



The Function of Cross Linker Carboxylic acid for TiO₂/Chitosan/SiO₂ Coated as Self Cleaning Fabrics

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ABSTRACT

The chemical compound TiO₂/Chitosan/SiO₂ is a photocatalyst with a self-cleaning capability against dye contaminations. Morphologically, it has an anatase structure with 13.1 nm of crystallite size, spherical shape, and E_g = 3.209 eV as characterized by X-ray diffraction, TEM, and UV-DRS. The self-cleaning capability of TiO₂/Chitosan/SiO₂ against the malachite green dye spot was optimized using two carboxylic acid cross-linkers namely 1,2,3,4- Buthane Tetra Carboxylic Acid (BTCA) and Chloro Acetic Acid (CAA). The optimization in enhanced the growth of ester covalent interaction with the functional groups of textile fiber was performed gradually in CAA and directly in BTCA to produce a self-cleaning textile. The self-cleaning efficiency of cross-linker under the UV irradiation (536 lux for 60 min.) was 96% and 69.96% in CAA and BTCA, respectively. The FT-IR analysis revealed that the ester covalent interaction among the cross-linker, cotton fiber, and TiO₂/Chitosan/SiO₂ nanocluster could be determined by the intensity change of C=O stretching of the functional group at 1700-1710 cm⁻¹. The intensity was higher in CAA (15.03%) than BTCA cross-link (12.04%). The superficial morphological feature of the cotton fiber as observed by SEM depicted that TiO₂/Chitosan/SiO₂ particles were dispersed more evenly in the CAA than BTCA. The TiO₂/Chitosan/SiO₂ nanocluster with a CAA cross-link is reliable to be used indesigning a high-quality self-cleaning textile.

Keywords: Cross linker, BTCA, CAA, self-cleaning, Malachite green.

INTRODUCTION

Textile is certainly needed infashion industries as well as various medical and office equipments, and other daily needs. The cotton textile is preferable as compared to the other materials due to its ease of maintenance, the strength, absorption, and affordability¹. However, the higher absorption

of cotton fiber makes it easy to be contaminated by dirt and dyes, thus it is also difficult to be removed out². As an alternative solution, some researchers modified the textile cotton fiber to acquire the self-cleaning capability against the dye spots contaminating the textile surface. The self-cleaning textile is practically effective to shorten the contact time of the dirt on the textile. Consequently, the dirt



could be easily cleaned and the deterioration of the textile fiber could be maximally prevented^{3,4}.

The nano-oxide metals including TiO_2 , ZnO or its composites are commonly used in modifying the cotton fiber due to their functional capability as the sunscreen, self-cleaning agents and antimicrobes³⁻⁵. The capabilities of the substances are related to their pivotal role as photocatalysts. Hence, they could remove the dye on the fiber by the photocatalytic mechanism. The previous study by Wijesena, applied this concept to develop the self-cleaning materials by using the TiO_2 and ZnO nanoparticles against the dye spots of methyl orange⁴. Moreover, Pakdel and Doud used TiO_2 and SiO_2 nanocomposites to enhance the functional capability of self-cleaning textile against various dyes including methyl orange^{4,6,7}, methylene blue^{3,8}, disperse yellow and C.I. reactive red⁹, and acid red¹⁰.

The coating of nano-oxide metal on the cotton fiber basically requires the cross-link agent, a carboxylic group-consisting compound, in order to promote the covalent interaction with the fiber cellulose and TiO_2 by means the electro statics interaction¹¹. The stability of TiO_2 - SiO_2 nanocluster's coating on the cotton fiber is determined by the type of carboxylic acid used as the cross-linker. A study by Karimi demonstrated that the use of succinate acid as across-linker in the TiO_2 - SiO_2 particle's coating could stand its stability up to 85% against washing, while it was only 11% without a cross-linker^{5,11,12}.

Furthermore, our previous study revealed that acrylic acid is an effective cross-linker to develop a textile acquiring the antimicrobe and self-cleaning capability against methylene blue dye⁴.

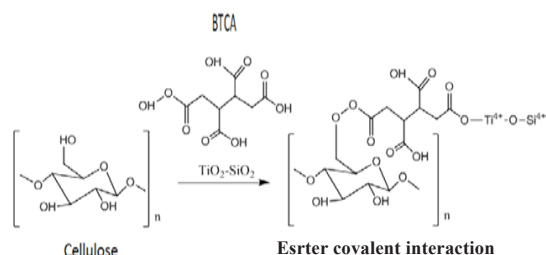


Fig. 1. Mechanism of ester covalent interaction among fiber cellulose, TiO_2 /Chitosan/ SiO_2 nanocluster and BTCA cross-link

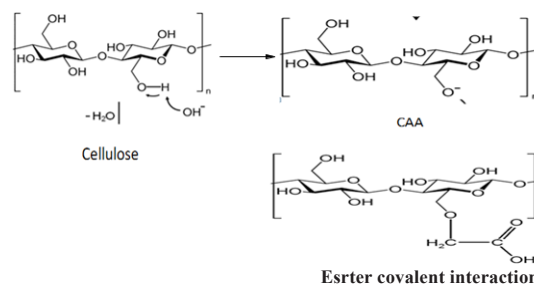


Fig. 2. Carboxymethylation mechanism of cellulose by sodium mono-chloroacetic⁴

In this present study, we used two cross-linkers including 1,2,3,4 butane tetra carboxylic acid (BTCA) and chloroacetic acid (CAA) with two different coating methods by means direct and gradual coating, respectively. It aimed to enhance the self-cleaning capability against the dye spot of malachite green on a textile cotton fiber with a densely TiO_2 /Chitosan/ SiO_2 coating.

EXPERIMENTAL

Materials

The instruments used in this study were magnetic stirrer, furnace, oven, analytical balance, spin coating machine, optic microscope, SEM-EDX (Hitachi S-3400N), FT-IR (Thermo Scientific: Nicolet iS10), XRD (X'Port PAN Analytical), UV-Vis DRS (Shimadzu UV-Vis 2450), and TEM (JEOL JEM 1400). The materials and chemicals were silky textile cotton, hydrochloric acid (HCl, Merck), acetic acid (CH_3COOH , Merck), aquadest, titanium isopropoxide ($\text{C}_{12}\text{H}_{28}\text{O}_4\text{Ti}$) (Aldrich 97%), diethanolamine ($\text{C}_4\text{H}_{11}\text{NO}_2$) (Merck), isopropanol ($\text{C}_3\text{H}_8\text{O}$, Merck), tetra ethyl ortho silicate ($\text{C}_8\text{H}_{20}\text{O}_4\text{Si}$, Merck), chitosan ($\text{C}_6\text{H}_{11}\text{NO}_4$)_n, 1,2,3,4-butane tetra carboxylic acid ($\text{C}_8\text{H}_{10}\text{O}_8$, BTCA, Merck), chloroacetic acid ($\text{C}_2\text{H}_3\text{O}_2\text{Cl}$, CAA, Merck), ethyl tri methyl ammonium bromide ($\text{C}_{13}\text{H}_{33}\text{N}(\text{CH}_3)_3\text{Br}$, Merck), detergent, sodium carbonate (Na_2CO_3), and malachite green ($\text{C}_{23}\text{H}_{26}\text{N}_2\text{Cl}$).

METHODS

Synthesis of TiO_2 /Chitosan/ SiO_2 nano cluster

The powder of TiO_2 /Chitosan/ SiO_2 nanocluster was synthesized using a sol-gel method with the titanium isopropoxide (TIP) and tetra ethyl ortho silicate as precursors. The sol solution consisted of A solution (TIP and DEA in isopropanol solvent; 1:2:2 in M) and B solution (TEOS and HCL 2 M in isopropanol; 1:2:2). The A and B solution

was homogenized separately for 30 min. in RT. The combination of A and B solution was prepared as a mixed sol with a composition of Ti and Si 3:2. Furthermore, the chitosan/acetic acid suspension (1:20) and CTAB (1:5) were added to the sol. The mixed sol was set at pH 10-11 and homogenized for 8 h followed by the heating at 110-120°C or 15 h to produce a gel. The gel was then calcinated at 500°C for 3 h to obtain the powder of TiO₂/Chitosan/SiO₂ nanocluster and subsequently morphologically characterized using XRD, UV-Vis DRS, and TEM.

Coating of textile cotton fiber

The textile cotton of size 64 m² was firstly washed using detergent 2 g/L and subsequently rinsed with aquadest and dried up at 80°C for 5 min. Furthermore, it was dewaxed using Na₂CO₃ 0.01 g in 25 mL aquadest for 5 min. at 100°C and rinsed with aquadest to adjust the pH 6-7, followed by heating at 80°C for 5 minute. The textile cotton was directly soaked in 1 M BTCA cross-link for 12 hours. In another treatment, the textile was firstly soaked into 2 M NaOH for 30 min. then into 1 M CAA. After the treatment using BTCA and CAA, the textile was heated at 80°C for 5 min. then coated using a suspension of 1% TiO₂/Chitosan/SiO₂ by means dip-spin coating for 90 min. It was then dried up at 80°C for 15 min. and subsequently analyzed using FT-IR, Photo Optics, XRD, and SEM- EDX.

Self-cleaning test of the textile cotton fiber

The self-cleaning test was carried out by observing the degradation of the malachite green dye spot on the coated cotton fiber under the UV irradiation (536 lux) in 0-2 h time window. The 4x4 cm textile dropped by 50 µL of 150 ppm malachite green was designated for a qualitative test, while the 1x1 cm textile soaked into 20 mL of 5 g/L malachite green was used for a quantitative test. The textile sample was observed in the darkroom for 30 min. and the absorption was subsequently noted as A₀. Furthermore, it was irradiated by UV light in 0-2 h then the absorption was noted as A. The dye degradation rate (Ef) was calculated by the formula as follow:

$$Ef = \frac{A_0 - A}{A_0} \times 100 \%$$

RESULTS AND DISCUSSION

Morphological characters of TiO₂/Chitosan/SiO₂ nanocluster

The TiO₂/Chitosan/SiO₂ nanocluster yielded

by the sol-gel synthesis method was identified using XRD, UV-Vis DRS, and TEM to determine the morphological characters related to its prospective application as a self-cleaning material. It was found that the nanocluster depicted anatase structure with 13.1 nm crystallite size at the highest intensity 2θ = 25.3°. The anatase intensity order of TiO₂/Chitosan/SiO₂ was 2θ = 25.3°; 36.93°; and 48° as elucidated by XRD analysis (Fig. 3). The crystallite size was calculated by the Scherrer formula as follow:

$$D = \frac{k \lambda}{\beta \cdot \cos \theta}$$

D (crystallite size), k (constant; 0.89)λ, (wavelength of X rays), β (value of full width at half maximum, FWHM), θ and (diffraction angle)^{6,13,14}.

The crystallite size could be modified by adding the dopant of SiO₂ and chitosan. The SiO₂ functions to form the pores and to extend the surface area^{15,16} while the chitosan plays a role as a template of porosity during the condensation of the crystallite and enhances the SiO₂ dispersion on TiO₂ surface¹⁶. It has been demonstrated that when the TiO₂ and SiO₂ were composited, it could inhibit the structural transformation of anatase to rutile phase¹⁵. Moreover, we have previously reported that the distribution of crystallite size was affected by the sol and gel preparation process¹⁸. The sol preparation for 8 h and gel polycondensation for 15 h noticeably increased the distributional uniformity of crystallite size of TiO₂/chitosan/SiO₂ nanocluster. The pattern of UV-DRS spectrum of TiO₂/chitosan/SiO₂ (presented in Fig. 3, left panel) was then converted using Plank equation [$E_g = \frac{h \cdot c}{\lambda}$] (Fig. 3, right panel) with E_g (band gap), h (Plank constant, 6.626 x 10⁻³⁴ J.s), c (light speed, 3 x 10⁸ m.s⁻¹) and (wavelength, in m). It was revealed that the maximum wavelength was 386.3 nm and the E_g was 3.209 eV. Hence, the photocatalytic reaction of the TiO₂/Chitosan/SiO₂ could be induced by the UV light (= 385 nm) with the energy equals the E_g value¹⁹.

The TEM pattern (Fig. 4) illustrates the 3-dimensional feature of TiO₂ hybridized with SiO₂ and chitosan. It was found that the TiO₂/Chitosan/SiO₂ nanocluster has a spherical crystallite shape and non-agglomerated structure. The SiO₂ and chitosan were amorph, and SiO₂ and TiO₂ formed a core-shell formation with the chitosan functioned as the cross-linker²⁰. The TEM-derived picture, in consistent with

the XRD spectral pattern, indicated that TiO_2 has the highest crystallite intensity at $2\theta = 25.3^\circ$ in anatase phase.

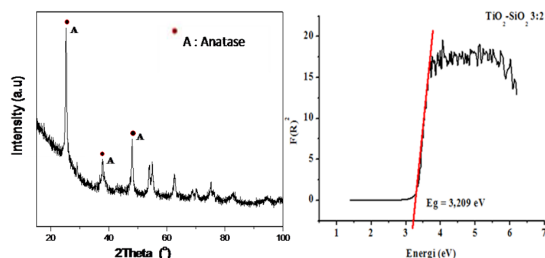


Fig. 3. The XRD and UV-DRS spectral patterns of $\text{TiO}_2/\text{Chitosan}/\text{SiO}_2$

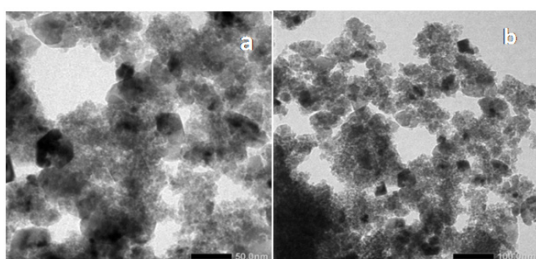


Fig. 4. TEM of $\text{TiO}_2/\text{chitosan}/\text{SiO}_2$ (Ti : Si : (3:2) at (a) 50 nm (b) 100 nm FT-IR analysis

The FT-IR analysis of the cotton fiber coated by $\text{TiO}_2/\text{Chitosan}/\text{SiO}_2$ with two cross-linkers (CAA and BTCA) produced the FT-IR spectrum as presented in Fig. 5. The patterns of the spectrum indicated that the intensity difference was observed at 1710 cm^{-1} identified as the covalent ester formation's zone (C=O stretching)²¹. The CAA cross-link has a higher intensity than BTCA, suggesting that the gradual growing of ester group in CAA could enhance the thickness of $\text{TiO}_2/\text{Chitosan}/\text{SiO}_2$ coating on the fiber by means the electrostatic interaction⁸.

The FT-IR spectrum of the uncoated fiber (Fig. 5a) depicted its absorbance at cm^{-1} with the intensity 10.1%, while the coated fiber by CAA cross-link (Fig. 5b) indicated the shifted wave number to 1710.04 cm^{-1} and the increased intensity to 15.03%. Likewise, the coated fiber by BTCA cross-link (Fig. 5c) also demonstrated the shifted wave number to 1708.5 cm^{-1} and increased intensity to 12.4%. The shiftings of the wave number indicated the chemical esterification's interaction between the cellulose of cotton fiber and the carboxylic cross-link as illustrated in Figure 1.

The cotton fiber coated by $\text{TiO}_2/\text{Chitosan}/\text{SiO}_2$ nanocluster with a CAA cross-link depicted the

different FT-IR spectrum as compared with BTCA cross-link. Interestingly, the absorbance intensity at 3400 cm^{-1} and 1529 cm^{-1} was also observed. The occurrence of the absorbance intensity at 3400 cm^{-1} might be resulted from the combination of carboxylic absorbance and alcoholic $-\text{OH}$ stretchings's absorbance. The absorbance intensity at 1529 cm^{-1} was reported as an absorbance of the carboxylic ionic group⁴.

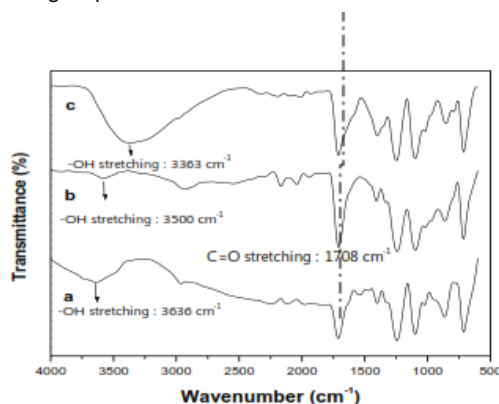


Fig. 5. The FT-IR of cotton fiber in (a) uncoated (b) coated with $\text{TiO}_2/\text{chitosan}/\text{SiO}_2$, 1 M BTCA (c) coated with $\text{TiO}_2/\text{chitosan}/\text{SiO}_2$, 1 M CAA

Morphological analysis using SEM-EDX

The morphological observation by using SEM suggested the difference in the features of cotton fiber treated with a CAA cross-link and BTCA cross-link (Fig. 6a-c). A cross-link plays a pivotal role in the formation of ester covalent interaction with the hydroxyl group of fiber, thereby the coating of the $\text{TiO}_2\text{-SiO}_2$ nanocluster on the textile. Meanwhile, the chitosan in $\text{TiO}_2\text{-SiO}_2$ provides the nitrogen base in order to enhance the amide covalent interaction and thereby trapping the $\text{TiO}_2\text{-SiO}_2$ by means the electrostatic interaction⁶. The difference in the cross-link determines the distributional uniformity of the $\text{TiO}_2/\text{Chitosan}/\text{SiO}_2$ nanoparticle on the textile fiber surface. It was found that in the CAA cross-link-treated fiber, the coating particles dispersed more evenly and densely on the surface of the textile as compared with the BTCA cross-link-treated fiber.

Chen *et al.*, reported that cotton fiber coated by TiO_2 depicted the rough surface feature. The roughness of the surface affects the self-cleaning capability of the fiber²². The results of SEM analysis (Fig. 6) and the pattern of EDX (Fig. 7), taken together, suggested that the technique of the growing an ester covalent interaction on the fiber determines

the amount of $\text{TiO}_2\text{-SiO}_2$ coating, its distributional uniformity as well as the stability of the coating. Based on the EDX analysis, the composition of C, O, Ti and Si elements was equal to the composition of Ti and Si used as the precursors in the $\text{TiO}_2\text{-SiO}_2$ synthesis (3:2 in M). The elements found in the cotton fiber coated by $\text{TiO}_2/\text{Chitosan}/\text{SiO}_2$ with a BTCA cross-link consisted of C = 27.6%, O = 17.97%, Ti = 2.36 %, and Si 0.90 %. Otherwise, the elements in the fiber with a CAA cross-link composed of C = 50.73 %, O = 38.64 %, Ti = 2.46 %, and Si 1.45%.

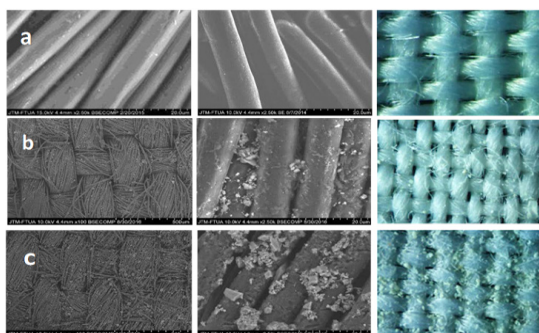


Fig. 6. The SEM pattern and optical feature of cotton fiber in (a) uncoated and (b) coated by $\text{TiO}_2/\text{chitosan}/\text{SiO}_2$ with a BTCA cross-link and (c) CAA cross-link

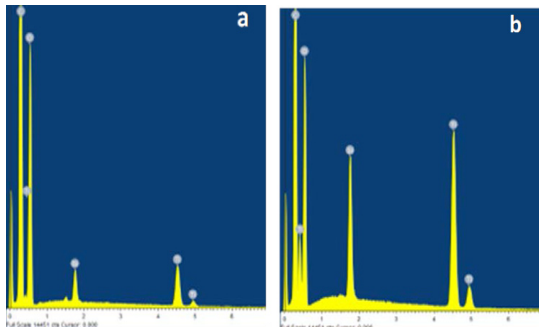


Fig. 7. The EDX pattern of cotton fiber coated by $\text{TiO}_2/\text{chitosan}/\text{SiO}_2$ (3 : 2) with (a) BTCA (b) CAA Cross link

Self-cleaning test

The self-cleaning capability of the cotton fiber coated by $\text{TiO}_2/\text{Chitosan}/\text{SiO}_2$ nanocluster against malachite green dye spot was evaluated both qualitatively and quantitatively. The qualitative test (Fig. 8) revealed that the cotton fiber coated by $\text{TiO}_2/\text{Chitosan}/\text{SiO}_2$ with a CAA cross-link acquired the capability to degrade the malachite green dye spot five times stronger as compared with BTCA cross-link. This result is in accordance with the findings by FT-IR and SEM analysis demonstrating that the CAA cross link noticeably elevated the abundance of $\text{TiO}_2/\text{Chitosan}/\text{SiO}_2$ on the textile fiber.

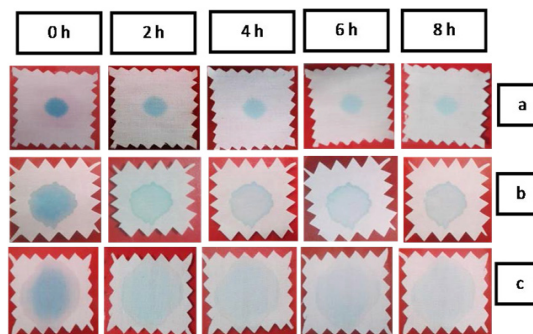


Fig. 8. Degradation of malachite green dye spot after UV irradiation for 0-8 h on the cotton fiber with (a) uncoated and (b) coated by $\text{TiO}_2/\text{chitosan}/\text{SiO}_2$ with BTCA cross link and (c) CAA cross-link

The quantitative test for the self-cleaning capability of the cotton textile was conducted by measuring the absorbance of malachite green. The result (Fig. 9) indicated that the efficiency of self-cleaning capability was higher in CAA cross-link (95.59%) as compared with BTCA cross-link (69.96%) under the UV irradiation for 60 minutes. This finding is also in accordance with the previous result by means qualitative test showing the cotton fiber treated by CAA cross-link acquired a higher degradation capability against malachite green as compared with BTCA cross-link.

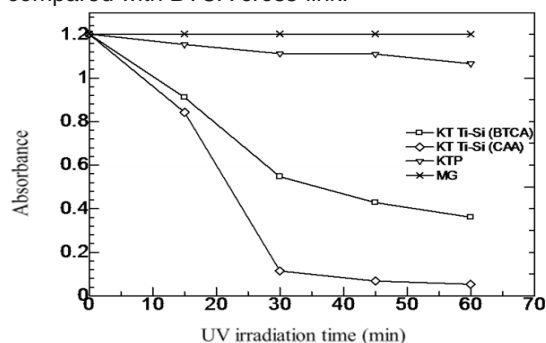


Fig. 9. The relationship curve of between UV radiation time and degradation rate of malachite green ($5.0 \text{ mg}\cdot\text{L}^{-1}$).

CONCLUSION

In this recent study, a self-cleaning textile cotton fiber coated by $\text{TiO}_2/\text{Chitosan}/\text{SiO}_2$ nanocluster was successfully developed. The $\text{TiO}_2/\text{Chitosan}/\text{SiO}_2$ morphologically depicted an anatase structure, with 13.1 nm of crystallite size and a band gap (E_g) = 3.20 eV. This particle acquired the self-cleaning capability against malachite green dye under the UV irradiation ($\lambda = 365 \text{ nm}$; 536 Lux). The increase of self-cleaning efficiency was determined by cross-link

functionalization in consistent with the abundance of TiO₂/Chitosan/SiO₂ coating on the cotton fiber. The gradual cross-link functionalization using CAA could highly optimize the self-cleaning efficiency (96.0%) as compared with BTCA (69.96%). The functional optimization of CAA was noticeably correlated with the morphological features revealed by SEM, XRD, and FT-IR analysis.

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