

## INVESTIGATING PRE-1949 CHINESE PAPER-BASED MATERIALS BY RAMAN SPECTROSCOPY: SHORT REVIEW (2000-2017)

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### Abstract

*Raman spectroscopy over the last two decades has shown its power and great potential in advancing our knowledge about the use of materials in the human past. Raman applications on paper-based materials are relatively few, however, compared to the countless case studies on other base materials. In this short review, I summarize post-2000 Raman applications on Chinese paper-based materials, in the hope of keeping non-Chinese scientists updated—which subjects have been investigated by Raman spectroscopy and to address what questions, how Raman applications shed light on the manufacture of pre-1949 Chinese paper-based materials, and what interesting topics arise from these Raman applications. I close my review by proposing a few topics worthy of exploration and investigation in future Raman applications.*

**Keywords:** Raman spectroscopy; Dyed papers; Indigo; Fiat money; Painting; Authenticity.

### Introduction

Raman spectroscopy is a powerful tool for identifying and characterizing phases, and it is ideal for studying art and archaeology materials in two aspects: *in situ* and non-destructive. While applied to art and archaeological artifacts, Raman spectroscopy helps researchers: recognize the materials from which an artifact is made [1, 2]; confirm degradation by-products developed upon the studied artifact [3, 4]; understand the degradation process [5, 6]; or evaluate conservation materials and the state of preservation [7, 8]. Case studies and review papers on Raman spectroscopy are too many to list. Some early or novel applications of Raman spectroscopy in art, archaeology and heritage science are well summarized in *R.J.H. Clark* [9, 10], *H.G. Edwards* [11] and *P. Vandenberg et al* [12, 13].

Raman spectroscopy - whether used alone or combined with other analytical approaches - sheds light on material use in the human past. Some aspects of human behavioral patterns can be understood through comparisons of Raman applications, for example, since when and in which locations did people begin to procure a particular kind of material? How they applied it to the making of artifacts, and to serve what purpose? Why they used it in a particular way? Countless Raman applications were - and still are - carried out to make a contribution to that end. The studied subjects show great diversity in materiality, culture and technology while crossing a wide range of scales in time and space.

In a global context, China has a short history of Raman applications to art and archaeology materials as well as a narrow range of subjects upon which Raman spectroscopy is applied. Raman investigations of ancient artifacts were rare in pre 2000 [14-16] but increased dramatically post 2000 (and this tendency continues until today). Overall, Raman analysis in Chinese case studies strongly focuses on coloring materials (pigment, ink and dye).

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Identification and characterization of base materials or degraded by-products are fewer. Raman investigation of the degradation process or conservation materials is rare or non-existent. Recently, Z. Feng *et al* [17] summarize post 2000 Raman applications in archaeology materials, according to which Chinese scholars apply Raman spectroscopy most commonly to base materials such as metal (bronze; lead; silver and gold), pottery and porcelain; less frequently to stone, jade and wood; and rarely to paper and fabric.

Undoubtedly, there is plenty of room for Raman applications in Chinese art and archaeology materials and, needless to say, Raman analysis has great potential in technical investigations of Chinese paper-based materials. (Unless specified otherwise, I use ‘Chinese paper-based materials’ to indicate paper sheets mainly made in hand papermaking as well as artifacts with handmade paper being a base material.) Why, then, Chinese paper-based materials are important and Raman applications on them are worth reviewing here? The reasons are as follows.

Firstly, Chinese paper-based materials are many (even if only the ancient ones are considered) but few were scientifically investigated due to the lack of suitable analytical methods. Conventional techniques—such as wet chemistry, x-ray diffraction (XRD) and scanning electronic microscopy (SEM)—are *destructive* and *require sampling*, sometimes massive given the size and weight of papers. *In situ* and non-destructive analyses are two distinct advantages that make Raman spectroscopy an ideal, in many cases, the only possible, approach for investigating paper-based materials.

Secondly, paper-based materials from a material science viewpoint are easily subject to degradation and decay and, if those ancient ones survive until today, they are valuable and of great aesthetic, scientific and historical values. Raman spectroscopy can identify and characterize fibre, pigment, dye, ink and filler, as well as paper degradation related to yellowing and ink-induced corrosion. Thus, Raman applications could generate new and reliable information for understanding ancient pulping and papermaking techniques and how papers were further processed or underwent degradation. They also help researchers evaluate the state of preservation and make decisions in the selection of conservation materials.

Thirdly, Raman spectroscopy has a promising application in the authenticity of Chinese calligraphy and paintings. Copies, imitations and forgeries of Chinese calligraphy and paintings are widespread in China than anywhere else in the world. Raman analysis reveals to us the artist’s preference regarding the use of paper, pigment, dye, ink, and the like. It might lay the basis for relative dating and evaluation of authenticity.

In this short review, I will summarize recent (2000–2017) Raman applications on pre-1949 Chinese paper-based materials and place emphasis on how Raman analysis helps to understand the manufacture or further processing of Chinese papers and paper-based materials. Specifically, I will introduce Raman identification and characterization of pigments and dyes; explain how they deepen our understanding of materials use in pre-1949 China; and in a few cases point out how Raman results can authenticate or date artifacts. I will close my review by summarizing issues that need further investigations in Raman applications.

## **Raman applications to Chinese paper-based materials**

Most paper-based materials mentioned in this review use handmade papers. Chinese hand papermaking has distinctive features, making its products unique in many aspects. For example, it makes use of: non-wood plant fibres for pulping; intensive papermaker’s hand labor; natural non-fibrous materials (lime, plant ash, plant juice) in pulping and sheet formation; and a mould designed specifically for sheeting papers. Chinese hand papermaking is made up of sophisticated and complex procedures and it usually takes months to years to prepare the plant raw materials into fibres. Xuan paper, known in the West as *rice paper*, is a well-studied example to demonstrate the technological complexity of Chinese pulping and hand papermaking. For details about the manufacture of Xuan paper, see T. Cao [18], H. Mullock [19] and F. Tsai and D. van der Reyden [20].

I will introduce Raman investigations of Chinese paper-based materials by the following categories: (1) dyed papers; (2) paintings of Chinese religious art; (3) fiat money as national currencies; (4) pawn tickets and bank receipts; (5) country postage stamps; and (6) books, notebooks and letters.

### (1) Dyed papers

‘Dyed paper’, as I use here, refers to the papers dyed by natural plant extracts, with or without writing and painting on them. Dyed papers, either recent or very ancient, are widely found in China. But they are little known to non-Chinese researchers. For this reason, I begin with a brief introduction of paper dyeing in ancient China.

The practice of dyeing paper took place early in China. Chinese records back in the second half of the 3<sup>rd</sup> century AD mention that paper was dyed yellow before used for writing [21]. As later documented, the yellow, natural dye was extracted from the barks of *Huangbo* (*Phellodendron amurense*), a deciduous tree [22, 23]. By 291 AD, papers dyed navy blue were used exclusively by the royal families of Xijin (Western Jin) [24]. Beginning in the 5<sup>th</sup> century AD, colored papers, yellow, red, blue, green, pink and so on, increased in prevalence [23]. In Sui and Tang dynasties (581–907 AD), full-time paperdyers worked in *Shuyuan* (private schools for classical learning). Many Buddhist manuscripts of Tang Dynasty had the paperdyers’ names written at the end of the writings [22]. Paper dyeing was widespread and commonly practiced from the Song Dynasty (960–1279 AD) onwards and many written texts document in detail the various paper dyeing techniques [24].

Chinese researchers believe that paper was dyed for three reasons: (1) Certain dye, such as red lead ( $Pb_3O_4$ ), prevents papers from bookworm infestations [23, 24]; (2) A colored (yellow) paper makes rewriting, when necessary, look more natural. It seems true especially given that in ancient China, texts were often rewritten by orpiment ( $As_2S_3$ ), a yellow pigment [23, 24]; and (3) Dyed papers are more enjoyable to write and read [24]. Many dyed papers were reserved for exclusive use or on particular occasions, e.g., the making of Buddhist manuscripts, official documents and so on [23, 24].

Although paper dyeing was documented early in China, researchers were unable to analyze dyed papers until more recently. *S.E.J. Bell et al* [25] report a dye identification by applying subtracted shifted Raman spectroscopy to the *Diamond Sutra*, hitherto the world’s oldest, dated to 868 AD, and printed Buddhist texts. The paper of *Diamond Sutra* was dyed yellow, and Raman analysis of the yellow dye suggests the presence of both berberine and palmatine (although berberine seems richer than palmatine in the investigated paper). This is the first reported Raman application to ancient Chinese dyed papers, and it confirms the use of plant extract from *Huangbo* (*Phellodendron amurense*) in paper dyeing back in the 9<sup>th</sup> century AD.

*T. Li* [26, 27] investigates two dyed paper fragments from Buddhist manuscripts, one in navy blue while the other in wine red, with an XpoloRA Raman spectrometer. The paper samples were unearthed from Khara Khoto, a Tangut city located in present-day western Inner Mongolia of North China, and they were dated to Western Xia (1038–1227 AD). The navy blue color has Raman peaks that match well with those of standard indigo (Fig. 1).

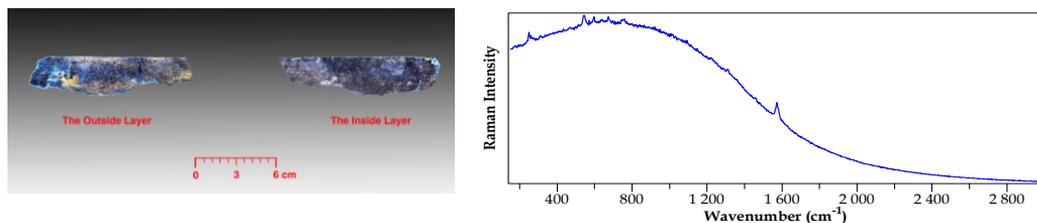


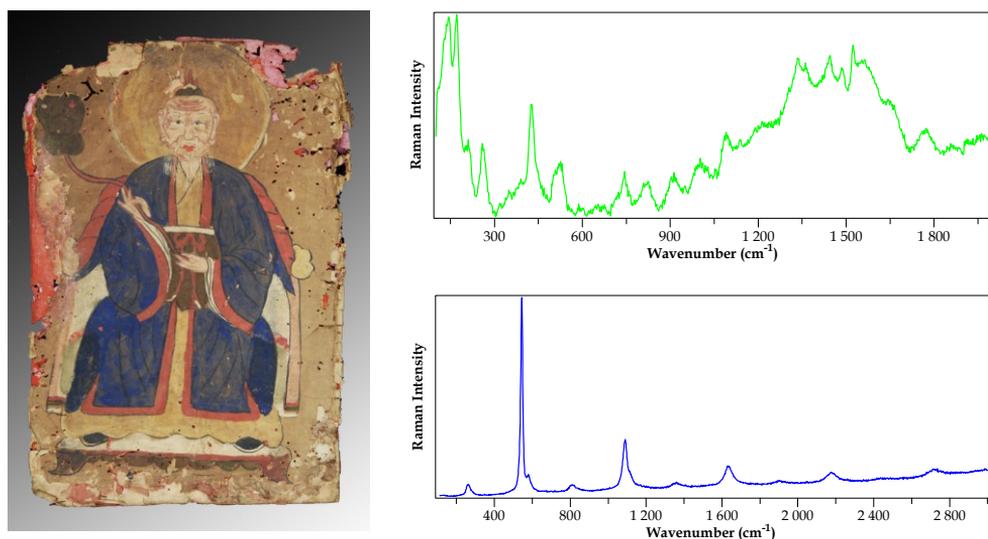
Fig. 1. Indigo-dyed 11<sup>th</sup> to 13<sup>th</sup> century Chinese Buddhist manuscript (*T. Li*, 2017)

The wine red had a strong luminescence background in its Raman spectra but a few Raman peaks are recognizable at 1174, 1227, 1278, 1358, 1404, 1511, and 1605 $cm^{-1}$ . Raman

peaks indicate an organic dye and they exclude the presence of safflower or logwood. *T. Li* [26] and *T. Li* [27] tentatively assign  $1174\text{cm}^{-1}$  to alizarin while the others to purpurin, both attributed to plant extract from madder dye plants (*Rubia tinctorum*). The indigo- and possibly madder-dyed papers are so far the earliest dyed papers examined by Chinese researchers with Raman spectroscopy.

### (2) *Paintings of Chinese religious art*

Traditional Chinese paintings are *hand-drawn on a paper base* using black ink and colored pigments (and less commonly natural dyes). They have a great diversity in subjects and contents, but religious figures are seen often.



**Fig. 2.** Emerald green (top right) and synthetic ultramarine blue (bottom right) as green and blue colors on a painting of Chinese Taoist figure [29]

*Q. He et al* [28] and *T. Li et al* [29] identify and characterize the pigments on a set of date- and author-unknown paintings of Chinese Taoist figures. Raman spectroscopy was the main tool for pigment identification but when uncertainty arose, it was complemented by diffuse reflectance spectroscopy (DRS), energy dispersive x-ray fluorescence (EDXRF), or micro x-ray diffraction ( $\mu\text{XRD}$ ). Raman analysis suggested that multiple pigments, cinnabar, emerald green, ultramarine blue, orpiment, carbon black, and white lead, were used to paint different colors. Microscopic examination and  $\mu\text{XRD}$  analysis of pigment particles further confirmed that ultramarine blue is synthetic rather than natural. Emerald green and synthetic ultramarine blue together (Fig. 2) placed the earliest possible manufacturing dates of the investigated paintings around 1830 AD. Additionally, *T. Li et al* [29] notice that white lead, when analyzed with higher energy from a shorter wavelength (such as 532nm), decomposes easily and transforms into massicot (orthorhombic  $\text{PbO}$ ). This is the first report of heat-induced decomposition of white lead on a paper base, therefore a caution for proper use of wavelength of Raman lasers.

### (3) *Fiat money as national currencies*

China is the country that first issued fiat money as regional or national currencies. As early as in 1023 AD, the Northern Song government issued a fiat money called *jiao zi* as regional paper currency. In the Yuan Dynasty (1279–1368 AD), fiat money became a national currency for the first time in human history and it remained so through the Early Ming (1368–1466 AD). In 1523 AD, the Ming government stopped issuing fiat money. Starting in 1853 AD,

the Qing government issued two paper currencies, *da qing bao chao*; *hu bu guan piao*, but both were soon abandoned in 1859 AD [30].

To understand pigment use on ancient Chinese fiat money, *T. Li* [26] and *J. Shi and T. Li* [30] apply Raman spectroscopy to three fiat money samples, *da ming bao chao*, radiocarbon dated to the first half of 15<sup>th</sup> century AD; *da qing bao chao* and *hu bu guan piao*, issued in 1859 AD and 1854–1858 AD. As revealed by Raman analysis, lead red ( $\text{Pb}_3\text{O}_4$ ) and carbon black account for red and black colors on the 15<sup>th</sup> century fiat money. The same red, blue, and black pigments are used on the two 19<sup>th</sup>-century fiat money and they are cinnabar, Prussian blue and carbon black according to Raman results (Fig. 3). Despite the small sample size, Raman analysis discloses two interesting facts: (1) different dynasties gave preference to different pigments in the making of fiat money; and (2) Western pigments, that is, pigments known to be first synthesized in the West, were applied in the manufacture of national currencies in middle 19<sup>th</sup> century China [31].

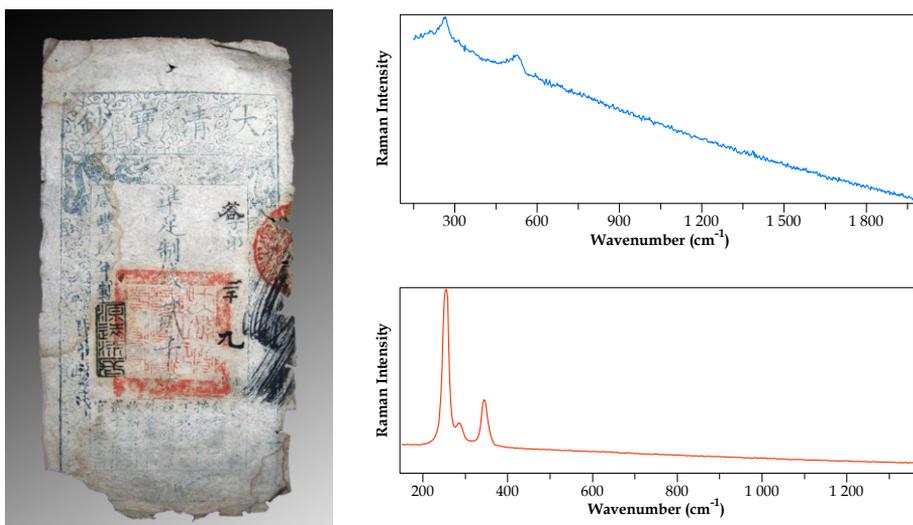


Fig. 3. Prussian blue (top right) and cinnabar (bottom right) on *da qing bao chao* [30]

#### (4) Pawn tickets and bank receipts

It is an old practice to travel with pawn tickets over heavy or valuable items (of course, people did so for other reasons as well). Pawnshops and pawn tickets in 19<sup>th</sup> and 20<sup>th</sup> century China were widespread, leaving behind an enormous amount of pawn tickets, most were used but some not.

*J. Shi et al* [32] apply Raman spectroscopy to investigate two colors - red and blue - on two unused pawn tickets, which were supposedly issued during the Republic of China (1912–1949 AD). Raman spectrum obtained from the red color show three peaks at 249, 280 and 338  $\text{cm}^{-1}$ , suggesting that cinnabar ( $\text{HgS}$ ) be used to print red. The pigment used to print blue, in its Raman spectrum, show Raman peaks at 260, 547, 581, 810, and 1093  $\text{cm}^{-1}$ . Noticing that the Raman peaks match well with those noticed for *Lapis lazuli*, a semi-precious stone, *J. Shi et al.* (2010) argue that blue pigment prepared from *Lapis lazuli*, known in many literature also as natural ultramarine blue, have been used on the investigated pawn tickets [32]. This conclusion is problematic (and very likely incorrect). As *T. Li* [31] has pointed out, it was more probable to use synthetic, instead of natural, ultramarine blue in printing during the Late Qing and the Republic of China, due to three facts: (1) no mines of *Lapis lazuli* have ever been discovered in China; (2) Raman spectroscopy alone do not suffice to distinguish between synthetic and

natural ultramarine blue, as the two share almost identical Raman peaks (especially in 100-2000  $\text{cm}^{-1}$ ); and (3) blue pigment made from *Lapis lazuli* are very expensive; it is unlikely that people in the manufacture of regional pawn tickets chose natural ultramarine blue over the synthetic one, especially given that the latter was cheap and used widely as blue pigments in the Late Qing and the Republic of China. For reliable identification, microscopic examination (with polarized light microscopy), or phase identification (by micro x-ray diffraction), of the blue pigment particles should be used for cross-check.

*J. Ji et al* [33] characterize multiple colors on a government bank receipt dated to 1945 AD. Diverse pigments are identified by Raman and scanning electron microscopy-energy dispersive x-ray spectroscopy (SEM-EDS) analyses. Both organic and inorganic ones are present, i.e., Red Pigment (RP-146 and RP-53:1), cinnabar, carbon black, Prussian blue and two types of realgar. Interestingly, printed colors (red and blue) on the bank note are prepared from modern, commercial pigments (such as Red Pigment and Prussian blue); while the red and yellow colors under the bank's seal contain traditional Chinese pigments (cinnabar and realgar). This case study, although unnecessarily an early example, shows how in printing and painting local traditions of pigment use gave way to the growing interest in commercial synthetic pigments.

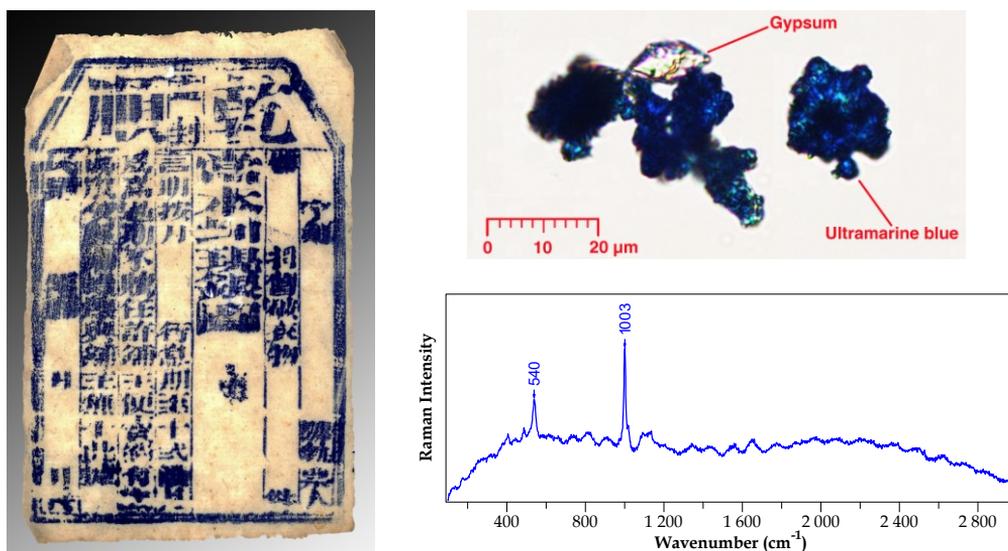


Fig. 4. Synthetic ultramarine blue (mixed with gypsum) on a Chinese pawn ticket [31]

*T. Li* [31] investigates a printed, unused pawn ticket that was issued in the year of 1924 AD by a private Chinese pawnshop. The pawn ticket is very well preserved, printed with one color only, blue. Raman analysis shows Raman peaks at 407, 485, 540, 1003, 1020, 1092, and 1132  $\text{cm}^{-1}$  (Fig. 4). Blue pigment, when removed from the pawn ticket and examined under a polarized light microscope, contains particles of two different colors and sizes, dominated by small rounded, bright blue particles, along with a few larger, diamond-shaped white, translucent particles. Raman peaks at 485, 539 and 1092  $\text{cm}^{-1}$  are attributable to ultramarine blue while the others to gypsum. *T. Li* [31] argues that synthetic ultramarine blue produces the blue color on pawn ticket, with gypsum being intentionally added in as a whiting pigment.

##### (5) Country postage stamps

The State Post of Imperial China issued its first set of postage stamps on October 1<sup>st</sup>, 1897 AD. To understand the pigments used on the early country postage stamps, in 2015, *W. Zhou et al* [34] investigate six engraved coiling dragon stamps, all plated and printed in the United Kingdom and issued in the end of 19<sup>th</sup> century imperial China, with Raman spectroscopy.

Not surprisingly, Raman identification confirms a predominant use of Western pigments which include lead (II) chromate, Prussian blue, synthetic ultramarine blue and chrome orange. In addition, red lead is used to print red. *W. Zhou et al* report the first Raman investigation of early Chinese stamps [34].

*Q. Gan et al* [35] investigate a green color on a Late Qing stamp, which was printed in London and issued in 1909 AD. Raman analysis of the green color shows Raman peaks at 145, 274, 332, 359, 377, 404, 504, 530, 597, 836, 2086, 2110, and 2145 $\text{cm}^{-1}$ . The elemental mapping analysis by SEM-EDS reports enriched iron (Fe), lead (Pb) and chromium (Cr) in the green area. From a color rendering perspective, *Q. Gan et al* [35] propose that Prussian blue and Pb(II) chromate are mixed to produce the green color. *J. Wang et al* [36] make similar attempts, by combining optical microscopy, Raman spectroscopy and X-ray fluorescence, to explain the color formation on a 19<sup>th</sup> to 20<sup>th</sup> century Chinese painting.

#### (6) Books, notebook and letters

Ancient Chinese books are noticed to often have Chinese characters hand-written or printed over the original texts, and pigments are used to serve the cover and correction purpose. Many 7<sup>th</sup> to 10<sup>th</sup> century Buddhist manuscripts discovered in the Dunhuang Library Cave have texts covered by orpiment ( $\text{As}_2\text{S}_3$ ) before rewriting is applied [23]. Recently, *S. Hao* [37] investigates a whitish cover pigment on a Chinese book printed around 1890 AD. SEM-EDS and Raman analyses together confirm that white lead is mainly contained in the white pigment. *S. Hao* [37] believes that this is a proved case of white lead functioning as *correction fluids*, despite that no organic components - such as animal glue and egg white, both used commonly in the manufacture of Chinese paintings or glues - are detected by Raman spectroscopy.

*L. Hu et al* [38] report Raman applications on a pre-1949 Chinese notebook (1934 AD) and a letter (1921 AD), both of which are dyed red and housed in Guangzhou Province of South China. Raman analysis of the red dye on the letter shows Raman peaks at 461, 734, 989, 1096, 1205, 1234, 1335, 1384, 1487, and 1596 $\text{cm}^{-1}$ . Red dye on the notebook, however, has Raman peaks at 712, 1000, 1140, 1239, 1325, 1419, and 1599 $\text{cm}^{-1}$ . *L. Hu et al* [38] argue that two different dyes are used for dyeing the notebook and the letter, respectively, given the different Raman peaks. They further point out that red dye on the notebook is prepared from smoking red, an imported Western pigment, while red dye on the letter - whose chemical composition can hardly be determined by Raman spectroscopy - is very likely prepared in local dyeing workshops in Guangzhou.

## Conclusions

Raman applications on pre-1949 Chinese paper-based materials - although only sporadic compared to the countless case studies on other base materials - have just started to show the power of Raman spectroscopy. Our understanding about Chinese papers and paper artifacts has been advanced especially on the following topics: paper dyeing by plant extracts; the manufacture of paper money; pigment or dye use on stamps, books, and documents; and pigments used for cover and correction purpose. Many interesting new questions arise from the reviewed Raman applications, including: dispersal of Western pigments (such as Prussian blue, synthetic ultramarine blue, emerald green and chrome orange) to East Asia in the 18<sup>th</sup> and 19<sup>th</sup> centuries; a shift of interest to commercial pigments and dyes and replacement of their Chinese counterparts; preference to some pigments and dyes over others in the manufacture of paper-based materials distributed and used on local, regional and national scales.

Gaps or limitations, on the other hand, do emerge as we reviewed the Chinese Raman applications. As far as paper-based materials are concerned, Raman analysis is powerful and reliable - very suitable for identifying and characterizing inorganic materials used as pigments, filling or covering pigments; its application to organic substances is rare, however. Admittedly, Raman spectroscopy is not the ideal technique for studying organic components, but successful case studies do exist (even though their studied materials are unnecessarily always on a paper base) [39-42]. Therefore, we would expect to see more trial-and-error Raman investigations of Chinese inks, seal pastes, plant and animal glues, and natural or commercial dyes. A most

relevant topic yet to explore is the dataset construction for accessible, searchable and downloadable standard Raman spectra. *J. Wang et al* [43] and *Z. Liu et al* [44] have published datasets for inorganic pigments most often used in ancient China, but many further studies are needed to complement their datasets or to construct completely new ones. For the same purpose, I shall emphasize that Raman applications must expand their interests to include raw materials documented to have been exploited for papermaking and printing. Last but not the least, many other kinds of Chinese paper artifacts have not been investigated by Raman spectroscopy (or any analytical approaches), including screens, umbrellas, kites, cloths, name cards, wallpapers, paper-cut, ceremonial papers and paper cards. They are worthy of investigation to extend our knowledge about different functions and uses of paper, pigment, dye, ink and the like.

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