(I)) are the most abundant collagen chains in skin, and with collagen Type III alpha-1 (collagen alpha-1(III)) provide the highest number of peptides. SM Tables 1 to 3 show the species markers for all three collagen chains that were used to discriminate sheep from goat. They are also compared to cow (*Bos taurus*), the closest domestic relative. Three samples, S3, S5, and S6 were identified as goat, while all others were confirmed as sheep (Table 4 and 5). Figure 14 shows the mass spectra of the Capra-specific marker in collagen alpha-2(I), GPSGEPGTAGPPGTPGPQGFLGPPGFLGLPGSR (Figure 14a) and its equivalent in Ovis sp. GPSGEPGTAGPPGTPGPQGLLGAPGFLGLPGSR (Figure 14b). These markers have been characterised before to differentiate sheep from goat in bones (Buckley et al. 2010). While none of the leather substrates was identified as bovine, traces of *Bos taurus* collagen were detected in sample S8 with four Bos sp. peptides identified from collagen alpha-2(I) (SM Table 2) and one from collagen alpha-1(III) (SM Table 3). This is likely part of the adhesive and not the leather itself.

Table 4. List of samples and proteomics identification of the leather substrate

Sample	Object no.	Metal	Leather identification
S1	9	Gold	Sheep
S2	9	Gold	Sheep
S3	8	Gold	Goat
S4	8	Gold	Sheep
S5	11	Silver	Goat
S6	11	Silver	Goat
S7	7	Gold	Sheep
S8	2	Silver	Sheep
S9	6	Gold	Sheep
S10	6	Gold	Sheep
S11	6	Gold	Sheep

Table 5. General results obtained from the NCBI Collagen bovidae + fish (imported January 06th, 2020) search on PEAKS PTM giving the number of PSM (Peptide-Spectrum Matches) and number of peptide sequences identified. Details are given for the main three collagen chains identified Col1A1 (collagen alpha-1(I)), Col1A2 (collagen alpha-2(I)) and Col3A1 (collagen alpha-1(III)): Score in -10lgP, %=percentage coverage, #=number of peptides

	PSM	Peptide sequences	Species id	Col1A1			Col1A2			Col3A1		
				Score	%	#	Score	%	#	Score	%	#
S1	3732	1076	*Ovis aries*	181.52	60	92	168.69	62	67	151.26	45	53
			Larimichthys crocea	170.96	60	99	163.87	63	76	-	-	-
S2	5611	1617	*Ovis aries*	166.32	58	78	155.09	59	59	137.36	45	50
			Larimichthys crocea	178.67	63	192	165.39	69	127	-	-	-
S3	5506	1526	*Capra hircus*	187.34	60	101	168.96	62	94	157.01	46	70
			Larimichthys crocea	174.14	61	139	165.49	67	101	-	-	-
S4	3904	1179	*Ovis aries*	184.96	59	99	170.13	58	67	147.3	44	53
			Larimichthys crocea	176.2	60	108	173.55	64	93	-	-	-
S5	4105	1213	*Capra hircus*	187.54	60	103	178.18	68	108	166.26	50	76

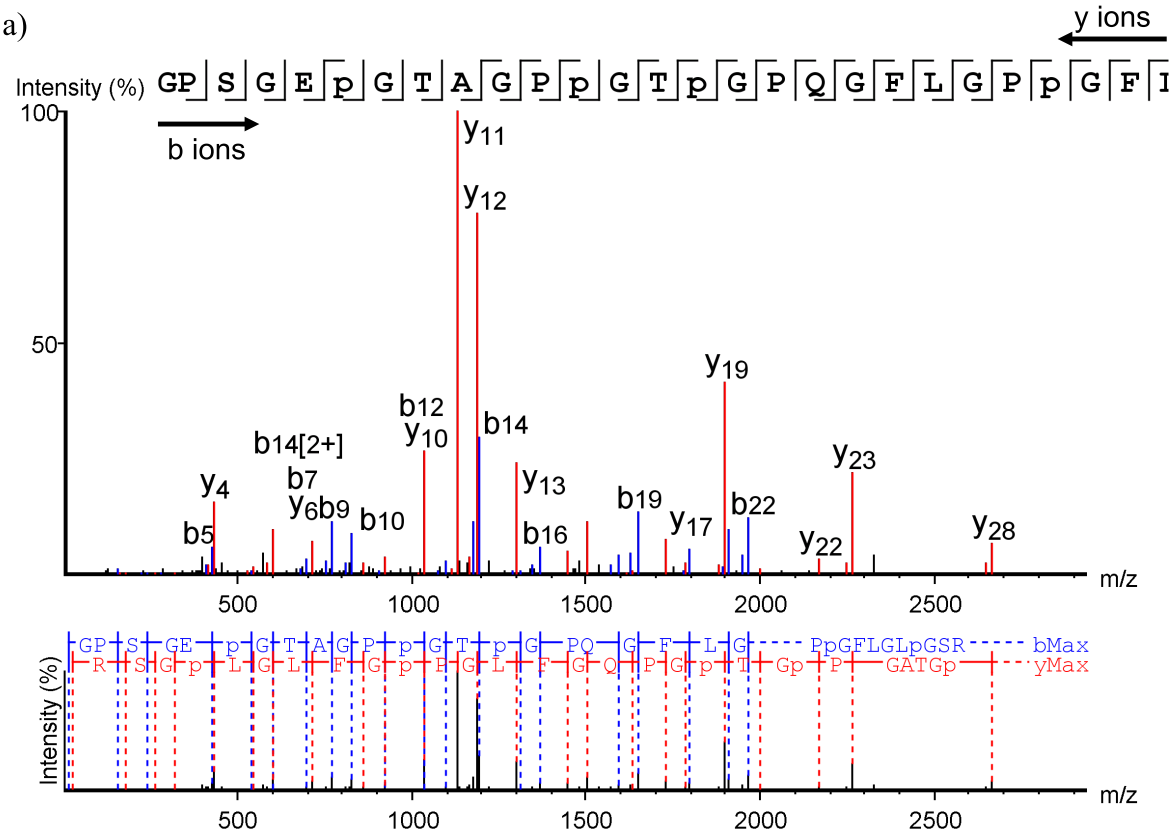
			Larimichthys crocea	172.71	58	110	164.46	64	81	-	-	-
S6	4216	1275	*Capra hircus*	191.79	60	104	178.1	65	104	146.46	50	73
			Larimichthys crocea	175.35	57	117	164.67	63	85	-	-	-
S7	5078	1455	*Ovis aries*	177.06	58	96	166.62	64	78	150.57	45	50
			Larimichthys crocea	179.71	61	140	171	67	110	-	-	-
S8	3867	1106	*Ovis aries*	191.88	63	92	183.92	63	72	158.11	46	60
			Larimichthys crocea	157.05	49	61	149.39	53	53	-	-	-
			Bos taurus	189.03	60	84	179.59	58	82	139.74	38	51
S9	4472	1214	*Ovis aries*	184.11	62	93	172.35	64	71	151.43	48	56
			Larimichthys crocea	168.2	60	105	166.12	65	81	-	-	-
S10	4352	1240	*Ovis aries*	164.85	58	79	153.77	58	55	115.52	37	38
			Larimichthys crocea	173.13	62	152	164.11	68	114	-	-	-
S11	3914	1140	*Ovis aries*	183.88	59	101	169.08	62	75	152.98	45	54
			Larimichthys crocea	167.33	56	104	160.1	62	78	-	-	-

Adhesive identification:

The search for the nature of the adhesive did not indicate the presence of non-collagenous proteins, such as egg or milk proteins. However, the NCBI collagen database containing fish revealed the presence of collagen from the species *Larimichthys crocea* or large yellow croaker, a marine fish from the croaker family (Sciaenidae), native to the northwestern Pacific Ocean. The species is important commercially and for this reason has had its genome mapped (Wu et al. 2014). In spite of the limited representation of fish collagen in public database, *L. crocea* collagen is identified in all samples with high number of peptides (Table 5, SM Figures 1 and 3) and similar protein coverage than the substrate collagen (e.g. 62% on average for fish collagen compared to 63% on average for the substrate for collagen alpha-2 (I)), giving high confidence that the collagen is from a species from the Larimichthys genus. The Larimichthys genus is composed of at least three species: *L. crocea* (large yellow croaker) (Cui et al. 2009), *L. polyactis* (small yellow croaker found in Yellow and East China seas) (Cheng et al. 2012), and *L. pamoides* (southern yellow croaker found in Australia and Papua New Guinea) (Munro 1964). A fourth species, L. *terengganui*, has recently been discovered in Peninsular Malaysia (Seah et al. 2015). Of all the Larimichthys, only *L. crocea* has been completely sequenced, while only mitochondrial DNA is available for *L. polyactis*. Possible peptides specific to *L. crocea* are shown in SM Tables 4 and 5, and SM Figures 2 and 4.

The identification of *Larimichthys crocea* is rather similar for all samples, with the exception of sample S8, where the protein percentage coverage is the lowest. As noted earlier, *Bos taurus* was also identified in this sample, albeit with less markers than *Ovis aries*. This indicates that the adhesive in S8 is likely a mixture of fish and bovine glue, and the lower coverage of the fish glue perhaps indicates a lower supply, which was compensated by the addition of hide glue from bovine.

a)


y ions
Intensity (%)
GP S G E p G T A G P p G T p G P Q G F L G P p G F I
b ions
100
50
y11
y12
y19
b12
y10
b14
b14[2+]
y23
y4
b7
y6b9
y13
b19
y17
b22
b10
b5
b16
y22
y28
m/z
500
1000
1500
2000
2500
GP S GE p G T A G P p G T p G PQ G F L G PpGFLGLpGSR bMax
R S G p L G L F G p P G L F G Q P G p T Gp P GATGp yMax
Intensity (%)
m/z
500
1000
1500
2000
2500

b)

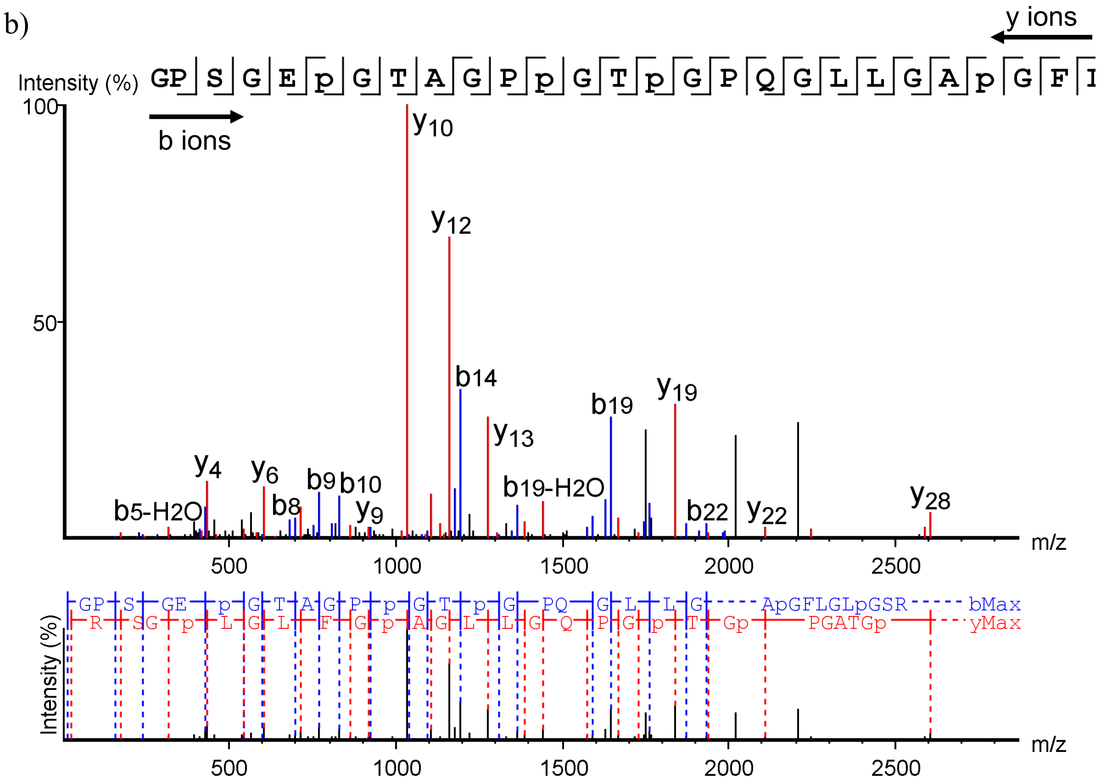


Figure 14. Mass spectra showing the b and y ions series corresponding respectively to peptide fragments from the amino terminus (extending from the left) and the carboxyl terminus (extending from the right) of (a) Peptide GPSGEP*GTAGPP*GTP*GPQGFLGPP*GFLGLP*GSR with 5 hydroxyprolines (P*) in sample S5: Molecular mass of the peptide is M=3092.4839, identified at a mass-to-charge ratio *m/z*=1031.8416 and PEAKs score of 46.15 (top) and; (b) Peptide GPSGEP*GTAGPP*GTP*GPQGLLGAP*GFLGLP*GSR with 5 hydroxyprolines (P*) in sample S10: Molecular mass of the peptide is M=3032.4839, identified at a mass-to-charge ratio *m/z*=1011.8407 and PEAKs score of 49.00 (bottom), obtained by nanoLC-Orbitrap MS/MS and analyzed in PEAKS 8.5 ©Smithsonian's Museum Conservation Institute

Discussion

As a result of the proteomic analysis, it was confirmed that "sheep and goat skins" are used as the base substrates of the "membrane threads" of the traditional Chinese children's hats. "Sheep leather gold" is a commonly known membrane thread in China. Both sheep and goat skins were found on a fish-shaped hat (object no. 8). This indicates that the raw materials of "sheep leather gold" could come from sheep or goat in the early 20th century. Moreover, fish collagen was also found in all samples and it was enlightening that the species of fish, yellow croaker, was matched with high confidence. The fish collagen is likely used in the form of fish glue to bind the metal onto the leather, as samples have noticeable adhesive layers beneath the metal layers when viewed under microscope (Figure 9). However, it cannot be ruled out that the glue was also used for fixing the "membrane threads" to the hats. Some of the metal strips are indeed adhered to the hats with glues rather than stitching. Nevertheless, the two findings correlate well with the ancient materials that were used for producing "leather gold" as well as its application as documented in the ancient encyclopaedia.

The use of "leather gold" dating to the 17th century was also reported in other texts, ranging from literary to historical and medical. It was described as goods and available in the trade market at that time. In a well-known Chinese novel "*The Plum in the Golden Vase*" (*Jin Ping Mei*), the hems of woman's costumes were decorated with "leather gold". More curiously, it could be used to cure fracture or injuries in Mongolia as cited in the ancient medical book "*Supplement to Compendium of Materia Medica*" (Temule 2011).

Leather gold embroidery is also known as "shadow embroidery". Leather gold is affixed as the backing of a motif, whereas suitable embroidery stitches would then be used to form the motifs. The sparkling effect of gold can be illustrated among the embroideries. This technique is said to be similar to an ancient embroidery technique which was described in a historical text "*History of Song*" (AD 960–1279, the Song dynasty). The embroidery work was combined with gold gilding to show the glittering of gold on the embroideries (Meng 2007).

Yellow croaker was identified which is likely one or the only component of the adhesive to bind the gold or silver strips (foils) onto the leather. There has been a long history of using fish glue in China since 475 BC (Pan et al. 2018). Dried swim bladder from the yellow croaker have been used to make fish glue (Lin 1939). It has been widely used in joining wood, especially for mortise and tenon joints, since ancient China (Zhang 2011). The use of fish glue was considered to be stronger and reversible in nature (Schellmann 2009). Tracing back to the record in the 17th century, fish glue made from the bladders and intestines of fish had been used to make bows, and *Seiaena schlegeli* (a now replaced scientific name designating a croaker fish) was used in Chekiang (nowadays Zhejiang Province) (Sung 1966). Various animal glues, including fish glue, were also implemented as binders in paint media during the Tang dynasty (AD 618-906) (Petukhova 2000).

Based on a Chinese online article written by the curator of Jincheng Museum about the making of "leather gold" in Jincheng of Shanxi in the olden days (Qing dynasty, AD 1644-1911), fish swim bladders, cape jasmine (*Gardenia jasminoides*) and Chinese gall (*Rhus chinensis)* were used. The latter two materials could possibly be used as antibacterial and tanning agents respectively (Guo 2011). Those literature findings on fish glue and leather gold reiterate the consistency of using traditional materials from the ancient time for the production of the children hats in the early 20th century.

Conclusion

The use of analytical tools such as microscopy, SEM-EDX, X-radiography and proteomics techniques provided insights about the decorative materials and fabrication techniques of these traditional children hats. In addition to textile fabrics like cotton and silk, the hats are composed of a variety of materials, in particular the metal-coated strips or foils made of organic materials. The strips or foils are made of gold or silver likely adhere onto sheep or goat leathers with fish glue from the croaker family. The leather types and glue were identified via proteomics, a powerful analytical technique for the species identification of skin and other animal tissues in minute amounts, notwithstanding still a destructive technique. The identification of adhesive is always challenging as the adhesive may not be easily isolated for analysis depending on its quantity, purity or structural condition.

Overall, the study provides valuable material information from historical and preservation perspectives. The composite nature of the children hats requires a stable environment to retard their deterioration, as well as good physical support for maintaining the shapes in storage. The recognition of the material types of the "gold" strips at the treatment stage cautioned the conservators to humidify the hats in a controlled manner for reshaping. The materials for fabricating the "leather gold" are largely in line with those used in ancient times, suggesting the making of "leather gold" could have also been inherited from the traditional ways. This reflects that the craftsmanship of children hats has passed down through families, from generation to generation, within the traditional cultural context.

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