ACS APPLIED MATERIALS & INTERFACES

Research Article

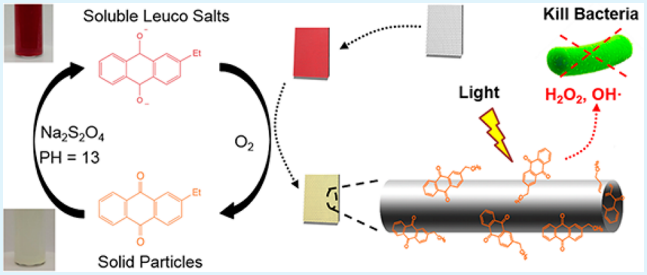
www.acsami.org

Antimicrobial Functions on Cellulose Materials Introduced by Anthraquinone Vat Dyes

Jingyuan Zhuo and Gang Sun*

Division of Textiles and Clothing, University of California, Davis, California 95616, United States

ABSTRACT: Many anthraquinone compounds have exhibited light-active properties in solutions and on materials under UVA or fluorescent light exposure. Two anthraquinone derivatives were incorporated onto cotton fabrics by a vat dyeing process. The dyed fabrics demonstrated light-induced biocidal functions, and the functions were durable against laundering and long-term light exposure. The structures and surface morphologies of the dyed fabrics were examined by using fourier transform infrared (FTIR) spectroscopy and scanning electron microscopy (SEM). Mechanical properties of the fabrics were measured by using a tensile tester. The results revealed that the anthraquinone compounds have different light-activities, resulting in different surface and mechanical impacts on the cotton cellulose.



KEYWORDS: *antimicrobial functions, vat dyeing, light-induced functions, anthraquinone species, cellulose materials, coloration and finishing*

1. INTRODUCTION

Aimed at preparation of antibacterial textiles for prevention of disease transmission through clothing materials, various technologies have been developed to chemically or physically incorporate biocides such as *N*-halamines,[1,2] quaternary ammonium,[3−7] and heavy metal silver (Ag)[8,9] onto surfaces of polymers, fibers, and fabrics. In addition, photosensitive chemicals such as TiO_2 nanoparticles[10−12] and porphyrin photosensitizers[13,14] could effectively generate reactive oxygen species (ROS) on polymer surfaces under light exposure, which could provide light-induced antimicrobial and self-cleaning functions. However, the use of the nanoparticles on textiles brings in concerns on human safety of the technology since the nanoparticles may come off from the surfaces of fibers and penetrate into the human body. The porphyrin compounds could be covalently linked onto polymers, but can mostly generate superactive singlet oxygen under light illumination, which has very short lifetime in air and thus is not very effective in providing antimicrobial effects on textiles.

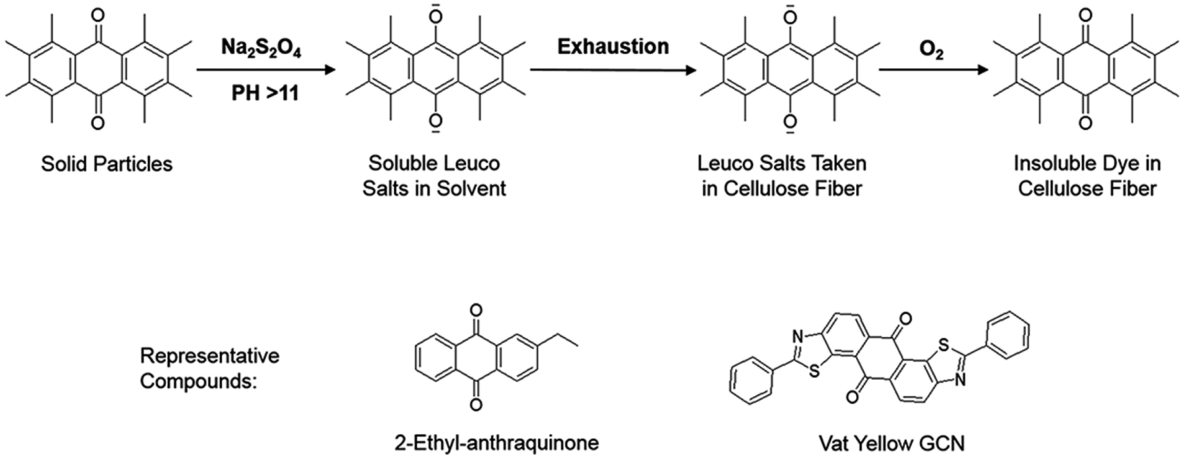
Recently, light-active properties of some anthraquinone compounds were discovered and employed in the development of light-induced antimicrobial cotton fabrics.[15,16] The light-active functions of the anthraquinone derivatives largely depend on the structures of the compounds and the environment in which the compounds are being surrounded.[17−20] Interestingly, anthraquinone compounds are the second abundant class of colorants based on chemical structures. Many natural colorants also contain the anthraquinone group, particularly those produced from aloe latex, fungi, senna, and some insects. The light active antimicrobial functions of the compounds are due to formation of triplet excited status of the anthraquinone structures and consequent production of reactive oxygen species (ROS) such as hydrogen peroxide in aqueous phase.[21] As a result, anthraquinone-2-carboxylic acid treated cotton has demonstrated excellent self-cleaning functions including antibacterial functions and decomposition of a pesticide.[15]

Although the incorporation of the light-active anthraquinone-2-carboxylic acid onto cotton cellulose was successful, the reaction and the treatment process were not practical[15] due to the use of the catalyst and long reaction time. Examining structures of light-active anthraquinone compounds, many of them possess structural features of vat dyes, which can be incorporated onto cotton cellulose by using commercial vat dyeing processes. During vat dyeing processes, anthraquinone structures are reduced to anthrahydroquinones, which will then react with sodium hydroxide to form water-soluble sodium phenolate of anthrahydroquinone, so-called leuco salts. The leuco salts can be easily exhausted onto cellulose through the vat dyeing process and then be oxidized back to water insoluble anthraquinone precursors inside the fibers. Such an approach could be advantageous for preparation of antimicrobial cotton fabrics due to the fact of achieving potential coloration and multiple functions in one wet treatment, an environmentally friendly process. Thus, light-active 2-ethylanthraquinone (2EtAQ), though not a real vat dye because of its low substantivity to cellulose, and a real vat dye, Vat Yellow GCN, possessing anthraquinone basic structure, were chosen in the trials.[22] Vat Yellow GCN, different from 2EtAQ, has high substantivity to cotton and could reach high exhaustion ratio on

Received: July 25, 2013
Accepted: September 30, 2013
Published: September 30, 2013

 © 2013 American Chemical Society

Scheme 1. Cotton Fabric Treatment with Anthraquinone Species through Vat Dyeing Processes



cotton fabrics. The use of Vat Yellow GCN can further confirm the concept and support the practicability of the technology. In this work, these two anthraquinone species were applied onto cotton through vat dyeing processes. The light-induced biocidal activities of the modified cotton fabrics were evaluated against both Gram-negative (*Escherichia coli*) and Gram-positive (*Staphylococcus aureus*) bacteria strains. Physical-chemical characteristics of the vat-dyed cottons were examined by Fourier transform infrared (FTIR) spectroscopy, scanning electron microscopy (SEM), and tensile stress measurements. The wash durability, reusability, and stability against light of the vat dyed fabrics were evaluated.

2. EXPERIMENTAL METHODS

2.1. Materials. Bleached and desized cotton fabrics (#400) were supplied by Testfabric, Inc. (West Pittston, PA). 2-Ethylanthraquinone (2EtAQ) and sodium dithionite were purchased from ACROS Organics (Pittsburgh, PA). Vat Yellow GCN (C.I. 67300) was obtained from Xuzhou Kedah Fine Chemicals Ltd. (Xuzhou, China). Other chemicals used in cotton treatments were supplied by either Fisher Scientific (Pittsburgh, PA) or EMD Chemicals (Gibbstown, NJ). Agar and nutrient broth for bacterial tests were obtained from BD Difco (Becton, Dickinson and Company, Franklin Lakes, NJ). All reagents were used as received without any further purification.

2.2. Treatment of Fabrics. 2EtAQ and Vat Yellow GCN (Scheme 1) were used in vat dyeing of cotton fabrics with concentrations varying from 1% to 9% (on weight of fabric, owf) for 2EtAQ and 0.5% to 3% (owf) for Vat Yellow GCN. A desired amount of the chemicals was dispersed evenly in water under alkaline conditions (pH > 11) and was then reacted with sodium dithionite (molar ratio of dye/sodium dithionite = 1:20) at 50 °C for 10 min. The compound was reduced to its leuco salt structure that is substantive to cellulose (Scheme 1). Cotton fabrics were immersed into the salt solution after it was diluted 20 times with distilled water, and the dyeing process was continued for 50 min with continuous agitation at room temperature. Sodium sulfate was added as an electrolyte into the dyeing baths to improve exhaustion of the compounds on cellulose materials, and the concentration was 80 g/L for 2EtAQ treatment and 60 g/L for Vat Yellow GCN. Upon the completion of dye exhaustion, the treated fabric samples were completely dried, and oxidation of the leuco-form compounds in the fabrics to the original anthraquinone compounds was carried out in the air at room temperature. All treated samples were then thoroughly washed in boiling detergent solutions for 30 min, rinsed, and dried at room temperature overnight.

2.3. Characterizations of Treated Fabrics. FTIR spectra of the treated cotton samples were recorded on a Nicolet 6700 FTIR spectrophotometer (Thermo Electron Co.) by using KBr pellets with acquisition conditions of spectral range of 4000−400 cm^{-1}, resolution at 4 cm^{-1}, and 64 accumulations. Surface morphologies of both treated and control samples before and after light exposure were examined by using a scanning electron microscope (Philips XL 30).

UVA exposure of the fabrics was conducted in a UV cross-linker (Spectrolinker XL-1000, Spectroline), with five 8 W UVA lamps (365 nm wavelength). The distance between the light source and samples were 12 cm. The light intensity in the cross-linker was 30 mW/cm^2.

The color change of the treated samples was measured by using a colorimeter (Color-Eye 7000A, GretagMacbeth) with a standard daylight source D65. Each measurement is expressed by CIE $L^*a^*b^*$ color scale. L^* indicates the lightness of samples with value scale from 0 (black) to 100 (white); a^* stands for the position between red (positive) and green (negative); b^* represents the yellow (positive) and blue (negative). The color difference between control and treated sample was expressed as ΔE (eq 1) based on International Commission on Illumination (CIE76).

$$\Delta E = \sqrt{(L^*_2 - L^*_1)^2 + (a^*_2 - a^*_1)^2 + (b^*_2 - b^*_1)^2} \quad (1)$$

where L^*_1, a^*_1, and b^*_1 represent attributes of a control sample and L^*_2, a^*_2, and b^*_2 are the corresponding parameters of a treated sample.

Tensile stresses of cotton fabrics were evaluated by using an INSTRON Tensile Tester (USA) according to modified D5034-09 Standard Test Method for Breaking Strength and Elongation of Textile Fabrics (Grab Test). The experimental data were averaged from five samples (1 in. × 6 in.).

Washing durability of the treated fabrics was evaluated by using a Launder-Ometer (Atlas Electric Devices Co.) following the AATCC Test Method 61-2003: Colorfastness to Laundering, Home and Commercial: Accelerated.

2.4. Antibacterial Functions of Treated Fabrics. Gram-negative bacterium, *E. coli* (K-12), and Gram-positive bacterium, *S. aureus* (ATCC 12600), were grown in nutrient broth and tryptic soy broth, respectively, at 37 °C under aerobic conditions for overnight (18−24 h) before usage.

Light-induced antimicrobial functions against *E. coli* were evaluated according to a modified AATCC test method 100. Overnight cultures of the midexponential-phase bacterium were diluted with phosphate buffered saline (PBS) to approximately10^5 CFU/mL. Two pieces of 3 × 3 cm^2 swatches of untreated (control I) and treated cotton fabrics were placed in separate sterile Petri dishes and inoculated with 300 μL of bacterial suspension, respectively. Then the samples were exposed to UVA (365 nm) light with different exposure durations in the UV cross-linker, while other control samples (control II, samples without UVA exposure) were stored under dark environment for the same duration. Afterward, each sample was placed into 30 mL of sterilized PBS solution. The mixture was shaken vigorously for 1 min. Then an aliquot of 0.1 mL of the mixture solution was taken out for serial dilutions and also placed on an agar plate.

In testing against *S. aureus*, swatches in size of 2 × 9 cm^2 of the untreated and treated cotton fabrics were placed in separate sterilized polystyrene centrifuge tubes (Corning 430055, Corning Inc.), and 3 mL of bacterial suspension with a concentration of approximately 10^4 CFU/mL was added into each tube. All tubes were illuminated under UVA (365 nm) light with different exposure durations. Control tubes with both samples were covered with aluminum film and put under dark environment for same durations. Then an aliquot of 0.1 mL of the mixture solution was taken out for serial dilutions and also was placed on an agar plate.

After incubation at 37 °C for 18 h, the agar plates were examined and the numbers of colony forming units (CFU) were counted manually. The microbial reduction rate was calculated according to the following equation (eq 2):

$$\text{reduction rate of bacteria (\%)} = \frac{B - A}{B} \times 100 \quad (2)$$

where B is the number of colony forming units of control II (without light exposure) and A is the number of colony forming units of light exposed samples.

3. RESULTS AND DISCUSSION

3.1. Structural Characterization of Vat Dyed Cotton. Anthraquinone and benzophenone compounds are light-active and could result in light-induced functions on cellulose, but the processes incorporating the chemicals onto cotton fabrics were unpractical.[15,23] However, the vat dyeing process provides a practical option of incorporating these compounds onto cotton fabrics. After experimental explorations, both 2EtAQ and Vat Yellow GCN were successfully applied onto cotton by the vat dyeing process. Structural confirmation of the incorporated anthraquinone compounds on the treated fabrics was conducted by FTIR spectroscopy, shown in Figure 1. New shoulders at 1671 and 1668 cm^{-1} are characteristic peaks of carbonyl groups in the anthraquinone structure, which could be observed on both 2EtAQ and Vat Yellow GCN treated cotton samples. Subtracted FTIR spectra (Figure 1A(b) and B(b)) of 2EtAQ and Vat Yellow GCN treated cotton samples by that of the control sample provide more characteristic information. In addition to the peak at 1671 cm^{-1} (C═O stretching), the peak at 1570 cm^{-1} in 2EtAQ treated sample corresponds to the aromatic C═C stretching in the anthraquinone structure, and a broad peak around 1668 cm^{-1} in Vat Yellow GCN dyed sample can be attributed to the combination of carbonyl stretching and C═C stretching in the anthraquinone structure. The C═C stretching vibration of phenyl ring in Vat Yellow GCN structure is responsible for the new peak in 1451 cm^{-1} in the subtraction spectrum. The new peaks in the subtracted spectra of the treated materials match well to the characteristic bands of pure 2EtAQ (Figure 1A(d)) or Vat Yellow GCN (Figure 1B(d)). These observations proved the successful incorporation of the anthraquinone species onto the cotton fibers by the vat dyeing process.

3.2. Light-Induced Antimicrobial Functions. The successful incorporation of anthraquinone compounds onto cellulose could bring light-active functions onto the fabrics. The most noticeable one is the light-induced antimicrobial functions of the vat dyed cotton fabrics, which were evaluated in vitro against both *E. coli* (Gram-negative) and *S. aureus* (Gram-positive) according to the testing methods. Both untreated and treated samples inoculated with bacterial suspensions were illuminated under the UVA light (365 nm) with a fluence dose of 30 mW/cm^2 for 30 or 60 min (equivalent to a fluence dose of 54 J/cm^2 or 108 J/cm^2). The bacterial reduction rates, determined by the ratio of colony counts from the 2EtAQ and Vat Yellow GCN treated and control samples, are shown in Table 1. According to the experimental results, the untreated cotton did not show any noticeable antimicrobial function, similar to the treated samples without light irradiation. Both *E. coli* and *S. aureus* appeared to be susceptible to the cotton fabrics treated with different concentrations of 2EtAQ and Vat Yellow GCN under light exposure. Upon illumination for 30

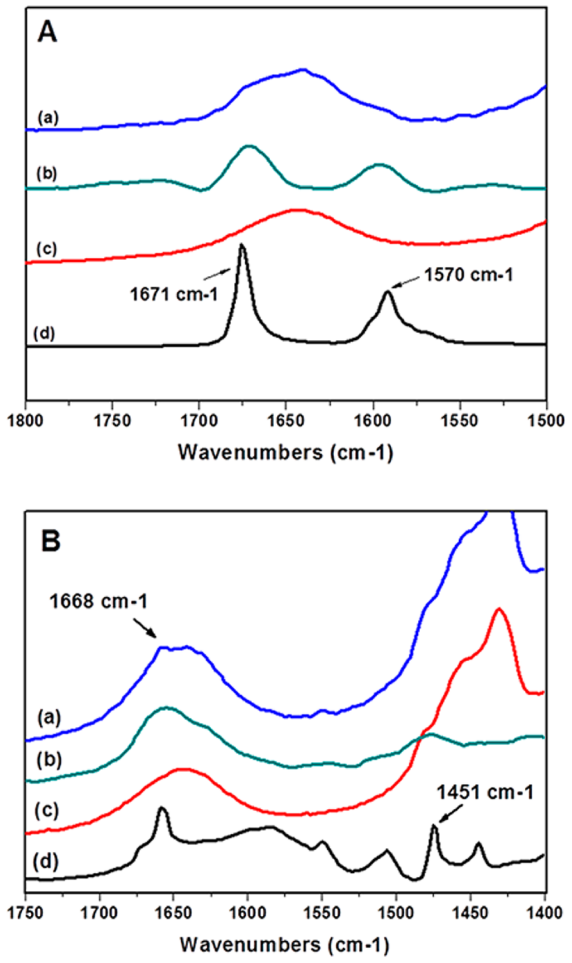


Figure 1. FTIR spectra of cotton fabrics: (a) treated cotton; (b) subtraction spectra of untreated cotton from treated cotton; (c) untreated cotton; (d) pure anthraquinone species. (A) 9% owf 2-ethylanthraquinone treated cotton; (B) 3% owf Vat Yellow GCN treated cotton.

Table 1. Light-Induced Antimicrobial Functions of Vat Dyed Cotton Fabrics

	reduction rate of bacterial count (%)			
	E. coli (10^5 CFU/mL)		*S. aureus* (10^4 CFU/mL)	
samples	30 min	60 min	30 min	60 min
untreated cotton	0.00%	0.00%	0.0%	0.0%
1% owf 2EtAQ-cotton	80.06%	99.99%	91.9%	99.9%
3% owf 2EtAQ-cotton	98.46%	99.99%	93.4%	99.9%
6% owf 2EtAQ-cotton	99.99%	99.99%	96.6%	99.9%
9% owf 2EtAQ-cotton	99.99%	99.99%	97.4%	99.9%
0.5% owf GCN-cotton	74.76%	99.99%	61.6%	99.5%
1.5% owf GCN-cotton	66.62%	99.99%	54.7%	99.6%
3% owf GCN-cotton	68.66%	99.99%	72.3%	99.2%

Table 2. Washing Durability of Antimicrobial Functions of 2-EtAQ and Vat Yellow GCN Treated Cotton Fabrics

	reduction rate of bacterial count (%)					
	E. coli (10^5 CFU/mL)			*S. aureus* (10^4 CFU/mL)		
samples	before wash	5 washes	10 washes	before wash	5 washes	10 washes
6% owf 2EtAQ-cotton	99.99%	99.99%	99.99%	99.9%	87.6%	67.6%
9% owf 2EtAQ-cotton	99.99%	99.99%	99.99%	99.9%	95.6%	61.9%
3% owf GCN-cotton	99.99%	99.99%	99.99%	99.9%	97.8%	86.8%

min, all treated samples demonstrated clear light-induced bactericidal effect against both Gram-positive and Gram-negative microorganisms. Due to the fact that 2EtAQ is a light active agent, at the same 3% owf concentration, the 2EtAQ treated cotton were at least 30% more powerful against both *E. coli* and *S. aureus* than the Vat Yellow GCN treated cotton, indicating that the anthraquinone structures affect their light-activity. The powerful light active functions of 2EtAQ was observed in solutions under UVA light (365 nm) under the same conditions in comparison to Vat Yellow GCN. With increasing amount of anthraquinone compounds incorporated, the fabrics demonstrated enhanced killing power under UVA against both *E. coli* and *S. aureus*. In fact, the weak light active functions of Vat Yellow GCN make it a commercial dye for cotton fabrics without concerns on color fading or other light-induced effect on the fabrics. All samples, after light exposure for 60 min, exhibited bacterial reduction rates of 99−99.99%.

It is also worthy to mention that the antibacterial tests against *S. aureus* were conducted in a bacterial suspension in polystyrene tubes, due to bacteria sensitivity to temperature and dryness. The tubes can partially block UVA irradiation and reduce the efficiency of light-induced activity. Therefore, the actual reduction rate against *S. aureus* by the treated samples will increase with direct light exposure on the fabrics.

Washing durability of the light-induced antimicrobial functions was evaluated by repeated laundering tests, and the results are shown in Table 2. All cotton fabrics were washed in a Launder-Ometer following AATCC standard 61, with one wash equivalent to five times regular home launderings. The results indicate that the anthraquinone species on cotton fibers could survive repeated laundry, though there was some loss in bacterial reduction in the tests against *S. aureus*, which was mainly caused by the loss of surface bound chemicals. The anthraquinone species trapped inside the fabrics, however, were stable and able to provide sufficient light dynamic inactivation function.

In addition, in terms of practical usage as light-induced biocidal materials, the samples should possess good stability against long-term light exposure and still remain efficient light-induced biocidal functions. To verify the light stability of the functions, both control and samples treated with selected concentrations of 2EtAQ and GCN were placed under UVA illumination for two continuous 60 min exposures, and their antimicrobial functions were evaluated. All fabrics samples did not reveal any reduction in the light-induced biocidal functions after such intensive light exposure (Table 3). Therefore, the functions on the cotton fabrics were basically unchanged within the tested lighting duration.

3.3. Scanning Electron Microscopy. Surface morphology of the control and treated cotton samples was examined by using SEM. SEM images of the control and treated samples before light exposure are presented in Figure 2a−c. No obvious structural changes are observed on the cotton fibers after the dyeing treatments. After UVA exposure for 8 h, SEM images of the samples were taken (Figure 2a′−c′). Significant changes were observed on surfaces of the cotton sample treated by 9% 2EtAQ, while the untreated (control) and Vat Yellow GCN dyed cotton samples remained intact. The noticeable changes on the 2EtAQ treated cotton fibers are grooves and cracks with exposed fibrils, and even some peel-offs on the surfaces of the fibers, damages possibly caused by reactive oxygen species generated by the light-active 2EtAQ on cellulose. The differences in light-induced damages on both 2EtAQ (9%) and GCN (3%) treated cotton fabrics were determined by the amounts and light-activities of the chemicals on the cotton fabrics, as well as their light-active properties. As a matter of fact, the light-induced biocidal properties attribute to the same reactive oxygen species generated on the surfaces of the fibers. Thus, very powerful light-induced activities could result in some physical damages to fibers and may have other concerns as well, and these potential impacts should be thoroughly examined.

Table 3. Light Stability of the Light-Induced Biocidal Functions on Fabrics

	E. coli (10^5 CFU/mL)		*S. aureus* (10^4 CFU/mL)	
samples	first run	second run	first run	second run
6% owf 2EtAQ-cotton	99.99%	99.99%	99.9%	99.9%
9% owf 2EtAQ-cotton	99.99%	99.99%	99.9%	99.9%
3% owf GCN-cotton	99.99%	99.99%	99.9%	99.9%

3.4. Mechanical Properties. Due to the light-induced surface damages on the treated fibers mechanical properties of the treated samples were investigated. First, the tensile stresses of the untreated and treated samples with different concentrations of chemicals before light exposure are shown in Figure 3a. The results indicate that the untreated fabrics possessed a tensile stress approximately 32.5 MPa, and the vat dyeing process did not cause much tensile losses to the cotton fabrics. On the other hand, tensile stresses of the fabrics were evaluated under different UVA exposure durations, and the results are shown in Figure 3b. The plain cotton clearly was unaffected by the UVA light exposure even with some the marginal variations. The UVA light illumination did not alter the mechanical properties of the Vat Yellow GCN treated cotton fabrics in the entire concentration range and under the longest exposure duration of 8 h. However, the UVA light clearly exhibited significant impact on the mechanical properties of the 2-EtAQ treated fabrics. The tensile losses intensified with prolonged light exposure times and increased concentration of 2EtAQ on the fabrics. After 8 h of light exposure, the 2EtAQ treated samples could lose 20% of the original tensile stress, which is a quite significant loss. The reduction of tensile stress of the 2-EtAQ treated fabrics coordinates very well with the observation of surface morphologies of the fibers from the SEM images. Such a negative impact of light-induced agents on the treated

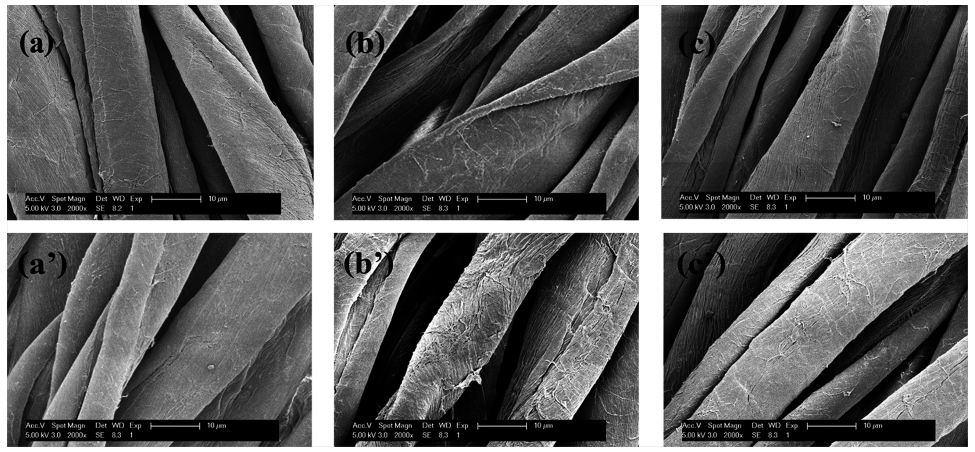


Figure 2. SEM images of cotton fabrics without light irradiation: (a) plain cotton, (b) 2EtAQ-cotton, and (c) Vat Yellow GCN-cotton. And after 8 h UVA irradiation: (a′) plain cotton, (b′) 2EtAQ-cotton, and (c′) Vat Yellow GCN-cotton.

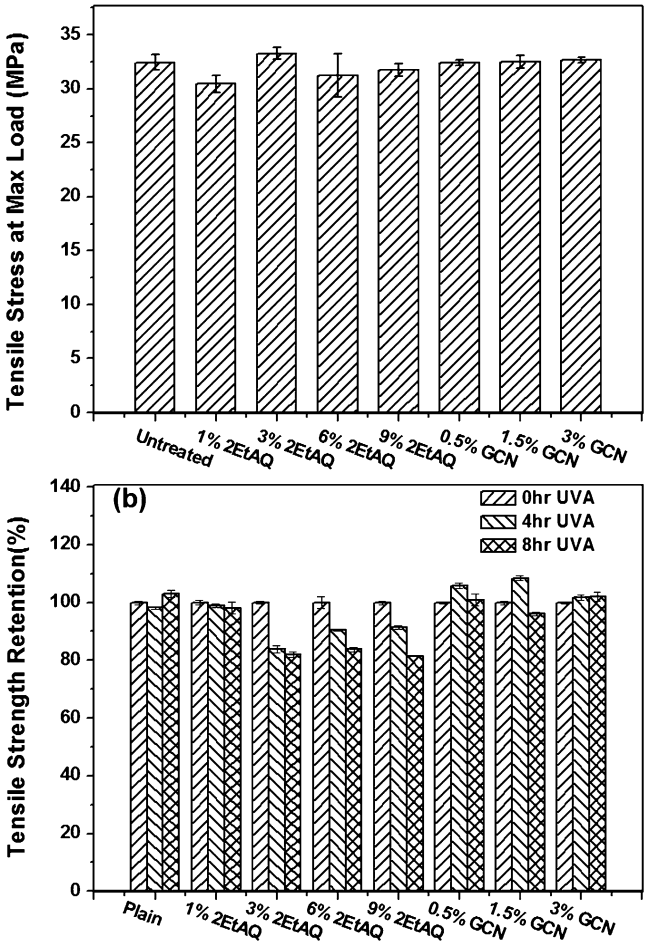


Figure 3. (a) Tensile stress of untreated and treated fabrics before light exposure. (b) Tensile stress retention (%) for 2-ethylanthraquinone and Vat Yellow GCN treated cotton before light (0 h) and after (4 and 8 h) UVA light (365 nm) illumination.

fabrics should be thoroughly and carefully managed, provided with the desired functions.

3.5. Color Fastness. Consequently, colors of the dyed fabrics could be affected by the light exposure. Thus, the colors of the vat dyed cottons were analyzed by using a colorimeter before and after UVA light exposure so as to examine the color fastness of the treated samples against long time light irradiation. Table 4 summarizes the color differences (ΔE values) of the 2EtAQ and Vat Yellow GCN dyed cotton fabrics.

Table 4. Color Changes of Fabrics before and after UVA Exposure[a]

samples	ΔE after 4 h UVA	ΔE after 8 h UVA
untreated cotton	1.31	1.28
1% owf 2EtAQ-cotton	9.89	11.47
3% owf 2EtAQ-cotton	12.62	14.78
6% owf 2EtAQ-cotton	12.74	16.24
9% owf 2EtAQ-cotton	13.25	16.77
0.5% owf GCN-cotton	2.15	6.24
1.5% owf GCN-cotton	2.21	2.86
3% owf GCN-cotton	2.25	2.91

[a]Results are averages of four trials.

The Vat Yellow GCN dyed cotton exhibited pretty good light stability with ΔE values in the range of 2−3, except the one with 0.5% at 8 h, which could be an error, while the 2EtAQ dyed fabrics all exhibited huge color differences. The results confirmed that Vat Yellow GCN dyed cotton possess excellent color fastness against UV light, a general requirement for light fastness of the product. The color changes of the 2EtAQ dyed cotton samples were most significant when they were exposed to UVA initially, and the follow-up light exposure would have less significant impact, which can be observed by comparing the difference of ΔE between 4 and 8 h. The major contributing factor to color changes is Δb^*, a yellowing effect, especially in the samples dyed with high 2EtAQ concentrations. The yellow color may be ascribed to the light-induced structural changes of the compound. In addition, the reactive oxygen species generated by the light-active species may accelerate the oxidation of cellulose structure, which also lead to yellow color, as well as the observed physical damages.

4. CONCLUSIONS

Both 2EtAQ and Vat Yellow GCN dyed cotton fabrics demonstrated light-induced antimicrobial effects against both Gram-negative and Gram-positive bacteria. The functions are durable against washing and are stable under long-term light exposure. 2-Ethylanthraquinone (2EtAQ) is a powerful light-active agent but not a good dye. 2EtAQ dyed fabrics could endure light-induced damages to colors and fibers due to its

high light-sensitivity. The Vat Yellow GCN dyed cotton fabrics also possessed good mechanical properties and limited color changes under light exposure, making Vat Yellow GCN a good multifunctional dye for textile applications. The results provide feasibility of using light-active vat dyes as functional agents.

AUTHOR INFORMATION

Corresponding Author

*Phone: 530-752-0840. E-mail: gysun@ucdavis.edu.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

J.Z. is grateful for a Jastro-Shields Graduate Student Research Grant from the University of California, Davis.

REFERENCES

(1) Sun, Y.; Sun, G. *Macromolecules* **2002**, *35*, 8909−8912.
(2) Cerkez, I.; Kocer, H. B.; Worley, S. D.; Broughton, R. M.; Huang, T. S. *Langmuir* **2011**, *27*, 4091−4097.
(3) Liu, J.; Sun, G. *Dyes Pigm.* **2008**, *77*, 380−386.
(4) Jia, Z.; Shen, D.; Xu, W. *Carbohydr. Res.* **2001**, *333*, 1−6.
(5) Cen, L.; Neoh, K. G.; Kang, E. T. *Langmuir* **2003**, *19*, 10295−10303.
(6) Tashiro, T. *Macromol. Mater. Eng.* **2001**, *286*, 63−87.
(7) Lee, S. B.; Koepsel, R. R.; Morley, S. W.; Matyjaszewski, K.; Sun, Y.; Russell, A. J. *Biomacromolecules* **2004**, *5*, 877−882.
(8) Kong, H.; Jang, J. *Langmuir* **2008**, *24*, 2051−2056.
(9) Yuranova, T.; Rincon, A. G.; Bozzi, A.; Parra, S.; Pulgarin, C.; Albers, P.; Kiwi, J. *J. Photochem. Photobiol., A* **2003**, *161*, 27−34.
(10) Wu, D.; Long, M.; Zhou, J.; Cai, W.; Zhu, X.; Chen, C.; Wu, Y. *Surf. Coat. Technol.* **2009**, *203*, 3728−3733.
(11) Tung, W. S.; Daoud, W. A. *J. Mater. Chem.* **2011**, *21*, 7858−7869.
(12) Qi, K.; Wang, X.; Xin, J. *Text. Res. J.* **2010**, *81*, 101−110.
(13) Feese, E.; Sadeghifar, H.; Gracz, H. S.; Argyropoulos, D. S.; Ghiladi, R. A. *Biomacromolecules* **2011**, *12*, 3528−3539.
(14) Ringot, C.; Sol, V.; Barriere, M.; Saad, N.; Bressollier, P.; Granet, R.; Couleaud, P.; Frochot, C.; Krausz, P. *Biomacromolecules* **2011**, *12*, 1716−1723.
(15) Liu, N.; Sun, G.; Zhu, J. *J. Mater. Chem.* **2011**, *21*, 15383−15390.
(16) Gorner, H. *Photochem. Photobiol.* **2003**, *77*, 171−179.
(17) Pullen, G. K.; Allen, N. S.; Edge, M.; Weddell, I.; Swart, R.; Catalina, F.; Navaratnam, S. *Eur. Polym. J.* **1996**, *32*, 943−955.
(18) Allen, N. S.; Pullen, G. K.; Shah, M.; Edge, M. *Polymer* **1995**, *36*, 4665−4674.
(19) Allen, N. S.; Pullen, G. K.; Shah, M.; Edge, M.; Hooldworth, D.; Weddell, I.; Swart, R.; Catalina, F. *J. Photochem. Photobiol., A* **1995**, *91*, 73−79.
(20) Diaz, A. N. *J. Photochem. Photobiol., A* **1990**, *53*, 141−167.
(21) Gorner, H. *Photochem. Photobiol. Sci.* **2006**, *5*, 1052−1058.
(22) Gee, G. A.; Phillips, G. O.; Richards, J. T. *J. Soc. Dyers Colour.* **1973**, *89*, 285−286.
(23) Hong, K. H.; Liu, N.; Sun, G. *Eur. Polym. J.* **2011**, *45*, 2443−2449.