Exploring the utility of silane cross-linkers for synthesis of superhydrophobic antibacterial fabrics

Agrawal, Neha

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**NANYANG
TECHNOLOGICAL
UNIVERSITY**

SINGAPORE

**EXPLORING THE UTILITY OF SILANE
CROSS-LINKERS FOR SYNTHESIS OF
SUPERHYDROPHOBIC ANTIBACTERIAL FABRICS**

AGRAWAL NEHA

SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

2018

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CROSS-LINKERS FOR SYNTHESIS OF
SUPERHYDROPHOBIC ANTIBACTERIAL FABRICS**

AGRAWAL NEHA

SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

A thesis submitted to the Nanyang Technological
University in partial fulfilment of the requirement for the
degree of Master of Engineering

2018

Statement of Originality

I hereby certify that the work embodied in this thesis is the result of original research and has not been submitted for a higher degree to any other University or Institution.

17 Dec 2018

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Date

Neha Agrawal

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Neha Agrawal

Supervisor Declaration Statement

I have reviewed the content and presentation style of this thesis and declare it is free of plagiarism and of sufficient grammatical clarity to be examined. To the best of my knowledge, the research and writing are those of the candidate except as acknowledged in the Author Attribution Statement. I confirm that the investigations were conducted in accord with the ethics policies and integrity standards of Nanyang Technological University and that the research data are presented honestly and without prejudice.

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Professor Chen Zhong

Authorship Attribution Statement

This thesis contains material from following papers under review/published in the following peer-reviewed journals where I was the first author.

Chapter 4 as Neha Agrawal, Pearlie Sijia Low, Eileen Wen Mei Fong, Yuekun Lai, Zhong Chen; Durable easy-cleaning and antibacterial cotton fabrics using fluorine-free silane coupling agents and CuO nanoparticles, *Nano Materials Science*. (Under review)

Chapter 5 as Neha Agrawal, Jasmine Si Jia Tan, Pearlie Sijia Low, Eileen Wen Mei Fong, Yuekun Lai, Zhong Chen; Green synthesis of robust superhydrophobic antibacterial and UV blocking cotton fabrics by dual stage silanization approach, *Advanced Materials Interfaces* (Accepted for publication)

The contributions of the co-authors are as follows:

- I co-designed the study with Prof Chen Zhong and performed all the laboratory work at the School of Materials Science and Engineering.
- All microscopy, including sample preparation, was conducted by me in the Facility for Analysis, Characterization, Testing and Simulation.
- Dr. Fong Wen Mei Eileen provided facilities in her laboratory for antibacterial experiments. Ms. Low Sijia Pearlie provided the training and guidance for obtaining the antibacterial test results.
- Ms. Tan Si Jia Jasmine provided high magnification FE-SEM images and EDS data at F.A.C.T.S. for Chapter 5 manuscript.
- Prof. Yuekun Lai, Soochow University, China provided the data for air permeability and flexural rigidity measurements.

17 Dec 2018

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Date

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Neha Agrawal

Abstract

Textiles are omnipresent materials which find various industrial and household applications in our everyday lives. Functionalization of the textiles with additional properties like superhydrophobicity and antibacterial activity can greatly improve their performance, especially in clothing and healthcare sectors. Despite the existing endeavours to incorporate these properties, fabrication of multi-functional fabrics of high durability through a scalable and eco-friendly technique remains a great challenge. The objective of this research involves developing novel routes of synthesis which are simple, inexpensive, eco-friendly, and can enhance the durability of the superhydrophobic antibacterial fabrics. In this thesis, two different fabrication techniques are reported which utilize fluorine-free silane coupling agents as cross-linkers for improving the durability. Metal-oxide nanoparticles have been employed to offer antibacterial activity and nanoscale roughness, essential to achieve superhydrophobicity and antibacterial functionality on the fabric. The role of the silane cross-linkers involves anchoring the nanoparticles to the fabric surface to enhance the robustness of the coating.

In the first synthesis technique, a low surface energy polymer, polydimethylsiloxane (PDMS) was deposited on cotton fabrics. Subsequently, copper oxide (CuO) nanoparticles were deposited on the PDMS coated fabrics with the aid of a silane cross-linker. Three silane cross-linkers, *viz.*, Aminoethylaminopropyltrimethoxysilane (AEAPTMS), Aminopropyltriethoxysilane (APTES), and Methacryloyloxypropyltrimethoxysilane (MPTMS), were explored for their applicability. The as-prepared fabrics displayed high superhydrophobicity and antibacterial performance with water contact angle (WCA) > 153°, water shedding angle (WSA) < 5°, and up to 99% antibacterial efficiency. It was found that 8 g/m² nanoparticle loading on the fabric surface was optimal in achieving maximum overall performance. The only observed limitation of this technique was the dark colour of the fabrics due to the agglomeration of the black CuO nanoparticles.

To overcome this drawback of the first synthesis technique, white zinc oxide (ZnO) nanoparticles were explored for their usage in the second technique. Here, ZnO

nanoparticles were deposited on the surface of the cotton fabrics using APTES silane cross-linker followed by modification with Hexadecyltrimethoxysilane (HDTMS), a low surface energy silane. The as-prepared fabrics with an optimized nanoparticle loading of 20 g/m² displayed high superhydrophobicity with WCA of 153.5° and WSA of 2.4° and up to 98% antibacterial efficiency. Additionally, the ZnO-treated fabrics displayed high UV blocking ability, more than 200 times of pristine cotton fabric. The fabrics synthesised through both the fabrication routes displayed superior durability against abrasion, ultrasonic washing and harsh chemical solutions. Moreover, the air permeability and flexibility of the fabric was not much compromised after the coatings.

The above-reported techniques are simple, cost-effective and demonstrate the ability to improve the durability of the synthesized coatings on the cotton fabrics. Both synthesis routes hold tremendous potential for large-scale production of multi-functional fabrics, especially for clothing and healthcare applications.

Lay Summary

Textiles are present everywhere around us. We use them every day for clothes, hospital bandages, food packaging, and various other household and industrial applications. The fabric materials used for clothing and healthcare however suffer from some drawbacks. Clothes tend to be easily stained with food and drinks, which increases the number of laundering needed, and results in the growth of germs. In the hospitals, the bedsheets, pillows, patient gowns get contaminated with blood which poses a severe risk of spreading infection. Therefore, by making fabrics that are stain-resistant and have antibacterial properties, these drawbacks can be overcome. In this study, stain-resistant and antibacterial cotton fabrics have been synthesized. Although extensive research has been done in the past in this field, most of these works reported poor durability of the coatings, use of harmful chemicals, or complicated synthesis procedures, which has limited the potential for these fabrics to be launched in the market. Therefore, in this work, efforts have been made to adopt eco-friendly and simple synthesis procedures for making durable stain-resistant and antibacterial fabrics. To introduce antibacterial activity, nanoparticles (particles whose size ranges from 1-100 nanometre or 10^{-9} metre) have been used that possess antibacterial properties. To improve the durability, a chemical called silane coupling agent has been used, which has two reactive ends. One end attaches itself to the nanoparticle and the other end to the fabric surface. In this way, it anchors the nanoparticles to the fabric firmly and maintains the longevity of the coating. In this work, two different techniques have been developed by which one can synthesize such robust multi-functional fabrics through an eco-friendly and simple synthesis process. These as-prepared fabrics through both routes displayed very high performance. Any water droplet fallen on the fabric surface could roll-off from the fabric with a slight tilt of the surface making it stain resistant and self-cleaning. The fabric was also able to kill 99% of the bacteria on the surface showing very high antibacterial activity. We also tested the durability of the fabric under common physical and chemical conditions. The fabric showed high resistance to abrasion, washing and different chemical solutions. Additionally, the breathability and flexibility of the fabric was also largely maintained after the coating ensuring that the comfortability will not be compromised during wearing. Therefore, through this work, it was possible to overcome some limitations of the previous techniques, taking this research one step closer to large-scale production of such multi-functional fabrics.

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Abbreviations

AATCC	American Association of Textile Chemists and Colorists
AEAPTMS	N-[3-(Trimethoxysilyl)propyl]ethylenediamine
APTES	(3-Aminopropyl)triethoxysilane
BTESE	1,2-Bis(triethoxysilyl)ethane
CAH	Contact Angle Hysteresis
FAS	nonafluorohexyltriethoxysilane
FE-SEM	Field Emission Scanning Electron Microscopy
FTIR	Fourier Transform Infrared Spectroscopy
HDTMS	Hexadecyltrimethoxysilane
LB	Luria Broth
MPTMS	3-(Trimethoxysilyl)propyl methacrylate
OD	Optical Density
OTES	Octyltriethoxysilane
PBS	Phosphate Buffered Saline
PDMS	Polydimethylsiloxane
ROS	Reactive Oxygen Species
THF	Tetrahydrofuran
UPF	Ultraviolet Protection Factor
UV	Ultra Violet
WCA	Water Contact Angle
WSA	Water Shedding Angle
XRD	X-Ray Diffraction

Chapter 1

Introduction

In this chapter, the motivation and significance for undertaking this research work are discussed. The existing issues faced by the current technology are raised. The objectives for enhancing the fabric performance are outlined along with scope of this research undertaking. Additionally, the significant contributions of this work are highlighted in this chapter.

1.1 Research motivation and significance

Textiles are ubiquitous materials that serve an everyday requirement of the people. Surface modification of the textiles has now gained attention as a way to impart additional properties to the fabric. Researchers have successfully demonstrated textiles which are self-cleaning [1, 2], antibacterial [3], self-healing [4], flame retardant [5], UV blocking [6, 7], electrically conductive [8] and even photocatalytic [9] for applications in healthcare, clothing, food-packaging, oil-water separation, and various other industrial and household applications.

Among various applications, textiles are mainly used for manufacturing clothes and garments. However, the clothes are easily stained with food and drinks, which not only diminishes the fabric appearance, but also results in foul odour and growth of microorganisms. In hospitals, textiles, mainly cotton and polyester are used for medical bandages, gauges, masks, patient bedsheets and gowns. However, these fabrics get easily soiled and contaminated with blood, pathogenic bacteria and germs which is undesirable especially in medical conditions [10, 11]. By making the clothes self-cleaning, and antibacterial, the performance of the fabrics will be greatly enhanced. The fabrics would become resistant to stain when water, milk, coffee, or soft-drink is spilled over it [12]. The self-cleaning nature would also facilitate reduced number of washes, which will save consumer effort, reduce energy consumption and retain the newness of the clothing. The bacteriostatic and bactericidal property of the antibacterial fabric material would prevent the bacterial adhesion and destroy the microorganisms.

Therefore, fabrication of self-cleaning antibacterial textiles will greatly improve their performance in clothing and healthcare applications, which is the primary motivation and significance of undertaking this study (Figure 1.1).

Figure 1.1 Advantages of using antimicrobial superhydrophobic fabrics in the clothing and healthcare industry

1.2 Problem statement

There are three primary requirements to obtain a self-cleaning antibacterial textile surface. For incorporating self-cleaning behaviour, the fabrics are usually induced with superhydrophobic property. Therefore, the presence of roughness along with low surface energy form the two primary requirements to obtain superhydrophobicity. The third requirement includes the use of an antibacterial agent to impart antibacterial functionality to the fabric. The most common strategy employed by the researchers involves the use of metal/metal-oxide nanoparticles which can perform the dual function of imparting roughness and antimicrobial activity [13]. The nanoparticles are then modified with a material of low surface energy to impart superhydrophobicity to the fabric. It is also essential that the nanoparticles should be exposed to the surface to obtain maximum possible antibacterial efficiency.

However, several challenges are faced by the current technology, which hinder the commercialization of such textiles. Most of the superhydrophobic coatings synthesized on the fabrics involve the use of long fluoro-alkyl chains for lowering the surface energy [14, 15]. These fluoro-alkyl chains are difficult to degrade and harmful to the environment [16]. Similar issue is faced when metal nanoparticles are used for antimicrobial activity or for inducing the surface roughness. If the coating is not stable, the nanoparticles are released from the surface and into the environment. Upon entering the body system through skin contact, inhalation or food items, they can cause severe harm to the body [17, 18]. Another drawback associated with the technology is the expensive cost [19] related to the complicated processes and equipment used for fabrication of these textiles [20]. This also hinders the scale-up of such processes due to high cost and complexity involved. The laundering durability of the superhydrophobic and antimicrobial textiles is significant when consumer markets are concerned. Even though researchers have been able to successfully fabricate such multifunctional textiles, the coating durability has not been optimised. There have been reports that after few washes, the multifunctional properties of the coating was lost [21]. Thus, in order to overcome these challenges, it is essential to develop a low-cost, eco-friendly, facile fabrication process which can also ensure high durability in superhydrophobic antibacterial fabrics. These features would then allow the commercialization of this technology to benefit society.

1.3 Objectives and scope

The objective of this research involves developing novel routes of synthesis that are simple, inexpensive, eco-friendly, and can enhance the durability of the superhydrophobic antibacterial textiles for clothing and healthcare applications. To achieve this goal, the role of silane coupling agents as cross-linkers was explored. Silane coupling agents are long chain molecules that consist of functional groups on each end. These functional groups can bond with organic and inorganic molecules thereby serving as an intermediary or as a cross-linker between two materials. In this study, the role of silane coupling agents as cross-linkers was explored for improving the durability of the multifunctional fabrics. It was envisaged that one end of the silane cross-linker could attach to the antibacterial metal-oxide nanoparticles and the other end could attach to the fabric substrate, thereby securing nanoparticles firmly to the

surface and preventing its release. This hypothesis displayed tremendous potential for providing a facile, cost-effective fabrication technique for synthesis of superhydrophobic antibacterial textiles. Moreover, fluorine-free silane cross-linkers would be utilized to overcome the toxicity issues usually involved with chemicals. Based on the above hypothesis and literature review, the key objectives and scopes of work of this project are as follows:

1. Develop coatings on cotton fabrics which offer superhydrophobic and antibacterial functionality
 - test different silane coupling agents which can be utilized as cross-linkers to bind the nanoparticles to the fabric substrate
 - optimize the loading of nanoparticles on the fabric surface for maximum performance
 - measure the performance of the synthesized fabrics
2. Understand the interaction among the nanoparticles, silane cross-linkers and fabric substrate
 - characterize the coating properties on the fabric
 - understand the bonding mechanism of different silane cross-linkers
 - understand the relationship between nanoparticle loading and fabric performance
3. Evaluate the durability of the developed coatings on the fabrics
 - conduct various durability tests to evaluate mechanical and chemical durability of the coating
 - measure coating performance after the tests to determine robustness of the synthesized fabrics

The outcome of this project would advance the research in this field and bring the multifunctional fabrics a step closer to commercialization. This fabrication technique can be utilized for exploring various other functionalities of fabrics apart from superhydrophobicity and antibacterial activity like UV blocking, electrical conductivity, flame retardance, self-healing ability and photocatalytic activity in the future. The role of silane coupling agents as cross-linkers can be extended to various

other substrates and nanoparticles for different surface engineering and coating applications.

1.4 Dissertation overview

The thesis explores the utility of silane cross-linkers for synthesis of superhydrophobic antibacterial fabrics. It is divided into 6 chapters.

Chapter 1 introduces the topic of study and the rationale for undertaking this research. It outlines the problem statement, the proposed solution along with objectives and scope for this work.

Chapter 2 provides an overview of the fundamentals for synthesis of superhydrophobic and antibacterial fabrics along with the theories of wetting behaviour. This chapter also highlights the role of nanoparticles in synthesis of such coatings and reviews the different nanoparticles which can be utilised for this application. Finally, this chapter reveals the existing research in this field and outlines the research gaps on which further research is needed.

Chapter 3 provides the experimental details. It also discusses the underlying principles of the fabrication techniques responsible for the synthesis of superhydrophobic antibacterial fabrics. Moreover, the chapter highlights the principles behind the different characterization techniques and durability tests undertaken to understand and evaluate the properties of the synthesized fabrics.

Chapter 4 elaborates the results obtained from the first fabrication technique resulting in CuO-Silane-PDMS-Cotton fabrics. It discusses in detail the outcomes obtained from the study, the achievements and its limitations.

Chapter 5 elaborates the results obtained from the second fabrication technique resulting in HDTMS-ZnO-APTES-Cotton fabrics. It discusses in detail the outcomes obtained from the study, the achievements and scope of improvement.

Finally, Chapter 6 draws together the threads of this thesis. It provides a results summary and verification of research hypothesis. It also provides a conclusion and the novel contributions of this research work. This chapter also discusses the scope for future work, which can be undertaken to further improve the research in this field. Moreover, this chapter also shares the reconnaissance work that has contributed in arriving at the main findings.

1.5 Findings and outcomes

This research has yielded several novel outcomes and helped make significant contributions to the field which are given as follows:

- Explored the role of silane cross-linkers for developing two facile, eco-friendly synthesis techniques for durable superhydrophobic antibacterial fabrics
- Optimized the nanoparticle loading on the fabric surface for maximizing coating performance
- Evaluated the longevity and robustness of the synthesized coating by various durability tests

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Chapter 2

Literature Review

In this chapter, the fundamental concepts behind the synthesis of superhydrophobic antibacterial fabrics are discussed. Essentially, presence of dual micro and nanoscale roughness, low-surface energy and an antibacterial agent form the three requirements to achieve superhydrophobic antibacterial coatings on fabrics. This chapter reviews the research conducted in this field to obtain such multifunctional fabrics and the different synthesis routes that have been elaborated. Most commonly, metal/metal-oxide nanoparticles are utilized as antibacterial agents such as silver, copper, copper oxide, titanium dioxide and zinc oxide. The role and the efficiency of these nanoparticles for synthesis has also been evaluated. Further, the research gaps identified after an extensive literature survey are revealed in this chapter.

2.1 Fundamentals of superhydrophobic self-cleaning fabric surfaces

The self-cleaning property of the Lotus leaves, well known as the ‘Lotus Effect’, was first studied by Barthlott and Ehler in 1977 [1]. The self-cleaning phenomenon is due to the presence of epidermal papillae on the lotus leaf surface that is covered with waxy hydrophobic epicuticular crystalloids. These structures provide dual micro and nanoscale roughness along with low surface energy to the leaf surface. This results in the surface having high water contact angle $>150^\circ$ and a low sliding angle $<10^\circ$. This property of the lotus leaf is therefore termed as ‘superhydrophobic or ultrahydrophobic’. A water droplet fallen on the leaf will experience a reduced contact area with the leaf surface and will roll-away carrying the dirt particles along with it (Figure 2.1). This ‘self-cleaning’ property has now found myriad applications in our day-to-day lives including textiles.

Figure 2.1 a) SEM image of the surface of Lotus leaf covered with micro and nanoscale structures; b) SEM image of wing surface of Cicada orni showing the dirt particles getting adhered to the surface of the water droplet; c) Mechanism displaying the self-cleaning effect observed due to the roughness and low surface energy of the substrate surface [1]

For the fabrication of superhydrophobic self-cleaning textiles, understanding the fundamentals responsible for the phenomenon becomes essential. The surface topography (micro and nanoscale roughness) and chemical composition (low surface energy) are two important criteria that determine the superhydrophobicity of a substrate surface. There are three fundamental theories available in this regard, which are detailed below.

2.1.1 Theories of wetting behavior

The first theory is based on the wettability of surfaces. One will notice that a water droplet fallen on a glass surface easily spreads on the surface while a water droplet on

a plastic surface does not spread easily. This phenomenon is due to the variation of wettability of different surfaces. Wetting or wettability is the degree to which a fluid spreads on a solid surface and it can be quantified using Young's equation. A liquid droplet placed on a smooth solid surface upon equilibrium forms an angle at the intervention of the solid, liquid and vapour phases called the equilibrium contact angle (Figure 2.2) and can be given by Young's Equation (2.1):

$$\cos\theta_E = \frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}} \quad (2.1)$$

where, θ_E is the equilibrium contact angle, γ_{SV} is the solid-vapour interfacial tension, γ_{SL} is the solid-liquid interfacial tension and γ_{LV} is the liquid-vapour interfacial tension.

Figure 2.2 Equilibrium contact angle of a liquid on a smooth solid surface following the Young's equation [2]

When $\theta_E = 0^\circ$, the wetting is termed as complete wetting and when θ_E is finite, the wetting is termed as partial wetting. When the liquid in consideration is water, the contact angle is referred to as the water contact angle (WCA). If a surface has $\text{WCA} < 90^\circ$, it is called a hydrophilic surface and if the $\text{WCA} > 90^\circ$ it is called a hydrophobic surface. Similarly, if the $\text{WCA} < 5^\circ$ it is called a superhydrophilic surface and if the $\text{WCA} > 150^\circ$ it is called a superhydrophobic /ultrahydrophobic surface (Figure 2.3).

The Young's equation is valid only for ideal solid surfaces which are smooth, flat, rigid and chemically homogeneous. However, most of the substances existing in nature have a rough surface architecture. Therefore, to account for the real surfaces, two regimes of wetting were developed by Wenzel and Cassie-Baxter respectively.

Figure 2.3 Representation of a) Superhydrophilic surface, b) Hydrophilic surface, c) Hydrophobic surface, d) Superhydrophobic surface [3]

In the Wenzel state of wetting [4], also referred to as the homogeneous type of wetting, the liquid enters the grooves present on the rough or topographically patterned substrate and wets it completely (Figure 2.4a). In such a case, the wetting is quantified by the equation (2.2):

$$\cos\theta_w = r\cos\theta_E \quad (2.2)$$

where, r is the roughness factor defined as the ratio of actual solid-liquid contact area to the geometrically projected area and θ_w is the apparent contact angle in the Wenzel regime. When $\theta_E > 90^\circ$, which implies that the smooth surface of the same material is hydrophobic, patterning the surface or increasing the surface roughness can help in improving the hydrophobic property of the material. This can be observed from equation (2) where the value of r is always greater than 1. If $\theta_E > 90^\circ$, θ_w will be higher than θ_E . On the other hand, if $\theta_E < 90^\circ$, which implies that the smooth surface is hydrophilic, the rough or patterned surface of the same material in Wenzel regime will become even more hydrophilic. In order to improve the hydrophobicity of acute angle surfaces, increasing the value of the roughness factor i.e. by having higher feature height, can greatly improve the hydrophobicity of the surface. Therefore, in order to obtain superhydrophobic surfaces, topography of the substrate or the roughness plays a key role. In the Wenzel regime, the liquid remains in complete contact with the solid surface by entering the grooves and thus, gets strongly adhered to the surface. This prevents the liquid droplet from rolling off easily and makes the surface unfavourable for self-cleaning.

The second regime of wetting is the Cassie-Baxter state of wetting [5], also called the heterogeneous type of wetting. Under this regime, the liquid droplet does not enter the grooves present on the substrate surface but instead, rests or floats on the isolated air

pockets trapped between the grooves (Figure 2.4b). In such a case, the wetting is governed by equation (2.3):

$$\cos\theta_{CB} = f_s \cos\theta_E + f_v \cos\theta_{LV} \quad (2.3)$$

where, $\cos\theta_{LV}$, the air-liquid equilibrium contact angle is equal to 180° and $f_s + f_v = 1$ where f_s is the fractional solid-liquid contact area and f_v is the fractional vapour-liquid contact area. Substituting the values in equation (2.3) yields equation (2.4):

$$\cos\theta_{CB} = f_s \cos\theta_E - (1 - f_s) \quad (2.4)$$

By increasing the surface roughness (higher height to area aspect ratio structures), the value of f_s gets lowered and better levels of hydrophobicity can be achieved. This results in θ_{CB} having a value much greater than θ_E . The Cassie-Baxter wetting regime is favourable for achieving the self-cleaning effect as the droplet can easily roll-off the surface due to the air-filled grooves of the rough surface. Therefore, for fabrication of superhydrophobic self-cleaning textiles, the surface should display the Cassie-Baxter regime of wetting.

Figure 2.4 Representation of the water droplet in the a) Wenzel state of wetting, b) Cassie-Baxter state of wetting [2]

2.1.2 Static contact angle, contact angle hysteresis and sliding angle

To prepare a self-cleaning superhydrophobic surface, the first requirement is that the static contact angle $\theta_E > 150^\circ$. It is measured by placing a sessile liquid drop (usually water) over the surface of the substrate (e.g. fabric surface). When the water drop achieves metastable equilibrium, two tangents are drawn on either side of the drop for measurement of θ_E and the average value of the measurement is reported as WCA. However, to characterize the superhydrophobic textiles completely, measurement of static contact angle is insufficient and the dynamic contact angle measurement is also

required [6]. A liquid droplet placed on a tilted surface displays two contact angles, namely the advancing contact angle θ_{Adv} (angle formed at the front of the droplet motion) and the receding contact angle θ_{Rec} (angle formed at the back of the droplet motion). The difference between the two angles is called the Contact Angle Hysteresis (CAH). The second requirement to achieve a superhydrophobic surface is that the CAH $< 10^\circ$. Such surfaces allow the liquid droplet to be easily rolled-off from the surface along with the dirt displaying a self-cleaning effect [7]. The CAH can be measured (Figure 2.5a) using an instrument with advanced videography system which also analyses the images digitally e.g. Kruss DSA (Germany) [7].

Another parameter for characterizing the superhydrophobic surfaces is the sliding angle (θ_{SA}). It is defined as the tilt angle of the surface at which the droplet completely rolls-off without the application of any external force [6]. Therefore, a good self-cleaning behaviour demands a low sliding angle, which can be measured by placing a known volume of liquid and tilting the plate at a constant speed. The tilt angle of the plate at which the droplet starts sliding is then measured as θ_{SA} for the surface (Figure 2.5b). In order to evaluate the superhydrophobicity of a surface, usually the sliding angle is measured as the value is very close to CAH, however, it is essential to note that they are not the same.

For macroscopically rough surfaces like fabrics, determining the sliding angle becomes difficult due to the fibres sticking out from the fabric surface. They tend to hold the droplet on the fabric and interfere with the sliding angle measurement. To overcome this issue, another parameter called the Water Shedding Angle (WSA) can be measured to gauge the quality of the superhydrophobic textiles for water repellency [8]. WSA can be defined as the minimum tilt angle of the substrate surface at which a droplet of a defined volume dropped from a defined height completely rolls-off from the surface (Figure 2.5c). For this measurement, the parameters which need to be controlled are: the angle of inclination of the substrate, the height from which the droplet is dropped on the substrate, and the drop volume [8]. Therefore, a textile surface can be termed superhydrophobic if the WCA $> 150^\circ$ and the WSA $< 10^\circ$.

Figure 2.5 Techniques for the measurement of a) Contact angle hysteresis, b) Sliding angle, c) Shedding angle [7]

2.2 Synthesis routes for superhydrophobic fabrics

In the past decade, many researchers have attempted to synthesize superhydrophobic fabrics. For their synthesis, a hierarchical structure comprising of dual scale roughness in combination with a low surface energy material is required. As fabric materials are made up of microscale fibres, the incorporation of nanoscale roughness coupled with low surface energy satisfies all the criteria to achieve superhydrophobicity. To introduce the nanoscale roughness, nanoparticles have been the most preferred solution for researchers.

Different routes have been explored to achieve superhydrophobicity on the fabrics. One of the routes involves the in-situ incorporation of the nanoparticles on the fabric surface followed by modification with a hydrophobic silane to obtain superhydrophobicity (Figure 2.6).

Figure 2.6 Synthesis route of superhydrophobic fabrics using nanoparticles and hydrophobic silanes

This approach was adopted by Yazdanshenas and Shateri-Khalilabad in their work [9] to synthesize superhydrophobic cotton fabrics by ultrasound irradiation. The in-situ deposition of silica (SiO_2) nanoparticles using tetraethylorthosilicate (TEOS) as the precursor was performed to achieve the nanoscale roughness. To eliminate the two-step process of inducing roughness followed by lowering the surface energy, the authors pre-treated the nanoparticles with hydrophobic octyltriethoxysilane before deposition on the fabric (Figure 2.7). This facile fabrication process resulted in WCA of $152.8^\circ \pm 2.6^\circ$ and WSA of 8° . Many other tests like water repellency and air permeability were conducted to measure the fabric performance. However, the superhydrophobicity was lost after 15 washing cycles, which revealed the limitation in the durability of such coatings.

Figure 2.7 Fabrication of superhydrophobic textiles using silica nanoparticles and octyltriethoxysilane [9]

In a similar work, Richard et al. successfully synthesized superhydrophobic cotton textile through an eco-friendly, cost effective technique [10]. Zinc hydroxide was utilised as a precursor for in-situ incorporation of zinc oxide nanoparticles on the surface of cotton fabric. The use of long-fluoro alkyl chains for lowering the surface energy was replaced with eco-friendly stearic acid (Figure 2.8). The fabric displayed a WCA of 151° and WSA $< 10^\circ$. Although the work provided a new direction to fabricate environmentally safe coatings, no washing test was carried out to determine the durability of the synthesized superhydrophobic fabric.

Figure 2.8 Synthesis of superhydrophobic textiles using zinc oxide nanoparticles and stearic acid [10]

In a recent work, effort has been made by Wang and co-workers to synthesize durable superhydrophobic fabrics which are fluorine-free [11]. Polydopamine nanoparticles were produced by self-polymerization of dopamine in an aqueous solution. Having a high surface energy, the nanoparticles were modified with hexadecyltrimethoxysilane to generate superhydrophobic cotton fabric surface with a very high WCA of 163° and a low sliding angle of 8.6° (Figure 2.9). The synthesized coating was durable as it retained its superhydrophobicity after 20 AATCC washing cycles. Moreover, the coating displayed self-healing behaviour against acid/base and plasma treatment.

Figure 2.9 Synthesis of superhydrophobic textiles using polydopamine nanoparticles and hexadecyltrimethoxy silane [11]

Another route explored for obtaining superhydrophobic fabrics involves the use of polymer as a substrate for the attachment of the nanoparticles as illustrated in Figure 2.10. Either the nanoparticles can be synthesized separately and then attached to the

polymer or grown in-situ on the polymer substrate. The prepared polymer nanocomposite is then deposited on the fabric surface.

Figure 2.10 Synthesis route of superhydrophobic fabrics by using polymer as a substrate for nanoparticle attachment

This approach was adopted by Zhang et al. where zinc oxide (ZnO) nanoparticles were used for the preparation of superhydrophobic cotton fabric for oil-water separation [12]. The nanoparticles were synthesized by using zinc nitrate as the precursor and stearic acid was used for lowering the surface energy. The prepared nanoparticles along with stearic acid were then dispersed in polystyrene (PS) to form polymer nanocomposite which was then drop-coated on the cotton fabric (Figure 2.11). The fabric displayed a WCA between 153° - 155° . The prepared coating was stable against air and extreme chemical environment. However, the work did not reveal any sliding angle measurement or washing tests, which are necessary to confirm the self-cleaning ability and durability of the synthesized fabrics.

Figure 2.11 Synthesis of superhydrophobic textiles by deposition of zinc oxide nanoparticles on polystyrene substrate and modification with stearic acid [12]

In a recent work by Zhu et al. [13], PDMS was employed as a low energy substrate for the deposition of ZnO nanoparticles for the synthesis of superhydrophobic cotton fabrics. The first step involved coating the cotton fabric with PDMS followed by in-

situ incorporation of ZnO nanoparticles. A thin layer of PDMS was coated over the nanoparticles to secure the particles in place and enhance the durability of the coating (Figure 2.12). This resulted in the fabrication of a superhydrophobic cotton fabric displaying a WCA higher than 160° . The fabric also displayed additional properties of UV blocking, self-cleaning and oil-water separation ability. The prepared coating displayed high durability by sustaining 20 accelerated washing cycles. This work is a fine example for facile synthesis of robust superhydrophobic fabrics for large-scale production.

Figure 2.12 Synthesis of superhydrophobic textiles by using PDMS as a substrate for attachment of zinc oxide nanoparticles [13]

2.3 Fundamentals of antibacterial fabric surfaces

Antibacterial fabrics, as the name suggests are those fabrics which either kill or prevent the growth of microorganisms on the surface of the fabric without causing any harm to the wearer or the surrounding environment [14]. In this section, the classification of the fabrics based on their function, type of treatment, the mechanism of antibacterial action and the measurement techniques for antibacterial activity has been discussed in detail. The success of different nanoparticles for superhydrophobic antibacterial fabrics has also been highlighted.

2.3.1 Introduction to antibacterial fabrics

Antibacterial fabrics are classified into two categories based on their function: biostatic and biocidal. Biostatic function involves preventing the adhesion and growth of the microorganisms on the fabric surface. This function only protects the textile material from the bacterial growth. It can neither protect the wearer nor prevent the transmission of diseases. Therefore, biostatic function is incorporated in the textiles only for odour control or for preservation of the textile material. On the other hand, biocidal function results in the death of the microorganisms thereby protecting the wearer from biological

attacks. Thus, biocidal property of the fabrics is more desirable in clothing and healthcare applications [15].

There are different approaches to induce antibacterial behaviour on the fabrics, which can be broadly classified as physical or chemical treatments. They involve:

- Impregnating the fibres of the textile material with the antibacterial agent
- Treating the fibrous material of the textile with the antibacterial agent during the pad-dry-cure process
- Incorporating the antibacterial agent on the fabric through covalent bonds
- Adding the antibacterial agent to the polymer melt during the synthesis of synthetic fabrics

The most favoured technique involves the incorporation of the antibacterial agent on the fabric surface by the formation of strong chemical bonds. As the durability of the treated fabric to multiple washes and abrasion depends on the type of bond present between the antimicrobial agent and the fibre surface, such chemical treatments allow efficient antibacterial activity due to the resistance of the strong chemical bonds to easy release of the antibacterial agent from the fibre surface [16].

Different antibacterial agents are available which can be utilised to chemically modify the fabric surfaces. However, before making the choice, it is essential to know the characteristics of an ideal biocidal material. An ideal antibacterial agent should [15]:

- show bactericidal activity against a wide spectrum of microorganisms
- not kill the non-pathogenic bacteria on the human skin
- not be toxic to the human body or the environment
- be durable against repeated washes
- not affect the physical strength or appearance of the fabric
- comply with the dyeing process
- be cost-effective

The antibacterial agents can be of two types. They can be either organic in nature, for example – chitosan, triclosan, formaldehyde, phenols, halamines etc. or they can be inorganic in nature, for example, metal ions (silver, copper, tin, zinc), quarternary ammonium salt etc. to name a few [15].

Among all the available organic and inorganic biocidal materials, nanoparticles of inorganic heavy metals (silver, copper etc.) have become very popular for use as antibacterial agent for textile materials. This is mainly due to their large surface to volume ratio which provides a higher number of active sites for the antibacterial reaction to take place [17]. Moreover, the inorganic antimicrobials also offer a higher stability and safety in comparison to the organic counterparts [18]. Nanoparticles of inorganic metal/metal oxide like silver, copper, copper oxide (CuO), zinc oxide, and titanium dioxide (TiO₂) are few examples which have been actively explored for their use as antibacterial agent for fabric treatment.

2.3.2 Modes of antibacterial action

A living microorganism (e.g. bacteria, fungi) consists of an outer cell wall which is responsible for maintaining the structure of the cell and protecting it from the external environment. Within the cell wall there exists a semi-permeable membrane, which is called the cell membrane. All the organelles which are the main components of the cell are contained within the boundaries of the cell membrane. For the microorganism to grow and proliferate, all the components of the cell should function effectively. The antibacterial agents incorporated on the textile surface damages either the cell wall or the cell membrane. They can also interfere with the enzymatic activity of the cell; damage the DNA or disturb the metabolic activity, all of which are essential for the cell survival. This results in the death of the microorganism and successful biocidal activity of the antibacterial agent [19].

Various researchers have made an attempt to explain the mechanism of antibacterial action of the nanoparticles, however, the accurate reasoning is still not well-established. In general, the bactericidal property of the inorganic nanoparticles is due to their large surface to volume ratio which provides an increased contact with the bacterial cell wall. Moreover, the antibacterial property of the nanoparticles also depends on their size, shape, morphology, size distribution and stability [18].

In a general opinion, different nanoparticles show their biocidal action through a combination of different mechanisms depending on their nature and chemistry (Figure 2.13). The most common route is by the production of Reactive Oxygen Species (ROS). Electrostatic interaction, DNA damage, disruption in the protein and enzymatic activity and photo killing are among other mechanisms responsible for antibacterial activity of the inorganic nanoparticles especially the metal/metal-oxide nanoparticles [20].

Figure 2.13 Different mechanisms of antibacterial action on a bacterial cell [20]

2.3.2.1 Generation of Reactive Oxygen Species

Upon contact of the metal/metal oxide nanoparticles with the bacteria, the nanoparticles enter into the cell through the cell membrane. After entering, they generate ROS either through cell-particle interaction, redox reactions or through the pre-existing functional groups on the nanoparticle surface. The ROS can be partially reduced forms of molecular oxygen like peroxide, superoxide or hydroxyl radicals. These interfere with the aerobic respiration process of the microorganism resulting in an oxidative stress within the cell. The oxidative stress affects the functioning of all the organelles including the proteins and enzymes, resulting in the death of the microorganism. Generation of ROS is one of the most common mechanisms of antibacterial action displayed by most biocidal nanoparticles [20].

2.3.2.2 *Electrostatic interaction*

The metal/metal-oxide nanoparticles are positively charged and the bacterial membranes are negatively charged. This results in an electrostatic interaction between the nanoparticles and the cell membrane. The nanoparticles are accumulated at the cell surface due to this interaction and eventually enter the bacterial cell introducing cytotoxicity. Moreover, the positively charged nanoparticles attach to the cell surface and disrupt the structure of the cell wall and membrane. The damage to the cell membrane promotes further entry of the nanoparticles within the cell and the leakage of all the essential cellular components resulting in microbial death. The strength of the electrostatic interaction directly correlates with the size of the nanoparticles. The smaller the size of the nanoparticles, the larger the surface area available, and therefore, the higher the electrostatic interaction between the nanoparticles and cell wall [20].

2.3.2.3 *DNA damage*

Metal ions are present inside a cell as they are important for the metabolic activities. However, their concentration is controlled as excess quantity can be detrimental. When the metal/metal oxide nanoparticles enter the bacterial cell through electrostatic interaction, the concentration of the metal ions inside the cells exceeds the permitted limit. As a result, they bind to the DNA and damage the helical structure. This eventually leads to the death of the microorganism. This mechanism is particularly characteristic of copper oxide nanoparticles [20].

2.3.2.4 *Protein and enzyme dysfunction*

The nanoparticles can also affect the protein and enzyme functioning which can lead to cell death. They oxidise the side chains of the amino acids, which results in the formation of carbonyl groups on the proteins. The protein carbonylation slows down the enzymatic activity and results in degradation of the proteins. The protein degradation disrupts the normal functioning of the cell resulting in bacterial death [20].

2.3.2.5 Photokilling

For nanoparticles of transition metals, the bactericidal activity can be initiated in the presence of light. The light causes DNA damage, and negatively affects the cell division and cell membrane. The light also initiates the generation of more ROS which kills the bacterial cells. Nanoparticles of TiO₂ and ZnO can show antibacterial activity through this mechanism [20].

2.3.3 Measurement of Antibacterial Activity

Antibacterial activity of the textile materials can be measured qualitatively and quantitatively. Qualitative analysis serves as a preliminary test to determine whether the fabric is antibacterial, while quantitative analysis helps in determining the efficiency of antibacterial action of the textile material. There are various test methods prescribed by different standards to measure the antibacterial activity of the textile materials qualitatively and quantitatively. In this report, the test methods standardized by American Association of Textile Chemists and Colorists (AATCC) to evaluate the antimicrobial activity of the treated fabrics qualitatively and quantitatively will be discussed [19].

The AATCC 147-2004 Antibacterial Parallel Streak test is a qualitative test method performed to obtain the biostatic activity of the fabric samples. It is a simple technique which is quick and easy to implement. In this method, the agar plates are inoculated with the bacterial cells. The gram-positive and gram-negative bacteria employed usually are *Staphylococcus aureus* (*S. aureus*) and *Escherichia coli* (*E. coli*) respectively. The fabric sample is placed over the bacteria inoculated plates and then incubated at 37°C for 18-24 hours [19]. After incubation, the results can be obtained. If the fabric shows antibacterial activity, there will be no bacterial growth observed immediately below the sample surface. If the sample also prevents the bacterial adhesion, a zone of inhibition will be formed around the sample [19]. The diameter of the zone can be measured for a qualitative evaluation of the antimicrobial efficiency of the textile surface (Figure 2.14). However, if the fabric is not antibacterial, no zone of inhibition will be observed.

Figure 2.14 Evaluation of antimicrobial efficiency of modified cotton fabrics by the AATCC 147-2004 test method. Formation of a) Zone of inhibition of 1.5 mm against *E. coli*, b) Zone of inhibition of 3 mm against *S. aureus* [21]

The AATCC 100-2004 test is a quantitative test method performed to obtain both the bacteriostatic and bactericidal activity of the fabric samples. In this technique, the bacterial cells are first allowed to grow in a growth enrichment broth to obtain a high concentration of the cells [22]. The fabric samples (both treated and untreated) are inoculated with the specific number of bacterial cells and then incubated at 37°C for 18-24 hours. After incubation for the stipulated time, serial dilution is carried out and the cells are spread on agar plates. These plates are then incubated at 37°C overnight to observe the growth of the colonies on the plates. Bacterial counts are then monitored for both the treated and the untreated samples [19]. If the fabric displays antibacterial activity, the number of colonies obtained for the treated sample will be lower than that obtained for the untreated sample. The antibacterial efficiency is measured in terms of percentage reduction of the colonies for the treated sample as compared to the untreated sample (Figure 2.15).

2.4 Use of nanoparticles for synthesis of superhydrophobic antibacterial fabrics

While a lot of research has been carried out for superhydrophobic fabrics and antibacterial fabrics separately, very few researchers have reported the synthesis of fabrics having both superhydrophobic and antibacterial functionalities. Nevertheless, different nanoparticles have been used to incorporate both properties to the fabric materials, the most common ones being silver, TiO₂, ZnO, copper, and CuO nanoparticles.

Figure 2.15 Schematic diagram showing the percentage reduction calculation procedure [23]

This section will discuss the use of different nanoparticles for the synthesis of superhydrophobic antibacterial textiles, with special emphasis on CuO and ZnO nanoparticles.

2.4.1 Silver (Ag) nanoparticles

Silver nanoparticles are one of the oldest and the most researched nanoparticles for use as antimicrobial agents. They show antibacterial effect against a large variety of microorganisms and are very popular for use as antimicrobial agents. Small quantities of nanoparticles are capable of showing high antibacterial activity by release of silver ions from the nanoparticles. These silver ions then prevent the cell division and cause DNA damage of the microbial cells [24]. Another mechanism involves release of ROS and free radicals which are capable of adhering to the bacterial cell wall and causing membrane damage ultimately causing cell death [25].

Khalil-Abad and Yazdanshenas [21] reported the synthesis of ‘superhydrophobic antibacterial cotton textiles’ by using silver nanoparticles. Silver micro-sized particles were deposited in-situ on the fabric surface employing silver nitrate as the precursor. The particles were further modified with octyltriethoxysilane (OTES) to lower the surface energy (Figure 2.16). This resulted in a superhydrophobic surface with a WCA of 151° . They reported the difficulty in measuring the sliding angle due to the inherent microscale roughness of cotton fibre. The coating however, displayed good antibacterial activity against both gram-positive and gram-negative bacteria. A zone of

inhibition of 1.5 mm and 3 mm were obtained for *E. coli* and *S. aureus* respectively. To check the durability of the coating, the fabric was subjected to ultrasonication for 30 minutes. No change in the superhydrophobic and antibacterial activity was observed proving the robustness of the synthesized coating.

Figure 2.16 a) Representation of the strategy followed for fabricating antimicrobial superhydrophobic textiles; b) SEM image of cotton fibre treated with Ag nanoparticles; c) SEM image of cotton fibre covered with Ag nanoparticles after OTES modification [21]

Xue et al. carried out a similar work where Ag nanoparticles were produced on cotton fibres by using silver-ammonium complex as the precursor (Figure 2.17a) [26]. The Ag-treated fabric was then modified with low surface energy hexadecyltrimethoxysilane (HDTMS) to yield a superhydrophobic surface with a static WCA of $157.3^\circ \pm 1.6$. Both qualitative and quantitative analysis for antibacterial activity was performed. A zone of inhibition of 6.84 mm was obtained and quantitative analysis revealed a 99.99% bacterial reduction (Figure 2.17b). The durability of the fabric was measured by mechanical stirring at room temperature in water for 10 minutes, 10 times. After the test, WCA was reduced to $151.5^\circ \pm 1.4^\circ$ however, the antibacterial activity remained the same.

Figure 2.17 a) Mechanism for the in-situ synthesis of silver nanoparticles over the cotton fibres;

b) Antibacterial activity of untreated cotton fabric (top) and HDTMS treated silver nanoparticle cotton fabric (bottom) [26]

2.4.2 Titanium dioxide (TiO₂) and zinc oxide (ZnO) nanoparticles

Among the metal-oxide nanoparticles, TiO₂ and ZnO have been extensively used for photocatalytic, and UV-blocking applications. Another application of these functional nanoparticles includes their antibacterial performance. Being transition metal oxides, upon photoactivation, both TiO₂ and ZnO release electron-hole pairs which interact with the cell membrane of the microorganism and cause cell death [27]. When compared with silver, they display much lower antibacterial activity. However, they have an advantage of white appearance and lower cost.

In a work by Karimi et al., TiO₂ nanoparticles were used effectively to synthesize an electroconductive, self-cleaning and antibacterial fabric using graphene-TiO₂ nanocomposite [28]. Graphene oxide was deposited on pristine cotton fabric by the oxidation of graphite following Hummer's method. Subsequently, graphene oxide was reduced and TiO₂ nanoparticles were nucleated on the fabric. The treated fabric displayed self-cleaning property against methylene blue, however, the contact angle data has not been published. The authors also reported that the treated fabric demonstrated excellent antibacterial and antifungal properties with 99% efficiency against both gram-positive and gram-negative bacteria (Figure 2.18). It was found that the high surface area of graphene aided in improving the antibacterial efficiency of TiO₂ nanoparticles.

Figure 2.18 A graph displaying the antimicrobial efficiency of raw cotton, graphene-oxide coated cotton, and TiO₂ modified graphene-oxide cotton [28]

In a recent work, ZnO nanoparticles were used in combination with octadecanethiol to produce superhydrophobic antibacterial cotton fabrics [29]. In the first step, pristine fabrics were dipped in a chloroform solution with ZnO nanoparticles suspended in it. After drying, they were dipped in octadecanethiol solution to obtain superhydrophobic fabrics with WCA of 161° and $SA < 2^\circ$. For measurement of antibacterial activity, the bacterial adhesion on the as-prepared fabric was reported which was significantly reduced for both *E. coli* and *S. aureus*, however, a bacterial reduction percentage was not reported. A washing test was conducted by subjecting the as-prepared fabrics to magnetic stirring in a detergent solution for 24 hours. The WCA fell to 151° and the SA rose to 20° , still retaining the hydrophobicity. However, no other durability measurements were conducted to determine the resistance of the coating to mechanical and chemical environments.

Figure 2.19 SEM images showing the adhesion on the ZnO-octadecanrthiol treated fabrics of a) *S. aureus*, b) *E. coli* [29]

2.4.3 Copper (Cu) and copper oxide (CuO) nanoparticles

Copper has been used as a biocide for decades, however, the use of copper nanoparticles as an antibacterial agent has only been explored recently. At the nanoscale, copper displays larger surface to volume ratio which makes it capable of bacterial cell damage unlike the micro-sized copper particles [25]. This is attributed to the large redox potential of copper nanoparticles. The Cu/CuO nanoparticles display antibacterial activity comparable to noble metals like gold and silver and are inexpensive. However, the dark colour of these nanoparticles forms its drawback.

Berendjchi et al. [30] reported the use of Cu nanoparticles for superhydrophobic antibacterial performance on cotton fabric. Silica sols were synthesized using the sol-gel method (Figure 2.20a). After deposition of the sols, the surface was treated with HDTMS to block the hydroxyl groups. The HDTMS treated silica sols were then doped with Cu nanoparticles. The deposition of Cu nanoparticles over the silica sols resulted in dual surface hierarchy and increased the air trapping capability of the treated cotton fabric (Figure 2.20b). This produced a superhydrophobic surface with WCA of 155° and an additional slippery property due to a low WSA of 24° . By employing the AATCC 100-2004 test method, the antibacterial property of the surface displayed 93% efficiency against *E. coli* and 99% efficiency against *S. aureus* bacteria. Although superhydrophobic antibacterial fabric surface was successfully synthesized, the durability of the coating was not tested. Moreover, the method of synthesis was complex and involved many steps, which hinders the scale-up of the process.

Figure 2.20 Representation of a) silica sol synthesized by sol-gel technique, b) HDTMS modified silica sol deposited on cotton substrate [30]

In a much recent work by Suryaprabha and Sethuraman [31], a known strategy was followed for creation of an antibacterial superhydrophobic cotton surface. In this work, Cu nanoparticles were coated on the fabric surface followed by treatment with stearic acid to obtain a self-cleaning surface with static WCA of 159° and sliding angle of 9° (Figure 2.21). The antibacterial property of the treated fabric was verified by the inhibition zone method. It was found that the inhibition zone was greater for the fabric with only the nanoparticles as compared to the fabric which was also treated with stearic acid. The laundering durability test revealed that continuous washing up to 10 washes resulted in the loss of superhydrophobicity of the fabric. However, the antibacterial activity after washing has not been reported. While this work highlights the stability of

the coating against blood, pH change, and mechanical wear, it reveals the scope of improvement of such coatings against continuous washing.

Figure 2.21 Treatment of normal cotton with copper nanoparticles and stearic acid to obtain antibacterial superhydrophobic textile surface [31]

A recent work by Yang et al. [32] involves the use of polydopamine as a substrate to bind the Cu nanoparticles for the synthesis of superhydrophobic antibacterial cotton fabric. Polydopamine being a strong adhesive and binder, was used for modifying the cotton substrate (Figure 2.22a,b). Cu nanoparticles were synthesized by in-situ reduction of copper sulphate also facilitated by polydopamine (Figure 2.22c). The roughness and the low surface energy resulted in a fabric displaying a WCA of 151.49° . The antibacterial activity of the synthesized coating was measured by the AATCC 100-2004 method. The fabric successfully demonstrated antibacterial activity of 99.99% which later dropped to 88.5% after 50 washes. The fabric retained its high contact angle after 50 washes establishing the high durability of the coating (Figure 2.22d). However, the major drawback of this work was the lack of superhydrophobic behaviour as the water droplet would not slide even at a 180° tilt of the fabric surface.

Figure 2.22 FE-SEM images of a) cotton fabric, b) polydopamine coated cotton fabric, c) copper coated polydopamine cotton fabric, d) copper coated polydopamine after 50 washes [32]

2.5 Research gaps in the existing synthesis routes for superhydrophobic antibacterial textiles

The literature review revealed that although Ag nanoparticles provide the highest antibacterial efficiency, they are very expensive for large-scale applications. Additionally, metal leaching is an environmental hazard, and therefore, unsuitable for use in the cloth industry [33]. While TiO₂ and ZnO provide an economical alternative to Ag nanoparticles and also have white appearance, their antibacterial efficiency is not as high. Therefore, a larger quantity of the nanoparticles may be required on the fabric surface to achieve high antibacterial activity. Cu/CuO nanoparticles display an antibacterial efficiency comparable to the noble metals and are inexpensive, however, their dark colour forms a limitation. Therefore, there exists a trade-off of properties between the nanoparticles. As a result, a suitable choice should be made based on the properties desired and the application sought for these multifunctional fabrics.

Most of the research also reveals poor durability of the coatings after which the superhydrophobicity is lost and there is considerable drop in the antibacterial efficiency. This is due to the loss of the nanoparticles from the coating. This not only affects the performance of the treated fabric, but also poses a serious health risk due to their release in the environment. Therefore, there exists a large scope for the improvement in the durability of such textiles by preventing the nanoparticle release from the fabric surface.

Some of the procedures followed to achieve such coatings are very complex and involve the use of expensive equipment which can hinder their scale-up. Additionally, some research works also utilize fluorine-based chemicals which induce toxicity in the environment and human body. Hence, another important area of improvement involves the use of safe, inexpensive raw materials and simple synthesis procedures for large-scale production of such multifunctional fabrics.

Therefore, through this research study, it is endeavoured to develop facile synthesis routes for the fabrication of inexpensive and durable superhydrophobic antibacterial fabrics.

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Chapter 3

Experimental Methodology

In this chapter, the rationale for the selection of silane cross-linkers and antibacterial nanoparticles is discussed. Three different silane cross-linkers were selected due to the multiple sites of attachment offered by them that aided in anchoring the nanoparticles to the fabric surface. Two different metal-oxide nanoparticles were chosen based on their antibacterial activity, colour, additional properties and non-toxicity to human cells. Additionally, the underlying principle and the detailed procedure for the two novel fabrication techniques for the synthesis of superhydrophobic antibacterial fabrics are discussed in this chapter. Lastly, the characterization techniques, antibacterial activity assessment method, durability tests and mechanical properties evaluation methods are highlighted in this chapter.

3.1 Rationale for selection of materials

This research study aims to develop novel techniques of synthesis that are simple, inexpensive and eco-friendly to fabricate durable superhydrophobic antibacterial fabrics. To achieve this goal, we proposed the use of silane coupling agents as cross-linkers which can bind the nanoparticles to the fabric surface, thereby considerably improving the durability. For this purpose, three different silane cross-linkers and two different nanoparticles were chosen for experimentation. The rationale for their selection will be given below.

3.1.1 Rationale for the selection of silane cross-linkers

Three silane coupling agents viz., N-[3-(Trimethoxysilyl)propyl]ethylenediamine, hereafter termed AEAPTMS, (3-Aminopropyl)triethoxysilane, hereafter termed APTES, and 3-(Trimethoxysilyl)propyl methacrylate, hereafter termed MPTMS were utilized for experimentation. To serve as a silane cross-linker, one end of these coupling agents should bind to the cellulose structure (cotton fabric) and the other end to the metal-oxide nanoparticles. The chemical structures of these silane chains are given in Figure 3.1.

Figure 3.1 Chemical structure of the silane cross-linkers AEAPTMS, APTES and MPTMS

AEAPTMS and APTES are amine-based silanes; the former consists of a primary and secondary amine group while the latter consists of a primary amine group only. These silane chains can undergo hydrolysis resulting in the replacement of the methoxy (for AEAPTMS) and ethoxy groups (for APTES) with the silanol groups as shown in Figure 3.2. This results in the presence of more than one reactive site on the silane chain.

Figure 3.2 Mechanism for hydrolysis of a) AEAPTMS b) APTES

After hydrolysis, the silanol groups of the silane (AEAPTMS and APTES) can attach to the cotton fabric and the amine group can attach to the metal-oxide nanoparticles through hydrogen bonding [1]. The reverse can also take place where the silanol groups attach to the metal-oxide nanoparticles and the amine groups engage in hydrogen bonding with the cellulose structure [1]. If the silane is present in excess, then these chains also cross-link among themselves [1]. While APTES offers two sites for attachment, AEAPTMS was chosen as it has the potential to offer three sites for attachment due to the additional secondary amine present in its chemical structure. The possible mechanism for attachment of AEAPTMS and APTES to CuO nanoparticles are displayed in Figure 3.3 and Figure 3.4, respectively.

Like AEAPTMS and APTES, MPTMS also offers dual sites of attachment. Instead of amine groups, it consists of carbonyl groups in its structure which can participate in hydrogen bonding. The methoxy groups of the unhydrolysed silane are replaced with silanol groups upon hydrolysis (Figure 3.5). These silanol groups can attach to the cellulose structure of the cotton fabric and the carbonyl groups can engage in hydrogen bonding with the metal-oxide nanoparticles [2]. Similarly, the silanol groups can bind with the nanoparticles and the carbonyl groups to the cellulose, thereby providing strong chemical bonds to hold the nanoparticles firmly to the fabric surface [2]. Moreover, the silanol groups of the silane can react with other silane chains to form siloxane linkages which can then attach to the nanoparticles and the fabric [2].

The possible mechanism for attachment of MPTMS to CuO nanoparticles is displayed in Figure 3.6.

Figure 3.3 Mechanism for attachment of AEAPTMS to CuO (or metal-oxide) nanoparticles

Figure 3.4 Mechanism for attachment of APTES to CuO (or metal-oxide) nanoparticles

Figure 3.5 Mechanism for hydrolysis of MPTMS

Figure 3.6 Mechanism for attachment of MPTMS to CuO or (metal-oxide) nanoparticles

Therefore, considering the potential of AEAPTMS, APTES and MPTMS in serving as silane cross-linkers due to their multiple sites of attachment, they were selected for fabrication purposes.

3.1.2 Rationale for the selection of nanoparticles

For the synthesis of superhydrophobic antibacterial fabrics, the presence of micro and nanoscale roughness, low surface energy and an antibacterial agent form the three primary requirements. Nanoparticles are able to perform a dual role by not only serving as an antibacterial agent, but also providing the nanoscale roughness required to realize superhydrophobicity. Various nanoparticles are available which can offer the required properties and have been reviewed in Chapter 2. The rationale for selection of the two different metal-oxide nanoparticles for this research study has been given below:

3.1.2.1 *Copper oxide nanoparticles*

Among the different nanoparticles reviewed in Chapter 2, copper oxide (CuO) nanoparticles displayed tremendous potential for use as an antibacterial agent. CuO nanoparticles are cheaper than silver and show better antibacterial activity than TiO₂ and ZnO [3]. Cu/CuO is also relatively non-toxic to human cells but shows strong bactericidal properties against large variety of microorganisms [4]. Its low cost of production and effective antibacterial activity makes it desirable for use as antimicrobial agent for textile application. Additionally, it has been found that CuO can be safely used on clothing textiles without causing any skin irritation to the wearer [5].

There is an existing concern about the release of metal/metal-oxide nanoparticles from the fabric surface into the environment or their consumption which can greatly affect the human health. Almost all metal nanoparticles if consumed in excess might cause severe damage to the human cells. Cu/CuO nanoparticles are no exception. If consumed in excess, it results in the generation of ROS within the body causing severe damage. However, there are enzymes secreted in the body which are responsible for copper homeostasis. If consumed in excess, the copper transporting adenosine triphosphates will remove the excess copper from the body as faeces, from the liver as a bile product or even from the mammary gland through milk [6]. Therefore, upon their release, the health risk is greatly reduced when using CuO nanoparticles. Hence, CuO nanoparticles provide the safest solution for achieving antibacterial activity on fabrics due to their high antibacterial efficiency, economical value and low toxicity concerns.

Most of the research has revolved around the use of Cu nanoparticles for antibacterial activity on fabrics and the use of CuO nanoparticles remains relatively unexplored. CuO nanoparticles not only offer the same advantages as Cu nanoparticles, but also provide Cu^{2+} ions which are essential for electrostatic interaction to observe bactericidal effects. Therefore, considering all the advantages, copper oxide nanoparticles were explored for their applicability in the synthesis of superhydrophobic antibacterial fabrics for our first fabrication technique.

3.1.2.2 Zinc oxide nanoparticles

After employing CuO nanoparticles for the first fabrication technique, few limitations were encountered. CuO nanoparticles turned the fabric grey/black in spite of the small quantity used. Moreover, the nanoparticles may undergo agglomeration even at moderate nanoparticle loading on the fabric. To overcome these drawbacks, the role of zinc oxide (ZnO) nanoparticles as an antibacterial agent was explored. ZnO nanoparticles are white in colour, and therefore do not induce any colour change on the white fabric. After initial experiments, a uniform distribution of the ZnO nanoparticles was observed on the fibre surface, thereby also overcoming the drawback of agglomeration.

ZnO nanoparticles display different morphologies and are known for their antibacterial activity against large number of bacterial species [7]. When compared to TiO_2 , they are far more biocompatible and non-toxic to human cells [7]. Zinc is also one of the important trace elements required in the human body in the absence of which many enzymes become inactive [8]. It is essential for cell growth [9], and also forms an important component for bones, teeth, enzymes and various proteins [8]. There have been no reports of carcinogenicity, genotoxicity or reproduction toxicity by the use of ZnO nanoparticles [8]. Moreover, it used as a lining in food packaging for its bacteriostatic and bactericidal effects to prevent spoilage of food items, confirming it is a biosafe material [7].

Apart from its antibacterial and antifungal properties, ZnO nanoparticles also display photo-oxidation and photocatalytic properties. They possess high optical absorption in

the UV-A (315 – 400 nm) and UV-B (280 – 315 nm) region [8] that not only enhances its antibacterial activity but also helps in UV blocking which can prove beneficial for clothing fabrics [7].

Therefore, considering the overall advantages offered by zinc oxide nanoparticles, they were utilised as an antibacterial agent for the second fabrication technique in the current work.

3.2 Materials

Cotton fabric with an individual fibre diameter of ~15 μm was obtained from Matex International Limited, Singapore. Aminoethylaminopropyltrimethoxysilane (AEAPTMS), Aminopropyltriethoxysilane (APTES), Methacryloyloxypropyltrimethoxysilane (MPTMS), Hexadecyltrimethoxysilane (HDTMS), Tetrahydrofuran (THF, anhydrous), Methanol (analytical reagent grade), CuO nanopowder (< 50 nm in diameter), ZnO nanopowder (<50 nm in diameter) and non-ionic detergent Triton X-100 were purchased from Sigma Aldrich and used without further purification. PDMS (Sylgard® 184, base and curing agent) was purchased from Dow Corning Corporation. *Escherichia coli* (*E. coli*, ATCC® 25922TM) and *Staphylococcus aureus* (*S. aureus*, ATCC® 25923TM) were purchased from the ATCC distribution partner Thermo Fisher Scientific, Singapore. BactoTM Agar, BactoTM Tryptone, BactoTM Yeast Extract were obtained from BD Lifesciences and Sodium Chloride EMSURE® was obtained from Merck. Phosphate Buffered Saline (PBS, 10x Ultrapure Grade) was obtained from Vivantis Technologies.

The cotton fabric was ultrasonically cleaned with ethanol and deionized water to remove possible impurities and dried for further processing.

3.3 Synthesis of CuO-Silane-PDMS-Cotton fabrics

The objective of this research involves developing novel methods which are simple, inexpensive, eco-friendly, and can enhance the durability of the superhydrophobic antibacterial fabrics. To realize this aim, a novel fabrication technique was developed. Polydimethylsiloxane (PDMS), a water-repellent, fluorine-free polymer was coated on the cotton fabrics for lowering the surface energy. PDMS is non-toxic, inexpensive, and

offers excellent chemical and mechanical stability, ideal for developing durable coatings on fabric materials. CuO nanoparticles, offering high antibacterial activity, were then attached to the PDMS through a silane cross-linker. The silane cross-linker provides additional chemical bonds between the nanoparticles and the PDMS coated cotton, securing them firmly to the fabric surface. We proposed that the use of silane cross-linkers would aid in enhancing the durability of the synthesized fabrics. Three silane cross-linkers were evaluated in the current study. The nanoparticle loading on the fabric was also optimized for maximum antibacterial proficiency. The detailed procedure for the synthesis of these superhydrophobic antibacterial fabrics is given below:

The fabrication procedure for the CuO-Silane-PDMS-Cotton fabrics is shown in Figure 3.7. First, the cotton fabrics were dip-coated with 1 wt % PDMS (prepared by mixing the base and curing agent in the ratio of 10:1, diluted with THF) and cured at 120 °C for 30 minutes to obtain PDMS coated cotton fabrics. Second, CuO nanoparticles were functionalized with a silane coupling agent. The silane was pre-hydrolysed in methanol (1 vol. %) where CuO nanoparticles (3.2, 8.0, 16 g/m² particle loading) were ultrasonically dispersed. Three different silanes AEAPTMS, APTES and MPTMS were explored for their applicability. Third, the PDMS coated cotton was immersed in the silane solution and magnetically stirred for 1 hour to allow the nanoparticle attachment. Thereafter, the fabric was heat treated at 100 °C for 1 hour and then washed with methanol to remove the unbound silane. This three-step process resulted in the synthesis of superhydrophobic antibacterial cotton fabrics. Different amount of nanoparticle was loaded to evaluate the effect on superhydrophobicity and antibacterial efficiency.

3.4 Synthesis of Cotton-ZnO-HDTMS fabrics

Another novel technique was developed for the synthesis of superhydrophobic antibacterial textiles. In this technique, antibacterial ZnO nanoparticles, offering white appearance and additional UV blocking property were anchored to the pristine cotton fabric using APTES silane cross-linker. To induce superhydrophobicity on the fabric surface, the ZnO-APTES-Cotton fabric was treated with HDTMS, a fluorine-free low surface energy silane. The nanoparticle loading on the fabric surface was optimized for maximum antibacterial efficiency and complete coverage of the fibre surface.

Figure 3.7 Schematic illustration of the three-step process for the synthesis of CuO-Silane-PDMS-Cotton fabrics

The detailed procedure for the synthesis of these superhydrophobic antibacterial fabrics has been given below:

The fabrication procedure for Cotton-ZnO-HDTMS fabrics is shown in Figure 3.8. First, ZnO nanoparticles were functionalized with APTES. The APTES was pre-hydrolysed in methanol (1 vol. %) where ZnO nanoparticles (4.0, 8.0, 12, 16, 20 and 24 g/m² particle loading) were ultrasonically dispersed. Second, cotton fabrics were immersed in the ZnO-APTES solution and magnetically stirred to allow the nanoparticle attachment on the fabric surface. Thereafter, the fabric was heat treated at 100 °C for 1 hour and then washed with methanol to remove the unbound silane. Third, the ZnO-APTES-Cotton fabrics were immersed in pre-hydrolysed solution of HDTMS (1 vol%) and stirred for two hours to allow the attachment of HDTMS over the nanoparticles and fabric surface. Thereafter, the fabric was heat treated at 100 °C for 1 hour and then washed with methanol to remove the unbound silane. This three-step process resulted in the synthesis of HDTMS-ZnO-APTES-Cotton fabrics. Different

amount of nanoparticles were loaded to evaluate the effect on superhydrophobicity and antibacterial efficiency on the fabrics.

Figure 3.8 Schematic illustration of the three-step process for the synthesis of HDTMS-ZnO-APTES-Cotton fabrics

3.5 Contact angle measurement

The wettability of the as-prepared fabrics via both synthesis techniques was measured using a contact angle goniometer OCA 20 (Dataphysics, Germany) and its corresponding software, SCA 20. Static water contact angle (WCA) and water shedding angle (WSA) was measured using this instrument. For the measurement of WCA, 5 μL of DI water was placed at five equidistant positions on the fabric. The mean and standard deviation were reported for three parallel tests. For the measurement of WSA, the stage of the instrument was tilted to a particular angle and a 13 μL water droplet was dropped vertically from a height of ~ 2 cm. The minimum angle of tilt at which the droplet rolls off from the fabric surface was regarded as WSA. The measurement was carried out at 5 equidistant positions and the mean and standard deviation were reported for three parallel tests.

3.6 Field Emission Scanning Electron Microscopy

To observe the distribution of the nanoparticles on the fabric surface, field emission scanning electron microscopy was performed using (FESEM) JEOL JSM-6340F. The images were obtained at an acceleration voltage of 5 kV under secondary electron imaging mode. 1 cm x 1cm of the fabric sample was placed on a conducting carbon tape and bordered with copper tape on all the four sides. As the fabric is non-conducting in nature, a thin layer of (~7 nm) of gold was sputter-coated on the sample before the SEM observation.

3.7 X-Ray Diffraction

To identify the phase of the crystalline nanoparticles attached to the fabric surface, X-Ray Diffraction (XRD) was performed using Thin Film Shimadzu XRD-6000 using Cu-K α radiation. The instrument was operated at 40 kV and 30 mA with step size of 0.02°/sec in 2 θ scan mode with a glancing angle of 5°. The scan range was 5° to 75° at a scan speed of 2°/minute. The obtained peaks were matched using the Match® phase identification software using the ICDD Database to identify the corresponding crystallographic planes and the crystal structure.

3.8 Fourier Transform Infrared Spectroscopy

To understand the mechanism responsible for the attachment of the nanoparticles to the PDMS coated cotton fabric in the first technique and to the pristine cotton fabric in the second technique by silane cross-linkers, Fourier Transform Infrared Spectroscopy (FTIR) was conducted. It was performed using FTIR Perkin Elmer Frontier. 32 scans were conducted per sample from 4000 cm⁻¹ to 600 cm⁻¹ with a resolution of 4 cm⁻¹ to obtain the transmittance data. Baseline correction was carried out and the curve was smoothened out to eliminate the noise. The significant peaks in the spectra were assigned to the possible chemical bonds in the sample.

3.9 Evaluation of antibacterial activity

The antibacterial activity of the as-prepared fabrics was assessed following the AATCC 100-2004 quantitative assessment method using microorganisms *E. coli* (ATCC® 25922™) and *S. aureus* (ATCC® 25923™). Fabric samples of dimension 5 cm x 5 cm were prepared especially for this analysis.

3.9.1 Preparation of agar plates

Prior to the antibacterial activity measurement, agar plates were prepared required for observing the growth of the colonies as shown in Figure 3.9. For the preparation of 1000 ml of LB Agar, a standard recipe was followed. 20 g of Bacto Agar, 10 g of Sodium Chloride, 10 g of Tryptone and 5 g of Yeast extract were weighed in a glass bottle and the volume was made up to 1000 ml by the addition of DI water. The solution was autoclaved at 121°C to obtain LB agar. Approximately 25 ml of the prepared LB agar was poured into 15 mm diameter sterilised Petri dishes and allowed to cool to room temperature to obtain the agar plates.

Figure 3.9 Preparation of agar plates for observing colonies growth for antibacterial activity assessment

3.9.2 Growth of bacterial culture

E. coli and *S. aureus* bacterial cultures were grown in LB media. For the preparation of 1000 ml of LB media, a similar recipe as LB agar was followed. 10 g of Sodium Chloride, 10 g of Tryptone and 5 g of Yeast extract were weighed in a glass bottle and the volume was made up to 1000 ml by addition of DI water. The solution was autoclaved at 121°C to obtain LB media. The bacterial cells were transferred to 20 ml

of LB media and were allowed to grow for 6-8 hours. After the stipulated time, the Optical Density (OD) of the culture was measured using a UV-Vis spectrophotometer. This was done to determine the number of colonies in the prepared culture media. 1 OD is equal to 10^9 CFU/ml. After the determination of the OD, the culture was centrifuged at 4000 rpm for 15 minutes to separate the cells from the media. The media was then decanted and the cells were re-suspended in 1 x PBS.

3.9.3 Inoculation of the fabric samples with bacterial culture

All the fabric samples were cut in circular shape of 4.8 cm in diameter and placed in 6 mm Petri dishes. A bare cotton fabric was also taken as a reference. An example of MPTMS treated fabric swatches has been displayed in Figure 3.10. The cells re-suspended in PBS were diluted further in 1 x PBS to obtain $\sim 10^5$ CFU/ml. 1ml of the diluted cell culture ($\sim 10^5$ CFU) was added to all the fabric samples. Further, 4ml of 1 x PBS was added to all the Petri dishes containing the samples to make sure the fabric is hydrated and the cells are in contact with the fabric surface. All the Petri dishes were then incubated at 37°C for 24 hours.

Figure 3.10 Swatches for antibacterial assessment of a) pristine cotton fabric; MPTMS-treated fabrics with nanoparticle loading of b) 3.2 g/m² c) 8 g/m² d) 16 g/m²

3.9.4 Serial dilution and plating of colonies

After the stipulated time, the cells were extracted from the fabric samples and serial dilution (Figure 3.11) was carried out by a factor of 5. 100 μ L of four different serial dilutions were spread on the previously prepared agar plates and were incubated overnight to observe the number of colonies (Figure 3.12)

Figure 3.11 Representation of the procedure for serial dilution (by a factor of 10)

Figure 3.12 Incubation of the petridishes to observe the colonies growth for measuring percentage bacterial reduction

The percentage reduction of the bacteria on the treated fabrics when compared to the pristine cotton fabric is given by the following formula in equation (3.1):

$$\% R = \frac{B-A}{B} \times 100 \quad (3.1)$$

where R is the reduction in bacterial count, A and B are the numbers of colonies observed for the untreated and treated fabrics respectively. Three parallel runs of each test fabric was conducted and an average value was reported. It is essential to note that colonies between 30 and 300 can only be counted on an agar plate.

3.10 UV blocking measurement

The UV blocking ability of the as-prepared fabrics was measured by the AATCC 183-2004 Test Method [10]. This assessment was conducted to determine the ultraviolet radiation (UV-R) blocked or transmitted by the fabrics for UV protection of the wearer. The UV-R transmission was measured on UV/Vis spectrophotometer Lambda 950 Perkin Elmer in the spectral range of 400 - 280 nm (400 – 315 nm constituting UV-A

and 315 – 280 nm constituting UV-B range) at a wavelength interval of 2 nm. From the obtained transmittance data, Ultraviolet Protection Factor (UPF) of the test fabrics was determined. UPF is defined as the ‘ratio of the average effective UVR irradiance for unprotected skin to the average effective UVR irradiance for skin protected by the test fabric’ [11]. It is calculated by the formula given in Equation 3.2.

$$UPF = \frac{\sum_{280\text{ nm}}^{400\text{ nm}} E_{\lambda} \times S_{\lambda} \times \Delta\lambda}{\sum_{280\text{ nm}}^{400\text{ nm}} E_{\lambda} \times S_{\lambda} \times T_{\lambda} \times \Delta\lambda} \quad (3.2)$$

where E_{λ} is the relative erythral spectral effectiveness, S_{λ} is the solar spectral irradiance, T_{λ} is the average spectral transmittance of the sample and $\Delta\lambda$ is the measured wavelength interval. For the fabrics to be UV blocking, the UPF rating should be greater than or equal to 50. Additionally, the average transmittance in the UV-A and the UV-B region for the test fabrics was calculated by the formulae given in Equation 3.3 and 3.4 respectively.

$$T(UV - A)_{av} = \frac{\sum_{315\text{ nm}}^{400\text{ nm}} T_{\lambda} \times \Delta\lambda}{\sum_{315\text{ nm}}^{400\text{ nm}} \Delta\lambda} \quad (3.3)$$

$$T(UV - B)_{av} = \frac{\sum_{280\text{ nm}}^{315\text{ nm}} T_{\lambda} \times \Delta\lambda}{\sum_{280\text{ nm}}^{315\text{ nm}} \Delta\lambda} \quad (3.4)$$

Three measurements were conducted per sample by rotating it at an angle of 45° each time. Moreover, three test samples of each fabric type were measured and an average value was reported.

3.11 Durability measurements

Durability measurements were conducted on the as-prepared fabric samples to determine their robustness against various physical and chemical environmental conditions.

3.11.1 Abrasion resistance test

The abrasion resistance was evaluated by applying a fixed pressure of 4 kPa on the as-prepared fabric surface with a pristine cotton fabric serving as the abrasion material

(Figure 3.13). The fabric was moved over the abradant surface normal to the direction of applied pressure at a speed of 3 cm/s for a distance of 11 cm in each cycle. After every 100 cycles, the contact angle was measured to determine the durability of the fabric against abrasion. Three samples of each fabric type were tested and the average value was reported.

Figure 3.13 The setup for abrasion testing of the superhydrophobic antibacterial fabrics

3.11.2 Washing durability test

For wash fastness measurement, Triton-X, a non-ionic detergent (1 g/L) was added to the as-prepared fabrics at a liquor ratio of 50:1 ml/g. Thereafter, the samples were subjected to washing in an ultrasound bath (275 W) at 40 ± 2 °C (Figure 3.14). After every 15 minutes, the samples were washed with DI water and dried in an oven at 120°C. Contact angle measurements were conducted after every such cycle to determine the durability of the as-prepared fabrics against washing. Three parallel runs were carried out and an average value was reported.

Figure 3.14 The setup for the ultrasonic washing of the superhydrophobic antibacterial fabrics

3.11.3 Chemical stability test

The chemical stability of the as-prepared fabrics was analysed by immersing the treated fabrics in aqueous solutions of HCl and NaOH with pH values ranging from 1 to 13 for a period of 24 hours. Contact angle was measured after 24 hours to determine the resistance of the fabrics to harsh chemical solutions. Three samples of each fabric type were tested and the average value was reported.

3.11.4 UV durability test

The UV durability of HDTMS-ZnO-APTES-Cotton fabrics was determined by exposure to UV lamp of 365nm wavelength at an irradiance of 72.6 mW/cm² for a period of 12 hours. The fabrics were placed at a distance of 10 cm from the UV bulbs. After every hour, the contact angle measurements were taken to determine the UV durability of the as-prepared fabrics. Three parallel runs were conducted and an average value was reported.

3.12 Air permeability and flexural rigidity assessment

The air permeability of the as-prepared fabrics was measured using a digital air permeability tester (YG461E-11), supplied by Wuhan Guoliang Instrument Co., Ltd., at a pressure of 400 Pa on a fabric area of 20 cm². The measurement of air permeability helps in determining the breathability of the fabric retained before and after the coating. The flexural rigidity of the as-prepared fabrics was tested using a fully automated fabric rigidity tester (YGB022D), manufactured by Shanghai Jinpeng Analytical Instrument Co. Ltd., at a fixed bending angle of 41.5°. Measurement of flexural rigidity is essential to determine the flexibility of the fabric after the deposition of the nanoparticles. Three parallel tests of each test fabric was conducted and the average value was reported.

3.13 Self-cleaning test

The self-cleaning ability of the HDTMS-ZnO-APTES-Cotton fabrics was evaluated to determine the stain resistance of the as-prepared fabrics. Graphite powder < 20 µm in

size was used as a model contaminant. The graphite powder was sprinkled on the pristine cotton fabric, ZnO-APTES-Cotton fabric and HDTMS-ZnO-APTES-Cotton fabric. Water droplets were then dropped on the fabric surface using a pipette to wash away the dirt and the self-cleaning ability was determined.

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Chapter 4

Results and Discussion: CuO-Silane-PDMS-Cotton fabrics

In this chapter, the performance of the superhydrophobic antibacterial Cotton-PDMS-CuO fabrics synthesized by the first synthesis technique are evaluated. The variation of the superhydrophobicity and antibacterial activity with nanoparticle loading was studied and the optimum amount was determined. FTIR analysis confirmed the role of the silane cross-linkers in anchoring the nanoparticles to the fabric surface. The as-prepared fabrics displayed high durability against abrasion, ultrasonic washing and harsh chemical solutions. Lastly, the air permeability and flexural rigidity tests revealed that the fabric breathability and flexibility was not compromised. Overall, the technique displays tremendous potential for clothing and healthcare fabrics production.

4.1 Introduction

To achieve the aim of developing durable superhydrophobic antibacterial fabrics, the first synthesis technique involved the fabrication of CuO-Silane-PDMS-Cotton fabrics. PDMS was coated on the cotton fabrics for lowering the surface energy. Antibacterial CuO nanoparticles were then attached to the PDMS coated cotton through a silane cross-linker. Three silane cross-linkers were explored for their applicability in the current study. The nanoparticle loading on the fabric was also optimized for maximum antibacterial proficiency. The surface morphology of the as-prepared fabrics was evaluated. FTIR analysis was conducted to confirm the chemical composition of fabric surface. The resistance of the as-prepared fabrics to abrasion, ultrasonic washing and harsh chemical solutions was assessed. Moreover, the air permeability and flexibility of the fabrics before and after the coating was evaluated. The results of these measurements are given below.

4.2 Surface morphology and contact angle analysis

A pristine cotton fabric (Figure 4.1a) consists of fibres with a smooth surface morphology (Figure 4.1b) comprising of hydroxyl ($-OH$) groups on its surface. The hydrophilicity induced by the hydroxyl groups causes a water droplet in contact with the surface to be easily absorbed within the fabric. When a uniform layer of PDMS is coated on the cotton fabric (Figure 4.1c), the fibres become water-repellent (Figure 4.1d). The inherent microscale roughness offered by the cotton fabric (due to arrangement of the fibres) coupled with low surface energy of PDMS displays highly hydrophobic behaviour with WCA of $146.5 \pm 1.1^\circ$ and WSA of $14.7 \pm 1.5^\circ$. The absence of dual scale architecture (micro and nanoscale roughness) on the PDMS coated cotton fabric hinders the display of superhydrophobicity. Figure 4.1e and Figure 4.1f present the WCA images of a pristine cotton fabric and PDMS coated cotton fabric respectively.

Upon depositing CuO nanoparticles on the PDMS coated cotton by using silane cross-linkers AEAPTMS, APTES, and MPTMS, the fabrics displayed superhydrophobic with

Figure 4.1 FE-SEM image of a) pristine cotton fabric, b) pristine cotton fibres, c) PDMS coated cotton fibres; d) photograph of water droplet on a pristine cotton fabric and PDMS coated cotton fabric; contact angle image of e) pristine cotton fabric, f) PDMS coated cotton fabric

WCA $> 150^\circ$ and WSA $< 10^\circ$. The effect of nanoparticle loading on WCA and WSA for the fabrics treated with the different cross-linkers has been shown in Figure 4.2a and Figure 4.2b, respectively. A general observation was an improvement in the superhydrophobicity (increase in WCA and decrease in WSA) of the as-prepared fabrics with an increase in the nanoparticle loading. This behaviour can be attributed to the higher surface roughness provided by the increased quantity of the well-distributed nanoparticles on the fabric surface. The surface morphology of the as-prepared fabrics treated with the silane cross-linkers with nanoparticle loading of 3.2 g/m^2 , 8 g/m^2 and 16 g/m^2 has been shown in Figure 4.3.

For the APTES and the MPTMS-treated fabrics, there was an enhancement in superhydrophobicity with an increase in the nanoparticle loading from 3.2 g/m^2 to 16 g/m^2 . The APTES-treated fabrics with a nanoparticle loading of 16 g/m^2 displayed a WCA of 154° and WSA of 5° . Similarly, the MPTMS-treated fabrics with a nanoparticle loading of 16 g/m^2 displayed a WCA of 153° and WSA of 4° . While this behaviour of improved superhydrophobicity with increased nanoparticle loading was significant for APTES and MPTMS treated fabrics, an anomalous behaviour was displayed by AEAPTMS-treated fabrics. For the AEAPTMS fabrics, there was an improvement in the superhydrophobic performance from 3.2 g/m^2 to 8 g/m^2 . However, with further

Figure 4.2 The effect of nanoparticle loading on a) WCA and b) WSA for the as-prepared fabrics treated with AEAPTMS, APTES and MPTMS

increase in nanoparticle loading to 16 g/m², there was no notable enhancement in WCA and there was even an increase in WSA. The observed anomaly is likely due to the chemical structure of AEAPTMS that consists of two amino groups on its silane chain (Figure. 1b). These amino groups can participate in hydrogen bonding with CuO nanoparticles due to the strong affinity between them, attracting more nanoparticles on a single chain of silane, and thereby, causing enhanced nanoparticle agglomeration. This reduces the amount of air that can be trapped in its microstructure causing a decreased superhydrophobic performance [1]. The surface morphology of the AEAPTMS-treated fabrics with nanoparticle loading of 8 g/m² and 16 g/m² are shown in Figure 4.3b and Figure 4.3c, respectively.

4.3 Chemical composition analysis

The chemical composition of the cotton fabric before and after PDMS and CuO deposition was investigated by FTIR analysis for all the as-prepared fabrics. Before the coating, the pristine cotton fabric displayed several strong peaks at 3335, 2900, and 1105 cm⁻¹ corresponding to -OH, C-H, and C-O-C glycosidic bond, respectively [2] (Figure 4.4). Upon coating the cotton fabric with PDMS (PDMS@Cotton fabric),

characteristic peaks at 1260 and 799 cm^{-1} of Si-C bond appeared confirming the presence of PDMS over the cotton fabric [3-5].

Figure 4.3 FE-SEM images of AEAPTMS-treated fabrics with CuO loading of a) 3.2 g/m^2 b) 8 g/m^2 c) 16 g/m^2 ; FE-SEM images of APTES-treated fabrics with CuO loading of d) 3.2 g/m^2 e) 8 g/m^2 f) 16 g/m^2 ; FE-SEM images of MPTMS-treated fabrics with CuO loading of d) 3.2 g/m^2 e) 8 g/m^2 f) 16 g/m^2

Figure 4.4 FTIR spectra of pristine cotton fabric and PDMS coated cotton fabric

To evaluate the chemical composition of the as-prepared fabrics after deposition of CuO using silane cross-linkers, the responsible mechanism for attachment was ascertained as explained in detail in Chapter 3 Section 3.2. To explain in brief, the CuO nanoparticles consist of hydroxyl groups on their surface. These hydroxyl groups can react with the silanol groups of the hydrolyzed silane cross-linkers by condensation reaction to form chemical bonds [6]. In addition, the nanoparticles can also engage in hydrogen bonding with the amino groups of the AEAPTMS and APTES silanes [7] or with the carbonyl groups of the MPTMS silane [6] [8]. This causes the firm attachment of nanoparticles to the silane cross-linkers. The silane can then anchor the nanoparticles to the PDMS through its silanol groups or the respective functional groups. To confirm this proposed mechanism, FTIR analysis was conducted.

Beginning with the AEAPTMS-treated fabrics, on performing the FTIR, a chemical similarity existed between the AEAPTMS-treated fabrics and PDMS coated cotton fabrics causing an overlap in their infrared spectra (Figure 4.5a). To observe the changes occurring on the PDMS coated cotton fabric after treatment with AEAPTMS and CuO, the spectra of PDMS coated cotton was subtracted from the AEAPTMS-treated fabric to obtain an after-subtraction spectrum (Figure 4.5b). Additionally, a spectra of pure AEAPTMS chemical was obtained (Figure 4.5c) which was then compared with the after-subtraction spectra of AEAPTMS-treated fabric to confirm its functional groups (Figure 4.5d).

The spectra of pure AEAPTMS chemical revealed peaks at 3372 and 2934 cm^{-1} corresponding to N-H stretching, and CH_2 bond stretching of primary amine respectively [9, 10]. The peak at 1595 cm^{-1} was characteristic of the primary NH_2 group [9]. The peaks at 1191 and 780 cm^{-1} were due to respectively C-N-C stretching and N-H bond vibration, characteristic of the secondary amine group [10]. Moreover, the peaks at 1461 , and 1074 cm^{-1} correspond to the CH_2 deformation vibration and the Si-O-Si bond peaking characteristic of pure AEAPTMS [9, 10]. On comparison with the after-subtraction spectra of AEAPTMS-treated fabrics, the FTIR revealed similar peaks at 1601 cm^{-1} which corresponds to the bond deformation of the amine (NH_2) group due to hydrogen bonding [9]. The peaks at 1462 , 1190 and 775 cm^{-1} corresponds to the CH_2 deformation vibration of $-\text{CH}_2\text{NH}_2$ primary amine, C-N-C stretching, and N-H bond

from the secondary amine, respectively, confirming the role of AEAPTMS in CuO attachment on the as-prepared fabrics [10, 11].

Figure 4.5 FTIR spectra of a) AEAPTMS-treated fabric, PDMS coated cotton fabric; b) After-subtraction spectra of AEAPTMS-treated fabric; c) pure AEAPTMS chemical; d) After-subtraction spectra of AEAPTMS-treated fabric, pure AEAPTMS chemical

Upon conducting FTIR for APTES-treated fabrics, a chemical similarity also existed with the PDMS coated cotton fabric similar to AEAPTMS causing an overlap in their infrared spectra (Figure 4.6a). Therefore, the spectra of PDMS coated cotton was subtracted from the APTES-treated fabric to obtain an after-subtraction spectra (Figure 4.6b). A spectra of pure APTES chemical was obtained (Figure 4.6c) which was compared with the after-subtraction spectra of APTES-treated fabrics to confirm its functional groups (Figure 4.6d).

The spectra of pure APTES chemical revealed peaks at 3364, 2973, 1572, 1391, and 1070 cm⁻¹ corresponding to N-H stretching, CH₃ stretching, NH₃⁺ bond deformation, CH₃ stretching and Si-O-Si bond peaking respectively. Upon comparison with the after-subtraction spectra of APTES-treated fabrics, similar peaks were obtained with most

characteristic peaks lying in the range of $1700 - 1300 \text{ cm}^{-1}$. The bend at 1638 cm^{-1} also present in the pure APTES chemical corresponds to the C=N imine bond due to the oxidation of the aminopropyl moiety [8]. Similarly, the peaks at $1566, 1484 \text{ cm}^{-1}$ correspond to the NH_3^+ deformation due to hydrogen bonding [7, 8]. The peaks at $1443, 1387 \text{ cm}^{-1}$ correspond to the asymmetric and symmetric deformation of the CH_3 groups, respectively. These peaks are characteristic of the pure APTES chemical, confirming the role of APTES in attaching CuO nanoparticles to the as-prepared fabrics [7].

Figure 4.6 FTIR spectra of a) APTES-treated fabric, PDMS coated cotton fabric; b) After subtraction spectra of APTES-treated fabric; c) pure APTES chemical; d) After-subtraction spectra of APTES-treated fabric, pure APTES chemical

For the FTIR of MPTMS-treated fabrics, there was no overlap in the spectra with the PDMS coated cotton and significant peaks were obtained (Figure 4.7). The peak at 1715 cm^{-1} for the MPTMS-treated fabric corresponds to the carbonyl group of MPTMS involved in hydrogen bonding [6]. A cumulative peak was displayed near 1640 cm^{-1} which was deconvoluted (by Gauss peak function) to produce two individual peaks. The deconvoluted peaks named as deconvoluted peak 1 at 1643 cm^{-1} and deconvoluted

peak 2 at 1637 cm^{-1} correspond to C=C bond of methacrylate group [10, 12], and –OH of adsorbed water [2] respectively. While the 1637 cm^{-1} peak due to adsorbed water was also present on the PDMS coated cotton fabric, the 1643 cm^{-1} peak due to methacrylate group was absent. This indicates the peak belongs to pure MPTMS, confirming its role in the attachment of CuO nanoparticles on the as-prepared fabrics.

Figure 4.7 FTIR spectra of PDMS coated cotton fabric, MPTMS-treated fabric and deconvoluted peaks 1 and 2

4.4 Antibacterial activity assessment

The antibacterial activity of the as-prepared fabrics was evaluated by the AATCC 100-2004 quantitative assessment technique [13]. The *E. coli* and *S. aureus* colonies observed on the agar plates were counted after 24 hours of incubation and the percentage reduction was calculated (Table 4.1). The assessment was conducted before and after the ultrasonic washing test. After the assessment, bacterial growth was observed for the untreated (pristine) cotton fabric which was used as control, thereby resulting in no antibacterial activity. The treated fabrics coated with CuO nanoparticles displayed high reduction in the bacterial growth for both *E. coli* and *S. aureus*, independent of the type of silane cross-linker used. Before washing of the as-prepared fabrics, with an increase in the nanoparticle loading from 3.2 g/m^2 to 8 g/m^2 , an improvement in the antibacterial efficiency of the fabric was observed. However, with further increase in nanoparticle loading up to 16 g/m^2 , no significant improvement in colony reduction was noticed. The fabrics with nanoparticle loading of 8 g/m^2 and 16

Table 4.1 Percentage reduction in the bacterial growth for the as-prepared fabrics with different nanoparticle loading treated with AEAPTMS, APTES, and MPTMS

Sample type (based on silane- crosslinker)	Nanoparticle loading (g/m ²)	Antibacterial Efficiency (%)			
		Escherichia coli		Staphylococcus aureus	
		Before Washing	After Washing	Before Washing	After Washing
AEAPTMS	3.2	97.6	96.4	96.9	95.8
	8	99.2	99.8	98.0	98.6
	16	99.7	98.9	97.1	96.9
APTES	3.2	98.4	97.1	95.4	91.9
	8	98.9	99.3	97.0	96.5
	16	99.4	99.3	97.4	96.2
MPTMS	3.2	98.9	97.3	96.0	92.8
	8	99.2	99.1	97.8	96.9
	16	99.4	99.5	98.3	97.1

g/m² displayed high reduction in the bacterial colonies with an efficiency greater than 99% for *E. coli* and upto 98% for *S. aureus* indicating high antibacterial performance of the as-prepared fabrics. After washing, there was a small decrease in the performance of the fabrics with 3.2 g/m² nanoparticle loading. However, the fabrics with 8 g/m² and 16 g/m² continued to display high antibacterial efficiency showing no pronounced performance decline upon washing. Therefore, nanoparticle loading of 8 g/m² was optimal in achieving high antibacterial performance before and after washing. As an example, the *E. coli* colony reduction for the APTES-treated fabrics with different nanoparticle loading before and after ultrasonic washing has been displayed in Figure 4.8. These results manifest the excellent performance and durability of the as-prepared fabrics through this novel route of fabrication. g/m² displayed high reduction in the bacterial colonies with an efficiency greater than 99% for *E. coli* and upto 98% for *S. aureus* indicating high antibacterial performance of the as-prepared fabrics. After washing, there was a small decrease in the performance of the fabrics with 3.2 g/m² nanoparticle loading. However, the fabrics with 8 g/m² and 16 g/m² continued to display high antibacterial efficiency showing no pronounced performance decline upon washing. Therefore, nanoparticle loading of 8 g/m² was optimal in achieving high antibacterial performance before and after washing. As an example, the *E. coli* colony

reduction for the APTES-treated fabrics with different nanoparticle loading before and after ultrasonic washing has been displayed in Figure 4.8. These results manifest the excellent performance and durability of the as-prepared fabrics through this novel route of fabrication.

Figure 4.8 a) Growth of *E. coli* colonies on untreated cotton fabric; Growth of *E. coli* colonies on APTES-treated fabrics before washing with CuO loading of b) 3.2 g/m² c) 8 g/m² d) 16 g/m²; Growth of *E. coli* colonies on APTES-treated fabrics after washing with CuO loading of e) 3.2 g/m² f) 8 g/m² g) 16 g/m²

4.5 UV blocking measurements

The UV blocking ability of the as-prepared fabrics was evaluated by the AATCC 183-2004 Test Method [14]. The UPF rating, the percentage transmission in the UV-A and the UV-B region was recorded. The pristine cotton fabric displays a low UPF rating of 7.9, insufficient to block the UV rays completely to safeguard the wearer (Figure 4.9a). Upon coating the fabrics with CuO, the as-prepared fabrics display UPF rating above 50, a requirement which ensures UV protection of the wearer (Figure 4.9b). The narrow band gap of the CuO nanoparticles results in absorption of the light in the visible and UV region, hence it also appears to be black. With an increase in the nanoparticle loading, the UPF rating of as-prepared fabrics was improved. Additionally, the fabrics displayed comparable UPF rating irrespective of the type of silane cross-linker used. The transmission of UV-A and UV-B rays through the CuO-treated fabrics is lower than 99%, manifesting excellent UV blocking ability of the as-prepared fabrics. Therefore, by the incorporation of CuO nanoparticles through this novel fabrication technique, the multi-functional fabric displays superhydrophobic, antibacterial and UV-blocking property making it desirable for clothing applications.

Figure 4.9 a) Transmittance of CuO-APTES-PDMS@Cotton fabric with different nanoparticle loading within the UV region; b) UPF ratings of as-prepared fabrics treated with different silane cross-linkers for various nanoparticle loadings

Table 4.2 Percentage transmission of the as-prepared fabrics in the UV-A and the UV-B region with different nanoparticle loading treated with AEPTMS, APTES and MPTMS

Sample type (based on silane-crosslinker)	Nanoparticle loading (g/m ²)	T (UVA) %	T (UVB) %
Pristine cotton fabric		17.8 ± 0.2	10.2 ± 0.2
AEPTMS	3.2	0.72 ± 0.20	0.64 ± 0.19
	8	0.18 ± 0.05	0.19 ± 0.04
	16	0.08 ± 0.02	0.09 ± 0.01
APTES	3.2	0.69 ± 0.36	0.57 ± 0.25
	8	0.23 ± 0.06	0.23 ± 0.06
	16	0.12 ± 0.01	0.12 ± 0.02
MPTMS	3.2	0.81 ± 0.41	0.65 ± 0.27
	8	0.19 ± 0.03	0.18 ± 0.02
	16	0.08 ± 0.01	0.08 ± 0.02

4.6 Durability assessments

It is vital for multi-functional fabrics to display lasting durability for industrial and household applications. For mechanical durability assessment, the as-prepared fabrics were subjected to dry abrasion resistance test and wet ultrasonic washing test. For the abrasion resistance measurement, the as-prepared fabrics were subjected to 500 cycles of abrasion with pristine cotton fabric serving as an abradant surface. With an increase in the number of abrasion cycles, there was a gradual decrease in the WCA. This was due to the lowering of the surface roughness against abrasion. With an increase in the nanoparticle loading, the as-prepared fabrics offered resistance against a higher number

of abrasion cycles. The originally higher surface roughness attributed to the fabrics with higher nanoparticle loading was responsible for the occurrence. Despite the variation in nanoparticle loading, the as-prepared fabrics displayed superior hydrophobicity up to 500 cycles of abrasion. Moreover, the fabrics revealed similar behaviour in WCA irrespective of the silane cross-linker used. These results not only prove the high durability of the as-prepared fabrics, but also manifest the reliability of this novel route of fabrication across different silane cross-linkers. The effect of abrasion cycles on as-prepared fabrics with different nanoparticle loading for all the silane cross-linkers is shown in Figure 4.10.

Figure 4.10 Effect of abrasion cycles on as-prepared fabrics with different CuO loadings treated with a) AEAPTMS b) APTES c) MPTMS

For the ultrasonic washing test, the as-prepared fabrics were subjected to harsh ultrasound treatment for a period of 90 minutes in the solution of a non-ionic detergent, Triton X-100. Contact angle measurements were taken after periodic intervals of 15 minutes. A gradual decrease in WCA was observed with an increase in the sonication time. This behaviour can be attributed to the sites of high temperature and pressure created on the surface of the as-prepared fabrics due to ultrasound, weakening the coating performance. For the treated fabrics with 16 g/m² nanoparticle loading, visible quantity of nanoparticles was released into the solution resulting in sharper decrease of WCA as compared to fabrics with 3.2 g/m² and 8 g/m² nanoparticle loading. The weak attachment of the excess nanoparticles on the surface could be responsible for the

nanoparticle release. Overall, despite the variation in the nanoparticle loading, the as-prepared fabrics displayed high hydrophobicity up to 90 minutes of harsh ultrasound washing treatment. Moreover, the fabrics displayed comparable behaviour with a very small variation in WCA across different silane cross-linkers. These results indicate the wash fastness of the as-prepared fabrics rendering them suitable for commercial applications. The effect of ultrasonic washing on the as-prepared fabrics with variation in sonication time for all the silane cross-linkers is shown in Figure 4.11.

Figure 4.11 Effect of ultrasonic washing on as-prepared fabrics with different CuO loadings treated with a) AEPTMS b) APTES c) MPTMS

Apart from the mechanical durability assessments, the chemical stability of the as-prepared fabrics was evaluated by the variation of WCA, after submerging them in aqueous solutions of NaOH and HCl with pH ranging from 1-13 for a period of 24 hours. In Figure 4.12, the effect of pH variation on the fabrics treated with highest nanoparticle loading of 16 g/m² across all silane cross-linkers has been shown. The as-prepared fabrics displayed high durability to the acidic and alkaline environments from pH values ranging from 3 to 11. At pH = 1, the CuO nanoparticles being a weak base, were completely dissolved by the strong acidic solution leaving the surface devoid of nanoparticles. The hydrophobicity, however, was retained due to the intrinsic strong resistance of PDMS to acidic treatments. At pH = 3, the acidic strength was weaker, and the performance of CuO nanoparticles was not compromised. At pH = 13, the nanoparticles remain unaffected, however, the PDMS coating was peeled off at a few

places causing a drop in WCA. Overall, the as-prepared fabrics showed satisfactory durability against chemical environments they are regularly exposed to in daily life.

Figure 4.12 Effect of pH on as-prepared fabrics treated with different silane cross-linkers with 16 g/m² CuO loading

4.7 Air permeability and flexural rigidity measurement

The air permeability and flexural rigidity of the as-prepared fabrics was evaluated before and after PDMS and CuO deposition (Figure 4.13). It was observed that the air permeability of the PDMS coated cotton was higher than the pristine cotton fabric. This was probably due to the binding of the individual cotton fibres together by the PDMS coating which resulted in more air flow through the fabric than the pristine cotton fabric. After incorporation of the nanoparticles, the air permeability was reduced. A general trend observed was a decrease in the air permeability with an increase in the nanoparticle loading. However, the overall decrease in the air permeability of the as-prepared fabrics was quite low when compared to the pristine cotton fabric, not affecting the breathability or comfort of these fabrics for clothing applications. The flexural rigidity of the PDMS coated cotton was lower than the pristine cotton fabric. This was probably due to the material properties of PDMS offering high elasticity and flexibility, thereby causing a reduction in the rigidity of the fabric. After deposition of the nanoparticles, there was an overall increase in the rigidity. However, it was

comparable to the pristine cotton fabric thereby not altering the fabric quality or wearer comfortability.

Figure 4.13 Variation of a) air permeability b) flexural rigidity of as-prepared fabrics with different nanoparticle loading treated with AEAPTMS, APTES and MPTMS

4.8 Summary

In this study, we report the successful fabrication of durable superhydrophobic antibacterial CuO-Silane-PDMS-Cotton fabrics through a novel and facile synthesis technique. Copper oxide nanoparticles were incorporated on the surface of PDMS coated cotton fabric by using fluorine-free silane coupling agents as cross-linkers for lasting durability. The as-prepared fabrics displayed excellent superhydrophobicity and antibacterial activity. We found that 8 g/m² nanoparticle loading on the fabric surface was optimal in achieving maximum performance. The reliability of the fabrication technique was confirmed by utilising three silane cross-linkers which displayed similar behaviour under all circumstances. Additionally, the fabrics displayed superior durability against abrasion, ultrasonic washing and harsh chemical environments. The antibacterial performance of the fabrics was not compromised even after ultrasonic washing. The breathability and flexibility of the as-prepared fabrics was also preserved. The only observed limitation of this technique was the dark colour of the fabrics due to the agglomeration of the copper oxide nanoparticles. Although the fabric has the potential to be dyed in different dark shades, it still poses a hindrance in its complete applicability for clothing fabrics. To overcome this drawback, in the second fabrication technique, zinc oxide nanoparticles were explored for their usage.

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Chapter 5

Results and Discussion: HDTMS-ZnO-APTES-Cotton fabrics

In this chapter, the performance of the superhydrophobic antibacterial HDTMS-ZnO-APTES-Cotton fabrics synthesized by the second synthesis technique is evaluated. The variation of the superhydrophobicity and antibacterial activity with nanoparticle loading was studied and the optimum amount was determined. Additionally, the superhydrophobicity, antibacterial activity, and UV-blocking property of the fabrics was evaluated. Chemical analysis confirmed the mechanisms for fabrication and phase identification for ZnO. The as-prepared fabrics displayed high durability against abrasion, ultrasonic washing, harsh chemical solutions and even UV irradiation. The air permeability and flexural rigidity tests revealed that the fabric breathability and flexibility was not compromised. This synthesis technique provides a novel route for fabrication of multifunctional textiles for large-scale applications.

5.1 Introduction

To achieve the aim of developing durable superhydrophobic antibacterial fabrics, the second synthesis technique is explored. Zinc oxide (ZnO) nanoparticles were chosen as potential antibacterial agents which could overcome the appearance issue with copper oxide nanoparticles. Additionally, they also displayed UV blocking properties which could prove beneficial for clothing applications. To achieve these goals, ZnO nanoparticles were anchored to the pristine cotton fabric employing APTES as a silane cross-linker. APTES was chosen among the previously explored silane cross-linkers due to its easy availability, popularity, and stability in the results. The ZnO coated fabric was then modified with HDTMS for lowering the surface energy. The nanoparticle loading on the as-prepared fabrics was also optimized based on surface morphology and antibacterial efficiency. FTIR and XRD analysis was conducted to confirm the chemical composition of the fabric surface. The resistance of the as-prepared fabrics to abrasion, ultrasonic washing, harsh chemical solutions and UV irradiation was assessed. Moreover, the air permeability and flexibility of the fabrics before and after the coating was evaluated. The results of these measurements are given below.

5.2 Nanoparticle loading optimization

To obtain the optimum loading of nanoparticles on the surface of the cotton fabric, samples with six different loading of ZnO nanoparticles were prepared. The surface morphology, contact angle and antibacterial efficiency of the as-prepared fabrics were evaluated. In Figure 5.1, FE-SEM images of 6 different samples with nanoparticle loading of 4, 8, 12, 16, 20, and 24 g/m² has been displayed. As can be seen in the figure, for nanoparticle loading of 4, 8 and 12 g/m², incomplete surface coverage was obtained. For samples with loading of 16 and 20 g/m², the entire surface of the fibre was completely covered with the ZnO nanoparticles. Upon further loading of nanoparticles up to 24 g/m², agglomeration took place resulting in poor coverage of the fabric surface. Therefore, based on surface morphology and coverage, samples with 16 and 20 g/m² nanoparticle loading were the most preferred options. Contact angle measurements and antibacterial tests were then conducted to further make a choice between the two quantities.

Figure 5.1 FE-SEM images of cotton fabrics coated with ZnO with nanoparticle loading of a) 4 g/m² b) 8 g/m² c) 12 g/m² d) 16 g/m² e) 20 g/m² f) 24 g/m²

For the contact angle measurement, a general trend was observed that there is an increase in WCA and a decrease of WSA with an increase in the nanoparticle loading on the fabric surface as shown in Figure 5.2. The highest superhydrophobic performance was displayed by 20 g/m² sample with the highest WCA of $153.5 \pm 1.1^\circ$ and lowest WSA of $2.4 \pm 1.2^\circ$. The higher roughness of the 20 g/m² sample as compared to 16 g/m² sample due to more nanoparticles on the surface was responsible for the observed phenomenon.

Figure 5.2 The variation of WCA and WSA with nanoparticle loading of ZnO on the cotton fabric

Antibacterial assessment was conducted with *E. coli* by the AATCC 100-2004 quantitative assessment technique and the antibacterial efficiency was calculated as seen in Table 5.1. With an increase in the nanoparticle loading, an increase in the antibacterial efficiency was observed. The highest efficiency of 99.2% was obtained for 24 g/m² sample with the highest quantity of nanoparticles on the fabric surface. Therefore, a clear co-relation existed between the quantity of nanoparticles on the surface and the antibacterial activity. However, as a choice has to be made between 16 and 20 g/m² samples, the latter displayed a higher efficiency of 98.8% as compared to the former.

Therefore, based on the cumulative results obtained from the three different evaluation methods, 20 g/m² nanoparticle loading of ZnO was considered optimal in achieving maximum performance for the as-prepared fabrics.

Table 5.1 Variation of antibacterial efficiency of as-prepared fabrics with ZnO nanoparticle loading

ZnO loading on cotton fabric (g/m²)	Antibacterial efficiency %
8	96.5
12	97.6
16	97.6
20	98.8
24	99.2

5.3 Surface morphology and contact angle analysis

After optimization of the nanoparticle loading on the fabric surface, a detailed analysis of surface morphology and contact angle was carried out before and after the coating. A pristine cotton fabric has a completely smooth morphology as shown in Figure 5.3a. The ZnO nanoparticles used for the fabrication were rod like in shape as shown in Figure 5.3b with size < 50 nm as provided by the manufacturer. After coating 20 g/m² ZnO nanoparticles over the pristine cotton fabric, the nanoparticles were uniformly distributed over the fabric surface displaying no visible agglomeration and completely covering the surface area of the fabric as can be seen in Figure 5.3c and 5.3d.

The chemical composition of the HDTMS-ZnO-APTES-Cotton fabrics was mapped using the EDS spectra and has been displayed in Figure 5.3e and 5.3f. The four main elements identified were C, O, Si, and Zn which were uniformly distributed over the fabric surface. The presence of gold was due to the sputter coating of the fabric sample for FE-SEM analysis. A small amount of aluminium impurity was detected. Moreover, nitrogen from APTES could not be detected by the EDS probably due to its low concentration causing an overlap of the spectrum with carbon and oxygen. The atomic ratio of C/O/Si/Zn was 55.86%/37.90%/1.28%/4.03%, confirming the successful synthesis of HDTMS-ZnO-APTES-Cotton fabrics.

Figure 5.3 FE-SEM images of a) pristine cotton fabric, b) ZnO nanoparticles, c) HDTMS-ZnO-APTES-Cotton fabric, d) higher magnification of HDTMS-ZnO-APTES-Cotton fabric; e) Element mapping of C, O, Si, Zn; f) EDS spectrum

Contact angle measurements were conducted to determine the surface wetting properties of the fabric before and after the coating and has been displayed in Figure 5.4. A pristine cotton fabric consists of hydroxyl groups on its surface owing to the cellulose structure, and therefore, absorbs water displaying hydrophilicity of the surface (Figure 5.4a). Upon incorporating 20 g/m² of ZnO nanoparticles on the fabric using APTES, a hydrophobic droplet was formed primarily due to the roughness created by ZnO. However, it was unstable and soon absorbed into the fabric. The goniometer image shown in Figure 5.4b is of an unstable water droplet with an attempt to capture

it before absorption. As a result, the droplet size obtained is slightly smaller displaying an average WCA of $145.8 \pm 3.2^\circ$. WSA could not be measured for the fabric as the droplet was absorbed very quickly upon tilting the surface. After coating the ZnO-APTES-Cotton fabric with HDTMS, a low surface energy silane, a superhydrophobic surface was obtained (Figure 5.4c) displaying a WCA of $153.5 \pm 1.1^\circ$ and WSA of $2.4 \pm 1.2^\circ$. The superhydrophobicity of the fabric has been displayed in Figure 5.5 where spherical water droplets (tainted with Rhodamine-B) are beaded over the fabric surface.

Figure 5.4 Goniometer images of a) pristine cotton fabric, b) ZnO-APTES-Cotton fabric, c) HDTMS-ZnO-APTES-Cotton fabric

Figure 5.5 Photograph of Rhodamine-B tainted water droplet on HDTMS-ZnO-APTES-Cotton fabric

5.4 Antibacterial activity assessment

The antibacterial activity of the as-prepared fabrics was evaluated by the AATCC 100-2004 quantitative assessment technique [1]. The *E. coli* and *S. aureus* colonies observed on the agar plates were counted after 24 hours of incubation and the percentage reduction was calculated as displayed in Table 5.2. Bacterial growth was observed for the pristine cotton fabric which was used as control, thereby resulting in no antibacterial activity. Upon deposition of ZnO nanoparticles using APTES, the fabrics displayed high reduction in the bacterial growth for both *E. coli* and *S. aureus* with upto 98%

efficiency. On further coating the fabric with HDTMS, no significant reduction in antibacterial activity was observed. Additionally, the antibacterial assessment of the HDTMS-ZnO-APTES-Cotton fabrics after ultrasonic washing for 2 hours was also carried out. There was a small decline in performance after washing, however, the antibacterial reduction upto 96% was maintained. These results confirm the excellent performance and durability of the as-prepared fabrics through this novel synthesis technique. The growth of the *E. coli* and *S. aureus* colonies on the agar plates are shown in Figure 5.6 and Figure 5.7, respectively.

Table 5.2 Percentage reduction in the bacterial growth for the HDTMS-ZnO-APTES-Cotton fabrics

Sample Name	Antibacterial Efficiency (%)	
	<i>Escherichia coli</i>	<i>Staphylococcus aureus</i>
ZnO-APTES-Cotton fabric	98.2	97.8
HDTMS-ZnO-APTES-Cotton fabric	98.4	96.7
HDTMS-ZnO-APTES-Cotton fabric (washed)	97.8	96.1

Figure 5.6 Growth of *E. coli* colonies on a) pristine cotton fabric b) ZnO-APTES-Cotton fabric c) HDTMS-ZnO-APTES-Cotton fabric d) HDTMS-ZnO-APTES-Cotton fabric (washed)

Figure 5.7 Growth of *S. aureus* colonies on a) pristine cotton fabric b) ZnO-APTES-Cotton fabric c) HDTMS-ZnO-APTES-Cotton fabric d) HDTMS-ZnO-APTES-Cotton fabric (washed)

5.5 Chemical composition analysis

To evaluate the chemical composition of the as-prepared fabrics after deposition of ZnO using APTES and further modification with HDTMS, the responsible mechanism for attachment was ascertained. ZnO nanoparticles consist of hydroxyl groups on its surface. Upon dispersion in APTES, these hydroxyl groups can either react with the silanol groups of the hydrolysed APTES or form hydrogen bonds with the amino group on the silane chain. This allows the attachment of the ZnO to APTES. When brought in contact with the pristine cotton fabric surface, these nanoparticles are then anchored to its surface by either the free silanol or amino groups of APTES. The possible mechanism for attachment is displayed in Figure 5.8. It is to be noted that the figure is only a representation of the possible bonds which might form and does not represent the quantity or size ratio of particles to silane in any way.

Figure 5.8 Mechanism displaying the attachment of APTES-treated ZnO to cotton fabric

Upon further modification with HDTMS, the silanol groups of HDTMS form bonds with the free hydroxyl groups present on cellulose structure, ZnO or APTES completing the coating process. The possible mechanism of attachment of HDTMS to the ZnO-APTES-Cotton fabric is shown in the Figure 5.9.

Figure 5.9 Mechanism displaying the attachment of HDTMS to ZnO-APTES-Cotton fabric

To verify the above mechanism, FTIR analysis was conducted as shown in Figure 5.10. Before the coating, the pristine cotton fabric displayed several strong peaks. The broad peak between $3600\text{--}3000\text{ cm}^{-1}$ is due to the hydroxyl --OH groups on the fabric surface. Other characteristic peaks at 2897 , 1636 , 1428 and 1315 cm^{-1} corresponding to asymmetric stretching of --CH_2 , --OH group due to adsorbed water, and deformation vibration of C--H groups, respectively [2]. After deposition of ZnO nanoparticles using APTES, there was decrease in the intensity of the broad peak between $3600\text{--}3000\text{ cm}^{-1}$

indicating that the -OH groups on the cellulose surface have been utilised for bonding. Additionally, a characteristic peak was obtained at 1561 cm^{-1} which corresponds to the deformation of NH_2 groups due hydrogen bonding [3], thereby confirming the role of APTES in ZnO attachment. After deposition of HDTMS, a new peak at 2856 cm^{-1} was obtained which corresponds to the symmetric stretching of the -CH_2 groups [4, 5]. Due to the long alkyl chain of HDTMS, the intensity of the peak is significantly high, confirming the presence of HDTMS on the fabric surface.

Figure 5.10 FTIR spectra of Cotton fabric, ZnO-APTES-Cotton fabric and HDTMS-ZnO-APTES-Cotton fabric

XRD analysis was conducted to identify the phase of the crystalline ZnO nanoparticles deposited on the fabric surface. Figure 5.11 shows the XRD patterns of the untreated and the ZnO treated fabric samples. All the samples contain the monoclinic crystal structure of cellulose I due to the cotton fabric which was confirmed by the presence of peaks at 14.97° , 16.49° , 22.73° and 34.57° corresponding to the (-110) , (110) , (200) , and (004) planes respectively (ICDD #00-056-1718). After modifying the fabric with ZnO nanoparticles using APTES, characteristic peaks of ZnO hexagonal zincite structure was obtained. This was confirmed by the presence of peaks at 32.01° , 34.63° , 36.43° , 47.69° , 56.77° , 63.09° , 68.15° and 69.25° which corresponds to (100) , (002) , (101) , (102) , (110) , (103) , (112) and (201) planes respectively (ICDD #04-006-2557). Moreover, no significant variation in peak position and peak intensity was observed

after coating with HDTMS which confirmed that HDTMS does not interfere with the ZnO phase upon deposition.

Figure 5.11 XRD patterns for phase identification of ZnO for HDTMS-ZnO-APTES-Cotton fabrics through various steps of sample preparation

5.6 UV blocking measurement

Pristine cotton fabric cannot protect the wearer from the harmful UV rays of the sun. To be shielded from the UV radiation, the fabric should have an Ultraviolet Protection Factor (also called as UPF rating) of 50. The UV blocking ability of the pristine cotton fabric and the ZnO-treated fabrics was evaluated by the AATCC 183-2004 Test Method [6]. The UPF rating, and the percentage transmission in the UV-A and the UV-B region is recorded in Table 5.3 and the graph displaying the transmittance curve is shown in Figure 5.12. The pristine cotton fabric displays a low UPF of 7.9, which will be unable to block the UV rays completely. The ZnO-treated fabrics, with and without HDTMS coating, both display very high UPF rating, over 200 times more than pristine cotton fabric. Additionally, the transmission of UV-A and UV-B rays through the ZnO-treated fabrics is lower than 99.5%, manifesting excellent UV blocking ability of the as-prepared fabrics. Therefore, by the incorporation of ZnO nanoparticles through this novel fabrication technique, the multi-functional fabric displays superhydrophobic,

antibacterial and additional UV-blocking property making it desirable for clothing applications.

Table 5.3 The UV-blocking parameters of HDTMS-ZnO-APTES-Cotton fabrics through various steps of sample preparation

Sample Type	T (UVA) %	T (UVB) %	UPF
Pristine Cotton fabric	17.8 ± 0.2	10.2 ± 0.2	7.9 ± 0.1
ZnO-APTES@Cotton fabric	0.3 ± 0.04	0.05 ± 0.01	1650.3 ± 349.1
HDTMS-ZnO-APTES@Cotton fabric	0.2 ± 0.06	0.05 ± 0.01	1769.2 ± 304.3

Figure 5.12 Variation of transmittance of HDTMS-ZnO-APTES-Cotton fabrics within the UV region

5.7 Durability measurements

For the fabrics to be commercially viable, it is essential for them to display lasting durability. Various durability assessments were conducted on the as-prepared fabrics and the analysis is given below.

For the abrasion resistance measurement, the as-prepared fabrics were subjected to 800 cycles of abrasion with pristine cotton fabric serving as an abradant surface. The performance of the fabrics to abrasion is displayed in Figure 5.13. With an increase in

the number of abrasion cycles, there was a gradual decrease in superhydrophobicity marked by a small decrease in WCA and an increase in WSA. Abrasion causes the wear of the fibres, damages the coating and affects the dual scale roughness essential for displaying superhydrophobicity. The HDTMS layer damage could have also been responsible in lowering of the WCA with increasing abrasion cycles. After 800 cycles of abrasion, the as-prepared fabrics displayed high durability confirming the robustness of the synthesized coating through this novel synthesis technique.

Figure 5.13 The effect of abrasion cycles on the WCA and WSA for HDTMS-ZnO-APTES-Cotton fabrics

To determine the wash-fastness of the as-prepared fabrics, they were subjected to ultrasonic washing for 2 hours in the solution of a non-ionic detergent, Triton-X. Contact angle measurements were taken at periodic intervals of 15 minutes. The effect of ultrasound treatment on the WCA and WSA of the as-prepared fabrics with respect to sonication time is recorded in Figure 5.14. Despite the high temperature and pressure regions created on the fabric surface due to the ultrasound waves, the fabrics displayed long lasting durability. There was only a small decrease in WCA from 151.9° to 148.9° and the WSA increased from 2.4° to 14.9°. This test confirmed the durability of the as-prepared fabrics to washing when used for clothing or healthcare applications.

Figure 5.14 The effect of ultrasonic washing on the WCA and WSA for HDTMS-ZnO-APTES-Cotton fabrics

The durability of the as-prepared fabrics to harsh chemical solutions was evaluated by submerging them in aqueous solutions of NaOH and HCl with pH ranging from pH = 1 to pH = 13 for a period of 24 hours. After the stipulated time, the effect of pH on the WCA and WSA of the fabrics was evaluated as shown in Figure 5.15. The as-prepared fabrics displayed high durability to the acidic and alkaline environments from pH values ranging from 3 to 11. The WCA remained $> 150^\circ$ and the WSA $< 15^\circ$ showing high resistance to chemical changes. However, at extreme pH conditions of pH = 1 and pH = 3, the performance of the coating was compromised. ZnO is an amphoteric oxide and therefore, reacts with both HCl and NaOH at extreme pH values resulting in the dissolution of the nanoparticles on the fabric surface. In such solutions, the WCA was reduced to 146° and the WSA rose to 25° for pH = 1 and 32° for pH = 13. However, such extreme chemical conditions are rarely encountered in everyday situations and therefore, the fabrics display satisfactory durability under commonly occurring chemical solutions.

To evaluate the longevity of the UV-blocking ability of the as-prepared fabrics, they were subjected to UV irradiance of 72.6 mW/cm^2 of 365 nm wavelength for a period of 12 hours. The variation of WCA and WSA of the as-prepared fabrics with the UV

irradiation time is displayed in Figure 5.16. Exposure to UV is known to cause degradation of a coating by causing chain scission reactions [7]. However, the ZnO

Figure 5.15 The effect of pH on the WCA and WSA for HDTMS-ZnO-APTES-Cotton fabrics

nanoparticles incorporated on the fabric surface absorbed the UV rays, thereby protecting the coating from undergoing degradation. As a result, despite continuous UV exposure for 12 hours, there was no significant reduction in the superhydrophobicity of the fabrics. The WCA dropped negligibly from 152.9° to 149.2° while the WSA increased from 1.9° to 9.7° still retaining the superhydrophobic performance. Hence, the fabrics displayed long lasting durability against UV irradiation making the fabrics useful for UV-blocking applications.

5.8 Air permeability and flexural rigidity measurements

The mechanical properties, air permeability and flexural rigidity of the as-prepared fabrics was evaluated before and after the coating and the data are reported in Table 5.4. After deposition of the ZnO nanoparticles on the pristine cotton fabric using APTES, the air permeability of the fabric reduced from 1895 mm/s to 1645 mm/s. This was due to the blocking of the air spaces between the fibres obstructing the air flow. After coating of HDTMS, the air permeability decreased marginally from 1645 mm/s to 1591 mm/s. Overall, the reduction in air permeability was low when compared to the

pristine cotton fabric, thereby not affecting the breathability or wearer comfort for clothing applications.

Figure 5.16 The effect of UV radiation on the WCA and WSA for HDTMS-ZnO-APTES-Cotton fabrics

A trend similar to air permeability was observed for flexural rigidity of the as-prepared fabrics. Upon coating the pristine cotton fabric with ZnO nanoparticles, the flexural rigidity of the fabric was increased. The rigidity was further increased after HDTMS coating. The overall flexural rigidity of HDTMS-ZnO-APTES-Cotton fabric was $50.7 \text{ mg} \times \text{cm}$ as compared to $36.5 \text{ mg} \times \text{cm}$ for pristine cotton fabric. Nevertheless, the flexural rigidity is still within the allowable range for clothes [8], hence proving its applicability for clothing and healthcare fabrics.

Table 5.4 Air permeability and flexural rigidity data for HDTMS-ZnO-APTES Cotton fabrics

Sample Type	Air permeability (mm/s)	Flexural rigidity (mg × cm)
Pristine cotton fabric	1895 ± 21.9	36.5
ZnO-APTES@Cotton fabric	1644.8 ± 48.9	44.1
HDTMS-ZnO-APTES@Cotton fabric	1591.1 ± 26.0	50.7

5.9 Self-cleaning application

For application in clothing, it is essential for the multi-functional fabrics to display self-cleaning behaviour which will prevent the clothes from accumulating dirt. To evaluate the self-cleaning ability of the as-prepared fabrics, graphite powder, a model contaminant, was sprinkled on the pristine cotton fabric, ZnO-APTES-Cotton fabric and HDTMS-ZnO-APTES-Cotton fabric as shown in Figure 5.17a. Water droplets were then dropped on the fabric surface using a pipette to wash away the dirt and the final outcome is displayed in Figure 5.17b. For the pristine cotton fabric, the dirt accumulated on the hydrophilic surface of the fabric leaving it stained and wet. For the ZnO-APTES-Cotton fabric, a similar result was obtained. Although the water droplets initially formed beads on the fabric surface, they were quickly absorbed leaving the dirt in its place. Despite the presence of dual-scale roughness, the absence of low surface energy prevented the ZnO-APTES-Cotton fabrics to display any self-cleaning behaviour. On the contrary, the HDTMS-ZnO-APTES-Cotton fabric, treated with HDTMS to lower the surface energy successfully displayed self-cleaning ability. Most of the dirt easily rolled away with the water droplets leaving the fabric surface clean and dry. Few dirt particles which were stuck between the fibres were easily removed by shaking the fabric slightly. Therefore, the results manifest the potential of the as-prepared fabrics for clothing applications.

Figure 5.17 Evaluation of self-cleaning behaviour of HDTMS-ZnO-APTES-Cotton fabrics a) before the test b) after the test

5.10 Summary

In this study, we report the successful fabrication of durable superhydrophobic antibacterial HDTMS-ZnO-APTES-Cotton fabrics through a novel and facile synthesis technique. Zinc oxide nanoparticles were deposited on the surface of the pristine cotton fabric using APTES which was further modified using HDTMS to obtain highly superhydrophobic and antibacterial fabrics. It was observed that nanoparticle loading of 20 g/m² was optimal in achieving maximum surface coverage and performance. The as-prepared fabrics also displayed high UV blocking ability, more than 200 times of pristine cotton fabric. The fabrics demonstrated superior durability against abrasion, ultrasonic washing, chemical solutions and UV irradiation. The breathability and flexural rigidity of the fabrics was not compromised. Most importantly, the fabrics retained their white appearance, thus making them suitable for all clothing and healthcare applications. This technique displays tremendous potential for various other surface engineering applications.

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Chapter 6

Conclusions and Recommendations for Future Work

In this chapter, a summary of the work constituting the thesis is discussed. The research hypothesis was verified and the novel technological and scientific contributions made through this study are elaborated upon. An overall conclusion highlighting the main results from the work is provided. This chapter also discusses the scope for future work. Further research can be conducted to incorporate additional properties over the fabrics apart from superhydrophobicity and antibacterial activity. Moreover, different antibacterial agents other than metal-oxide nanoparticles can also be explored. This chapter concludes with the reconnaissance work which formed an important study for deriving the second synthesis technique but could not be included in the main chapters due to few drawbacks. Overall, this chapter draws together the threads of this thesis and highlights the scope for further improvement which can take this research forward in the future.

6.1 General summary

Synthesis of multi-functional fabrics for industrial and household applications has been heavily researched and various techniques and materials to achieve such coatings on the fabrics are available. However, the drawback of the existing research is the poor durability of such synthesized coatings hindering its commercialization.

In this thesis, the utility of silane cross-linkers for the synthesis of durable superhydrophobic antibacterial fabrics was explored by two novel techniques.

In the first technique, PDMS was deposited over the cotton fabrics followed by deposition of copper oxide nanoparticles using silane cross-linkers. Three different silanes were explored for their utility. The nanoparticle loading on the fabric surface was optimized and 8 g/m^2 CuO loading was found optimal in achieving maximum performance. CuO nanoparticles rendered the fabric black in colour limiting its application as clothing fabrics.

In the second technique, zinc oxide nanoparticles were incorporated on the surface of the pristine cotton fabric using a silane cross-linker. The fabric was further modified with low surface energy silane to obtain superhydrophobic antibacterial fabrics. The optimized nanoparticle loading was 20 g/m^2 for maximum surface coverage and performance. The white appearance of the fabrics was retained. Additionally, the fabric displayed UV blocking ability due to ZnO nanoparticles.

For both the fabrication techniques, durability assessments like abrasion test, ultrasonic washing test and chemical stability tests were conducted and the fabrics displayed very high durability confirming the role of silane cross-linkers in improving the robustness of the coatings.

By conducting this research, it has been possible to successfully prove that the durability of the coatings can be improved by introducing additional chemical bonds in the form of silane cross-linkers. This would allow the fabrics to be commercialized for various applications.

6.2 Verification of research hypothesis

The objective of this research involved developing novel techniques of synthesis which are simple, inexpensive, eco-friendly, and can enhance the durability of the superhydrophobic antibacterial fabrics for clothing and healthcare applications. To achieve this goal, we explored the role of silane coupling agents as cross-linkers which could anchor the metal-oxide nanoparticles to the fabric substrate, and substantially improve the durability. Moreover, fluorine-free silane cross-linkers were to be utilized to overcome the toxicity issues usually involved with chemicals. Based on the hypothesis, the research objectives were fulfilled as follows:

Two different types of coatings were developed on cotton fabrics which offer superhydrophobic and antibacterial functionality

- Three different silane coupling agents were successfully tested which could be utilized as cross-linkers to bind the nanoparticles to the fabric substrate. All the silanes displayed comparable performance manifesting the reliability of the techniques.
- The nanoparticle loading on the fabric substrates was optimised for both the fabrication techniques based on the type of nanoparticle used.
- The performance of the fabrics for their superhydrophobicity and antibacterial activity was evaluated.

The interaction among the nanoparticles, silane cross-linker and fabric substrate was understood through different characterization techniques

- FE-SEM helped in visualizing the surface morphology and nanoparticle distribution over the fabric substrate.
- Chemical analysis like FTIR confirmed the bonding mechanism between the nanoparticles, silane cross-linkers and the fabric substrate
- The relationship between nanoparticle loading and coating performance was understood through contact angle measurements and antibacterial assessments

The durability of the developed coatings on the fabrics was evaluated by various techniques

- Abrasion test, ultrasonic washing test and chemical stability test were conducted which proved the mechanical and chemical stability of the coatings.
- UV durability test was conducted for the HDTMS-ZnO-APTES-Cotton fabrics which confirmed the robustness of the fabric against continuous UV exposure.

6.3 Novel contributions

Based on the studies carried out for this work, the technological and scientific contributions made are given as follows:

6.3.1 Technological contributions

- Explored the role of silane cross-linkers for developing two facile, eco-friendly synthesis procedures for durable superhydrophobic antibacterial fabrics
- Optimized the nanoparticle loading on the fabric surface based on the type of nanoparticle used
- Conducted various durability tests to confirm the robustness of the synthesized coatings
- This technique is simple and can be applied to any other system for various other surface engineering and coating applications.

6.3.2 Scientific contributions

- Understood the mechanisms responsible for anchoring the nanoparticles to the fabric by the aid of silane cross-linkers

6.4 Overall conclusion

Textiles are essential in various day-to-day applications. By incorporating additional properties like superhydrophobicity and antibacterial activity, their utility can be further enhanced especially for clothing and healthcare sectors. In our work, two new synthesis techniques have been reported which are simple, eco-friendly for long lasting superhydrophobic antibacterial fabrics. Silane coupling agents were utilized as cross-linkers for anchoring antibacterial nanoparticles to the fabric surface. In the first synthesis technique, CuO-Silane-PDMS-Cotton fabrics were prepared with WCA >

153° and WSA < 5° and upto 99% antibacterial efficiency. 8 g/m² nanoparticle loading was optimum in achieving maximum performance. Three different silane cross-linkers confirmed the reliability of the technique. Moreover, the as-prepared fabrics displayed high durability against 500 cycles of abrasion, 90 minutes of ultrasonic washing and chemical solutions with pH ranging from 1 to 13 for a period of 24 hours. The breathability and flexibility of the fabric was also retained successfully after the coating. In the second synthesis technique, HDTMS-ZnO-APTES-Cotton fabrics were prepared with optimized nanoparticle loading of 20 g/m². The as-prepared fabrics displayed WCA of 153.5° and WSA of 2.4° with upto 98% antibacterial efficiency. The fabrics also demonstrated high durability against 800 cycles of abrasion, 120 minutes of ultrasonic washing and chemical solutions with pH ranging from 1 to 13 for a period of 24 hours. The breathability and flexibility of the fabric was not compromised ensuring wearer comfortability. The above-reported techniques are simple, cost-effective and demonstrate the ability to increase the longevity of the synthesized coatings on the cotton fabrics. Both synthesis routes hold tremendous potential for large-scale production of multi-functional fabrics, especially for clothing and healthcare applications.

6.5 Suggestion for future work

This study focuses on the synthesis of superhydrophobic antibacterial fabrics through new fabrication techniques. This work has been successful in highlighting the role of silane cross-linkers for improving the durability of multi-functional fabrics. Future work can be carried out to incorporate additional functionalities to the fabric apart from superhydrophobicity and antibacterial activity. In this work, metal-oxide nanoparticles have been utilised to provide antibacterial functionality to the fabric. Despite an improvement in the durability, they still pose a risk of entering the environment and human body. Future work can be conducted to utilise other antibacterial agents for this purpose.

6.5.1 Research to incorporate additional functions apart from superhydrophobicity and antibacterial activity

While silane cross-linkers have been successful in providing durability for synthesis of superhydrophobic antibacterial fabrics, their utility can be further extended to synthesize fabrics which offer additional functionalities. In a recent work, flame retardancy and antibacterial functionality were combined together on a cotton fabric using a combination of cyclotriphosphazene, polydopamine and silver nanoparticles [1]. Dopamine was autopolymerized on the surface of cotton fabric to produce polydopamine with simultaneous hydrolysis of cyclotriphosphazene. Thereafter, silver nanoparticles were in-situ grown on the surface to produce flame retardant and antibacterial coatings. In another work, superhydrophobic flame retardant coatings were synthesized on cotton fabrics via a trilayer coating [2]. First, 2,5-Dimercapto-1,3,4-thiadiazole was deposited on the fabric surface with the aid of copper. Second, the in-situ reduction of silver nitrate was conducted which resulted in silver particles. Third, Octadecyltriethoxysilane was coated to produce superhydrophobic flame retardant cotton fabrics. By drawing inspiration from these articles, our work can be further extended to incorporate flame retardancy function together with superhydrophobicity and antibacterial activity by using a combination of nanoparticles, silane cross-linkers and flame retardancy agents.

6.5.2 Research to utilise other antibacterial agents apart from metal-oxide nanoparticles

While metal-oxide nanoparticles like CuO and ZnO offer high antibacterial activity, upon release they can enter the environment and human body. Due to their toxicity, they can cause severe damage both to marine organisms and human beings. Therefore, there is a need to replace the metal-oxide nanoparticles with more natural moieties. In recent years, the use of chitosan in nanoparticle form has gained interest of researchers. Chitosan is a naturally occurring polysaccharide which is abundantly available. It consists of hydroxyl and amine functional groups in its structure. Chitosan offers antibacterial properties due to the presence of amino group at C-2 position [3]. In a past work, hybrid ZnO/Chitosan nanoparticles were deposited on cotton fabric through

sonochemical treatment to offer high antibacterial activity to the cotton fabric [4]. However, after 10 washing cycles, the stability of the coating was severely affected. This work can be further improved by employing silane cross-linkers for anchoring the chitosan nanoparticles to the fabric for lasting durability. Therefore, for future work, there exists tremendous scope to utilise different antibacterial agents like chitosan nanoparticles or quaternary ammonium salts for antibacterial performance coupled with silane coupling agents for enhanced coating robustness and durability.

6.6 Reconnaissance work

Before arriving at the second synthesis technique mentioned in the thesis utilizing ZnO nanoparticles, APTES and HDTMS silane for obtaining superhydrophobic antibacterial fabrics, another route was explored. This route did not yield satisfactory results and was modified, which is how the second synthesis technique was derived.

The rationale behind the route was simple. It was desired to attach the CuO nanoparticles directly to the fabric, and then modify it with a low surface energy silane to obtain superhydrophobic antibacterial fabrics. While investigating different silane cross-linkers, a new class of silanes called the dipodal silanes looked promising. These dipodal silanes consist of two silane groups on both the ends instead of a terminal functional group, hence the name dipodal silanes. For serving as a cross-linker, a very simple dipodal silane molecule - 1,2-Bis(triethoxysilyl)ethane (BTESE) was chosen (Figure 6.1a). It was hypothesized that one silane group would bind to the hydroxyl groups on the cellulose structure, and the other would bind to the hydroxyl groups on the nanoparticle surface and therefore, attach the nanoparticles to the fabric surface. For hydrophobic modification, nonafluorohexyltriethoxysilane (FAS), a relatively short fluoro-alkyl silane was selected (Figure 6.1b).

A similar experimental methodology was followed as the previously mentioned techniques for synthesis. Pristine cotton fabrics were dipped in CuO-BTESE solution and were heat treated to obtain CuO-BTESE-Cotton fabrics. Upon conducting the experiment, the CuO nanoparticles attached successfully to the cotton fabric surface. The second step involved modifying it with FAS to achieve superhydrophobicity.

Figure 6.1 a) Silane cross-linker 1,2-Bis(triethoxysilyl)ethane (BTESE) b) Silane hydrophobe nonafluorohexyltriethoxysilane (FAS)

However, on dipping the CuO-BTESE-Cotton fabric in FAS, no surface modification took place. This was due to the inability of FAS to attach to the fabric surface. It was postulated that the extensive cross-linking of BTESE in the form of a network around the CuO nanoparticles and over the fabric surface prevented the attachment of FAS due to lack of hydroxyl groups available for attachment. One of the popular techniques to breakdown cross-linked chains involves the exposure to UV irradiation. To test the hypothesis, the CuO-BTESE-Cotton fabric was exposed to UV rays from a 470W lamp at a distance of 12 cm for few minutes, and then dipped in FAS for coating. The technique was successful, and the fabric surface turned superhydrophobic due to the successful attachment of FAS. The step-by-step process for synthesis of FAS-CuO-BTESE-Cotton fabrics is displayed in Figure 6.2.

Figure 6.2 Experimental methodology for synthesis of FAS-CuO-BTESE-Cotton fabrics

After the process finalization, the UV irradiation time was optimized to achieve the maximum superhydrophobic performance. The CuO-BTESE-Cotton fabrics were exposed to different time periods of 15, 30, 45, 60, 75 and 90 minutes of UV irradiation and then coated with FAS to evaluate the WCA and WSA. The variation of UV irradiation time with WCA and WSA values is displayed in Figure 6.3. From the figure, the WCA was highest for UV exposure of 30 minutes and declined for longer periods. Similarly, WSA was lowest for 30 minutes of UV irradiation, and increased for longer exposure times. Therefore, 30 minutes was considered as the optimum time for achieving highest superhydrophobic performance on the as-prepared cotton fabrics.

Figure 6.3 Variation of WCA and WSA of FAS-CuO-BTESE-Cotton fabrics with UV irradiation time

To confirm the hypothesis of extensive cross-linking by BTESE followed by scission of the cross-linked chains by UV exposure, FTIR analysis was carried out. CuO-BTESE-Cotton fabrics were exposed to 0, 30 and 60 minutes of UV and immediately subjected to FTIR to observe the changes in the chemical composition of the fabric (Figure 6.4). As can be seen in the figure, significant changes were obtained for various peaks. The peaks at 1105 and 1003 cm^{-1} correspond to asymmetric Si-O-C stretching [5] and Si-O stretching in $(\text{SiO})_n$ [5], respectively. The intensity of these peaks was reduced for fabrics exposed to UV, slightly more reduced for 30 minutes exposure as

compared to 60 minutes. These peaks are indicative of the possible cross-linking taking place between the various BTESE chains together as they correspond to Si-O-Si and Si-O-C linkages. The reduction in the peak intensity is an indicator of these bonds being broken down by the UV treatment. The peaks at 1261 and 801 cm^{-1} correspond to symmetrical deformation vibration of CH_3 in Si-CH_3 , [6, 7] and rocking of CH_3 in $\equiv\text{Si-CH}_3$ [6], respectively. The intensity of these peaks was increased for fabrics exposed to UV, slightly more increased for 30 minutes exposure as compared to 60 minutes. The increase in the intensity of the peaks indicate that the scission of the Si-O-Si and Si-O-C groups has resulted in the formation of more Si- CH_3 groups, reducing the extensive cross-linking and probably exposing surface of the fabric and the CuO nanoparticles facilitating FAS attachment after UV exposure. Therefore, FTIR analysis confirmed the procedure and mechanism behind this route of fabrication.

Figure 6.4 FTIR spectra displaying the effect of UV exposure on CuO-BTESE-Cotton fabrics

However, few drawbacks were identified with this fabrication route, and are given below:

- Upon conducting the antibacterial assessment to evaluate the antibacterial activity of the as-prepared fabrics, a lot of nanoparticle release was observed, revealing the poor durability of the fabric.

- The stability of the silane hydrophobe FAS was quite poor. After 2-3 months of use, the FAS stopped functioning, and continuously new FAS had to be purchased which revealed that FAS had a poor stability as it expired much before its expiry date.

Due to the above-stated drawbacks, the technique was modified. APTES was used instead of BTESE as a silane cross-linker as it had shown a lot of stability during the first synthesis technique. HDTMS was used to replace FAS as it not only had better stability but was also an eco-friendlier variant of the silane hydrophobe.

However, upon using APTES as a silane cross-linker, it was found that UV exposure was no longer a requirement to achieve superhydrophobicity. The HDTMS chains could easily attach to the APTES-treated fabric due to the presence of the free amino groups. Therefore, the technique was simplified even further to arrive at the second synthesis technique using ZnO nanoparticles, APTES silane cross-linker and HDTMS silane hydrophobe.

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