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Original article

Chinese handmade mulberry paper: Generation of reactive oxygen species and sensitivity to photodegradation

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ABSTRACT

Handmade mulberry paper is a traditional bark paper of China dating back nearly two millennia and is still a popular medium used today for preserving and restoring Asian paper artefacts. In the present study, samples of modern Chinese mulberry paper from different traditional manufacturers were artificially aged by exposure to UVA radiation. Their degradation patterns and associated generation of superoxide anions and hydrogen peroxides were determined by means of various spectroscopic techniques following our previous approach. Furthermore, electron spin resonance (ESR) spectroscopy using 5,5-dimethyl-1-pyrroline-N-oxide (DMPO) as a spin-trapping agent was employed to detect hydroxyl radicals in irradiated paper as well as to provide additional information for the photodegradation mechanism. Like *Xuan* paper, Chinese handmade mulberry paper exhibited blue fluorescence ($\lambda ex = 340-400$ nm; $\lambda em = 450-480$ nm) consistent with it originating from a number of naturally-occurring hydroxylcoumarins. UVA irradiation of papers of different origins resulted in varying changes to the fluorescent species, which, together with the hydrolysis or formation of chromophores absorbing in the visible region, leads to the photobleaching or photoyellowing of paper. The extent of photodiscolouration of different papers correlate with their relative rates of the production of reactive oxygen species (ROS), including hydrogen peroxides, superoxide anions and hydroxyl radicals. SEM-EDS analyses revealed that the Chinese mulberry paper studied in the work had high levels of calcium and phosphorous, together with a much lesser amount of potassium, iron and copper, which probably originate from details in their manufacturing methods. Papers containing high concentrations of these metal ions also exhibited higher yields of ROS, which contribute to a higher level of oxidative stress and thereby affects their photostability. The main mechanism for the photodegradation of Chinese mulberry paper is proposed to be a sensitised oxidation via the formation of activated ROS, catalysed by the presence of transition metal ions, particularly ferric and cupric, and was accelerated by other factors such as moisture. This study has provided detailed knowledge for the photodegradation process of Chinese mulberry paper, which aims to assist the development of effective treatments for the restoration of important paper cultural heritage objects.

1. Introduction and research aims

Mulberry paper, also known in Chinese as *Sangpi* or *Hanpi* paper, is a Chinese handmade paper of significant cultural and heritage value. Manufactured from the inner bark fibres of mulberry (*Morus alba*) or paper mulberry (*Broussonetia papyrifera*), this type of paper is thin, soft, glossy, fine and absorbent. In ancient China, mulberry papers were extensively used for writing and bookmaking in the Tang dynasty (AD 618–907) and has continued during the Ming and Qing dynasties (AD 1368–1912) as evidenced by many Dunhuang and Turfan manuscripts [1]. Historically it was the principal paper used for bank notes, book covers, clothing and furnishings [2].

The advent of making mulberry paper in China dates back to the invention of bark paper by Cai Lun in the Eastern Han dynasty (AD 25–220) [2]. The methods of papermaking were recorded in the book "*Tian Gung Kai Wu*" by Song Ying-Xing (AD 1587–1666), where he described the harvest of paper mulberry barks and the treatment with fluid lime for fibre preparation [3]. The basic processes of making Chinese mulberry paper were similar to that for bamboo paper, including the preparation of raw materials by soaking, pounding,

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boiling, cleansing and bleaching (by exposure to sunlight and treatment with wood ashes); casting and draining the pulp on a screen; and drying the sheet by heat [2]. Song also described an economical method of making mulberry paper in the southern areas of China using sixty percent of mulberry bark with forty percent of tender bamboo or seventy percent of bark and bamboo mixed with thirty percent of rice stalks [3]. In East Asia, the methods of making mulberry paper in Korea and Japan, namely *Hanji* and *Washi* paper respectively, have been founded on the Chinese manufacturing procedure of mulberry paper, which continued to develop with their own tools and techniques [4].

Traditional handmade paper made exclusively of mulberry bark is still produced today in some areas of China to meet the needs of artists and conservators. One of the common uses of mulberry paper is to serve as the backing material for the mounting of artwork, a significant process in the decoration of new works of art or in the conservation of antique pieces. It is believed that the survival of many historic Chinese paintings and calligraphies on paper is largely due to the extraordinary durability of the backing paper used [2]. However, after the middle of the 20th century, the scale of handmade mulberry paper production in China rapidly declined, making this traditional papermaking technology in danger of being lost. This problem has been exacerbated by traditional papermills in China being mainly family-operated and the quality of paper varies according to materials, manufacturing techniques and regions. These factors raise concerns about the selection and quality control of mulberry paper suitable for conservation uses.

As a lignocellulosic material, mulberry paper is subject to deterioration caused by light, moisture, temperature, microorganisms and chemical pollutants, apparent as embrittlement and discoloration (fading, yellowing and foxing) [5]. Most of these result in loss of aesthetic properties and often the irreversible degradation of important documents and works of art. The Korean *Hanji* paper has been extensively investigated regarding its conservation suitability, and the impacts of pulping agents [6], beeswax coatings [7] and preservatives [8] on the properties and permanence of paper have been reported. By contrast, investigations on the permanence and durability of Chinese mulberry paper are rare and most studies are confined to descriptions of the optical or mechanical changes of paper during thermal ageing [9,10]. Little is known about the photodegradation of Chinese mulberry paper and the underlying mechanisms responsible for this degradation are far from understood. Our previous report on *Xuan* paper [11], another Chinese bark paper, used multiple non-destructive spectroscopic methods to evaluate the lightfastness of the handmade paper. The mechanism for the photodegradation of *Xuan* paper was interpreted in terms of a sensitised photooxidation triggered by the photoactive fluorescent species present in the fibre. And the relative rates of discolouration (e.g. photoyellowing) of different Chinese handmade papers correlates with their concomitant formation of reactive oxygen species (ROS) [12].

This paper reports a mechanistic study on the photodegradation of modern Chinese handmade mulberry paper informed by the detection and measurement of various reactive oxygen species. Using our previous approach [11,12], the morphology and elemental contents of different paper samples were determined by scanning electron microscopy with energy dispersive spectroscopy (SEM-EDS). The optical appearance changes of paper samples occurring during UVA-photoageing under wet or dry conditions were determined by 3D-fluorescence and reflectance spectroscopy, and the kinetics of photolytic formation of superoxide ions and hydrogen peroxides were determined by colorimetric assays. Furthermore, hydroxyl radicals in photoaged papers were directly detected by electron spin resonance (ESR) spectroscopy combined with spin-trapping. The objective of the study is to contribute to a better understanding of the mechanisms that culminate in the discolouration of important documents or works of art on mulberry paper, in order to guide the selection of appropriate paper for conservation or developing suitable restoration treatments. In addition, as part of an ongoing study, the results can be compared with similar work that has been carried out on Chinese *Xuan* paper and bamboo paper [11,12].

2. Materials and methods

2.1. Paper samples

Three samples of traditional mulberry paper were selected for this work, which were all sourced from reputable papermaking provinces of China. Sample M1 is an unbleached paper made in 2014 at Moyu County of Hotan, northwest Xinjiang Uygur Autonomous Region. The traditional craft of making mulberry paper in Hotan areas may have originated from the Silk Road since the Tang dynasty and was listed as a National Intangible Cultural Heritage of China in 2016. Samples M2 and M3 were collected from Wenzhou and Jing County in 2008, which are reputed areas for producing high-quality mulberry paper since the Song dynasty [3]. As summarised in Table 1, M1 and M3 were made from 100% mulberry barks and M2 was produced from mixed pulp fibres of mulberry and coniferous wood. The use of auxiliary agents also varied regionally. For instance, M2 and M3 were manufactured in the southern areas where lime and wood ash were often employed in the traditional pulping and bleaching process. By contrast, M1, the sample from northwestern China, was made from pulps in which poplar soda was used as the alkali. Other chemical additives were not disclosed.

After collection, paper samples were stored in polyethylene bags in the dark at 4 °C prior to use. The surface pH of each paper sample, before and after UVA photoageing, was non-destructively measured according to Tappi T 529 om-04 using a combination flat-head electrode (InLab Surface pH electrode, Mettler Toledo, Switzerland) and a Mettler Toledo SevenCompact S210 pH meter. The accuracy in pH determinations was average pH $< \pm 0.02$ units ($n = 3$).

2.2. UVA-Irradiation

Paper samples weighing 0.2 g (dry weight) for wet or dry irradiation were exposed at a distance of 10 cm to two 15 W blacklight UVA lamps (Spectronics XX-15A, USA). The UV radiation spectrum ranged from 320–400 nm with a maximum output at 365 nm and a spectrally-integrated intensity in the range of 2.5–3.5 mW.cm^{-2}. Wet irradiations were performed by soaking the test pieces of paper in 2 mL of double-distilled water in a sealed polyethylene container with an optical transmission of 75–80% over the spectral range of the irradiating source from 350 to 400 nm. The radiation intensity inside the container was attenuated by 0.17–0.23 mW.cm^{-2} compared with that of dry irradiation as measured by a Spectronics AccuMax XF-1000 radiometer equipped with a XS-365 UVA sensor.

2.3. Morphological characterisation

The morphology of mulberry papers was observed with a Hitachi S-4800 field emission scanning electron microscope (FESEM, Hitachi High-Technologies, Japan) with an EDS attachment for elemental analysis and mapping. The samples were sputter-coated with gold to reduce electrostatic charging.

2.4. Fluorescence and reflectance spectroscopy

Fluorescence spectral measurements were performed using a Horiba Jobin-Yvon Fluorolog-3 spectrofluorometer (Edison, USA) with a “front-face” excitation/detection configuration. Excitation