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Investigating Prevention of UV Damage to Hair Using Raman Spectroscopy

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Synopsis

The goal of this work is to demonstrate the impact of UV and potential protective materials on hair fiber cuticle protein structure using Raman spectroscopy.

INTRODUCTION

Damage is a top consumer hair care concern because it can result in a variety of undesirable effects, including breakage, unmanageability, fly-aways, dry-feeling hair, lack of shine, and split ends. The need for protection against hair damage follows directly from the impact of many hair-related habits and treatments, as well as environmental exposure, on hair fiber structure. In this work, ultraviolet (UV) radiation was chosen as a model insult because of the fact that exposure is difficult to avoid altogether, UV tends to exacerbate the damaging effects of other treatments, and there is no standardization or analogous sun protection factor (SPF) index for hair fibers. Although there are many facets involved in the interaction between UV and hair fibers, this work builds on the following key facts from literature: UV has sufficient energy to break disulfide bonds (1), which are integral to hair fiber structural integrity. UV also tends to damage the cuticle before the cortex (2–4). Kuzuhara has illustrated the utility of Raman spectroscopy for measuring hair fiber cuticle protein structure (5–8). The goal of this work, therefore, is to demonstrate the impact of UV and potential protective materials on hair fiber cuticle protein structure using Raman spectroscopy. This work focuses only on one measure of UV damage and protection.

METHODS

Whole fibers of unpigmented hair were used in this work with and without treatment with neat solutions of six commercially available raw materials (materials A–F) advertised

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by the manufacturers as being UV protectants. Hair fibers were treated with materials of interest, exposed to a controlled amount of UV, and analyzed using Raman spectroscopy.

The Atlas Suntest XXL+ (Atlas Material Testing Solutions, Mount Prospect, IL) with daylight filters gave UV exposure from 300 to 400 nm. The irradiance was set at 62 W/m^2, which gave a total energy of 5.4 MJ/m^2 over the course of 24 h. This exposure level was in line with Signori's low UV exposure level: a few hours per day over the course of about 1 mo (1). The black standard temperature, the highest temperature the sample surfaces could reach, was set at 65°C. The relative humidity was fixed at 55%.

Raman spectra were collected using a XPlora Plus spectrometer (Horiba Scientific, Piscataway, NJ). The use of unpigmented hair eliminated fluorescence and required minimal sample preparation. Raman provided a direct measure of disulfide content and good spatial resolution with a spot size of approximately 0.5 μm. At least three hair fibers for each treatment were fixed to aluminum foil–covered microscope slides, as shown in Figure 1.

Spectra from 200 to 3,200 1/cm were taken starting at the surface of the hair fiber and into the hair fiber at 0.5 μm intervals to 3 μm toward the fiber center, giving information on the protein structure of the cuticle. These spectra were averaged, and at least three hair fibers for each treatment were analyzed. The 785-nm laser was used at full power (100 mW at the laser source) through a ×100 objective, and 1,200 g/mm with 10-s acquisition time and three accumulations gave good signal to noise. The spectra were baselined using linear chords connected to the spectra. Spectra were normalized to peaks that did not show significant change upon the UV exposure used in this study: Phe at 1,003 1/cm, CH_2 bending at 1,448 1/cm, amide I at 1,655 1/cm, and CH signatures at approximately 2,920 1/cm.

Raman data can provide quantitative information; two approaches are shown in Figure 2. The double-cursor approach to extracting data is favorable because it requires the least amount of data manipulation, but this technique cannot resolve overlapping peaks. Gaussian/Lorentzian peak fitting allows for peak deconvolution but involves the inherent uncertainty of mathematical peak fitting routines. Prior knowledge of anticipated peak positions and reasonable initial parameters prove helpful in using this approach to peak fitting.

The Raman peaks for the different conformations of the disulfide bond appear at different wavenumbers (9). The disulfide peak can be deconvoluted using Gaussian/Lorentzian peak fitting. However, for simplicity in this work due to the presence of treatment materials in addition to hair fibers, the disulfide peak at about 505–511 1/cm was chosen as representative of the hair fiber disulfide content. Gaussian/Lorentzian peak fitting was

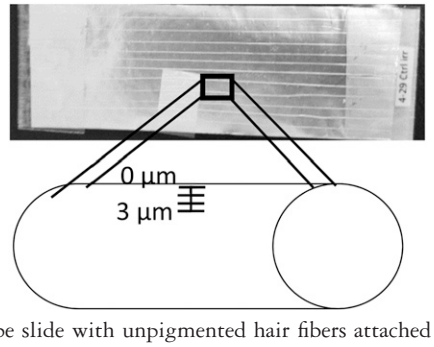
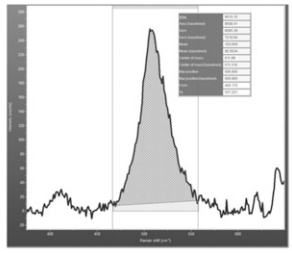
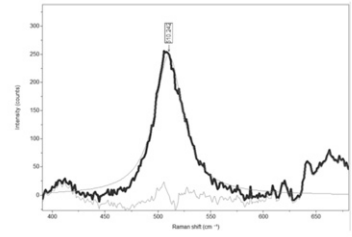


Figure 1. Example microscope slide with unpigmented hair fibers attached and hair fiber schematic with Raman spectrum acquisition position indicator.





	Double-Cursor	Gaussian/Lorentzian Peak Fitting
Advantage	least amount of data manipulation	can resolve overlapping peaks **key for studying impact of materials*
Disadvantage	cannot resolve overlapping peaks	uncertainty in fitting

Figure 2. Approaches to quantifying Raman peak information.

crucial for understanding the potential protective effects of treatment materials A–F on hair fiber protein structure because these materials have Raman spectra of their own. An example of peak fitting for 440–600 1/cm for a Material B–treated, irradiated hair fiber is shown in Figure 3. Material B has a strong peak near 488 1/cm which overlaps with the disulfide signature from the hair fiber. Peak fitting was important for separating the potential effect of the treatment material from the hair fiber structure.

RESULTS AND DISCUSSION

Baselined, normalized spectra for the cuticle of untreated, nonirradiated unpigmented hair fibers and unpigmented hair fibers subjected to 24 h of 62 W/m^2 UV radiation (5.4 MJ/m^2) are shown in Figure 4. Tentative peak assignments from literature (5–14) are also given

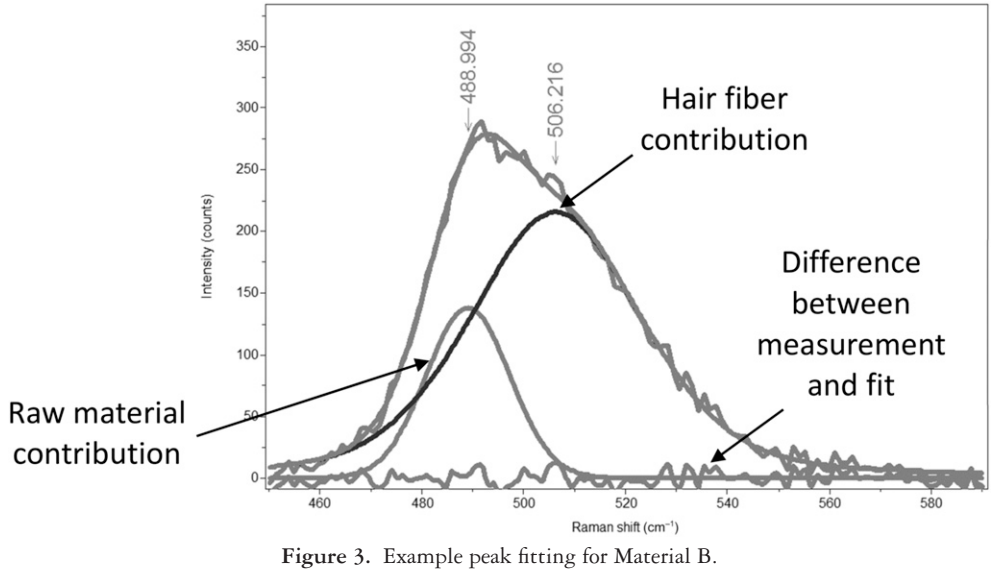


Figure 3. Example peak fitting for Material B.

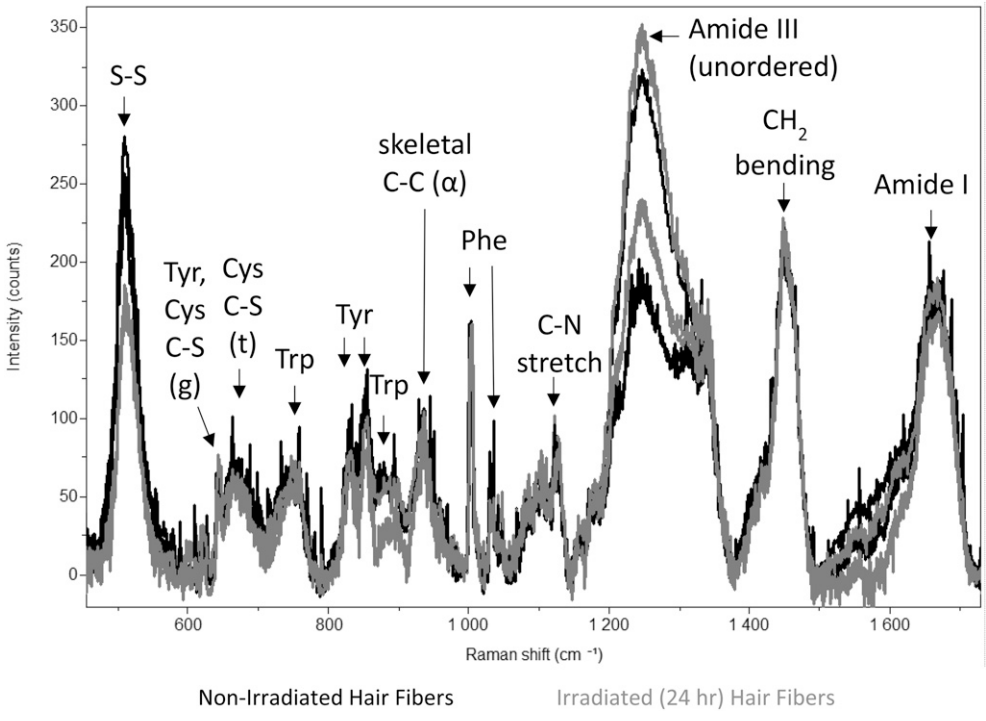


Figure 4. Raman spectra of the cuticle of unpigmented hair fibers that have not undergone irradiation (non-irradiated hair fibers) and that have undergone 24 h of 62 W/m^2 UV irradiation (5.4 MJ/m^2).

in the figure. Key differences appear with disulfide and amide III. Disulfide content decreases on 24-h UV exposure, indicating damage to the hair fiber cuticle. The influence of UV on amide III was less clear and is not addressed in this work.

As discussed in the Methods section, Raman spectra were normalized to peaks that did not change significantly on 24 h of UV exposure. Because of its importance to hair fiber structure, normalized disulfide peak height was investigated for all treatments. Figure 5 shows the disulfide peak height normalized to the peak height values for Phe, CH_2 bending, amide I, and CH signature around 2,920 1/cm. Using all available peaks for normalization allows for analysis of hair fibers treated with materials even if the treatment material Raman signature overlaps with some of the hair fiber peaks used for normalization. Comparing the nonirradiated versus irradiated hair fibers in Figure 5 shows a clear decrease in normalized disulfide bond intensity, consistent with Figure 4. The treatment materials, with the exception of Material B, showed disulfide content consistent with or lower than disulfide content of the untreated, irradiated hair. Material B appears to show some promise for disulfide protection. However, this protection needs to be verified with a secondary method because of the peak fitting required to separate the contribution from hair fiber disulfide from the raw material signature at 488 1/cm. In addition, materials A–F could potentially provide benefits if delivered from formulations, which were not evaluated in this work. They could potentially also have a protective effect on other measures of UV damage to hair, which were also not evaluated as part of this work.

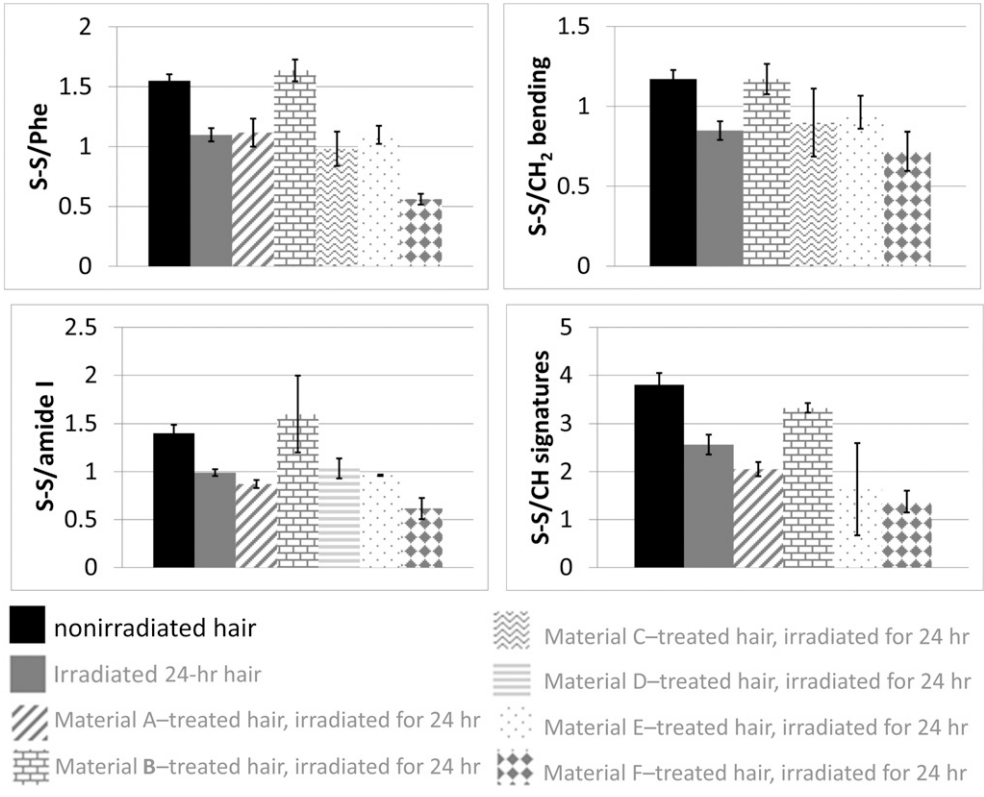


Figure 5. Disulfide peak height normalized to Phe, CH_2 bending, amide I, and CH signatures peak heights.

CONCLUSIONS

In conclusion, this work has illustrated the utility of Raman spectroscopy for understanding the impact of UV on hair fiber protein structure, particularly in the decrease of disulfide band intensity. The protective effect of potential treatment materials was evaluated, and one promising treatment material was identified for further study. Future directions include addressing additional Raman signatures, spatial variation within the hair fiber, and complementing Raman with infrared measurements.

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