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Crosslinking of cotton cellulose with succinic acid in the presence of titanium dioxide nano-catalyst under UV irradiation

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Abstract The nanometer titanium dioxide (TiO_2), succinic acid (SUA), and the mixture of nano- TiO_2 and SUA were dispersed or dissolved in pure water, then irradiated with UV at the wavelength of 254 nm under stirring for different time periods respectively. The pH and conductivity values and UV-vis spectra of those solutions were recorded immediately. The powders obtained from the filtrated and vacuum dried from those solutions were examined with Fourier Transform Infrared Spectroscopy and Wide Angle X-Ray Diffraction meter. It shows that the crystalline structure and IR and UV-vis spectra of SUA adsorbed on nano-TiO_2 particles are changed. The photo-reduced succinic acid in the presence of nanometer titanium dioxide under UV irradiation can create aldehyde group on SUA and free radical of SUA to improve the catalytic effects of crosslinking reaction between SUA and cotton cellulose.

Keywords Catalyst · Nanometer titanium dioxide · Succinic acid · Photo-reduction · Irradiation · Crosslinking reaction

Introduction

It is well known that the electron of the nanometer titanium dioxide (TiO_2) particle at valence band will be excited to the conduction band under the irradiation of ultraviolet (UV) light whose wavelength is lower than 400 nm for a few microsecond (μs) to rise the electron to the surface of the nanometer particle [1, 2]. This phenomenon is called as photo-reduction that can reduce the water molecule and hydroxyl ion, which could be absorbed on the surface of the nanometer particle, in the reaction system to create a series reaction shown as Scheme 1 [1, 3].

The use of nanometer titanium dioxide or other nanometer materials as the catalyst was investigated for many years to enhance the catalytic effect [4–8] on the improvement of some properties of the treated materials. Using the nanometer grade TiO_2 as catalyst [9] to improve the crease recovery property of the silk fabrics was studied. Those facts adumbrate that the functional groups of the acid crosslinking agents therefore could interact with nanometer titanium dioxide to enhance the crosslinking between cellulose molecules. However, the detailed information for the mechanism of crosslinking and the photo-reduction of succinic acid in the presence of the nanometer grade TiO_2 catalyst is lacking.

In this study, we will use succinic acid as crosslinking agents in the presence of nanometer TiO_2 as catalyst under the irradiation of UV light whose wavelength is 254 nm. The crease recovery angle and tensile strength of the treated fabrics will be determined and the Fourier Transform Infrared Spectroscopy and Wide Angle X-ray Diffraction of the TiO_2/succinic acid samples and the conductivity, pH values and UV-vis spectroscopy obtained from the various conditions of UV irradiated TiO_2/succinic acid water solutions will also be analyzed to investigate the mechanism of crosslinking with succinic acid and the photo-reduction of the succinic acid crosslinking agent in the presence of the nanometer grade TiO_2 catalyst in water medium.

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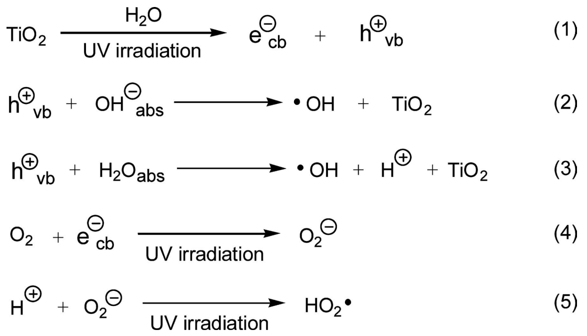


$$TiO_2 \xrightarrow[\text{UV irradiation}]{H_2O} e^{\ominus}_{cb} + h^{\oplus}_{vb} \quad (1)$$

$$h^{\oplus}_{vb} + OH^{\ominus}_{abs} \longrightarrow \bullet OH + TiO_2 \quad (2)$$

$$h^{\oplus}_{vb} + H_2O_{abs} \longrightarrow \bullet OH + H^{\oplus} + TiO_2 \quad (3)$$

$$O_2 + e^{\ominus}_{cb} \xrightarrow[\text{UV irradiation}]{} O_2^{\ominus} \quad (4)$$

$$H^{\oplus} + O_2^{\ominus} \xrightarrow[\text{UV irradiation}]{} HO_2\bullet \quad (5)$$

Scheme 1 The possible photo-reduction of nano-TiO_2 under UV irradiation

Experimental

Materials

In this study, we used desized, scoured, and bleached cotton fabric, 32s × 32s ends (77) and picks (66).

The crosslinking agent was succinic acid (SUA) and was supplied by First Chemical Co., Taipei, Taiwan. The nanometer titanium dioxide powder (<7 nm) was an anatase and a tetrahedral crystal (density: 3.90 g/cm^3, hardness: 5.5–6.0, energy level: 3.2 eV) and was supplied by Sachtleben Chemie (GmbH) Co., Germany. Other chemicals used were all reagent grade.

Methods

Cotton fabric samples were padded twice to about 85% wet pickup with freshly prepared (2, 4, 6, 8, and 10% w/w) aqueous solutions of the mixtures of succinic acid and the various concentrations of nanometer titanium dioxide catalyst. Padded fabrics were dried at 60°C for 3 min, UV (254 nm) irradiated for various time periods, soaped, washed, and dried.

Tensile strengths of the treated fabrics were measured on an Instron tensile tester (KAO-TIEH, AT-7010 D1, Machinery Industrial Co., Ltd., Taichung, Taiwan) according to the method of ASTM D1682-64. ASTM standard D 1295-67 was used to determine dry and wet crease recovery angles.

The nanometer titanium dioxide alone (1.0 gram), succinic acid alone (1.0 gram), and the mixture of nanometer titanium dioxide and succinic acid (1 gram/9 grams) were dispersed or dissolved in water to form a solution of 100 grams. Those solutions were irradiated with UV at the wavelength of 254 nm under stirring at 25°C for different time periods (0, 1, and 5 h, respectively). Then, the conductivity values and the pH values of those dispersed or aqueous solutions were examined immediately with conductivity meter (SUNTEX conductivity meter SC-170, Suntex Instruments Co., Ltd., Taipei, Taiwan) and pH meter (Suntex SP-2200 Microprocessor PH/ORP meter, Suntex Instruments Co., Ltd., Taipei, Taiwan), respectively.

Surface reflectance of infrared spectroscopic measurement of the solid powders filtrated and vacuum dried from the following samples were recorded. These were (a) nano-TiO_2 alone, (b) succinic acid alone, (c) the mixture of nano-TiO_2 (0.1 wt%) and SUA (1 wt%). They were irradiated under UV light (254 nm) for 0 hr and 5 hr, respectively. All those solid samples were recorded directly on the Fourier Transform Infrared Spectroscopy (FT-IR, FTIR Spectrum One *Perkin Elmer,* New Jersey, U.S.A.) that has the equipment of Attenuated Total Reflectance.

Five samples of dispersed or aqueous solutions were prepared, which were (a) 1 wt% of succinic acid alone under UV irradiation for 0 hr, (b) 1 wt% of succinic acid alone under UV irradiation for 5 hr, (c) the mixture of nano-TiO_2 (0.1 wt%) and SUA (1 wt%) under the UV irradiation for 0 hr, (d) 0.1 wt% of nano-TiO_2 alone under UV irradiation for 0 hr, and (e) the mixture of nano-TiO_2 (0.1 wt%) and SUA (1 wt%) under the UV irradiation for 5 hr, respectively. The upper layer of these dispersed or aqueous solutions after stirring and irradiation for 3 min was drawn and was examined with UV-vis spectroscopy (UV/VIS spectrophotometers V-560, Japan Spectroscopic Co., Ltd., Tokyo, Japan).

For confirming the crosslinking reaction between the SUA molecule and cellulose molecule, infrared spectra of the three samples were obtained using a KBr disk technique [10]. These samples were (a) carboxymethylcellulose (CMC was selected as a model molecule of cotton cellulose for the un-solubility of cellulose powder in water), (b) SUA, and (c) CMC/SUA: CMC was dissolved in water and mixed with the SUA at the mole ratio of 1 to 1 in the presence of nano-TiO_2 catalyst (10 wt% of CMC/SUA), then irradiated under the UV light (254 nm) at room temperature for 40 min on a piece of glass. Samples were prepared to give a dry weight about 1.8 mg after storage in 1-dram vials over P_2O_5 for 3 days. Spectral-grade KBr (250–300 mg) was ground, transferred to individual sample vials, dried in an oven at approximately 200°C for several hours, and stored in an oven at 110°C. All the samples and KBr were mixed, ground and dried in 1-dram vials over P_2O_5 for 3 days, the samples were then pressed in an evacuated die under suitable pressure. A Fourier transform infrared spectrophotometer (Model FT/IR-3, JASCO Inc., Tokyo, Japan) was used to obtain spectra and investigate the reaction between SUA and cellulose in the presence of nano-TiO_2 catalyst under UV irradiation.

Additionally, four samples were examined with the wide angle X-ray diffraction (WAXD) using a X-ray Powder Diffractometer XRD (MXP18, MAC Science, Yokohama, Japan) equipped with a Ni-filtered CuKα radiation operated at 40 kV and 30 mA. Each sample was scanned in the reflection mode from 5° to 60° at a scanning rate of 1.8°/min. These samples were obtained from the filtrated and vacuum dried powders of (a) nano-TiO_2 alone, (b) the mixture of nano-TiO_2 (0.1 wt%) and SUA (1 wt%) dispersed solution irradiated with UV for 0 hr, (c) the mixture of nano-TiO_2 (0.1 wt%) and SUA (1 wt%) dispersed solution irradiated with UV for 5 hr, and (d) SUA alone, respectively.

Results and discussion

Physical properties

The dry crease recovery angle (DCRA), wet crease recovery angle (WCRA), and tensile strength retention (TSR) of the fabrics treated with succinic acid (SUA) under different conditions catalyzed with nanometer titanium dioxide (nano-TiO_2) are listed in Table 1. The data in this table show that the DCRA and WCRA values for the various treated fabric samples are gradually increased with the increasing of the concentration of succinic acid (SUA) and irradiation time period, but TSR values decreased for all cases. Those results indicate that the catalytic effect of the nano-TiO_2 is strongly depended on the time period of irradiation that is the longer the time period of irradiation the higher the catalytic effect of crosslinking.

Additionally, it is interesting to find that the DCRA and WCRA values for the various treated fabric samples are gradually increased with the increasing of nano-TiO_2 catalyst concentration then decreased as the catalyst concentration used is kept increasing, but the TSR values are gradually decreased with the increasing of catalyst concentration. Those results obtained from the higher catalyst concentrations used are somewhat different from those results obtained from normal crosslinking reaction catalyzed with metallic salts such as magnesium chloride and zinc nitrate, which is that the higher DCRA and WCRA of the treated fabrics would respond the lower TSR [11, 12]. This difference of lower DCRA and WCRA under the condition of higher nano-TiO_2 catalyst concentrations used may be caused by the damage of cellulose fiber and crosslinking agent under UV irradiation.

The catalytic effects of the nanometer titanium dioxide catalyst on the crosslinking reaction interest us to investigate the crosslinking reaction and the photo-reduction of succinic acid crosslinking agent in the presence of the nanometer titanium dioxide catalyst under UV irradiation.

Photo-reduction of succinic acid in the presence of Nano-TiO_2

In order to confirm the possible reaction of SUA in the presence of nano-TiO_2 under UV irradiation, the following series of investigations on the FTIR (surface reflection) of the solid powder samples obtained from the solutions under various conditions are discussed. Figure 1(a), the IR spectra of nano-TiO_2 without UV irradiation, shows no obvious important and interesting absorption band. The important and interesting absorption band of SUA without UV irradiation shown in Fig. 1(b) is the carbonyl group at about 1682 cm^{-1}. The carbonyl group of succinic acid at about 1682 cm^{-1} is almost no change as the succinic acid was mixed with nano-TiO_2 and was not irradiated with UV (Fig. 1(c)); however, there is a new absorption band generated at about 1560 cm^{-1}, which is believed to be the $–COO^-$ group [13]. Those results may be caused by the hydrolysis of succinic acid in the presence of nanometer titanium dioxide in the water medium.

For the investigation of the effect of UV light irradiation on the photo-reduction of SUA, the IR spectra of the samples of nano-TiO_2, SUA, and the mixture of nano-TiO_2 and SUA under the UV light irradiation for 5 hr are examined and shown in Figs. 2(a)–(c), respectively. From the comparison between Figs. 2(a) and 1(a) and that between Figs. 2(b)

Table 1 Physical properties of the treated fabrics catalyzed with nanometer titanium dioxide

	Treating conditions			Physical properties		
Crosslinking agents	Agents conc. (%)	Cat. conc. (%)	Irradiation time (min)	Dry crease recovery angle (W + F)°	Wry crease recovery angle (W + F)°	Tensile strength retention (%)
Control	–	–	–	199	169	100
	2	0.8	30	202	164	97.4
	4	0.8	30	210	169	96.2
	6	0.8	30	214	173	95.5
	8	0.8	30	216	174	94.5
	10	1.0	30	213	173	93.2
SUA	10	0.8	30	217	175	94.1
	10	0.6	30	215	172	95.4
	10	0.4	30	210	168	96.6
	10	0.2	30	198	158	98.0
	10	0.8	5	200	171	97.2
	10	0.8	15	208	172	96.1
	10	0.8	45	218	176	92.9

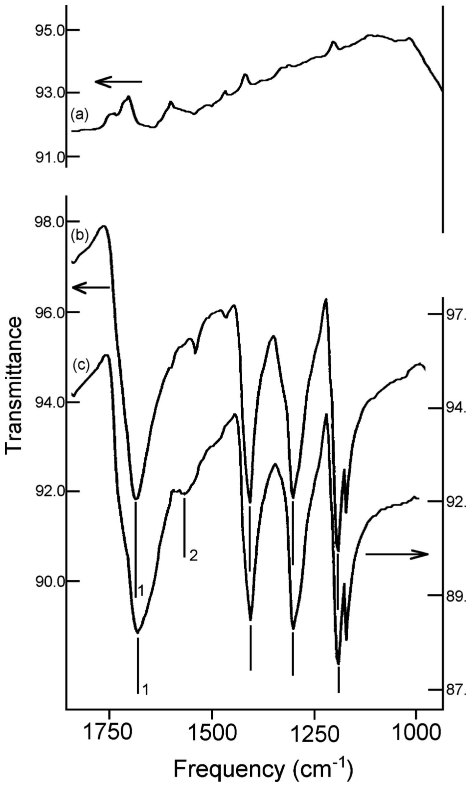


Fig. 1 The IR spectra of the powders filtrated and vacuum dried from the following water solutions of (a) nano-TiO_2 alone, (b) succinic acid alone, and (c) the mixture of nano-TiO_2 and SUA under the UV irradiation for 0 hr. 1.1682 cm^{-1}, 2.1560 cm^{-1}

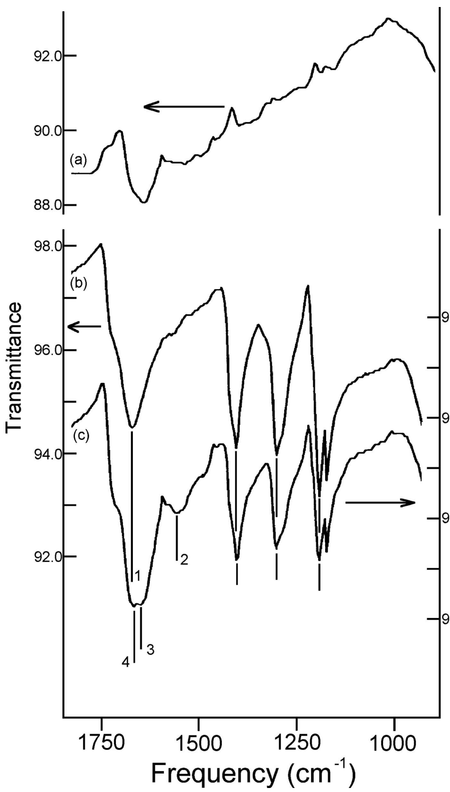


Fig. 2 The IR spectra of the powders filtrated and vacuum dried from the following water solutions of (a) nano-TiO_2 alone, (b) succinic acid alone, and (c) the mixture of nano-TiO_2 and SUA under the UV irradiation for 5 hr. 1.1682 cm^{-1}, 2.1556 cm^{-1}, 3.1647 cm^{-1}, 4.1668 cm^{-1}

and 1(b), we find that there is no significant change on the absorption bands of nano-TiO_2 alone and SUA alone after 5 hrs' UV irradiation. However, the carbonyl group at 1682 cm^{-1} shifts to 1668 cm^{-1} shown in Fig. 2(c), which is the spectrum of TiO_2/SUA after the UV irradiation for 5 hr. This result supports the existence of photo-reduction of SUA in the presence of nano-TiO_2 under UV irradiation. Figure 2(c) also reveals two new absorption bands at about 1556 cm^{-1} and 1647 cm^{-1}. The former is believed to be the $–COO^-$ group [13], which is also appearing in Fig. 1(c) (0 hr's UV irradiation) but a slight shift. The latter accounts for the photo-reduction of SUA. The slight shift for the $-COO^-$ from 1560 cm^{-1} (Fig. 1(c)) to 1556 cm^{-1} (Fig. 2(c)) possibly caused by the change of environment after 5 hrs' UV irradiation. At the same time, a new absorption band at about 1647 cm^{-1} is found in Fig. 2(c), which is believed to be the aldehyde group [13] photo-reduced from the carboxylic acid of succinic acid.

From Figs. 1 to 2, we suggest that the carboxylic acid group of succinic acid can be adsorbed on the surface of nanometer titanium dioxide particle under UV irradiation. At the same time, the carboxylic acid group of succinic acid could be photo-reduced to form the aldehyde group to provide the crosslinking ability of succinic acid. Our previous studies [14, 15] showed that the functional group of aldehyde is well to react with the hydroxyl group of cotton cellulose.

Figures 3(a) and (b), the UV-vis spectra of water solution of succinic acid irradiated with UV light for 0 hr and water solution of succinic acid irradiated with UV light for 5 hr, respectively show that there is no change after 5 hrs' UV irradiating that is there is no change on the chemical structure of succinic acid after UV irradiating. In order to assure whether the structure of succinic acid in water is affected by nanometer titanium dioxide, the UV-vis spectra of water solution containing SUA and nano-TiO_2 irradiated with UV light for 0 hr and water solution of containing SUA and nano-TiO_2 irradiated with UV light for 5 hr are examined (Figs. 3(c) and (e)). From the comparison between these two figures, it can be found that the absorption peak at about 310 nm is becoming palpable, but a sharp peak is appearing at around 339 nm. This may be attributed to the formation of free radical of water and SUA molecules after UV irradiation (photo-reduction) in the presence of nano-TiO_2. Additionally, it is interesting to find that the absorption peak at around 339 nm is shifting and broadening and is increasing significantly on the value of absorbance after 5 hrs' irradiation (Fig. 3(e)) as compared with that in Fig. 3(c) of 0 hr's irradiation and that in Fig. 3(d) of nano-TiO_2 having 0 hr's

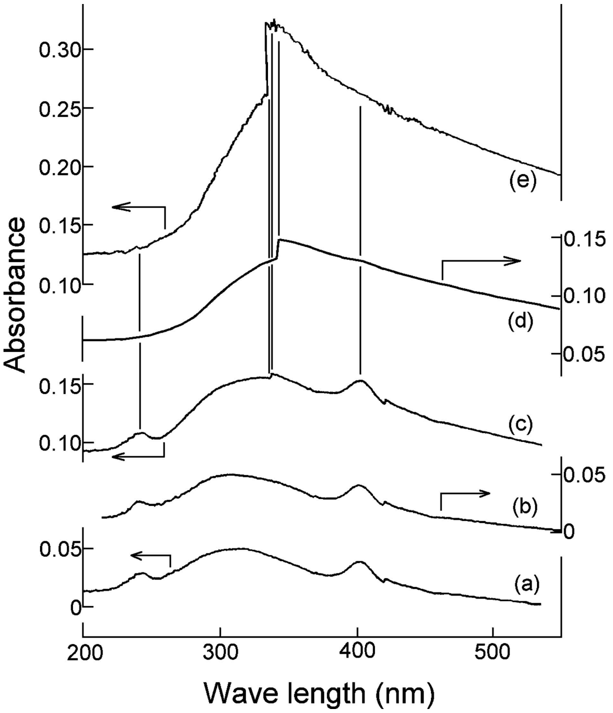


Fig. 3 The UV-vis spectra of (a) 1 wt% of succinic acid alone under UV irradiation for 0 hr, (b) 1 wt% of succinic acid alone under UV irradiation for 5 hr, (c) the mixture of nano-TiO_2 (0.1 wt%) and SUA (1 wt%) under the UV irradiation for 0 hr, (d) 0.1 wt% of nano-TiO_2 alone under UV irradiation for 0 hr, and (e) the mixture of nano-TiO_2 (0.1 wt%) and SUA (1 wt%) under the UV irradiation for 5 hr, respectively

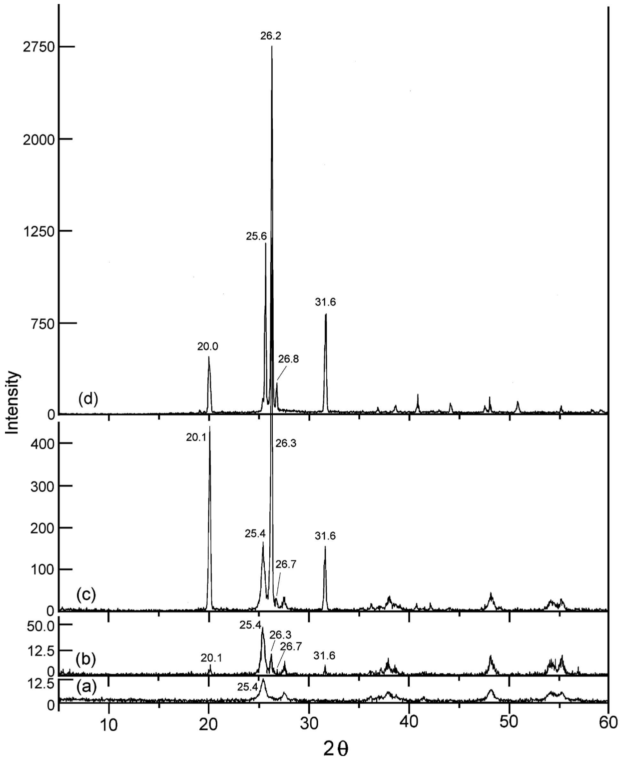


Fig. 4 The patterns of the wide angle X-ray diffraction for the samples obtained from filtrated and vacuum dried powders of the (a) nano-TiO_2 alone, (b) SUA/nano-TiO_2 water solution irradiated with UV for 0 hr, (c) SUA/nano-TiO_2 water solution irradiated with UV for 5 hr, and (d) succinic acid alone

irradiation. Those changes around 339 nm may be caused by the increase of the photo-reduction of SUA and nano-TiO_2 in water medium after UV irradiation discussed in above section of FT-IR spectra. Again, from this result we can assure that the photo-reduction of SUA could be occurred to improve the crosslinking ability. On the other hand, the absorption bands at about 244 nm and 403 nm of the SUA (Figs. 3(a)–(c)) are disappeared by the overlapping for the elevation of the value of absorbance in Fig. 3(e). The significant elevation of absorbance might also be caused by the photo-reduction of the SUA in the presence of nano-TiO_2 under UV irradiation.

The pattern of SUA alone (Fig. 4(d)) shows that the main diffraction peaks are those about 20.0°, 25.6°, 26.2°, 26.8°, and 31.6°. From the comparison of nano-TiO_2 alone (Fig. 4(a)), SUA/nano-TiO_2 without irradiation (Fig. 4(b)), SUA/nano-TiO_2 with 5 hrs' irradiation (Fig. 4(c)), and SUA alone (Fig. 4(d)), we find that the diffraction peaks for nano-TiO_2 are all existed, but the diffraction peaks for the SUA adsorbed on nano-TiO_2 particles only 20.1°, 26.3°, 26.7°, and 31.6° are existed, 25.6° is disappeared or overlapped with the diffraction peak for nano-TiO_2 at about 25.4°. Prolonging the time period of UV irradiation does not change the main peaks of the X-ray patterns (Figs. 4(b) to (c)). Additionally, the strength of X-ray diffraction for SUA which was absorbed on the nano-TiO_2 particles under 0 hr's irradiation is significant lower than that for SUA which was absorbed on the nano-TiO_2 particles under 5 hrs' irradiation. This result is agreeing with the smaller value of absorbed percentage listed in Table 2. There among, the diffraction peak at about 26.8° decreases significantly from the comparison of intensity of the ratios of 26.8°/31.6° in Fig. 4(d) and 26.7°/31.6° in Fig. 4(c). Those results of the slight shift and the change in diffraction strength of diffraction peaks reveal that the crystalline structure is different for SUA and the SUA adsorbed on nano-TiO_2 particles. This phenomenon is probably caused by the photo-reduction of SUA in the presence of nano-TiO_2 under UV irradiation discusses in Figs. 1 and 2.

If the pure water contains a simple compound such as nanometer titanium dioxide alone under the irradiation of UV light, the conductivity values of the nanometer titanium dioxide water solutions will be affected only by the hydrogen ion, hydroxyl ion, free radical, and the polar functional groups. Therefore, the pH values of a stable solution will have a corresponding value of conductivity. Table 2 shows that the pure water has the pH value of 6.85 and the conductivity of 3.29. As nano-TiO_2 particles are added into the pure

Table 2 The values of pH and conductivity of water, water solution containing nanometer titanium dioxide, and water solution containing nanometer titanium dioxide and succinic acid under various time periods of UV irradiation

	Treating condition			Properties	
Number of samples	Nano TiO_2 conc. (wt%)	Succinic acid conc. (wt%)	Irradiation time period (hr)	PH value	Conductivity (μs/cm)
1	0	0	0	6.85	3.29
2	1	0	0	3.54	53
3	1	0	1	4.29	58
4	1	0	5	5.07	65
5	0	10	0	2.20	1990
6	0	10	1	2.20	2020
7	0	10	5	2.17	2330
8	1	10	0	2.24	2130
9	1	10	1	2.24	2740
10	1	10	5	2.24	2890

Note: The concentration of SUA in liquid phase for sample 8, 9, and 10 are 99.5, 95.5, and 84.9 wt%, respectively

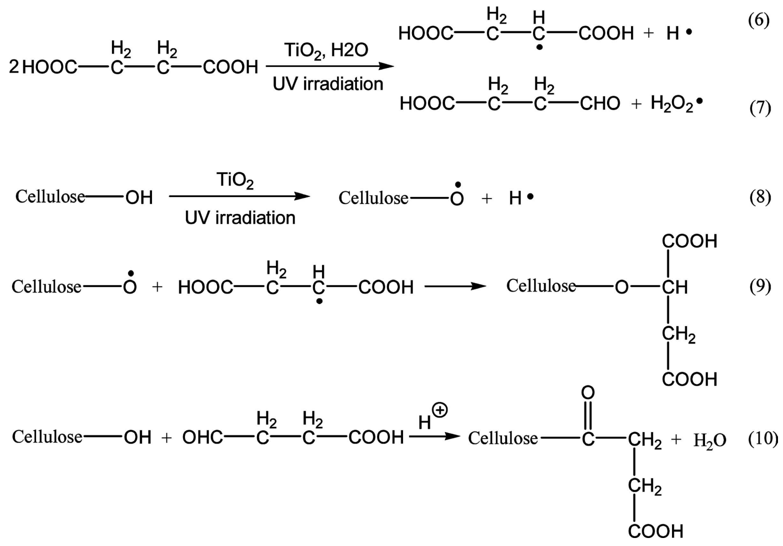
water, the pH value is decreased to 3.54 and the conductivity value is increased to 53. The slight increase of acidity and conductivity of the pure water containing nano-TiO_2 particles might be the residue of acid after production. Prolonging UV irradiation time period increases the values of pH and conductivity but only slightly. As succinic acid alone is added into the pure water, the pH values are decreased and the conductivity values are increased significantly. Prolonging UV irradiation time period scarce changes the pH value but increases the conductivity value. However, the addition of both SUA and nano-TiO_2 particles into the pure water makes the pH value decreasing significantly but the same as those of succinic acid alone. Meanwhile, the conductivity values of the pure water containing SUA/nano-TiO_2 are increased significantly and are higher than the summation of SUA alone and nano-TiO_2 alone for all UV irradiation time periods. The significantly increase on the conductivity values but scarcely change on the pH values for the pure water containing both SUA and nano-TiO_2 should be attributed to the photo-reduction among water, SUA, and nano-TiO_2 under UV irradiation that will liberate a lot amount of free radicals.

First, the liberation of the OH and O_2H free radicals and the ions from the Eqs. (1) to (5) of Scheme 1 shown in the section of introduction could explain that the pH and the values of conductivity of pure water containing TiO_2 particles irradiated with UV are higher than that of pure water and are increased with the increasing of irradiation time period (samples 2–4 of Table 2). It is well known that organic acid molecules could partially hydrolyze in water medium to liberate the hydrogen ions, which could significantly increase the acidity and conductivity of pure water contained the SUA (sample 5 of Table 2). We believe that the further hydrolysis of SUA could be occurred after prolonging UV irradiation time period, which could further increase the acidity and conductivity of SUA water solution (samples 6 and 7 of Table 2). As the SUA and nano-TiO_2 were added to the pure water at once, the acidities of the both (sample 2 and sample 5 of Table 2) are neutralized to have the pH value slightly higher than SUA alone, whereas the conductivity value is raised. After prolonging UV irradiation time period, the hydrolysis of SUA and the consumption of hydrogen ions (Eq. (5) of Scheme 1) might be in the state of balance and, therefore the acidity values of the solutions are remaining constant; however, the sustaining generation of free radical (Eqs. (2), (3), and (5) of Scheme 1) could increase the conductivity of solutions (samples 8, 9, and 10 of Table 2).

Mechanism of crosslinking reaction

For confirming the possible crosslinking reaction mechanism between the SUA molecules and cellulose molecule, Carboxymethylcellulose (CMC) was selected as a model molecule of cotton cellulose for the un-solubility of cellulose powder in water. The interesting and important absorbing bands are that of –CH$\underline{\text{OH}}$ (1060 cm^{-1}) [13] for CMC (Fig. 5(a)). After the sample of the mixture of CMC and SUA in the presence of nano-TiO_2 catalyst was irradiated, the IR spectra (Fig. 5(c)) were changed significantly. This spectrum shows that there is a new absorption band at about 1045 cm^{-1} appears and the original absorption band at about 1060 cm^{-1} still exists. This new generated absorbing band is believed to be an ether bond [13]. In addition, Fig. 5(c) reveals another new absorption band generated at about 1708 cm^{-1} as compared with that in Fig. 5(b) for the SUA alone. This is referred to be the formation of ketone group [13]. The ether and ketone groups generated for the sample of CMC/SUA clearly indicate that the crosslinking reaction between cellulose molecules and SUA molecules is occurred. We suggest that the crosslinking reaction in this study has two main ways shown in Scheme 2.

From the predominant base on the experiment results shown in this paper, we suggest that the crosslinkig reaction of succinic acid catalyzed by nanometer titanium dioxide under UV irradiation is that of following. First, the succinic acid molecules adsorbed on the surface of the nanometer



Scheme 2 The possible crosslinking reaction catalyzed with nano-TiO_2 under UV irradiation

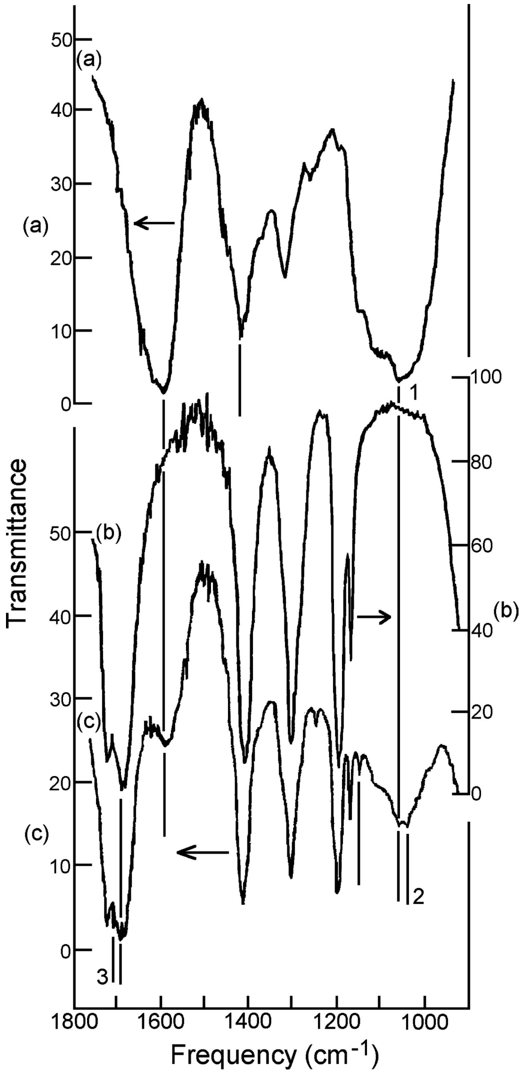


Fig. 5 The IR spectra of the (a) carboxymethylcellulose alone, (b) SUA alone, and (c) irradiated the mixture of CMC and SUA. 1.1060 cm^{-1}, 2.1045 cm^{-1}, 3.1708 cm^{-1}

titanium dioxide particles are subjected to the reaction of photo-reduction under UV irradiation to form the SUA free radicals (Eq. (6) of Scheme 2) and the aldehyde group contained in SUA (Eq. (7) of Scheme 2). The free SUA radical is then contacting with the free radical of cellulose molecule (Eq. (8) of Scheme 2) generated from photo-reduction under UV irradiation to complete the free radical crosslinking reaction (Eq. (9) of Scheme 2) [16–18]. On the other hand, the aldehyde group of SUA (Eq. (7) of Scheme 2) could crosslink with cellulose molecules by reacting the hydroxyl group of cellulose in the presence acid catalyst [14, 15]. Additionally, the photo-reduction under UV irradiation will also break the cellulose molecular chain on the surface of cotton fibers [19], which will increase the stress concentration of cellulose molecular chains as they are bearing stretch so as to decrease the strength of the treated fabrics. However, as the concentrations of nano-TiO_2 catalyst used were higher than the specific value, the crease recovery of the treated fabrics will not keep on increasing and the tensile strength (Table 1) will keep on decreasing for the damage of cotton fiber and crosslinking agent by photo-reduction.

Conclusions

In this study, we used succinic acid crosslinking agents in the presence of nanometer TiO_2 catalyst under the irradiation of UV light to study the crosslinking reaction and the photo-reduction of succinic acid. We find that the carboxylic acid group of succinic acid can be photo-reduced to form the aldehyde group. The crystalline structure of SUA adsorbed on nanometer TiO_2 particles can be changed under UV irradiation. The photo-reduction of succinic acid in the presence of nanometer titanium dioxide in water medium under UV irradiation can increase the values of conductivity for the creation of free radicals. We suggest that the crosslinking reactions in this study are the reaction between aldehyde group of succinic acid and the hydroxyl group of cellulose and the reaction between free radical of succinic acid and the free radical of cellulose. The stress concentration caused by crosslinks and the damage caused by the photo-reduction is the main factors to decrease the tensile strength of the treated fibers.

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