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Influence of Illumination on Paper and Silk used in Chinese Traditional Painting and Calligraphy Based on Raman Spectroscopy in Museum

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ABSTRACT
As the substrate of Chinese traditional painting and calligraphy, the paper and silk are susceptible to optical radiation in the museum illumination and appear mechanical damage such as brittleness, chalking, deformation, etc. However, there is no effective method now of quantitatively evaluating the mechanical damage of cultural relics caused by illumination. In this paper, Raman spectroscopy used in the analytical chemistry field was introduced into the illumination research of the cultural relics in museum. The four light sources with different center wavelengths of 450nm, 510nm, 583nm, and 650nm, which constitute the spectra of the white light-emitting-diode (LED), were used as the light sources. As experimental specimens, the paper and silk specimens were illuminated by the above light sources for half of a year. Raman spectra of specimens before and after illumination were detected. By analyzing the variations of Raman characteristic peak intensity, the relative damage coefficients of four light sources on the microscopic molecular structure of the paper and silk specimens were studied, respectively. Finally, white LED illumination, namely the spectral irradiance distribution (SPD) of white LED, for the paper and silk should be designed according to the corresponding relative damage coefficients, respectively. Simultaneously, the paper proposed a new research method of studying mechanical damage of cultural relics based on Raman spectroscopy.

KEYWORDS
Museum illumination, paper and silk, Raman spectroscopy, illumination damage

INTRODUCTION
Chinese traditional painting and calligraphy (CTPC) are recognized as the treasures of oriental art in the world (Dang et al. 2013). However, according to the photochemical stability grading standard of museum exhibits formulated by the Commission Internationale de L'Eclairage (CIE) (2004), CTPC belong to the highest level of light sensitivity. The paper consisting of plant fibres and silk consisting of protein molecules are used as the substrates of CTPC, both of which are natural organic substances with unstable properties (Proniewicz et al. 2001; Shao et al. 2005). At present, the illumination damage research mainly uses the color difference to evaluate the influence of museum illumination on color fading and discoloration of cultural relics (Dang et al. 2017, 2018; Pinilla et al. 2016; Farke et al. 2016). As non-staining organic substrates, the illumination damage to the substrates is mainly mechanical damage caused by the microscopic molecular structure changes, which cannot be evaluated by the color difference. Therefore, there is an urgent need for a method to study microscopic molecular structure damage of the paper and silk substrates under illumination of museum light sources.

Raman spectroscopy is an analytical method based on Raman scattering principle and an effective method of accurately evaluating the microscopic damage to substances. Like human fingerprints, each substance has its Raman spectral characteristic bands, namely Raman

characteristic peaks, which correspond to the major molecular functional groups of the substance. When the substance is irradiated with the incident light with energy E (E= hν, where h is Planck's constant and ν is the frequency of light), energy exchange between the substance and the light occurs when photons of the incident light collide with molecules inside the substance, which is manifested as changes of photon frequency and characteristic peak intensity. Huang (Huang et al. 2016) analyzed the content of unsaturated fatty acids in different edible oils by calculating the peak intensity of different Raman spectra. According to Alves (Alves et al. 2016), Raman peak intensities of cellulose's spectral peaks were used to characterize the fibre structure and its changes in different acid and alkali environments. Monti (Monti et al. 2001) evaluated the amount of silk I form in the silk specimens by calculating the Raman intensity ratio. It can be seen that changes in the microscopic molecular structure inside the substance can be further quantified by Raman peak intensity.

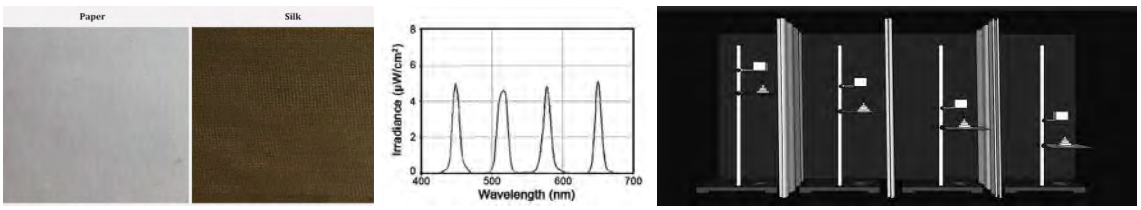
The white light-emitting-diode (LED) spectra currently meeting the requirements of low correlated color temperature (CCT $\leqslant$ 4000K) and high color rendering (Ra $\geqslant$ 90) formulated by the lighting code of Museum (2009) mainly include four monochromatic light spectra of red, yellow, green and blue. By adjusting the ratios of them, Red, Yellow, Green and Blue (RYGB) type white LED with low CCT and high Ra can be achieved, which was defined by Dang et al. (2017). Therefore, determining the quantified damage of four monochromatic light spectra on the paper and silk substrates is of great significance for obtaining new white LED spectra suitable for illuminating CTPC.

In this research, Raman spectroscopy was innovatively introduced into the illumination study of museum cultural relics. The four monochromatic light spectra were used as experimental light sources. The peak intensity of the Raman spectra was used as an evaluation index. The change of microscopic molecular structure inside the paper and silk specimens before and after illumination was characterized by the variations of Raman peak intensity. By analyzing the degree of microscopic damage to the paper and silk specimens caused by four monochromatic light spectra, the problem that cannot quantitatively studying the mechanical damage to the paper and silk substrates at present could be solved.

EXPERIMENT PROCESS

Experimental specimens

In accordance with traditional techniques, the paper and silk specimens used in CTPC were prepared by the National Museum of China. Then two specimens were cut into the same size and combined together, as shown in Figure 1(a).



(a) (b) (c)

Figure 1. (a)The paper and silk specimens. (b) The SPDs of four monochromatic light sources used in illumination experiment. (c) The illumination experiment scene.

Experimental light sources

Four light sources with different center wavelengths of 450nm, 510nm, 583nm, and 650nm

were fabricated by using a museum-specific tungsten halogen lamp combined with a 20nm wide narrowband filter and an infrared filter. By using a spectrophotometer, the SPDs of four monochromatic light sources were detected, as shown in Figure 1(b).

Illumination methodology

The illumination methodology was in accordance with the previous study, which was clearly defined by Dang et al. (2017). The experimental scene is shown in Figure 1(c).

Experiment program

The analytical process was as follows. First, before the illumination experiment, Raman shift and Raman peak intensity of specimens as a control group was detected by Raman spectrometer, whose resolution was set at 1.496 cm^{-1}. The specimens were excited with the 780nm line of a diode laser. After illumination experiment, the Raman data of the illuminated specimens were detected again as the experimental group. Then Raman spectrogram of Raman peak intensity varying with Raman shift was plotted. Raman characteristic peaks of the specimens were selected. Then, the peak intensity values of the selected peak before and after illumination were read by the Origin software. By using Eq. (1), the difference ΔI of Raman peak intensities before and after the illumination experiment were obtained.

$$\Delta I = \left| I_1 - I_0 \right| \tag{1}$$

Where I_0 and I_1 are the peak intensity values of the selected peak before and after illumination, respectively. The smaller the ΔI, the lower the microscopic damage degree of specimens. By comparing microscopic damage degree caused by different monochromatic light sources to the paper and silk specimens, the relative damage coefficients of different light sources on the microscopic molecular structure of the paper and silk specimens were obtained.

EXPERIMENT RESULT

Paper

Paper consists of mostly bonded cellulose fibres that are held together by strong intramolecular hydrogen bonds that promote aggregation of single chains into highly oriented structure. These aggregates are ordered up to even 80% ‘crystalline forms’. The unordered rest is called ‘amorphous form’, which was defined by Proniewicz et al. (2001). Owing to the influence of illumination environment and its own characteristics, the microscopic molecular structure of the paper can be easily damaged. Therefore, Raman spectroscopy was introduced to evaluate microscopic damage of different monochromatic light sources to the paper.

Raman spectra of the paper specimens before and after illumination experiment are shown in Figure 2. The abscissa represents Raman shift, that is, the frequency shift of the scattered light relative to the incident light after the incident light is scattered by the substrate specimens. Raman shift is recorded in wavenumbers, which is commonly expressed by inverse centimetres (cm^{-1}) in Raman spectra; the vertical axis represents the intensity of Raman scattered light. The solid Raman spectral line represents the Raman spectra before illumination and the dotted one represents the Raman spectra after illumination. The Raman peaks in the dotted Raman spectral line were obtained by the redshift of the Raman peaks in solid Raman spectral line. Taking the Raman spectra of the paper specimens illuminated by the 510nm light source as an example, the Raman peak at 895 cm^{-1} in solid spectral line was red-shifted to 897 cm^{-1} in dotted spectral line. The following Figure 3 is analogous.

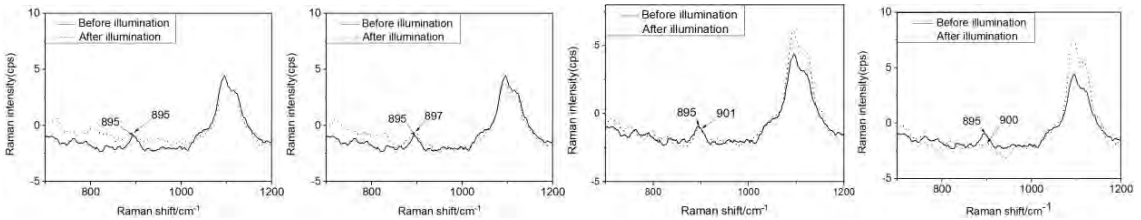


Figure 2. Raman spectra of the paper specimens under illumination of (a) 450 nm monochromatic light spectrum, (b) 510 nm monochromatic light spectrum, (c) 583 nm monochromatic light spectrum, and (d) 650 nm monochromatic light spectrum.

It could be seen from the solid spectral line in Figure 2, the Raman peak with medium intensity is 895 cm^{-1}. According to Proniewicz et al. (2001), they found that the intensity of 900 cm^{-1} peak was sensitive to the amount of crystalline versus amorphous structure of cellulose. It was also found *I900* was proportional to the amount of disorder in the cellulose (Wiley and Atalla, 1987). Therefore, Raman peak intensity *I895* was selected to characterize the microscopic damage of different monochromatic light sources to the paper specimens.

The variations in Raman peak intensity of the paper under four light sources were analyzed. As shown in Figure 2(b), the paper illuminated by 510 nm light source was taken as an example. According to the solid Raman spectral line obtained before illumination, the Raman peak intensity of 895 cm^{-1} was read by the Origin software as I_0; according to the dotted Raman spectral line obtained after illumination, the intensity of Raman band at 897 cm^{-1} was read as I_1. By using Eq. (1), Raman peak intensity difference ΔI could be obtained. Similarly, the ΔI of the paper specimens illuminated by the rest light sources were calculated. By defining ΔI 0.4278 of the paper specimens illuminated by 450 nm light source was 1.0000, through conversion the relative damage coefficient of four light sources to the paper specimens was 1.0000: 0.9093: 0.3714: 1.9780. The calculation results are shown in Table 1.

Table 1. The comparison of the paper's Raman peak intensity differences under illumination of four types of monochromatic light sources

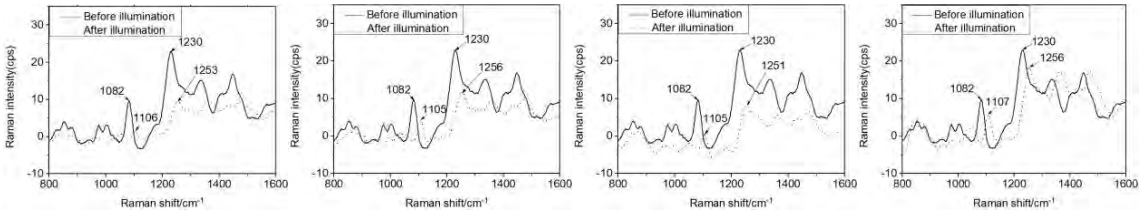
Measure / Light sources	Before illumination	After illumination	Calculation	Through conversion
	I_0	I_1	$\Delta I = \lvert I_1 - I_0 \rvert$	
450nm	-0.9361	-0.5083	0.4278	1.0000
510nm		-0.5471	0.3890	0.9093
583nm		-1.0950	0.1589	0.3714
650nm		-1.7823	0.8462	1.9780

Silk

Silk fibroin contained in silk is natural polymer fibre protein, which was defined by Shao et al. (2005). Exposure to light will cause significant changes in these organic components of silk.

Raman spectrum changes of the silk specimens before and after the illumination are shown in Figure 3. In solid Raman spectral line, the strongest peak is 1230 cm^{-1} and medium Raman peak is 1082 cm^{-1}. According to Shao et al. (2005), the peak intensities at 1232 and 1087 cm^{-1} corresponding to C-N bond decreased after UV/ozone irradiation, indicating that UV/ozone irradiation causes peptide chain breaks and confirming that photodegradation occurs at the C-N bond. Silk phototendering is caused by peptide fission initially at the weaker C-N bond,

which leads to loss of fibre strength (Setoyama, 1982). We selected *I1082* and *I1230* to comprehensive characterize the microscopic damage of light sources to the silk specimens.



a) b) c) d)

Figure 3. Raman spectra of the silk specimens under illumination of (a) 450 nm monochromatic light spectrum, (b) 510 nm monochromatic light spectrum, (c) 583 nm monochromatic light spectrum, and (d) 650 nm monochromatic light spectrum.

The variations of Raman peak intensities under illumination of four light sources were analyzed. Silk specimen illuminated by 510 nm light source was taken as an example. According to solid Raman spectral line detected before illumination, the intensity values of 1082 and 1230 cm^{-1} Raman peaks were read as I_0 and I_0', respectively; according to the dotted Raman spectral line detected after illumination, the intensity values of the Raman peaks at 1105 and 1256 cm^{-1} were read as I_1 and I_1', respectively. By using Eq. (1), based on I_0 and I_1, Raman peak intensity difference ΔI was calculated; based on I_0' and I_1', $\Delta I'$ was calculated. Then, $\Delta I''$ was obtained by calculating the average value of ΔI and $\Delta I'$. Similarly, the ΔI'' of the silk specimens illuminated by the rest light sources were calculated. By defining $\Delta I''$ 10.8402 of the silk specimens under illumination of the 450nm light source was 1.0000, through conversion the relative damage coefficient of four light sources to the silk specimens was 1.0000: 0.7740: 1.1046: 0.3846. The calculation results are shown in Table 2.

Table 2. The comparison of the silk's Raman peak intensity differences under illumination of four types of monochromatic light sources

Measure / Light sources	Before illumination		After illumination		Calculation		Average	Through conversion
	I_0	I_0'	I_1	I_1'	ΔI	ΔI'	ΔI''	
450nm	9.6050	22.9035	1.4985	9.3297	8.1065	13.5738	10.8402	1.0000
510nm			4.1123	11.6151	5.4927	11.2884	8.3906	0.7740
583nm			0.3696	8.1909	9.2354	14.7126	11.9740	1,1046
650nm			5.7272	18. 4442	3.8778	4.4593	4.1686	0.3846

DISCUSSIONS

There are different damage degrees caused by light sources with different center wavelengths of 450nm, 510nm, 583nm, and 650nm. According to Table 1, the ratio of four light spectra constituting white LED used in illuminating the paper, namely the SPD of white LED, should be based on the relative damage coefficient of 450nm: 510nm: 583nm: 650nm =1.0000: 0.9093: 0.3714: 1.9780. According to Table 2, the ratio of four light spectra constituting white LED used in illuminating the silk, namely the SPD of white LED, should be based on the relative damage coefficient of 450nm: 510nm: 583nm: 650nm =1.0000: 0.7740:1.1046:0.3846. The larger the influence coefficient value, the greater the damage caused by the monochromatic light to the paper and silk substrates. The coefficients can be used as selection

criteria for WLEDs that are suitable for illumination in museum paper and silk relics

CONCLUSION

The research method of studying illumination damage based on Raman spectroscopy proposed in this paper can evaluate the mechanical damage to substrates from the microscopic level.

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