FUNCTIONALIZATION OF COTTON FABRIC WITH ZnO/PVA FOR ANTIBACTERIAL TEXTILE APPLICATION

TAN LEE YAE

MASTER OF ENGINEERING SCIENCE

LEE KONG CHIAN FACULTY OF ENGINEERING SCIENCE
UNIVERSITI TUNKU ABDUL RAHMAN
OCTOBER 2018

ABSTRACT

FUNCTIONALIZATION OF COTTON FABRIC WITH ZnO/PVA FOR ANTIBACTERIAL TEXTILE APPLICATION

The characteristics of ZnO/PVA on the cotton in term of mechanical strength, surface morphologies, chemical structure, composition, crystal size of ZnO and antibacterial performance were investigated. Range of ZnO compositions (0.1, 0.15, 0.2, 0.25 M) were cooperated with polyvinyl alcohol (PVA) solution (5, 10, 15, 20 g in 200 ml of water).The cotton was padded in the PVA/ZnO solution and dried it at 70 ℃ for overnight. It was found that all the treated samples had abundant particles deposited on fibers and fibers are attached together. The corresponding EDX result showed carbon, oxygen and zinc elements presented on the treated cotton fabric. From EDX mapping, Zn element was presented uniformly over the cotton fabric. For XRD result, there was peak at 31.96°, 34.66°, 36.46°, 47.92° and 56.73° attributed to the characteristic peak of ZnO which revealed hexagonal wurtzite structure of the synthesized ZnO NPs. The crystal size of ZnO in the sample was calculated Debye-Scherer formula was approximately 25~42 nm. Based on FTIR result, the decreasing order of hydroxyl peak of treated samples indicated the bonding was formed between ZnO, PVA and cotton. The antibacterial efficiencies against S.aureus and E.coli increase when ZnO and PVA dosage increase. Generally, the optimal formulation of antibacterial cotton fabric at 0.25 M ZnO / 15 g PVA as the coated fabric has highest strength against tearing and considerable antibacterial properties against S. aureus and E. coli growth.

ACKNOWLEDGEMENT

I would like to thank everyone who had contributed to the successful completion of this project. I would like to express my gratitude to my research supervisor, Dr. Lee Tin Sin and my co-supervisor, Dr. Bee Soo Tueen for their invaluable advice, guidance andenormous patience throughout the development of the research.

In addition, I would also like to express my gratitude to my loving parent and friends who had helped and given me encouragement in order to complete this report with passion and dedication.

Last, this work was supported by Universiti Tunku Abdul Rahman (UTAR) through Universiti Tunku Abdul Rahman Research Fund (UTARRF) under project number 6200/T54.

APPROVAL SHEET

This dissertation/thesis entitled "**FUNCTIONALIZATION OF COTTON FABRIC WITH ZnO/PVA FOR ANTIBACTERIAL TEXTILE APPLICATION**" was prepared by TAN LEE YAE and submitted as partial fulfillment of the requirements for the degree of Master of Engineering Science at Universiti Tunku Abdul Rahman.

Approved by:

(Ir. Dr Lee Tin Sin) Date:…………………..
Supervisor
Department of Chemical Engineering
Lee Kong Chian Faculty of Engineering Science
Universiti Tunku Abdul Rahman

(Ir. Dr Bee Soo Tueen) Date:…………………..
Co-supervisor
Department of Chemical Engineering
Lee Kong Chian Faculty of Engineering Science
Universiti Tunku Abdul Rahman

LEE KONG CHIAN FACULTY OF ENGINEERING SCIENCE
UNIVERSITI TUNKU ABDUL RAHMAN

Date: __________________

SUBMISSION DISSERTATION

It is hereby certified that **TAN LEE YAE** (ID No: **17UEM00216**) has completed this dissertation entitled "FUNCTIONALIZATION OF COTTON FABRIC WITH ZnO/PVA FOR ANTIBACTERIAL TEXTILE APPLICATION" under the supervision of Ir. Dr Lee Tin Sin (Supervisor) from the Department of Chemical Engineering, Lee Kong Chian Faculty of Engineering Science, and Ir. Dr Bee Soo Tueen (Co-Supervisor) from the Department of Chemical Engineering, Lee Kong Chian Faculty of Engineering Science.

I understand that University will upload softcopy of my dissertation in pdf format into UTAR Institutional Repository, which may be made accessible to UTAR community and public.

Yours truly,

____
(TAN LEE YAE)

DECLARATION

I hereby declare that the dissertation is based on my original work except for quotations and citations which have been duly acknowledged. I also declare that it has not been previously or concurrently submitted for any other degree at UTAR or other institutions.

Name ______________________________
(TAN LEE YAE)

Date ______________________________

TABLE OF CONTENTS

CHAPTERS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

AALL	ambient artificial laboratory light
ATRP	atom transfer radical polymerization
BCD	β-cyclodextrin
BTCA	butanetetracarboxylic acid
BZ	benzedine
CA	citric acid
CMC	carboxymethylcellulose
CMC	cell membrane complex
CSH	cell surface hydrophobicity
CTAB	cetyl trimethyl ammonium bromide
CTS-O-MPEG	chitosan-O methoxy polyethylene glycol
DBD	dielectric-barrier discharge
DMDHEU	dimethyloldihydroxyethylene urea
DMDMS	dimethyl dimethoxysilane
ED	ethylenediamine
EG	ethylene glycol
EPS	extracellular polymeric substances
HBP-NH_2	hyperbranched polymer
HL60	myeloblastic leukemia cells
HMTETA	hexamethyltriethyylene tetramine
HMW-CS	high molecular weight of chitosan
LMW-CS	low molecular weight of chitosan
LSPR	localized surface plasmon resonance
MCT-CD	monochlorotriazinyl-β-cyclodextrin

MIC	minimum bactericidal concentration
MRSA	Methicillin-Resistant Staphyloccus aureus
NPs	nanoparticles
NSL	natural sunlight
PBMCs	peripheral blood mononuclear cells
PDADMAC	poly(diallyldimethylammonium chloride)
P(DMDAAC-AGE-MAA)	polymer diallyl dimethyl ammonium chloride-allyl glycidyl ether-methacrylic
PEG	polyethylene glycol
PEM	polyelectrolyte multilayers
PET	poly (ethylene terephthalate) or polyester
PET/WO	polyester blended wool
PVA	polyvinyl alcohol
PVP	polyvinylpyrrolidone
ROS	reactive oxygen species
SF	silk fibroin
SHP	sodium hypophosphite
TCEP	tris (2-carboxyethyl) phosphine
TEOS	tetraethoxysilane
TTIB	titanium butoxide
TTIP	titanium isopropoxide
WO	wool

CHAPTER 1

INTRODUCTION

1.1 Background

Cotton fabric, one of the natural cellulose materials are notable and versatile with wide application in daily human life due to its outstanding characteristics namely, softness, biodegradability hygroscopicity, affinity to skin and regeneration property (Lin et al., 2008, Saravanan et al., 2009). However, the features of cotton fabric possesses conducive environment such as carbon source, optimal temperature and moisture for microorganism's growth. The microorganism's damage could lead to mechanical strength loss, stains formation, excretion of foul odor product, resulting in an adverse effect on health of the human beings (Hebeish et al., 2011b, Hebeish et al., 2011a, Zhang et al., 2008). With raising consciousness of human being toward the hygiene and health, the need of the antibacterial textile is increasingly expanding. To date, the antibacterial agent has applied on the textile including chitosan (Ali et al., 2011), triclosan (Kalyon and Olgun, 2001), quaternary ammonium compounds (Sun et al., 2005), nanoparticles of noble metals and metal oxides (Jiang et al., 2011, Joshi et al., 2007, Mary et al., 2009, Montazer and Seifollahzadeh, 2011, Vasilev et al., 2010, Xia et al., 2011). In this study, ZnO which possesses antibacterial property and safe for human use will be applied to coat on cotton fabric to prevent microorganisms' growth (Tan et al.). ZnO has been widely used in cosmetic products, ointments, lotions and sunscreens to provide strong protection against UV exposure owing to the ability to block spectrum of UVB (280-315 nm) and UVA (315-400 nm) However, the common obstacle in metal based antibacterial textile application is absence of chemical bonds between metal oxide and organic cellulose fibers which will lead to weak adherence of ZnO on antibacterial textiles. Recently, PVA has been applied in wound dressing formulations due to its nontoxic and biocompatible. Increasing the amount of PVA leads to increasing of air and water permeability which can be attributed to the increase in the extent of the structure opening(Abou-Okeil et al., 2012). PVA membranes were used for biomedical materials (Koyano et al., 2000). PVA can be stabilized the dispersion of nanoparticles due to its amphiphilic characteristic. In the PVA interface, there is presence large quantity of free hydroxide group (OH^-) which able to form hydrogen bonding with the surrounding molecules while hydrophobic long hydrocarbon chain creates physical barrier to the desired crystal growth (Stanković et al., 2013). Dip coating, one of the most promising to synthesis and impregnation of nanoparticles on textile application has been spurred great interest. The process could be defined as depositing aqueous-based liquid phase coating solutions onto the surface of any substrate (Shaban et al., 2016). Generally, target materials are dissolved in solutions which directly coated on the surface of substrate, then the sedimentary wet coating has been evaporated to obtain dry film. It has been proven as effective approach to synthesize nanoparticle at milder operation condition with high large surface and quality of ZnO structure can be obtained.

1.2 Problem Statements

Textile such as cotton, wool, nylon, etc can be a potential microorganism’s propagation site. Its optimum conditions such as optimal humidity, temperature and carbon source are conducive for microorganism growth. Thus, in order to enhance the health of wearer, ZnO have shown antibacterial effects on many microorganisms was cooperated with PVA as stabilizer. The problem statements for this study are as follow:

1. What is the synthesis technique to develop ZnO/PVA grafted cotton fabrics?
2. What are characteristics of ZnO/PVA grafted cotton fabrics in term of surface morphologies, chemical structure, crystal size of ZnO, bonding and mechanical strength?
3. What are the effect of ZnO and PVA concentrations on antibacterial activities against E.coli and S.aureus by disc diffusion method?
4. What is the optimal formulation for antibacterial cotton fabric?

1.3 Aims and Objectives

The objectives of this study are to investigate the characteristics of the ZnO/PVA on the cotton. The aims and objectives of the project further divided as follows:

1. To develop ZnO/PVA grafted cotton fabrics.
2. To evaluate the characteristics of ZnO/PVA grafted cotton fabrics in

terms of surface morphologies, chemical structure, crystal size of ZnO, bonding and mechanical strength.

3. To study the effect of ZnO and PVA concentrations on antibacterial activities against S.aureus and E.coli growth by a disc diffusion method.
4. To determine the optimal formulation for antibacterial cotton fabric.

1.4 Scope of Study

This study mainly focuses on analyzing the characteristics of ZnO/PVA grafted cotton fabrics based on the different concentration of ZnO and PVA on antibacterial performance against S.aureus and E.coli growth.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

Textile has been widely used for clothing application since thousand years ago. Among these are wool, silk, cotton, nylon, etc. However, the vulnerability of microorganisms attacking on textile could be a serious problem. The optimal moisture affinity and natural feature of those textiles could be favorable for microorganism’s hostility particularly those used in wound dressing, sportswear, underclothes, infant wear, and sportswear which induce increased chances of contacting bacteria (Li et al., 2017). The infection caused by pathogenic microorganisms, particularly Escherichia coli, Staphylococcus aureus, and Klebstella pneumoniae should be controlled as the proliferation of microorganisms on textile could lead to dramatic effects such as deterioration of textile strength, defacement, and odors which can contaminate the textile as well as endanger the wearer (Chandrasekar et al., 2014).

Generally, the impacts of microorganism on textile material could be performed by two main ways, namely assimilation and degradation. Their metabolites revealed in occurrence of spots on textile surface, formation of bubbles on colored surface of textile materials, induction of bond breaks in fibrous materials, penetration into cavity of natural fiber, and adverse effect on mechanical strength, mass loss, alteration of chemical properties, and other properties (Wilkie et al., 2014).

Owing to the improvement of healthcare concern related with the infection of diseases by various microorganisms, multifunctional textile has been developed so as to impede the growth of bacteria onto the textile where it will lead to adverse hygiene effect on wearer. Nanotechnology is an advance technology that gaining interest to be used on coating nanoparticles on textile to avoid degradation and discoloration by microorganisms at the same time prevent propagation of bacteria. Over the past few contracts, metal based nanoparticles (NPs) whose structures endowed excellent functionality and ability to improve pristine textile in term of physical, chemical, and biological have been studied as one of the most promising route to produce antibacterial textile. To date, the common metallic based NPs used in development of antibacterial textile are Ag, ZnO, Cu based, and TiO_2. Also, there is a scarce researches on other metal based NPs namely, iron based, CeO_2, Au, SiO_2, Ni, and Pt which have been investigated to be applied on biocidal textile field. These metallic based materials have their own unique properties beside antibacterial feature which further improve the textile finishing.

Given the increase in the number of investigations and developments on the properties of suitable metal based NPs and their efficiencies on antibacterial property, this review mainly focus on comprehensive compilation on published metal based NPs used to synthesize antibacterial textile finishing and the proposed synthesis techniques. Moreover, it also concerned with the mechanisms of action against bacterial cell death as well as the factors influence the efficiency of antibacterial performance.

2.2 Type of textile

Textile can be categorized into three main sources namely, animal based, plant based, and synthetic based textile. Each of them has its own unique characteristics which are applied on different textile fields such as medical textile, sportswear, children’s wear, furniture’s upholstery, and so on.

2.2.1 Animal based textile

Animal based textiles to be discussed are originated from wool and silk. Wool widely used on textile applications are the one made from goat, sheep, camel, and rabbit which possessed high extent of warmth (Wilkie et al., 2014). Whereas, silk is an animal fiber produced from cocoon with its softness in fame.

2.2.1.1 Wool

Wool is a natural animal fiber which mainly constitutes of fibrous protein substance, called keratin which contains more sulphur content compared to other types of protein. These filaments of keratin are aligned in continuous fiber axis in cortical cell, bounded by a lipid membrane called cell membrane complex (CMC). The keratin fibers with disulphide crosslinks between individual polypeptide chains have improved fabric's strength and thermal stability. Although the advantages of excellent in chemical resistance and other mechanical strength, the presence of cysteine bonds are susceptible to sunlight, caused the fabric weakened by prolonged exposure to sunlight (Wilkie et al., 2014). Moreover, the wool fabric is subjected to microorganism's damage. The keratin is a major component of wool, acts as a nutrition and energy source for microbes and bacteria growth. As a consequence, the microorganism's propagation on wool fabric induced health problems such as skin irritating (Mura et al., 2015). There are several researchers have been studied the antibacterial activity of wool fabric functionalized with different potential NPs such as Ag (Klemenčič et al., 2013, Yu et al., 2015b, Rehan et al., 2015, Tang et al., 2012, Boroumand et al., 2015, Hosseinkhani et al., 2012, Barani et al., 2012), Cu (Heliopoulos et al., 2013, Shariatinia et al., 2015), TiO_2(Behzadnia et al., 2015, Behzadnia et al., 2014), and SiO_2(Wang et al., 2007). The features of wool facilitate the bonding formation with NPs which favorable to a long term antibacterial performance. Based on the literature (Klemenčič et al., 2013), amino acids and sulphurs in the wool fibers provide binding sites for silver to form stable silver mercaptides. Moreover, the non-keratinous cell membrane cortex region which is light cross-linked exhibits high water absorbency which able to absorb up to 30-38% of its original weight. It is proposed that these reasons result the high affinity of nanoparticle's adsorption on wool fabric. As a consequence, it generates excellent antimicrobial efficiency of wool fabric in the long run. According to Heliopoulos et al, the use of alginate increases the copper sorbing capacity due to its structure comprised of abundant carboxylic groups (-COOH) that able forming bonds with mercapto groups, carboxylic or sulphonic groups of wool keratin, thus offer excellent antibacterial effect (Heliopoulos et al., 2013). The CMC lipid layer inside cortical cell of wool fiber making the surface of wool hydrophobic, thus this feature, in particular results the difficulties in process of dyeing and finishing of fabric. Embedment of silica nanoparticles not only promotes the uptake of nanoparticles on wool, it also alters the wettability of wool gives the wool to be super-hydrophilic (Klemenčič et al., 2013, Yu et al., 2015b, Rehan et al., 2015, Tang et al., 2012).

2.2.1.2 Silk

The raw silk comprises of two major components called fibroin and sericin. However, the raw silk is not suitable to be used as textile application directly. This is probably due to once the presence of sericin inside the human body, it is detected as an antigenic factor by T-cells and triggers immulogic reaction. Thus, extraction of sericin is necessary before further processing and the process is known as degumming process. Upon degumming silk or silk fibroin (SF), it appears shiny and feel soft to touch and is highly demand in textile industry (Çalamak et al., 2014). Silk fibroin produces from the cocoon Bombyx mori, in particular, is widely used in medical wound dressing due to its inherently biocompatibility, proper strength, morphologic flexibility, biodegradability, and permeability (Çalamak et al., 2014, Koh et al., 2015). Despite of the advantages, the natural protein fiber of silk serves as a carbon and nitrogen sources for microorganism's growth (Lu et al., 2014). Adherence of microorganism adversely deteriorates the strength by deformation the surface and also alters the original color by means of microbial secretions or spores (Park et al., 2008). Thus, the development of multifunctional silk textile particularly on antibacterial aspect by using nanostructure metal based materials have been studied such as CeO_2(Lu et al., 2014), Ag (Yu et al., 2015a, Li et al., 2011), TiO_2 (Li et al., 2011), and Au (Tang et al., 2014).

2.2.2 Plant-based textile

Cotton and bamboo pulp are two main sources for plant-derived textiles. They are widely used on clothing due to its abundance, comfortability, soft, and breathable natural fiber. Moreover, there is semi-synthetic textile which is derived from natural sources, known as viscose or rayon (Wilkie et al., 2014).

2.2.2.1 Cotton

Cotton, composes of celluloses and hemicelluloses, is the most abundant natural polymer can be found on the Earth. Cotton is linked with a range from as low as 15 or less to as high as 7000-10,000 of linear, straight chain of D-glucose units through condensation by means of β ($1\rightarrow4$)-glycosidic bonds. Due to the cellulose as one of the renewable carbon source, cotton is susceptible for microbial degradation. Different degradation mechanisms could be resulted by vary of microorganisms involved. Attacking of fungi initiates from the cracks on the surface of cotton fiber or at the fiber ends and degradation occurs from the internal to external layer of the fibers. Whereas, it is opposed from the cotton degradation by bacteria where the process begins from fiber surface extends throughout to the internal layers of fibers. In general, the depolymerization of cellulose is the primary cause for deterioration of cotton in term of weight and strength (Reese, 2013). Biodegradation of cotton causes discoloration, foul smelling, appearance disfiguration, and hygiene issue in the products (Muthu, 2014). In order to suppress the negative impacts of microorganism’s adherence on cotton fabric, there are numerous of studies on metal based NPs coated on cotton fabric for aiming antibacterial purpose; such as Ag (Maryan et al., 2015, Ibrahim and Hassan, 2016), ZnO (Petkova et al., 2016), Cu (Yang et al., 2017), and Fe_3O_4(Rastgoo et al., 2016).

2.2.2.2 Bamboo

Bamboo based textile has been commonly used due to its wicking property, excellent water absorption, and permeability. The natural hollowness in the horizontal cross sections, making bamboo has numerous micro-holes and micro-gaps to absorb and evaporate the moisture of human skin readily. This special feature creates superb ventilation and thus inhibits the growth of bacteria. As comparison with cotton, bamboo has been discovered more eco-friendly in term of land use, irrigation, and pesticide adoption. The propagation rate of bamboo is considered as one of the fastest growing plants, which at 3 to 4 years growth rate. Moreover, bamboo fiber demands less amount of dye and thus less waste produced to the environment (Murthy, 2016). Bamboo is a natural biopolymer made up of lignocellulose, which categorized as the grass family Poacease (Teli and Sheikh, 2013). Bamboo fiber has been found that it has excellent antibacterial and bacteriostatic bio-agent due to the presence of bambocane substance in the fiber (Wilkie et al., 2014, Tausif et al., 2015). However due to the hydrolysis alkalization process and multi-stage bleaching in the refining process, the intrinsic antibacterial feature disappeared (Tausif et al., 2015). Thus, imparted ZnO (Zhang et al., 2013b), Ag (Tang et al., 2015), and Au (Tang et al., 2015) on bamboo pulp fabric have been studied and the results have revealed the modified fabrics possessed antibacterial activity.

2.2.2.3 Viscose/rayon

Viscose or rayon is regenerated fiber derived from natural resource such as wool pulp or bamboo pulp. It is classified as semi-synthetic fiber which comprises of cellulose macromolecules made up of glucopyranose rings link with β-1, 4-glycoside bond and each of glucopyranose ring has composed of three hydroxyl alcohols. Thereby, this is conducive for hydrogen bonding formation between hydroxyl group of viscose and water, making viscose hydrophilic, breathable, and cool (Kramar et al., 2013). The versatility of bamboo viscose fiber is widely employed in the production of sanitary, apparel, geotextile, hygiene, composites, and filtration fabrics. As similar to cotton, the cellulosic components serve as a nutrient for microbial growth and cause the viscose fabric's degradation (Tausif et al., 2015). Thereby, several studies have been reported on coating metal based materials on viscose fabric namely, Ag (Kramar et al., 2013, Teli and Sheikh, 2012, Abou-Okeil et al., 2012, Emam et al., 2014, Rehan et al., 2017, Fahmy et al., 2013), TiO_2 (Fahmy et al., 2013), Cu based material (Teli and Sheikh, 2013, Kramar et al., 2013, Mekewi et al., 2012), Zn (Mekewi et al., 2012), Ni (Mekewi et al., 2012) and SiO_2(El-Gabry et al., 2013).

2.2.3 Synthetic-based textile

Synthetic textiles are textiles produced from man-synthesis such as nylon, polyester and acrylic, which made up by joining monomers into long polymer chains. These textiles endow different features that some might not inherited by that produced from natural sources such as waterproof, elasticity, wrinkle-free, flame resistant, etc (Deopura et al., 2008).

2.2.3.1 Polyester

Polyester fabric is a man-made fabric constitutes of poly (ethylene terephthalate) (PET) that made up of almost 50 % of all fiber materials with considerable strength, chemical resistance with dimensional stability (Pasquet et al., 2014, Gaminian and Montazer, 2017). The outstanding of characteristics such as better elasticity, wrinkle and shrinkage resistance, pleat retention, good easy care properties, not undermined by sunlight and weather making polyester extensively used as children’s wear, lingerie, raincoat, pants, shirts, sport-wears, separates, jackets, blouses, and dress. Also, by blending polyester with wool, the composite endowed features to eliminate crushing and reduce fading, which it has widely employed on furniture’s upholstery and fiberfill in pillows (Deopura et al., 2008). However, the hydrophobicity of PET leads to poor adhesion of the coating, thereby shorten the durability of finishing treatment. This is due to the presence of benzene rings and $–CH_2CH_2-$ groups in PET that endow non-polar characteristic causes it not capable to form hydrogen bonds with other molecules (Sirelkhatim et al., 2015). Moreover, the lack of hydrophilic property brings the fabric susceptible to generate and accumulate static electric charge, hard to clean during laundering and prone to gather up dirt which might deteriorate the hygiene and health of wearer

(Gaminian and Montazer, 2017). According to recent studies, the authors are focused on modification of polyester into more hydrophilic at the same time endowed antibacterial property. Among the modification agents are Ag (Harifi and Montazer, 2015) and Pt (Shahidi and Ghoranneviss, 2011). Blending both natural and synthetic fibers is an important treatment to produce wide variety of yarns with desirable attributes and at the mean time covers up negative characteristics of both fibers. Blending polyester with cotton synthesizes fabric inherits merits of polyester and cotton such as wear and easy care property and high moisture absorbency, respectively. Meanwhile, it reduces the features such as poor moisture absorption and static dissipation from polyester and poor crease retention and wrinkle recovery from cotton (Deopura et al., 2008). Rastgoo et al. have studied to produce blended polyester/cotton fabric with antibacterial, magnetic, photoactive, and sonocatalytic properties via sonosynthesis of magnetite iron oxide NPs (Rastgoo et al., 2016). Hanh et al. have immobilized Ag NPs on peco bed sheets (65 % polyester, 35 % cotton) for antibacterial performance evaluation (Hanh et al., 2016). The results proved that the modified peco bed sheet successfully inhibited the growth of the clinical breed such as S. aureus, Acinetobacter spp, K. pneumonia, Escherichia coli, Proteus, Enterobacter spp, S. epidermidis, P. aeruginosa, S. pneumoniaea and Provindencia spp. Klemenčičet al. have compared the antibacterial performances of Ag based on 3 different types of coated fabric namely, wool (WO), polyester (PET), and polyester blended wool (PET/WO) (Klemenčič et al., 2013). The results demonstrated that all the modified fabrics did facilitate the bacterial reduction to a lesser or greater extent, which strongly depend not only on the concentration of Ag adherence on fabric but also the feature of fabric itself. According to the results, PET had the lowest concentration of adsorbed Ag, followed by PET/WO and WO fabric yet their antibacterial performance exhibited in opposite trend. This could be due to the bonding between Ag and wool. The high affinity of Ag to sulphur in the cuticles of the wool fiber tends to form stable silver mercaptide, thus making it harder to release silver cations. Whereas, the high antibacterial activity on PET fabric is attributed to the weak physical bonding with Ag, where silver cations are more readily to be leached into surrounding. Moreover, PET possesses structure with more aromatic, higher crystalline and hydrophobic than wool fabric, caused it to have much more resistant to microbial adherence and it is inherited on blended PET/WO as well where the wettability decreases which impairs the microbial growth.

2.2.3.2 Polyamide/nylon

Polyamide, also known as nylon is made up of monomers with one molecules having acid group (COOH) attached its end with another molecules containing amine group (NH_2). Generally, there are two main compounds have found widespread used in textile industry which are polyamide 6, 6 and polyamide 6. Due to high stretchability and elasticity recovery properties, it is widely used in women's lingerie and hosiery. Its abrasion resistance and low absorbency favor the use in produce sport-wear, raincoats, ski and snow apparel, and so on (Deopura et al., 2008). There are several researches on synthesis multifunctional nylon fabric coated with metal NPs having electroconductivity, UV protection, antibacterial properties, etc. There are Ag (Montazer et al., 2014, Montazer and Nia, 2015, Montazer et al., 2012b, Montazer et al., 2012a) and Cu (Komeily-Nia et al., 2013). Blending nylon with cotton has found to have high abrasion resistance and comfortability and it is used in labor cloth, uniform, and dressing (Meftahi et al., 2015). Accordingly, Meftahi et al. have employed ZnO/TiO_2 nanocomposite on nylon/cotton and have found there is considerable improvement in light, washing fastness, and antibacterial efficiencies against E.coli and S.Aureus.

2.2.3.3 Acrylic

Acrylic fabric as one of the synthetic fabrics is typically used in textile field due to its wool-like feel, resilient and resistant to outdoor exposure, and chemical substances (Ma and Sun, 2005). Mekewi et al. have introduced Cu, Zn and Ni chelated on acrylic and viscose fabrics with aliphatic and aromatic amines as binding agents and have found that acrylic fabric more favor to metal uptake and copper chelated amine coated for both fabrics have higher microorganism’s hostility resistance compared with that those Zn and Ni coated fabrics (Mekewi et al., 2012). The elevated metal ions uptake by acrylic fabric is attributed to the presence of tactical isotactic structure. The structure capable to form coordinate bonding with the pendant acrylonitrile groups of acrylic polymer chain and via ionic bonding with the carboxylic groups of acrylic molecules.

2.3 Type of metal-based antibacterial agents on textile

Metal based NPs on textile on the basis of containing excellent antibacterial property have been studied. Among those are Ag, ZnO, Cu-based, TiO_2 and other minor metals namely; iron based, CeO_2, Au, SiO_2, Ni and Pt. They are functionalized on textile either in dispersed form or incorporation with polymer matrix to enhance its antibacterial activity.

2.3.1 Silver nanoparticles (Ag NPs)

Ag NPs is one of the most promising metal based bactericidal and therapeutic agents that has been widely used in numerous industry fields. It is reported that silver is very versatile to inhibit approximate 650 species of bacteria. The manufacturing of Ag grafted textiles have been expanded for domestic, medical, and other functions. In medical application, it is applied to bandages, wounds dressings, and surgical thread. While for domestic clothing, it is used for sportswear, underwear, and military uniform (Sataev et al., 2014). Its antibacterial effectiveness is superb compared to other metal based materials such as Cu based, ZnO, and TiO_2. Ren et al. have published their study that the minimum bactericidal concentration (MIC) of a range of microorganism strains needed for CuO, Cu, Cu_2O and ZnO are higher compared to Ag (Ren et al., 2009). Silver endows high antibacterial action even with small dose usage and it is not harmful to human being. According to Lee and Jeong, colloidal silvers with nano-sized (2~3 nm and 30 nm) particles on textile fabric have ability to kill 99 % of S.aureus and K.pneumoniae and are proven skin-innoxious when come into contact with human skin (Lee and Jeong, 2005). In order to manufacture effective antimicrobial-functionalized fabric, it must be well-understand the mechanisms of action against bacteria. However, the published literatures are varied with conditions where physical and chemical modification can be resulted and altered the interaction with bacteria of interest. The method of synthesis the material, additive or capping agent involved, bacteria strain used, nature of test to assess it and so on could lead to different outcomes. Yet, most researchers have intuitively attributed the inhibition growth of bacterial cell by Ag is due to presence of Ag^+ ions and Ag NPs. According to Quay and Stellacci, Ag NPs agglomerate around the bacterial membrane and cause diminution bacterial membrane integrity and as a result leading to cellular death. This physical mode of antibacterial action relies on the size of Ag NPs to facilitate the penetration of these particles through the cell membrane to the intracellular matrix and trigger cytotoxic mechanism. Moreover, several studies revealed that Ag NPs causes formation of reactive oxygen species (ROS) which accumulate to create very high oxidative stress inside the cell and inactivate the cell. The role of Ag^+ ions on inhibition microorganism growth relies on high affinities for organic phosphates, amines, and specially thiols. Those chemical compound can be found mainly on DNA, peptides (component of membrane-bound or intracellular component), and cofactor. Silver is categorized as oligo-dynamic metal and acts as a bridging agent to form bonds with several thiols cause the irreversible aggregation of thiol-bearing molecules and subsequently inactivate the biological system of bacterial cell. Compared to other antibiotic agent, Ag^+ ions can bind non-specifically to broad range of targets, disturbing the cellular metabolism and leading to cell death (Le Ouay and Stellacci, 2015). Incorporation of other constituents inside the NPs system could also enhance to the antibacterial property on modified fabric. Among these additives are TiO_2/SiO_2/alginate (Mura et al., 2015), silica (Klemenčič et al., 2013, Tang et al., 2012), trisodium citrate (Rehan et al., 2015), Sodium bisulphite and sodium dithionite (Hosseinkhani et al., 2012), tris (2-carboxyethyl) phosphine (TCEP) (Yu et al., 2015b, Yu et al., 2015a), lecithin (Barani et al., 2012), glucose (Maryan et al., 2015), butyl arylate (Ibrahim and Hassan, 2016), chitosan/polyvinyl alcohol (PVA) (Abou-Okeil et al., 2012), ethylene glycol (EG)/polyvinylpyrrolidone (PVP) (Rehan et al., 2017, Nateghi and Shateri-Khalilabad, 2015), Tinosan/dimethyloldihydroxyethylene urea (DMDHEU)/PVP (Fahmy et al., 2013), TiO_2/Fe_3O_4(Harifi and Montazer, 2015), ammonia complex (Montazer et al., 2014), Tollen-s agent (Montazer and Nia, 2015), Tollen’s agent/PVP (Montazer et al., 2012b), 1,2,3,4-butanetetracarboxylic acid (BTCA)/sodium hypophosphite (SHP) (Montazer et al., 2012a), hexadecyltrimethoxysilane (Shateri-Khalilabad et al., 2017), polypyrrole (Babu et al., 2012), carboxymethylcellulose (CMC) (Bozaci et al., 2015), chitosan (Hanh et al., 2014), starch (Raza et al., 2015, El-Rafie et al., 2014), sodium alginate (Su et al., 2017), alginate (Zahran et al., 2014), chitosan-O methoxy polyethylene glycol (CTS-O-MPEG) (Abdel-Mohsen et al., 2012), monochlorotriazinyl-β-cyclodextrin (MCT-CD) and β-cyclodextrin (βCD) (Hebeish et al., 2014), polyethylene glycol (PEG) (Hebeish et al., 2015), xanthan gum (Emam and Zahran, 2015), poly(diallyldimethylammonium chloride) (PDADMAC) (Dubas et al., 2006), Tragacanth gum/CA/SHP

(Montazer et al., 2016), AgBr-TiO_2/DMDMS/TEOS (Rana et al., 2016), amino-terminated hyperbranched polymer (HBP-NH_2) (Zhang et al., 2013a)and sulfated β-cyclodextrin (Selvam et al., 2012), mercaptopropyltriethoxysilane (Kwak et al., 2015), ciprofloxacin and cefobid (Ibrahim et al., 2017).

According to Tang et al., Ag endows localized surface plasmon resonance (LSPR) which results to obtain different colors with different morphologies through photo-induction method. The mixture of nanoprisms and nanospheres tend to synthesize green color ofAg NPs. Blue color of Ag NPs are obtained from solution with almost all nanoprisms structure of Ag while red and yellow color are obtained with nanodisks structure. This phenomena could be explained due to the anisotropic property of Ag. Different shapes possess different plasmon resonance modes. From Tang et al. experimental result, the bands at long wavelength of 601-710 nm resulted Ag nanoplates while 440 – 500 nm formed Ag nanodisk which regards being caused by the in-plane dipole plasmon resonance mode. Conversely, the out-of-plane quadrupole plasmon resonance mode of Ag nanoparticles is shown at the wavelength at 330 – 340 nm of the Ag nanoplates. The green Ag nanoparticle solution at band centered at 401 nm is proposed to be attributed to the in-plane dipole plasmon resonance mode of Ag nanospheres (Tang et al., 2012). However, when the size of particle reduced, the electronic band structure begins revealing quantum size influences under the critical size of that material. Particle size decreases to 1 - 2 nm, the discrete energy levels incline to fix to the molecular energy level. At this level, there is no metallic band structure accessible to demonstrate surface plasmon effects and it loses its characteristic color and Ag no longer behave as metal. The existence of silica on Ag NPs coated fabric could enhance the color of modified fabric as well as prevent the Ag NPs from agglomeration (Nischala et al., 2011).

2.3.1.1 Synthesis method

There are many different application techniques have been studied on coating Ag NPs onto textile materials. Among these included: pad dry cure method (Mura et al., 2015, Klemenčič et al., 2013, Abou-Okeil et al., 2012, Fahmy et al., 2013, Montazer et al., 2012b, Montazer et al., 2012a, Lee and Jeong, 2005, Bozaci et al., 2015, El-Rafie et al., 2014, Zahran et al., 2014, Abdel-Mohsen et al., 2012, Hebeish et al., 2014, Hebeish et al., 2015, Emam and Zahran, 2015, Montazer et al., 2016, Selvam et al., 2012, El-Rafie et al., 2012, Balakumaran et al., 2016), dip and dry (Nateghi and Shateri-Khalilabad, 2015), ex-situ immersion (Tang et al., 2012, Zhang et al., 2013a), direct sorption (Rehan et al., 2015, Hosseinkhani et al., 2012, Barani et al., 2012, Maryan et al., 2015, Emam et al., 2014, Montazer and Nia, 2015, Shateri-Khalilabad et al., 2017, Babu et al., 2012, Emam et al., 2017, Emam et al., 2016), spray coating (Rana et al., 2016), thermal reduction (Kwak et al., 2015), hydrothermal (Raza et al., 2015), microwave (Rehan et al., 2017, Su et al., 2017), gamma irradiation (Hanh et al., 2016, Hanh et al., 2014), sonochemical (Ibrahim and Hassan, 2016, Harifi and Montazer, 2015, Montazer et al., 2014), electroless plating (Yu et al., 2015b, Yu et al., 2015a), plasma treatment

(Kramar et al., 2013, Ibrahim et al., 2017, Deng et al., 2015), and self-assembly (Dubas et al., 2006).

The ex-situ synthesis of Ag grafted textile via pad dry cure method has been widely used in many researches. Figure 2.1 illustrates steps of coating Ag NPs onto fabric via pad dry cure process. Ag NPs are first prepared either via wet chemical (Lee and Jeong, 2005, Bozaci et al., 2015, El-Rafie et al., 2014, Zahran et al., 2014, Abdel-Mohsen et al., 2012, Hebeish et al., 2014, Hebeish et al., 2015, Emam and Zahran, 2015, Montazer et al., 2016, Selvam et al., 2012), or biomass filtrate (El-Rafie et al., 2012, Balakumaran et al., 2016) before padding the textile into Ag NPs colloidal solution, drying and finally curing. However, due to weak interaction on fabric surface itself without any penetration into yarn level causes it not permanent against washing. Thus, impregnation of capping agent either synthetic polymer (Fahmy et al., 2013, Montazer et al., 2012b, Montazer et al., 2012a, Lee and Jeong, 2005, Hebeish et al., 2014, Hebeish et al., 2015), or natural biological agent (Zahran et al., 2014, Emam and Zahran, 2015, Montazer et al., 2016) facilitates the stability of Ag NPs on textile.

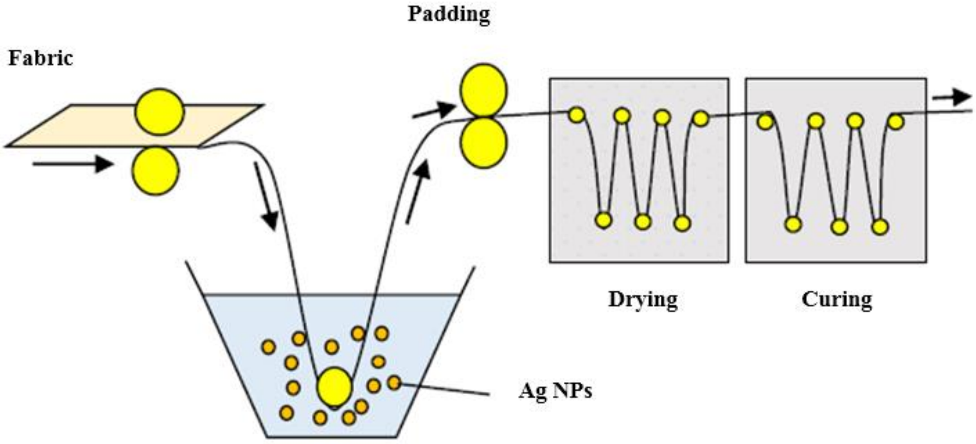


Figure 2.1: Steps of coating Ag NPs onto fabric via pad dry cure method (Lee and Jeong, 2005).

The incorporation of Ag NPs onto textile through in-situ immersion, generally carried out in two steps namely, pre-activation and sorption. The purpose of pre-activation is to swell the fiber matrix inside the textile to facilitate the diffusion of Ag NPs into fibers. The alkali based material or reducing agent used in pre-activation step is to fully dissociate COOH in cellulose and thus increases the affinity of Ag NPs adherence on textile. The advantages of this method are facile, cheap, and can be carried out at mild reaction conditions (Emam et al., 2015). The reducing agents used in pre-activation step that have been studied are trisodium citrate (Rehan et al., 2015) and sulphur-based materials (Hosseinkhani et al., 2012), potassium hydroxide (Shateri-Khalilabad et al., 2017), and sodium hydroxide (Emam et al., 2015). The combination of pre-oxidation of textile before carry out in-situ synthesis Ag NPs onto fabric has been studied as well. Montazer and Nia have reported to use potassium permanganate to oxidize polyamide chains which lead to increased functional groups that served as active sites for loading more Ag NPs on fabric surface. Incorporation of ultrasound bath shortens the processing time and energy consumption in coating process (Montazer and Nia, 2015). Emam et al. have made comparison with both solventless sorption and padding methods on deposition Ag NPs on cotton fabric. Based on the result, sorption method has higher efficiency on loading Ag NPs on textile compared to padding method by 10 times. This could be due to the higher tendency for the Ag^+ ion in the solution undergone reduction to form Ag than compared to padding method that carried out in oven (Emam et al., 2016).

Thermal reduction method of silver carbamate complex in organic solvent has been studied to synthesize Ag NPs. The advantage of this method is able to produce stable Ag NPs without creating inorganic ions except amine and carbon dioxide by reducing silver carbamate at low temperature. In Kwak et al. study, Ag NPs have assembled on cotton fabric by using 3-mercaptopropyltriethoxysilane and transparent alcoholic solution of organometallic silver 2-ethylhexylcarbamate under thermal heating at low temperature 130℃. Figure 2.2 illustrates the 3-mercaptopropyltriethoxysilane reacts with hydroxyl groups of cotton to create a –SH groups monolayer followed by decomposition silver carbamate complex to silver metal through thermolysis.The synthesized Ag NPs conveyed a homogeneous and continuous layer of silver metal on fabric with average size of 20 to 100 nm exhibited high conductivity, electric resistance, and antibacterial performance against E.coli and S.aureus (Kwak et al., 2015). Hydrothermal technique is also extensively used in synthesis nano-structure of Ag on textile application. Raza et al. have studied the impregnation of Ag NPs on enzymatic starch pre-treated cotton fabric under autoclave conditions of 103.42 kPa, 121℃ for 15 min. Figure2.3 shows the impregnation mechanism of Ag Ns on cotton fabric under pressurized heating treatment. At this condition, the aldehyde terminal of starch able to reduce silver ions which bound to the anionic oxygen site of cotton fabric to silver atom and stabilized the NPs on fabric surface. The obtained surface of treated cotton fabric revealed multi-functions of antibacterial activity, hydrophobicity, tensile strength, and is rougher than pristine cotton fabric (Raza et al., 2015). The microwave heating synthesis is advantageous over conventional heating due to its rapid nucleation sites generation and thus enhances the reaction rates. Supply of energy by mean of electromagnetic field directly to the material results fast heating. Su et al. have synthesized sodium alginate-grafted Ag NPs on cotton fabric through microwave irradiation under various conditions by manipulated sodium alginate concentration (0.5-2 %), volume of reducing agent aniline (50,100, 150 μL) and duration of heat treatment (30-240 s) in order to investigate the effects on antibacterial performance (Su et al., 2017). Moreover, Rehan et al. used combination of microwave heating and polyol method to synthesize Ag NPs on viscose fabric with incorporation of PEG as reducing agent and PVP as stabilizing agent. The microwave power has increased from 50 W to 90 W increased the kinetics of reaction and production of localized heat at reaction sites, thereby increased the reaction rate. As a consequence, the reduction rate of silver ions accelerated thus enhanced the antibacterial performance (Rehan et al., 2017).

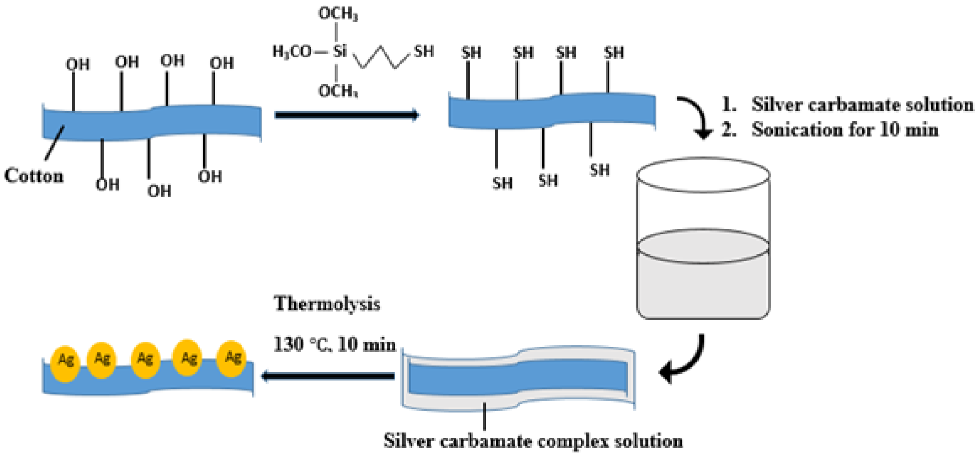


Figure 2.2: Preparation of Ag NPs coated by thermolysis using silver carbamate complex (Kwak et al., 2015).

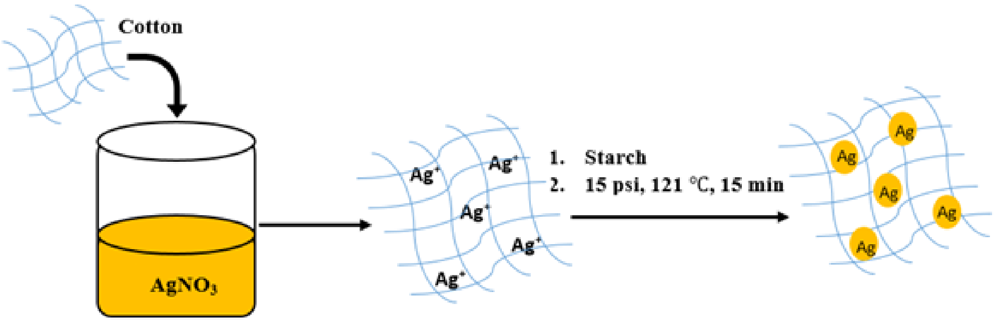


Figure 2.3: Impregnation of Ag NPs on cotton fabric by hydrothermal (Raza et al., 2015).

Using gamma, γ irradiation to produce hydrated electrons and radicals of hydrogen, reduce the silver ions to silvers and immobilize it on the fabric has been studied (Hanh et al., 2016). Influences of absorbed dose and $AgNO_3$ solution concentration on impregnation of Ag NPs on fabric with chitosan as additive has been investigated by Hanh et al. (Hanh et al., 2016, Hanh et al., 2014). The absorbed dose serves a vital part in synthesis and growth of Ag NPs. As reference to the results, nanoparticles did not form in low dose but appeared at high dose. Whereas, increased concentration of $AgNO_3$ from 0.5

to 5 mM enhanced the Ag content on cotton fabric and thus improved the inhibition of bacterial growth.

Sonosynthesis has been proven as effective approach to synthesize NPs at mild operation condition due to its unique capability of generation energy by acoustic cavitation mean. Harifi and Montazer have used sonosynthetic method to deposit $TiO_2/Fe_3O_4/Ag$ nanocomposites fabricated on polyester fabric to impart enhanced antibacterial, magnetic and self-cleaning features with considerable hydrophilicity/hydrophobicity at mild temperature. The formation, growth and implosion of bubbles, micro-turbulence, shock waves, and presence of localized hot zones induced smaller size NPs and intensified mass transfer onto the textile lead to strong physical adsorption (Harifi and Montazer, 2015). Montazer et al. have applied ultrasound to synthesize silver complex $[Ag(NH_3)_2]^+$ before crosslinked with polyamide chain found that the synthesized Ag NPs homogenous deposited on polyamide fabric surface with the particle sizes range of 20 nm to 150 nm, exhibited antibacterial properties against E.coli and S.aureus (Montazer et al., 2014). Ibrahim and Hassan have synthesized Ag NPs coated cotton fabric using fungus Alternaria alternate to synthesize Ag NPs, after that applied ultrasound to ensure homogeneous dispersion before treated fabric subjected to gramma irradiation and thermal curing (Ibrahim and Hassan, 2016).

Chemical electroless plating is another method employed for coating Ag NPs onto textile surface. Yu et al. have metalized silk and wool fabrics by using tris (2-carboxyethyl) phosphine (TCEP) as reducer to create thiol groups and –SH groups on corresponding fabrics for serving catalytic seeds to form complexes ions between fabrics and silver ions (Yu et al., 2015b, Yu et al., 2015a). The whole coating process is illustrated in Figure 2.4The chemical interaction of catalytic seeds with silk fibers will lead to better bonding and adhesion between fiber and metal layer. However, this method has drawbacks related with the utilization costly materials and difficulty to create reactive groups on the fiber's surface.

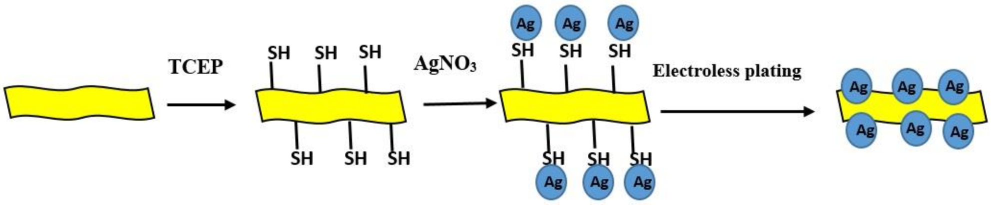


Figure 2.4: The process of silver fiber electroless plating (Yu et al., 2015a).

Plasma treatment coating involves interaction of high energy with quasineutral gas such as electrons, ions, and excited molecules atoms under electric or both electric and magnetic fields condition. These particles can be used to alter the textile surface chemically and physically. Generally, there are two common plasma approaches that are applied to modify the textile namely, atmospheric pressure plasma and dielectric-barrier discharge (DBD). As for the atmospheric pressure plasma technique, its discharge employs high flow rate of inert carrier gas (Mather, 2009). Deng et al. have impregnated Ag NPs on PET fabric through double layer of plasma deposited organosilicon thin film which served as a reservation platform for Ag immobilization and controlled the adherence of Ag on fabric. The concentration of silver in double layer coatings has been successfully suppressed the growth of E.coli and S.aureus at 100 % reduction at Ag NPs content of 7 at % (Deng et al., 2015). Ibrahim et al. have pre-surface modified different types of fabric namely, cotton, linen, viscose, and lyocell to create active sites (-NH_2 groups) for loading Ag NPs onto fabric surface by using N_2 plasma with the DBD as plasma source. The evaluation of antibacterial performance of modified fabric arranged in decreasing order: lyocell > viscose > cotton > linen (Ibrahim et al., 2017). On the other hand, the coating principle of DBD is through bombardment of fabric surface with high speed electrons by using a pulsed voltage upon an electrode pair with one electrode shielded by a dielectric material. The dielectric limits the flow of current and distributes over the whole fabric, improves the uniformity during the treatment (Mather, 2009). Kramar et al. have studied the aging effect of using DBD with different exposure times (1, 7, 14, 21 days) on wettability and sorption ability of bactericidal ions, Ag^+ and Cu^{2+} ions on viscose fabric. Obtained results showed that both types of ion possessed different sorption capabilities and antibacterial performances at different post-plasma treatment durations (Kramar et al., 2013).

Polyelectrolyte multilayers (PEM) formed by layer-by-layer self-assembly on coating NPs onto textile application has been gained interest due to its simplicity for development of nanoscale structure with high stability. This process is carried out by successive dipping alternative polycations and polyanions followed by rinsing in water. The coating replies on the interactions between hydrophobic and electrostatic features as the thickness and properties in a film can be exquisitely adjusted. Dubas et al. have implemented Ag NPs coated nylon and silk fabrics by using layer-by-layer deposition approach on investigation their antibacterial activity. The use of anionic poly (methacrylic acid) capped Ag NPs on silk and nylon fibers with cationic poly (diallyldimethylammonium chloride) (PDADMAC) formed 20 layers between them have obtained. Based on the results, the affinity for PEM on the nylon was lower compared with silk fabric due to their different fiber structures. The silk endows carboxylic functional groups inside the natural protein fiber, facilitates the adhesion of PDADMAC and the growth of film layers. Whereas, nylon has lower surface charge which non-conducive for deposition of PEM, thus leading to slower and lesser amount of immobilized NPs. As a consequences, the deposition of 20 PDADMAC/PMA coated Ag layers onto the fibers cause 50 % bacteria in reduction for the nylon and 80 % for the silk fiber (Dubas et al., 2006).

2.3.2 Zinc oxide nanoparticles (ZnO NPs)

ZnO is II-VI semiconductor group and owns three forms namely, hexagonal wurtzite, cubic zinblende, and rarely observed cubic rocksalt. As compared with zinblende form, wurtzite structure is more thermodynamically stable in room temperature. The metastable zincblende can be stabilized through growth techniques (Sirelkhatim et al., 2015). Due to its unique lattice structure, it exhibits piezoelectric property and has widely used in piezoelectric devices, sensors, and elctro-acoustic transducers. ZnO is a n-type semiconductor, endows relatively wide direct band gap (~ 3.3 eV) with high excitonic binding energy (60 meV) at ambient environment and results it potentially applied on electronic field such as solar cells, gas sensors, varistor, photodiodes, and UV light emitting devices. Furthermore, ZnO possesses high optical absorption and catalytic activities which favorable its use in anti-reflection coatings, UV absorbers, photo-catalysis, and catalyst. ZnO also can be utilized in ointments, lotions and sunscreens to protect skin from UV illumination due to it serves as the broadest spectrum UVA (315-400 nm) and UVB (280-315 nm) reflector (Sirelkhatim et al., 2015, Dastjerdi and Montazer, 2010). Recently, there are numerous studies investigated the use of ZnO NPs as antibacterial agent on diverse fields such as food (Venkatasubbu et al., 2016), textile (Selvam et al., 2012, Shaheen et al., 2016, Krishnaveni and Thambidurai, 2013, Sivakumar et al., 2010, Selvam and Sundrarajan, 2012, Wang et al., 2016, Svetlichnyi et al., 2016, Barani, 2014, Ghayempour and Montazer, 2017, Abramov et al., 2009, Perelshtein et al., 2015, Prasad et al., 2016, Gao et al., 2014, Çakır et al., 2012, Staneva et al., 2015, Aladpoosh and Montazer, 2015, Dhandapani et al., 2014)91-106], and biomedical applications (Mirzaei and Darroudi, 2017). Devanand Venkatasubbu et al. have applied ZnO on food pathogens namely, Salmonella typhi, Klebsiella pneumonia, and Shigella flexneri for investigation its antibacterial performance (Venkatasubbu et al., 2016). Liedtke and Vahjen have shown the antibacterial effect of ZnO NPs against 75 intestinal bacteria. According to the literature, ZnO NP is an amphoteric molecule and has displayed higher solubility in acidic environment. The results showed that the intestinal bacteria’s resistance against ZnO NPs is species specific and cannot be assigned based on their taxonomic origin (Liedtke and Vahjen, 2012). Premanathan et al. have studied the toxicity of ZnO NPs against the inhibition growth of prokaryotic and eukaryotic cells.

The authors have used normal peripheral blood mononuclear cells (PBMCs) and human myeloblastic leukemia cells (HL60) to evaluate the cytotoxicity of ZnO NPs and at the same time, antibacterial activity of ZnO NPs against Gram positive bacteria Staphylococcus aureus as well as the Gram-negative bacteria Escherichia coli and Pseudomonas aeruginosa have been tested. The results showed that ZnO possessed abilities to kill cancerous HL60 cells and those Gram-negative and positive bacteria through two mechanisms namely, generation of ROS and induction of apoptosis (Premanathan et al., 2011). However, up-to-date, the cytotoxicity of ZnO on mammalian cells is scarce and need more significant and clear published literature before translating into medical-use. The synthesis of ZnO NPs coated materials usually are done by addition of additive or supporting matrix to stabilize and increase durability of ZnO. ZnO is susceptible to agglomerate in water owing to high polarity of water result deposition to occurs (Liedtke and Vahjen, 2012). Thus, ZnO has been incorporated with many capping agents on synthesis ZnO nanocomposite coated on textile such as multi-amide compound (Zhang et al., 2013b), sulfated β-cyclodextrin (Selvam et al., 2012), hexamethyltriethyylene tetramine (HMTETA) (Shaheen et al., 2016), chitosan (Krishnaveni and Thambidurai, 2013, Wang et al., 2016), acacia (Sivakumar et al., 2010), poly-N-vinyl-2-pyrrolidone (PVP) (Selvam et al., 2012), silica (Barani, 2014), Tragacanth gum (Ghayempour and Montazer, 2017), cellulose (Petkova et al., 2016), polymer diallyl dimethyl ammonium chloride-allyl glycidyl ether-methacrylic P(DMDAAC-AGE-MAA) (Gao et al., 2014), polystyrene-block-poly (acrylic acid) (Prasad et al., 2016), hydrogel (Staneva et al., 2015) and sodium alginate (Varaprasad et al., 2016).

There are several proposed ZnO antibacterial mechanisms namely, direct physical contact with cell walls and destruction of cell membrane's integrity, dissolution of ZnO NPs, and ROS formation. Figure 2.5 illustrates the different proposed mechanisms of ZnO NPs to inhibit bacterial growth. The ROS such as hydrogen peroxide (H_2O_2), superoxide anion (O^{2-}) and hydroxide (OH^-) involve the damge of cellular components such as DNA, lipids and proteins, thus trigger cell death. The released Zn^{2+} induces active transport inhibition and amino acid metabolism as well as enzyme system disruption. Those are the effects responsible for inhibition growth of bacterial cell. The mechanisms are dependent on the presence of UV illumination and morphology of ZnO (Sirelkhatim et al., 2015). Based on the Joe et al. report, the toxicity mechanisms of ZnO against S.aureus and K. pneumoniae under absence of light condition has revealed that the inhibition of bacteria is due to the physical attachment of ZnO on cell wall and increasing release of Zn^{2+} ions in bacterial cytoplasm(Joe et al., 2017). However, Ma et al. presented their studies on comparison of phototoxicity and antibacterial performance of ZnO under natural sunlight (NSL) and ambient artificial laboratory light (AALL) illumination with different ZnO particle sizes. As regarding the phototoxicity, both nano-ZnO and bulk ZnO under NSL had higher methylene blue degradation which occurred as fast as 2 hours than those samples under AALL exposure which only observed after 24 hours. The extent of toxicity under 2 hour-NSL was higher than under 24 hour-exposure AALL. Both conditions seemed to be mediated with different antibacterial mechanisms against Caenorhabditis elegans growth as no significant methylene blue degradation under AALL indicated bare or none generation of ROS such as O_2^-

and $^{-}$OH. It should be noted that no phototoxicity of ZnO under AALL but NSL. The spectrum of sunlight used in the study is assumed to be treated as typical radiation spectrum though it is varied by geographical conditions, atmospheric variability, weather conditions, and so on. Yet, it is estimated around 8~9 % of solar energy falls in the UV electromagnetic region which is sufficiently to activate ZnO to generate ROS and can eventually causes lipid peroxidation and leads to cell death. Whereas, the source of AALL is typical “white cool” fluorescent lamp which possesses negligible amount of UV (less than 400 nm) illumination which is deficient to excite the ZnO to create hydroxyl radials and superoxide ions. It is found that the UV exposure under fluorescent lamps for eight hours is corresponding to one minute of sunlight exposure. Moreover, based on the data obtained, the dissolution of ZnO is estimated to be 5.6 mg/L of Zn is seemed not to be the cause for mortality of bacteria. Thus, the possible mechanism for increasing lipid peroxidation and mortality of C.elegans under AALL for 24 hours exposure could be due to the oxidative stress occurred within the bacterial cell. The precise mechanisms of ZnO antibacterial activity in the absence of light are highly debate and need further understand. On the other hand, the particle size plays a major role in influencing the degree of toxicity for ZnO. The results showed the nano-sized ZnO (60 ± 25 nm) had greater methylene blue degradation percentage compared with bulk ZnO (550 ± 256 nm) (Ma et al., 2011). This is good agreement with Čepin et al. studies that have found the antibacterial activity of E.coli is clearly particle-size dependent (Čepin et al., 2015).

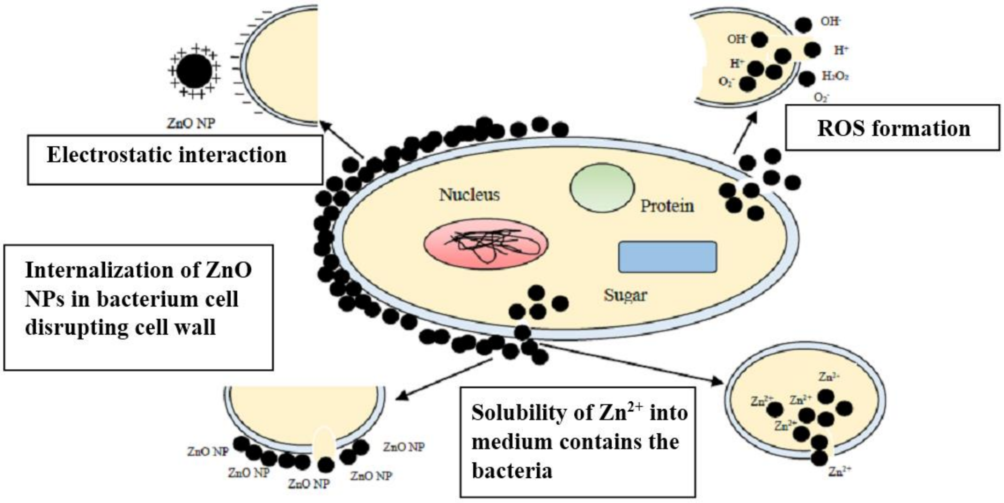


Figure 2.5: Different mechanisms of ZnO NPs on inhibition microorganism's growth namely electrostatic interaction, internalization of ZnO-NPs into bacteria, Zn^{2+} ions release and ROS formation (Sirelkhatim et al., 2015).

2.3.2.1 Synthesis method

There are several ZnO NPs coating techniques has been studied such as pad dry cure (Selvam et al., 2012, Shaheen et al., 2016, Selvam and Sundrarajan, 2012, Barani, 2014, Prasad et al., 2016), spraying and dipping (Çakır et al., 2012), hydrothermal (Krishnaveni and Thambidurai, 2013, Sivakumar et al., 2010), sonochemical (Ghayempour and Montazer, 2017, Perelshtein et al., 2015, Varaprasad et al., 2016, Petkova et al., 2016), plasma treatment (Wang et al., 2007), and pulse laser ablation (Svetlichnyi et al., 2016).

Shaheen et al. have developed amine based material with hexamethyltriethylene tetramine (HMTETA) as precursor which provided alkaline condition for formation of ZnO NPs on cotton fabric by pad dry cure approach, found imparted antibacterial characteristics and UV protection (Shaheen et al., 2016). Selvam and Sundrarajan have functionalized poly-N-vinyl-2-pyrrolidone (PVP) on cotton fiber surface exhibited improved reactive dying and antibacterial activity via pad dry cure approach (Selvam and Sundrarajan, 2012). Barani has applied Zn NPs on cotton fabric by embedding them into silica matrix via two different ways of procedure and compared its effects on morphological, structural, thermal, and antibacterial properties. First method, the fabric was immersed into the sol solution, dried and cured the treated fabric before immersed into zinc nitrate solution, finally treated with sodium hydroxide solution and dried it. The second method was adding the zinc nitrate into solution before immersed fabric into solution, after that dried and cured the treated fabric. The treated fabric was then mixed with sodium hydroxide and dried it. The results showed that the agglomeration of nanoparticles occurred on first method compared to that second method which produced spherical nanoparticles. Thus, the antibacterial properties against S.aureus and E.coli demonstrated higher for fabric treated by second method compared with first method due to its higher surface area exposure (Barani, 2014). Cakır et al. have used reverse micelle cores of PS-b-PAA to form ZnO NPs by atom transfer radical polymerization (ATRP) and dip-coated on cotton fabric for giving long term self-cleaning, UV-protective, and antibacterial properties (Prasad et al., 2016). Besides that, Prasad et al. have made comparison in effectiveness of adhesion of ZnO on cotton fabric between spraying and dipping approaches. As a results, the spraying process had 3 times more formation of ZnO NPs than spraying process while exhibited considerably similar antibacterial reduction (Çakır et al., 2012).

In situ synthesis of ZnO NPs on bamboo pulp fabric with incorporation of multi-amide compound which served as a template to entrap ZnO NPs through hydrothermal impregnation method for rendering UV protective and antibacterial properties have been presented by Zhang et al (Zhang et al., 2013b). Sivakumar et al. have synthesized ZnO flower-like nanorods coated on cotton fabric with the additives chaconne and acacia as antibacterial agent and binder, respectively through hydrothermal synthesis followed by direct immersion approach (Sivakumar et al., 2010). Dhandapani et al. have synthesized ZnO NPs grafted cotton fabric using ureolytic bacteria, Serratia ureilytica to produce biogenic ammonia as the base materials for ZnO NPs synthesis on cotton fabric at temperature 50℃ for different durations (30, 60, 90 min). The results showed that the ZnO morphologies changed upon varied heat treatment duration times. From treatment time 30 to 60 min, the spherical ZnO with particle sizes changed from 170-250 nm to 300-600 nm with evident agglomeration was observed. Further heat treatment of fabric to 90 min caused progressive of ZnO NPs growth with grain sizes of 185-360 nm nanoflower shaped nanoparticles. The cotton fabric with treatment for 90 min exhibited greater antibacterial efficiencies against E.coli and S.aureus compared to that 30 min and 60 min. The reason behind the increased antibacterial activity with prolonged treatment leading to high chance for ZnO NPs crystal growth (Dhandapani et al., 2014).

Combination of enzymatic pre-activation of cotton fiber and sonochemical coating of ZnO NPs on fabric has been investigated by Petkova et al. The ultrasound is applied to boost the enzymatic hydrolysis rate and establish the cotton surface more reducing sugars which act as an anchoring points with ZnO NPs to increase the durability of antibacterial effect. The controlled ultrasound amplitude accelerates the mass transfer from the processing solution towards cotton fiber without damaging the fiber, subsequently enhanced uniformity of enzymatic treatment within shorter period (Petkova et al., 2016). Application of natural polymer as stabilizing agent on synthesis ZnO nanocomposite onto the cotton fabric through sonochemical approach has been studied. Ghayempour and Montazer used Tragacanth gum, a natural polysaccharide as stabilizing, reducing and binding agent for in-situ synthesis of ZnO NPs on cotton fabric via ultrasound irradiation. Figure 2.6 proposed the mechanism of in-situ synthesis of ZnO NPs on the fabric itself. Sodium hydroxide reduces the hydroxyl groups and carboxylic groups of Tragacanth gum to $–O^-$ and $-COO^-$ and ionizes cellulose to cellulosate with negative charge. The Zn ions from zinc nitrate solution bond with hydroxyl groups and carboxyl groups from Tragacanth gum and cotton before sonicate to form ZnO NPs. The analysis showed that the star-like ZnO NPs with average particle size of 62 nm with antibacterial properties against S.aureus, E.coli and C.albicans were observed [98]. Varaprasad et al. has successfully fabricated sodium alginate-ZnO NPs grafted cotton fabric by sonochemical mean. The synthesized ZnO NPs revealed a rod-like shape alignment with average grain size of 25 ± 5 nm with good inhibition microbial growth of E.coli (Varaprasad et al., 2016). Perelshtein et al. have conducted scale-up sonochemical coating of medical textile with ZnO NPs as antibacterial agent. The clinical comparisons have made with two different conditions where 21 patients used ZnO NPs coated medical textile while another 16 patients used normal medical textile. The results demonstrated that the patients using modified textiles were less contaminated with nosomonial pathagens and the textiles did not show toxicity compared to that uncoated NPs textile (Perelshtein et al., 2015).

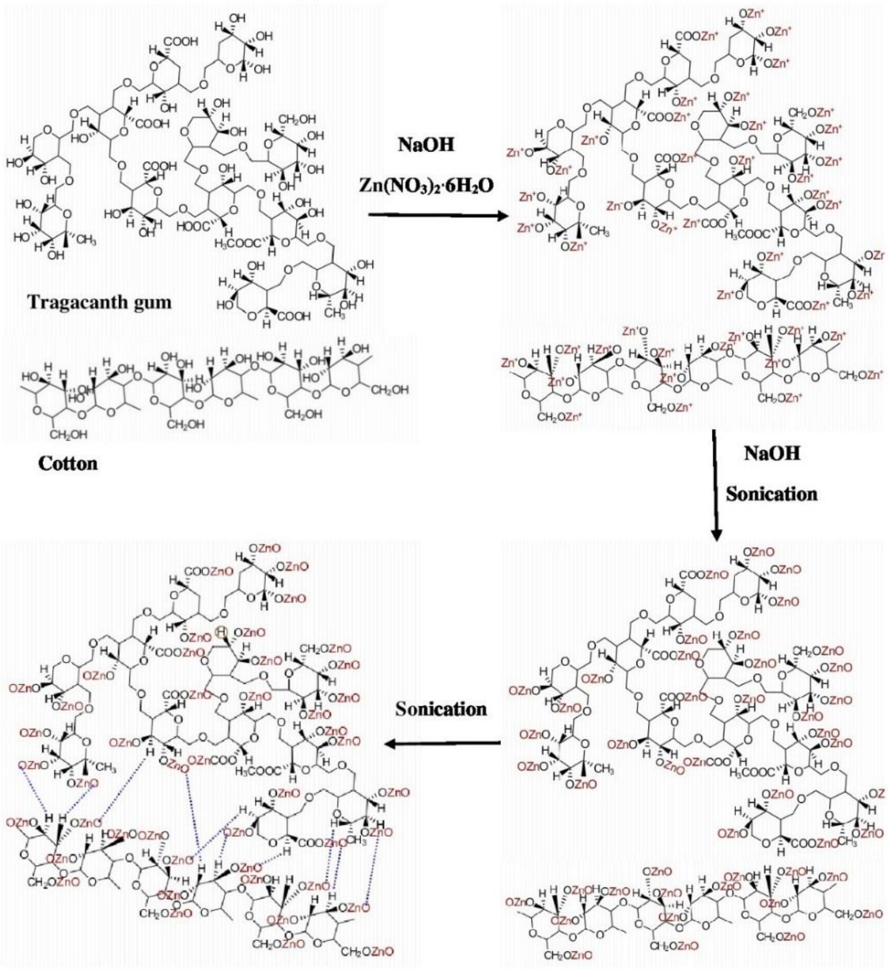


Figure 2.6: The proposed reactions of in-situ synthesis of ZnO NPs on the cotton fabric (Ghayempour and Montazer, 2017).

Plasma pre-treatment for coating ZnO NPs on textile to impart antibacterial property has been investigated by Wang et al. The cotton was pre-treated by cold oxygen plasma and the ZnO/chitosan nanocomposite was coated on treated cotton via facile pad dry cure method. There was a significant enhancement of UV resistance and antibacterial activity of the modified cotton fabric (Wang et al., 2016). Svetlichnyi et al. have proposed to apply pulsed laser ablation for synthesis ZnO NPs in the stable dispersion form under two different types of system namely, water and ethanol. In the case of water system, there were mixture of crystalline forms with different grain sizes and tend to agglomerate. They appeared in spherical, hexagons and rod-like shaped in corresponding particle sizes of 150 nm, 50 to 80 nm and 10-30 nm in width and up to 70 nm in length, respectively. Whereas, the ZnO NPs synthesized from ethanol system mostly consisted of flat square plates from 10 to 60 nm. Thus, the composites synthesized from ethanol dispersions revealed larger inhibition zones than those synthesized from water dispersion system (Svetlichnyi et al., 2016).

2.3.3 Copper-based nanoparticles (Cu-based NPs)

Copper is an excellent electrical and thermal conductivity due to its electronic structure, thus it is widely used in electrical equipment. It is found that copper and its derivatives such as copper oxide have antibacterial features and are applied on diverse fields. Basically, there are two forms of copper oxide that found to have antibacterial property namely; copper oxide (CuO) and copper (II) oxide or cupric oxide (Cu_2O). They are categorized as semiconducting material with monoclinic in structure (Ren et al., 2009). However, CuO appears to be more attractive compared to Cu_2O due to its simplicity and stability. The valence state of CuO (+2) is more stable than valence state of Cu_2O (+1) making CuO able to withstand high temperature above 1020℃ (Ananth et al., 2015). Owing to its excellent superconductivity and serves as a critical p-type semiconductor, CuO has been favorably applied on diverse fields such as catalysis, gas sensors, batteries, solar energy conversion, field emission emitters, and high temperature conductors. Moreover, CuO endows narrow band gap making it having photovoltaic and photoconductive functionalities (Ren et al., 2009). Recent studies have proven CuO in nano-sized possesses antibacterial activity either in suspended or incorporated into matrices (Teli and Sheikh, 2013, Kramar et al., 2013, Ren et al., 2009, Ananth et al., 2015). In order to sustain its antibacterial performance efficiency and durability, it is more preferable to be coated with supporting polymer matrix. This could be explained by two main principles: 1. Polymer facilitates the release of ions in a long term by capping nanoparticles on the material; 2. Polymer enhances the exposure of nanoparticles to the outside environment by increased the surface area, thus creates high probability of reaching and inhibiting the surrounding bacteria (Tamayo et al., 2016). Currently, there are different polymers have been studied as matrix for immobilization of CuO NPs for antibacterial hostility resistance namely: bamboo-rayon (Teli and Sheikh, 2013), nylon (Komeily-Nia et al., 2013), agar (Shankar et al., 2014), bovine-serum albumin (Rastogi and Arunachalam, 2013), carboxymethyl cellulose hydrogel (Yadollahi et al., 2015), cellulose (Llorens et al., 2012), chitosan (Ancona et al., 2014), cotton (Perelshtein et al., 2009), epoxy resin (Das et al., 2014), high-density polyethylene (Bikiaris and Triantafyllidis, 2013), hydrogel based on acrylamide and acrylic acid (Pourbeyram and Mohammadi, 2014). According to Ananth et al., the antimicrobial performance is depend on numerous factors such as surface area and morphology of structure. Selection of suitable synthesis methods and conditions could directly result differences in size and shape and thus, influence the antibacterial performance. As mentioned above, the literature has reported the synthesis of CuO using wet chemical and hydrothermal methods with copper (II) nitrate trihydrate as source of copper and polyethylene glycol as surfactant with different conditions. In wet chemical approach, the temperature of the solution was varied at 75 ℃ and 100 ℃ and the samples were denoted as CuO 75 and CuO 100. Whereas, in hydrothermal method, the sample was synthesized at 150℃ and denoted as HYD 150. The effect of incorporation of PEG on particle structure was determined via FESEM and its impact on inhibition growth of four bacterial strains namely S.iniae, E.coli, V.anguillarum and S.parauberis through disc diffusion method have been carried out. All the CuO samples without PEG tend to be aggregated compared with the samples with PEG as adhesion agent appeared in fine dispersion. This could be explained that PEG facilitates the reduction of Gibb’s free energy while samples without surfactant prone to aggregation to reduce Gibb’s free energy. For morphology aspect, HYD 150 had plate-like particle while CuO 75 and CuO 100 exhibited rice-grain-like and needle-like particle, respectively. However, particle size, morphology, and extend of aggregation changed when PEG concentration varied. In comparison in term of shape-dependent antibacterial performance, nanoplate-like CuO synthesized by hydrothermal method has discovered to have larger zone of inhibitory zone compared to CuO 75 and CuO 100. This could be due to the interaction with bacterial cell wall rely on the morphology of particles, thus resulted different extent of damages to the bacteria and inhibits the growth (Ananth et al., 2015). Generally, there are three mechanisms associated with antibacterial activities by CuO nanocomposites namely, release of Cu ions, Cu nanoparticles, and biofilm inhibition. Inhibition growth of bacteria by copper ions mainly resulted from generation of ROS, caused increase in cell permeability for copper ions diffuse into bacterial intracellular matrix. The copper ions bind to the DNA and cross-link to the nucleic acid strands, caused disorder helical structure and as a consequence caused protein and nucleic acid denaturation and cell unable to replicate and died. Moreover, the overwhelmed of ROS could potentially resulted outbreak of oxidative stress, and burst within the bacterial cell (Tamayo et al., 2016, Dodd et al., 2007). Release of copper nanoparticles mechanism depends on its particle size and surface charge. For particle between the ranges of 10 to 100 nm, the copper particle attaches to cell membrane by endocytosis while particle less than 10 nm, its hydrophobicity or hydrophilicity on surface plays a crucial factor for the interaction with cell membrane (lipid bilayer). Penetration of copper into membrane releases copper ions and triggers copper ions mechanism. Biofilm formation is where the active outer layer of copper particles reduces significantly the cell surface hydrophobicity (CSH) and extracellular polymeric substances (EPS) causes the attachment of copper particles around the cell membrane, consequently it results similar copper nanoparticle mechanism on inhibition bacteria growth (Tamayo et al., 2016).

2.3.3.1 Synthesis method

There are various methods to synthesize Cu based NPs either Cu NPs or CuO NPs coated fabric have been developed such as chemical reduction (Heliopoulos et al., 2013, Yang et al., 2017, Teli and Sheikh, 2013, Komeily-Nia et al., 2013), ultrasound irradiation (Shariatinia et al., 2015, Abramov et al., 2009, Perelshtein et al., 2009, Abramova et al., 2013), and metal chelation technique (Mekewi et al., 2012).

Komeily-Nia et al. have in situ synthesized Cu NPs on nylon fabric with incorporation of ascorbic acid as reducer and cetyl trimethyl ammonium bromide (CTAB) as capping agent through facile chemical reduction technique. The results showed that most of the synthesized Cu NPs were spherical, with minor presence of nano-wired shaped that owned grain size less than 100 nm. The inherited property of surface plasmon absorbance showed colorant effect on fabric. CTAB as cationic surfactant has affected the particle size which resulted smaller particles with improved antibacterial properties (Komeily-Nia et al., 2013). Helipoulos et al. have prepared alginate-Cu NPs coated wool fabric via chemical reduction, exhibited good bacterial reduction against E.coli. There is a difference in copper loading between wool/copper fabric and wool/alginate/copper as the presence of alginate has the ability to hold up more than 170.0 mg/g of copper ions (Heliopoulos et al., 2013). Moreover, Teli and Sheikh have studied the antibacterial characteristic of acrylamide-Cu NPs grafted bamboo rayon fabric by chemical reduction synthesis. Addition of acrylamide on coating served as a binding sites for attachment of Cu NPs on the fabric surface and thus enhanced the bacterial reduction (Teli and Sheikh, 2013). Yang et al. have impregnated Cu NPs on cotton fabric with the use of polydopamine as reductant and binder found exhibited durable sticky superhydrophobicity and considerable antibacterial activity. According to the analysis, it has found that there are mainly consisted of metallic state of Cu with the minor presence of CuO on the cotton surface. The strong adhesive property between Cu NPs and poly-dopamine enable modified fabric still able to inhibit growth of bacteria even it had washed 30 and 50 cycles with 95.5 % and 88.5 % reduction of initial E.coli presented (Yang et al., 2017).

Perelshtein et al. have prepared CuO NPs coated cotton fabric via in situ one-step ultrasound method and found that the process lead a homogeneous dispersion of CuO NPs with 15 nm in size, owned significant bactericidal effect against E.coli and S.aureus (Perelshtein et al., 2009). The synthesis of CuO NPs is through the reaction with Cu ions with ammonia to form deep blue solution of ammonium complex ions accompanied by hydrolysis and sonochemical mirojets. The chemical reaction pathways to form CuO NPs are depicted as following:

$$Cu^{2+}_{(aq)} + 4NH_3{\cdot}H_2O_{(aq)} \rightarrow [Cu(NH_3)_4]^{2+}_{(aq)} + 4H_2O \quad (1)$$

$$[Cu(NH_3)_4]^{2+}_{(aq)} + 2OH^-_{(aq)} + 4H_2O \rightarrow Cu(OH)_{2(s)} + 4NH_3{\cdot}H_2O_{(aq)} \quad (2)$$

$$Cu(OH)_{2(s)} \xrightarrow{\Delta} CuO_{(s)} \quad (3)$$

According to Mekewi et al., antibacterial CuO NPs coated into textile using ultrasonic cavitation has synthesized ellipsoidal shape and particle sizes range from 200 to 400 nm with considerable antibacterial activity against Escherichia coli, Klebsiella pneumoniae, Staphyloccus aureus, and Methicillin-Resistant Staphyloccus aureus (MRSA) (Abramova et al., 2013). Shariatinia et al. have used two nano-sized copper(II) complexes including phosphoric triamide ligands with formula $Cu(NO_3)_2L_2$ and $Cu(CH_3COO)_2L_2$ where L represents $4\text{-}NO_2C_6H_4NHP(O)(NC_4H_8O)_2$ coated on nylon and wool fabrics, endowed yellow and green color, respectively with spherical morphology in average grain sizes of 17-20 nm. The complexes were synthesized through sonochemical approach and the yielded fabrics possessed excellent wash fastness and antibacterial activity against Bacillus subtilis while poor in lightfastness (Shariatinia et al., 2015). The pilot scale sonochemical coating of CuO NPs onto cotton fabric produced biocidal property has been studied by Abramov et al. According to the results, it revealed that the coating is homogeneous with particle sizes range from 10 to 20 nm. It is found that the homogeneity of metal deposition on fabric depends on the precursor concentration as well as velocity of bandage passing between the sonicated plates (Abramov et al., 2009).

Mekewi and co-workers have presented antibacterial synthetic viscose and acrylic fabrics by using metal chelation Cu NPs to enhance antibacterial activities against E.coli and S.aureus. The fabric has undergone amination with different types of chemical namely, ethylenediamine (ED) and benzedine (Bz) and the effect on its affinity to metal chelation of Cu which indirectly influence the antibacterial activity has been studied. The results showed that benzedine treated fabric is more favorable for Cu metal uptake than those fabric treated with ED owing to Bz molecules binding affinity to translation metal ions through the nitrogen lone pairs. As a consequence, benzedine treated fabric has more prominent microorganism’s hostility resistance (Mekewi et al., 2012).

2.3.4 Titanium oxide nanoparticles (TiO_2 NPs)

TiO_2 exists in three famous crystalline structures known as anatase, rutile, and brookite. Compared to anatase and brookite, rutile is the most thermally stable due to its more compact structure. When anatase and rutile heated under high temperature, crystal growth induced and altered the phase stability and ultimately caused anatase and brookite are irreversibly transformed to the rutile. Rutile has excellent characteristics such as greater chemical stability, higher refraction index, and higher specific gravity compared to anatase and brookite, making it mostly used in pigments industry. Anatase in nanosize-structure is metastable at ambient room temperature while rutile phase is stable at room temperature in particle size beyond ~14 nm. Thus, thermodynamic stability is particle size dependent and it is important in determination performance of TiO_2 in different applications. Due to its stability at nano-structure, anatase is favorably used in photocatalysis due to its high surface area. Its high photocatalytic property able to generate electrons and electric hole pairs by absorption of UV illumination. The created electrons and holes react with oxygen and water to form O_2^- and hydroxyl radicals. This ROS generation is postulated could be the agent to kill the bacteria cell under presence of light (Shaikh et al., 2016). Wu et al. have been successfully deposited TiO_2 in anatase with particle size 3~5 nm on cotton fabrics, possessed distinct bactericidal activity and self-cleaning under the fluorescent light. It proposes that the antibacterial efficiency is due to the photocatalytic effect of TiO_2 coated fabric, leading to destruction of cell wall and membrane by ROS (Wu et al., 2009). However, due to its wide energy band gap between conduction and valence bands which is approximately 3.2 eV, it requires high energy to create electrons and electric hole pairs. Thus, researchers have been added noble metal and additive material to extend the light absorption property of TiO_2 from UV to visible light range, which resulted in high generation of ROS. These included silver/polysiloxane (XPs) (Dastjerdi et al., 2010), chitosan (El-Shafei et al., 2015), chitosan/AgCl (Arain et al., 2013, Goyal et al., 2016), and sericin/polycarboxylic acid (Doakhan et al., 2013). Notably, Ag-TiO_2 coated cotton fabrics have been studied due to the shifting of UV-vis absorption spectrum to long wavelength (> 400 nm), thus enable the enhancement of antibacterial activity under fluorescent light. Ag serves as an electron traps facilitating electron-hole separation by generation a local electric field which accelerates the electron excitation from valence band to conduction band (Dastjerdi and Montazer, 2010). According to Daoud et al. literature, it suggested that the cytotoxicity of TiO_2 not only occurred under the presence of light but the reduction of bacteria cells under dark condition have been observed due to the non-sustenance nature of TiO_2 by serving as a protecting shield against formation of biofilm (Daoud et al., 2005).

2.3.4.1 Synthesis method

There are several techniques in preparation of TiO_2 coated fabric namely, pad-dry-cure method (Li et al., 2011, Meftahi et al., 2015, Selvam et al., 2012, Wu et al., 2009, Dastjerdi et al., 2010, El-Shafei et al., 2015, Arain et al., 2013, Doakhan et al., 2013, Daoud et al., 2005) and sonosynthesis (Goyal et al., 2016, Behzadnia et al., 2014) in which all of these methods are carried out at low temperature.

For pad-dry-cure method, Dastjerdi et al. have synthesized polysiloxane/silver on the TiO_2 polyester fabric to test the effect on antibacterial activity against S.aureus and E.coli (Dastjerdi et al., 2010). Arain et al. have studied the effect of different blend ratios of chitosan to AgCl/TiO_2 coated onto fabric on antibacterial activity against S.aureus and E.coli via pad-dry-cure method. Increasing concentration of chitosan not only showed better antibacterial activity but had advantages on tensile strength, fabric stiffness, and wrinkle recovery angle (Arain et al., 2013). Doakhan et al. have prepared sericin/TiO_2 grafted cotton fabric with polycarboxylic acid as cross-linking agent via pad-dry-cure method. The presence of sericin acted as a glue to bind the TiO_2 on cotton and at the same time facilitated antibacterial activity against S.aureus and E.coli. Its poly cationic feature which has ability to interact with negatively charged bacterial cell membrane, reduce cell membrane integrity and ultimately leading to cell death (Doakhan et al., 2013). El-Shafei et al. have applied TiO_2 (0-9 %) on cotton fabric with the presence of different amounts of BTCA (0-8 %), SHP (0-8 %), and chitosan (0-10 %) through pad-dry-cure approach, exhibited flame retardant and antibacterial properties (El-Shafei et al., 2015). Li et al. have designed nano-sized TiO_2 and Ag/TiO_2 functionalized silk textile with the aid of 3-(3,4-dyhydroxyphenyl) propionic acid (DHBPA), 1,2,3,4 butanetetracarboxylic acid (BTCA), dimethyloldihydroxyethyleneurea (DMDHEU), and sodium hypophosphite (SHP) which served as enhancing antiviral property, bridge crosslink, color property, and catalyst, respectively through pad-dry-cure method. It is observed that TiO_2 had a diameter around 20 nm with irregular structure and was surrounded by nano-sized Ag with grain size approximately 5 nm which enhanced photocatalysis and thereby increased the antibacterial activity against E. coli, S. aureus, and P. aeruginosa (Li et al., 2011). Wu et al. have used tetrabutyl titanate as precursor for TiO_2 production via pad dry cure technique. The synthesized TiO_2 possessed dominant anatase crystalline morphology with almost uniform in size 3~5 nm dispersing on cotton fabric surface. The coated fabric showed self-cleaning ability in photocatalytic decolor of dyes and antibacterial activity (Wu et al., 2009). Daoud et al. have used titanium isopropoxide as source for TiO_2 via pad dry cure method. The TiO_2 characterized semi-spherical morphology with particle size around 10 nm in diameter on cotton surface. The authors have compared the antibacterial assessment under UV radiation and dark conditions and found that both conditions possessed reduction of bacteria but with coated fabric under UV irradiation had higher cytotoxicity compared with that under absence of light (Daoud et al., 2005).

Immobilization TiO_2 onto textile material can be through in-situ sonosynthesis approach. This method not only able to reduce surface of textile, but also enhance the washing fast ability by trapping the nanoparticles inside the textile matrix. The simplicity of this method also provides the formation of TiO_2 on textile in one single step and without involving of annealing process. Goyal et al. have studied the role of chitosan with different molecular weights, low molecular weight (LMW-CS) and high molecular weight (HMW-CS) of chitosan on coating TiO_2 onto cotton fabric via sonosynthesis method. Figure 2.7 depicts the stabilization mechanism of adding HMW-CS, LMW-CS, and ionic polymers which are PVA and PEG on TiO_2 NPs. Incorporation of CS enhances the chemical bonding by forming of hydrogen bonding between hydroxyl groups of TiO_2 NPs and polar groups of CS. The cationic behavior of CS due to the presence of $–NH_3^+$ on molecules increase the ξ potential and stabilize the TiO_2 dispersions on cotton. Also, the role of steric hindrance by using a non-ionic polymer acts as stabilizing agent on TiO_2/CS dispersion on cotton. Both LMW-CS and HMW-CS coated with TiO_2 on cotton had self-cleaning, UV-protection, and antibacterial activity. Yet, with HMW-CS samples, there was an increase in TiO_2 particle size and dispersion stability due to its high molecular weight able to create a thicker layer around the TiO_2 before the repulsion suppressed the deposition of further chains.(Goyal et al., 2016). Behzadnia et al. have used sonochemical method at 60-65 ℃ to produce TiO_2 coated wool fabric by using two different precursors namely, titanium isopropoxide (TTIP) and titanium butoxide (TTIB). The synthesized TiO_2 resulted the formation of both anatase and rutile phases with self-cleaning, antibacterial, and hydrophilicity properties. The samples with TTIB have found to have higher photocatalytic activity compared to samples with TTIP. This could be due to the longer hydrocarbon chain changes the band gap of TiO_2 but persuades several localized occupied states in the gap (Behzadnia et al., 2014).

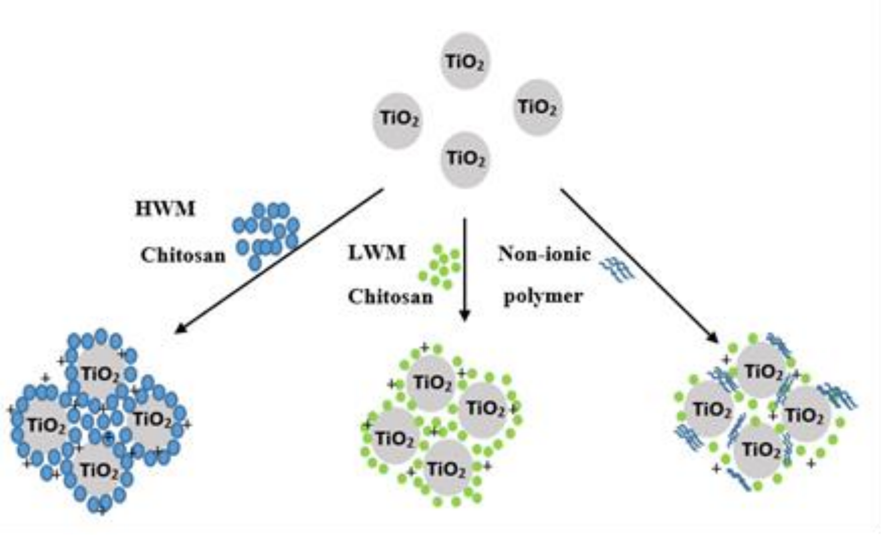


Figure 2.7: Suggested stability mechanism for TiO_2 NPs deposition in the presence of polymers (Goyal et al., 2016).

2.3.5 Other metal based nanoparticles

There are also embedment of other metal based antibacterial agents such as iron based (Rastgoo et al., 2016), CeO_2 (Lu et al., 2014, Rajan et al., 2017), Au (Tang et al., 2014, Tang et al., 2015, Ganesan and Prabu, 2015, Velmurugan et al., 2016), Ni (Mekewi et al., 2012), SiO_2(El-Gabry et al., 2013, Wang et al., 2007), and Pt (Shahidi and Ghoranneviss, 2011). For iron based NPs, Rastgoo et al. have prepared Fe_3O_4 on blended cotton/polyester fabric via ultrasound mediation exhibited magnetic, photocatalytic, sonocatalytic, and antibacterial characteristics (Rastgoo et al., 2016).

CeO_2 is one of the most abundant rare earth metal oxides, which categorized in lanthanide series with two stable oxidation forms trivalent state (+3) and tetravalent state (+4). The ability in reversible switching between two oxidation states along with the oxygen vacancies by surface defects making it possesses antioxidative ability which is widely applied on biomedical field by regenerating free-radical-scavengers. Moreover, its relatively smaller band gap compared to ZnO and TiO_2, leading it as alternative UV absorbent for sunscreen, photocatalyst, textile fiber coating, and so on (Lu et al., 2014). The toxicity of CeO_2 on microorganisms has been studied by Rajan et al. (Rajan et al., 2017), and Lu et al. (Lu et al., 2014). Lu et al. have immobilized CeO_2 NPs on silk fabric via simple dip-coating approach, found endowed UV-shielding ability and antibacterial activity. The synthesized CeO_2 NPs tend to agglomerate and lead to larger particle sizes ranging from 20 to 30 nm which might affect the efficiency of antibacterial performance. In order to enhance microbicidal effect of CeO_2 on treated fabric, Rajan et al. have incorporated allicin on coating via wet chemical method found to have more effective on inhibition growth of E.coli and S.aureus.

Most of the studies regarding the synthesis of Au NPs coated textile use chloroauric acid ($HAuCl_4$) as source of Au. Tang et al. have functionalized Au NPs coated bamboo pulp fabric through facile chemical reduction method without any stabilizing agent used. The results indicated that the morphology of Au NPs depend on the concentration $HAuCl_4$ solution, which induced different colorant effect owing to their localized surface plasmon resonance (LSPR) property. The imparted fabric showed excellent fastness to light, UV protection, and antibacterial activity (Tang et al., 2015). Tang and co-workers also have presented another literature based on the in situ of Au NPs coated silk fabric by using same method. The Au NPs coated silk fabric possessed remarkable antibacterial activity, UV protective, and thermal conductivity (Tang et al., 2014). Moreover, there are researches on synthesis Au NPs coated textile with additional reducing agent either synthetic or natural. Ganesan and Gurumallesh Prabu have synthesized antibacterial Au NPs coated cotton fabric with $HAuCl_4$ as precursor and extract of Acorus calamus rhizome as green reducer via pad dry cure method. The results revealed that the size of Au NPs depend on the concentration of precursor. At low concentration, NPs showed homogenous in size with spherical morphology at particle size in below 100 nm. Whereas, at high concentration of precursor, the synthesized nanoparticles showed in bigger size in spherical structure at grain sizes between 100 to 500 nm. The treated fabric showed improved antibacterial activity and UV blocking property compared to that untreated fabric (Ganesan and Prabu, 2015). Velmurugan et al. have compared three different modes of synthesis Au NPs on cotton, silk, and leather namely, green, chemical, and combination of green and chemical composite techniques. For green synthesis, natural leaf powder extract, Ginkgo biloba Linn is used as reducer while for chemical route, KBH_4 is used as reducing agent. Combination of both syntheses using both reducing agents in the synthesis process. Based on the observation, it is found that composite syntheses had more dead bacterial cells than in green and chemical synthesis. The treated leather is less affinity to take up Au NPs than silk and cotton due to its collagen bundles interconnected with large elastic fibers. Moreover, the incorporation of G.biloba leaf extract is responsible for enhancing high antibacterial activity (Velmurugan et al., 2016).

Application of monodisperse silicon on development of multifunctional textile has been studied (El-Gabry et al., 2013, Wang et al., 2007). El-Gabry et al. have incorporated acrylate based copolymer as binder on coating nano-sized silica on viscose and polyester fabrics through conventional pad dry cure method. It is found that percentage of reduction E.coli bacteria before and after 10 laundering cycles is higher for acrylate/silica treated fabric compared to pristine and solely silica coated fabrics, indicated the conducive trapping effect on the treated fabric. Wang et al. have prepared nano-silica with additional loading of Ag via plasma irradiation treatment found to have spherical particles with average grain size of 60 nm, exhibited high effective in inhibition of bacteria growth and good water resisting feature.

For Pt NPs, Shahidi and Ghoranneviss have investigated the antibacterial feature of Pt on polyester fabric with different natural and synthetic dyes via DC magnetron sputtering mean. It revealed that the platinum itself did not show any antibacterial activity without presence of any derivatives of antibacterial agent (Shahidi and Ghoranneviss, 2011).

CHAPTER 3

METHODOLOGY

3.1 Material

Zinc acetate ($Zn(CH_3COO)_2 \cdot 2H_2O$) (97%), sodium hydroxide (NaOH) (99%), polyvinyl alcohol (PVA) (89% degree of hydrolysis), ethanol (C_2H_5OH) (99%) were purchased from Merck Co. A 100% plain-woven cotton fabric was used in this study. All the chemicals and agents were of analytical grade, and distilled water was used throughout the work.

3.2 Synthesis of ZnO/PVA cotton fabric

ZnO/PVA was synthesized on the surface of cotton fibers through ex-situ dip coating method. ZnO were synthesized by preparing $Zn(CH_3COO)_2 \cdot 2H_2O$ range from 0.10, 0.15, 0.20, 0.25 M (in 50 ml distilled water) was then dropwised with excess NaOH solution (1 M) under stirring. Two layers were formed with white precipitate ZnO settled on the bottom and by-products, sodium acetate ($NaCH_3COO$) and water were formed on the upper layer. The sodium acetate was dissociated in the water and the solution was centrifuged to get ZnO. After that, PVA solution (5, 10, 15, 20 g in 200 ml of distilled water) was prepared under water bath at 100 ℃ for 4 hour until all the PVA powders were dissolved. PVA solution was then poured inside ZnO and the solution was swirled to achieve homogenous dispersed phase. A cotton fabric with a 7 × 7 cm^2 was soaked inside ethanol solution for 10 min before coating process. The cotton was padded in the PVA/ZnO solution. The finishing was dried at 70 ℃ for overnight.

3.3 Scanning Electron Microscope (SEM)

The surface morphology of the samples was scanned using Hitachi Scanning Electron Microscope model BS 340 TESLA. This instrument was operated at the electron beam voltage of 20 to 30 KV. The 1000× magnification power was chosen and the scanning photographs were recorded. Before carried out the scanning, the specimen was cut into smaller piece and was coated with thin layer of gold.

3.4 Energy Dispersive X-ray spectroscopy (EDX)

Energy Dispersive X-ray spectroscopy (EDX) was used to find out the elemental composition of coated samples.Before carried out the scanning, the specimen was cut into smaller piece and was coated with thin layer of gold.

3.5 X-ray Diffraction Analysis (XRD)

The crystalline structure of ZnO was determined by using Shimadzu XRD 6000 diffractometer with Cu-Kα radiation source at λ, 1.542 Å. The gold-coated specimen was mounted on a goniometer to position the specimen at selected orientation for scanning. The scanning operation was carried out in a 2 θ range from 10 ° to 60 ° with step size of 0.02 at 2 ° min^{-1}. The operating voltage and current was 40 kV and 30 mA respectively. The scanning pattern was recorded by using Rigaku software. The average crystal size of ZnO was calculated using Debye-Scherrer equation as follow (Ghayempour and Montazer, 2017):

$$d = \frac{k\lambda}{\beta \cos\theta} \tag{4}$$

Where Scherrer constant, K (0.92), λ is wavelength of X-rays, Bragg diffraction angle, θ and full-width at half maximum of the peak, β related to ZnO.

3.6 Fourier Transform Infrared Spectroscopy (FTIR)

To identification of chemical bonding of the samples, Fourier Transform Infrared Spectroscopy (FTIR) was employed by using Perkin Elmer Spectrum One. The vibration frequency of pure cotton fabric, ZnO, PVA, ZnO/PVA and ZnO/PVA cotton fabric were obtained to identify the presence of certain functional groups. The specimen was loaded in the sample holder inside the compartment of the equipment under the λ range between 4000 cm^{-1}

– 400 cm^{-1}. For typical solid sample, the “Force Gauge” was set to be around 80. The transmission spectrum data was then can be collected and recorded.

3.7 Tensile Test

The mechanical test was used to test the tensile strength of the samples. The dimension used was 60 mm × 6 mm × 0.5 mm. The Instron Universal Testing Machine (Model 4302 Series IX) was used as testing machine where the specimen was loaded in the grip of the machine. The tensile measurement for every different formulation sample was used from average 5 samples and the data results were then generated through Bluehill software.

3.8 Antibacterial Test

The antibacterial efficiency of ZnO/PVA cotton fabric against S.aureus and E.coli was determined by disc diffusion method (Kirby-Baucer method) through the measurements of inhibition zone surrounding the treated samples. The 1×10^8 of bacteria were prepared by using 0.5 McFarland standard and swabbed over the surface of sterile nutrient agar plates. The treated cotton fabric with diameter of 0.5 cm was gently pressed on the swabbed agar surface and incubated at 37°C for 24 hour. The antibacterial property of treated cotton fabric is calculated by the mean value of inhibition zone as shown as following equation (Emam et al., 2015):

$$\mathrm{W} = \frac{\mathrm{T} - \mathrm{D}}{2} \tag{5}$$

Where W is the width of the inhibition zone in mm, T is the total diameter included fabric patch and clear zone where no bacteria grown and D is the diameter of fabric patch.

CHAPTER 4

RESULTS AND DISCUSSIONS

4.1 ZnO synthesis mechanism

The fabrication of ZnO/PVA cotton fabric is carried out by utilized zinc acetate and excess sodium hydroxide. It is an acid-base reaction. The possible reaction is shown in Equation 6-8. The main product, zinc hydroxide, $Zn(OH)_2$ and by-products, sodium acetate CH_3COONa and water H_2O are formed. Excess sodium hydroxide is to provide alkaline condition for ZnO formation. According to Mamady et al., the alkaline $[HO^-]$ / $[Zn^{2+}]$ ratio affects the ZnO formation. For $[HO^-]$ / $[Zn^{2+}]$ ratio< 2, zinc hydroxide (Zn (OH_2) is preferably formed. Conversely, for $[HO^-]$ / $[Zn^{2+}]$ ratio ≥ 2, the structural and crystallinity growth showed the ZnO structure is crystallized. In fact, the number of OH^- must at least twice that of Zn^{2+} in order for the synthesis of hydrated hydroxides [$(Zn(OH)_2)$ and Zn-OH groups] as precursor at a previous process of nucleation for ZnO formation (Conde et al., 2011). As reference to Table 1, shows the concentration of sodium hydroxide and zinc acetate and $[HO^-]$ / $[Zn^{2+}]$ ratio used in this study. The $[HO^-]$ / $[Zn^{2+}]$ ratio is between 4 and 10 which provide favorable condition for ZnO formation. The advantage of this synthesis ZnO route is ability for good control of particle nucleation and growth processes without require for ripening or annealing process.

In order to control the ZnO NPs size, the synthesized ZnO is dispersed into the long chain PVA polymer matrix as a template capable of maintaining size distribution and good uniformity. The cellulose of cotton is reduced with ethanol to ionize to cellulosate with negative charge facilitates the bonding with ZnO/PVA. The intra- and intermolecular hydrogen bonding is the hindrance to dissolution and bonding formation with surrounding molecules. The enthanolysis is used to degrade the cellulose fiber wall layer and weaken the cell wall structure allowing ZnO accessibility to the inner core of fiber. These chemically modified surfaces attributed vital condition in ZnO NPs fabrication and assembling. The possible mechanism for coating ZnO/PVA on cotton is proposed in Figure. 4.1.

$$(Zn(CH_3COO)_2 2H_2O) + 2NaOH \rightarrow Zn(OH)_2 + 2CH_3COONa + 2H_2O \quad (6)$$

$$Zn(OH)_2 + 2H_2O \rightarrow Zn(OH)_4^{2-} + 2H^+ \quad (7)$$

$$Zn(OH)_4^{2-} \rightarrow ZnO + H_2O + 2OH^- \quad (8)$$

Table 4.1: Concentration of sodium hydroxide and zinc acetate and respective $[HO^-] / [Zn^{2+}]$ ratio

Zinc acetate concentration [M]	**Sodium hydroxide concentration [M]**	**$[HO^-] / [Zn^{2+}]$**
0.1	1	10
0.15	1	6.67
0.20	1	5
0.25	1	4

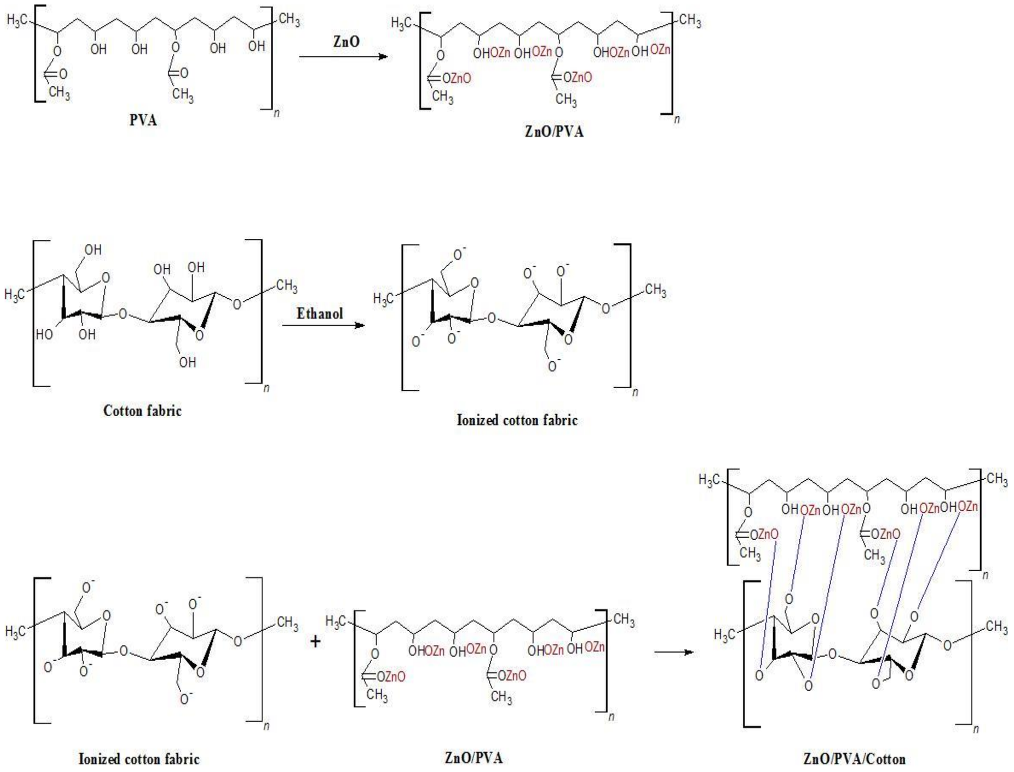


Figure 4.1: The possible mechanism for coating ZnO/PVA on cotton fabric.

4.2 SEM

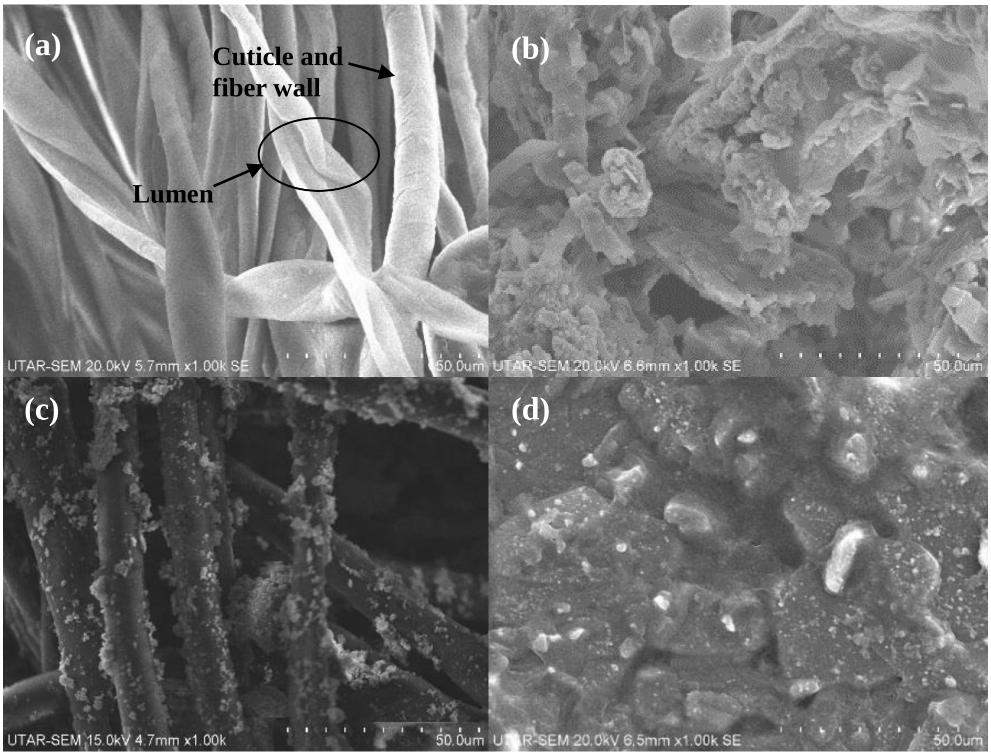
SEM is used to observe the surface morphology of untreated cotton fabric and cotton fabric treated with ZnO/PVA as showed in Figure 4.2. The SEM image of pristine cotton fabric in Figure 4.2(a) showed individual lengthwise warp yarns are held smooth surface without attached with any particles on the surface. The cotton fibers resemble twisted ribbons or a collapsed and twisted tubes. These twists are called convolutions (Grishanov, 2011). The mature pristine cotton endowed convolute and convex/concave structures with loosely detached individual fibers. In fact, the cotton structure comprises of cuticle, fiber wall and lumen. As reference to Figure 4.2 (a), the cuticle and fiber wall are the outer layers underneath the cellulose fibrils which protects the fibrils from chemical and mechanical damages. Underneath the fiber wall, there is an abundant, well-arranged system of continuous, very fine capillaries. These capillaries serve greatly to cotton’s wipe-dry performance Also, through the observation from the Figure 4.2 (a), cotton fibers are collapsed inward, hollow canal which resulting kidney-shaped cross section of cotton fibers are called lumen. The hollow lumen is resulting from the evaporation of cell sap after the cotton boll burst open during the growth period. As the sap evaporates, the atmospheric pressure on the outside is greater than pressure inside the fiber and leading to fiber wall shrinks, collapse, lumen become smaller and the fiber develops convolution. The characteristics of convolutions and hollow lumen not only provide comfortable and compatible to human skin due to the countless minute air space exists between them (Kljun et al., 2014).

The ZnO is synthesized through zinc acetate and sodium hydroxide is displayed with agglomeration with non-uniform shapes inset of Figure 4.2(b). ZnO is highly insoluble in water system, thus it is vulnerable to agglomerate in water owing to high polarity of water leading to deposition (Tan et al.). To our knowledge, dielectric constant dominantly influences the kinetic of nucleation and growth of crystallites. In a word, water has high dielectric constant which favor the nucleation and growth of ZnO into large crystallites (Chen and Chang, 2004). Also, nanoparticles tend to agglomerate and form large-sized aggregates due to the existence of inter-particle forces and surface energy. Thus, this is a common problem encounter in nanotechnology that nanoparticles incline to reduce its excess surface energy by forming large crystals (Nanda et al., 2003).

Based on Figure 4.2(c), the ZnO NPs agglomerated severely on the cotton fibers. The intrinsic property of ZnO as inorganic metallic oxide has poor compatibility and stability to organic system hindered it on textile application. Also, from the observation, cotton has mercerized in cylindrical shapes and has very few convolutions. This is due to the alkali ethanol causes the cotton fibers to swell, penetrate to the amorphous regions of the fibers. Ethanol caused weakening in the cell wall structure and built up osmotic pressure inside the fiber led to swelling phenomenon. The swelling increase the fiber thickness and fiber contraction occurs. Mercerization results tougher, smoother and more regular, enabling it to reflect incident light more evenly (Qin et al., 2008).

Thus, in order to overcome the aggregation of ZnO, PVA polymer is applied into ZnO NPs. PVA polymer possesses amphiphilic property has ability to prevent fine crystalline precipitate from agglomeration into large bulk particles. PVA structure comprises of hydrophilic of large number of free hydroxyl groups forming hydrogen bonding with ZnO while on the other side facing hydrophobic long chain of hydrocarbon which inhibit further growth of ZnO, forming physical barrier to the preferred growth of ZnO crystals as shown in Figure 4.2(d). The uniform dispersion of ZnO NPs and good affinity between ZnO and PVA led to reduction density of crack deflection sites and enhanced miscibility of PVA polymer phases (Pouton, 2006).

A close examination on the sample in Figure 4.2(e) that ZnO/PVA is deposited on fibers and fibers are bonded together. The reason behind these phenomena is aroused from coupling effect of PVA, which acts as adhesive agent to connect ZnO and cellulose fibers. Polymeric adsorption is effectively stabilized the dispersion of inorganic ZnO particles in the organic cotton material through combination of electrostatic and chemical interaction, hydrogen bonding formation and Van der Waals force (Sudha et al., 2013). There is a clear difference between cotton solely with ZnO and cotton with ZnO/PVA. The surface of ZnO /cotton is rough with increased diameter of cotton fibers and ZnO is agglomerated in bulk form. Conversely, ZnO/PVA cotton visualized the homogenous dispersed phase provided uniform properties over cotton fabric. The stabilization of ZnO NPs over cotton fabric is crucial for antibacterial activities as it facilitates the penetration of ZnO into intracellular matrix and triggers cytotoxic mechanisms.



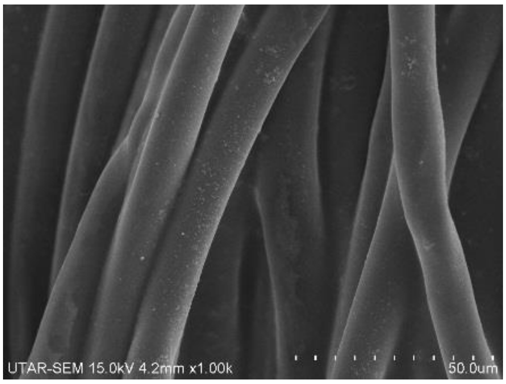
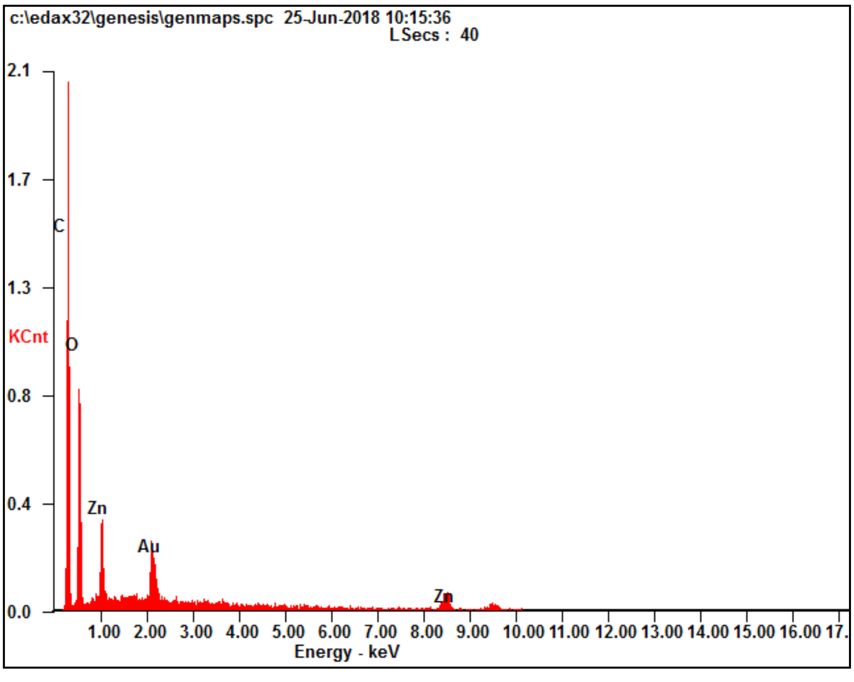


Figure 4.2: SEM images of (a) pristine cotton, (b) ZnO, (c) ZnO/cotton, (d) ZnO/PVA, (e) ZnO/PVA cotton.

4.3 EDX

The elemental identification and composition analysis of ZnO/PVA cotton is investigated through energy dispersive X-ray characteristics test (EDX). The corresponding EDX result in Figure 4.3 shows the spectrum of ZnO/PVA cotton. As reference to the figure, the result indicates the ZnO/PVA cotton comprises of carbon, oxygen, zinc elements, along with trace amount of gold element. From quantitative analysis revealed that carbon concentration is highest at 0.3 KeV which originated from aliphatic hydrocarbon from cotton and PVA. Also, there is a strong signal of oxygen at 0.5 KeV is contributed from cotton, PVA and ZnO. The oxygen from cotton is come from the three hydroxyl groups, one primary and two secondary and oxygen bridges linked by C-1 to C-4 (Qin et al., 2008). On the other hand, the oxygen detected from PVA structure is come from the ester group and hydroxyl group presented in the structure (Halima, 2016). The characteristic peaks at approximately 1.0 and 8.6 KeV confirmed the presence of Zn on the surface of cotton fibers with the loading percentage of 1.64 atomic %. The minor amount of Au as coating agent before testing to make the sample conductive and give the accurate analysis result. These test results are in line with other research work (Shaban et al., 2016).

The contribution of ZnO over the cotton fabric is investigated using Mapping images (Figure 4.4a-c). The carbon, oxygen and zinc elements are found in the treated cotton which displayed in red, green and blue respectively in Figure 4.4a-c. The high concentration of carbon and oxygen in the structure are contributed from the cotton fabric and PVA while zinc element can be observed in their mapping images as well. Based on the image, the presence of zinc element demonstrates uniform distribution stabilized on the cotton fabric. The results obtained from the SEM morphology and spectrum and mappings from EDX are clear evidence of the deposition of ZnO on the surface of cotton fabric.



Element	***Wt%***	***At%***
CK	**50.11**	**64.53**
OK	**34.30**	**33.16**
AuM	**08.67**	**00.68**
ZnK	**06.93**	**01.64**
Matrix	**Correction**	**ZAF**

Figure 4.3: EDX spectrum and composition of ZnO/PVA cotton.

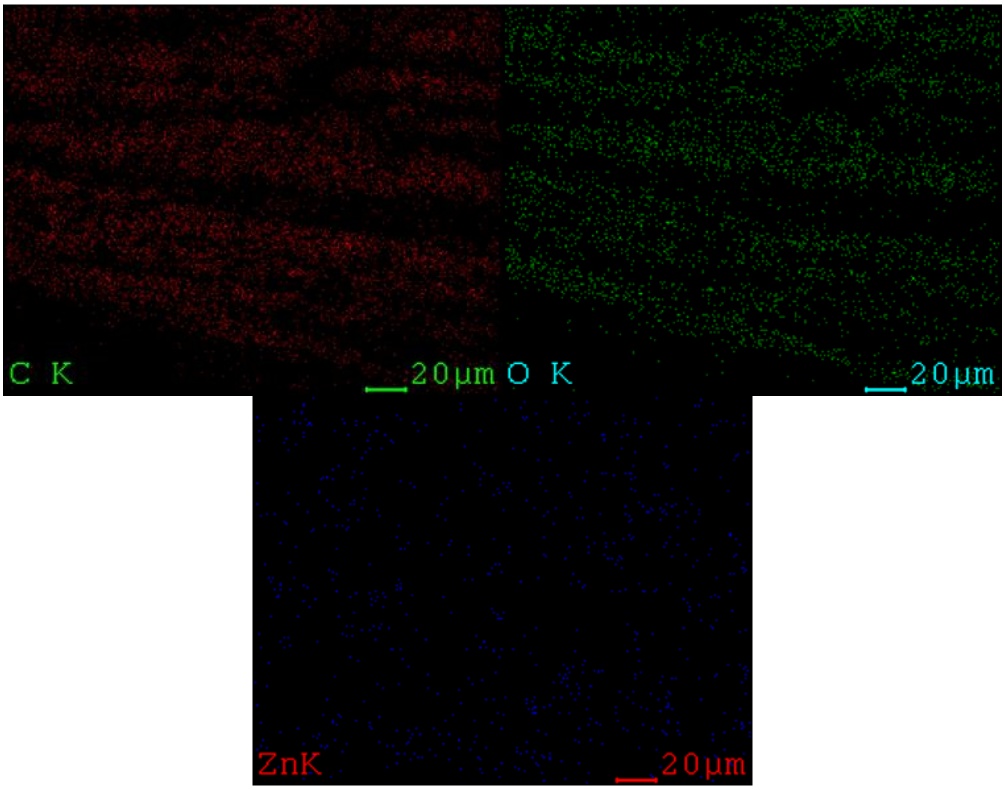


Figure 4.4: EDX mapping images of (a) Carbon (b) Oxygen and (c) Zinc elements.

4.4 XRD

XRD primarily used in this study is to determine the compound identification and grain size of ZnO crystallite of treated cotton fabric. Figure

4.5 revealed the XRD diffraction peak of synthesized ZnO NPs prepared by dip coating method. Based on the figure, there is diffraction peaks at 31.71°, 34.37°, 36.02°, 47.48° and 56.53° which assigned to {100}, {002}, {101}, {102}, and {110} indicated hexagonal wurtzite structure of the synthesized ZnO. In the wurtzite structure, the oxygen ions, O^{2-} are arranged in a hexagonal close packed model with zinc ions, Zn^{2+} filling half the tetrahedral sites. The O^{2-} and Zn^{2+} ions coordinated tetrahedrally and stacked alternately to each other along the c-axis. The lattice parameters of synthesized ZnO for dominant peaks at {100}, {002} and {101} are compared with the published Joint Committee on Powder Diffraction Standards (JCPDS) card 036-1451 of wurtzite structure of ZnO. The comparison result is tabulated in Table 4.2. The values for 2 theta and d spacing obtained are consistent with JCPDS data of wurtzite ZnO. The full width at half-maximum (FWHM) for synthesized ZnO are summarized in Table 2. The lattice constant a and c for {100} and {002} are calculated by using equations (9) and (10),

$$a = {}^{\lambda}/_{\sqrt{3}sin\theta} \tag{9}$$

$$c = {}^{\lambda}/_{sin\theta} \tag{10}$$

The a and c obtained for synthesized ZnO are 0.325 nm and 0.52 nm respectively whereas lattice constants of ideal unstrained ZnO are a = 0.324 nm and c = 0.52 nm, indicate that there is minor strain exerts on the synthesized ZnO NPs compared to that of ideal unstrained ZnO. The ZnO bond length, L is calculated by using equation (11) and (12),

$$L = \sqrt{\left(\frac{a^2}{3} + \left(\frac{1}{2} - u\right)^2 c^2\right)} \tag{11}$$

$$u = \frac{a^2}{3c^2} + 0.25 \tag{12}$$

Where u is the positional parameter for wurtzite structure and is used to measure of the quantity by which each atom is displaced with respect to the next along c axis. The calculated ZnO bond length is 1.9723 Å which is near to the ideal unstrained ZnO (1.9767 Å), thus indicates there is minor compressive strain of the ZnO deposition (Apeh etal., 2018), (Bindu and Thomas, 2014).

The XRD spectra of pristine cotton fabric, 0.1 M ZnO/PVA cotton fabric and 0.25 M ZnO /PVA cotton fabric are shown in Figure 4.6. In Figure 4.6(a), the spectra represented the pristine cotton fabric. There is a broad and large reflection peak at low and medium 2θ about 14.78°, 16.56°, 22.74° and 37.8° and 44.12° which represented the cellulosic fibers of characteristic of the {101}, {101}, {002}, and {040} (Barani, 2014). The main reflection peaks at 14.78° and 16.56° are contributed to amorphous phase of cotton fiber while 22.74° is due to the crystalline phase (Moafi et al., 2011, Barani, 2014). Thus, based on the results, it is in line with research work of Nickerson. The cellulose in pure cotton fabric comprises of two distinct states of aggregations namely, a crystalline and a non-crystalline. The cellulose possesses three free hydroxyl groups demonstrate a strong tendency to interact or to become associated through hydrogen bonding. This chemical bonding tends to arrange cellulose molecules in parallel to the fiber direction. Thus, the crystallinity of cellulose depends on the extent to which molecules become parallel. Higher the degree of orientation of the cellulose becomes, the more favorable conditions are for further crystallization. It is known that some characteristics, such as tenacity depend upon the degree crystallinity of the cellulose structure (Nickerson, 1942).

Figure. 4.6(b) and Figure. 4.6(c) showed XRD spectra of ZnO /PVA cotton with 0.1 M and 0.25 M of ZnO concentrations. The new reflection peaks presented at 31.96°, 34.66°, 36.46°, 47.92° and 56.73° attributed to the characteristic peak of ZnO which assigned to {100}, {002}, {101}, {102}, and {110} indicated hexagonal wurtzite structure of the synthesized ZnO. The reflection peak at {101} is the strongest indicates the synthesized ZnO nano-crystals have a preferential crystallographic {101} orientation. In both XRD patterns, no other impurity such as $Zn(OH)_2$ which confirm the purity of ZnO structure has obtained. In addition, the intensity of cellulose became weak compared to pristine cotton fabric. This could be attributed to the ZnO NPs coated on the cellulose surface which makes it difficult to detect the diffraction data of cellulose. The intensity of ZnO diffraction peaks is higher and sharper in the 0.25 M ZnO/PVA cotton fabric than 0.1 M ZnO/PVA cotton fabric due to the higher ZnO content. The sharper and intense diffraction peaks suggest the high crystallinity produced in the structure (Zanni et al., 2016). The crystal size of ZnO in the sample was calculated Debye-Scherer formula was approximately 25~42 nm.

Table 4.2: Comparison of lattice parameters for synthesized ZnO and JCPDS data

{h k l}	**$2\theta_{XRD}$[°]**	**$2\theta_{JCPDS}$[°]**	**d_{XRD} [Å]**	**d_{JCPDS} [Å]**	**FWHM [°]**
{100}	31.71	31.77	2.82	2.81	0.37

{002}	34.37	34.42	2.61	2.603	0.25
{101}	36.20	36.25	2.48	2.48	0.34

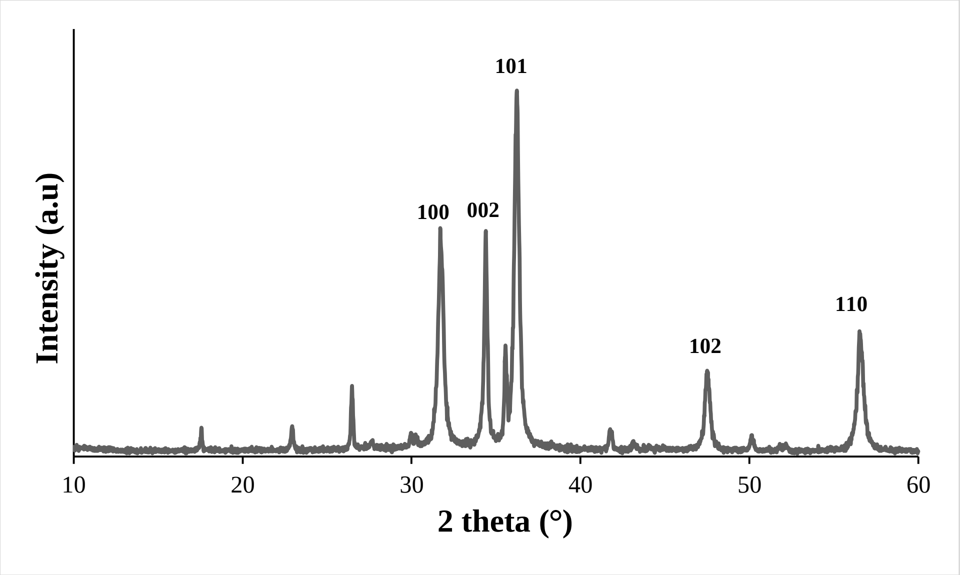


Figure 4.5: XRD spectrum of synthesized ZnO NPs.

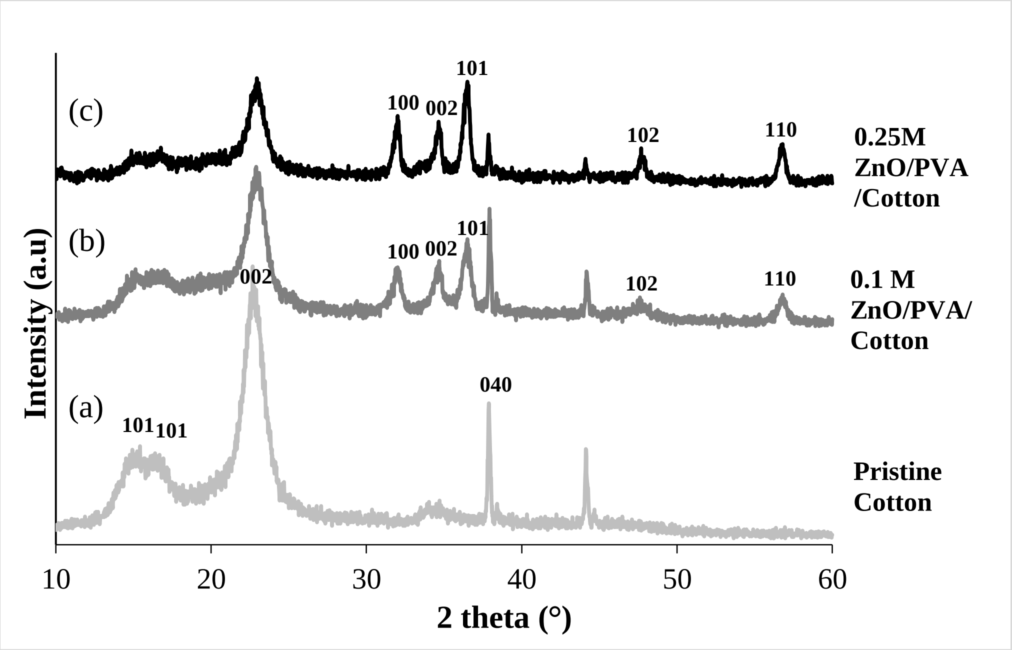


Figure 4.6: XRD spectra of (a) pristine cotton, (b) 0.1 M ZnO/PVA cotton, (c) 0.25 M ZnO/PVA cotton.

4.5 FTIR

FTIR is a tool to investigate whether there is bonding between ZnO, PVA and cotton fabric. Figure 4.7 presented the FTIR spectra of chemical structure of ZnO, PVA, ZnO/PVA, pure cotton and ZnO/PVA cotton in 4000-400 cm^{-1} region. The characteristic peaks of ZnO structure in Figure. 4.7(a) including absorption bands in the 3371 cm^{-1}, 1500-1400 cm^{-1} and 868 cm^{-1} that aroused due to the vibration and stretching of hydroxyl group respectively, which are related to the absorbed water on the surface of the samples (Samavati et al., 2016). The spectrum for pure PVA is illustrated in Figure. 4.7(b). The presence of broad band at 3272 cm^{-1} assigned to the PVA chemical structure endows large content of hydroxyl group while the peak at 2927 cm^{-1} corresponded to the asymmetric CH_2 bond stretching (Yuan, 2011), (Roy et al., 2013). The peak at 1715 cm^{-1} and 1558 cm^{-1} are assigned to the stretching and vibration band of carbonyl –C=O (Gunasekaran et al., 2009). The peaks at 1400-1200 cm^{-1} resulted from CH_2 and CH_3 bending while the band at 1084 cm^{-1} and 829 cm^{-1} resulted from the C–O stretching vibration and C–C stretching, respectively (Mansour et al., 2015). To determine whether any covalent bond formed between ZnO and PVA, the FTIR spectrum of ZnO /PVA composite film is performed and illustrated in Figure. 4.7(c). Based on the result, the decreasing order of hydroxyl peak occurred as ZnO > PVA > ZnO/PVA composite. The decrease of this band is attributed to the hydrogen bonding formed between ZnO and PVA, altered the electron cloud transformation of hydroxyl groups present in PVA, thus leading to weak hydroxyl group bonding being detected. The characteristic peaks of cellulose structure are presented in Figure. 4.7(d). The spectra of hydroxyl groups in

3327cm^{-1}, aliphatic C-H in 2891cm^{-1}, and C-O-C bond in 1024cm^{-1}are critical peaks for pure cellulose fibers (Ghayempour and Montazer, 2017). After fabrication ZnO/PVA onto cotton fabric, the intensity of hydroxyl group decreased, suggesting the hydrogen bonding formed between ZnO, PVA and cotton. Also, a slight increment in the intensity of the C-H stretching is observed in treated cotton. This is due to the presence of CH bonds in the chemical structure of PVA and cotton.

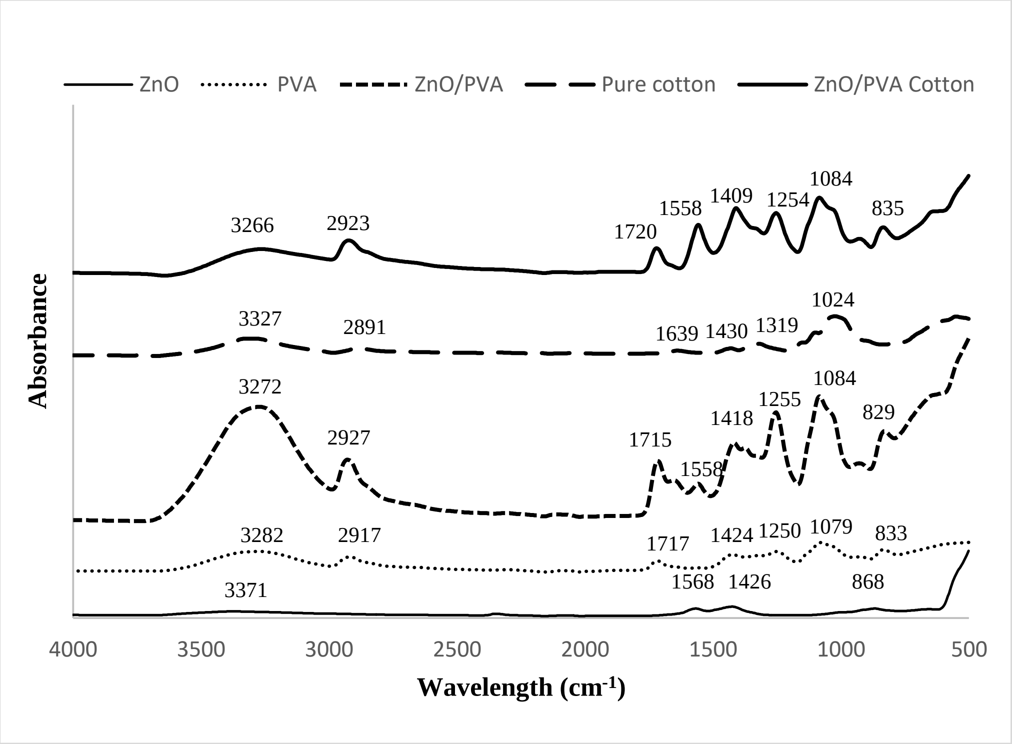


Figure 4.7: FTIR spectra of (a) ZnO, (b) PVA, (c) ZnO/PVA, (d) pure cotton and e) ZnO/PVA cotton.

4.6 Tensile Strength

Tensile strength is vital characteristic for textile application. High strength and strong cotton fabric favorable for many field such wound dressing, sportswear and etc. In this study, the cotton fabric used is plain woven fabric where the weft alternates over and under the warp. Untreated plain woven cotton fabric has weak tensile strength. According to Campbell research work, the strength and stiffness of plain woven fabric is reduced due to its waviness or yarn crimp. The style of plain weave is the repeated exchanges of position from top to bottom made by each yarn. The wavy pattern of fiber accelerated the matrix cracking under tension. More in-plane waviness, the matrix and loaded yarns are stretched unevenly with each other and hence vulnerable to tear (Campbell Jr, 2003).

As reference to Figure 4.8, the tensile strength of ZnO/PVA cotton fabric with different dosage of ZnO and PVA has changed significantly. This could be explained based on several justifications, namely, alkali pretreatment before coating ZnO/PVA, PVA and ZnO concentrations respectively.

All the treated cotton fabric with ZnO and PVA has undergone ethanol pre-treatment before coating. The ethanol reacts with the hydroxyl group of cellulose fiber lead to destruction of fibers split into filaments. It can be observed in Figure 4.9, after the ethanol treatment the cellulose fiber dissolute and breaks into smaller fibrils. This phenomenon is known as fibrillation. The fibrillation stage enhances effective surface area available for interact with matrix and thus increases the interfacial adhesion. Also, ethanol could improve the adhesive properties of fabric surface by eliminating natural and artificial impurities consequently creating a rough surface topography (Cao et al., 2006). Similar finding has been studied by Cao et al., who studied the mechanical properties of biodegradable composite reinforced with Bagasse fiber before and after alkali treatments and found out the enhancement in terms of the increase in fiber roughness and contact area after alkali treatment.

Generally, incorporation of PVA enhances the tensile strength of ZnO/cotton fabric as shown on Figure. 4.8. Based on the result, the tensile strength of PVA/ZnO cotton fabric where PVA amount at 15 g and 20 g were comparatively higher than at 5 g and 10 g regardless of ZnO concentration. Tensile strength for samples with 15 g and 20 g of PVA are between 3.59 MPa to 4.58 MPa whereas tensile strength for samples at 5 g and 10 g of PVA are between 2.12 MPa to 3.83 MPa. Increase of tensile strength is due to the PVA has outstanding coupling of two components with reactive groups, thus enhancing the interaction and mechanical strength (Rana et al., 2016). It is known that nanoparticles exhibit high tendency of agglomeration. The nano-sized of ZnO could adverse the cotton fabric properties due to particle-particle interaction of ZnO NPs. PVA acts as coupling agent, presence of large hydroxyl groups in the structure formed intermolecular hydrogen bonding with ZnO.

Also, the extent formation of hydrogen bonding with surrounding molecules depends on the hydrolysis degree of PVA. In this study, the PVA used is 89% degree of hydrolysis with molecular weight of 15000 which categorized as partially hydrolyzed grades. PVA with low degree of hydrolysis (below 98%) as well as molecular weight favorable formation of intermolecular hydrogen bonding (Chan et al., 1999). This could be explained by the significant quantities of residual hydrophobic acetate groups present in PVA structure induces steric hindrance from interaction between the hydroxyl groups in the PVA molecules, thus dominant the formation of intermolecular hydrogen bonding. Likewise, low molecular weights tend to crosslink easily with surrounding molecules than high molecular weight of PVA, exhibit greater intermolecular interaction. These increased the intermolecular interaction resulting higher tensile strength. In addition, in weaving the wrap is lengthwise thread in a roll while weft is the transverse thread to create textile. Introducing PVA/ZnO into the void between warp and weft yarn improves tensile strength of fabric. Also, it reduces the defects and weak points in yarn under the stretching process.

The effect of further increased of PVA from 15 g to 20 g deteriorated the tensile strength of treated fabric. At this stage, the proportion of PVA is extremely greater than the proportion of ZnO dosage. Cotton fabrics treated with 15 g of PVA, the ZnO interaction, dispersion, stress transfer and morphology have all reached maximized to optimum condition. Further addition of PVA, the reinforcing effect of ZnO disappeared and this directly affected the orientation of PVA arrangement become rigid and the chains are entangled very weakly due to lack of intermolecular hydrogen bonding with ZnO NPs. Excessive PVA induces disentanglement, sliding and slippage, thus vulnerable to tear when stress is applied (Virtanen et al., 2014).

In term of ZnO concentration effect, the tensile strength decreased from 0.1 M to 0.15 M, then increased from 0.15 M to 0.25 M. The deterioration of tensile strength when ZnO loading amount increase from 0.1 M to 0.15 M could be attributed to the ZnO behave as a lubricant in the PVA structure and induces the chain sliding effect, making it vulnerable to tear (Sin et al., 2013). Low concentration of ZnO NPs has weak interfacial interactions thus lower the efficiency of the ZnO in strengthening of PVA matrix in the treated cotton fabric (Akbari and Bagheri, 2007).

Meanwhile, increase of tensile strength from 0.20 M to 0.25 M is explained by increasing of ZnO weight fraction leads to homogenous and continuous interface that may create a strong PVA polymer network enhancing the tensile property of treated cotton fabric. Increased nano-sized of ZnO into the PVA matrix acts as load transfer agent and reinforcement, enhances the toughness of treated cotton fabric. Improvement in toughness attributed to suppression of PVA polymer chain mobility. This is resulted by the better interactions of increasing number of hard-particles or altering the properties of the polymer surrounding particle surface, enhance energy for crack propagation (Chen et al., 2008). This result is in line with the research work from Zhang and coworkers, investigated the increased particle loading amount, decreased average inter-particle distance until a mechanically couple network is formed at the critical inter-particle distances (Zhang et al., 2006). Also, increasing of crystallinity and entanglement between ZnO NPs and PVA which make it difficult in chain sliding and lead to enhancement the tensile strength of the treated cotton fabric. Increased of ZnO NPs within the PVA matrix attributes low slipping power by forming complex and non-uniform matrix, resists sliding of the molecules past each other and hence resulted more strength of the treated cotton fabric. More bonding able to form when increase ZnO concentration, thus more interaction between PVA and ZnO. ZnO and PVA are held together by means of covalent forces reduced slippage with the presence of intermolecular forces.

In conclusion, the optimal formulation for antibacterial cotton fabric application is at 0.25M ZnO with 15 g of PVA as it possesses highest tensile strength. High strength is vital performance property of fabric as to provide strong durability, stability and tenacity based on different end usage.

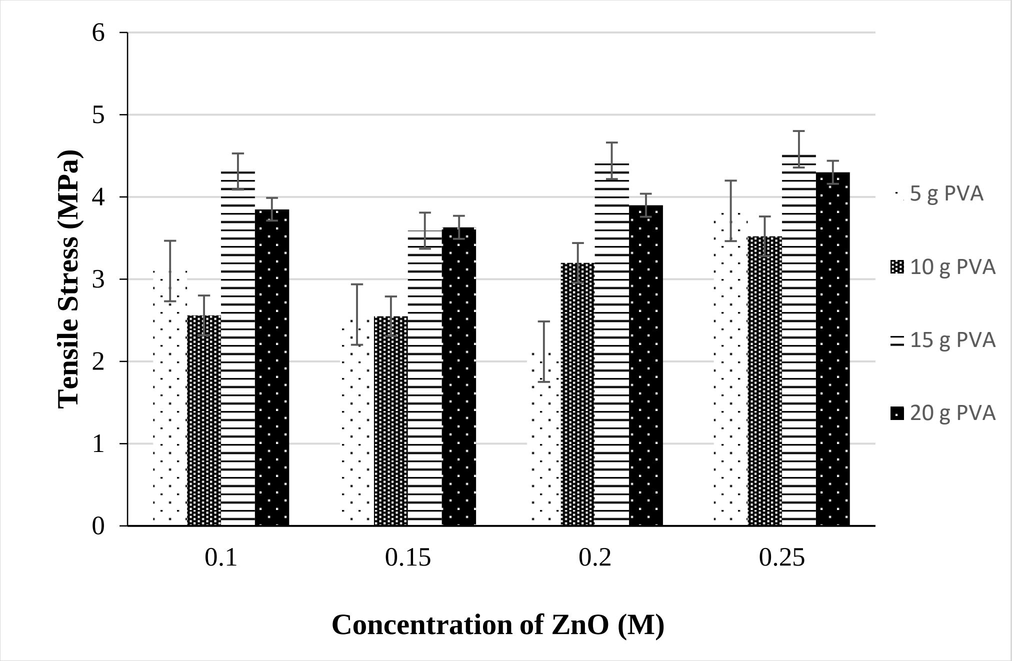


Figure 4.8: Tensile strength of ZnO/PVA cotton.

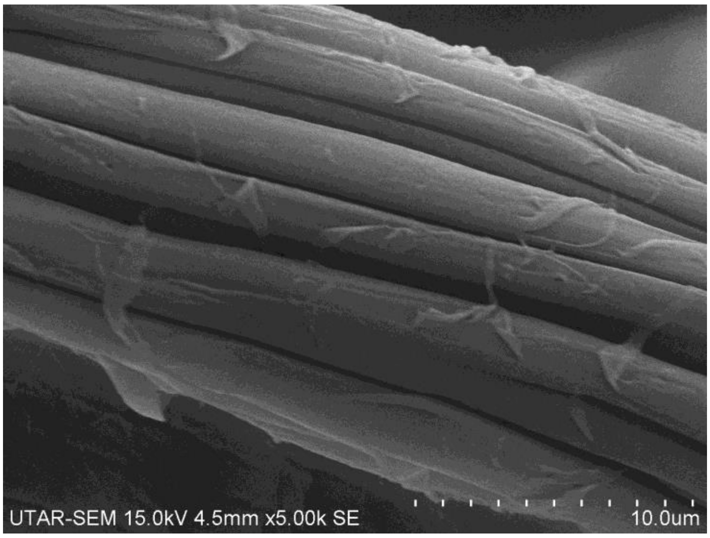


Figure 4.9: Cotton fabric after ethanol treatment.

4.7 Antibacterial Test

The susceptibilities of S.aureus and E.coli to ZnO incorporated with PVA at different loading amount fabricated onto cotton fabric are studied. The bacteria efficiencies against S.aureus and E.coli are measured by disc diffusion method in term of the width of inhibition zone. The width of the inhibition zone for S.aureus and E.coli are obtained after 24 hour incubation. The interpretation of inhibition zone for ZnO concentration (0.1, 0.15, 0.2, 0.25 M) doped with the PVA (5, 10, 15, 20 g) against S.aureus growth is shown in Figure 4.10 and Table. 4.3 while the E.coli is displayed in Figure. 4.11 and Table. 4.4.

As reference to Figure 4.10 and 4.11, each Petri dish is placed with 3 ZnO/PVA cotton discs (white color circular discs) of same formulation to get mean zone diameter to make sure reliable results are obtained. The growth medium used is Trytone soya agar which provide nutrient for bacteria growth. Standardized inoculums of 1×10^8 CFU is used and swabbed over the petri disk. After 24 hour incubation, there is presence of clear circular area surrounded ZnO/PVA cotton discs where bacteria have not grown. A larger zone of inhibition zone indicates that the bacteria are sensitive to the ZnO in the disc. It is found that all the treated fabric exhibited satisfied inhibition zone, increased with increasing ZnO and PVA amount for both bacteria. For S.aureus, the inhibition zone increased from 2.05 mm to 5.79 mm. On the other hand, for E.coli, the inhibition zone increased from 1.07 mm to 4.21 mm.

For the effect of ZnO NPs concentration on antibacterial efficiency, higher ZnO concentration in the cotton fabric induces more reactive oxygen species (ROS) such as superoxide anion (O^{2-}) and hydroxide (OH^-) and hydrogen peroxide (H_2O_2). (Barani, 2014). According to Amna et al., O^2 and $OH^-$are too large to penetrate into intracellular matrix, remain outer surface of the bacteria disrupt cell wall integrity. On the other hand, H_2O_2 molecules able to penentrate through bacterial cell wall, accumulate and create high oxidative stress inside the cell and leading to cell death.

Another suggested mechanism is dissolution of ZnO NPs into Zn^{2+} ions which act as antibacterial agent. Zn^{2+} ions have significant effect in the active transport inhibition, enzyme system disruption and amino acid metabolism (Sirelkhatim et al., 2015). Zn^{2+} ions aroused generation of ROS in bacterial cells and lead to DNA damage. This resulted from a liberate of catalytic binding of Zn^{2+} ions to DNA with release of OH radicals and by reacting H_2O_2 with metal caused the strand breaks in DNA and subsequently modified DNA base-pairs and deoxyribose fragmentation. Zn^{2+} ions substitution into DNA structure formed irreversible complex formation with DNA as shown in Figure 4.12. G (guanine)≡ C (cytosine) and A (adenine) = T (thymine) pairs resulted by hydrogen bonding with Zn^{2+} ions. As a result, DNA damage inhibits bacterial growth, metabolism and replication function and leading to cell death (Ishida, 2018).

Incorporation of PVA has ability to disperse the ZnO NPs homogeneously over the cotton fabric. PVA acts as a stabilizer prevent ZnO from agglomeration and improve antibacterial function of ZnO. ZnO possesses significant antibacterial properties when particle size is in nanometer range as nano-sized enable ZnO disrupt the bacterial cell wall integrity and facilitate the penetration of these particles through cell membrane to the intracellular matrix and trigger cytotoxic mechanism (Sirelkhatim et al., 2015). This justification is supported by the research work of Jiang and his coworkers, concluded nanoscale of ZnO had greater antibacterial effect than micronscale (Jiang et al., 2009).

Conversely, it is found also that the inhibition zone of S.aureus is comparatively greater than that of E.coli regardless of ZnO and PVA concentration. S.aureus is representative of Gram positive bacteria whereas E.coli is representative of Gram negative bacteria. The distinguishing difference between these two groups of bacteria is the thickness of the cell wall and the presence of specific appendices in outer membrane in Gram negative bacteria only that attributed to the different of sensitivity toward ZnO NPs. Gram positive bacteria have thick peptidoglycan structure while Gram negative bacteria have thin peptidoglycan layer with additional membrane. The feature of Gram negative bacteria creates additional permeability barrier and consequences in the need for transport mechanisms across the membrane. Also, this additional membrane imbedded lipids, proteins and lipopolysaccharides in their cell membrane whereas Gram-positive do not. Lipoplysaccharides or known as endotoxin is essential component for bacterial survival which provided protection against outside attack. Lipopolysaccharide is comprised of three components namely, lipid A, highly conserved core polysaccharide and O-antigen. The lipid A is responsible for the major bioactivity of lipopolysaccharide and it is cell-associated, released when the bacteria cell wall break (Wang and Quinn, 2010). This is the reason for the obtained smaller inhibition zone of E.coli compared to that of the S.aureus. Thus, based on the tensile strength and antibacterial efficiency results, the optimal formulation for antibacterial textile is at 0.25M ZnO with 15 g of PVA as it has highest tensile strength and considerable antibacterial efficiencies in inhibition of microorganism growth against S.aureus and E.coli.

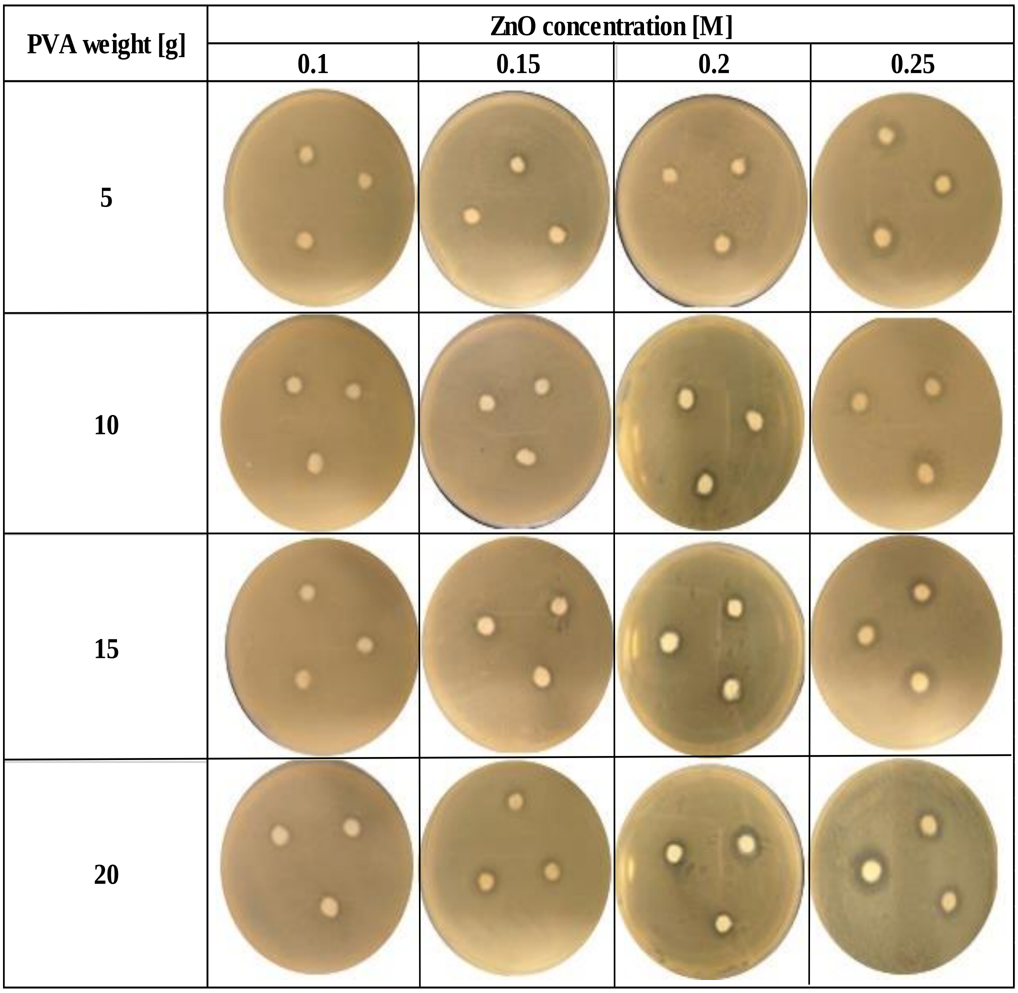


Figure 4.10: Antibacterial activity of ZnO/PVA cotton against S.aureus growth using disc diffusion method.

Table 4.3: Antibacterial activity test of ZnO/PVA/cotton against S.aureus growth

	Inhibition zone [mm]			
	ZnO concentration [M]			
PVA weight [g]	**0.1**	**0.15**	**0.2**	**0.25**
5	2.05	2.72	3.15	4.38
10	2.49	2.75	3.76	4.57
15	2.58	3.06	3.86	4.77
20	2.62	3.08	3.88	5.79

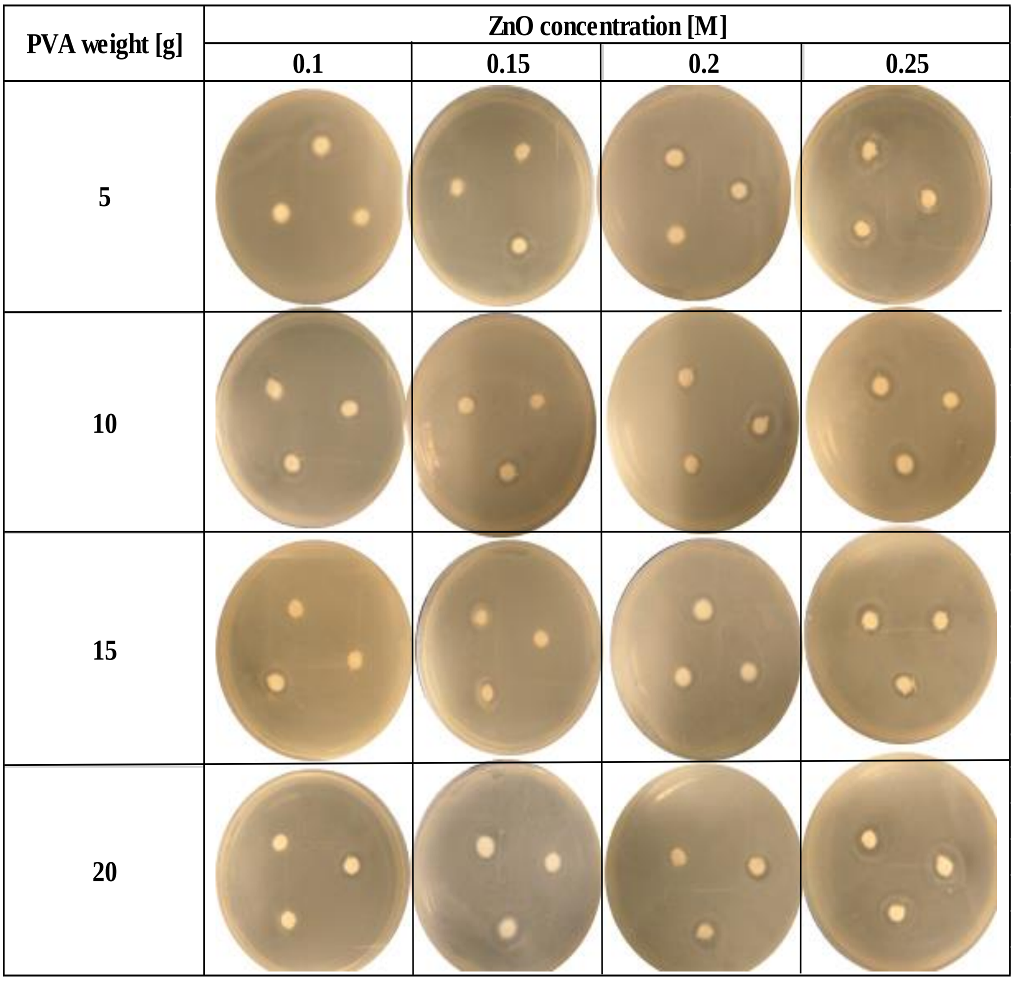


Figure 4.11: Antibacterial activity of ZnO/PVA cotton against E.coli growth using disc diffusion method.

Table 4.4 Antibacterial activity test of ZnO/PVA/cotton against E.coli growth

	Inhibition zone [mm]			
	ZnO concentration [M]			
PVA weight [g]	**0.1**	**0.15**	**0.2**	**0.25**
5	1.07	1.75	2.84	3.61
10	1.37	1.84	2.89	3.89
15	1.19	2.24	3.12	3.85
20	1.25	2.55	3.19	4.21

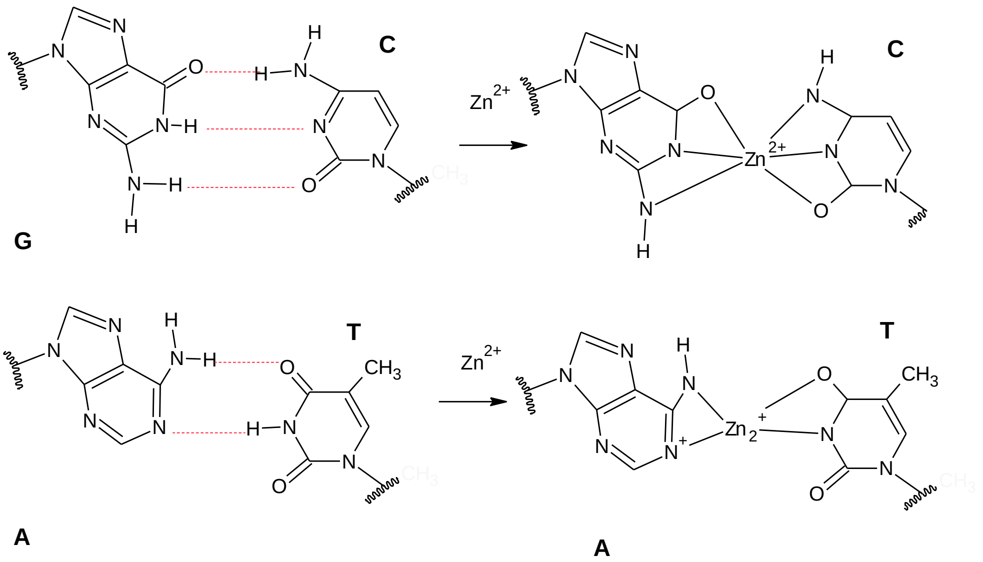


Figure 4.12: The mechanism of Zn^{2+} substitution into DNA base pairing of G-C, A-T pairs. a) Stable form of 6–coordinated Zn complex formation with G≡C base pair, b) Unstable form of 4-coordinated Zn complex formation with A=T base pair (Ishida, 2018).

CHAPTER 5

CONCLUSION

5.1 Conclusion

Overall, all the objectives of this study have accomplished. The results of this study have reconnected with its corresponding objective as follow:

1. To develop ZnO/PVA grafted cotton fabric.

   The fabrication of ZnO/PVA cotton fabric has carried out through dip coating method.

2. To evaluate the characteristics of ZnO/PVA grafted cotton fabric in terms of surface morphologies, chemical structure, crystal size of ZnO, bonding and mechanical strength.

   In this work, the morphological appearance of the nanosized ZnO particles dispersed uniformly over the fabric. Hexagonal wurtzite ZnO were synthesized on the cotton fabric in conjunction with PVA as stabilizer. The crystal size of ZnO NPs were approximately 25 ~ 42 nm. The weakening of hydroxyl peak intensity of ZnO/PVA cotton reflected the formation of intermolecular hydrogen bonding. ZnO/PVA coated fabric exhibited higher strength with increasing ZnO NPs and PVA due to increasing bonding formed.

3. To study the effect of ZnO and PVA concentrations on activities against S.aureus and E.coli growth by a disc diffusion method.

Increased both of ZnO and PVA concentrations on cotton fabric have improved antibacterial activities against the S.aureus and E.coli growth.

4. To determine the optimal formulation for antibacterial cotton fabric.

   The optimal formulation for antibacterial cotton fabric was at 0.25 M ZnO / 15 g PVA as it has highest strength when tearing and considerable antibacterial properties against S.aureus and E.coli growth.

5.2 Future Works

The metal based materials have spurred interests in application on antimicrobial textile due to their excellent features. Regarding to the development of those antibacterial agents on textile field, its adherence onto fabric should be strong in order to prevent leaching into environment and leading to pollution. Thus, to ensure there is chemical reaction between the agent and textile fiber, pre-treatment on the textile fiber before coating enable creating more concentration of functional groups which serve as a binding sites for absorption. Moreover, the finishing textile's effectiveness and durability also depend on the type of polymer used, the antibacterial agents, and synthesis technique used in the production.

Incorporation antimicrobial agent on polymer matrix able to promote a slower release during usage and prolonged its antibacterial function period of textile wear. Upon the environmental protection priority, the utilization of green natural biopolymers extracted from either animals or plants, such as chitosan, sericin, alginate, and so on which are renewable and environment-friendly are potential to be a critical resources for future sustainable multifunctional textile. The type of antibacterial agents endow different modes of action on biocidal mechanisms associated with their chemical, structure and affinity extent to particular target sites within microbial cells. The most desirable agents to be antibacterial candidates on textile are the ones own biocidal at low dosing levels as well as durable functionality. On the other hand, the synthesis techniques should be provide high efficiency, economical, practical without creating ecological hazard. There are new technologies such as plasma treatment, ultrasound, UV radiation, etc have been investigated to replace conventional processes. The employment of dry plasma treatment does not use harmful chemical solutions (solvent-free process) and does not contaminated water or induces mechanical hazards for modified textile. In addition, through ultrasound and UV irradiation can enhance the dispersion of antibacterial agent onto the textile, thus increase antibacterial power. Another green approach that is gaining attention is modified with the promotion of specific reaction catalyzed by enzymes such as glycosidases, proteases, laccase, and lipases.

Therefore, for future development aspects, researchers should put more efforts in opening up more environmental-friendly synthesis approaches and encourage the involvement of green agents which possess potential long term antibacterial benefits without pose consequent risks to human health and surrounding medium.

REFERENCES

Abdel-Mohsen, A., Abdel-Rahman, R. M., Hrdina, R., Imramovský, A., Burgert, L. & Aly, A. 2012. Antibacterial cotton fabrics treated with core–shell nanoparticles. *International journal of biological macromolecules,* 50**,** pp. 1245-1253.

Abou-Okeil, A., Sheta, A., Amr, A. & Ali, M. A. 2012. Wound dressing based on nonwoven viscose fabrics. *Carbohydrate polymers,* 90**,** pp. 658-666.

Abramov, O., Gedanken, A., Koltypin, Y., Perkas, N., Perelshtein, I., Joyce, E. & Mason, T. 2009. Pilot scale sonochemical coating of nanoparticles onto textiles to produce biocidal fabrics. *Surface and coatings Technology,* 204**,** pp. 718-722.

Abramova, A., Gedanken, A., Popov, V., Ooi, E.-H., Mason, T. J., Joyce, E. M., Beddow, J., Perelshtein, I. & Bayazitov, V. 2013. A sonochemical technology for coating of textiles with antibacterial nanoparticles and equipment for itsimplementation. *Materials Letters,* 96**,** pp. 121-124.

Akbari, B. & Bagheri, R. 2007. Deformation mechanism of epoxy/clay nanocomposite. *European polymer journal,* 43**,** pp. 782-788.

Aladpoosh, R. & Montazer, M. 2015. The role of cellulosic chains of cotton in biosynthesis of ZnO nanorods producing multifunctional properties: Mechanism, characterizations and features. *Carbohydrate polymers,* 126**,** pp. 122-129.

Ali, S. W., Joshi, M. & Rajendran, S. 2011. Novel, Self-Assembled Antimicrobial Textile Coating Containing Chitosan Nanoparticles. *Aatcc Review,* 11**,** pp.

Ananth, A., Dharaneedharan, S., Heo, M.-S. & Mok, Y. S. 2015. Copper oxide nanomaterials: Synthesis, characterization and structure-specific antibacterial performance. *Chemical Engineering Journal,* 262**,** pp. 179-188.

Ancona, A., Sportelli, M., Trapani, A., Picca, R., Palazzo, C., Bonerba, E., Mezzapesa, F., Tantillo, G., Trapani, G. & Cioffi, N. 2014. Synthesis and characterization of hybrid copper–chitosan nano-antimicrobials by fmtosecond laser-ablation in liquids. *Materials Letters,* 136**,** pp. 397-400.

Arain, R. A., Khatri, Z., Memon, M. H. & Kim, I.-S. 2013. Antibacterial property and characterization of cotton fabric treated with chitosan/AgCl–TiO2 colloid. *Carbohydrate polymers,* 96**,** pp. 326-331.

Apeh, O. O., Chime, U., Agbo, S., Ezugwu, S., Taziwa, R., Meyer, E., Sutta, P., Maaza, M. & Ezema, F. 2018. Properties of nanostructured ZnO thin films synthesized using a modified aqueous chemical growth method. Materials Research Express.

Babu, K. F., Dhandapani, P., Maruthamuthu, S. & Kulandainathan, M. A. 2012. One pot synthesis of polypyrrole silver nanocomposite on cotton fabrics for multifunctional property. *Carbohydrate polymers,* 90**,** pp. 1557-1563.

Balakumaran, M., Ramachandran, R., Jagadeeswari, S. & Kalaichelvan, P. 2016. In vitro biological properties and characterization of nanosilver coated cotton fabrics–an application for antimicrobial textile finishing. *International Biodeterioration & Biodegradation,* 107**,** pp. 48-55.

Barani, H. 2014. Preparation of antibacterial coating based on in situ synthesis of ZnO/SiO2 hybrid nanocomposite on cotton fabric. *Applied Surface Science,* 320**,** pp. 429-434.

Barani, H., Montazer, M., Samadi, N. & Toliyat, T. 2012. In situ synthesis of nano silver/lecithin on wool: enhancing nanoparticles diffusion. *Colloids and Surfaces B: Biointerfaces,* 92**,** pp. 9-15.

Behzadnia, A., Montazer, M. & Rad, M. M. 2015. Simultaneous sonosynthesis and sonofabrication of N-doped ZnO/TiO2 core–shell nanocomposite on wool fabric: Introducing various properties specially nano photo bleaching. *Ultrasonics sonochemistry,* 27**,** pp. 10-21.

Behzadnia, A., Montazer, M., Rashidi, A. & Rad, M. M. 2014. Sonosynthesis of nano TiO2 on wool using titanium isopropoxide or butoxide in acidic media producing multifunctional fabric. *Ultrasonics sonochemistry,* 21**,** pp. 1815-1826.

Bikiaris, D. N. & Triantafyllidis, K. S. 2013. HDPE/Cu-nanofiber nanocomposites with enhanced antibacterial and oxygen barrier properties appropriate for food packaging applications. *Materials Letters,* 93**,** pp. 1-4.

Bindu, P. & Thomas, S. 2014. Estimation of lattice strain in ZnO nanoparticles: X-ray peak profile analysis. Journal of Theoretical and Applied Physics, 8, pp. 123-134.

Boroumand, M. N., Montazer, M., Simon, F., Liesiene, J., Šaponjic, Z. & Dutschk, V. 2015. Novel method for synthesis of silver nanoparticles and their application on wool. *Applied surface science,* 346**,** pp. 477-483.

Bozaci, E., Akar, E., Ozdogan, E., Demir, A., Altinisik, A. & Seki, Y. 2015. Application of carboxymethylcellulose hydrogel based silver nanocomposites on cotton fabrics for antibacterial property. *Carbohydrate polymers,* 134**,** pp. 128-135.

Çakır, B. A., Budama, L., Topel, Ö. & Hoda, N. 2012. Synthesis of ZnO nanoparticles using PS-b-PAA reverse micelle cores for UV protective, self-cleaning and antibacterial textile applications. *Colloids and Surfaces A: Physicochemical and Engineering Aspects,* 414**,** pp. 132-139.

Çalamak, S., Erdoğdu, C., Özalp, M. & Ulubayram, K. 2014. Silk fibroin based antibacterial bionanotextiles as wound dressing materials. *Materials Science and Engineering: C,* 43**,** pp. 11-20.

Campbell Jr, F. C. 2003. *Manufacturing processes for advanced composites,* Elsevier.

Cao, Y., Shibata, S. & Fukumoto, I. 2006. Mechanical properties of biodegradable composites reinforced with bagasse fibre before and after alkali treatments. *Composites part A: Applied science and Manufacturing,* 37**,** pp. 423-429.

Čepin, M., Hribar, G., Caserman, S. & Orel, Z. C. 2015. Morphological impact of zinc oxide particles on the antibacterial activity and human epithelia toxicity. *Materials Science and Engineering: C,* 52**,** pp. 204-211.

Chan, L. W., Hao, J. S. & Heng, P. W. S. 1999. Evaluation of permeability and mechanical properties of composite polyvinyl alcohol films. *Chemical and pharmaceutical bulletin,* 47**,** pp. 1412-1416.

Chandrasekar, S., Vijayakumar, S. & Rajendran, R. 2014. Application of chitosan and herbal nanocomposites to develop antibacterial medical textile. *Biomedicine & Aging Pathology,* 4**,** pp. 59-64.

Chen, C., Justice, R. S., Schaefer, D. W. & Baur, J. W. 2008. Highly dispersed nanosilica–epoxy resins with enhanced mechanical properties. *Polymer,* 49**,** pp. 3805-3815.

Chen, H.-I. & Chang, H.-Y. 2004. Homogeneous precipitation of cerium dioxide nanoparticles in alcohol/water mixed solvents. *Colloids and Surfaces A: Physicochemical and Engineering Aspects,* 242**,** pp. 61-69.

Conde, M. N., Dakhsi, K., Zouihri, H., Abdelouahdi, K., Laanab, L., Benaissa, M. & Jaber, B. 2011. Preparation of ZnO nanoparticles without any annealing and ripening treatment. *Journal of Materials Science and Engineering. A,* 1**,** pp. 985.

Daoud, W. A., Xin, J. H. & Zhang, Y.-H. 2005. Surface functionalization of cellulose fibers with titanium dioxide nanoparticles and their combined bactericidal activities. *Surface science,* 599**,** pp. 69-75.

Das, G., Kalita, R. D., Gogoi, P., Buragohain, A. K. & Karak, N. 2014. Antibacterial activities of copper nanoparticle-decorated organically modified montmorillonite/epoxy nanocomposites. *Applied Clay Science,* 90**,** pp. 18-26.

Dastjerdi, R. & Montazer, M. 2010. A review on the application of inorganic nano-structured materials in the modification of textiles: focus on anti-microbial properties. *Colloids and Surfaces B: Biointerfaces,* 79**,** pp. 5-18.

Dastjerdi, R., Montazer, M. & Shahsavan, S. 2010. A novel technique for producing durable multifunctional textiles using nanocomposite coating. *Colloids and Surfaces B: Biointerfaces,* 81**,** pp. 32-41.

Deng, X., Nikiforov, A., Vujosevic, D., Vuksanovic, V., Mugoša, B., Cvelbar, U., De Geyter, N., Morent, R. & Leys, C. 2015. Antibacterial activity of nano-silver non-woven fabric prepared by atmospheric pressure plasma deposition. *Materials Letters,* 149**,** pp. 95-99.

Deopura, B., Alagirusamy, R., Joshi, M. & Gupta, B. 2008. *Polyesters and polyamides,* Elsevier.

Dhandapani, P., Siddarth, A. S., Kamalasekaran, S., Maruthamuthu, S. & Rajagopal, G. 2014. Bio-approach: ureolytic bacteria mediated synthesis of ZnO nanocrystals on cotton fabric and evaluation of their antibacterial properties. *Carbohydrate polymers,* 103**,** pp. 448-455.

Doakhan, S., Montazer, M., Rashidi, A., Moniri, R. & Moghadam, M. 2013. Influence of sericin/TiO2 nanocomposite on cotton fabric: Part 1. Enhanced antibacterial effect. *Carbohydrate polymers,* 94**,** pp. 737-748.

Dodd, C. E., Richards, P. J. & Aldsworth, T. G. 2007. Suicide through stress: a bacterial response to sub-lethal injury in the food environment. *International journal of food microbiology,* 120**,** pp. 46-50.

Dubas, S. T., Kumlangdudsana, P. & Potiyaraj, P. 2006. Layer-by-layer deposition of antimicrobial silver nanoparticles on textile fibers. *Colloids and Surfaces A: Physicochemical and Engineering Aspects,* 289**,** pp. 105-109.

El-Gabry, L., Allam, O. & Hakeim, O. 2013. Surface functionalization of viscose and polyester fabrics toward antibacterial and coloration properties. *Carbohydrate polymers,* 92**,** pp. 353-359.

El-Rafie, M., Ahmed, H. B. & Zahran, M. 2014. Characterization of nanosilver coated cotton fabrics and evaluation of its antibacterial efficacy. *Carbohydrate polymers,* 107**,** pp. 174-181.

El-Rafie, M., Shaheen, T. I., Mohamed, A. & Hebeish, A. 2012. Bio-synthesis and applications of silver nanoparticles onto cotton fabrics. *Carbohydrate polymers,* 90**,** pp. 915-920.

El-Shafei, A., Elshemy, M. & Abou-Okeil, A. 2015. Eco-friendly finishing agent for cotton fabrics to improve flame retardant and antibacterial properties. *Carbohydrate polymers,* 118**,** pp. 83-90.

Emam, H. E., Ahmed, H. B. & Bechtold, T. 2017. In-situ deposition of Cu2O micro-needles for biologically active textiles and their release properties. *Carbohydrate polymers,* 165**,** pp. 255-265.

Emam, H. E., Mowafi, S., Mashaly, H. M. & Rehan, M. 2014. Production of antibacterial colored viscose fibers using in situ prepared spherical Ag nanoparticles. *Carbohydrate polymers,* 110**,** pp. 148-155.

Emam, H. E., Saleh, N., Nagy, K. S. & Zahran, M. 2015. Functionalization of medical cotton by direct incorporation of silver nanoparticles. *International journal of biological macromolecules,* 78**,** pp. 249-256.

Emam, H. E., Saleh, N., Nagy, K. S. & Zahran, M. 2016. Instantly AgNPs deposition through facile solventless technique for poly-functional cotton fabrics. *International journal of biological macromolecules,* 84**,** pp. 308-318.

Emam, H. E. & Zahran, M. K. 2015. Ag0 nanoparticles containing cotton fabric: Synthesis, characterization, color data and antibacterial action. *International journal of biological macromolecules,* 75**,** pp. 106-114.

Fahmy, H., Eid, R., Hashem, S. & Amr, A. 2013. Enhancing some functional properties of viscose fabric. *Carbohydrate polymers,* 92**,** pp. 1539-1545.

Gaminian, H. & Montazer, M. 2017. Simultaneous nano TiO2 sensitization, application and stabilization on polyester fabric using madder and NaOH producing enhanced self-cleaning with hydrophilic properties under visible light. *Journal of Photochemistry and Photobiology A: Chemistry,* 332**,** pp. 158-166.

Ganesan, R. & Prabu, H. G. 2015. Synthesis of gold nanoparticles using herbal Acorus calamus rhizome extract and coating on cotton fabric for antibacterial and UV blocking applications. *Arabian Journal of Chemistry***,** pp.

Gao, D., Chen, C., Ma, J., Duan, X. & Zhang, J. 2014. Preparation, characterization and antibacterial functionalization of cotton fabric using dimethyl diallyl ammonium chloride-allyl glycidyl ether-methacrylic/nano-ZnO composite. *Chemical Engineering Journal,* 258**,** pp. 85-92.

Ghayempour, S. & Montazer, M. 2017. Ultrasound irradiation based in-situ synthesis of star-like Tragacanth gum/zinc oxide nanoparticles on cotton fabric. *Ultrasonics sonochemistry,* 34**,** pp. 458-465.

Goyal, N., Rastogi, D., Jassal, M. & Agrawal, A. K. 2016. Chitosan as a potential stabilizing agent for titania nanoparticle dispersions for preparation of multifunctional cotton fabric. *Carbohydrate polymers,* 154**,** pp. 167-175.

Grishanov, S. 2011. Structure and properties of textile materials. *Handbook of Textile and Industrial Dyeing.* Elsevier.

Gunasekaran, S., Sailatha, E., Seshadri, S. & Kumaresan, S. 2009. FTIR, FT Raman spectra and molecular structural confirmation of isoniazid. pp.

Halima, N. B. 2016. Poly (vinyl alcohol): review of its promising applications and insights into biodegradation. *RSC Advances,* 6**,** pp. 39823-39832.

Hanh, T. T., Thu, N. T., Hien, N. Q., An, P. N., Loan, T. T. K. & Hoa, P. T. 2016. Preparation of silver nanoparticles fabrics against multidrug-resistant bacteria. *Radiation Physics and Chemistry,* 121**,** pp. 87-92.

Hanh, T. T., Van Phu, D., Thu, N. T. & Hien, N. Q. 2014. Gamma irradiation of cotton fabrics in AgNO3 solution for preparation of antibacterial fabrics. *Carbohydrate polymers,* 101**,** pp. 1243-1248.

Harifi, T. & Montazer, M. 2015. A robust super-paramagnetic TiO2: Fe3O4: Ag nanocomposite with enhanced photo and bio activities on polyester fabric via one step sonosynthesis. *Ultrasonics sonochemistry,* 27**,** pp. 543-551.

Hebeish, A., Abdel-Mohdy, F., Fouda, M. M., Elsaid, Z., Essam, S., Tammam, G. & Drees, E. A. 2011a. Green synthesis of easy care and antimicrobial cotton fabrics. *Carbohydrate Polymers,* 86**,** pp. 1684-1691.

Hebeish, A., El-Bisi, M. & El-Shafei, A. 2015. Green synthesis of silver nanoparticles and their application to cotton fabrics. *International journal of biological macromolecules,* 72**,** pp. 1384-1390.

Hebeish, A., El-Naggar, M., Fouda, M. M., Ramadan, M., Al-Deyab, S. S. & El-Rafie, M. 2011b. Highly effective antibacterial textiles containing green synthesized silver nanoparticles. *Carbohydrate Polymers,* 86**,** pp. 936-940.

Hebeish, A., El-Shafei, A., Sharaf, S. & Zaghloul, S. 2014. Development of improved nanosilver-based antibacterial textiles via synthesis of versatile chemically modified cotton fabrics. *Carbohydrate polymers,* 113**,** pp. 455-462.

Heliopoulos, N. S., Papageorgiou, S. K., Galeou, A., Favvas, E. P., Katsaros, F. K. & Stamatakis, K. 2013. Effect of copper and copper alginate treatment on wool fabric. Study of textile and antibacterial properties. *Surface and Coatings Technology,* 235**,** pp. 24-31.

Hosseinkhani, M., Montazer, M., Eskandarnejad, S. & Rahimi, M. 2012. Simultaneous in situ synthesis of nano silver and wool fiber fineness enhancement using sulphur based reducing agents. *Colloids and Surfaces A: Physicochemical and Engineering Aspects,* 415**,** pp. 431-438.

Ibrahim, H. M. & Hassan, M. S. 2016. Characterization and antimicrobial properties of cotton fabric loaded with green synthesized silver nanoparticles. *Carbohydrate polymers,* 151**,** pp. 841-850.

Ibrahim, N. A., Eid, B. M. & Abdel-Aziz, M. S. 2017. Effect of plasma superficial treatments on antibacterial functionalization and coloration of cellulosic fabrics. *Applied Surface Science,* 392**,** pp. 1126-1133.

Ishida, T. 2018. Antibacterial Mechanism of Bacteriolyses of Bacterial Cell Walls by Zinc（Ⅱ）Ion Induced Activations of PGN Autolysins, and DNA damages. *Journal of Genes and Proteins,* 2017.

Jiang, T., Liu, L. & Yao, J. 2011. In situ deposition of silver nanoparticles on the cotton fabrics. *Fibers and polymers,* 12**,** pp. 620.

Jiang, W., Mashayekhi, H. & Xing, B. 2009. Bacterial toxicity comparison between nano-and micro-scaled oxide particles. *Environmental pollution,* 157**,** pp. 1619-1625.

Joe, A., Park, S.-H., Shim, K.-D., Kim, D.-J., Jhee, K.-H., Lee, H.-W., Heo, C.-H., Kim, H.-M. & Jang, E.-S. 2017. Antibacterial mechanism of ZnO nanoparticles under dark conditions. *Journal of Industrial and Engineering Chemistry,* 45**,** pp. 430-439.

Joshi, M., Ali, S. W. & Rajendran, S. 2007. Antibacterial finishing of polyester/cotton blend fabrics using neem (Azadirachta indica): a natural bioactive agent. *Journal of Applied Polymer Science,* 106**,** pp. 793-800.

Kalyon, B. D. & Olgun, U. 2001. Antibacterial efficacy of triclosan-incorporated polymers. *American journal of infection control,* 29**,** pp. 124-125.

Klemenčič, D., Tomšič, B., Kovač, F., Žerjav, M., Simončič, A. & Simončič, B. 2013. Antimicrobial wool, polyester and a wool/polyester blend created by silver particles embedded in a silica matrix. *Colloids and Surfaces B: Biointerfaces,* 111**,** pp. 517-522.

Kljun, A., El-Dessouky, H. M., Benians, T. A., Goubet, F., Meulewaeter, F., Knox, J. P. & Blackburn, R. S. 2014. Analysis of the physical properties of developing cotton fibres. *European Polymer Journal,* 51**,** pp. 57-68.

Koh, L.-D., Cheng, Y., Teng, C.-P., Khin, Y.-W., Loh, X.-J., Tee, S.-Y., Low, M., Ye, E., Yu, H.-D. & Zhang, Y.-W. 2015. Structures, mechanical properties and applications of silk fibroin materials. *Progress in Polymer Science,* 46**,** pp. 86-110.

Komeily-Nia, Z., Montazer, M. & Latifi, M. 2013. Synthesis of nano copper/nylon composite using ascorbic acid and CTAB. *Colloids and Surfaces A: Physicochemical and Engineering Aspects,* 439**,** pp. 167-175.

Koyano, T., Koshizaki, N., Umehara, H., Nagura, M. & Minoura, N. 2000. Surface states of PVA/chitosan blended hydrogels. *Polymer,* 41**,** pp. 4461-4465.

Kramar, A., Prysiazhnyi, V., Dojčinović, B., Mihajlovski, K., Obradović, B., Kuraica, M. & Kostić, M. 2013. Antimicrobial viscose fabric prepared by treatment in DBD and subsequent deposition of silver and copper ions—Investigation of plasma aging effect. *Surface and Coatings Technology,* 234**,** pp. 92-99.

Krishnaveni, R. & Thambidurai, S. 2013. Industrial method of cotton fabric finishing with chitosan–ZnO composite for anti-bacterial and thermal stability. *Industrial crops and products,* 47**,** pp. 160-167.

Kwak, W.-G., Oh, M. H. & Gong, M.-S. 2015. Preparation of silver-coated cotton fabrics using silver carbamate via thermal reduction and their properties. *Carbohydrate polymers,* 115**,** pp. 317-324.

Le Ouay, B. & Stellacci, F. 2015. Antibacterial activity of silver nanoparticles: a surface science insight. *Nano Today,* 10**,** pp. 339-354.

Lee, H. J. & Jeong, S. H. 2005. Bacteriostasis and skin innoxiousness of nanosize silver colloids on textile fabrics. *Textile Research Journal,* 75**,** pp. 551-556.

Li, G., Liu, H., Zhao, H., Gao, Y., Wang, J., Jiang, H. & Boughton, R. 2011. Chemical assembly of TiO2 and TiO2@ Ag nanoparticles on silk fiber to produce multifunctional fabrics. *Journal of colloid and interface science,* 358**,** pp. 307-315.

Li, J., He, J. & Huang, Y. 2017. Role of alginate in antibacterial finishing of textiles. *International journal of biological macromolecules,* 94**,** pp. 466-473.

Liedtke, J. & Vahjen, W. 2012. In vitro antibacterial activity of zinc oxide on a broad range of reference strains of intestinal origin. *Veterinary microbiology,* 160**,** pp. 251-255.

Lin, H., Yao, L., Chen, Y. & Wang, H. 2008. Structure and properties of silk fibroin modified cotton. *Fibers and Polymers,* 9**,** pp. 113-120.

Llorens, A., Lloret, E., Picouet, P. & Fernandez, A. 2012. Study of the antifungal potential of novel cellulose/copper composites as absorbent materials for fruit juices. *International journal of food microbiology,* 158**,** pp. 113-119.

Lu, Z., Mao, C., Meng, M., Liu, S., Tian, Y., Yu, L., Sun, B. & Li, C. M. 2014. Fabrication of CeO2 nanoparticle-modified silk for UV protection and antibacterial applications. *Journal of colloid and interface science,* 435**,** pp. 8-14.

Ma, H., Kabengi, N., Bertsch, P., Unrine, J., Glenn, T. & Williams, P. 2011. Comparative phototoxicity of nanoparticulate and bulk ZnO to a free-living nematode Caenorhabditis elegans: the importance of illumination mode and primary particle size. *Environmental Pollution,* 159**,** pp. 1473-1480.

Ma, M. & Sun, G. 2005. Antimicrobial cationic dyes. Part 3: simultaneous dyeing and antimicrobial finishing of acrylic fabrics. *Dyes and pigments,* 66**,** pp. 33-41.

Mansour, A., Mansour, S. & Abdo, M. 2015. Improvement structural and optical properties of zno/pva nanocomposites. *IOSR J. Appl. Phys,* 7**,** pp. 60-69.

Mary, G., Bajpai, S. & Chand, N. 2009. Copper (II) ions and copper nanoparticles-loaded chemically modified cotton cellulose fibers with fair antibacterial properties. *Journal of Applied Polymer Science,* 113**,** pp. 757-766.

Maryan, A. S., Montazer, M. & Harifi, T. 2015. Synthesis of nano silver on cellulosic denim fabric producing yellow colored garment with antibacterial properties. *Carbohydrate polymers,* 115**,** pp. 568-574.

Mather, R. 2009. Surface modification of textiles by plasma treatments. *Surface modification of textiles.* Elsevier.

Meftahi, A., Yadegari, F., Alibakhshi, S., Vatandoost, S. & Mohammadi, H. 2015. Finishing of Nylon/Cotton Fabric with ZnO/TiO2 Nanocomposite. *Procedia Materials Science,* 11**,** pp. 600-604.

Mekewi, M., El-Sayed, A. A., Amin, M. & Said, H. I. 2012. Imparting permanent antimicrobial activity onto viscose and acrylic fabrics. *International journal of biological macromolecules,* 50**,** pp. 1055-1062.

Mirzaei, H. & Darroudi, M. 2017. Zinc oxide nanoparticles: Biological synthesis and biomedical applications. *Ceramics International,* 43**,** pp. 907-914.

Moafi, H. F., Shojaie, A. F. & Zanjanchi, M. A. 2011. Photocatalytic self-cleaning properties of cellulosic fibers modified by nano-sized zinc oxide. *Thin Solid Films,* 519**,** pp. 3641-3646.

Montazer, M., Keshvari, A. & Kahali, P. 2016. Tragacanth gum/nano silver hydrogel on cotton fabric: In-situ synthesis and antibacterial properties. *Carbohydrate polymers,* 154**,** pp. 257-266.

Montazer, M. & Nia, Z. K. 2015. Conductive nylon fabric through in situ synthesis of nano-silver: Preparation and characterization. *Materials Science and Engineering: C,* 56**,** pp. 341-347.

Montazer, M. & Seifollahzadeh, S. 2011. Enhanced self-cleaning, antibacterial and UV protection properties of nano TiO2 treated textile through enzymatic pretreatment. *Photochemistry and photobiology,* 87**,** pp. 877-883.

Montazer, M., Shamei, A. & Alimohammadi, F. 2012a. Stabilized nanosilver loaded nylon knitted fabric using BTCA without yellowing. *Progress in Organic Coatings,* 74**,** pp. 270-276.

Montazer, M., Shamei, A. & Alimohammadi, F. 2012b. Synthesizing and stabilizing silver nanoparticles on polyamide fabric using silver-ammonia/PVP/UVC. *Progress in Organic Coatings,* 75**,** pp. 379-385.

Montazer, M., Shamei, A. & Alimohammadi, F. 2014. Synthesis of nanosilver on polyamide fabric using silver/ammonia complex. *Materials Science and Engineering: C,* 38**,** pp. 170-176.

Mura, S., Greppi, G., Malfatti, L., Lasio, B., Sanna, V., Mura, M. E., Marceddu, S. & Lugliè, A. 2015. Multifunctionalization of wool fabrics through nanoparticles: A chemical route towards smart textiles. *Journal of colloid and interface science,* 456**,** pp. 85-92.

Murthy, H. S. 2016. *Introduction to Textile Fibres*, CRC Press.

Muthu, S. S. 2014. *Roadmap to sustainable textiles and clothing: Eco-friendly raw materials, technologies, and processing methods*, Springer.

Nanda, K., Maisels, A., Kruis, F., Fissan, H. & Stappert, S. 2003. Higher surface energy of free nanoparticles. *Physical review letters,* 91**,** pp. 106102.

Nateghi, M. R. & Shateri-Khalilabad, M. 2015. Silver nanowire-functionalized cotton fabric. *Carbohydrate polymers,* 117**,** pp. 160-168.

Nickerson, R. 1942. Structure, Properties, and Utilization of Cotton-Influences of Common Agencies on Behavior. *Industrial & Engineering Chemistry,* 34**,** pp. 1149-1154.

Nischala, K., Rao, T. N. & Hebalkar, N. 2011. Silica–silver core–shell particles for antibacterial textile application. *Colloids and Surfaces B: Biointerfaces,* 82**,** pp. 203-208.

Park, D. J., Lee, M. H., Woo, Y. I., Han, D.-W., Choi, J. B., Kim, J. K., Hyun, S. O., Chung, K.-H. & Park, J.-C. 2008. Sterilization of microorganisms in silk fabrics by microwave-induced argon plasma treatment at atmospheric pressure. *Surface and coatings technology,* 202**,** pp. 5773-5778.

Pasquet, V., Behary, N. & Perwuelz, A. 2014. Environmental impacts of chemical/ecotechnological/biotechnological hydrophilisation of polyester fabrics. *Journal of cleaner production,* 65**,** pp. 551-560.

Perelshtein, I., Applerot, G., Perkas, N., Wehrschuetz-Sigl, E., Hasmann, A., Guebitz, G. & Gedanken, A. 2009. CuO–cotton nanocomposite: Formation, morphology, and antibacterial activity. *Surface and Coatings Technology,* 204**,** pp. 54-57.

Perelshtein, I., Lipovsky, A., Perkas, N., Tzanov, T., Arguirova, M., Leseva, M. & Gedanken, A. 2015. Making the hospital a safer place by sonochemical coating of all its textiles with antibacterial nanoparticles. *Ultrasonics sonochemistry,* 25**,** pp. 82-88.

Petkova, P., Francesko, A., Perelshtein, I., Gedanken, A. & Tzanov, T. 2016. Simultaneous sonochemical-enzymatic coating of medical textiles with antibacterial ZnO nanoparticles. *Ultrasonics sonochemistry,* 29**,** pp. 244-250.

Pourbeyram, S. & Mohammadi, S. 2014. Synthesis and characterization of highly stable and water dispersible hydrogel–copper nanocomposite. *Journal of Non-Crystalline Solids,* 402**,** pp. 58-63.

Pouton, C. W. 2006. Formulation of poorly water-soluble drugs for oral administration: physicochemical and physiological issues and the lipid formulation classification system. *European journal of pharmaceutical sciences,* 29**,** pp. 278-287.

Prasad, V., Arputharaj, A., Bharimalla, A., Patil, P. & Vigneshwaran, N. 2016. Durable multifunctional finishing of cotton fabrics by in situ synthesis of nano-ZnO. *Applied Surface Science,* 390**,** pp. 936-940.

Premanathan, M., Karthikeyan, K., Jeyasubramanian, K. & Manivannan, G. 2011. Selective toxicity of ZnO nanoparticles toward Gram-positive bacteria and cancer cells by apoptosis through lipid peroxidation. *Nanomedicine: Nanotechnology, Biology and Medicine,* 7**,** pp. 184-192.

Qin, C., Soykeabkaew, N., Xiuyuan, N. & Peijs, T. 2008. The effect of fibre volume fraction and mercerization on the properties of all-cellulose composites. *Carbohydrate Polymers,* 71**,** pp. 458-467.

Rajan, S. T., Karthika, M., Balaji, U., Muthappan, A. & Subramanian, B. 2017. Functional finishing of medical fabrics using CeO2/allicin nanocomposite for wound dressings. *Journal of Alloys and Compounds,* 695**,** pp. 747-752.

Rana, M., Hao, B., Mu, L., Chen, L. & Ma, P.-C. 2016. Development of multi-functional cotton fabrics with Ag/AgBr–TiO2 nanocomposite coating. *Composites Science and Technology,* 122**,** pp. 104-112.

Rastgoo, M., Montazer, M., Malek, R. M., Harifi, T. & Rad, M. M. 2016. Ultrasound mediation for one-pot sonosynthesis and deposition of magnetite nanoparticles on cotton/polyester fabric as a novel magnetic, photocatalytic, sonocatalytic, antibacterial and antifungal textile. *Ultrasonics sonochemistry,* 31**,** pp. 257-266.

Rastogi, L. & Arunachalam, J. 2013. Synthesis and characterization of bovine serum albumin–copper nanocomposites for antibacterial applications. *Colloids and Surfaces B: Biointerfaces,* 108**,** pp. 134-141.

Raza, Z. A., Rehman, A., Mohsin, M., Bajwa, S. Z., Anwar, F., Naeem, A. & Ahmad, N. 2015. Development of antibacterial cellulosic fabric via clean impregnation of silver nanoparticles. *Journal of Cleaner Production,* 101**,** pp. 377-386.

Reese, E. T. 2013. *Advances in Enzymic Hydrolysis of Cellulose and Related Materials: Including a Bibliography for the Years 1950–1961,* Elsevier.

Rehan, M., Mashaly, H. M., Mowafi, S., El-Kheir, A. A. & Emam, H. E. 2015. Multi-functional textile design using in-situ Ag NPs incorporation into natural fabric matrix. *Dyes and Pigments,* 118**,** pp. 9-17.

Rehan, M., Mowafi, S., Aly, S. A., Elshemy, N. S. & Haggag, K. 2017. Microwave-heating for in-situ Ag NPs preparation into viscose fibers. *European Polymer Journal,* 86**,** pp. 68-84.

Ren, G., Hu, D., Cheng, E. W., Vargas-Reus, M. A., Reip, P. & Allaker, R. P. 2009. Characterisation of copper oxide nanoparticles for antimicrobial applications. *International journal of antimicrobial agents,* 33**,** pp. 587-590.

Roy, A. S., Gupta, S., Sindhu, S., Parveen, A. & Ramamurthy, P. C. 2013. Dielectric properties of novel PVA/ZnO hybrid nanocomposite films. *Composites Part B: Engineering,* 47**,** pp. 314-319.

Samavati, A., Ismail, A., Nur, H., Othaman, Z. & Mustafa, M. 2016. Spectral features and antibacterial properties of Cu-doped ZnO nanoparticles prepared by sol-gel methodProject supported by the Universiti Teknologi Malaysia (UTM)(Grant No. R. J1300000. 7809.4 F626). Dr. Samavati is thankful to RMC for postdoctoral grants. *Chinese Physics B,* 25**,** pp. 077803.

Saravanan, D., Vasanthi, N. & Ramachandran, T. 2009. A review on influential behaviour of biopolishing on dyeability and certain physico-mechanical properties of cotton fabrics. *Carbohydrate polymers,* 76**,** pp. 1-7.

Sataev, M., Koshkarbaeva, S., Tleuova, A., Perni, S., Aidarova, S. & Prokopovich, P. 2014. Novel process for coating textile materials with silver to prepare antimicrobial fabrics. *Colloids and Surfaces A: Physicochemical and Engineering Aspects,* 442**,** pp. 146-151.

Selvam, S., Gandhi, R. R., Suresh, J., Gowri, S., Ravikumar, S. & Sundrarajan, M. 2012. Antibacterial effect of novel synthesized sulfated β-cyclodextrin crosslinked cotton fabric and its improved antibacterial activities with ZnO, TiO2 and Ag nanoparticles coating. *International journal of pharmaceutics,* 434**,** pp. 366-374.

Selvam, S. & Sundrarajan, M. 2012. Functionalization of cotton fabric with PVP/ZnO nanoparticles for improved reactive dyeability and antibacterial activity. *Carbohydrate polymers,* 87**,** pp. 1419-1424.

Shaban, M., Abdallah, S. & Khalek, A. A. 2016. Characterization and photocatalytic properties of cotton fibers modified with ZnO nanoparticles using sol–gel spin coating technique. *Beni-Suef University Journal of Basic and Applied Sciences,* 5**,** pp. 277-283.

Shaheen, T. I., El-Naggar, M. E., Abdelgawad, A. M. & Hebeish, A. 2016. Durable antibacterial and UV protections of in situ synthesized zinc oxide nanoparticles onto cotton fabrics. *International journal of biological macromolecules,* 83**,** pp. 426-432.

Shahidi, S. & Ghoranneviss, M. 2011. Investigation on dye ability and antibacterial activity of nanolayer platinum coated polyester fabric using DC magnetron sputtering. *Progress in Organic Coatings,* 70**,** pp. 300-303.

Shaikh, S. F., Mane, R. S., Min, B. K., Hwang, Y. J. & Joo, O.-S. 2016. D-sorbitol-induced phase control of TiO 2 nanoparticles and its application for dye-sensitized solar cells. *Scientific reports,* 6**,** pp. 20103.

Shankar, S., Teng, X. & Rhim, J.-W. 2014. Properties and characterization of agar/CuNP bionanocomposite films prepared with different copper salts and reducing agents. *Carbohydrate polymers,* 114**,** pp. 484-492.

Shariatinia, Z., Shekarriz, S., Mousavi, H. S. M., Maghsoudi, N. & Nikfar, Z. 2015. Disperse dyeing and antibacterial properties of nylon and wool fibers using two novel nanosized copper (II) complexes bearing phosphoramide ligands. *Arabian Journal of Chemistry***,** pp.

Shateri-Khalilabad, M., Yazdanshenas, M. E. & Etemadifar, A. 2017. Fabricating multifunctional silver nanoparticles-coated cotton fabric. *Arabian Journal of Chemistry,* 10**,** pp. S2355-S2362.

Sin, L. T., Bee, S.-T., Tee, T.-T., Kadhum, A. a. H., Ma, C., Rahmat, A. & Veerasamy, P. 2013. Characterization of α-tocopherol as interacting agent in polyvinyl alcohol–starch blends. *Carbohydrate polymers,* 98**,** pp. 1281-1287.

Sirelkhatim, A., Mahmud, S., Seeni, A., Kaus, N. H. M., Ann, L. C., Bakhori, S. K. M., Hasan, H. & Mohamad, D. 2015. Review on zinc oxide nanoparticles: antibacterial activity and toxicity mechanism. *Nano-Micro Letters,* 7**,** pp. 219-242.

Sivakumar, P., Balaji, S., Prabhawathi, V., Neelakandan, R., Manoharan, P. & Doble, M. 2010. Effective antibacterial adhesive coating on cotton fabric using ZnO nanorods and chalcone. *Carbohydrate Polymers,* 79**,** pp. 717-723.

Staneva, D., Atanasova, D., Vasileva-Tonkova, E., Lukanova, V. & Grabchev, I. 2015. A cotton fabric modified with a hydrogel containing ZnO nanoparticles. Preparation and properties study. *Applied Surface Science,* 345**,** pp. 72-80.

Stanković, A., Dimitrijević, S. & Uskoković, D. 2013. Influence of size scale and morphology on antibacterial properties of ZnO powders hydrothemally synthesized using different surface stabilizing agents. *Colloids and Surfaces B: Biointerfaces,* 102**,** pp. 21-28.

Su, C.-H., Kumar, G. V., Adhikary, S., Velusamy, P., Pandian, K. & Anbu, P. 2017. Preparation of cotton fabric using sodium alginate-coated nanoparticles to protect against nosocomial pathogens. *Biochemical engineering journal,* 117**,** pp. 28-35.

Sudha, M., Senthilkumar, S., Hariharan, R., Suganthi, A. & Rajarajan, M. 2013. Synthesis, characterization and study of photocatalytic activity of surface modified ZnO nanoparticles by PEG capping. *Journal of sol-gel science and technology,* 65**,** pp. 301-310.

Sun, J.-Y., Li, J., Qiu, X.-L. & Qing, F.-L. 2005. Synthesis and structure-activity relationship (SAR) of novel perfluoroalkyl-containing quaternary ammonium salts. *Journal of fluorine chemistry,* 126**,** pp. 1425-1431.

Svetlichnyi, V., Shabalina, A., Lapin, I., Goncharova, D. & Nemoykina, A. 2016. ZnO nanoparticles obtained by pulsed laser ablation and their composite with cotton fabric: Preparation and study of antibacterial activity. *Applied Surface Science,* 372**,** pp. 20-29.

Tamayo, L., Azócar, M., Kogan, M., Riveros, A. & Páez, M. 2016. Copper-polymer nanocomposites: An excellent and cost-effective biocide for use on antibacterial surfaces. *Materials Science and Engineering: C,* 69**,** pp. 1391-1409.

Tan, L. Y., Sin, L. T., Bee, S. T., Ratnam, C. T., Woo, K. K., Tee, T. T. & Rahmat, A. R. A review of antimicrobial fabric containing nanostructures metal-based compound. *Journal of Vinyl and Additive Technology***,** pp.

Tang, B., Sun, L., Kaur, J., Yu, Y. & Wang, X. 2014. In-situ synthesis of gold nanoparticles for multifunctionalization of silk fabrics. *Dyes and pigments,* 103**,** pp. 183-190.

Tang, B., Sun, L., Li, J., Kaur, J., Zhu, H., Qin, S., Yao, Y., Chen, W. & Wang, X. 2015. Functionalization of bamboo pulp fabrics with noble metal nanoparticles. *Dyes and Pigments,* 113**,** pp. 289-298.

Tang, B., Wang, J., Xu, S., Afrin, T., Tao, J., Xu, W., Sun, L. & Wang, X. 2012. Function improvement of wool fabric based on surface assembly of silica and silver nanoparticles. *Chemical engineering journal,* 185**,** pp. 366-373.

Tausif, M., Ahmad, F., Hussain, U., Basit, A. & Hussain, T. 2015. A comparative study of mechanical and comfort properties of bamboo viscose as an eco-friendly alternative to conventional cotton fibre in polyester blended knitted fabrics. *Journal of Cleaner Production,* 89**,** pp. 110-115.

Teli, M. & Sheikh, J. 2012. Antibacterial and acid and cationic dyeable bamboo cellulose (rayon) fabric on grafting. *Carbohydrate polymers,* 88**,** pp. 1281-1287.

Teli, M. & Sheikh, J. 2013. Modified bamboo rayon–copper nanoparticle composites as antibacterial textiles. *International journal of biological macromolecules,* 61**,** pp. 302-307.

Varaprasad, K., Raghavendra, G. M., Jayaramudu, T. & Seo, J. 2016. Nano zinc oxide–sodium alginate antibacterial cellulose fibres. *Carbohydrate polymers,* 135**,** pp. 349-355.

Vasilev, K., Sah, V. R., Goreham, R. V., Ndi, C., Short, R. D. & Griesser, H. J. 2010. Antibacterial surfaces by adsorptive binding of polyvinyl-sulphonate-stabilized silver nanoparticles. *Nanotechnology,* 21**,** pp. 215102.

Velmurugan, P., Shim, J., Bang, K.-S. & Oh, B.-T. 2016. Gold nanoparticles mediated coloring of fabrics and leather for antibacterial activity. *Journal of Photochemistry and Photobiology B: Biology,* 160**,** pp. 102-109.

Venkatasubbu, G. D., Baskar, R., Anusuya, T., Seshan, C. A. & Chelliah, R. 2016. Toxicity mechanism of titanium dioxide and zinc oxide nanoparticles against food pathogens. *Colloids and Surfaces B: Biointerfaces,* 148**,** pp. 600-606.

Virtanen, S., Vartianen, J., Setälä, H., Tammelin, T. & Vuoti, S. 2014. Modified nanofibrillated cellulose–polyvinyl alcohol films with improved mechanical performance. *Rsc Advances,* 4**,** pp. 11343-11350.

Wang, C., Lv, J., Ren, Y., Zhou, Q., Chen, J., Zhi, T., Lu, Z., Gao, D., Ma, Z. & Jin, L. 2016. Cotton fabric with plasma pretreatment and ZnO/Carboxymethyl chitosan composite finishing for durable UV resistance and antibacterial property. *Carbohydrate polymers,* 138**,** pp. 106-113.

Wang, S., Hou, W., Wei, L., Jia, H., Liu, X. & Xu, B. 2007. Antibacterial activity of nano-SiO2 antibacterial agent grafted on wool surface. *Surface and Coatings Technology,* 202**,** pp. 460-465.

Wang, X. & Quinn, P. J. 2010. Endotoxins: lipopolysaccharides of gram-negative bacteria. *Endotoxins: Structure, Function and Recognition.* Springer.

Wilkie, C. A., Geuskens, G. & De Matos Lobo, V. M. 2014. *Handbook of Research on Functional Materials: Principles, Capabilities and Limitations,* CRC Press.

Wu, D., Long, M., Zhou, J., Cai, W., Zhu, X., Chen, C. & Wu, Y. 2009. Synthesis and characterization of self-cleaning cotton fabrics modified by TiO2 through a facile approach. *Surface and Coatings Technology,* 203**,** pp. 3728-3733.

Xia, N., Cai, Y., Jiang, T. & Yao, J. 2011. Green synthesis of silver nanoparticles by chemical reduction with hyaluronan. *Carbohydrate polymers,* 86**,** pp. 956-961.

Yadollahi, M., Gholamali, I., Namazi, H. & Aghazadeh, M. 2015. Synthesis and characterization of antibacterial carboxymethylcellulose/CuO bio-nanocomposite hydrogels. *International journal of biological macromolecules,* 73**,** pp. 109-114.

Yang, J., Xu, H., Zhang, L., Zhong, Y., Sui, X. & Mao, Z. 2017. Lasting superhydrophobicity and antibacterial activity of Cu nanoparticles immobilized on the surface of dopamine modified cotton fabrics. *Surface and Coatings Technology,* 309**,** pp. 149-154.

Yu, D., Kang, G., Tian, W., Lin, L. & Wang, W. 2015a. Preparation of conductive silk fabric with antibacterial properties by electroless silver plating. *Applied Surface Science,* 357**,** pp. 1157-1162.

Yu, D., Tian, W., Sun, B., Li, Y., Wang, W. & Tian, W. 2015b. Preparation of silver-plated wool fabric with antibacterial and anti-mould properties. *Materials Letters,* 151**,** pp. 1-4.

Yuan, X. 2011. Enhanced interfacial interaction for effective reinforcement of poly (vinyl alcohol) nanocomposites at low loading of graphene. *Polymer bulletin,* 67**,** pp. 1785-1797.

Zahran, M., Ahmed, H. B. & El-Rafie, M. 2014. Surface modification of cotton fabrics for antibacterial application by coating with AgNPs–alginate composite. *Carbohydrate polymers,* 108**,** pp. 145-152.

Zanni, E., Chandraiahgari, C. R., De Bellis, G., Montereali, M. R., Armiento, G., Ballirano, P., Polimeni, A., Sarto, M. S. & Uccelletti, D. 2016. Zinc oxide nanorods-decorated graphene nanoplatelets: a promising antimicrobial agent against the cariogenic bacterium Streptococcus mutans. *Nanomaterials,* 6**,** pp. 179.

Zhang, D., Chen, L., Zang, C., Chen, Y. & Lin, H. 2013a. Antibacterial cotton fabric grafted with silver nanoparticles and its excellent laundering durability. *Carbohydrate polymers,* 92**,** pp. 2088-2094.

Zhang, F., Chen, Y., Lin, H., Wang, H. & Zhao, B. 2008. HBP-NH2 grafted cotton fiber: Preparation and salt-free dyeing properties. *Carbohydrate polymers,* 74**,** pp. 250-256.

Zhang, G., Morikawa, H., Chen, Y. & Miura, M. 2013b. In-situ synthesis of ZnO nanoparticles on bamboo pulp fabric. *Materials Letters,* 97**,** pp. 184-186.

Zhang, H., Zhang, Z., Friedrich, K. & Eger, C. 2006. Property improvements of in situ epoxy nanocomposites with reduced interparticle distance at high nanosilica content. *Acta Materialia,* 54**,** pp. 1833-1842.

LIST OF PUBLICATIONS

Tan, L., Sin, L., Bee, S., Ratnam, C., Woo, K., Tee, T. and Rahmat, A. 2017. A review of antimicrobial fabric containing nanostructures metal-based compound. *Journal of Vinyl and Additive Technology*, 25, pp.3-27.

Tan, L., Sin, L., Bee, S., Ratnam, C., Woo, K., Tee, T. and Rahmat, A. Functionalization of cotton fabric with ZnO/PVA for antibacterial textile. *Solid State Phenomena.*