GROWTH CONTROL OF ZnO-TiO₂/CHITOSAN NANOROD ON COTTON TEXTILE FIBER BASED ON DIFFERENT CHLORO ACETIC MOLAR COMPOSITION AS CROSS LINKER

Yetria Rilda^{1,*}, Dyah Rahayu Ratyaningsih¹, Yulia Eka Putri¹, Refinel¹
Syukri¹, Anthoni Agustien² and Hilfi Pardi³

¹Department of Chemistry, Faculty Mathematics and Natural Sciences of Andalas University,
Kampus Unand Limau Manis Padang, 25163, Indonesia

²Department of Biology, Faculty Mathematics and Natural Sciences of Andalas University,
Kampus Unand Limau Manis Padang, 25163, Indonesia

³Department of Chemistry Education, Faculty of Teacher Training and Education Maritim Raja
Ali Haji University, Senggarang, Tanjungpinang 29111, Indonesia

*E-mail: yetriarilda@sci.fmipa.ac.id

ABSTRACT

The objective of this research was to synthesize ZnO-TiO₂/chitosan patterned nanorods with the molar composition of Zn and Ti at 3: 1 and pH of 13.0 using the Zinc Nitrate precursor as a source of ZnO and Titanium Iso Propoxide as doped TiO₂. ZnO-TiO₂/chitosan nanorods (Zn-Ti NRd) were later grown on textile cotton fibers by dip-spin-coating technique through the optimization of the cross-linker function of Chloroacetic Acid (CAA) and NaOH base based on the differences in the molar composition, 3:1, 2:1, 1:1 and 1:2. The interaction of hydroxyl groups between the cellulose fibers - CA carboxylic groups and Zn-TiNRd showed the intensity of C=O stretching at 1700 cm⁻¹ which was indicated as covalent ester interaction. With respect to the results of XRD characterization, Zn-Ti NRd crystals measuring 38.8 nm and SEM-EDX and TEM-SAED showed nanorod patterned particles. Moreover, photocatalytic activity showed an increase in the antibacterial properties of Zn-Ti NRd against *Bacillus subtilis* (ATCC 6633) with a zone of inhibition recorded as 23 mm after 24 hours of ultraviolet irradiation at 1:2 CAA and NaOH molar composition. An increase was observed in the mechanical properties of the fiber-based on the measured tensile strength of 25 cm with warp direction of 227 kg, feed direction at 154 kg and the tear strength by 0.64 kg and 0.56 kg respectively.

Keywords: Nanorods, ZnO-TiO₂/chitosan, Chloroacetic Acid, Mechanics, *B. subtilis* (ATCC 6633)

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INTRODUCTION

Zinc Oxide (ZnO) is a semiconductor metal oxide compound with a band gap of 3.37 eV and 60 meV hole electron bond which makes it show absorption when ultraviolet -Visible light is used as a source of photons.¹ ZnO has magnetic and piezoelectric as well as conductivity and photocatalyst properties.^{2,3} Its photocatalytic nature is due to the excitation-electron process of the valence and conduction band when photons are absorbed to form electron-holes which consequently free the pair of free radicals (ROS) after contact with Water and Oxygen. However, the free radicals (•OH) and (•O₂)⁴ are oxidative in most organic compounds such as microbial, dyes, peptides.^{4,5} ZnO compounds have been widely used in several fields, for example, they are used as additives in the cosmetics, paint, and textile industries.⁶ ZnO has several advantages one of which is the growth of cheaper, non-toxic, and environmentally friendly large-scale ZnO nanorods.⁷ The performance of these nanorods can, however, be improved through the formation of composites with doped TiO₂ and chitosan to modify their morphology such as size, structure, and surface area.⁸ Wijesena (2015)⁹ reported that TiO₂ and ZnO photocatalyst nano-coatings were more effective and economical for the preparation of anti-bacterial textiles. Rilda et al., (2019)¹⁰ also

reported that the use of TiO_2 compounds modified with SiO_2 and chitosan has been proven to be superior for the preparation of multi functional cotton textiles with anti-bacterial, anti-fungal, and anti-stain properties.^{10,11} Moreover, the use of photocatalytic processes like Advanced Oxidation Process (AOPs) has been able to completely destroy the microbial with 99% efficiency, overcome the problem of bacterial cell contamination, reduce the risk of infection, and also interesting to be applied in several fields including medical textiles.¹²⁻¹⁵

In this paper, $\text{ZnO-TiO}_2/\text{chitosan}$ nanorods (ZnO NRd) were synthesized by the simpler and more economical precipitation method. The growth of ZnO NRd in textile fibers was used as a cross-linker of CAA with NaOH substitution base and further used for the preparation of anti-bacterial textiles. The chemical composition, morphology and photocatalytic properties of ZnO NRd in textile cotton fibers were analyzed and the mechanism of photocatalysis was discussed.

EXPERIMENTAL

Instruments

The equipment used include Ultraviolet-Visible Spectrophotometer (Thermo Scientific Evolution 201 UV-Vis Spectrophotometer), SEM-EDX (Hitachi 5-3400N), XRD (X'Port PAN Analytical), FT-IR (Thermo Scientific: Nicolet iS10), UV-Vis (Shimadzu UV-Vis 2450), TG-DTA, TEM-SAED (Philips CM 12 Analysis Docuversion 3.2 image analysis system) and tensile strength (KJ-C045).

Materials

The materials used include cotton textiles, zinc nitrate (Merck), ZnO (Merck), titanium isopropoxide (Aldrich 97%), NaOH (Merck), $\text{C}_6\text{H}_{12}\text{N}_4$ (Merck), diethanol amines (Merck), isopropanol (Merck), commercial chitosan, chloroacetic acid (Merck), CTAB (Merck), acetic acid (Merck), nutrient agar media (NA), and the *Bacillus subtilis* bacterial culture (ATCC 6633) (College of Life Sciences, ITB).

Research Procedures

Synthesis of $\text{ZnO-TiO}_2/\text{Chitosan}$ Powder

ZnO seed at 0.1 M was dissolved in aquabides and added to a mixture of $\text{Zn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ at 0.1 M, NaOH at 0.4 M and Hexamethylenetetramine at 0.2 M, and the mixture denoted as (A) was homogenized at 60 °C for 2 hours. The mixture (B) consists of TIP and DEA in isopropanol at 1: 2: 2 M solvent and homogenized for 30 minutes. The mixtures (A) and (B) were added to CTAB (1: 0.2) M and chitosan (1: 0.2) M and homogenized for 4 hours, dried at 110 °C for 12 hours, and calcined at 600 °C for 7 hours.

$\text{ZnO-TiO}_2/\text{Chitosan}$ Coatings in Textile Cotton Fibers

Textile cotton at 8x8 cm was dewaxed with Na_2CO_3 3.7×10^{-3} M, washed with aquadest, and dip-coated with a cross-link of chloroacetic acid (CAA) and NaOH varied at a molar composition of 3:1, 2:1, 1:1, and 1:2 Molar for 12 hours. It was later dried at 70 °C for 15 minutes. The cotton fiber was coated with $\text{ZnO-TiO}_2/\text{chitosan}$ 1% using the dip-spin coating method for 90 minutes.

Anti-Bacterial Test of Textile Cotton Fibers

Bacillus subtilis bacterial isolate (ATCC 6633) was inoculated on NA media provided in the Petridish by scraping bacterial isolates in a zig-zag manner after which a 0.6 mm textile fiber was placed on the surface of the media. The incubation was conducted in a UV incubator with an intensity of 536 Lux for 24-48 hours and the zone of inhibition was measured at 2 cross-sectional points.

RESULTS AND DISCUSSION

Synthesis of ZnO/Chitosan and $\text{ZnO-TiO}_2/\text{Chitosan}$ Powder

Analysis of FT-IR

The FT-IR analysis aimed to discover the interactions between organic and inorganic compounds from the composition of the raw material used in the material preparation process. The specific peaks of functional groups were described as intermolecular interactions in chemical processes. Figure-1 shows the difference in intensity between ZnO/Chitosan and $\text{ZnO-TiO}_2/\text{Chitosan}$ in the -OH range and the

substitution of the TiO_2 caused a shift in intensity to a larger wave number. At wave numbers $3445\text{--}3455\text{ cm}^{-1}$ and N-O at $2100\text{--}2200\text{ cm}^{-1}$, the active absorption was chitosan groups while $1600\text{--}1650\text{ cm}^{-1}$ area indicated buckling vibrations - NH amide and Zn-OH . Moreover, there was an indication of the methyl group (CH_3) at wave number $1400\text{--}1450\text{ cm}^{-1}$ while at the range of $850\text{--}900\text{ cm}^{-1}$, an intensity of Zn and O was observed. Furthermore, at $500\text{--}750\text{ cm}^{-1}$, the intensity of Zn-O-Ti increased with the substituted Ti .¹⁶

Fig.-1: FT-IR Spectrum of (a) ZnO/Chitosan (b) $\text{ZnO-TiO}_2/\text{Chitosan}$

Analysis of Scanning Electron Microscopy - Expensive Diffraction X-Ray (SEM-EDX)

This was conducted to observe and determine the quantitative composition of elements contained in the material. Figure-2 shows the morphology of the ZnO NRd synthesized at pH 13 to be shaped like bars or nanorods with a particle size of 3 micrometers in length and 400 nanometers in diameter. The EDX test showed the initial composition of the ratio between the elements in the ZnO NRd nanomaterial formed, Zn and Ti , was 3:1. Moreover, the EDX composition for ZnO and TiO_2 was approximately the same and was found to be O at 77.15%, Ti at 6.15%, and Zn at 19.7%.

Fig.-2: Morphological Patterns (a) SEM and (b) Analysis of EDX from $\text{ZnO-TiO}_2/\text{Chitosan}$

Analysis of Transmission Electron Microscopy (TEM)

The TEM and SAED patterns of the ZnO NRd powder are shown in Figure-3. It was discovered that the TEM's particle distribution was in the three-dimensional form of the rod while SAED particles were arranged regularly to form a crystalline pattern. TEM observations were conducted from calcination at $600\text{ }^\circ\text{C}$ and each of them gave a diameter of crystallite size in the scale range of 38.8 nm.

Fig.-3: Patterns (a) TEM and (b) SAED: 3 Dimensional Patterns of ZnO-TiO₂/Chitosan Nanorods Crystals

ZnO-TiO₂/Chitosan Coating in Textile Cotton Fibers

The growth of ZnO NRd in textile cotton fibers was strongly influenced by the type of cross-link used due to the presence of a carboxylic group needed for the interaction with the hydroxyl cellulose group of the fibers in a covalent ester to ensure the compound is coated.¹⁷ The composition of the Chloroacetic Acid (CAA) was varied with NaOH bases at 3:1, 2:1, 1:1, and 1:2. The growth started with the dyeing textile cotton fibers in the composition of each cross-link for 12 hours and followed by coating with the ZnO NRd suspension through the use of spin coating for 90 minutes. Indications of the coating were visually observed based on the increase in the weight of the textile cotton as shown in Figure-4.

Fig.-4: Conversion of Textile Mass after the Growth of ZnO-TiO₂/Chitosan Nanorods with Differences in the Molar Composition of Cross-links of CAA and NaOH (a) 3: 1 (b) 1: 2 (c) 2: 1 and (d) 1: 2

Figure-4 shows an increase in the mass of textile cotton fibers with different CAA and NaOH compositions. In 1:2 and 1:1, the greatest increase in mass growth of ZnO NRd was observed and the textile cotton fibers were not too rigid but slightly moist. The interactions formed between functional groups were studied based on the mechanism in Figure-4. It further showed the carboxymethylation of cellulose was conducted through hydroxide substitution in the mono-chloroacetate compound to grow carboxylic groups gradually to achieve esterification interactions on the cross-link of CAA and fibers in the ZnO NRd coating process.

FT-IR Analysis of Textile Cotton Fibers

FT-IR analysis was conducted to identify functional groups contained in a nanomaterial consisting of organic and inorganic compositions reacting with each other. In this study, it was used to determine whether there was an interaction between cellulose in cotton fibers and cross-linkers of CAA and ZnO NRd.

Fig.-5: Carboxymethylation Mechanism of Cellulose with Sodium Mono-chloroacetic⁹

Therefore, Figure-6 shows the difference in the spectrum of cotton fiber coated with cross-link of carboxylic acid CAA and NaOH without ZnO NRd and cotton fiber coated with ZnO NRd and cross-link of CAA with different NaOH compositions of 3:1, 2:1, 1:1, and 1:2. Furthermore, the difference in the composition of the substitution bases shows the variations in the intensity of the C=O stretching carbonyl group in the absorption band 1710 cm^{-1} .

This shows the interaction between the hydroxyl groups of textile fiber cellulose with CAA cross-links was conducted in covalent esters. However, the absorption intensity at 1710 cm^{-1} increased with more substitution of the hydroxyl groups of NaOH bases on the mono-chloro side of the CAA. With the use of the ZnO NRd coating, there was the production of a lower intensity than without coating. It was assumed that the cotton fibers conducted by the growth of ZnO NRd interacted in covalent esters.¹⁸ The C=O stretching group was not only derived from cellulose fibers in textile cotton but also from the esterification interactions between cellulose and CAA cross-link compounds that produced a higher absorption peak. Moreover, there was a reduction in the intensity of the absorption peak of 1710 cm^{-1} during the reaction of cotton fiber coated with ZnO NRd and CAA binder due to the fact that the carboxylic group originating from the CAA interacted electrostatically with Zn-Ti to reduce the absorption intensity of C=O stretching. Figure-6 shows the comparison of the intensity of C=O stretching based on the variations of the compositions, 3:1, 2:1, 1:1 and 1:2 and the greatest decrease in absorption intensity shows the composition where ZnO NRd coating is more optimal.

Characterization of SEM-EDX of Textile Cotton Fibers

The morphology of textile cotton coated with ZnO NRd has the particles scattered or distributed in all parts of the fiber with the carboxymethylation of the CAA and NaOH cross-link coating process as observed through the use of Scanning Microscope Electron (SEM). Figure-7 shows (a) the cotton without coating gives the shape of a shiny whole fiber because it is wrapped in pectin and wax.

However, the ZnO NRd coated textile cotton fibers had a rough morphology and the particles were evenly distributed in the presence of CAA cross-links. There was more ZnO NRd coating with more optimal reactions of carboxymethylation reactions through the interaction of CAA in an alkaline atmosphere in

accordance with the mechanism of carboxymethylation as shown in Fig.-5. Moreover, textile cotton fibers with a ratio of 1:2 were more coated with ZnO NRd than 1:1 and according to EDX analysis, the composition of the fiber after modification included O at 52.58%, Ti at 1.99%, Zn at 3.15%, C at 39.35%, and P at 2.93%.

Fig.-6: FT-IR Spectrum of Textile Fiber Coatings on Differences in Composition of CAA and NaOH (a) Without Coating (b) Cross-linker of CAA/NaOH 1:1 (c) CAA/NaOH 3:1 and ZnO NRd (d) CAA/NaOH 2:1 ZnO NRd (e) CAA/NaOH 1:1 ZnO NRd (f) CAA/NaOH 1:2 ZnO NRd

Fig.-7: Cotton Surface Morphology at 150x and 1500x magnification (a) Without Coating (b) CAA and NaOH (1: 1) (c) CAA and NaOH (1: 2)

The higher C and O content is due to the presence of ZnO NRd while the phosphorus content was because of the monosodium phosphate (NaH_2PO_4) which was used as a catalyst to increase the intensity of carbonyl esters and also observed to have contributed to the refractory properties of the cotton fibers.¹⁹

Thermal Analysis of Textile Cotton Fibers

When the material was heated, there was mass decomposition because of the high temperature. Therefore, the Thermogravimetric Analysis (TGA) analysis correlated with Differential Thermal Analysis (DTA) in Figure-8 shows the mass stability of the textile cotton fiber against heat. The modification of the fiber properties with ZnO NRd has the ability to increase its stability to heat by 100 °C than without ZnO NRd which was observed to reduce to 300 °C from 400 °C. The DTA curves describe the differential of the reduction in mass of a material to heat.

Fig.-8: TGA (a), DTA (b). Analysis of (a) Uncoated Cotton and (b) ZnO-TiO₂/Chitosan Coated Cotton Fabrics

The DTA analysis shows there is an exothermic peak in the temperature range of 110-170 °C through the process of loss of water molecules and decomposition of organic residues from textile fibers at 110-200 °C. Moreover, the evaporation at 100-200 °C occurred in the free volume area or the empty portion between the crosslinking polymer molecules or composites.²⁰ At the start of the heating process, the curve pattern showed the mass reduction was linear at the initial stage of the pyrolysis process and it was assumed there was damage to the cellulose compound. As the temperature rose, the mass of the textile cotton decreased or decomposed and began to experience a massive mass decrease in the temperature range of 200-350 °C to indicate the degradation of organic compounds. The ZnO NRd coated textile cotton modified with the addition of the NaH_2PO_4 catalyst had a significant reduction in weight compared to cotton without coating. This is due to the presence of phosphorus in the coated cotton fibers which contribute to its refractory properties.

Mechanical Analysis of Textile Cotton Fibers

Tensile strength is a measure of the maximum load a material has the ability to hold before it is damaged. The measurement of the tensile strength of cotton fibers is based on its length or warp direction and width or feed direction.²¹⁻²⁵ Table-2 shows the composition at 1:2 has higher tensile strength with warp direction at 227 kg and feed direction at 154 kg while 1:1 has a smaller value with a warp direction of 221 kg. This, therefore, means more hydroxyl group substitution leads to more ZnO NRd coatings and, consequently, increased tensile strength and tear properties of textile fibers.

Anti-bacterial Properties of Textile Cotton Fibers

Bacillus subtilis bacterial cells are Gram-positive bacteria that are pathogenic to humans by causing meningitis, endocarditis, eye infections, and others. They are generally used as indicators of anti-bacterial testing because they have a broad microbial spectrum.

Table 1-: Data of Mechanical Properties of Textile Cotton Fibers on the Composition of CAA and NaOH

Test Type		Textile fibers of CAA and NaOH		Test Standards
		1:2	1:1	
Tensile Strength of fabric/2.5 cm	Warp Direction, N (kg)	23.1 (227)	22.5 (221)	SNI 0276:2009 The way of the lint ribbon Clamp 50x105 mm CRE type
	Feed direction, N (kg)	15.7 (154)	15.7 (154)	
Elastic	Warp direction, N (kg)	9.72	9.26	
	Feed direction, N (kg)	15.1	14.8	
Tear strength (Elmendorf)	Warp direction, N (kg)	7.7 (0.78)	7.4 (0.75)	SNI ISO 13937-1:2010
	Feed direction, N (kg)	6.3 (0.64)	5.5 (0.56)

Fig.-9: Zones of Textile Cotton Inhibition (a) Without Coating (b) ZnO-TiO₂/Chitosan Coating with Cross-links of CAA and NaOH (1: 2)Table- 2: *Bacillus subtilis* Inhibition Zone (mm) on the Difference in the Composition of CAA and NaOH

Textile Samples	Inhibition Zone (mm)	
	<i>Pseudomonas Aeruginosa</i> Bacteria	
a. Without treatment	-	
b. Positive control of azithromycin	24.0	
c. CAA and NaOH (1:1)	10.2	
d. ZnO-TiO ₂ /chitosan CAA and NaOH (1:1)	17.0	
e. ZnO-TiO ₂ /chitosan CAA and NaOH (1:2)	23.0	
f. ZnO-TiO ₂ /chitosan CAA and NaOH (2:1)	16.0	

However, anti-bacterial properties are known based on the size of the fiber inhibition in bacterial growth. Therefore, the inhibition zone of the textile cotton coated with ZnO NRd with a molar composition of CAA and NaOH at 1:2 was 23 mm and this value is greater than for 1:1 which was 17 mm. This indicates more ZnO NRd coated textile fiber produced greater effectiveness of the anti-bacterial properties.

CONCLUSION

The synthesis of ZnO NRd nanoparticles was successfully conducted using the precipitation method at a pH of 13.0. The material obtained used to coat textile cotton fibers using a dip-spin method to modify its anti-bacterial functions and properties against *Bacillus subtilis* (ATCC 6633). Moreover, the increased effectiveness of anti-bacterial textiles was determined by the optimization of the NaOH substituted Chloroacetic acid (CAA) cross-link function as an active site for the formation of covalent ester interactions between the fiber-cross linker and ZnO NRd. It was discovered that the molar composition of CAA and NaOH at 1:2 had the highest inhibitory efficiency against the bacterium *Bacillus subtilis* (ATCC 6633) with an inhibition zone of 23 mm. This process also improved the mechanical properties of textile fibers to tensile strength/25 cm with a warp direction of 227 kg, feed direction of 154 kg and tear strength. The warp direction was 0.64 kg, and the feed direction was 0.56 kg.

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