Journal of Cultural Heritage 15 (2014) 331–335

Available online at
SciVerse ScienceDirect
www.sciencedirect.com

Elsevier Masson France
EM|consulte
www.em-consulte.com/en

Short note

A note on Chinese Bamboo paper: The impact of modern manufacturing processes on its photostability

Ying Tang[a,*], Gerald J. Smith[b,1]

[a] Beijing Key Laboratory of Plant Resources Research and Development, School of Sciences, Beijing Technology and Business University, 11 Fucheng Road, 100048 Beijing, China
[b] School of Chemical and Physical Sciences, Victoria University of Wellington, PO Box 600, Wellington, New Zealand

ARTICLE INFO

Article history:
Received 17 February 2013
Accepted 27 May 2013
Available online 1 July 2013

Keywords:
Bamboo paper
Chinese handmade paper
Manufacturing techniques
Fluorescence
Photodegradation
Reactive oxygen species

ABSTRACT

Papermaking has a special place in the cultural heritage of China. Papers made from different types of plant fibers were, and are still used for particular applications. Bamboo paper is a handmade paper that has been traditionally used for book printing and restoration of ancient paper objects since antiquity in China, whereas *Xuan* paper, the subject of recent previous study, is used for traditional Chinese calligraphy and painting. Following our previous approach on *Xuan* paper, four modern Bamboo papers manufactured using traditional or chemically-facilitated techniques were artificially aged by UVA radiation and changes to their optical properties were evaluated by reflectance and 3D-fluorescence spectroscopies. Paper samples produced by different methods displayed different fluorescence spectra and UVA photolysis of paper resulted in decreases in the fluorescence intensities and reflectance values, manifested as differing photoyellowing of the papers. Assays of reactive oxygen species, ROS, revealed that papers made by chemically-assisted pulping methods generally produce more hydrogen peroxide or superoxide radicals than those made by traditional methods, which correlates with their relative yellowing rates. Different spatial distributions of calcium and chlorine were also observed by SEM/EDS analysis in the chemically-manufactured papers, probably arising from the specific pulping and/or bleaching chemicals used in their manufacture.

1. Research aims

This study reports the fluorescence and photochemical characteristics of Bamboo paper upon exposure to UVA radiation as well as the effects of different manufacturing techniques on the optical properties and photostabilities of paper. Four types of Bamboo paper manufactured using traditional or chemically-facilitated methods were investigated. Their photooxidative stresses associated with the production of hydrogen peroxide and superoxide radicals during irradiation were measured and relative photostabilities were assessed by reflectance and 3D-fluorescence spectroscopies. Scanning electron microscopy with energy dispersive spectroscopy (SEM/EDS) was employed to examine the morphological and elemental characteristics of paper. The objective is to provide fundamental knowledge for how production techniques, especially the use of synthetic chemical agents, determine the relative photostabilities of Bamboo paper. This contributes not only to the conservation of Asian paper artefacts but also to the preservation of traditional papermaking crafts.

2. Introduction

Bamboo paper, also known as *Lianshi* paper, is a type of Chinese handmade paper of significant cultural and heritage value. Bamboo paper features the qualities of whiteness, softness and thin form, and has been used extensively for printed books throughout history [1]. Today, this paper is still produced in some areas of China to meet needs of artists as well as for the restoration of ancient paper objects. In 2006, the craft of making Bamboo paper was listed as a National Intangible Cultural Heritage of China [2].

Bamboo paper is manufactured from pulped young twigs of bamboo (*Phyllostachys aurea*), a plant that was extensively cultivated in China and has been a major source of papermaking fiber since the 8th century [3]. Traditionally the paper was made using natural materials, hand-tools, utensils and naturally-occurring reagents. Step-by-step processes of the manufacture were well documented by Song Ying-Xing (AD 1587–1666) in his book "*Tian Gung Kai Wu* (The Exploitation of the Works of Nature)" [4] as well as in Needham's multi-volumed work, "Science and Civilisation in China" [3]. General procedures include: "removing the green" by

* Corresponding author. Tel./fax: +86 1068984917.
E-mail addresses: tangying@th.btbu.edu.cn, ytjenny@gmail.com (Y. Tang), gerald.smith@vuw.ac.nz (G.J. Smith).
1 Tel.: +64 44635547; fax: +64 44635237.

1296-2074/$ – see front matter © 2013 Elsevier Masson SAS. All rights reserved.
http://dx.doi.org/10.1016/j.culher.2013.05.004

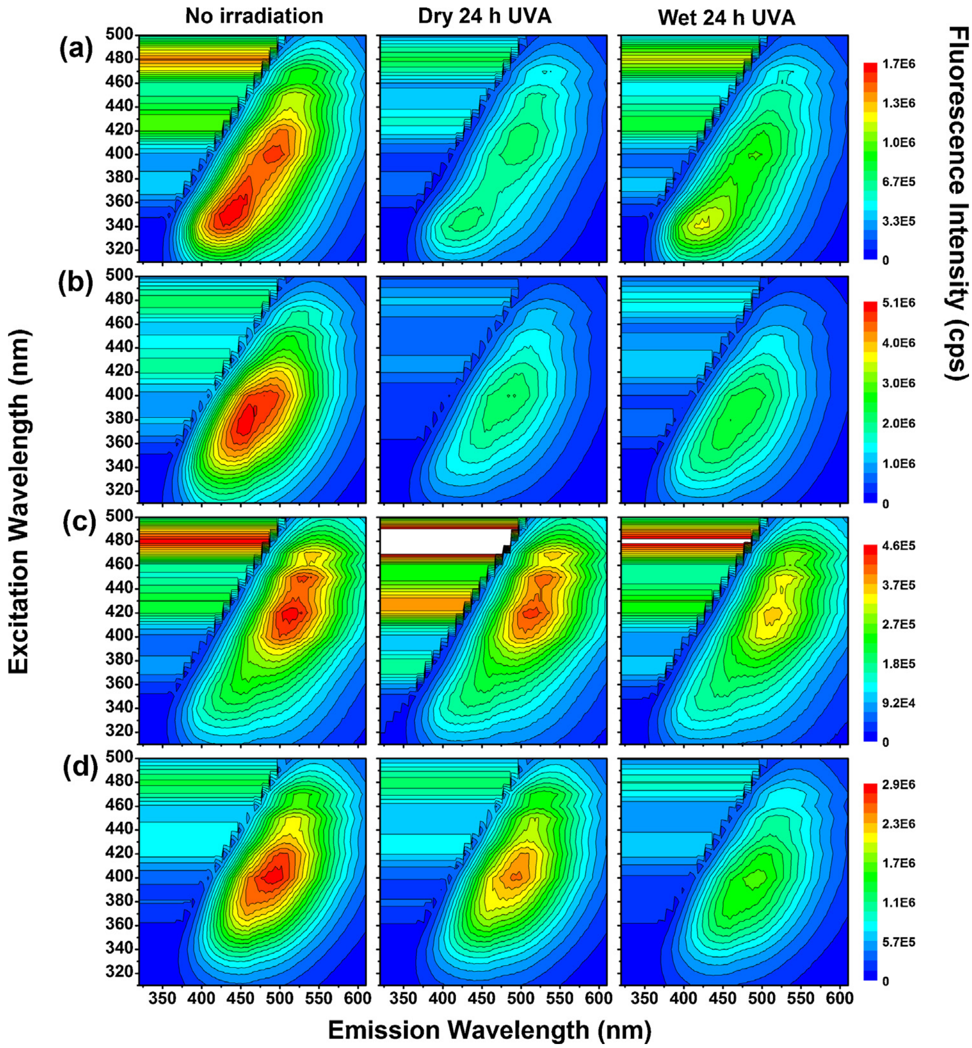

Fig. 1. 3D-fluorescence spectra of four Bamboo papers B1 (a), B2 (b), B3 (c) and B4 (d) before (left side) and after 24 hrs of UVA irradiation, under dry (middle) or wet (right side) conditions.

repeated soaking, pounding, cooking, rinsing, and solar bleaching of the plant materials; forming paper sheets by casting the pulp on a perforated screen; pressing the sheets to expel water; and finally drying on a heated brick wall. The traditional manufacture of Bamboo paper is an arduous and painstaking process, and may take about eight months to one year to produce the sheets of paper [4]. From the 20th century, synthetic chemical reagents have been employed to accelerate the manufacturing process [5,6]. For example, calcium hypochlorite has been used in the preparation of pulps instead of traditional solar bleaching, and sodium hydroxide, in the cooking/thermal hydrolysis stage [1,6]. However, papers produced using these present-day techniques are generally considered inferior in quality, especially with regard to lightfastness, to the traditionally-manufactured paper [7]. Concerns are raised about their appropriateness for paper conservation, and the traditional papermaking crafts are in danger of being lost [6].

Unlike the famous *Xuan* paper [8], reports of scientific research on Bamboo paper are comparatively rare and most have been confined to ethnographic field studies of the paper handcrafts in different regions of China [1,5,6,9]. These reports have contained some preliminary investigations of the relationship between the permanence of the paper and its methods of manufacture. For example, Su's study revealed that Bamboo papers produced by traditional solar bleaching and repeated thermal treatment with alkaline solutions made by dissolving lime or extractions of wood ash in water retained their whiteness and strength during accelerated thermal ageing better than those made by modern methods [1,6]. However, there has to date, been no quantitative evaluations of the photostability or lightfastness of Bamboo paper nor an elucidation of the underlying mechanisms. Our recent work on *Xuan* paper was the first fluorescence and photochemical study of Chinese handmade paper during artificial photoageing, in which a novel approach was developed to assess the yellowing rate of paper by spectroscopic changes together with assays of the concomitant formation of reactive oxygen species [10].

3. Experimental

3.1. Materials

The Bamboo papers investigated were sourced from Fuyang County, China, where the tradition of making Bamboo paper has been maintained for many years. Paper samples labelled as B1-B4 were manufactured using either traditional or chemically-assisted methods. As stated in Table 1, B1-B2 were of the same origin and were both made from traditional pulps (heating with aqueous extracts of wood ash or lime water), but the latter had been treated with calcium hypochlorite instead of exposure to sunlight. The samples of paper types, B3-B4, were produced from chemical

Table 1
List of Bamboo paper investigated in this paper.

No.	Pulping agent	Bleaching agent	Manufacturer	Origin
B1	Wood ash	Sun bleach	*A-De*	Fuyang
B2	Lime	Bleaching powder	*A-De*	Fuyang
B3	NaOH	Unbleached	*Xin-San-Yuan*	Fuyang
B4	NaOH	Bleaching powder	*Xin-San-Yuan*	Fuyang

pulps by a different manufacturer in which sodium hydroxide was used as the alkali although the pH has not been disclosed. Similarly, other additives which could impact on the stability were not disclosed. Sample B4 had also been chemically bleached while B3 was an unbleached paper.

3.2. Methods

0.2 g of paper samples were exposed to UVA radiation from a pair of 6 W "blacklight" UV fluorescent lamps (NEC FL6BL-B) with a maximum output at 366 nm at a distance of 1 cm from the paper sample. This configuration gave a uniform illumination field over the samples with a spectrally integrated intensity of 4.2 mW.cm^{-2} between wavelengths of 350 nm and 400 nm at the surface of the sample. The samples were irradiated in the presence of water and without added water. The "wet" irradiations were performed by immersing the test pieces of paper in 2 mL of double-distilled water sealed within a polyethylene film container having a transmission of 80% over the UV photolysis wavelength range from 350 to 400 nm. Because the heat output from the fluorescent lamps was low, the temperature of the samples could be maintained at room temperature (~20 °C) by forced air cooling. The wet paper samples were air-dried at ambient temperature after irradiation before the fluorescence and reflectance spectroscopic measurements. Spectroscopic characterizations including 3D-fluorescence and UV-Vis reflectance spectroscopy as well as the scanning electron microscopic examination of paper were performed using identical experimental methods to those detailed in the previous work on *Xuan* paper [10]. Photoinduced yields of H_2O_2 and $O_2^{\bullet-}$ in the irradiated papers were also measured using the previous colorimetric xylenol assay [10,11]. Further details of the methods used are presented in references [10] and [11].

4. Results and discussion

4.1. Optical effects of manufacture and UVA radiation

Fig. 1 shows the 3D-fluorescence spectra of the four samples of Bamboo paper before and after 24 hrs of UVA irradiation. Irrespective of the pulping methods, solar-bleached and unbleached papers (B1 and B3) displayed fluorescence excitation/emission spectra indicative of the presence of multiple fluorophores. This is in contrast with the chemically-bleached papers that displayed only one fluorophore emitting in the blue spectral region with the maxima at 450 nm for B2 and at 475 nm for B4. This blue fluorophore was attributed to the presence of a number of naturally-occurring hydroxycoumarins which has also been observed on the traditional *Xuan* paper [10]. The absence of other minor fluorophores absorbing at longer wavelengths in B2 and B4 suggests these fluorophores/chromophores were removed by the chemical bleaching agents, which gives an enhanced reflectance/whiteness level compared to their solar-bleached or unbleached counterparts shown in Fig. 2.

Exposure of the Bamboo papers to UVA radiation resulted in reductions in fluorescence yields (Fig. 1) and reflectance across the visible spectrum from 400 to 600 nm (Fig. 2). The largest changes in the reflectance spectra were observed for irradiation of B2, the paper made from traditional pulp but bleached with chemical agents, following UVA irradiation of the dry paper. Interestingly, papers produced from traditional pulps (B1-B2) displayed greater reductions in the paper's fluorescence intensities and reflectance values when irradiated dry as opposed to wet. This is in contrast to the more rapid photoyellowing with wet irradiations observed in the papers produced from chemical pulps (B3-B4). It is therefore concluded that the different fluorescence/reflectance spectral characteristics of papers depend on their manufacturing methods. Their relative photostabilities after 24 hrs of UVA irradiation follow the trend B1≈B3 > B4 > B2 when irradiated in the dry state which contrasts with the trend B1 > B2 > B3≈B4 when irradiated in the presence of water, as determined by declines in reflectance across the visible spectrum (Fig. 2).

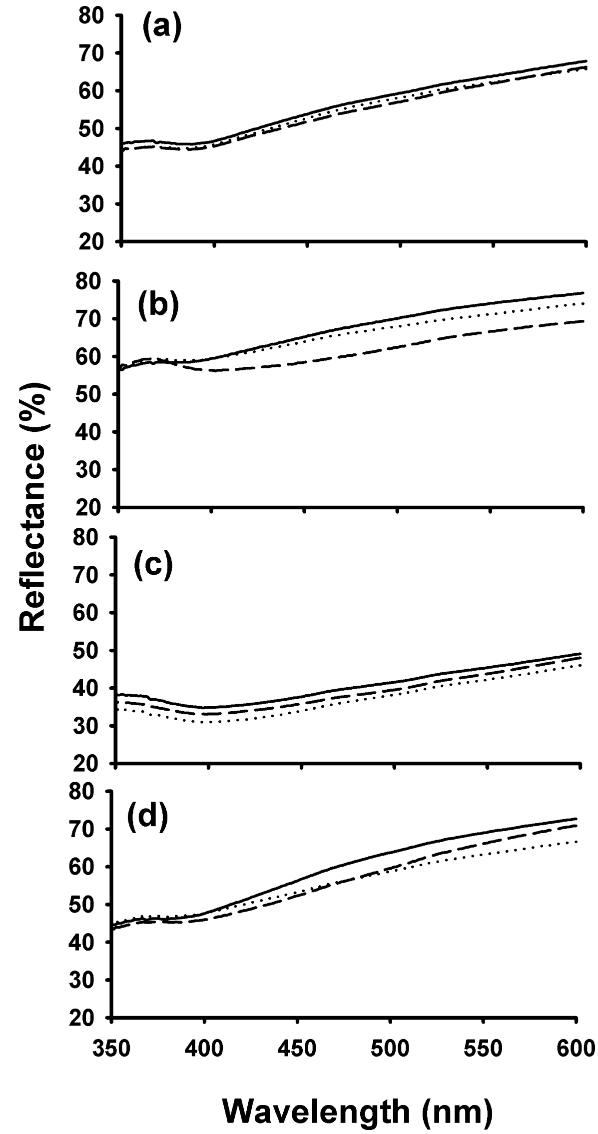

Fig. 2. UV-Vis reflectance spectra of Bamboo papers B1 (a), B2 (b), B3 (c), and B4 (d) before (solid line) and after 24 hrs of UVA irradiation, under dry (dashed line) or wet (dotted line) conditions.

4.2. Photogeneration of peroxide and superoxide

The kinetics of UVA-induced generation of ROS in the four Bamboo papers studied in the presence of water is shown in Fig. 3. The highest yield of H_2O_2 was observed from irradiation of B3, the unbleached paper. When many of the visible chromophores

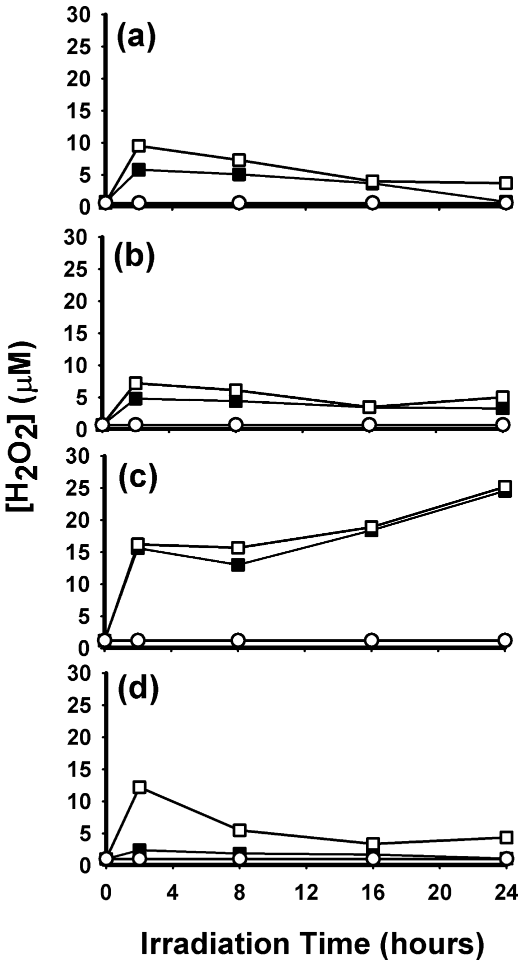

Fig. 3. Photoproduction of hydrogen peroxide in UVA-irradiated Bamboo papers B1 (a), B2 (b), B3 (c) and B4 (d) with the addition of SOD (□) or catalase (○) in comparison to the paper only (■). Each data point in the graph is the mean of three replicate measurements.

are removed from chemically-bleached paper, as occurs in type B4, only trace amounts of H_2O_2 were detected on photolysis. This suggests that the yellow chromophores, associated with lignin present in the unbleached paper, contribute significantly to the photoinduced peroxide production. The formation of $O_2^{\bullet-}$ is indicated by an enhancement of H_2O_2 production in the presence of superoxide dismutase (SOD) with the highest yield observed in B4 following 2 hrs of irradiation. Because the addition of catalase to all samples did not alter the amount of Fe(III) formed in the analytical system, it is inferred there was no oxidants, other than hydrogen peroxide and its precursors, were produced (e.g. alkyl peroxides) by photolysis[11]. The levels of photoinduced H_2O_2 and $O_2^{\bullet-}$ formed are associated with the UVA-induced degradation of the papers studied. This can be interpreted in terms of sensitized photooxidation via a mechanism of electron transfer from some fluorescent species (e.g. hydroxycoumarins) present in the fiber in their excited singlet states. This photodegradation mechanism has been proposed previously for traditional *Xuan* paper subjected to UVA photolysis [10].

It is apparent that the chemically-pulped papers (B3, B4) produced more peroxide or superoxide than those made from traditional pulps (B1, B2). However, in the cases of the traditionally-pulped papers, the two bleaching methods used, i.e. exposure to sunlight (B1) or calcium hypochlorite (B2), did not significantly affect the yields of photoinduced of hydrogen peroxide.

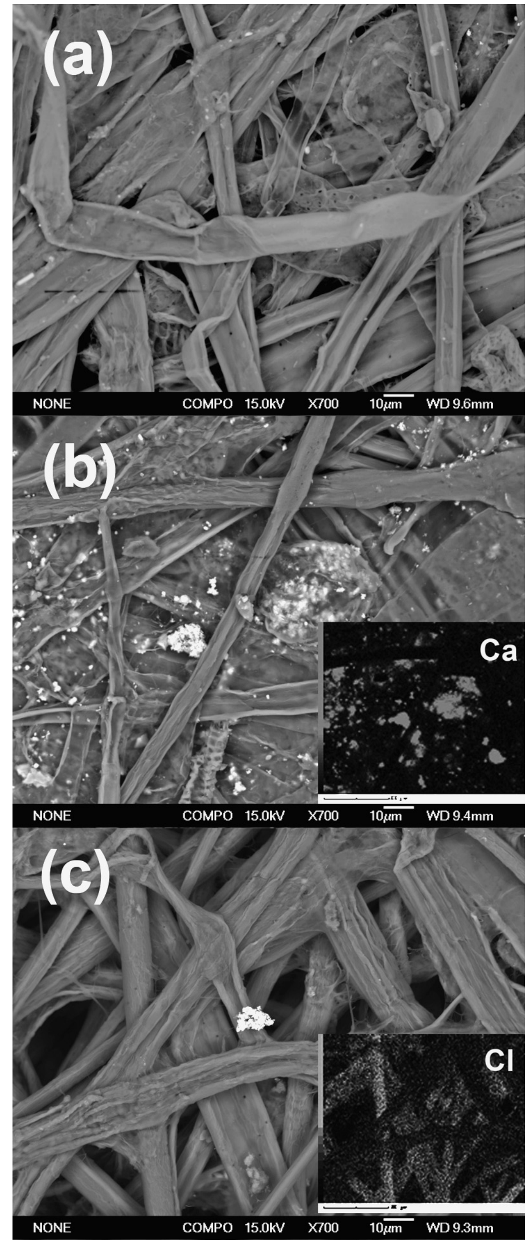

Fig. 4. SEM backscattered images of Bamboo papers B1 (a), B2 (b) and B4 (c) with EDS mapping of chlorine (Cl) and calcium (Ca) for B2 and B4 respectively. All papers were investigated at 700× magnification.

This is consistent with the observation that the paper B1 and B2 are more photostable than B3 and B4 following 24 hrs of "wet" irradiation.

4.3. Morphological and elemental characteristics

The use of synthetic chemical reagents in producing paper B4 have resulted in an enhanced fiber deformation and adhesion between the component fibers compared with the undamaged, well-separated fibers present in the traditional paper, B1 (Fig. S1). Paper samples treated with chemical reagents have also exhibited relatively high levels of calcium and/or chlorine as demonstrated in electron-backscatter SEM images with associated EDS mapping (Fig. 4 and Fig. S2). Calcium-containing particles were observed in paper B2 and are probably associated with residues of chemical bleach such as calcium chloride and calcium hypochlorite.

In the presence of water, these chemicals are expected to oxidize and bleach the coloured photoproducts thereby reducing the photoyellowing of paper under wet conditions (Fig. 2b). Calcium precipitates are also likely to be formed in the "lime-cooking" process used in the traditional pulping and were shown to protect *Xuan* paper from increasing acidity during hydrothermal ageing [10]. Paper B4 exhibited fibers impregnated with high levels of chlorine, suggesting there are chlorinated organic compounds bonded to the surface of the paper after pulping with sodium hydroxide.

5. Conclusions

The traditionally manufactured and unbleached papers have multiple fluorophores while the chemically-bleached papers possess only a single fluorophore. Exposure of the papers to UVA radiation resulted in decreases in the fluorescence intensities and reflectance values throughout the visible spectrum which results in a duller yellower appearance after irradiation. The concomitant photogeneration of hydrogen peroxide and superoxide radicals showed that papers manufactured from chemical pulps generally produce more peroxide or superoxide than those made from traditionally produced pulps, which is attributed to the additional fluorophores/photosensitizing species present in chemically-facilitated pulped paper. SEM/EDS analysis indicates that Bamboo papers produced by chemical-facilitated methods exhibit different levels and spatial distributions of calcium and chlorine from those observed in paper produced by traditional methods which is a consequence of the different pulping and/or bleaching chemicals used in their manufacture.

This work has thereby provided some insight into how manufacturing techniques and the use of synthetic chemicals affect the optical properties and lightfastness of Bamboo paper. The results of this research will inform conservators and restorers of books printed on bamboo paper of the photostability issues that attend the use of chemically-pulped bamboo paper in their practice.

Acknowledgement

The authors wish to thank the Department of Scientific History and Archaeometry, Graduate University of Chinese Academy of Sciences (Beijing, China) for providing the paper samples. G.J.S. acknowledges the New Zealand Ministry of Science and Innovation, contract VICX0803, for support.

Appendix A. Supplementary data

Supplementary data (Figs. S1 and S2) associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.culher.2013.05.004.

References

[1] J. Su, Conservation of the papermaking crafts of Lianshi paper, Master Thesis, Fudan University, China, 2008.

[2] Ministry of Culture P.R. China, The First List of National Intangible Cultural Heritages (2006), http://www.ihchina.cn/main.jsp (last visited 17/02/2013).

[3] J. Needham, T.H. Tsien, Science and Civilisation in China: Volume 5, Chemistry and Chemical Technology; Part 1, Paper and Printing, Cambridge University Press, UK, 1985.

[4] Y.X. Song, Tian Gung Kai Wu, Guangdong Education Publishing House, Guang Zhou, China, 2011.

[5] R.Q. Liu, Lianshi paper-researches on acient paper, Paper and Paper Making 31 (2012) 62–66.

[6] J. Su, G. Chen, The handicraft of Lianshi paper and preliminary investigation of paper permenance, in: Preceedings of The Fifth Annual Conference Symposia of Chinese Cultural Heritage Conservation Technique Association, Science Press, Beijing, 2008, pp. 314–319.

[7] G. Chen, Current situation and questions for Bamboo paper used in the restoration of ancient books and archives, Arch. Sci. Study 1 (2012) 80–84.

[8] H. Mullock, Xuan paper, Paper Conservator 19 (1995) 23–30.

[9] X.Y. Fang, D.T. Wu, Z.H. Yan, R.S. Gan, L.X. Shi, W.L. Zhong, Research and investigation about Lianshi Paper at Jiangxi province, Yanshan county, J. Beijing Inst. Graphic Commun. 18 (2010) 8–17.

[10] Y. Tang, G.J. Smith, Fluorescence and photodegradation of Xuan paper: the photostability of traditional Chinese handmade paper, J. Cult. Herit. (2012), http://dx.doi.org/10.1016/j.culher.2012.11.002 [In press].

[11] K.R. Millington, G. Maurdev, The generation of superoxide and hydrogen peroxide by exposure of fluorescent whitening agents to UVA radiation and its relevance to the rapid photoyellowing of whitened wool, J. Photochem. Photobiol. A 165 (2004) 177–185.