Photoinduced Decolorization of 2, 6-Dichloroindophenol by 2-Anthraquinone Sulfonate Treated Nylon

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Ⓢ *Supporting Information*

ABSTRACT: Photoactive 2-anthraquinone sulfonate sodium (2-AQS) can produce hydroxyl radical and other reactive oxygen species under UVA irradiation. Because of its acid dye like feature, 2-AQS was immobilized onto nylon fibers through an acid dyeing process, and the dyed nylon was employed as a photoactive self-cleaning material. As a model study, decolorization of representative colorants such as 2,6-dichloroindophenol (DCIP) by the material was investigated. The results revealed that DCIP was first absorbed on the fibers and then degraded by hydroxyl radicals and other reactive oxygen species generated by 2-AQS on the surfaces upon UVA exposure. The photo degradation pathway of DCIP was further studied by directly using aqueous 2-AQS solution, and the degraded products in the solutions were analyzed by LC-MS. Different light sources and hydrogen donors were investigated in degradation of DCIP. The photoactive functions on the 2-AQS-dyed nylon fibers were quite durable and maintained similar decolorization effect of DCIP after five repeated tests.

KEYWORDS: anthraquinone, decolorization, hydroxyl radical, photoactive
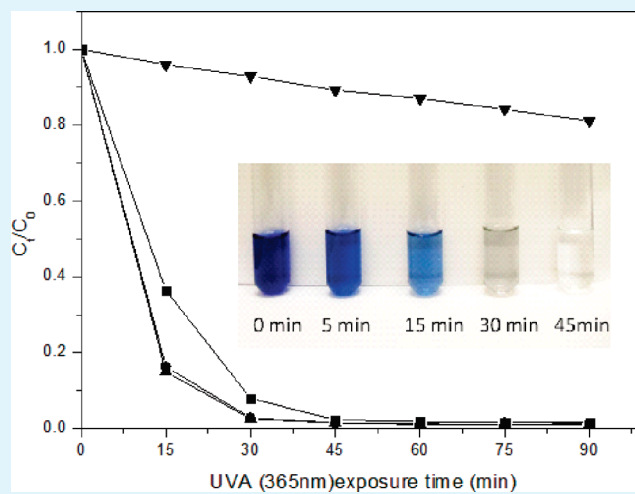
INTRODUCTION

Self-cleaning/self-decontaminating/self-detoxifying fibrous materials have received a lot of attentions in recent years.[1−13] Those materials, possessing the so-called "smart" functions, could acquire the functions by incorporating highly efficient photoactive agents, including inorganic compounds such as TiO$_2$,[1−8] ZnO[9] and organic ones like rose bengal,[10] methylene blue,[11,12] and anthraquinone 2-sulfonate.[13] Upon light exposure, the photosensitive compounds will be excited to singlet and then triplet states by intersystem crossing, which could generate hydroxyl radical, singlet oxygen and other reactive oxygen species with existence of oxygen media.[14] These highly reactive oxygen species are capable of breaking down various chemical and biological agents,[14] which serve as the photoinduced self-cleaning functions.

Most of the photoinduced self-cleaning textiles are TiO$_2$ based, which have successfully demonstrated capability of decolorizing a variety of dyes, decomposing organic compounds and killing pathogenic microorganism.[1−8] TiO$_2$ has been coated onto wool-polyamide, polyester, and cotton textile fabrics through the sol−gel process.[1−4] However, the harsh acidic condition could easily cause 50% reduction of tearing strength on the materials.[5−7] As an inorganic compound, TiO$_2$ has poor affinity toward the majority of organic fibers, which largely limited its immobilization methods on fiber surfaces.

As a popular organic photosensitizer used in water solutions, rose bengal has also been applied onto fibers, and the products have demonstrated strong detoxifying effects under light exposure.[10,15] However, its excited triplet state could be efficiently quenched by oxygen to produce singlet oxygen. The quantum yield of singlet oxygen for rose bengal is 0.76.[16,17] Although singlet oxygen is an exceptionally reactive chemical intermediate and could oxidize many toxic organic compounds, it cannot compete with hydroxyl radicals in final minerization of organic compounds.[14] Besides, under light exposure, rose bengal itself undergoes severe photobleaching process.[10,18] After 5 times of exposure, only around one-third of the dye was left on the fabric.[10]

In this study, we tried to develop textile materials with photoinduced functions from organic dyes such as 2-anthraquinone sulfonate sodium salt (2-AQS) that has inherent interactions with the fibers. 2-AQS has been reported as a "good photosensitizer" and is able to produce hydroxyl radicals and other reactive oxygen species under light exposure.[13,19−23] Because of its acid dye like structure, 2-AQS can be easily incorporated onto polyamide and protein fibers. In a previous study, antibacterial functions of 2-AQS treated wool, nylon and silk fabrics were demonstrated under UVA irradiation.[13] In this
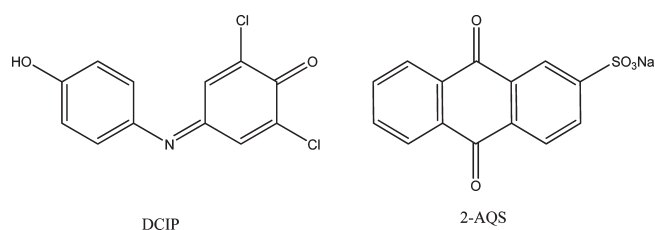
Figure 1. The structure of DCIP and 2-AQS.

study, we report the decolorization of 2, 6-dichloroindophenol (DCIP) by 2-AQS treated nylon samples under light exposure. To better understand the decolorization pathway, a model study was conducted in 2-AQS aqueous solution with two different hydrogen donors. The degradation products and intermediates were analyzed by LC-MS and compared with photodegradation of 2, 6-dichloroindophenol (DCIP) products in aqueous dispersions of TiO_2.[24,25]

■ MATERIALS AND METHODS

Materials. 2, 6-dichloroindophenol (DCIP) and 2-anthraquinone sulfonate sodium salt (2-AQS) were purchased from Sigma-Aldrich. (Milwaukee WI) (Figure 1). Nylon 6,6 filament taffeta (#306A) was purchased from Testfabrics Inc. (West Pittston, PA). All other chemicals were supplied by major chemical vendors and used as received. Except the water used for HPLC mobile phase, all water used in this study was deionized water.

Apparatus and Conditions. UVA irradiation was conducted in a Spectrolinker XL-1000 UV cross-linker (Spectroline, USA), with five 8w lamps in 365 or 312 nm wavelength, or cool white light. The distance between the UV lamps and the material is 12 cm. The UVA light intensity is $1.3-2.0$ mW/cm^2. UV—vis absorption spectra were taken with an Evolution 600 UV—visible spectrophotometer (Thermo Scientific, USA) in a wavelength range of $300-800$ nm.

The LC-MS analyses were performed using a Waters e2695 liquid chromatography system, equipped with Waters 2998 photodiode array (PDA) detector and Waters Micromass ZQ (ESI-MS). The flow rate was set at 0.33 mL/min, and the injection volume was 10 μL. The detection wavelength was set from 190 to 800 nm. Instrument control and data acquisition were performed using Micromass MassLynx software (version 4.1) (Waters Co., Milford, MA, USA). The mobile phase contains 60% water with 0.1% hydrofluoric acid (HF) and 40% acetonitrile with 0.1% HF.

The mass spectrometer conditions were as follows: capillary voltage, 3.0 kV; cone voltage, 60 eV; source temperature, 125 °C; desolvation temperature, 350 °C; desolvation gas flow, 250 L/h. A reverse phase C18 column (5 μm particle size, 4.6 by 150 mm) was used.

Dye Nylon with 2-AQS. 2-Anthraquinone sulfonate sodium (2-AQS) has acid dye feature, which will dissociate to anionic anthraquinone sulfonate in aqueous solution. Under acidic condition, the anthraquinone sulfonate would interact with protonated amino end groups of polyamide (nylon) when an acid dyeing process was employed. Sulfuric acid was used to adjust solution pH 3 and protonate the amino groups on the polymer. Sodium sulfate was used as an electrolyte in assisting interactions between 2-AQS with the polymer, and its concentration was 5 times of that of the sulfuric acid. The dyeing process was conducted on a laboratory scale dyeing machine (Atlas, USA). Dyeing bath temperature was raised from room temperature to 49° by a heating rate of 5 °C/min, and then was increased to 95° by a rate of 0.5 °C/min and kept at 95° for 60 min. The rotation speed was 35 rd/min, and the dye concentration was ranging from 0.5 to 1.5% on weight
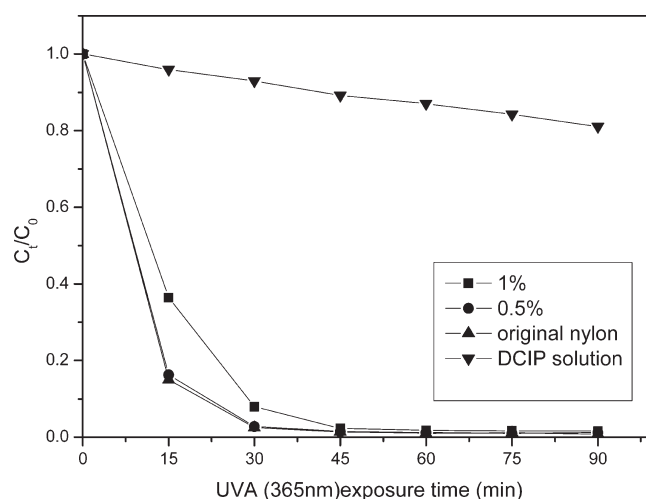

Figure 2. Concentration changes of DCIP solutions (initial conc = 0.2 mM) containing nylon dyed with 0.5% (circle) and 1% (square) 2-AQS solutions, original nylon (up triangle), and without any fabric (down triangle) under UVA irradiation.

of fabric (owf). Dyed fabric was washed in hot water for 30 min to remove unbonded 2-AQS.

Decolorization of DCIP by 2-AQS-Treated Nylon. Decolorization of DCIP by 2-AQS-dyed nylon was evaluated by analyzing the concentration changes of DCIP using the UV—vis spectrometer. The dyed nylon in size of 12×10 cm^2 was put inside of a 50 mL centrifuge tube. Ten milliliters of 0.2 mM DCIP solution was added into the centrifuge tube and then exposed under UVA light for 15 min, 30 min, 45 min, 60 min, 75 min and 90 min, respectively. The UV—visible absorbance of the solution was measured and the maximum absorbance of DCIP in the visible range (600 nm) was recorded after different irradiation durations. The distance between fabric and light source was 12 cm. The original nylon (untreated nylon) chosen as a control was placed in same DCIP solution in another tube which was exposed under the same condition. A colorimeter (Color Eye 7000A) with D65 light source was applied to quantitatively measure color changes of the nylon fabric. Each measurement was expressed in the CIE $L^*a^*b^*$ system. L^* stands for lightness and varied from 0 (black) to 100 (white); a^* represents red (positive) and green (negative); and b^* is positive for yellow color and negative for blue color. Thus, compared with CIE $L^*a^*b^*$ values of a standard sample, negative ΔL^* means darker, more red gives positive Δa^*, and positive Δb^* is more yellow.

Decolorization of DCIP by 2-AQS Solution. 2-AQS solution instead of its dyed nylon was used in these tests to study the decolorization mechanism. Six centrifuge tube (10-cm dia.); each was filled with 10 mL of a 0.2 mM solution of DCIP, 1 mL of 0.6 mM AQS, and 0 or 2 mL of isopropanol or DMSO were placed in the UV cross-linker. The tubes were put flat and exposed under UVA light for 10, 30, 60, 90, and 120 min, respectively. At each interval, the UV—visible absorbance was measured and the maximum absorbance in the visible range (600 nm) was recorded. The dye concentration measured from the unexposed sample served as the initial concentration (C_0) for calculating the C_t/C_0 ratio.

■ RESULTS AND DISCUSSIONS

Decolorization of DCIP by 2-AQS-Dyed Nylon. 2-AQS-dyed nylon is in faint yellowish color. A photoinduced decolorization test was conducted by immersing a piece of 12×10 cm^2 of the fabric inside of a 50 mL transparent centrifuge tube containing
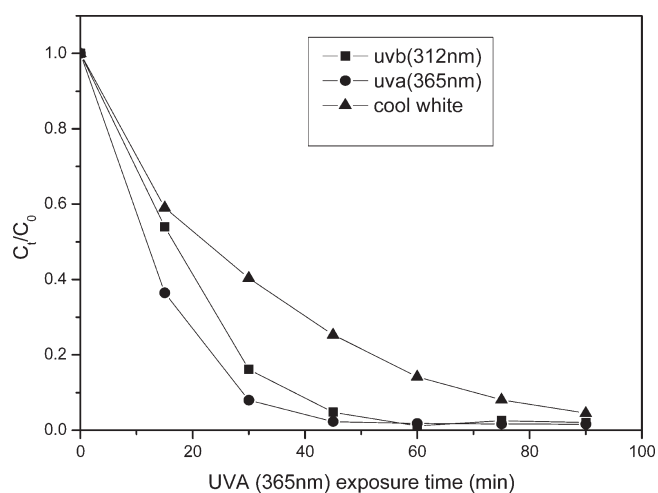
Figure 3. Concentration changes of DCIP solutions with 2-AQS-dyed nylon under different light sources: UVB light (square), UVA light (circle), cool white (up triangle) (initial DCIP conc = 0.2 mM).
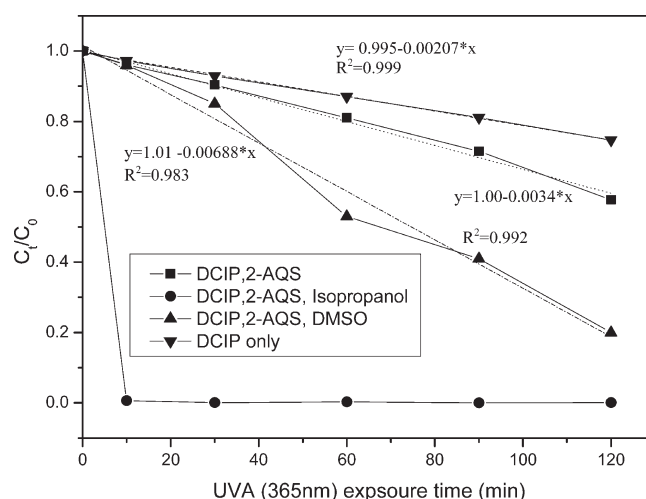

Figure 4. Concentration changes of DCIP solutions containing DCIP only (down triangle) and its linear fit (dash line); DCIP and 2-AQS (square) and its linear fit (dot line); DCIP, 2-AQS, and DMSO (up triangle) and its linear fit (dash-dot line); DCIP, 2-AQS, and isopropanol (circle) (initial DCIP = 0.2 mM).

Table 1. Reaction Rate and Correlation Constant for the Degradation of DCIP in Three Different Solutions

solutions	k_{obs} (M/l)	R^2
DCIP	−0.00207	0.999
DCIP and 2-AQS	−0.0034	0.992
DCIP,2-AQS,DMSO	−0.00688	0.983

10 mL of 0.2 mM DCIP solution. The tube was exposed to UVA (365 nm) light in the UV cross-linker. After different durations of the light exposure, the color changes of the DCIP solution was visually observed, changing from blue to colorless. UV–vis absorbance of the DCIP solutions were measured at 600 nm (λ_{max} of DCIP), and corresponding concentration changes of DCIP are presented in Figure 2. The concentration of DCIP dropped more than 60% during the first 15 min of the UVA irradiation in an aqueous solution containing the nylon dyed with 0.5% 2-AQS and 1% AQS, as well as by the original nylon (nylon without any treatment). The decoloration effect of the original nylon fabric was caused by the absorption of DCIP onto the fibers, similar phenomena were observed for the nylon samples dyed with 0.5% 2-AQS and 1% 2-AQS, respectively. However, the blue color on the original nylon fabric stayed almost unchanged during the entire 90 min UVA exposure process and afterward, while the blue color on the fabric samples dyed with 2-AQS gradually disappeared. The specific color changes on these exposed fabrics were measured by a colorimeter (Color-Eye 7000A, GretagMacbath, USA) and are shown in Table 2. The Δb values between the nylon samples with and without exposure to DCIP clearly indicate the fabric became blue after exposing to DCIP, whereas the dyed samples were not so significant. Because more 2-AQS could be incorporated on the nylon in more concentrated 2-AQS solution (1%), there are less dyeing or binding sites available for DCIP on the surfaces, and more DCIP will stay in the solution. This may explain that the concentration changes of DCIP in the 1% dyed nylon system were slightly slower than the solutions with 0.5% dyed nylon. Generally, speaking, 2-AQS will change to a triplet excited state upon the UVA irradiation, which could abstract hydrogen atoms easily from good donors such as weaker N–H bonds in nylon (polyamide), resulting in AQS and polymer radicals. Triplet radicals of 2-AQS could interact with oxygen and produce hydroxyl radicals and reactive oxygen species, which could oxidize DCIP.[19] Thus, photodecolorization of DCIP by the 2-AQS-dyed nylon substrate could be a result of the above mechanisms.

Influence of Different Light Sources. So far, the results have proven that under a short exposure time to UVA (365 nm)

irradiation 2-AQS-dyed nylon could completely decolorize DCIP . UVB and cool white light sources were explored in the decolorization of DCIP as well. The nylon sample treated by 1% AQS was used in the comparison tests under different light sources including UVA (365 nm), UVB (312 nm), and cool white light, and the results are shown in Figure 3. The results revealed that the UVA light demonstrated the most powerful decolorization ability against DCIP among these light sources. The UVB (312 nm) irradiation was not as efficient as the UVA light in generating reactive oxygen species, though UVB may directly decolorize DCIP. The lowest DCIP decolorization efficiency by the fabric was observed for cool white light, however, this result is still surprisingly promising considering that only five 8 W cool white lamps were used in the test. In addition, after extended exposure time (90 min) the 2-AQS treated nylon could almost completely decolorized DCIP under the cool white light, making such materials capable of providing light-active self-cleaning functions.

Decoloration of DCIP by 2-AQS in Solution. In fact, the photoactive functions of 2-AQS were found only on several fabrics including nylon 66, nylon 6, wool and silk, all possessing amide structures.[13,23] On the basis of the proposed mechanism,[26] a hydrogen donor is necessary to generate powerful reactive oxygen species. To clearly understand the reaction mechanism, we conducted a model study in 2-AQS aqueous solutions using DMSO or isopropanol as a hydrogen donor (Figure 4). Obviously, the decrease of DCIP concentration caused by the UVA irradiation was less significant compared with the other three
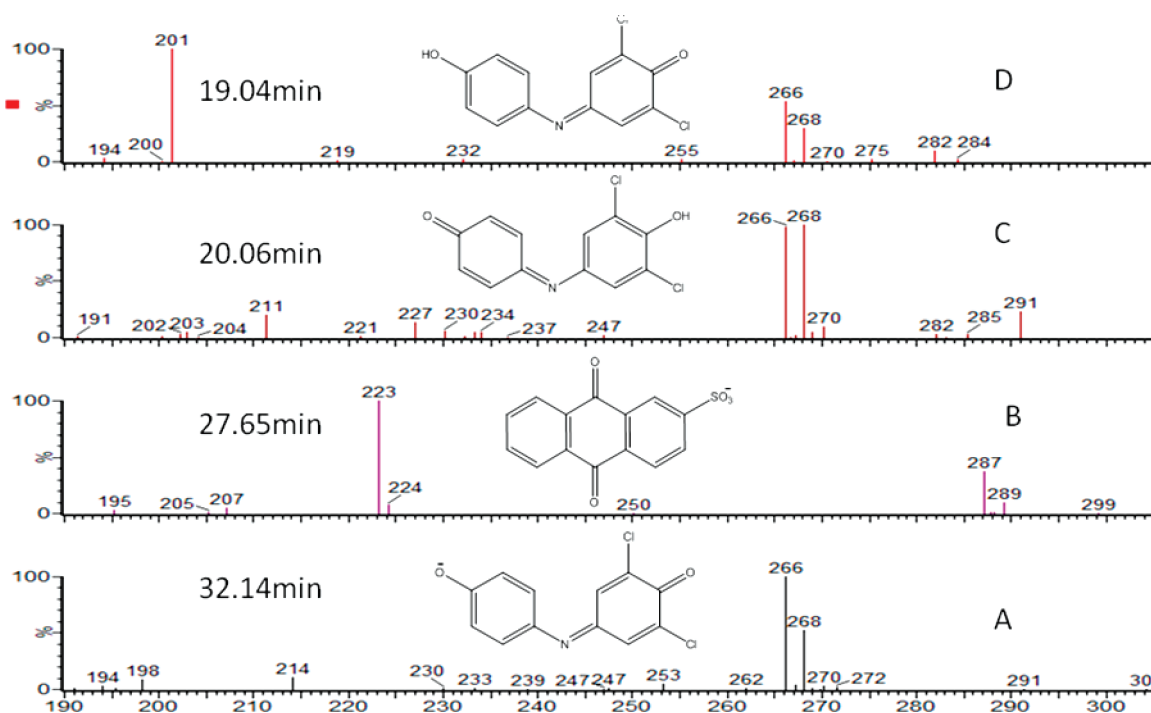
Figure 5. Mass spectra of degradation products and intermediates of in solution A—D.
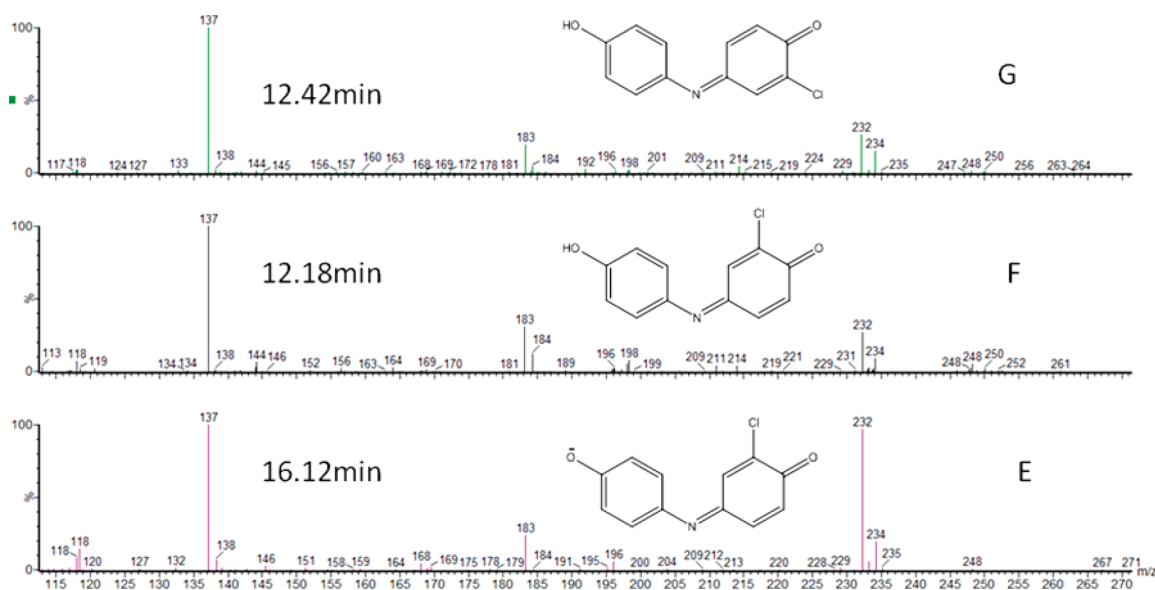

Figure 6. Mass spectra of degradation products and intermediates of DCIP E—G.

samples. 2-AQS in the solution exhibited photoinduced activity in decolorizing DCIP. But, when DMSO or isopropanol was added into the mixture, the decolorization process was accelerated, and isopropanol was the most efficient cocatalyst. This suggests that in the presence of isopropanol, 2-AQS produces most reactive oxygen species in the solution under the UVA irradiation, followed by DMSO, and water. Compared with water and DMSO, isopropanol forms the most stable intermediate secondary radical, stabilized by hyper-conjugation effect of methyl group.[26] DMSO promotes the formation of hydroxyl radicals due to the weaker C—H bonding in the chemical structure. Water molecule has a stronger O—H bonding energy

which may explain why it needs longer time to decolorize DCIP without isopropanol or DMSO in aqueous solution. Such results also proved that N—H bonds, which are the weakest in nylon, should have served as hydrogen donors in the system.

Carefully examining the results of three solution systems containing only DCIP, DCIP and 2-AQS, DCIP, and 2-AQS and DMSO (Figure 4), the degradation of DCIP follows pseudo-zero-order kinetics under the tested condition. For a zero-order kinetic model, the rate law is $r = -(dC)/t = k$, where r is the oxidation rate of the reactant (mM/min), k is the rate constant of the reaction (mM/min), C is the concentration of DCIP (mM), t the illumination time (min). The plots of C_t/C_0 versus time

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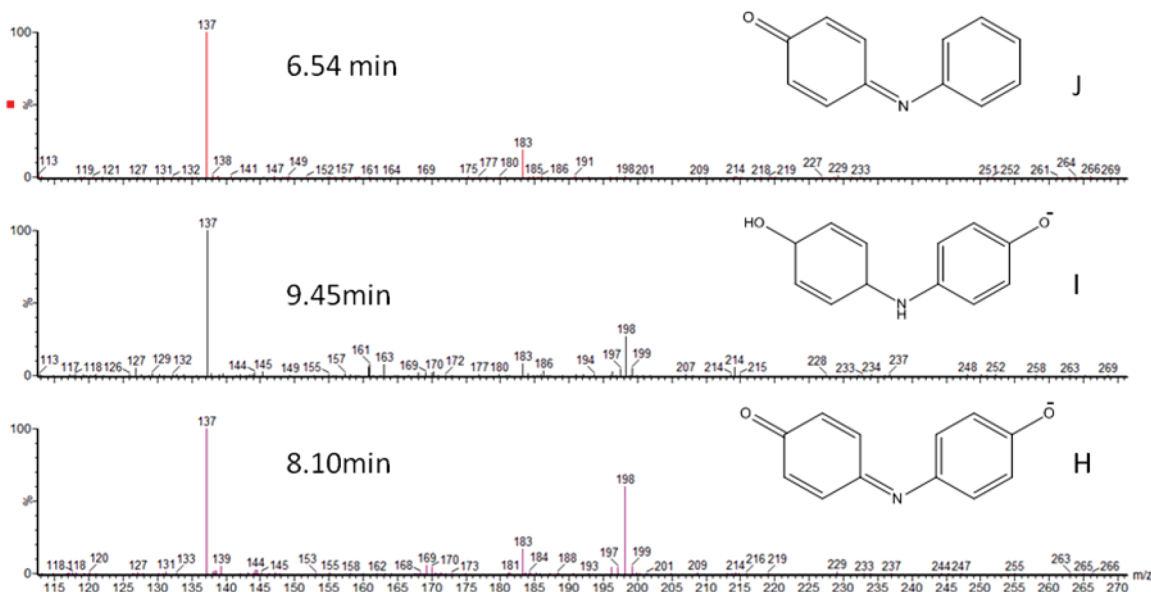
Figure 7. Mass spectra of degradation products and intermediate of DCIP H—J.

displayed excellent linear fit, with the smallest correlation constant larger than 0.98. The rate constants were calculated and listed in Table 1. The rate constant is independent of the concentration of the reactant(s). Increasing the concentration of the reacting species will not speed up or slow down the rate of the reaction.

Identification of Degradation Products and Intermediate Compounds. Because DCIP and its degraded products were easily absorbed on the fabric, the analysis of the structures was relatively difficult. However, with proper mixture ratios of DCIP, 2-AQS, and iso-propanol in solution, these fragments and intermediates of DCIP formed during the UVA exposure process were analyzed by LC-MS. LC analysis illustrated that a number of intermediate compounds formed as the concentration of the DCIP decreased. Three peaks shown in the chromatogram spectra of the original solution are related to DCIP. Study showed that under acidic condition, DCIP will change to pink color because of the addition of one H onto the structure (eq 1), producing two isomers, with one structure dominates because of the steric hindrance effect from two chlorine atoms. On the basis of the UV—vis absorbance data of these three peaks, the peak at 32.14 min (compound A) was assigned to the original DCIP structure. Compound B is 2-AQS in the solution. Compound C at 20.06 (dominates) and compound D at 19.04 min were assigned to two isomers of DCIPH (Figure 5). In Figure 2, it is noted that continuous UVA light exposure will also decolorize DCIP in a slow speed. The LC-MS analysis demonstrated that the DCIP eventually was transferred to compounds C and D without using 2-AQS. No further degradation was observed.

DCIP (blue)   DCIPH (pink)   (1)
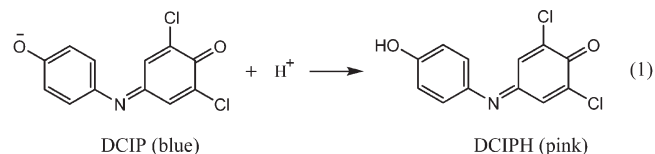
Three intermediates separated at 16.12, 12.18, 12.42 min (peaks E, F, and G respectively) appeared at the earlier stage
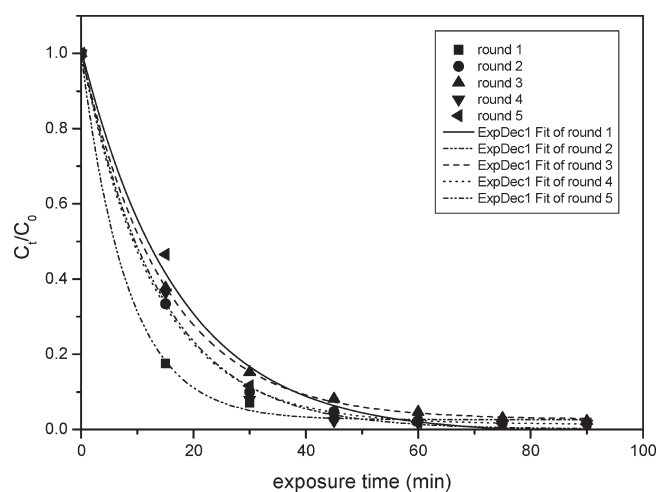

Figure 8. Repeated decolorization of DCIP (initial conc = 0.2 mM) by the 2-AQS-dyed nylon.

of photoexposure and then gradually vanished during the process. These structures are the fragments of DCIP, including the one losing one chlorine (peak E), and two isomers after adding one hydrogen atom and losing one chlorine (peaks F and G, Figure 6). Three other intermediates peaked at 8.10, 9.45, 6.54 min (peaks H, I, and J) increased gradually and became dominant peaks during the photodecolorization process. Mass spectrometer data interpreted peak at 9.45 min as the fragment of DCIP after losing two chlorine atoms (Figure 7). And accordingly the peak at 8.10 min was the fragment adding one hydrogen atom. The last detectable fragment of DCIP was the one lost two chlorine atoms and one oxygen atom. Our results are consistent with the reported photodegradation intermediates of DCIP in TiO$_2$ suspension solution.[24,25] The appearance time, accumulation, and diminishment of these intermediate indicate that the oxidation reaction could start by hydroxyl radicals attacking chlorine on the benzene ring, followed by attacking the second chlorine and the ketone bond.

Table 2. Color Coordinates of Undyed, Dyed, and UVA Exposed Samples

	L	a	b	ΔL	Δa	Δb
original nylon (standard)	74.95	−0.70	−3.61			
nylon dyed with 0.5% 2 AQS	74.73	−0.78	−2.87	−0.22	−0.08	0.74
nylon dyed with 1% 2-AQS	74.48	−0.68	−2.20	−0.47	−0.02	1.40
original nylon after 1st round	68.45	−7.58	−11.67	−6.50	−6.88	−8.06
nylon dyed with 0.5% 2-AQS after 1st round	74.76	−1.79	−0.16	−0.19	−1.09	3.44
nylon dyed with 1% 2-AQS after 1st round	73.81	−1.75	1.06	−1.14	−1.04	4.67
nylon dyed with 1% 2-AQS after 2nd round	72.81	−1.67	3.07	−2.14	−0.96	6.68
nylon dyed with 1% 2-AQS after 3rd round	72.41	−1.09	2.91	−2.54	−0.38	6.52
nylon dyed with 1% 2-AQS after 4th round	71.55	−0.79	1.65	−3.41	−0.08	5.26
nylon dyed with 1% 2-AQS after 5th round	70.91	−0.80	1.46	−4.04	−0.10	5.07

Durability Test. A major concern about the practical applications of these photoactive materials is their durability under continuous light exposure. To evaluate the durability of photodegradation activity, the 2-AQS-dyed nylon was used in DCIP solution and exposed to the UVA (365 nm) illumination. Afterward the same fabric was placed into another fresh DCIP solution and exposed to the UVA again. The same process was repeated five times (Figure 8). Even after five cycles of UVA irradiation, no significant difference of the photodecolorization ability of DCIP was observed on the same fabric. In addition, the color changes of the same 2-AQS treated nylon after each cycle of UVA irradiation were also recorded. The results demonstrated that 2-AQS treated nylon initially absorbed DCIP and the whole fabric showed blue color of DCIP. After the UV irradiation process, the blue color diminished because DCIP was decolorized. Color changes of the 2-AQS-dyed fabric were observed after each of five cycles of irradiations. The fabric become yellower and darker (Table 2), because of the side reactions of 2-AQS with water or nylon.

An HPLC study of solution samples also demonstrated 11% consumption of 2-AQS in the mixture solution of 2-AQS, isopropanol and DCIP after 80 min of UVA exposure. Mass spectrometer data suggested that products including several coupling compounds of 2-AQS and isopropanol and products added one hydroxyl radical on 2-AQS (see the Supporting Information, Figures 1 and 2)

CONCLUSIONS

In this study, 2-AQS-dyed nylon was used to degrade DCIP in aqueous solution under light irradiation. DCIP was initially adsorbed onto the fabric, and then degraded on the surface of the fabric quickly. The decolorization of DCIP solution was affected by different light sources and different hydrogen donors such as isopropanol or DMSO. When these hydrogen donors were added in 2-AQS solutions, degradation of DCIP could be accelerated. In aqueous solutions containing DCIP, 2-AQS with or without a hydrogen donor, the degradation of DCIP followed zero order kinetic models, indicating concentration change of DCIP will not affect the reaction rate. The degradation pathway of DCIP in aqueous solution could be caused by hydroxyl radicals attacking one chlorine atom of the compound, which could also be the mechanism on the 2-AQS-dyed nylon fabric. The results showed that the 2-AQS-dyed nylon was durable, and after five times of repeated tests still maintained similar decolorization ability against DCIP.

ASSOCIATED CONTENT

S **Supporting Information.** Two additional figures (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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