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M.Sc. in Textile Engineering

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**REPUBLIC OF TURKEY**

**GAZİANTEP UNIVERSITY**

**GRADUATE SCHOOL OF NATURAL & APPLIED SCIENCES**

# DEVELOPMENT OF FUNCTIONAL TECHNICAL TEXTILES WITH $TiO_2$ NANOPARTICLE BASED NANOCOMPOSITES & NANOHYBRIDS

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**June 2020**

**I hereby declare that all information in this document has been obtained and presented in accordance with academic rules and ethical conduct. I also declare that, as required by these rules and conduct, I have fully cited and referenced all material and results that are not original to this work.**

**Yeşim ÖZKOYUNCU**

## ABSTRACT

### DEVELOPMENT OF FUNCTIONAL TECHNICAL TEXTILES WITH $TiO_2$ NANOPARTICLE BASED NANOCOMPOSITES & NANOHYBRIDS

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**M.Sc. in Textile Engineering**
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The development of nanotechnology and its importance in the textile industry have been investigated in detail together with advancing technology every single day. Nanotechnology becomes very popular in textile finishing processes. It provides more functional properties in comparison with traditional textile applications. In this study, nano titanium dioxide ($TiO_2$) was coated with silver nanoparticles (Ag) and gold nanoparticles (Au). After preparing $TiO_2$@Ag, $TiO_2$@Au nano chemicals, their dimensional analyses were carried out. These nano chemicals were applied on cotton/polyester fabric with using the traditional pad-dry-cure and novel electrospraying methods. Processing conditions for the electrospraying method and properties of suspensions were determined. The electrospraying method provided less chemical agent usage compared to the traditional pad-dry-cure method. In addition, fabrics were modified with functional end group-containing carboxylic acids thiol (mercaptan) before they were coated with nano-chemicals in order to form a strong covalent bond of metal-sulphur (M-S) between nano chemicals and the thiol groups in the functional end on the surface of fabrics. The water contact angle measurements were conducted for the control and the coated fabrics. Superhydrophobic fabric surfaces were successfully obtained for the coated fabrics. Nano $TiO_2$, $TiO_2$@Ag, $TiO_2$@Au chemicals have also a photocatalytic property. Therefore, the satisfactory self-cleaning properties for the coated fabrics have been observed under UV light. The fabric comfort properties were interpreted by testing the water vapor transmission rate (WVTR) and air permeability of the modified fabrics. Our results suggested that the comfort characteristics of the coated fabrics did not change significantly compared to the control fabric. Antibacterial properties of the coated fabrics with $TiO_2$, $TiO_2$@Au, and $TiO_2$@Ag nano chemicals were determined. Also, the durabilities of the obtained functionalities on the surface of the coated fabrics were examined by means of SEM images taken before and after washing and abrasion treatments. Our results showed that the coating is durable and the coated fabrics are highly antibacterial with other desired functional properties.



**Key Words:** Nanotechnology, Nano $TiO_2$, Nano Au, Nano Ag, Nano $TiO_2$@Ag, Nano $TiO_2$@Au, Thiol, Pad-Dry-Cure, Electrospraying, Superhydrophobic, Antibacterial, Self-Cleaning Fabric, Medical Textiles

# ÖZET

## $TiO_2$ NANOPARÇACIK BAZLI NANOKOMPOZİTLER & NANOHİBRİTLER İLE FONKSİYONEL TEKNİK TEKSTİLLERİN GELİŞTİRİLMESİ

**ÖZKOYUNCU, Yeşim**
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Gün geçtikçe ilerleyen teknoloji ile birlikte, nanoteknolojinin tekstil endüstrisinde önem kazanması detaylı olarak araştırılmıştır. Nanoteknoloji, tekstil bitim işlemlerinde oldukça popüler hale gelmekte olup geleneksel uygulamalara kıyasla daha fazla fonksiyonel özellik kazandırmaya yardımcı olmaktadır. Bu çalışmada, nano boyutta titanyum dioksit ($TiO_2$), nano boyuttaki gümüş (Ag) ve altın (Au) ile kaplanmıştır. Hazırlanan $TiO_2$@Ag, $TiO_2$@Au nano kimyasallarının boyutsal analizleri yapılmıştır. Bu nanokimyasallar, geleneksel emdirme-kurutma ve yenilikçi elektrospreyleme yöntemleri kullanılarak pamuk/polyester kumaş üzerine kaplanmıştır. Elektrospreyleme yöntemi için gerekli işlem koşulları ve süspansiyonların özellikleri belirlenmiştir. Elektrospreyleme yöntemi, geleneksel emdirme-kurutma yöntemine kıyasla daha az kimyasal ajan kullanımı sağlamıştır. Ayrıca kumaş, nanokimyasallar ile kaplanmadan önce tiyol (merkaptan) fonksiyonel uç grubu içeren karboksilli asitler ile modifiye edilerek, kumaş yüzeyinde fonksiyonel uç halinde oluşturulan tiyol gruplarının nano kimyasallar ile kuvvetli metal-kükürt (M-S) kovalent bağ oluşturması sağlanmıştır. İşlem görmemiş kumaş ve kaplanmış kumaşlar için su temas açısı ölçümleri yapılmıştır. Süperhidrofobik kumaş yüzeyleri, kaplanmış kumaşlar için başarıyla elde edilmiştir. Nano $TiO_2$, $TiO_2$@Ag, $TiO_2$@Au kimyasallarının fotokatalitik etkiye sahip olması sebebiyle, yapılan kumaş kirletme deneyleri sonrası UV ışık altında kaplanmış kumaşların tatmin edici derecede kendini temizleme etkisi gözlemlenmiştir. Modifiye edilmiş kumaşların su buharı iletim oranları (WVTR) ve hava geçirgenlikleri test edilerek kumaş konfor özellikleri belirlenmiştir. Sonuçlar, kaplanmış kumaşların konfor özelliklerinin işlem görmemiş kumaş ile karşılaştırıldığında önemli ölçüde değişmediğini göstermektedir. $TiO_2$, $TiO_2$@Au ve $TiO_2$@Ag nanokimyasalları ile kaplanan kumaşların antibakteriyel özellikleri tayin edilmiştir. Ayrıca, yapılan kaplamanın dayanıklılığı, yıkama ve aşınma işlemlerinden önce ve sonra alınan SEM görüntüleri ile incelenmiştir. Elde edilen sonuçlar, kaplamanın dayanıklı olduğunu ve yüksek antibakteriyel özellikle beraber diğer fonksiyonel özellikleri barındırabildiğini göstermiştir.



**Anahtar Kelimeler:** Nanoteknoloji, Nano $TiO_2$, Nano Au, Nano Ag, Nano $TiO_2$@Ag, Nano $TiO_2$@Au, Tiyol, Emdirme-Kurutma Yöntemi, Elektrospreyleme, Süperhidrofobik, Antibakteriyel, Kendini Temizleyen Kumaş, Medikal Tekstiller

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| | |
|---|---|
| **$TiO_2$** | Titanium Dioxide |
| **Au** | Gold |
| **Ag** | Silver |
| **ES** | Electrospray |
| **PDC** | Pad-Dry-Cure |
| **SEM** | Scanning Electron Microscope |
| **NNI** | National Nanotechnology Initiative |
| **WCA** | Water Contact Angle |
| **TCD** | Tip to Collector Distance |
| **DMSO** | Dimethyl Sulfoxide |
| **DMF** | Dimetilformamid |
| **$H_2SO_4$** | Sulphuric Acid |
| **ZnO** | Zinc Oxide |
| **$CeO_2$** | Cerium Oxide |
| **$MgCl_2$** | Magnesium Chloride |
| **$SiO_2$** | Silicon Dioxide |
| **$ZrO_2$** | Zirconium Oxide |
| **$AgNO_3$** | Silver Nitrate |
| **$HAuCl_4.3H_2O$** | Gold(iii) Chloride Hydrate |
| **$NaBH_4$** | Sodium Borohydride |

# CHAPTER 1

# INTRODUCTION

Nanotechnology is not nearly the size of very little things this is the revolutionary science and all importance at the molecular scale. The practical applications of nanotechnology are far-reaching and could include medical, military applications, computing, and astronomy which takes place on a tiny scale - larger than the level of atoms and molecules, but within the range of 1-100 nanometers. The objective of nanometer technology is to produce products of special functions with new physical and chemical features by making atoms, molecules, and matters presenting their features directly in the length of a nanometer (Rezaei and Mosaddeghi, 2006).

At the present time, there is a new revolution in the textile industry with the apparition of new technologies that could add significant functions and properties to the textile materials. Textile coloring, digital printing on textiles, smart fabrics, and high-performance functional textiles have been positioned in development in the textile industry (Rivero et al., 2015). The nanoparticles are salutary used in finishing for obtaining soil release; stain resistance; water repellent; flame retardation; self-cleaning; wrinkle resistance; moisture management; antibacterial, antistatic, and UV protection; improvement of dyeability, etc. So, inclusion nanoparticles into a textile can affect a lot of properties, including shrinkage, strength, and electric and thermal conductivity (Mishra and Militky 2019).

Several scientific studies available in the world have been inspired by nature. The hydrophobic surface can be defined as the non-wettable surface which means that water contact angle (WCA) is higher than 90° between the hydrophobic surface with a water droplet. A high static water contact angle and a low sliding angle provide the high-water repellent surface that means a superhydrophobic surface which has contact angles of water droplet above 150°. Lotus leaf is an inherently hydrophobic material which has a micron-level rough surface and epicuticular wax on the leaves which are defined as superhydrophobic. On the other hand, achieved a the superhydrophobic

surface that has about 150 that wash the dirt off on the surface by water droplets roll off easily that keep the surface clean themselves (Acatay et al. 2004; Lee and Michielsen 2006; Mishra et al. 2019).

Self-cleaning is one of the functional technologies inspired by nature that draws great interest all over the world by reason of its wide range of applications. A lot of surface in nature reveals self-cleaning property on surfaces which can prove being cleaned themselves without any laundering actions. Self-cleaning textiles can be carried out by two strategies. Firstly, the superhydrophobicity effect supports the self-cleaning property. When considering the lotus leaves, that have high water contact angle with invisible nano roughness on the surface and low sliding angle. Nearly spherical water droplets take place on their surfaces which can move in all directions without constraint and then pick up dirt particles on the leaf surface. And the second strategy is these surfaces have photocatalysis property (Ganesh et al., 2011; Liu and Jiang, 2012). With decreasing cleaning efforts, reducing the consumption of water and energy, saving time and laundering cost, and being environmentally friendly with providing these features, the Self-cleaning notion makes a contribution in various industries not only in the clothing industry (Saad et al., 2016).

Microorganisms are present everywhere all around the earth even inside human bodies which have a great number of types. Textile materials are along about suitable for the growth of microorganisms due to the natural features of the textiles are exposed to heat and moisture during their usage of in daily life. Antibacterial term amounts to an agent that either kills various microorganisms or decelerate the growth of these organisms. Many nanoparticles show the antimicrobial effect that has metal and metal oxides properties as silver, titanium dioxide, zinc oxide, and copper II oxide (Hardin and Kim, 2016; Ibrahim, 2015; Zille et al., 2014).

Electrospray can achieve success to guide for the development of nanotechnology. Production of nanoparticle, microparticle, and their thin-film occurrence and nanocapsule, microcapsule formation can be effectually taking place by the electrospray method. Being more environmentally friendly, inexpensive operating costs, low material utilization of electrospray provides many versatile advantages which can be devised that electrospraying will increasingly be used in the medical field, food industries, biotechnology, microelectronics, and modern material

technologies. Filters, biological tissue, mask, intelligent garment producing are manufactured by electrospinning production (Jaworek and Sobczyk, 2008).

### 1.1 The Aim of the Thesis

The purpose of this thesis is to develop and produce advanced technical textile products by preparing nanoparticles and nano-sized coating them on the textile surface with electrospray applique method that is different from the traditional textile coating method. Electrospraying is a recently developed, easy, and less expensive method of wet textile finishing application. Also, the electrospray method allows a very low amount of chemical uses so that is environmentally friendly since chemical material will not be wasted at the end of the process. In this way, that is aimed at high functional efficiency on the textile surface with very little chemical usage by coating at the nano-level. And practically, advantages and disadvantages were compared between the most commonly used traditional pad dry methods with the electrospray method.

With the application of nanomaterial on the fabric surface, nano-size roughness to be formed on the surface which provides increasing of the contact angle between water and fabric surface, thus superhydrophobic property was obtained on the surface and thus providing the self-cleaning function feature has been supported. Considering that the self-cleaning feature can be achieved in two ways on the surface, firstly the surface roughness provides a high contact angle of the surface that separates the stain from the fabric surface with low-level effect and the second way is a photocatalytic effect. The self-destruction of the stains is provided on the fabric surface under UV light by the photocatalytic effect. Photocatalysts are defined as substances that promote reactions by absorbing the light without being altered themselves. Titanium dioxide is an excellent photocatalyst with applications in various fields. The first step of the study was also determined as the synthesis of $Au@TiO_2$ and $Ag@TiO_2$ nanoparticles by a coating of nano $TiO_2$ with Au and Ag nanoparticles that show photocatalytic properties themselves. Antibacterial properties on the fabric that is intended by used nanometals (Au, Ag).

The second step of the study is to determine the electrospraying parameters and suspension concentrations for prepared nano $TiO_2$, $TiO_2$@Au, and $TiO_2$@Ag nano chemicals to apply them for cotton/polyester woven fabrics.

At the same time, the fabrics were treatment with carboxylic acid (COOH) containing the thiol (SH) functional group before coating with the nanomaterial. The fabric surface containing thiol end groups make metal-sulphur (M-S) strong covalent bond with nanomaterials that was determined as another aim for increasing strength of coating fabrics.

## 1.2 Structure of the Thesis

The literature review about the development of nanotechnology, implementations of textile with obtaining functional properties due to using of nanotechnology, dwelled on especially water repellency and self-cleaning of the textile, other enhanced features of textile through nanotechnology applications and application method as electrospray, padding, and parameter of them that given is given in Chapter 2. In Chapter 3, our study is explained in detail. Materials and methodology, analysis of prepared nanoparticle material for establishing of coating of nanoparticle, application of them over the fabric with electrospray and padding method, and various testing of coated fabric for proving intended to obtain functional properties as the superhydrophobic and self-cleaning effect that are imparted. Chapter 4 is another study about the antibacterial effects of coating fabrics with prepared nanomaterials with also electrospraying and padding methods. The antibacterial effect is discussed after washing fastness tests and various comfort tests are applied coated fabrics with nanomaterials. In chapter 5, the conclusions of this study and recommendations for further studies are presented.

# CHAPTER 2

# LITERATURE REVIEW

## 2.1 Nanomaterials

Nanotechnology mentions the branch of science and engineering which comprises producing, devices, structures, and systems by directing atoms and molecules at the nanoscale, i.e. having one or more dimensions of the order of 100 nanometers or less which is defined by the National Nanotechnology Initiative (NNI). Nanotechnology is the research of extremely small structures (Mishra and Militky, 2019). The prefix "nano" word comes from Greek what means "dwarf". The word "nano" describes very small or so little size (Nikalje, 2015).

The improvement in the field of nanotechnology commenced in 1958 and that development has been shown in Table 2.1 (Nikalje, 2015). Feynman made speech who called "There's plenty of room at the bottom" to the American Physical Society's West Coast section. He created a vision of what would later be called nanotechnology, imagining "that we could arrange atoms one by one, just as we want them" (Sawhney et al., 2008).

**Table 2.1** Periodical development in nanotechnology (Nikalje, 2015)

| *Year* | *Development in Nanotechnology* |
|---|---|
| ***1959*** | R. Feynman initiated the thought process |
| ***1974*** | The term nanotechnology was used by Taniguchi for the first time. |
| ***1981*** | IBM Scanning Tunneling Microscope |
| ***1985*** | "Bucky Ball" |
| ***1986*** | The first book on nanotechnology Engines of Creation published by K. Eric Drexler, Atomic Force Microscope |
| ***1989*** | IBM logo was made with individual atoms |
| ***1991*** | S. Iijima discovered Carbon Nanotube for the first time. |
| ***1999*** | 1st nanomedicine book by R. Freitas "Nanomedicine" was published |
| ***2000*** | For the first time, the National Nanotechnology Initiative was launched |
| ***2001*** | For developing theory of nanometer-scale electronic devices and for synthesis and characterization of carbon nanotubes and nanowires, Feynman Prize in Nanotechnology was awarded |
| ***2002*** | Feynman Prize in Nanotechnology was awarded for using DNA to enable the self-assembly of new structures and for advancing our ability to model molecular machine systems. |
| ***2003*** | Feynman Prize in Nanotechnology was awarded for modeling the molecular and electronic structures of new materials and for integrating single molecule biological motors with nano-scale silicon devices. |
| ***2004*** | The first policy conference on advanced nanotech was held. The first center for nanomechanical systems was established, Feynman Prize in Nanotechnology was an award for designing stable protein structures and for constructing a novel enzyme with an altered function. |
| ***2005-2010*** | 3D Nanosystems like robotics, 3D networking, and active nano products that change their state during use were prepared. |
| ***2011*** | The era of molecular nanotechnology started |

Commonly used prefixes for the various powers of 10 are listed in Table 2.2. Prefixes according to the International System of Units (SI) give multiples of that unit.

Table 2.2 Some prefixes for SI Units

| | | |
|---|---|---|
| *yotta (Y)* | $10^{24}$ | 1 septillion |
| *zetta (Z)* | $10^{21}$ | 1 sextillion |
| *exa (E)* | $10^{18}$ | 1 quintillion |
| *peta (P)* | $10^{15}$ | 1 quadrillion |
| *tera (T)* | $10^{12}$ | 1 trillion |
| *giga (G)* | $10^{9}$ | 1 billion |
| *mega (M)* | $10^{6}$ | 1 million |
| *kilo (k)* | $10^{3}$ | 1 thousand |
| *hecto (h)* | $10^{2}$ | 1 hundred |
| *deka (da)* | 10 | 1 ten |
| *deci (d)* | $10^{-1}$ | 1 tenth |
| *centi (c)* | $10^{-2}$ | 1 hundredth |
| *milli (m)* | $10^{-3}$ | 1 thousandth |
| *micro (μ)* | $10^{-6}$ | 1 millionth |
| *nano (n)* | $10^{-9}$ | 1 billionth |
| *pico (p)* | $10^{-12}$ | 1 trillionth |
| *femto (f)* | $10^{-15}$ | 1 quadrillionth |
| *atto (a)* | $10^{-18}$ | 1 quintillionth |
| *zepto (z)* | $10^{-21}$ | 1 sextillionth |
| *yocto (y)* | $10^{-24}$ | 1 septillionth |

The several nanoparticles, composites, coatings are produced by using physical, chemical, or mechanical process whom characteristics can be regulated surface tension, PH, concentration, processing of preparation, etc. Two major different approaches are used to get nanoparticles “top-down” and “bottom-up" strategies. Top-down approaches are used to produce structures with long-range order and for making macroscopic connections with mechanical comminution, while bottom-up approaches are more suitable for building up short-range by chemical processes order at nanoscale dimensions (Raab et al., 2011).

In recent times, nanotechnology has an important impact on its increasing multifarious applications. A wide area of usage of nanotechnology takes place in branches of science, technology, and industry such as material and material science, chemistry, biology, medicine, buildings industry, environmental science, textile, physic science,

etc. which can provide unknowingly a lot of advantage in our daily lives. Sunglasses, wrinkle-free shirts, computer hard drives, even cosmetic products are some of them (Chaurasia, 2017).

### 2.1.1 Nanotechnology Applications in Textiles

Nanoparticles have all-purpose applications in the textile industry. Frequently, finishing processes in textile can salutarily answer the purpose of the selected nanomaterials. Particles at nano-scale that are used in finishing for obtaining water repellent coatings, antistatic treatment and UV protection, flame retardant, antibacterial, wrinkle resistance, self-cleaning, insect protection and so on (Joshi and Bhattacharyya, 2011; Wong et al., 2006; Yetisen et al., 2016). Nanotechnology applications in the textile branch usually in this way; carbon nanotubes, aerogels, nanofibrous layer, zeolites, dendrimers, self-assembled monolayers, nanoparticles textiles (Yetisen et al., 2016).

The intended use of nanotechnology in the textile industry is lower energy consumption, chemical usage that is to say accordingly which provides low cost, high performance. Because of these reasons, these advantages increase the preference of nanotechnology (Black, 2009).

#### 2.1.1.1 Water Repellence

Water repellency has been becoming like one of the major goals for textile finishing by textile scientists and manufacturers for centuries which gain importance when considering the end use of the textile (Park et al., 2015). Water repellent textiles mean to repel water from the on the textile surface that describes how well a fabric resists the absorption, adsorption, and penetration of water on the surface of a fabric. The contact angle between water and the fabric surface is measured and that identify quantitatively surface energy of the substrate method. Water repellency textiles as distinct from waterproof textiles have diminished surface tension via a hydrophobic compound which is permeable to water vapor and air due to having not filing pores on the textile surface with finishing treatment. Droplets of water are situated spherical

shape on the textile surface. The tendency of textiles to resist wetting come to existence by a high static water contact angle (WCA) and a low sliding angle (Bashari et al., 2018; Chinta et al., 2013; Park et al., 2015).

In 1805, Thomas Young explain surface wettability consisting of the contact angle θ by analyzing the forces acting at a fluid droplet on the solid surface encircled by a gas which shows the thermal dynamic equilibrium relations of interface energy of the surface. Young's Equation is on the basis of an impeccable system where the solid surface is smooth and homogeneous (Park et al., 2015; Yan et al., 2011). The contact angle, $\theta_C$, is the angle formed by a liquid at the three-phase boundary where the liquid, vapor, and solid intersect in showed Figure 2.1.

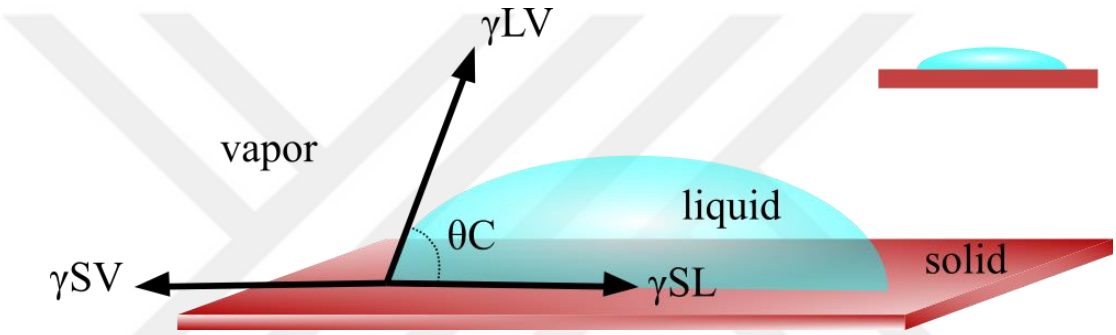



**Figure 2.1** Young's model for static contact angle in relation to interfacial tensions of solid/liquid/vapor phases

Young's equilibrium (Equation 2.1) clarifies the wettability of the surface under fluid drops with the relationship of static contact angle, the interfacial tension between solid and vapor phases, and interfacial tension between the liquid and vapor phases which is fundamentally a force balance in the horizontal direction. (Lee and Michielsen, 2006).

$$\gamma SV = \gamma SL + \gamma LV \cos\theta C \qquad (2.1)$$

where

γSV Interfacial tension between the solid and vapor,

γSL Interfacial tension between the solid and liquid,

γLV Interfacial tension between the liquid and vapor,

θC Contact angle of water on the surface.

The surface has less than 90° water contact angle, in that case, the surface is defined as "hydrophilic" which gives a strong affinity to water. Though, when the contact angle is greater than 90° at that the surface is defined as "hydrophobic" that show strongly repels toward the water. Superhydrophobic surfaces, such as the leaves of the lotus plant, the contact angle of a water droplet with the surface is bigger than 150° and these are shown in Figure 2.2 (Latthe et al., 2014; Özdoğan et al., 2006).

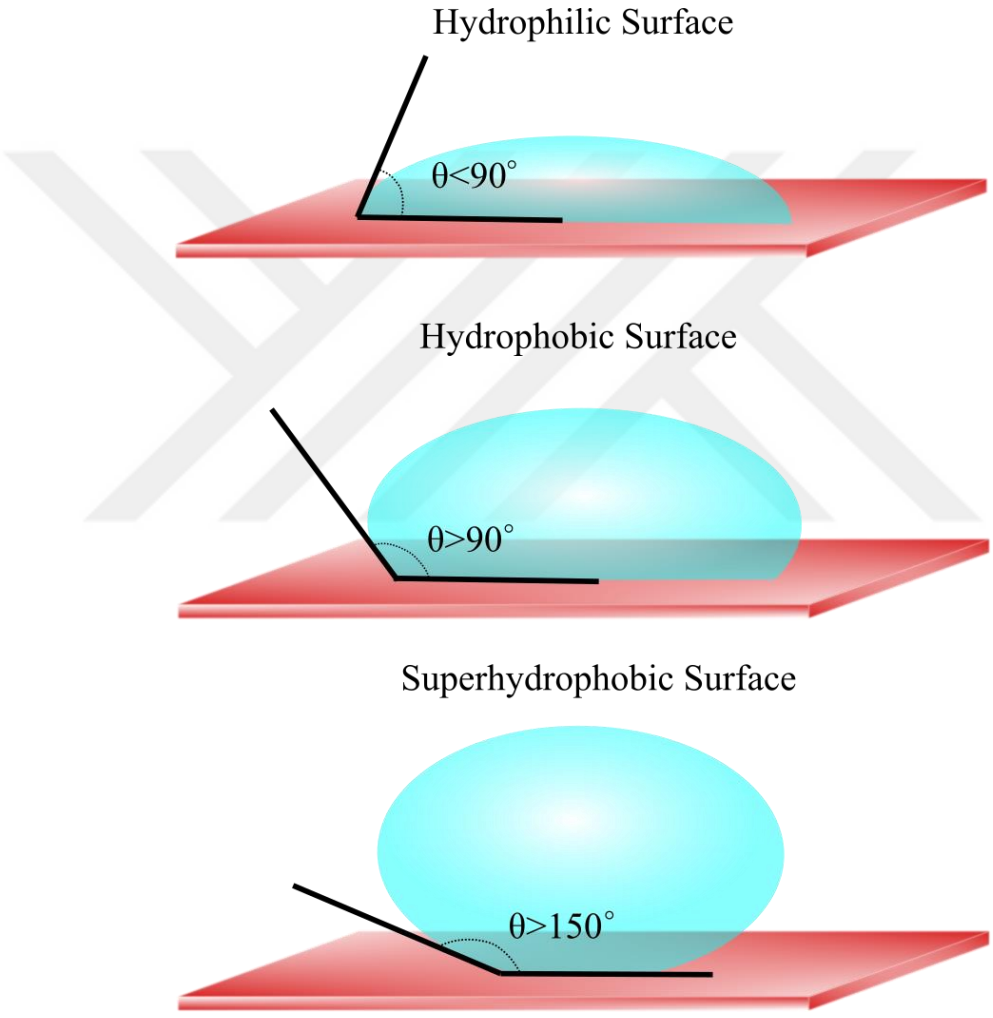



**Figure 2.2** Hydrophilic surface, hydrophobic surface and superhydrophobic surface with their water contact angles

In this case, the wettability of the surface is established by the chemical structure of the solid surface. According to Young's Theorem, at an equilibrium state, a solid phase

with low surface free energy (γSV) would give large interfacial tension (γSL) of the solid surface and fluid drop, and the large static contact angle of the liquid phase. Consequently, superhydrophobic textiles can be constituted with lowering the free surface energy of the solid surface with using repellent agents for the surface without making creating roughness at the surface (Bhushan et al., 2009; Karunakaran et al., 2011; Lee and Michielsen, 2006; Park et al., 2015; Yan et al., 2011).

Young's model has a limitation explanation about solid surface wettability by reason of many solid surfaces hold certain about roughness in daily life. The Wenzel and Cassie Baxter models are commonly employed to correlate surface roughness with the existing water contact angle(Liu and Jiang, 2012; Wenzel, 1936). In 1936, Wenzel's model is described a model to clarify the relationship between surface roughness and contact angle that more certain estimate about wettability for the uneven surface Wenzel's Model is described by the following equation (Equation 2.2):

$$\cos\theta W = r \cos\theta Y \tag{2.2}$$

where θW is the apparent contact angle in the Wenzel model, θY is Young's contact angle, and r is the surface roughness factor given by the ratio of rough to planar surface areas (Wenzel, 1936).

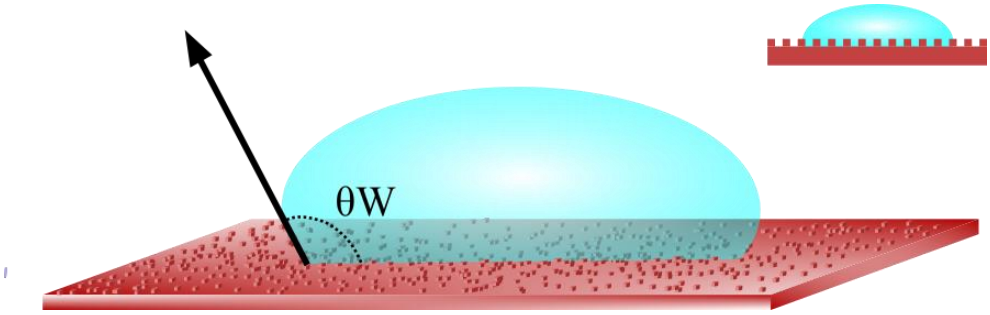



**Figure 2.3** Wenzel's model

In the Wenzel model (Figure 2.3), the fluid droplet is contacted with the solid surface so (r) is always greater than one. A hydrophobic surface (θY > 90◦) becomes more hydrophobic (θW > θY) when rough, whereas a hydrophilic surface (θY < 90◦) shows increased hydrophilicity (θW < θY). Wenzel expressed that with an increased surface roughness;

- a hydrophobic surface will become more hydrophobic,
- a hydrophilic surface will become more hydrophilic.

Despite the fact that trend is generally made a deduction, the Wenzel model is not enough when one is dealing with a heterogeneous surface so the Cassie-Baxter model was proposed (Liu and Jiang, 2012; Özdoğan et al., 2006; Park et al., 2015; Wenzel, 1936).

In the case of the Cassie-Baxter model, this is supposed the heterogeneous contact where the liquid is not completely in contact with the surface due to the tamped air pocket between the fluid droplet and the surface for more complicated systems that are representative of water-surface relations in nature. Trap air between the water droplet and the surface is considered for Cassie and Baxter equation that is described by the following equation (Equation 2.3) (Cassie and Baxter, 1944):

$$\cos\theta CB = fs\,(\cos\theta Y + 1) - 1 \qquad (2.3)$$

where,

θCB contact angle of water predicted by Cassie-Baxter's model

*f*s the surface fraction of the solid

θY contact angle at the flat surface (from Young's model).

Cassie-Baxter's research explains that obtaining superhydrophobic surfaces can be carried out with using the single method which reduces free surface energy that provides to enlarge the contact area between liquid and air with small-scale roughness on the surface. Cassie Baxter's model is shown in Figure 2.4 (Cassie and Baxter, 1944; Liu and Jiang, 2012).

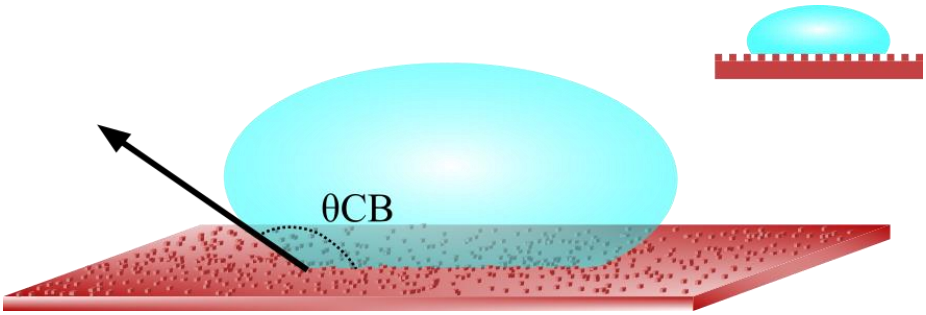



**Figure 2.4** Cassie Baxter's model

Chen et al. (2018) applied successfully nano-$TiO_2$ and the combination of polyvinyl silsesquioxane (PVS) on the cotton fabric for UV-blocking, superhydrophobic characteristic. They have prepared $TiO_2$ nanosuspensions at various ratios, and have used nano-$TiO_2$ particles in the PVS film layer on the surface of cotton fibers by covalent Ti–O–Si bonds. Water repellent properties of the functional cotton fabrics have been developed with an increase in the amount of add-on by them. SEM micrographs of the functional cotton fabrics treated with composite coatings of the PVS polymer and nano-$TiO_2$ with an increasing amount (Figure 2.5).

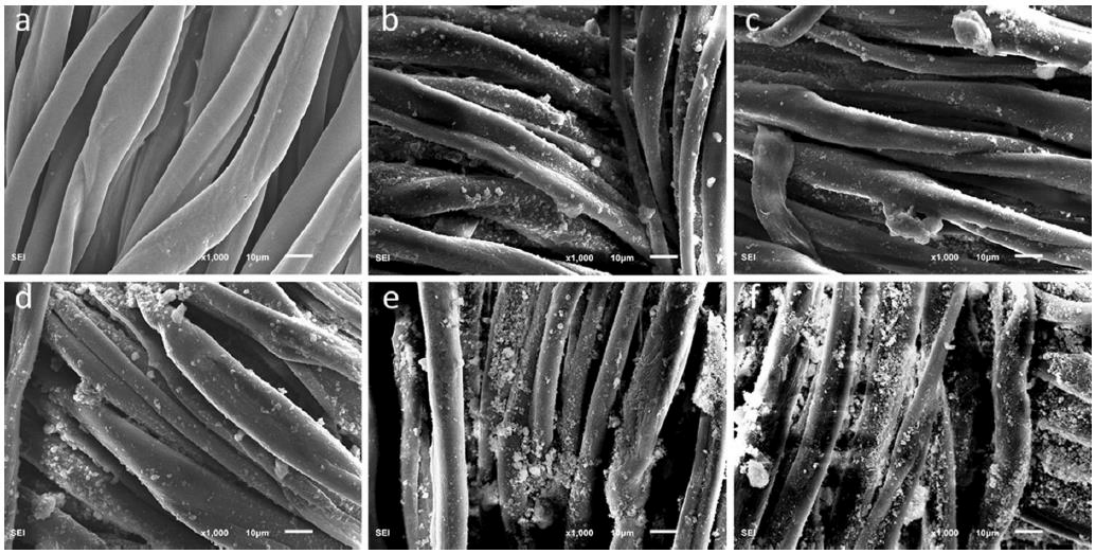



**Figure 2.5** SEM micrographs of the functional cotton fabrics treated with composite coatings of the PVS polymer and nano-$TiO_2$ a) cotton fabric without nano $TiO_2$ b) 0.5% w/v nano $TiO_2$ c) 1% w/v nano $TiO_2$ d) 2% w/v nano $TiO_2$ e) 3% w/v nano $TiO_2$ f) 5% w/v nano $TiO_2$

Their measurement of the water contact angles has been taken as from 152° for 0.5% w/v nano $TiO_2$ to 162° for 5% w/v nano $TiO_2$. They have reported the composite coatings combined with the PVS polymer and nano-$TiO_2$ can demonstrate high superhydrophobicity for the cotton fabrics.

Montazer et al. (2013) have treated a cotton fabric with nano titanium dioxide and have used 1,2,3,4 butane tetracarboxylic acid as a cross-linking agent. They measured the water drop absorption time by treated cotton fabric with $TiO_2$ nanoparticles that are shown in Figure 2.6.

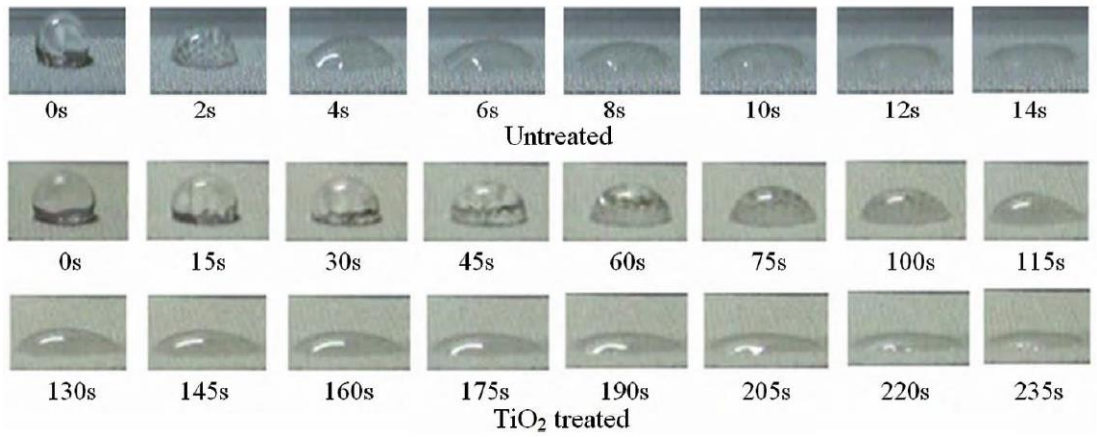



**Figure 2.6** Waterdrop absorption time with untreated nano $TiO_2$ and treated nano $TiO_2$

Nano $TiO_2$ application constituted a nano rough layer on the cotton fibers. For bleached and mercerized cotton fabric without untreated, the existence time of water droplet has taken 14 seconds, in spite of that, treated this cotton fabric with $TiO_2$ nanoparticles has held about 235 seconds water drops. In this study with these results, obtaining the superhydrophobic surface was occurred with coating $TiO_2$ nanoparticle through creating nano roughness.

Pakdel et al. (2013) used nano $TiO_2$ and $TiO_2/SiO_2$ nano compounds at various ratios by low-temperature sol-gel method on the 100% wool fabric in their study. They have prepared nano $TiO_2$ suspensions with blended TTIP, acetic acid, hydrochloric acid, and distilled water. $TiO_2/SiO_2$ nanocomposite suspensions have taken 70:30, 50:50 and 30:70 concentration ratios. The self-cleaning and hydrophilicity properties have analyzed by them on the wool fabric.

In their study, they have observed that present of silica in the suspension raised hydrophilicity characteristic with performed water contact angle measurements on the wool fabric surface. When $TiO_2/SiO_2$ at 70:30 ratio reduced slowly water contact angle, $TiO_2/SiO_2$ at 50:50 and 30:70 ratios created hydrophilic fabric and reduced water contact angle to zero. As shown in Figure 2.7, the untreated wool fabric has given 129.04° contact angle, with only applied $TiO_2$ nanoparticles water contact angle was taken 118.3°, increasing $SiO_2$ ratio, water contact has decreased firstly 111.1°

behind that have seen 0°. Figure 2.7 shows the water droplets on the wool fabrics with untreated and treated by prepared nanoparticles. Coated wool fabric with $TiO_2/SiO_2$ 50:50 and 30:70 suddenly have absorbed water droplets.

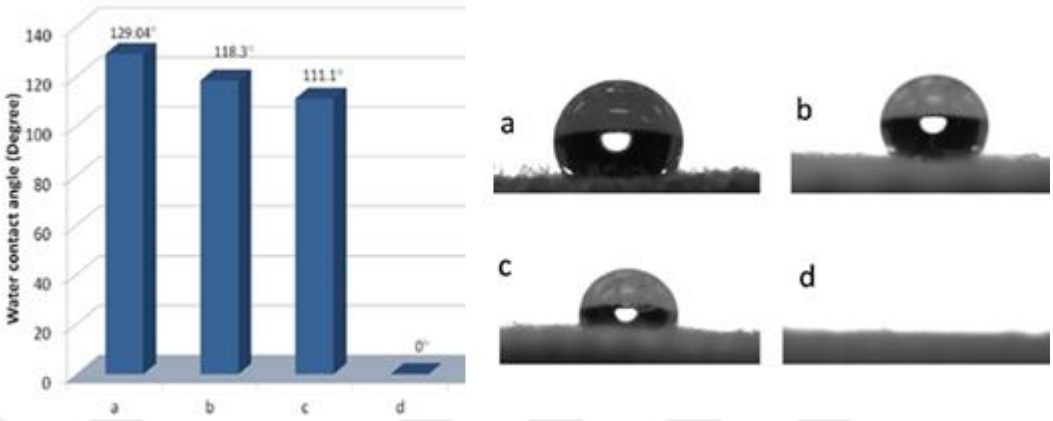



**Figure 2.7** Water contact angles and water droplets on wool samples: (a) untreated wool; wool fabrics treated with (b) $TiO_2$, (c) $TiO_2/SiO_2$ 70:30, (d) $TiO_2/SiO_2$ 50:50, or 30:70

In literature, the application of nanoparticle on the fabric generally provide hydrophobically characterization with the development of roughness at nano scaled on the surface. But in this article, the opposite state the result is investigated for finding direction in our own study. The research team has interpreted these results that the surface energy of wool fabrics has increased with increasing surface acidity providing a higher concentration of hydroxyl groups. Ti-O-Si bonds have provided a higher content of hydroxyl groups, due to, absorbing more hydroxyl groups on the surface of the photocatalyst.

Xue et al. (2008) prepared their suspensions as transparent bright $TiO_2$ by a traditional hydrolysis process with tetrabutyl titanate, and anhydrous ethanol, acetic acid, stearic acid, 1H, 1H, 2H, 2H perfluorodecyltrichlorosilane. They have coated the cotton fabrics by $TiO_2$ with padding in the ethanol suspension containing $TiO_2$ for 10 minutes. With obtaining surface roughness, they provided successfully superhydrophobic cotton fabric by measurement of water contact angle.

Ramaratnam et al. (2007) have purposed to obtain ultrahydrophobic coatings by using non-fluorinated silica nanoparticles and polymers to the fiber surface. Polyester fabric [poly (ethylene terephthalate) (PET)] is used in this study with the difference of other searched studies. Firstly, they have processed polyester fabrics with various solvents for removing other contaminants and any finishes, that is to say, fabrics were cleaned. After fabrics have been treated with sodium hydroxide (NaOH) for increasing the reactivity, by this means, carboxyl and hydroxyl groups have taken place on the fabric surface. Silica nanoparticles have been prepared with an ultrathin PGMA reactive layer that was deposited on the fiber surface. Carboxy, hydroxy functional groups have occurred on the nano-silica coated fabric. They have achieved a superhydrophobic surface by nano silica coating with taken higher from 150 water contact angle measurements. Also, nano coating surfaces have coated again with prepared polymeric solutions that have been shown more increasing water contact angles on the coated surface.

#### 2.1.1.2 Self-Cleaning Properties

Self-cleaning property is attracted attention by a lot of researchers, especially in the new smart textile industry. Self- cleaning textile can provide benefits by means of the ability to clean without need using any laundering (Ganesh et al., 2011). Nowadays, nanotechnology provides many approaches to the development of self-cleaning textiles which provides not only technically benefited in this sector, in daily life as well as fresh clothes, and also many benefits. At the same time, the self-cleaning properties of textiles can increase the durability of the fabric. (Bashari et al., 2018).

Two concepts for self-cleaning finishing of textiles become the main topic of conversation. In the first approach, superhydrophobic property on the surface with roughness at nano or microscale accompanied by low sliding angle provide dirt and pollutants retiring from the surface so the self-cleaning property is ensured which that is to say "lotus effect" (Özdoğan et al., 2006; Yan et al., 2011). The second approach is the photocatalytic characteristic on the surface. Some catalytic nanoparticles such as titanium oxide, zinc oxide, etc. which can chemically decompose pollutants and other impurities when exposed to sunlight. The UV light, oxygen, and air humidity are

required for the working of the function. These are inspired by the photosynthesis process in nature (Malik et al., 2018; Samal et al., 2015; Yuranova et al., 2006).

Barthlott and Neinhuis in the 1990s analyzed various kinds of lotus leaves who researched the effects of factors on the stain particle size, rain intensity and thus removing these pollutants with rolling of a water droplet on the surface that accordingly impact of self-cleaning on the superhydrophobic lotus leaf (Barthlott and Neinhuis, 1997). The lotus leaf has nanoscale and microscale a mass of closely packed points and trough on the surface morphology which is covered in a wax material due to could not adhering water droplets (Karthick and Maheshwari, 2008). Barthlott and his team identified and named "Lotus Effect" for a self-cleaning property on the surfaces, through that found out already in the 1970s (Barthlott and Neinhuis, 1997). In Figure 2.8., Scanning electron microscope image of the lotus leaf surface is shown and with a very low roll-off angle, dirt and pollutants are moved away.

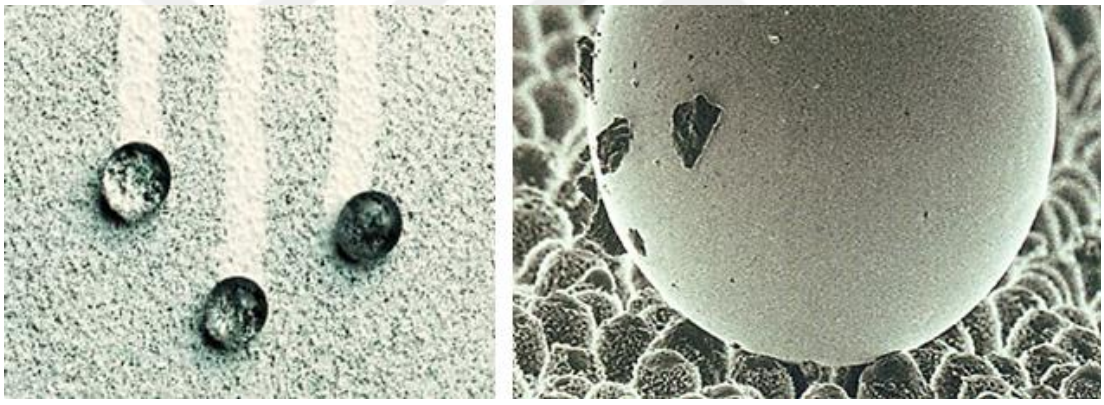


**Figure 2.8** SEM image of the lotus leaf surface and self-cleaning property with lotus effect (Özdoğan et al., 2006)

In the scope of the water repellency, water repellent mechanisms by nanoroughness surfaces are mentioned with theorems in the previous one title in this study. The Wenzel Equation and the Cassie–Baxter Equation models which explained the obtaining of the hydrophobic surface with roughness on the surface.

In the rough surface, dirt particles on the surface have very low adhesion energy due to the allow small contact area. As a result, superhydrophobic surface enables to take

out exactly pollutant against a smooth surface. The smooth surfaces have higher adhesion energy that provides an only change of location of dirt particle on surfaces that is not enough removing completely on the surface. The adhesion energy between the pollutant particle and the smooth surface is comparing with higher than between the particle and the water drop (Bashari et al., 2018). Removing of dirt on the surface with surface roughness and relocation of dirt particles on the smooth surface which is schematically shown in Figure 2.9.

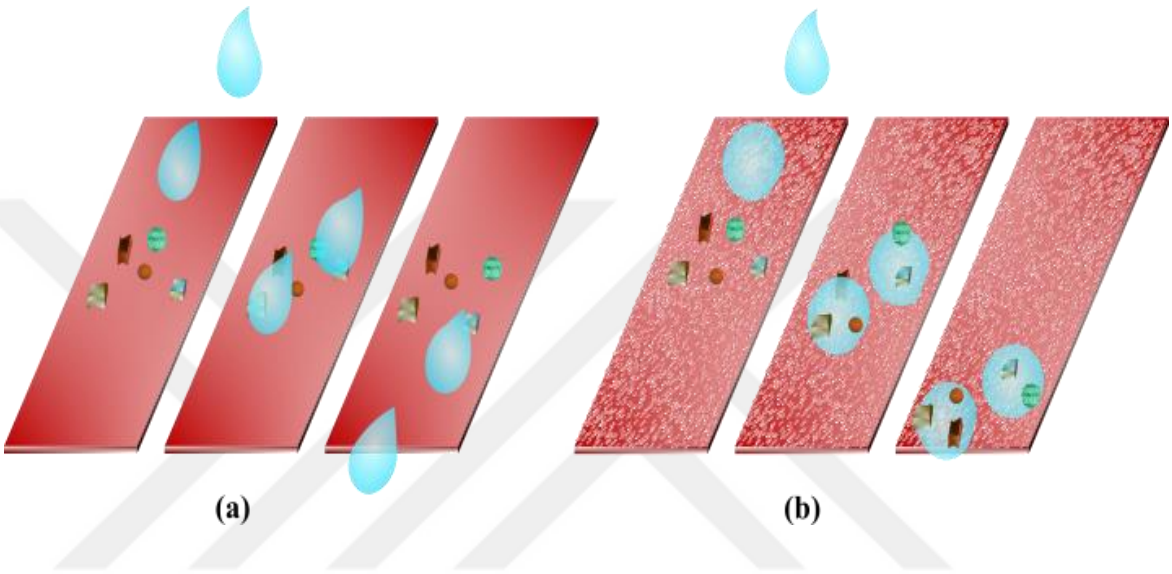



**Figure 2.9** (a) Smooth surface and (b) Rough surface for movement of the pollutant from the surface

The second approach is the photocatalytic characteristic on the surface for the self-cleaning property. Photocatalytic is a process that chemically breaks down dirt and other impurities by taking advantage of the exposing sunlight with photoreaction with the availability of catalyst which process is called “photocatalysis”. Photosynthesis process of the green leaves has constitutively been the source of inspiration with using sunlight for the photocatalytic process (Saad et al., 2016). Photoreaction cause for decomposing the organic impurities into air and water by photocatalysts (Banerjee et al., 2015).

In the mechanism of the photocatalytic reaction, ultraviolet light (UV) is used in the main for initiator reaction (Kumar, 2015). Stimulation of electron on the photocatalyst

surface has occurred with the energy equal to or higher than its band gap. These electrons run away from the valence band to the conduction band, guiding to the formation of electron-hole pairs in the surface-excited negative charged electrons (e-) in the carrying band, and the positively charged holes (H) in the valence band. Occurring pairs can get trapped or relink and give a reaction with other materials that induce redox reactions at the surface. The positive electric holes and water procure hydroxyl radicals ($OH^-$). The negative electrons (e-) and oxygen compound to form superoxide radical anions ($O_2^-$). In conclusion, carbon dioxide ($CO_2$) and water ($H_2O$) will be comprised of oxidizing organic compounds by highly active oxygen type (Figure 2.10). By this means, organic substances in the air such as bacteria, viruses, and odor molecules can be decomposed by photocatalyst (Castellote and Bengtsson, 2011; Saravanan et al., 2017).

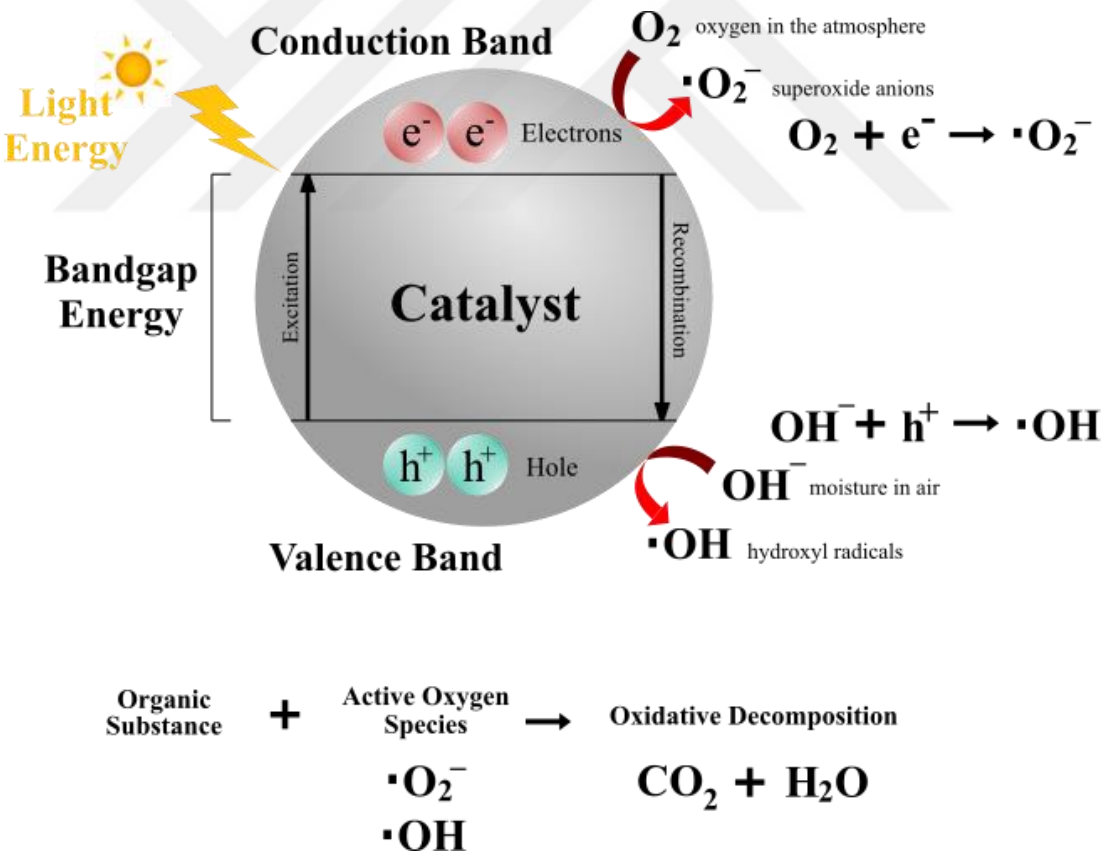



**Figure 2.10** Schematic exemplifications of semiconductor photocatalytic mechanism

Karimi et al. (2010) have aspired to obtain self-cleaning cotton fabrics through coated fabrics with $TiO_2$ nanoparticle. They have prepared various $TiO_2$ suspensions as 0.1, 0.3, 0.5, 1, and 1.5 weight percent and have used succinic acid for cross-linking agents to bind $TiO_2$ suspensions to the cotton fabric surface. As shown in Figure 2.11, in coating fabric without using the cross-linking agent, nanoparticle distributions on the surface have been seen more heterogeneous presence over the cotton surface.

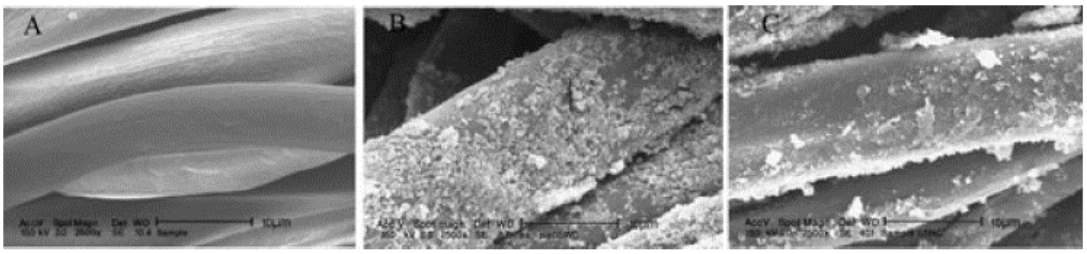



**Figure 2.11** SEM images of (A) untreated cotton fabric, (B) cross-link and (C) non-cross-link–coated cotton fabrics with 0.5% $TiO_2$

They have selected coating fabric with 1% $TiO_2$ in consequence of their taken results. They have used organic staining agents as tea and sour cherry juice under the radiation of 20 and 400 W lamps. According to their study, tea stains have been almost wholly extinguished, as to sour cherry stain have been critically removed. Here, using the cross-linking method surpass. Organic stains have photocatalytic broken up in contrast with synthetic stains. The effect of the wavelength of the ultraviolet light source was observed for photocatalytic self-cleaning tests in their study (Figure 2.12).

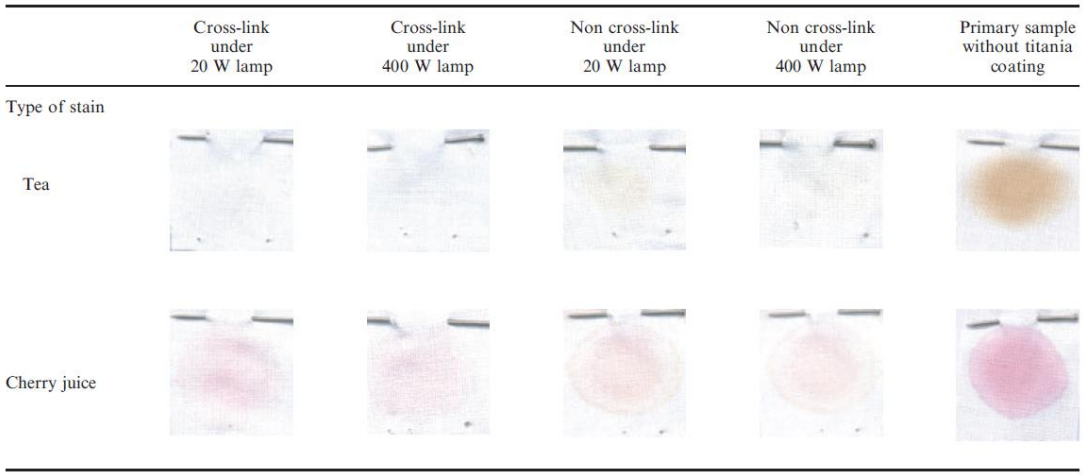



**Figure 2.12** Treated fabrics with 1% $TiO_2$ and self-cleaning study of them with stained with tea and sour cherry

### 2.1.1.3 Antibacterial Characteristic

Regenerated textile materials in addition to natural textile fibers convenient to grow odor-generating bacteria, such as Gram-negative and Gram-positive bacteria in spite of hydrophobic synthetic textile materials. On the whole, synthetic fibers have a high strength level to microbes due to this do not have antagonists which have developed to break them down. Many of them are more hydrophobic then natural fibers so they do not ensure necessary conditions for living microbes such as the moisture (Ibrahim, 2015). In addition, various textile processes, using auxiliaries and base fabrics until obtaining the final product which can show influence over the antimicrobial performance of the textile (Hardin and Kim, 2016).

Microorganisms on the textile materials which are hazardous organisms on human health that also cause unwanted odors, mildew, color changing, staining. For this reason, the marketplace for the antimicrobial characteristic shows an increase quickly by taking an interest in cleanliness and personal health. On this topic, antibacterial textiles benefit to prevent increasing of the negative effect of microorganisms on the human body such as allergic reactions, illness-causing organisms (Palamutcu et al., 2011). Textile materials in daily use, dress, carpets, curtains, clothes, towels, bed, bath, linens, upholstery fabric, pillows, etc provide living space for the microorganism

which can be expatriated on the human body. Used textile such as into hospital, sports industry, and in the military field is given priority (Bonin, 2008).

Bacteriostats and bacteriocides create two categories of antibacterial finishing agents according to their method of effect on dangerous bacteria. In this connection, established release mechanisms (i.e., leaching types) and contact formal (i.e., bacteria must contact the immobilized antibacterial agent) show the importance.

- Metals and metal salts,
- quaternary ammonium compounds,
- triclosan, chitosan,
- N-halamine, and peroxy acid,
- some dyes (organic or inorganic)
- immobilized enzymes, and
- inorganic nanostructured materials have been used to provide an antibacterial activity for textile materials (Dastjerdi and Montazer, 2010; Khalil-Abad and Yazdanshenas, 2010; Rodriguez et al., 2014).

#### 2.1.1.4 UV-Protection

Ultraviolet (UV) radiations, visible light, infrared (IR) radiation are findable in the sun's radiations. These radiations have a respectively different wavelength in nanometer. The primary source of UV radiations in nature is the sun. The UV radiation is classified into UVA, UVB, and UVC.

- 
- wavelength.
- UVB is the mid-strength UV wavelength in 280–320 nanometers.
- UVC is found in 200–280 nm range which is the weakest UV wavelength (Belkin et al., 1994).

UV light within 40 - 400nm range can cause various harms to organic matters. UVA is contributing to making premature skin aging and skin cancer, wrinkling, cataracts, and eye damage because of its possibility to penetrate into the dermis layer of human

skin. UVB only penetrates into the epidermis layer that can burn the superficial layers of skin. Meanwhile, UVC does not reach onto the earth that is absorbed by the ozone layer. The harmful impacts of ultraviolet (UV) radiation are having an increased effect on the world (Ramirez and Schneider, 2003).

Textiles can be used in sun-protection applications for many centuries. But many textile materials absorb ultraviolet radiation and come over a quick photolytic and photo-oxidative reaction that effects in their photodegradation. The energy of the photons in the ultraviolet region will be effective to break chemical bonds in these materials and to constitute free radicals. These getting free radicals give a reaction with polymers to obtain oxy and peroxy radicals and cause breaking out of chain until two free radicals are combined together and stable nonradical combinations are created (Schindler and Hauser, 2004).

UV-protective agents are used such as $TiO_2$, $CeO_2$, and ZnO in inorganic oxides which are having band gap energies conforming to absorption spectra and refractive index. For this reason, light below wavelengths has enough energy for electrons exciting and is absorbed by metal oxides. At the same time, light with wavelength longer than the band gap wavelength will not be absorbed (Tsuzuki and Wang, 2010).

#### 2.1.1.5 Anti-Static

Electrostatic charges build up on textile fibers due to the owned low humidity of textile materials and in dry conditions. Not only textile comfort properties, but static electricity is also an undesirable feature until the textile final product is obtained which can be dangerous in a flammable atmosphere. The synthetic fiber as nylon and polyester because due to their structures absorb lower water in spite of that cellulosic fibers have higher moisture that is a primary determinant for accumulating of static charge (Choudhury et al., 2011). Because of these reasons, the anti-static feature of textile materials has become significant. So, research study with respect to the development of the anti-static properties of textiles by using nanotechnology application was carried out. Electrically conductive nano chemicals can be used as anti-static agents. These conductive materials help to effectually spread the electrostatic charge which is accumulated on the textile surface. For instance, nao

titanium dioxide, zinc oxide, nano antimony-doped tin oxide, and silane nanosol could perform for anti-static properties to, especially synthetic fibers (Patra and Gouda, 2014).

On the other hand, an antistatic agent can use to eliminate static electricity build upon the surface usually caused by the triboelectric effect that looks like a surfactant effect; the hydrophobic area interacts with the surface of the material, while the hydrophilic side interacts with the moisture of the air and establishes bond the water molecules. Silane nanosol enhances anti-static properties, as the silane gel particles on fiber absorb moisture in the air by amino and hydroxyl groups and bound water (Xu et al., 2005).

#### 2.1.1.6 Wrinkle Resistance

Synthetics textile products have resistance to wrinkles by themselves and effectively stability due to they do not absorb water as efficiently such as polyester, nylon, acrylic, and olefin. But, cellulosic textiles such as cotton wrinkles easily and has the probability to shrink after laundering due to the hydrophilic characteristic of them and their chemical structure(Das et al., 2014).

Wrinkle resistance occurs to stop the molecules from moving when in contact with water or other external stress (Das et al., 2014). Various cross-linking can be used as chemical or physical for creating wrinkle resistance textile materials such as dimethylol dihydroxy ethylene urea (DMDHEU), dimethylol ethyltriazone, trimethylol melamine, and methylol urea agents. The other examples of cross-linking agents used in the wrinkle-resistant treatment include isocyanates, epoxides, divinyl sulphone, aldehydes, chlorohydrins, N-methylol compounds, and polycarboxylic acids. DMDHEU is the most commonly used durable press products finish chemical. These agents are low costs but they can show notably carcinogen effect and have a lot of damage such as causing harmful dermatological effects and having environmental damage (Lam et al., 2011).

With the development of nanotechnology, nano chemicals such as nano titanium dioxide and nano-silica can be used to (as a catalyst/ co-catalyst for these reactions)

become an alternative way to reduce the minimum the formation of free formaldehyde and fabric strength loss. Nano-titanium dioxide can be exercised with carboxylic acid as a catalyst under UV radiation to catalyze the cross-linking reaction between the cellulose molecule on the fabric and this acid. Samples are available in the literature such as nano-silica has been used with maleic anhydride as a catalyst that could successfully improve the wrinkle resistance of silk in the result (Yuen et al., 2009). And Liao et. al in 2002 worked the non-formaldehyde wrinkle resistant finishing of cotton fabrics by preparing carboxylic acid as a crosslinking agent with the compound catalyst of nano titanium dioxide ($TiO_2$), Ag, $MgCl_2$, $SiO_2$ and $ZrO_2$ (Liao et al., 2002).

#### 2.1.1.7 Flame Retardant

Flame retardancy or fire resistance textiles provide resistance to the flame source. There are two principles to make fabric flame retardant. Firstly, usable specific fibers which provide characteristically resistant to fire with the chemical formulation of them. In another principle, with applications of flame retardants finish agents on the textile surface, the flame retardants property is provided (Horrocks, 1975).

In nanotechnology applications, colloidal antimony pentoxide is developed as flame retardant agents which are used as fine particle dispersion, for use as flame retardant synergist with halogenated flame-retardants (the ratio of halogen to antimony is 5:1 to 2:1). Nano antimony pentoxide is applied with halogenated flame retardants for a flame retardant finish for textile (Morshed et al., 2010).

## 2.2 Application Methods of Finishing Materials

Textile finishing means that is the process for using to create desired effects at the textile materials before putting into the final form after it's manufactured. That can be provided for aesthetic appearance, functional profits, or obtaining useful characteristics with chemical and mechanical processes for making the fabric more appealing to the consumer (Gashti et al., 2016). Various finishing techniques can be applied at different stages during the production until the end product which position as spraying, exhausting, coating, pad-drying, etc. (Bashari et al., 2018)

With each passing day, nanotechnology coatings based are taken place widely in the chemical finishing of the textile industry which is rapidly growing in the world with functionalization of textiles (Bashari et al., 2018; Chaurasia, 2017). Nanoparticles gain success with their size-related properties and high surface area-to-volume ratio along with providing more functional properties (Gashti et al., 2016).

Various finishing method in textile is developed due to the increasing interest for nanocoating. Electrospraying coating is one of them which create a route for nanoparticle' application on the textile surface (Jaworek and Sobczyk, 2008).

### 2.2.1 Electrospraying Method

Electrospray is a method of generating liquid atomization using electrical forces that disperse fluid or for the fine aerosol resulting so that is sometimes called electrohydrodynamic atomization (EHDA) (Jaworek and Sobczyk, 2008).

In basically the electrospraying method, an emitter supplies a high voltage for fluid by means of emitting a fluid jet through its peak. The nozzle provides the transition of liquid which is charged thus Taylor cone form has occurred on the nozzle tip. Passing fluid has load much electrical force until a critical point. Thus, charged fluid droplet is obtained based on electrospray process parameters with a dispersed high electrical current through Coulomb repulsion. Obtaining micro or nanoscaled droplets coat the intended materials upon the collector (Bock et al., 2012).

Actually, electrospraying considerably has a simple and cheap process when parameters of the process ideally set. So, intended morphology, size, construction, etc. will be easily obtained (Marinov et al., 2019). That includes constitutively,

- a high voltage source,
- a syringe pump for feeding and syringe
- needle,
- a collector as grounding.

In this process, the intended prepared polymer solution is filled into a conductive nozzle of a syringe. The polymer solution is fed with a set rate through the syringe pump. High voltage is connected to the nozzle and so, the capillary needle head will highly be charged by a high voltage source. Obtaining charged droplet on tip of the needle depends on consisting of the electrical area between charged needle and grounding collector. This droplet size is affected by many parameters of the process for instance distance of collector to the needle, the amount of applied voltage, the viscosity of the solution, etc. (Jaworek and Sobczyk, 2008).

The droplet shape is changed from the spherical shape to conic shape with increasing voltage power that shape is called Taylor Cone. The fluid acting pumped with rate through into a fine uninterrupted mist of droplets that fly rapidly. In usual, when the liquid begins to exit the needle, it charges up and assumes a conical shape, referred to as the Taylor cone, in honor of Geoffrey Taylor who explained the happenings in 1964. The liquid assumes this shape because when charged up, a conical shape can take more charge than a sphere (Taylor, 1964).

After changing of droplet shape as conical with reaching critical voltage so spraying comprises of electrical force. The solvent of polymer solution evaporates until on grounding collector during the flight of sprayed droplets (Bock et al., 2012; Jadhav et al., 2011).

Production of micron- or nano-sized particulates can be primary one of their advantages with reference to electrospray parameters. Surface coating at the nanoscale becomes possible that contribute for nanotechnology area. Furthermore, the structure of droplet and droplet size can be controllable create significance for many applying by electrospray parameters such as electrical area, feeding rate. So that employed in various sectors such as automotive, building trade, medical, food, textile, etc (Jaworek and Sobczyk, 2008).

The electrospraying is diversified several modes which are dripping, micro-dripping, spindle, multi-spindle, cone-jet, oscillating-jet, precession, and multi-jet modes in the literature. Types of spraying depend on the pattern of displacement of the beam, the pattern of jet movement, the shape of the meniscus, and the road of a disintegration of

the droplets (Castillo-Orozco et al., 2017; Khan et al., 2013). Some forms of the electrospray modes are expressed schematically in Figure 2.13.

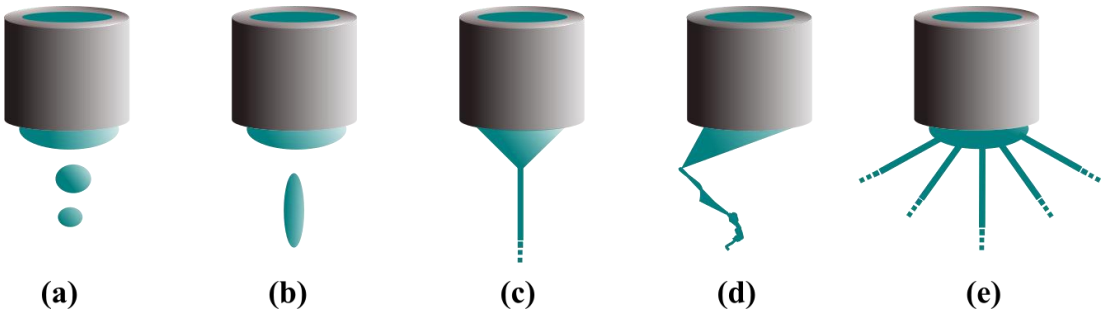



**Figure 2.13** Several modes of electrospraying; (a) dripping mode, (b) spindle mode, (c) cone-jet mode, (d) oscillating-jet mode, (e) multi-jet mode

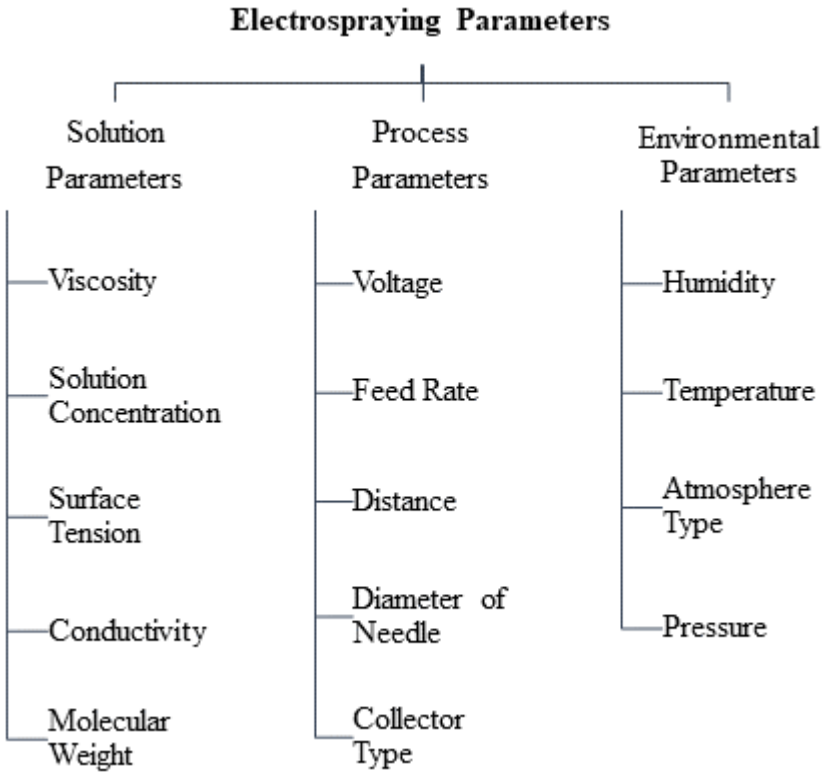
The relation between electrical force and surface tension and discharged kinetic energy of fluid define these electrospraying modes (Zarrabi et al. 2012). The cone-jet mode is the most objective mode of spraying in this case meniscus fluid takes regularly form and axisymmetric cone with through simultaneously capillary axis which is the in the main desirable mode due to providing an opportunity for very thin jetting, the ability of consistent production, conducting to uniformity, controlled size of spraying and uninterrupted electrospray pattern (Castillo-Orozco et al., 2017; Jaworek and Sobczyk, 2008).

#### 2.2.1.1 Electrospraying Process Parameters

There are various parameters on how to determine the electrospraying process. These are broadly classified into three groups: solution, process, ambient parameters. With the understanding of these parameters, that is possible to create spraying on the surface coating with different morphology by varying the parameters.

In general terms, overall the electrospray parameter is given in Table 2.3. However, within this study, the selected parameter of the electrospray process has been discoursed and described.

**Table 2.3** Parameters of electrospraying method




#### 2.2.1.1.1 Solution Parameters

The properties of the polymer solution have the most important impact in the electrospraying process and the resultant coating morphology to devise a consistent product and to modify the size arrangement of the particles.

##### 2.2.1.1.1.1 Viscosity

The viscosity of the liquid is a measurement of its demonstrated strength in contrast to gradual deformation by tensile stress or shear stress (Ku and Kim, 2002). Viscosity and surface tension of polymer is affected by the changing of polymer concentration and molecular weight, all these terms of viscosity, polymer concentration, and molecular weight of the polymer are linked with each other which are the main factors for determining the possibility of electrospraying morphological properties of particles

producing. The viscosity of the polymer can be arranged with preparing solution concentration (Bock et al., 2012).

At the same time, the length of the polymer chain affects the molecular weight of the polymer which typifies an effect on the viscosity of the solution since the polymer length will decide the amount of complication of the polymer chains in the solvent. When the viscosity is increased which means that there is a higher amount of polymer chains entanglement in the solution (Li and Wang, 2016).

If the polymer viscosity is low enough, the jet is destabilized and hence fine spherical droplet at micro-scaled is formed so the electrospraying process can take place. For decreasing viscosity, the polymer solution can be diluted with a set amount of solvent. So, droplet size is affected substantially by the viscosity of the solution (Ku and Kim, 2002).

#### 2.2.1.1.1.2 Concentration

Polymer concentration has shown the effect over the viscosity of solution accordingly over other processing parameters which has an excellent impression on particle and fiber or coating formations during electrospraying and electrospinning process (Jadhav et al., 2011).

The polymer concentration depends on the ratio of solvent which is set to provide a threshold concentration of polymer. That threshold concentration designate electrospinning or electrospraying behavior that represents entanglement of the polymer chain (Li and Wang, 2016).

During of formation of the coating on the surface, low concentration cause nano and microparticles have occurred. The particle size of droplets can increase with the additive concentration ratio. Even, with a continued increase of concentration, fiber formation is taken place instead of coating. The reason is that polymeric chains become tangled with close to each other. For this reason, concentration for the formation of the coating must set ideally level (Jaworek and Sobczyk, 2008).

#### 2.2.1.1.1.3 Surface Tension

Surface tension is the energy, or action by unit area or force per unit length, required for raising the surface area of a fluid due to intermolecular forces between the liquid's molecules at the liquid's outer limits, that is to say, surface molecules have puller force by the internal molecules, this is called surface tension. The surface tension of having fluidity surface trends to keep the smallest possible surface area (Jadhav et al., 2011).

When a droplet of waterfalls from the air such as rain, the droplet usually obtains a spherical shape. The fluid surface property that causes this happening is known as surface tension (Hermans et al., 2017) The surfactants can add to decreasing the surface tension of the liquid besides that, several ingredients can procure lower surface tension. Decreasing of surface tension that provides more uniform distribution spraying with comprising of nanomaterials (Li and Wang, 2016).

In electrospraying, the charges on the polymer solution should be ideal enough to overcome the surface tension of the solution. Formation of electrospray process mode especially cone-jet mode is influenced electrical area between meniscus of liquid and supplied electrical force at this stage, the surface tension of liquid gets involved for production cone-jet mode droplets at micro or nanoscale (Bock et al., 2012).

#### 2.2.1.1.1.4 Conductivity

Conductivity is the measurement that can be defined as material conducts electricity, measured as the ratio of the current density in the material to the electric field (Lee et al., 2010). Conductivity should be ideally brought polymer solution such that the pusher forces within the solution are able to surpass the surface tension of the solution for initiating of the electrospray process. Consisting of droplet size effects from the conductivity of the polymer or its solvent. When the polymer solution has high electrical conductivity, the size of droplets can be observed lower and providing disseminative of liquid drops at the desired level depending on the other electrospraying parameters such as voltage. Due to, procuring larger accumulation electrical area is obtained with transporting more charge (Bock et al., 2012).

The availability of several acids, bases, mineral salts, dissolved carbon dioxide, and mixing chemically non-interacting constituents can considerably raise the conductivity of the solvent (Li and Wang, 2016).

#### 2.2.1.1.2 Process Parameters

Process parameters of the electrospraying come into prominence inasmuch with solution parameters which are significantly the various outside factors on the electrospinning jet. These comprise;

- voltage,
- flow rate,
- the distance between the needle tip and collector
- type of collector,
- the diameter of the needle.

##### 2.2.1.1.2.1 Voltage

The voltage is a critical process parameter which influences the formation of the electrospray process (Nguyen–Vu et al., 2017). With applying voltage, the polymer solution is induced with an electrical charge and the electrostatic force in the solution overcomes the surface tension of the solution. So, charging solution droplets in the tip of the nozzle with an external electrical field are dimensionally distributed above the surface at Taylor cone form during jet (Marginean et al., 2009).

Herewith, Coulombic energy and electrostatic impulsion connecting the surface charge these two electrostatic forces comprise droplets at lower particle size with high voltage applying. For this reason, these droplets can be overflowed from the nozzle following the performance of these electrostatic synergies into a conical cone. Even so, other parameters have an impact such as the concentration of polymer and the distance between needle and collector, in other words, the flight time of the electrospray's jet and also faster solvent evaporation can be encouraged by voltage (Nguyen–Vu et al., 2017).

#### 2.2.1.1.2.2 Feed Rate

The flow rate of the polymer solution defines the amount of solution present at the needle tip during electrospraying. The feed rate is the state when the gravity force is the predominant performance on the primary drop at commencing electrospraying (Li and Wang, 2016). Understanding the feed rate parameter that makes it possible the material's behavior identification of particle size in the electrospray process. That is to say, the formation of the droplet size is influenced by the feeding rate (Nguyen–Vu et al., 2017).

There is yielding feeding rate for the formation of Taylor cone mode with given ideally voltage. In other words, arranging of the feed rate of solution supports the dimension of liquid drop depending on the cone-jet mode (Bock et al., 2012).

When all other parameters are kept stable, if the high feed rate is set, the large particle size of droplets takes place at electrospray. Due to the flying time of polymer solution is not enough for drying from tips of the needle to the collector that is to say solvent does not completely evaporate at this time. Therefore, a low feed rate guides to shorter droplet size which causes the greater volatilization of the solvent (Jaworek et al., 2009).

#### 2.2.1.1.2.3 Distance

The formation of electrospray droplets takes place between the tip of the nozzle and collector which can be effect flight time of drop and electrical area. Accordingly, can affect the size of droplets and occurred to characterize finished product morphology through the evaporation of the solvent of the polymer (Zaouk et al., 2000).

When the voltage is held as consistent, if this tip to collector distance (TCD) is decreased, the electrical area will increase wherein the inverse proportion relationship will be observed. As a result, the size of the droplet will be influenced so taking place stability of cone-jet will be affected mode through evaporation of the polymer solvent (Bock et al., 2012).

#### 2.2.1.1.3 Environmental Parameters

Environmental parameters especially humidity and temperature show many influences over solution properties and electrospraying processes as productivity and product morphology.

##### 2.2.1.1.3.1 Humidity

Evaporation of the polymer solvent is directly influenced by humidity in the air. Other parameters are affected as well as between the conductivity of the solvent That said, too high humidity can be an obstacle to the performance of an electrostatic process due to electrospraying is performed at environmental conditions. For instance, when high humidity was found, that induce the occurrence of pores on the fiber surface at the electrospinning process that It was observed in the studies (Li and Wang, 2016).

##### 2.2.1.1.3.2 Temperature

The temperature parameter affects the electrospraying process. The evaporation rate of polymer solvent and correspondingly polymer properties such as viscosity can be shown an alteration thereby, the production of electrospray can be influenced (Marinov et al., 2019).

### 2.2.2 Padding Method

The padding application method is one of the traditional methods of finishing. Padding is based on the working principle that fabric is impregnated in a chemical solution bath then removing surplus chemical over the fabric by squeezing roller and then drying (Schindler and Hauser, 2004). When the fabric is passing during the process, chemical solutions make the crosslinking the fabric with final drying (Holme, 1993).

In a chemical solution bath, the dipping process takes place the immersion of the fabric in at rough or pan containing the finishing chemical solution then with nipping, the fabric passes between the two squeeze rolls. The squeeze rollers are sometimes called

a mangle which can be done rubber and other metals. This pressure determines the percent wet pick-up between rollers (Schindler and Hauser, 2004). Percent wet pick-up is mean as the weight of liquid picked up by the fabric after padding expressed as a percentage of the original dry fabric weight (Namboodri and Duke, 1979; Schindler and Hauser, 2004).

There are also disadvantages as there are advantages such as getting high spring back angles for dry creases of this method. This method has low cost and providing a uniform coating on the fabric, but effective results may not be shown. With increasing concentration, saving water may be possible. Making a process setting can be effective for functional advantages (Gashti et al., 2016; Ramachandran et al., 2009; Schindler and Hauser, 2004).

# CHAPTER 3

# FORMATION OF SUPERHYDROPHOBIC AND SELF-CLEANING SURFACES WITH MODIFIED BICOMPONENT CORE/SHELL NANOPARTICLES BY USING NOVEL ELECTROSPRAYING METHOD

## 3.1 Abstract

In this study, $TiO_2$ nanoparticles were coated with Ag and Au metal in the form of core@shell structure to not only increase the photocatalytic activity of $TiO_2$ but also to enable covalent bonding the nanoparticles to the surface by means of the metal-sulphur bond. Also, the surface was modified with 12-mercaptododecanoic acid to obtain a thiolated cellulose-containing textile surface which both improves the hydrophobicity of the surface due to the long hydrocarbon chain and enables covalent bonding of metal coated nanoparticles to the textile surface. The structural characterization of $TiO_2$@Au and $TiO_2$@Ag nanoparticles were performed using UV-VIS spectrophotometer and Zetasizer. The physicochemical properties of nanoparticle suspensions prepared at different concentrations were measured to determine the suitability of these suspensions for electrospraying. The coated nanoparticles were applied to the thiolated textile surface using conventional pad-dry-cure and novel electrospraying methods. After the coating applications, water contact angle measurements and photodegradation of staining agents under the UV irradiation were obtained to evaluate hydrophobic and photocatalytic properties of the modified surfaces. Results demonstrated that thiolated textile surfaces coated with comparatively very low amount of $TiO_2$@Au and $TiO_2$@Ag via electrospraying showed the closest superhydrophobic characteristic and $TiO_2$@Au provided the highest photocatalytic performance.

## 3.2 Introduction

In the textile industry, nanotechnology can be used either to form nanofibers or to functionalize surfaces for obtaining advanced functional properties. There is a great interest on the use of nanotechnology to develop several technical textiles for medical applications (Nikalje, 2015; Patra and Gouda, 2014), protective textiles (Black, 2009; Qian and Hinestroza, 2004; Tsuzuki and Wang, 2010; Wong et al., 2006), and outdoor textiles (Morganti et al., 2013; Gashti et al., 2016; Sawhney et al., 2008).

In many technical textile products, hydrophobicity is desired to achieve required advance protection on the textile surfaces. Hydrophobicity can be obtained either reducing the surface energy by coating the surface with silicones (Artus et al., 2006), fluorocarbons (Dasdemir and Ibili, 2017; Di Mundo et al., 2008), etc. or increasing roughness of the textile surface (Lee, 2009). If the surface tension of the liquid is higher than the surface tension of the textile material, the fabric cannot be wettable otherwise, liquid dissipates on the surface and then penetrates into the fabric due to its low surface tension.

Superhydrophobicity can be achieved when the water contact angle on the surface is equal or greater than 150° and the sliding angle is less than 10° (Bhushan et al., 2009; Ramaratnam et al., 2007; Xue et al., 2010). Lotus leaf is a great example for the superhydrophobic surface in nature. It has both unique non-polar wax coated surface and surface architecture. The waxy surface having non-polar methyl group reduces the surface tension of the leaf that provides the hydrophobicity. The surface architecture having micro/nanostructures provides advanced roughness on the surface and reduces the contact point which provides superhydrophobicity and self-cleaning properties (Lee and Michielsen, 2006; Stegmaier et al., 2008). Researchers have been inspired from the lotus leaf and have tried to mimic its properties using several techniques and materials (Karthick and Maheshwari, 2008; Latthe et al., 2014; Özdoğan et al., 2006; Ramaratnam et al., 2018; Roach et al., 2008).

To obtain superhydrophobic textile surfaces, various nanomaterials have been used such as $TiO_2$ (Afzal et al., 2014; Xue et al., 2008), $SiO_2$ (Karunakaran et al., 2011; Pakdel et al., 2013; Rilda et al., 2016; Xu et al., 2015), ZnO (Qing et al., 2015; Uğur et al., 2010), silver (Khalil-Abad and Yazdanshenas, 2010; Xue et al., 2012), and

carbon nanotubes (Shahidi and Moazzenchi, 2018). Among these materials, $TiO_2$ nanoparticles are more popular, because they are not only non-toxic and low-cost materials but also have high photocatalytic activity and chemical stability (Rana et al., 2016).

$TiO_2$ is an effective photocatalyst that can decompose nearly any organic compound when it is exposed to UV irradiation. Therefore, it has been used in many applications including wastewater treatment and self-cleaning. Even though there are many metal oxide photocatalysts such as ZnO (Rajbongshi and Samdarshi, 2014), Ag (Zheng et al., 2008), $Fe_2O_3$ (Gao et al., 2007), $SnO_2$ (Li et al., 2013), and ZnS (Lee and Wu, 2017), $TiO_2$ (Kumar, 2015), and its composites are the most popular photocatalysts used on textiles (Saad et al., 2016).

Obtaining self-cleaning property on the surface of the textiles is highly desired for the most technical textile applications such as protective suits, medical gowns, etc. Therefore, there are many efforts to attain self-cleaning surfaces with the use of the photocatalytic $TiO_2$ nanoparticles (Abbas et al., 2018; Gupta et al., 2008; Qi et al., 2011; Yuranova et al., 2006). Wu et al. (2009) coated cotton fabric with $TiO_2$ nanoparticles using the dip-coating method. They evaluated the degradation of staining agents under UV irradiation. Also, the durability of the coating against washing was determined. It was found that after the washing the photocatalytic performance of the cotton fabric surface decreased due to weak adhesion between $TiO_2$ nanoparticles and cotton fabric surface. Karimi et al (2010) prepared $TiO_2$ suspensions at various concentrations and used succinic acid for cross-linking agents to covalently bind $TiO_2$ nanoparticles onto the cotton fabric surface for improving the adhesion of the $TiO_2$ nanoparticles onto the surface. They investigated the photocatalytic activity and stain degradation performance of the cross-linked and non-cross-linked $TiO_2$ nanoparticles to the surface depending on the power of the illumination source. They observed more stain degradation performance when cross-linked $TiO_2$ nanoparticles were used and the higher power for illumination source was selected.

In addition to the photocatalytic property of $TiO_2$ nanoparticles, it can be obtained hydrophobic property from nanoparticles present on the surface due to the increment of the surface roughness. Montazer et al. (2013) coated cotton fabric with $TiO_2$ nanoparticles using 1,2,3,4 butane tetracarboxylic acid (BTCA) cross-linking agent.

They measured the water drop absorption time for $TiO_2$-treated cotton fabric. The duration of water droplet stayed on the surface of untreated fabrics was recorded as 14 seconds, while that of treated fabrics was found to be approximately 235 seconds. This demonstrates that the hydrophobic characteristic of the fabric was enhanced with $TiO_2$ nanoparticle coating as a result of achieving surface roughness.

In order to improve the adhesion between nanoparticles and fabric surfaces, thiolated carboxylic acid was also used as a linking agent (Park et al., 2012). For this purpose, Park and co-workers (2012) used mercaptoacetic acid to obtain thiol modified surfaces which can be used to covalently bind metallic nanoparticles to the surface. The thiol-modified surface was used for the attachment of silver nanoparticles to the surface via metal-sulphur bonding. This approach can be used to obtain functional fabric surfaces with the modification of the different type of In order to apply or coat nanoparticles onto the textile surface, various methods can be used such as sol-gel (Gupta et al., 2008; Kumar, 2015; Mahltig et al., 2005), layer-by-layer deposition, dip-coating (Chang et al., 2014), pad-dry-cure (Wiener et al., 2017), sputtering, plasma (Balu et al., 2008), chemical vapor deposition (Ma et al., 2005), etc. In addition to them, there is also a novel method called electrospraying (electrohydrodynamic spraying) which is an emerging coating method. This method allows the atomization of fluid by means of electrical forces which can decrease the droplet size down to less than 100 nm (Bošković and Bugarski, 2019; Jaworek and Sobczyk, 2008). The smaller droplet size enables to reach the higher surface area, thinner coating, less chemical consumption on the applied surface which is significant for several applications. Also, the other advantage of this process is that it does not require any subsequent drying process since the great portion of the solvent evaporates during the electrohydrodynamic spraying process. Thus, it can be considered as a cost-saving coating method due to the above-mentioned advantages.

In this study, it is aimed to obtain superhydrophobic and self-cleaning textile surfaces. For this purpose, nano titanium dioxide ($TiO_2$) was coated with silver (Ag) and gold (Au) layers to obtain bicomponent core/shell structure namely $TiO_2$@Ag and $TiO_2$@Au nanoparticle suspensions. Particle sizes, zeta potential, and UV-vis absorbance wavelengths of $TiO_2$@Ag and $TiO_2$@Au were measured to verify core/shell structural formation. Cotton/polyester fabric surfaces were coated with bare

$TiO_2$, $TiO_2$@Ag, and $TiO_2$@Au using conventional pad-dry-cure and novel electrospraying methods. Before they were coated with nano-chemicals, the fabric surfaces were initially modified with the 12-mercaptododecanoic acid to obtain covalent bonds via metal-sulphur (M-S) between metal coated nanoparticles and thiolated fabric surfaces. The structural characterization of $TiO_2$@Au and $TiO_2$@Ag nanoparticles were performed using UV-VIS spectrophotometer and Zetasizer. The physicochemical properties (viscosity, surface tension, and conductivity) of nanoparticle suspensions prepared at different concentrations were measured to determine the suitability of these suspensions for electrospraying. The coated nanoparticles were applied to the thiolated textile surface using the electrospraying technique. The conventional pad-dry-cure method is also used as a coating method for comparison purpose. After the coating applications, water contact angle measurements were acquired from the textile surfaces to evaluate hydrophobicity. Also, the photocatalytic performance of the coated textile surfaces was evaluated by photodegradation of staining agents under the UV irradiation. Scanning electron microscope (SEM) images were obtained for the morphological characterization of the coated fabric surface.

## 3.3 Materials and Methods

### 3.3.1 Materials and Preparation of Nanoparticles

Cotton/Polyester blended (35%/65%) white woven fabric weighing 110 (±5) $g.m^{-2}$ was used. Three sets of 1 gram of $TiO_2$ nanoparticles (*Sigma-Aldrich* Product No:718467, nanopowder, 21 nm primary particle size, ≥99.5% trace metals basis) were weighed and dissolved in 100 mL of water and then ultrasonicated to obtain homogeneous suspensions. One of these suspensions was used as a control sample. 0.2 grams of silver nitrate ($AgNO_3$) (*Sigma-Aldrich* Product No: 85228, puriss. p.a., ≥99.5%) and 0.2 grams of gold(iii) chloride hydrate ($HAuCl_4.3H_2O$) (*Sigma-Aldrich* Product No: 254169, 99.995% trace metals basis) were added separately into each $TiO_2$ suspension to coat $TiO_2$ with silver and gold metal shells, respectively. Schematic illustration of the preparation of $TiO_2$@Au and $TiO_2$@Ag nanoparticles was demonstrated in Figure 3.1.

In a separate manner, 20 mL of 1% w/v Sodium Borohydride ($NaBH_4$) reducing agent was freshly prepared. Reduction of the $Ag^+$ and $Au^{3+}$ were achieved by the dropwise addition of 10 mL of $NaBH_4$ (1% w/v) into the mixture. A comparison of the color of bare $TiO_2$ and prepared $TiO_2$@Ag and $TiO_2$@Au nanoparticles were shown in Figure 3.2. The color of the bare $TiO_2$ turned from white to brown and pink/red when the bare $TiO_2$ were coated with Ag and Au, respectively.

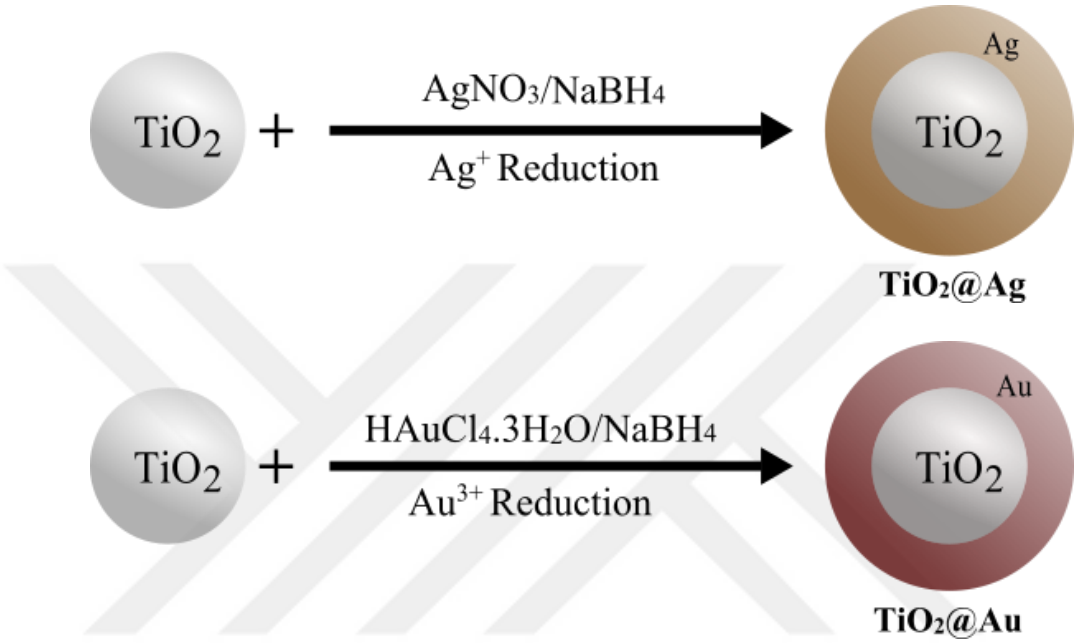
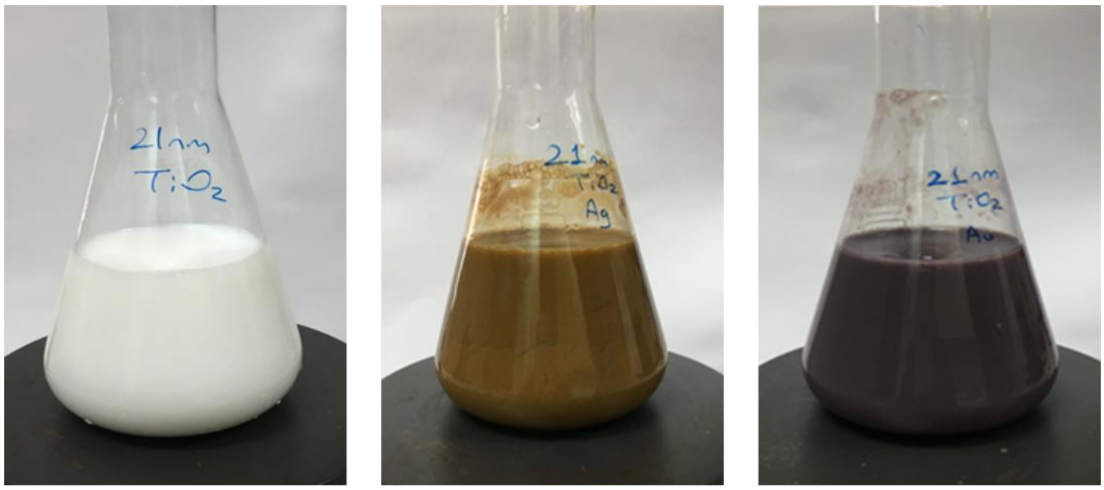



**Figure 3.1** Preparation of $TiO_2$@Ag and $TiO_2$@Au nanoparticles




**$TiO_2$** **$TiO_2$@Ag** **$TiO_2$@Au**

**Figure 3.2** Comparison of the color of bare $TiO_2$, prepared $TiO_2$@Ag and $TiO_2$@Au nanoparticle suspensions

To remove the unreduced Ag and Au ions remaining in the suspension, all the suspensions were centrifuged at 2000 rpm for two minutes and washed with water three times. Finally, 1% w/v $TiO_2$@Ag and $TiO_2$@Au nanoparticle suspensions were obtained as previously reported by Baysal et al. (2011). All these suspensions were diluted with isopropyl alcohol to obtain 0.9%, 0.5%, and 0.1% (w/v) nano chemical concentration for further coating applications.

### 3.3.2 Characterizations of Nanoparticle Suspensions

UV-vis absorption measurements of colloidal suspensions of $TiO_2$, $TiO_2$@Au, and $TiO_2$@Ag were performed using Thermo Scientific - Evolution 201 Spectrophotometer. Size distribution and zeta potential measurements were taken at 25°C for three times with the MALVERN Zetasizer Nano ZS instrument.

Physicochemical properties of suspensions including viscosity, conductivity, and surface tension were measured to determine their electrospraying characteristics. Four viscosity measurements for each suspension were taken at 25 °C and 200 rpm with using Brookfield DV III Ultra Programmable Rheometer device and a spindle number of 18. Seven surface tension measurements for each suspension were taken by using

KSV Theta Optical Tensiometer. For the conductivity measurements of suspensions, Orion 4 Star Plus pH Meter device was used and four measurements were taken from each sample at 25 °C.

### 3.3.3 Surface Modification of Cellulose Containing Fabrics

The surface of the cotton/polyester blended fabric was modified with using 12-mercaptododecanoic acid (*Sigma-Aldrich* Product No: 675067, 96%, $C_{12}H_{24}O_2S$) in an acidic environment. Schematic illustration of the surface modification of cellulose containing fabric is shown in Figure 3.3.

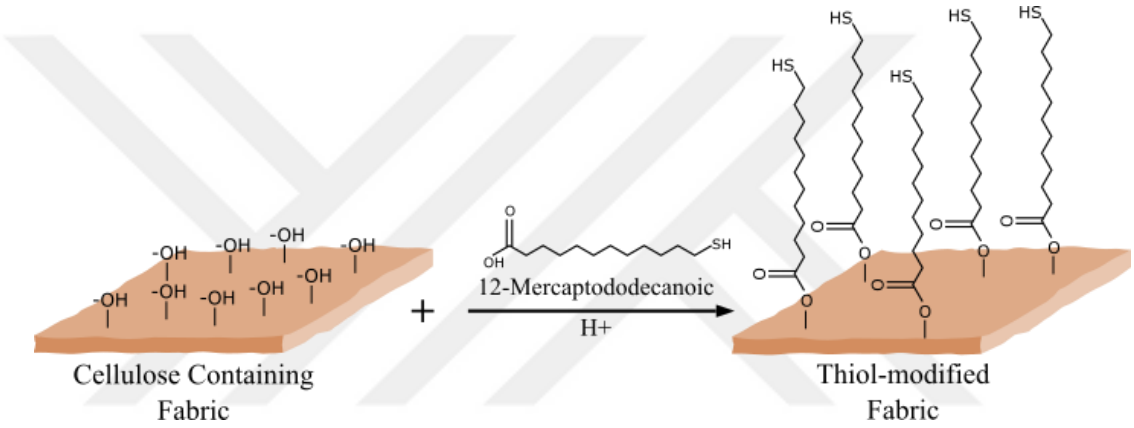



**Figure 3.3** Surface modification of cellulose containing fabric with 12-mercaptododecanoic acid (thiol)

To determine the ideal recipe, five different batches were prepared and named as A, B, C, D, and E (Table 3.1).

**Table 3.1** Prepared thiol solutions at various concentration and ratios

| | **A** | **B** | **C** | **D** | **E** |
|---|---|---|---|---|---|
| **12-Mercaptododecanoic Acid** | 0.0464 gr | 0.2 gr | 0.2 gr | 0.1 gr | 0.1 gr |
| **Acetic Acid** | 14.4 mL | - | - | 14 mL | 14 mL |
| **Dimethyl Sulfoxide (DMSO)** | - | 20 mL | - | - | - |
| **Dimetilformamid (DMF)** | - | - | 20 mL | - | - |
| **Sulphuric Acid ($H_2SO_4$)** | 0.3 mL | 10 mL | 10 mL | 10 mL | 5 mL |
| **Distilled Water** | 250 mL | 500 mL | 500 mL | 250 mL | 250 mL |
| **Fabric*** | 30 gr (9 piece) | 20 gr (6 piece) | 20 gr (6 piece) | 10 gr (3 piece) | 10 gr (3 piece) |
| **Temperature** | 40°C | 60°C | 60°C | 100°C | 100°C |
| **Holding Time** | 4 days | 5 days | 5 days | 1 day | 1 day |

**20cm x 20cm, cellulose containing woven fabrics*

Bare $TiO_2$ and prepared $TiO_2$@Ag and $TiO_2$@Au nanoparticle suspensions were applied onto the thiol-modified fabrics. Schematic illustrations of the coating of the thiol-modified fabric with $TiO_2$, $TiO_2$@Ag, and $TiO_2$@Au nanoparticles were depicted in Figure 3.4.

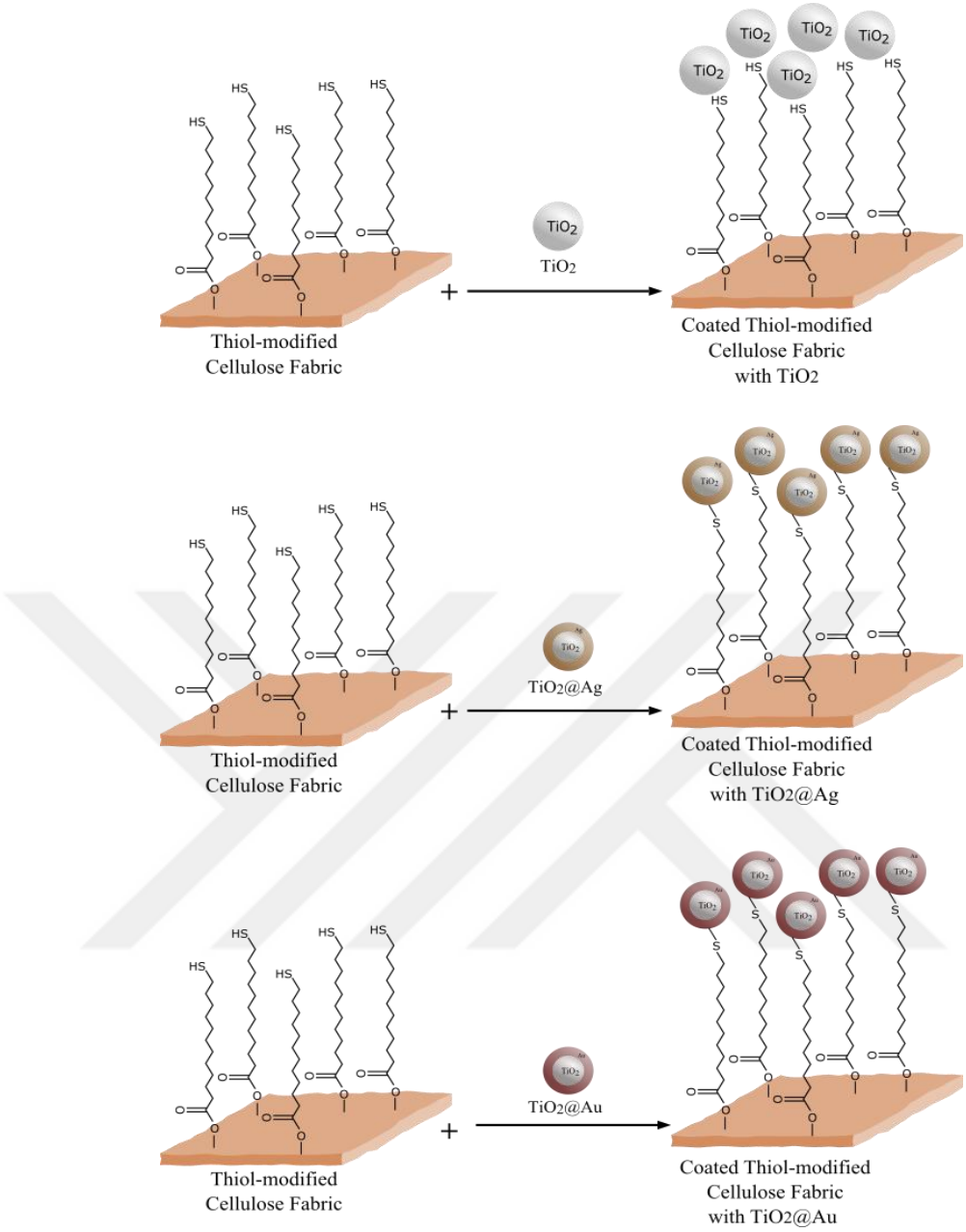



**Figure 3.4** Schematic illustrations of coating of the thiol-modified fabric with $TiO_2$, $TiO_2$@Ag, and $TiO_2$@Au nanoparticles

The application of nanoparticles onto the textile fabric surface was conducted using two different approaches or methods. In the first approach, a novel electrospraying technique was used. For this purpose, a laboratory-type electrospraying set up which contains 100 kV- 20W ES100P Model Gamma high voltage power supply and New Era NE-1000X pump was used. Vertical electrospraying configuration was chosen in which the fabric (10 cm x 10 cm) was placed on top of the grounded metal collector placed at the bottom (Figure 3.5). For all electrospraying trials the flow rate, the applied voltage, and tip to collector distance were kept constant as 20 $\mu l.min^{-1}$, 10 kV, and 10 cm, respectively.

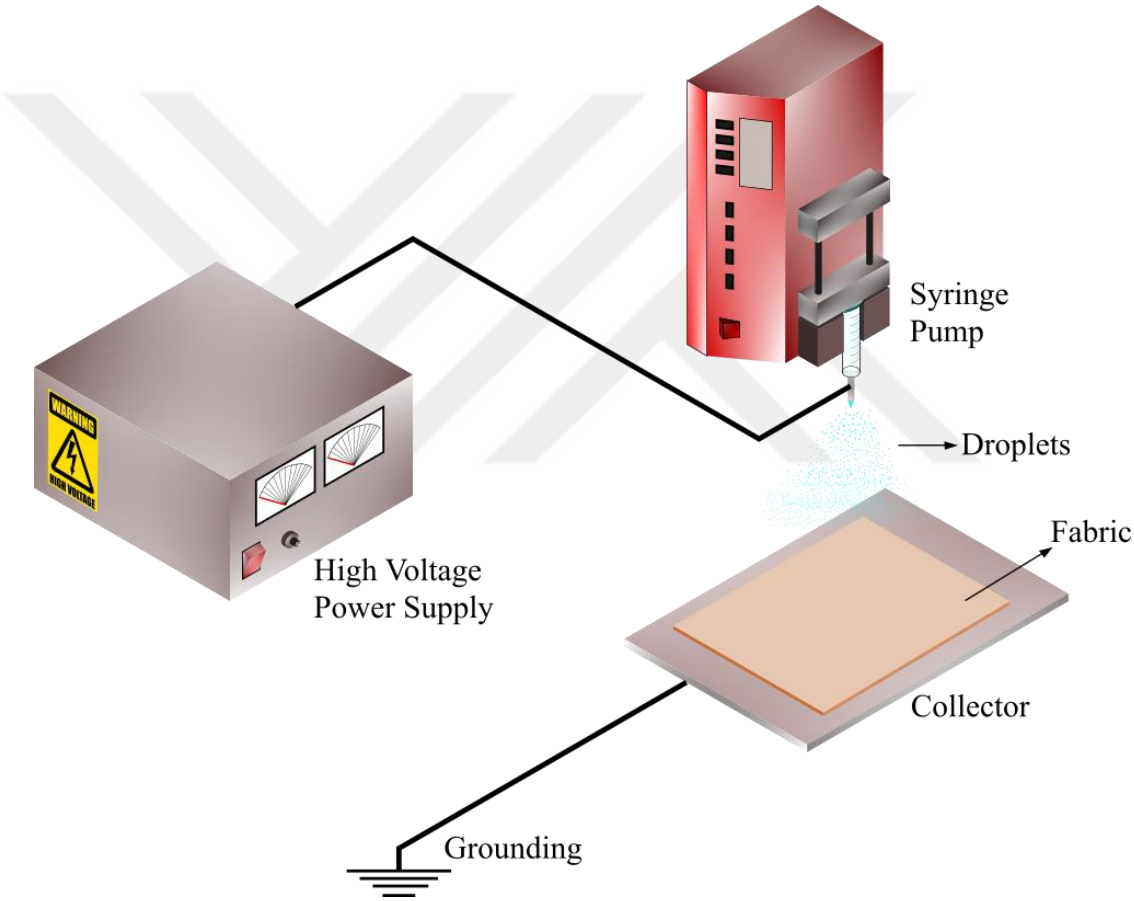



**Figure 3.5** Schematic representation of the electrospraying coating process

In the second approach, a traditional textile coating method named pad-dry-cure was used to coat the fabric with nanomaterials. For this purpose, fabric samples (10 cm x 10 cm) were immersed into the nanoparticle suspension containing bath of laboratory type padding machine (Prowhite Testing Equipment with a model no: PDF01-

A/0601001). Fabrics stayed in the bath for 10 seconds and they were squeezed between two rotating (2 $m.min^{-1}$) pressure rollers at 300 kPa (Figure 3.6).

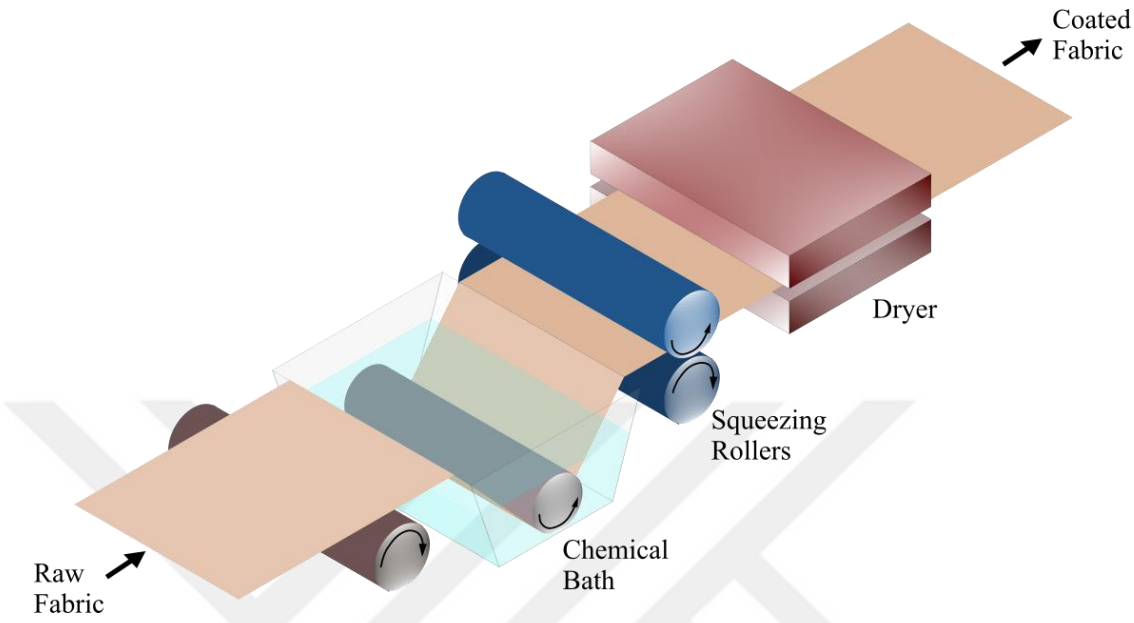



**Figure 3.6** Schematic illustration of the pad-dry-cure coating method

After the coating application, electrosprayed and padded fabric samples were dried at 110 °C for 5 minutes to achieve chemical fixation of chemicals onto the fabric surface.

### 3.3.4 Characterization of Modified Fabrics

#### 3.3.4.1 Measurement of Water Contact Angle (WCA) for Water Repellency

Water contact angle measurements were taken from uncoated and coated fabric surfaces according to ASTM D7334-08 standard (sessile water droplet technique). Theta Optical Tensiometer was used for testing. From each sample, seven repeats were taken and the average was reported.

#### 3.3.4.2 Evaluation of Self-cleaning Fabric via Photocatalytic Property

The self-cleaning characteristic of coated fabric with prepared different nanoparticle was compared on the color removal of coffee stains on fabrics under UV radiation. Coated fabrics were stained with the coffee solution (1gr Nescafe Gold soluble coffee was mixed 30 mL hot water). Stained fabrics were exposed to BLX-254 VILBER LOURMAT laboratory type UV radiation device. (254nm Tube, Power: 80 W). After 8 hours, 16 hours, and 24 hours, stained sample fabrics were photographed for comparison.

#### 3.3.4.3 Surface Morphology and Elemental Analysis

The surface morphology of the coated samples was examined using JEOL JSM-6390 scanning electron microscopy. SEM images were determined under the same conditions for coated fabrics which is in 2500,5000,10000 and 20000 magnifications, 4kV accelerating voltage, and 12 to 15 mm working distance.

## 3.4 Results and Discussions

### 3.4.1 Characterization of $TiO_2$, $TiO_2$@Ag, and $TiO_2$@Au Nanoparticle Suspensions

Silver and gold salts were reduced onto the $TiO_2$ nanoparticles to obtain core/shell structure consisting of $TiO_2$@Ag and $TiO_2$@Au nanoparticle suspensions. It is well known that UV-Vis. absorption spectroscopy is widely used for the characterization of nanostructures having optical properties such as Ag and Au nanoparticles. Therefore, the absorption spectra of colloidal $TiO_2$@Au and $TiO_2$@Ag nanoparticle suspensions were compared with that of the individual $TiO_2$ nanoparticle suspension (Figure 3.7). Bare $TiO_2$ nanoparticles did not demonstrate any absorption peak. However, when the bare $TiO_2$ nanoparticle suspension coated with Ag and Au layers, absorption spectra at 410 nm for $TiO_2$@Ag and 540 nm for $TiO_2$@Au were obtained. The maximum absorption peaks seen on the spectra are due to the optical properties of Ag and Au layers on the bare $TiO_2$ nanoparticles. Similar absorption spectra for Ag

nanoparticles have been reported by Paramelle et al. (2014). In Ag nanoparticles, electrons on the conduction and valence band move freely and closely which demonstrates rise to a surface plasmon resonance through the collective oscillation of electrons of Ag nanoparticles in resonance with the light (Patil, 2015). Also, there are some supporting results regarding to surface plasmon resonance wavelength of Au nanostructures (Ngo et al., 2015; Seol et al., 2011).

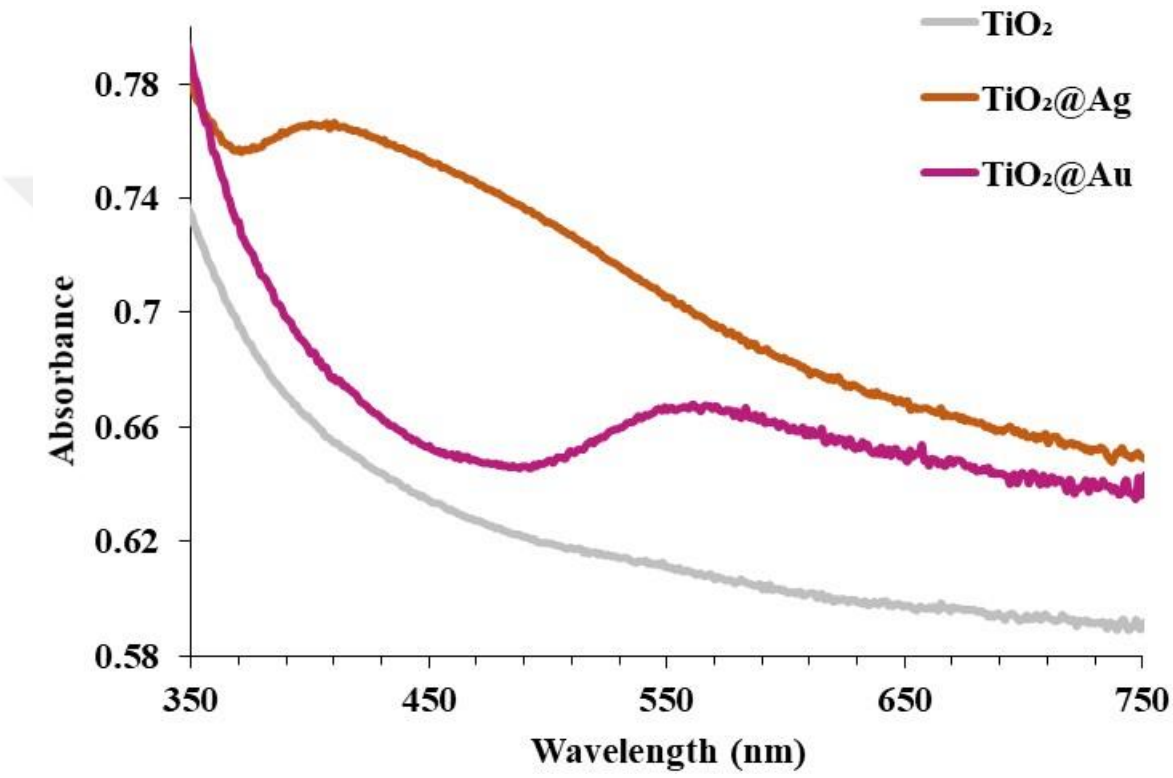



**Figure 3.7** UV-Vis. absorption spectra of bare $TiO_2$, prepared $TiO_2$@Ag and $TiO_2$@Au nanoparticle suspensions

In order to determine whether the $TiO_2$ nanoparticles were coated with Ag and Au, size distributions and zeta potentials of bare $TiO_2$, $TiO_2$@Ag, and $TiO_2$@Au were measured (Figure 3.8 and 3.9). According to results shown in Figure 3.8, while the size of the bare $TiO_2$ nanoparticles was about 227 nm, those of the Ag and Au coated $TiO_2$ nanoparticles were about 418 nm and 519 nm, respectively. The increments in the sizes of $TiO_2$ nanoparticles are due to the shell formation of metals onto bare $TiO_2$

nanoparticles. These results indicate that bare $TiO_2$ are successfully coated with Ag and Au metal layers. Previous studies also reported a similar increase in the size of the $TiO_2$ nanoparticles after they were coated with Ag and Au metal layer (Baysal et al., 2011; Gunduz et al., 2011).

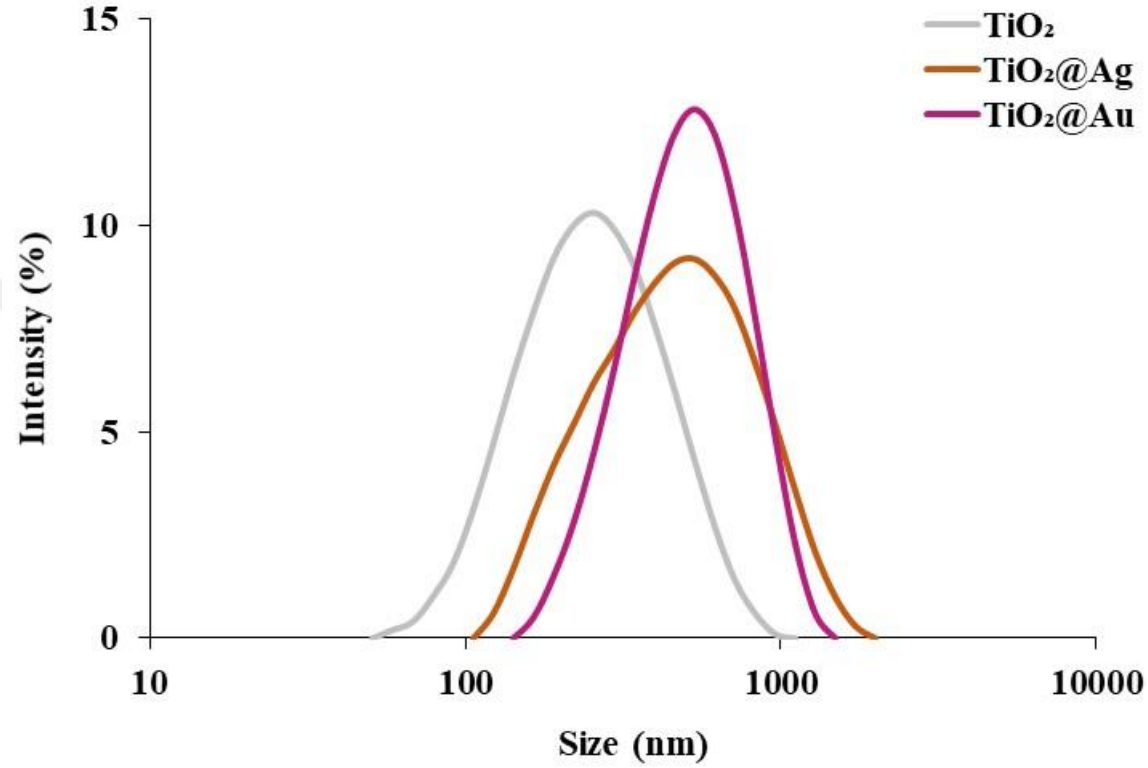



**Figure 3.8** Size distributions of bare $TiO_2$, prepared $TiO_2$@Ag and $TiO_2$@Au nanoparticle suspensions

The zeta potential measurement of the bare $TiO_2$, $TiO_2$@Ag, and $TiO_2$@Au nanoparticle suspensions are shown in Figure 3.9.

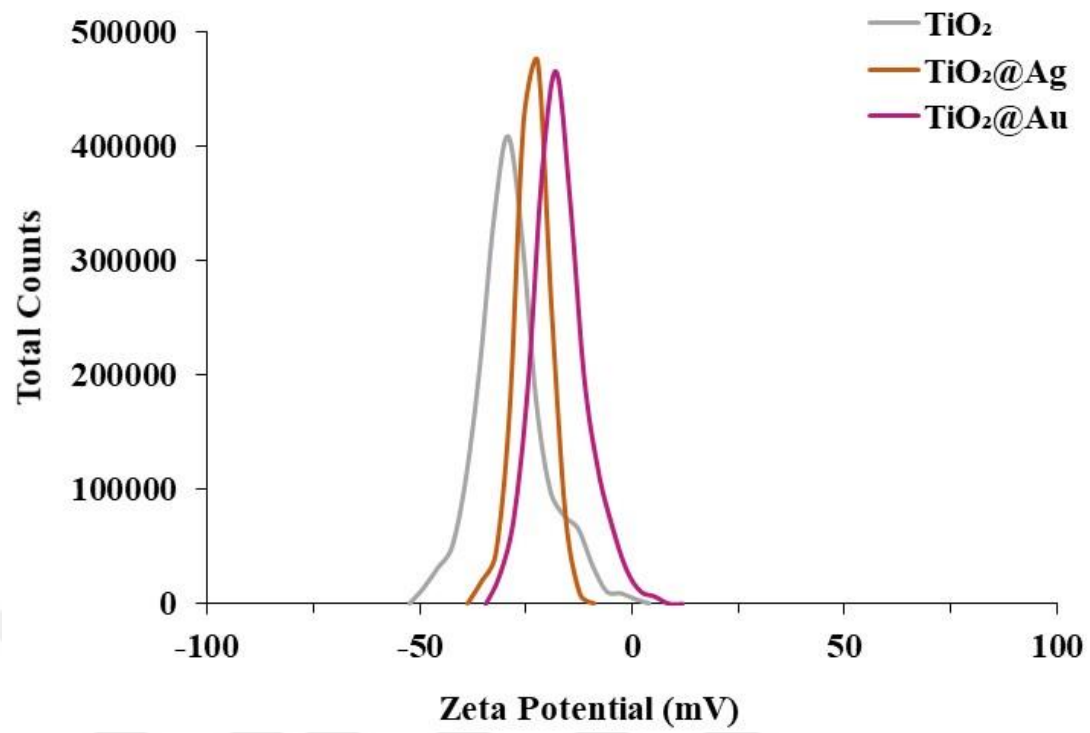



**Figure 3.9** Zeta potentials of bare $TiO_2$, prepared $TiO_2$@Ag and $TiO_2$@Au nanoparticle suspensions

While the zeta potential of bare $TiO_2$ nanoparticle was -28.3 mV, after the coating with Ag and Au layers the zeta potentials obtained as -23.4 mV and -16.9 mV, respectively. The zeta potential changes are due to the modification of bare $TiO_2$ nanoparticle surfaces with the metal layer. These results demonstrate that the bare $TiO_2$ nanoparticles were successfully coated with the metal layers.

Viscosity measurement results of the bare $TiO_2$ and prepared $TiO_2$@Ag, $TiO_2$@Au nanoparticle suspensions at different nanoparticle concentrations are shown in Figure 3.10. The viscosity values of the nanoparticle suspensions ranged from 1.12 to 3.04 mPa.s at 0.1% and 0.5% nanoparticle concentrations. The viscosity values of the nanoparticle suspensions usually increase with the increase in concentration (Khedkar et al., 2013; Mishra et al., 2014). This behavior was observed when the concentration rose from 0.1% to 0.5% as expected. However, when the nanoparticle concentration was 0.9%, the viscosity decreased. The huge decrease of viscosity value at 0.9% nanoparticle concentration could be due to the chemical precipitation of nanoparticle.

This can be caused by the agglomeration of the nanoparticles at comparatively higher concentration values in which the distance in between the nanoparticles decreased and the higher attraction occurred between nanoparticles (Duan et al., 2011).

Measured viscosity values were found at the low range which did not pose a problem for the suitability of electrospraying at 0.1% and 0.5% nanoparticle concentration. Since, 1 mPa.s - 22 mPa.s viscosity value range was considered as the proper viscosity for the electrospraying process (Jaworek et al., 2009).

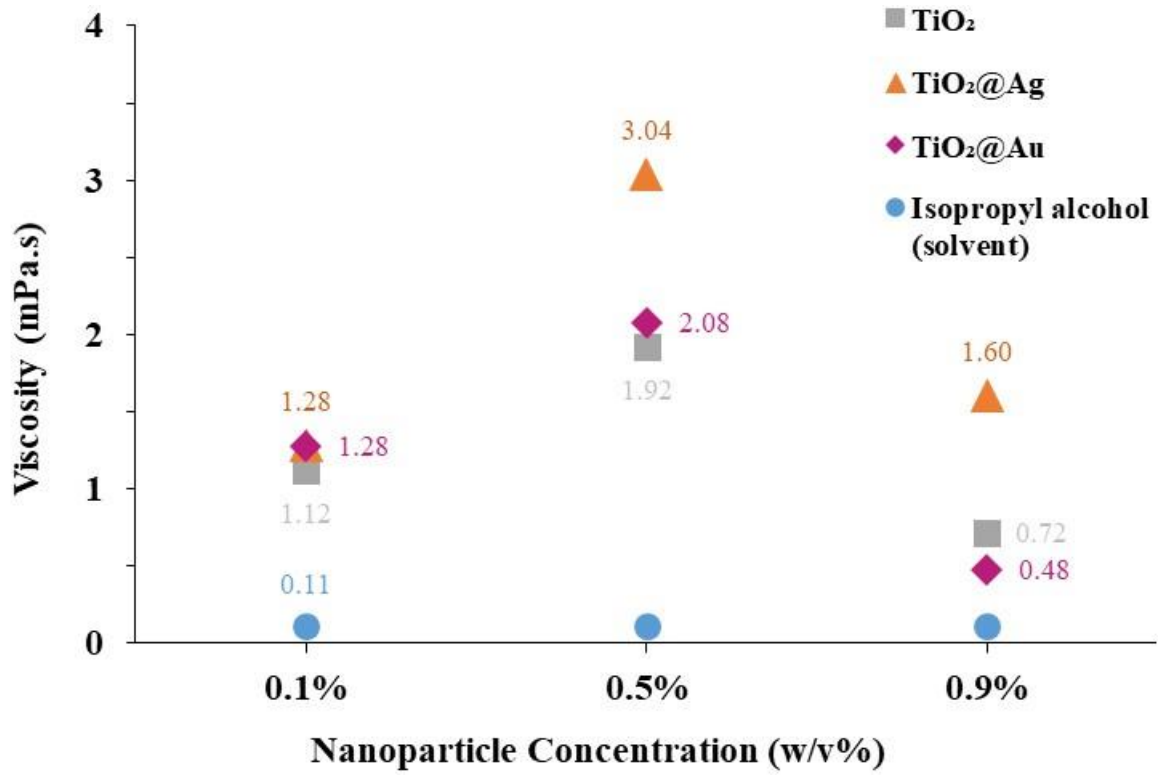



**Figure 3.10** Viscosities of bare $TiO_2$, prepared $TiO_2$@Ag and $TiO_2$@Au nanoparticle suspensions

The conductivity of nanoparticle suspensions was measured for three concentrations (0.1%, 0.5% and 0.9%) (Figure 3.11). The electrical conductivities of nano $TiO_2$ suspensions increased from 5.18 $\mu S.cm^{-1}$ to 47.33 $\mu S.cm^{-1}$ with increasing of nanoparticle concentration. When the bare $TiO_2$ coated with the silver and gold layer the conductivity of these suspensions also increased depending on the nanoparticle

concentrations. The increment in the conductivity of coated nanoparticle suspensions is due to the metallic layer on the bare $TiO_2$ which is known as good conductors because of the sharing electron easily. Our results are consistent with the previously published studies (Bi et al., 2014; Ganguly et al., 2015; Senthilkumar and Rajendran, 2018; Smitha et al., 2014).

The conductivity of a suspension is an important parameter for the electrospraying process. Smith (1986) reported that the conductivity value of an electrospraying solution should be greater than $10^{-11}$ $\mu S.cm^{-1}$. The measured conductivities of the prepared suspensions were well above the limit of electrosprayable conductivity value. Thus, the prepared suspensions were suitable for electrospraying in terms of conductivity.

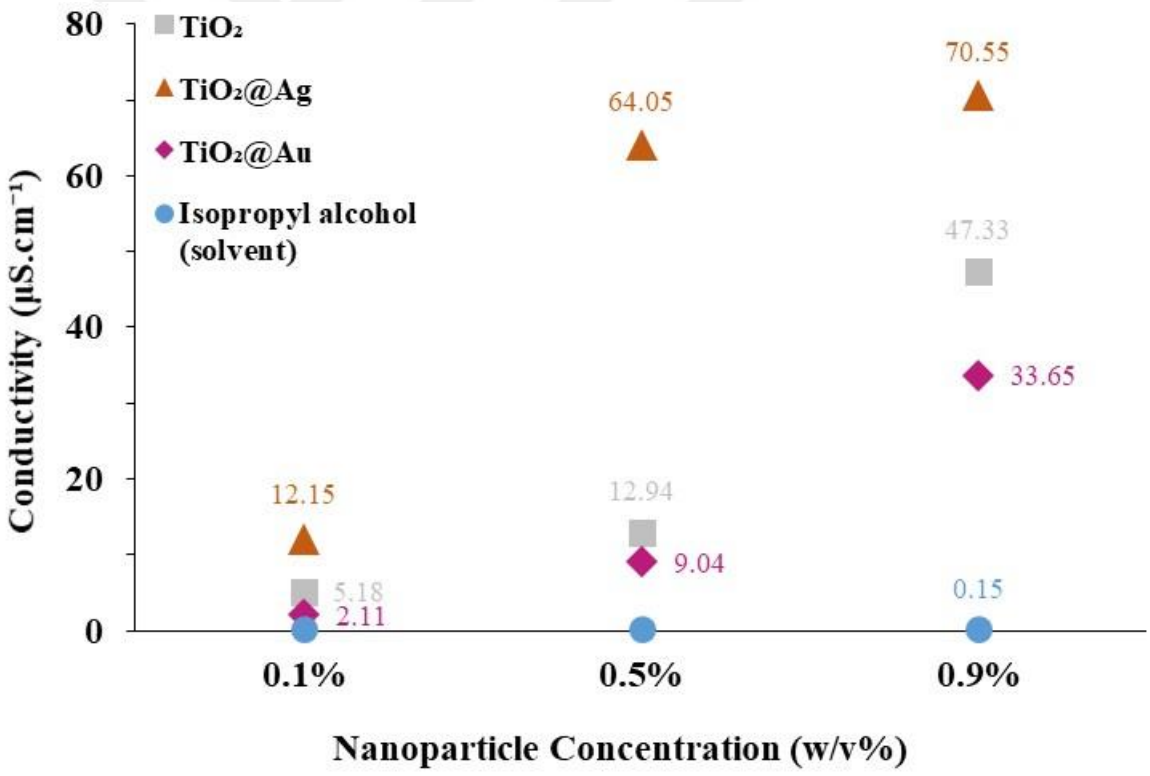



**Figure 3.11** Conductivities of bare $TiO_2$, prepared $TiO_2$@Ag and $TiO_2$@Au nanoparticle suspensions

For nanoparticle suspensions, there is a deficiency of consistent studies in the literature on the effect of nanoparticle concentration on surface tension, contact angle, and wetting behavior. The surface tension of all nanoparticle suspension was measured for all concentrations that is shown in Figure 3.12. The surface tension measurements of prepared $TiO_2$@Ag, and $TiO_2$@Au nanoparticle suspensions were shown a small piece decrease with the increasing concentration ratios of suspension respectively from 22.25 $mN.m^{-1}$ and 22.42 $mN.m^{-1}$ to 21.42 $mN.m^{-1}$ and 21.72 $mN.m^{-1}$ at 0.1% and 0.5% concentration. Radiom et al. (2010) have studied above surface tension results at higher concentrations, they have taken the lower surface tension measurement with increasing concentration ratios of the nanoparticle suspension. This study of them has confirmed our surface tension results for coated nanoparticle as $TiO_2$@Au and $TiO_2$@Ag suspensions at 0.1% and 0.5% concentration. However, surface tension measurements of $TiO_2$ nanoparticle suspension showed an increase. Subsequently, $TiO_2$@Au and $TiO_2$@Ag suspensions at 0.9% concentration that showed an upward trend. These showed aggregation and chemical precipitation at 0.9% concentration. Thus, the rise of surface tension measurement at 0.9% concentrations which was interpreted depending upon the aggregation of nanoparticle suspension. Prepared metal-coated nanoparticles at 0.9% concentration during characterization measurements were proved aggregation and precipitation (Zhang, 2014). The obtained highest surface tension results at 0.1% and 0.5% concentrations that were not shown a negative effect over the electrospray process. However, 0.9% concentration ratio of the suspension is not sufficient for the electrospraying application method for this reason the main concentration was selected 0.5% according to its results.

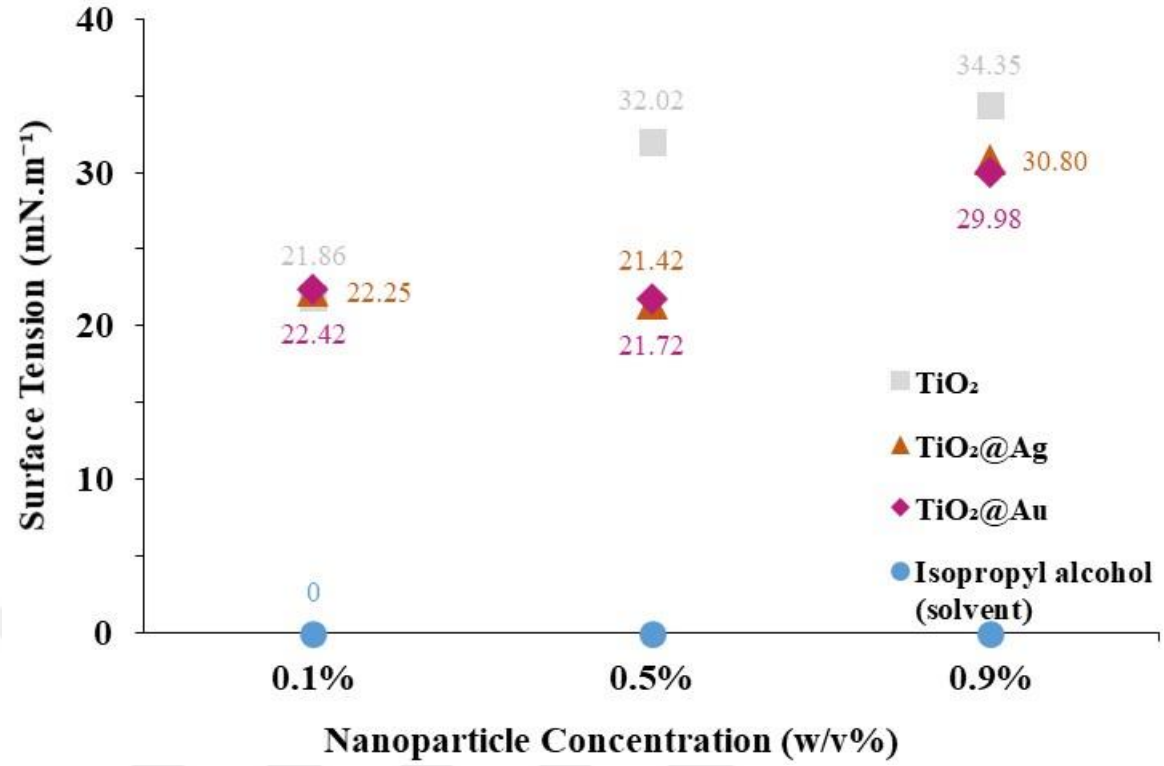



**Figure 3.12** Surface tensions of bare $TiO_2$, prepared $TiO_2$@Ag and $TiO_2$@Au nanoparticle suspensions

### 3.4.2 Selection of Thiol-modification Recipe

In order to determine the best performing thiol-modification recipe, the water contact angles of surfaces were measured. Figure 3.13 shows the comparison of the water contact angles of control fabric and thiol modified fabrics prepared using five different recipes. The water contact angle of control fabric (52.4°) increased after the thiol modification (with Recipe A: 97.6°, B: 87.4°, C: 87.7°, D: 65.2°, and E: 66.5°) as expected. This is due to the hydrophobic characteristic of mercaptododecanoic acid in the thiol modification recipes. The highest water contact angle (97.6°) was obtained in recipe A. This could be due to the great amount of thiolated molecules attached to the fabric surfaces. Therefore, in the following studies for the thiol modification of the fabric recipe A was chosen.

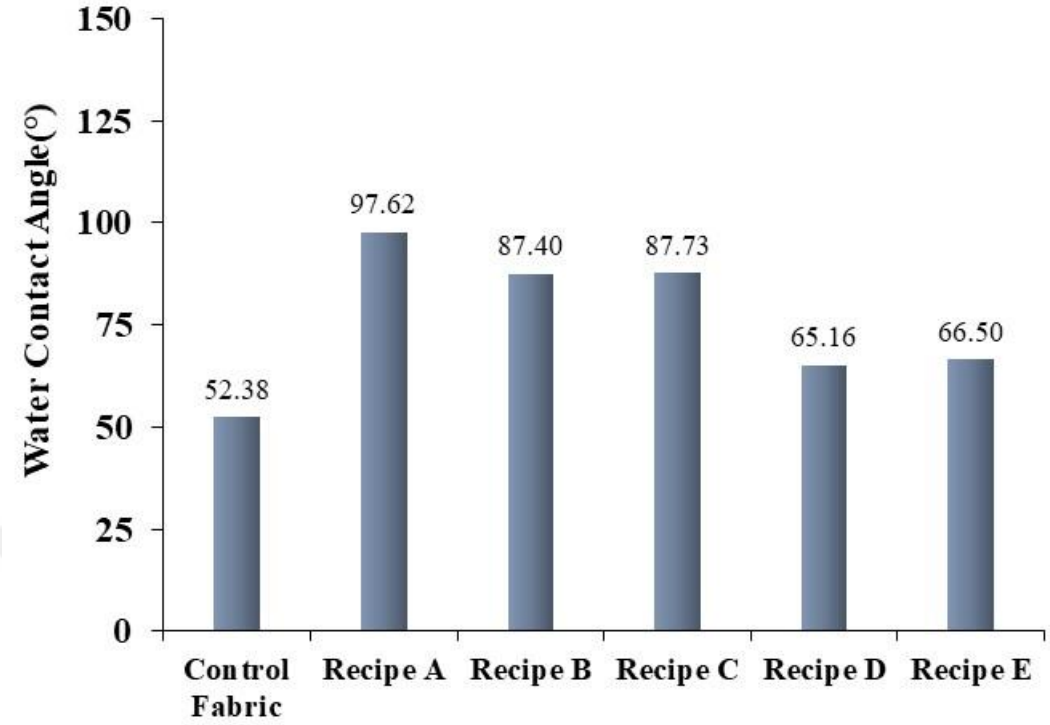



**Figure 3.13** Water contact angles of fabric surfaces modified with thiol using different recipes

### 3.4.3 Determination of the Hydrophobic Characteristics of Modified Fabric Surfaces with Different Coating Applications

A novel electrospraying coating method was used to coat the fabric surfaces with the prepared nanoparticles suspensions having three different concentrations (0.1%, 0.5%, and 0.9%). Also, well-known conventional method named pad-dry-cure was used for comparison. Water contact angles (WCAs) of the fabric surfaces were measured to determine hydrophobic characteristics attained after the coating applications. Figure 3.14 obviously reveals that the WCA values of the coated fabrics with $TiO_2$ nanoparticle at 0.5% concentration was improved from 94.1° to 111.5° and from 97.1° to 117.3° after electrospraying and padding applications, respectively. When $TiO_2$@Au nanoparticles were used, WCA values of the coated fabrics with at 0.5% concentration was improved from 107.2° to 113.0° for electrosprayed and from 118.4° to 137.9° for padded (Figure 3.15). The WCA values of the coated cotton/polyester

fabrics with $TiO_2$@Ag nanoparticle at 0.5% concentration was improved from 100.1° to 106.5° for electrosprayed and from 103.8° to 128.2° for padded (shown in Figure 3.16).

As the concentration of nanoparticle suspensions increased, WCA has increased for both the padding method and the electrospray method. As expected, for electrosprayed fabric WCA are lower than from padded fabrics the reason for this is taken the amount of chemical matter for the absorption of coated fabric as weight gains ratio. Even so, as requested hydrophilic fabric having about 53° WCA that has become to have a hydrophobic character with significantly increasing WCA due to the creation of roughness by the use of prepared nanoparticles in suspensions on the all coated fabric surface.

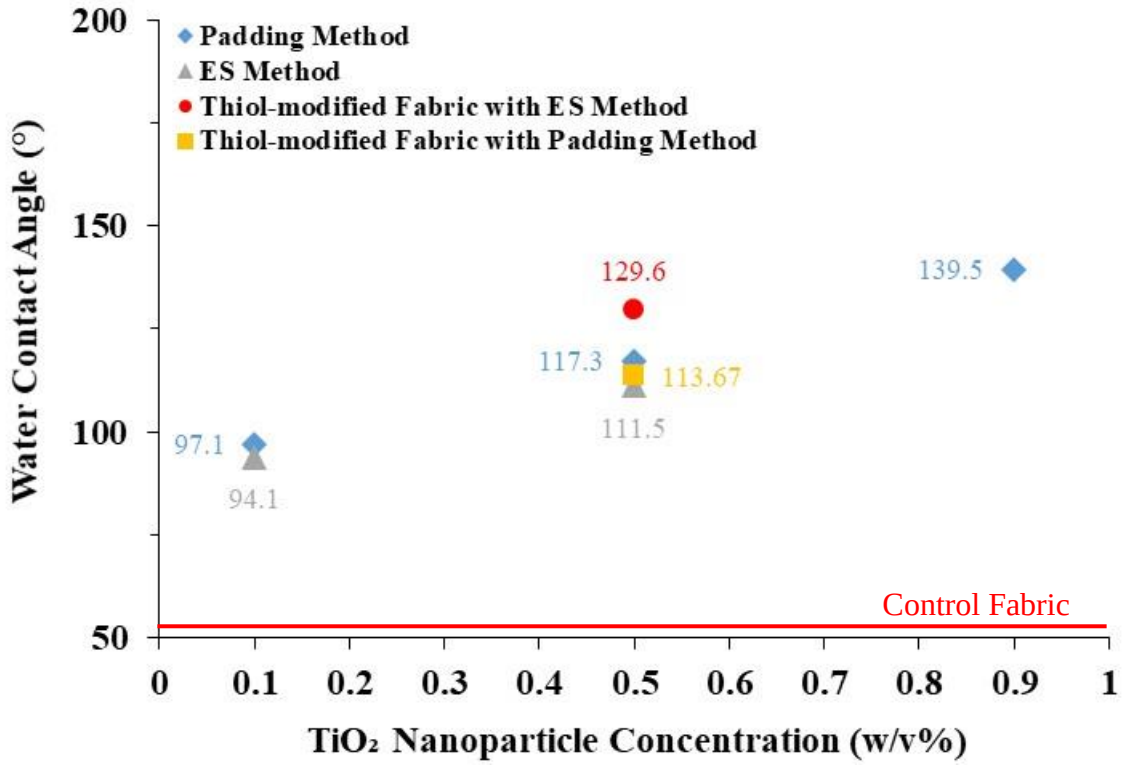



**Figure 3.14** Water contact angles of coated fabric with $TiO_2$ nanoparticle at 0.1%, 0.5%, and 0.9% nanoparticle concentrations

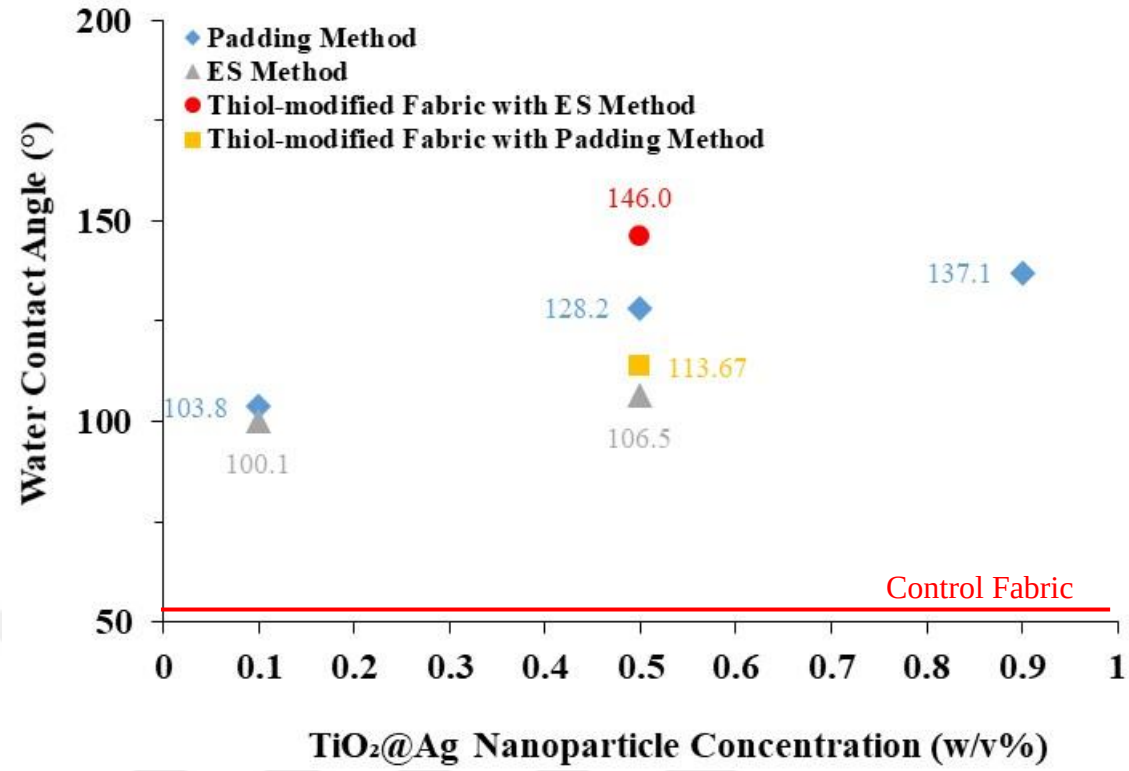



**Figure 3.15** Water contact angles of coated fabric with $TiO_2$@Ag nanoparticle at 0.1%, 0.5%, and 0.9% nanoparticle concentrations

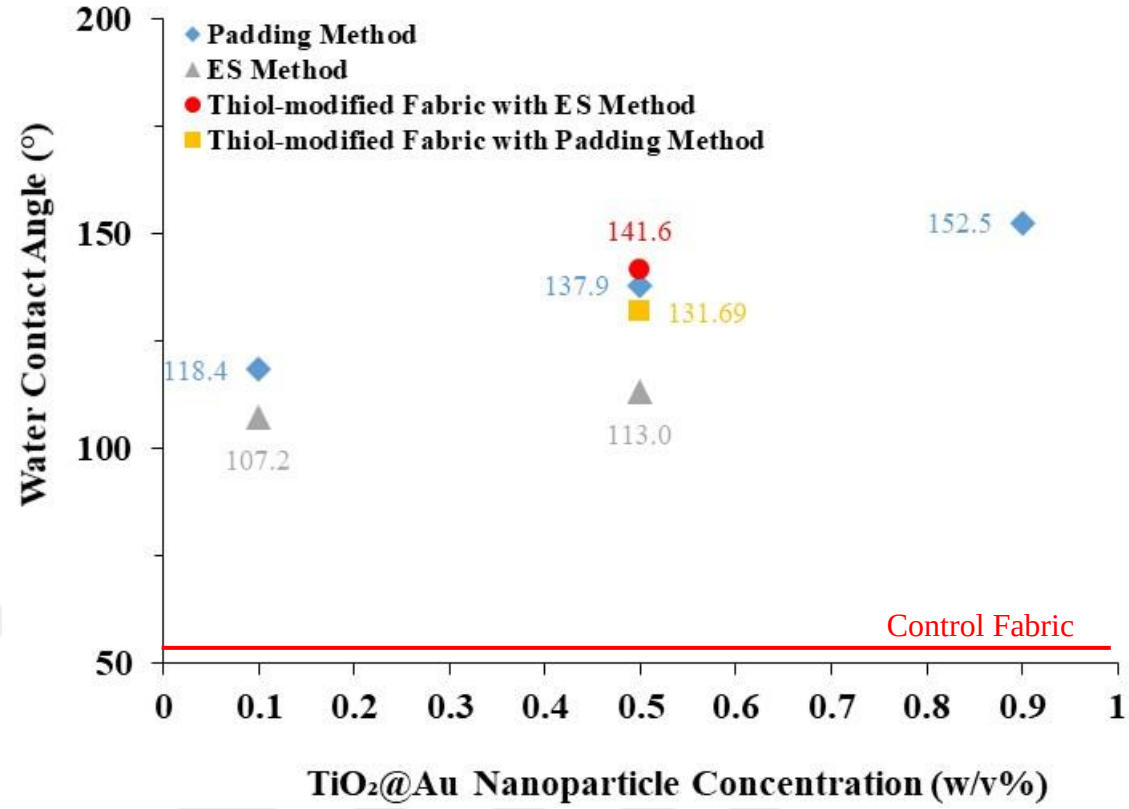



**Figure 3.16** Water contact angles of coated fabric with $TiO_2$@Au nanoparticle at 0.1%, 0.5%, and 0.9% nanoparticle concentrations

The WCA of selected thiol-modified fabric was found to be about 97° before the coating of nanoparticles. After the application of $TiO_2$, $TiO_2$@Au and, $TiO_2$@Ag nanoparticle, WCA results of electrosprayed thiol-modified fabrics showed changing respectively about 129.6°, 141.6°, and 146.0°. Thus, the superhydrophobic characteristic was achieved for each nanoparticle suspensions compared to not thiol-modified raw fabrics. When the thiol-modified fabric coated with the padding method at the same concentration over the electrospray method, lower WCA measurements were obtained as about 113.7°, 131.7°, and 113.6°. Besides that, coated bare $TiO_2$ nanosuspension with thiol modified fabric although it contains no strong bonds between nano chemical and fabric that show high uniformity with increasing WCA on the surface. This situation has been interpreted that using thiol with 12 carbons chain increased the intended hydrophobicity of the fabric. The WCA values of the coated cotton/polyester fabrics with $TiO_2$, $TiO_2$@Au, and $TiO_2$@Ag nanoparticle at 0.9% concentration was respectively performed as 139.5°, 152.5° and 137.1° for padded.

With the concentration of nanoparticles increasing, the surface roughness of the cotton/polyester fabrics gradually increased. Even though not use of any covalent bonding or crosslinking agents, WCA results of the coated fabrics at 0.9% concentration were taken quite high due to the formation of large-sized nano- $TiO_2$ aggregations embedded in the nanoparticle suspension which provided development on the hydrophobicity of the treated cotton/polyester fabrics. When each result compared with one another, coated fabrics with $TiO_2$, $TiO_2$@Au, and $TiO_2$@Ag nanoparticle at the same concentrations have clearly released. These results in which prepared $TiO_2$@Au and $TiO_2$@Ag as core@shell nanoparticles have given higher WCA values than WCA values of coated fabric with only $TiO_2$ nanoparticles. The superhydrophobicity characteristic of the treated cotton/polyester fabrics can mainly occur to two factors. The first one is that the coated surfaces of the treated cotton/polyester fabrics having low surface energy(Khalil-Abad and Yazdanshenas, 2010; Lee, 2009; Ma et al., 2005; Park et al., 2015), and secondly, the coated fabric having the increased surface roughness resulting from micro or nanostructures by addition of nanoparticles(Qing et al., 2015; Roach et al., 2008). The coated nanomaterial in the core@shell form that has constituted more roughness of the fabric surfaces caused hydrophobicity. Yan et al. (2011) have published a paper using nanoparticles that corroborate our data over the superhydrophobic effect of roughness by nanoparticle coating on the surface.

### 3.4.4 Weight Gains of Electrosprayed and Padded Fabrics

After using electrospraying and padding applications for coating, we determined the weight gains of coated fabrics (Table 3.2). Weight gains of the electrosprayed fabrics were found to be in between 0.0005% and 0.002%, while those of padded fabrics were ranged in between 1.17% and 5.98% depending upon concentration ratio. The amount of chemicals accumulated on the surface of the fabric increased with increasing the concentration for both coating methods. The important outcome of this study is the achievement of coating with low amount of the nanoparticles which can be fulfilled by using the electrospraying technique.

**Table 3.2** Weight gains of padded and electrosprayed (ES) fabrics after the coating with different nanoparticle concentrations

| Weight Gain (%) | | | | | | | |
|---|---|---|---|---|---|---|---|
| **Methods** | | **Electrospraying** | | | **Padding** | | |
| **Concentrations** | | **0.1%** | **0.5%** | **0.9%** | **0.1%** | **0.5%** | **0.9%** |
| **Nanoparticles** | **$TiO_2$** | 0.0005 | 0.0007 | - | 1.17 | 2.3586 | 5.53 |
| | **$TiO_2$@Ag** | 0.0023 | 0.0022 | - | 1.84 | 2.8514 | 6.92 |
| | **$TiO_2$@Au** | 0.0016 | 0.0020 | - | 1.56 | 2.6071 | 5.98 |

### 3.4.5 Self-cleaning Properties of Coated Fabrics under UV Radiation

As shown in Figure 3.17, two droplets of the coffee staining agent have fallen on the sample fabric, hydrophilic untreated cotton/polyester fabric absorbed suddenly, but, obtaining the hydrophobic property of coated fabric samples absorbed staining agents as slowly at the moment of installation in a word at zero hours.

After 8 hours, when the untreated cotton/polyester fabric did not give any changing, the coffee staining over coated fabrics with $TiO_2$ nanoparticle which showed noticeably removal on the fabric surface. The same observed result can be said for coated fabrics with $TiO_2$@Au nanoparticles. However, no change of color cannot be said for coated fabric with $TiO_2$@Ag nanoparticles.

After 16 hours, removal of the coffee stain was relatively observed in a small way for coated sample fabrics by $TiO_2$ and $TiO_2$@Au nanoparticle. Coated fabric with $TiO_2$@Ag nanoparticle was not very successful in the complete decomposition of stains under the visible light and only some slight enhancements were observed that are shown in Figure 3.17.

As finally after 24 hours, even though some promising results were obtained, the coating of $TiO_2$@Ag nanoparticle was not very successful in the complete decomposition of stains under the visible light and only some slight recovery was seen by comparison untreated cotton/polyester fabric. However, the self-cleaning feature of

samples treated with coated sample fabrics with $TiO_2$ and $TiO_2$@Au nanoparticles was obviously higher than $TiO_2$@Ag treated samples.

$TiO_2$ and $TiO_2$@Au showed the highest self-cleaning performance in comparison with untreated sample fabric and even treated the fabric with $TiO_2$@Ag. We have already demonstrated that the self-cleaning property of titanium dioxide on cotton/polyester fabric could be augmented. And, the presence of gold has been helpful in intensifying the self-cleaning activity of fabrics. Based on the images, optimizing the concentration of gold seems to be important due to the gold's coloring side effects on the fabrics particularly at higher concentrations (Pakdel et al., 2013). Even though some promising results were obtained, the coating of $TiO_2$@Ag nanoparticle was not very successful in the complete decomposition of stains under the visible light and only some very slight enhancements were observed.

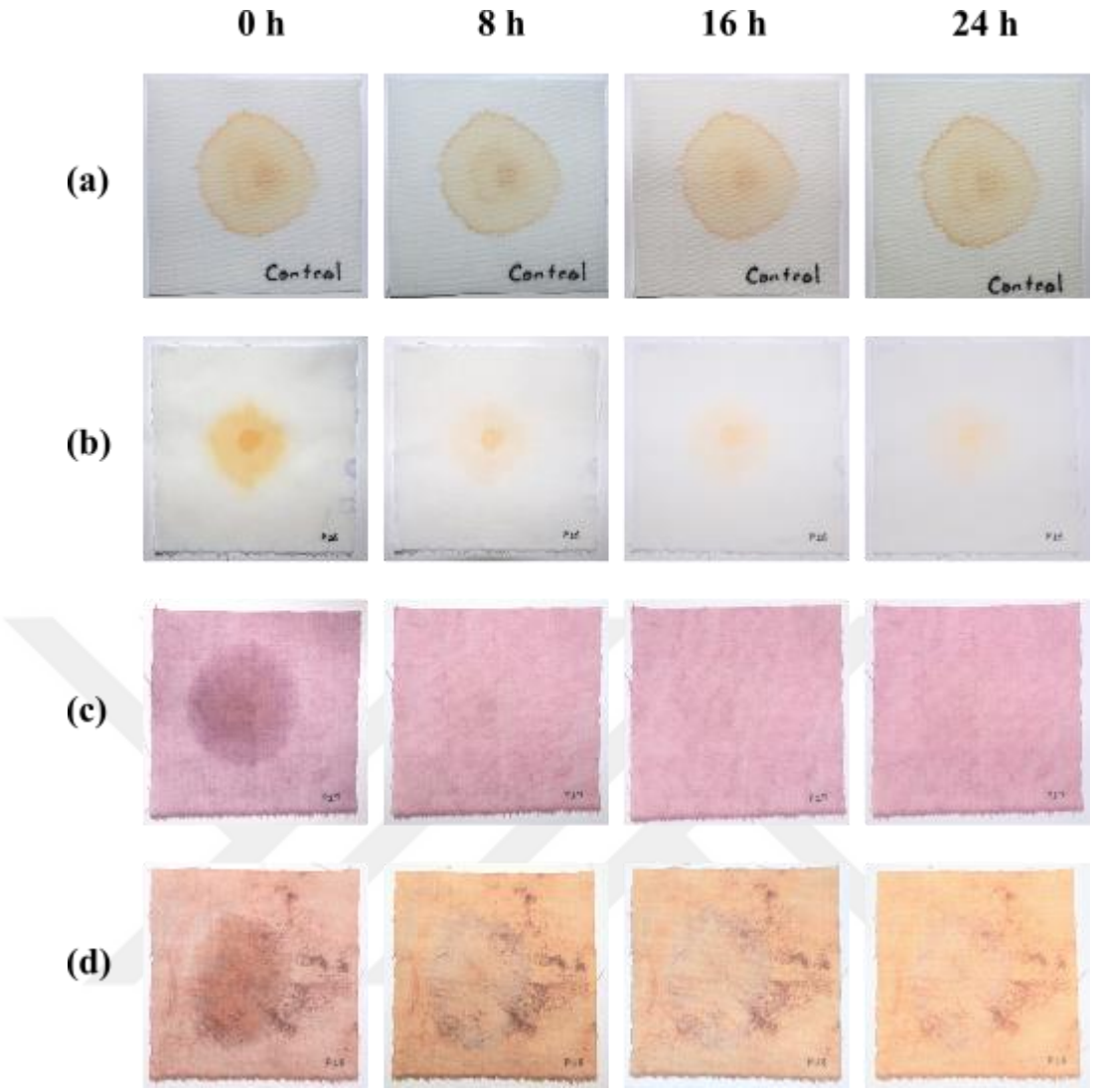



**Figure 3.17** Stain decomposition test of coated fabric samples with the coffee stain after 0, 4, 8 and 24 h under UV radiation simulator (a: untreated fabric, b: $TiO_2$-treated fabrics, c: $TiO_2$@Au-treated fabrics, d: $TiO_2$@Ag-treated fabrics)

### 3.4.6 Morphological Analysis of Coated Surfaces

SEM images of the coated fabric surfaces with nanomaterials were obtained to better understand the improvement on hydrophobic and photocatalytic properties. Figure 3.18 shows the SEM images of control fabric and coated fabrics by using electrospraying (ES) and padding methods with $TiO_2$@Au. It was observed that there were more surface coatings for padded fabrics than electrosprayed fabrics. This was

expected since high amount of nanoparticles were used and consumed during the padding application. Also, the padding method created a thin film surface on the fiber.

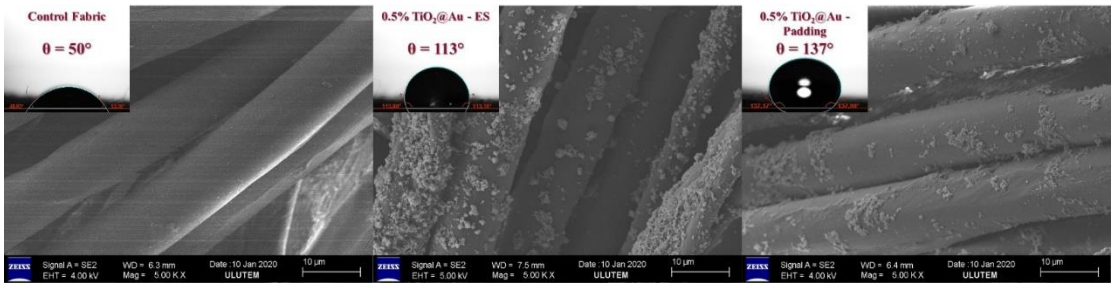



**Figure 3.18** SEM images of control fabric and coated fabrics by using electrospraying (ES) and padding methods with $TiO_2$@Au

Figure 3.19 shows the SEM images of bare and thiollated fabric coated by using the electrospraying method with $TiO_2$@Ag and $TiO_2$@Au. We determined a uniform nanoparticle distribution for the thiolated fabric surfaces coated with $TiO_2$@Ag and $TiO_2$@Au. Also, thilation of fabric surface increased the number of the binding nanoparticles to the surface by means of the metal-sulphur bond. Thus, a surface roughness at nano-size was achieved on the surfaces which improved hydrophobic characteristics of the surfaces.

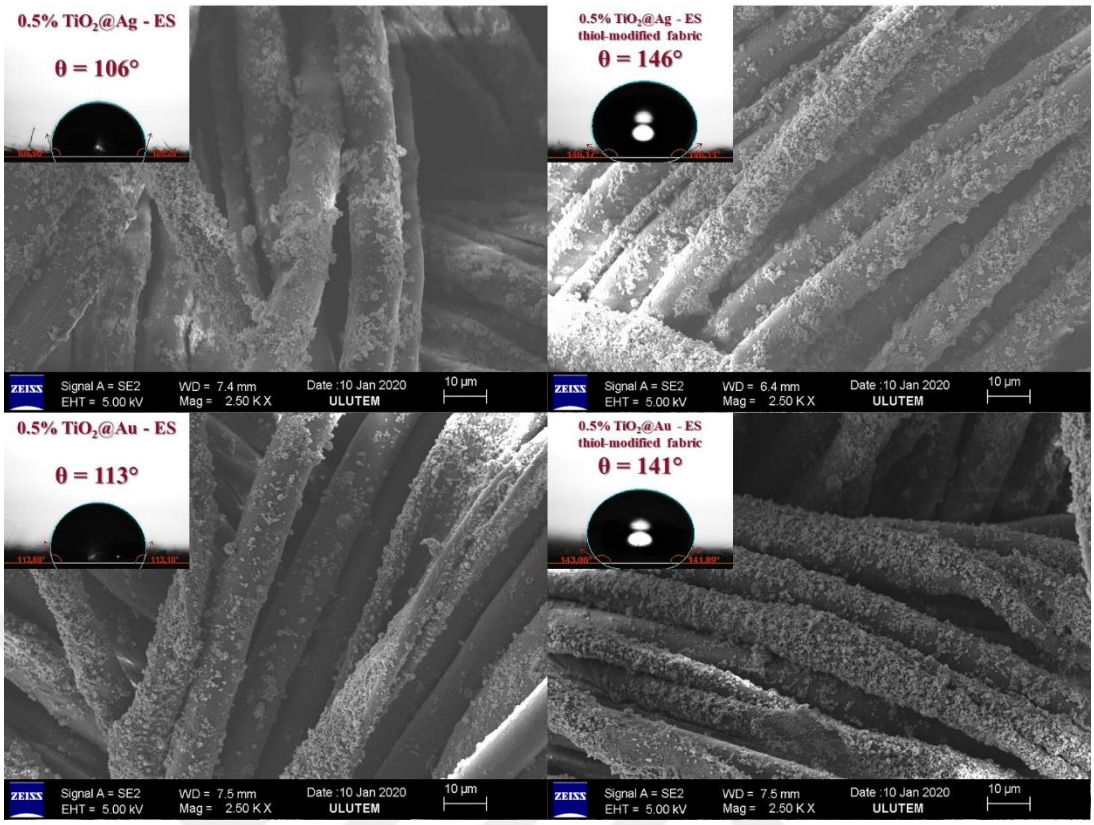



**Figure 3.19** SEM images of bare and thiollated fabric coated by using electrospraying method with $TiO_2$@Ag and $TiO_2$@Au

Figure 3.20 shows that the concentration of nanoparticle suspensions increased, WCA has increased for both padding method and the electrospray method. For $TiO_2$@Au nanoparticle suspension coating with padding method which shown an increase with increasing concentration ratios.

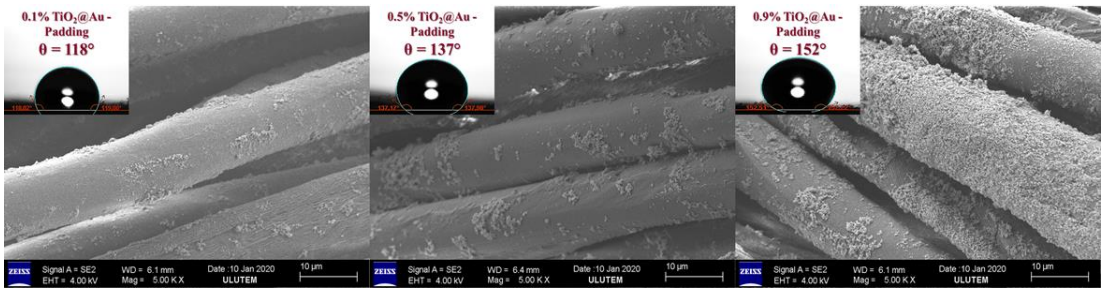



**Figure 3.20** SEM picture of concentration effect on coated fabric with $TiO_2$@Au nanoparticle suspension by using the padding method.

When the thiol-modified fabric coated with the padding method at the same concentration over the electrospray method, lower WCA measurements were obtained as about 113.7°, 131.7°, and 113.6°. Because the padding method created a thin film surface on the fiber (Figure 3.21).

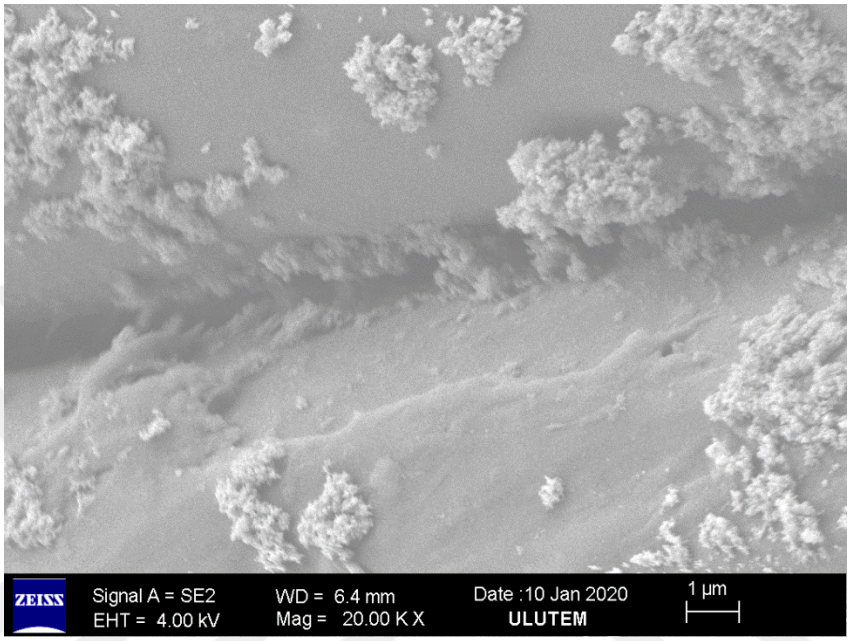



**Figure 3.21** SEM pictures of thiol-modified coated with 0.5% $TiO_2$@Au by using the padding method.

# CHAPTER 4

# ANTIBACTERIAL SURFACES BY NANOPARTICLES TREATED ELECTROSPRAYED COATINGS FABRIC

## 4.1 Abstract

This paper deals with the antibacterial activity of cotton/polyester woven cotton fabrics treated with the traditional padding and innovative electrospraying processes. Two bacteria, Escherichia coli, and Staphylococcus aureus were employed to assess the antibacterial activity of fabric samples finished with bare nano $TiO_2$ and in the form of core@shell structure coated nano $TiO_2$@Au and $TiO_2$@Ag. Also, the surface was modified with 12-mercaptododecanoic acid to obtain a thiolated cellulose-containing textile surface that enables the covalent bonding of metal coated nanoparticles to the textile surface. The coated nanoparticles were applied to the thiolated textile surfaces for determining antibacterial efficiencies. The antibacterial activities of fabric samples against E. coli and S. aureus were determined quantitatively after both washing and abrasion. The microstructural characteristics and surface morphology of the fabric samples were investigated by SEM analyses. Our results suggest that metal-coated nanoparticles imparted good and durable antibacterial activity for thiol-modified fabrics and raw cotton/polyester fabrics which can be a good candidate for antibacterial textiles. The water vapor permeability and air permeability test results indicated that the coated fabrics with nanoparticle materials did not significantly influence the comfort properties.

## 4.2 Introduction

Functional textiles are those that provide additional functions such as UV protection (Sawhney et al., 2008; Yetisen et al., 2016), self-cleaning (Banerjee et al., 2015; Morshed et al., 2010; Pakdel et al., 2013; Yuranova et al., 2006), lotus effect (Karthick and Maheshwari, 2008; Özdoğan et al., 2006; Stegmaier et al., 2008),

superhydrophobicity (Acatay et al., 2004; Lee and Michielsen, 2006; Xue et al., 2012), fire retardation (Bashari et al., 2018), antibacterial action (Ibrahim, 2015; Khalil-Abad and Yazdanshenas, 2010; Morshed et al., 2010), etc. in addition to performing their routine job. So, the researchers have focused their attention on the development of multifunctional textiles due to growing market demand. These development require the use of nanotechnology or nanomaterials to either deposit nanoparticles on textiles to functionalize them or to obtain nanofibers that are used to produce textile materials with functional features (Bashari et al., 2018; Joshi and Bhattacharyya, 2011; Morshed et al., 2010; Rivero et al., 2015).

A significant example of such functional textiles is antibacterial fabrics which have recently drawn the attention. Because of the textiles' large surface area and capacity to maintain moisture, they are considered to be beneficial to the development of micro-organisms, such as bacteria and fungi, which can be contained nearly anywhere and can rapidly reproduce based on the amounts of moisture, nutrients, and temperature (Gao and Cranston, 2008; Windler et al., 2013). Antibacterial textiles have aroused interest by scientific researchers and consumers to draw concern in minimizing the possibility of contamination or infection in medical areas, crowded places such as hospitals, cinemas, theatres, shopping centers and schools, and even home or office environments (Ibrahim, 2015; Marambio-Jones and Hoek, 2010).

For the antibacterial effect, many nanoparticles are used like nano-sized CuO, ZnO, $TiO_2$, Ag (Hasan et al., 2013). Due to its durability, low cost, biocompatibility, non-toxicity, photocatalytic and antibacterial efficiency, $TiO_2$ is one of the most researched materials among various nanoparticles. Wang et al. (2014) report that changing nano-$TiO_2$ concentration in the finishing solution had a significant impact on the finished fabric's antibacterial efficiency. According to this analysis, the finished fabric exhibited stronger antibacterial activity with over 90% antibacterial effectiveness when the adjusted nano $TiO_2$ concentration in the finishing solution was greater than 5 g/L. Also, metallic ions and compounds often offered some degree of sterilizing effect. It is believed that oxygen in the air or water is converted into active oxygen species through catalysis with the metallic ions such that the organic compounds are dissolved to produce a sterilizing effect (Palza, 2015; Xu and Imlay, 2012). Metals such as gold and silver have long been known to form stable colloids of nanosized

particles. Mirjalili et al. (2016) developed polycaprolactone-based antibacterial electrospun nanofibers including silver-loaded zirconium phosphate (nano-AgZr) nanoparticles for wound dressing application. Also, Inbakumar et al. (2012) recorded a process which integrates Ag nanoparticles into the cotton fabric. This fabric was tested against E. coli for its antibacterial behavior. Silver oxide nanoparticles were prepared and covered with an acrylic binder on the bleached cotton fabrics. Results suggested that the fabric's Ag content is a key factor in regulating its antibacterial performance.

Breathable barrier fabrics protect the human body from external heat, wind, and water in many extreme climatic conditions and at the same time allow the moist vapor to be properly transferred. They enable water vapor to flow and also prevent liquid water droplets from entering. The breathability of the fabric is the ability of the clothing to enable the transmission by diffusion of moisture vapor and thus promote the evaporative cooling (Mukhopadhyay and Kumar, 2008; Painter, 1996). Textiles which are both water-repellent and breathable advance to become functional performance clothing and to give the wearer a greater degree of comfort. Water repellence and permeability to moisture are two functions which contradict each other (Jin et al., 2016). New material production technology needs to be developed for achieving adequate barrier efficiency and comfort satisfaction at the same time. Electrospraying coating as an effective and promising technique provides the extremely fine coating with small pore size and high surface area at the nanoscale in which fabric breathing characteristics and fluid barrier characteristics can be provided (Ju et al., 2009). Electrospraying is a low-cost method that can turn into particles to stable nano and monodisperse droplets which can produce thin uniform coatings (Kavadiya et al., 2017; Ku and Kim, 2002; Zarrabi et al., 2012). Electrospraying technique as electrostatic deposition has advantages compared with other traditional coating methods because they allow preparing coatings at the nanoscale on multiple substrates with uses of the low chemical amount (Dasdemir and Ibili, 2017; Jaworek and Sobczyk, 2008). In the method, positively charged droplets are created from the tip of a liquid jet by applying a high voltage and are pushed towards a grounded collector. When the solvent evaporates, particles are collected on the substrate with the electrostatic repulsion effect as a thin coating. The other benefit of this method is also that no corresponding drying phase is needed because the vast portion of the solvent

evaporates during the electrohydrodynamic spraying method (Bošković and Bugarski, 2019; Dasdemir and Ibili, 2017; Jaworek et al., 2009; Nguyen–Vu et al., 2017).

In this work, we studied the antibacterial activity of photoactive coatings prepared as the metal from the coating of $TiO_2$@Ag $TiO_2$@Au nanoparticle suspensions. Nanoparticle suspensions were padded and electrosprayed on the control and thiol-modified cotton/polyester fabrics. The antibacterial efficiencies were assayed using means of cultures of the gram-positive bacterium Staphylococcus aureus and gram-negative Escherichia coli bacteria. The bioactivity of coatings was studied by quantifying the number of culturable bacteria and by visualizing the formation of coated fabrics. Also, the comfort performance of coated fabrics was tested.

## 4.3 Materials and Methods

### 4.3.1 Preparation of Nanoparticle Suspensions and Modification of Cellulose Containing Fabrics with Nanoparticles

Preparation of the nanoparticle suspensions which is used in this study was explained in detail in chapter ***"3.3.1. Materials and Preparation of Nanoparticles"***

Also, the application of nanoparticle suspension onto the textile fabric surface was conducted using two different methods which were pad-dry-cure (Figure 4.1) and electrospraying methods (Figure 4.2). The details of used two application methods were mentioned in chapter ***"3.3.3. Surface Modification of Cellulose Containing Fabrics"***


**Figure 4.1** Laboratory type of padding machine

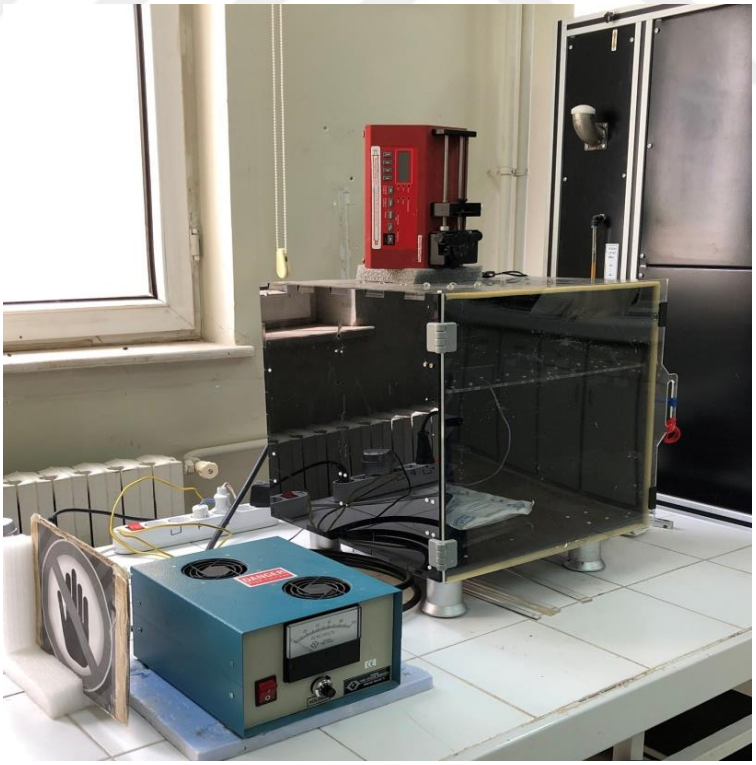


**Figure 4.2** Laboratory type electrospraying set up

### 4.3.2 Characterization of Modified Fabric

#### 4.3.2.1 Washing

The laundering test was used to ensure that the metal nanoparticle agents were still on the surface of the fabric after washing and evaluate the durability of coated fabric surfaces. After the washing, antibacterial efficiencies of coated fabrics were evaluated and SEM images of the coated surfaces with nanoparticle were examined.

The washing test was applied to all coated fabric samples based on ISO 105 C06-A2S method with 10 accelerated laundering cycles. Laboratory type washing machine was used. After the washing process, fabric samples were dried as flat without any additional stretching or twisting. Fabric specimens were cut as 100 mm x 40 mm sizes. Laundering solution was prepared with using 1 gr of sodium borate and 4 gr of SDC ECE phosphate reference detergent b per 1lt of water.

The washing test machine was set at 40 °C. According to the washing method, 120 ml prepared solution and fabric were added in a stainless steel container with ten steel balls. They were put in a machine and heated at 40 °C for 30 minutes, this process was accepted as a laundering cycle and that was repeated until 10 launderings. After 10 laundering cycles, all samples were rinsed twice for 1 min in two separate 100 ml portions of water at 40 °C and they were dried at ambient conditions.

#### 4.3.2.2 The Abrasion Test

AATCC Test Method 8-2001 was used to determine the abrasiveness of coated fabric with a Crockmeter rubbing strength tester. Fabric samples were cut at 50 mm × 130 mm size and they were placed on a lower pad, 10 cycles were rubbed with a white fabric fixed on a peg in the upper rubbing neck. The peg's rubbing motion with 10 cycles back and forth allowed nanoparticle coated fibers from the lower coated surface of sample fabrics to be transferred to the white fabric placed on the upper platform. The basic configuration of the integrated Crockmeter has features that are a full turn of the handle, 15mm in diameter peg pushed back and forth in a straight with together 9N vertical pressure on the sample fabric surface.

#### 4.3.2.3 Antibacterial Test

The antibacterial activity of coated fabric samples was quantitatively evaluated and compared with two non-spore forming bacteria, which are gram-positive Staphylococcus aureus (ATCC = 25923) and one gram-negative Escherichia coli (ATCC = 25922) according to using AATCC 100 test method.

According to AATCC 100 test method, fabric specimens were cut as 4.8 ± 0.1 cm in diameter. 100 µl of bacterial culture solution containing $1 \times 10^5$ CFU (colony-forming units)/ml of bacteria in nutrient agar was prepared and poured on fabric samples. After exposure to the bacteria with a contact time of 1 hour, that was named as "0" contact time, prepared bacteria solutions in each jar were inoculated on nutrient agar plates. Plates were incubated at 37°C for 24 hours. Bacteria solutions which were impregnated onto treated fabric samples were vortexed and incubated into the drying-oven to wait at 37°C for 24 hours. After that, the same process was applied, waited bacteria solutions were inoculated on nutrient agar plates and all plates were incubated for a further at 37°C for 48 hours ("1" contact time). The results of '0' and '1' contact time assays were recorded as CFUs per milliliter. Based on the ratio of the number of bacteria in "1" contact time to the number of bacteria in "0" contact time, the amount of decrease in bacteria was determined as % value (Equation 4.1).

$$\text{Bacterial reduction } (\%) = \frac{(B-A)}{B} \times 100 \qquad (4.1)$$

A is the number of bacteria recovered from the inoculated treated test sample swatches in the jar incubated after 24 hours, and B is the number of bacteria recovered from the inoculated treated test sample swatches in the jar after 1 hour. If A > B, the sample is not antibacterial (Gao and Cranston, 2008; Ibrahim, 2015).

#### 4.3.2.4 Determining Comfort Properties of Coated Fabric

Air permeability and water vapor transmission of the fabric are intended parameters to assess the breathability of clothing, especially for wearer comfort.

In SDL ATLAS M261 (Figure 4.3)., the water vapor transmission rate (WVTR) of untreated and all treated fabrics were calculated in compliance with BS EN 7209. The

method evaluates reduced weight within the time of the water vaporization used for a cup. The method determines the rate of water mass transfer from eight cups via fabric, with two covered with reference fabric and the other six covered with test samples. For each test sample, three distinct specimens were taken. Subsequently, the sample cups were supplied with 46 ml of distilled water to provide a constant distance between the surface of water and fabric. Then, the samples were covered on the cups and glued. The rings of the cup were closed over the fabric sample to prevent any slip. Cups covered with sample fabric were put on the turn-table. After 1 hour of turn-table rotating, the cups were weighed on a precision scale that was the first measurement. After 5 hours, the second measurement was taken with the weight of each sample cup. After the test was completed the difference between the two measurements was calculated as $g.m^{-2}.24\ h^{-1}$ at the same ambient temperature and humidity.

**Figure 4.3** Water vapor permeability tester

In addition, air permeability tests for such fabrics were carried out in compliance with the ASTM D737-04 specification in the SDL ATLAS M021A air permeability tester (Figure 4.4). Fabrics were prepared as 20 $cm^2$ for the test and placed over the airflow tube. Through pressure difference between two sides of the fabric, airflow was supplied into the fabric structure. The means of ten different measurements were taken for all fabrics at 100 Pa pressure as $cm^3/s/cm^2$ unit.

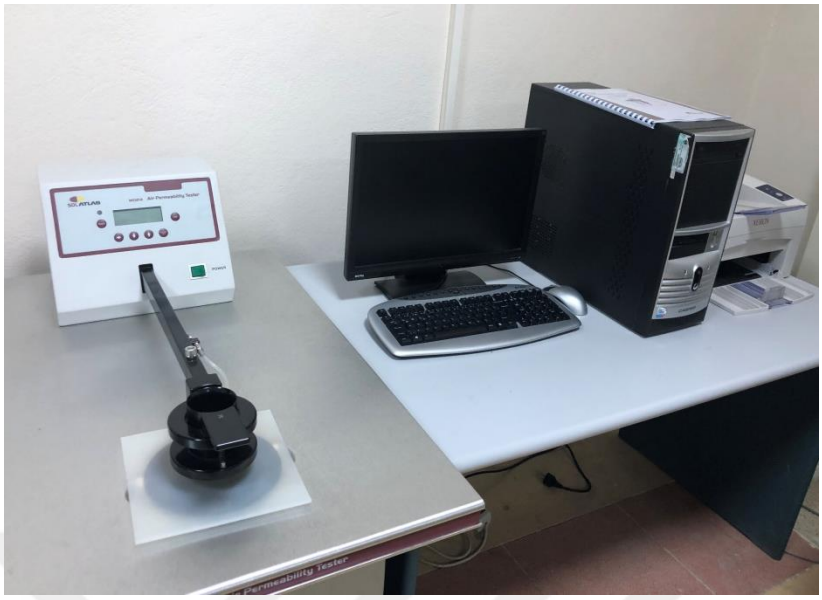


**Figure 4.4** Air permeability tester

#### 4.3.2.5 Surface Morphology and Elemental Analysis

The surface morphology of the coated samples was examined using JEOL JSM-6390 scanning electron microscopy. Samples were coated with gold/palladium (Au/Pd) ultra-thin film at 2–20 nm thickness in order to increase both the signal to noise ratio and the number of secondary electrons that can be detected from the surface of the specimen before analysis. SEM images were determined under the same conditions for coated fabrics which is in 2500,5000,10000 and 20000 magnifications, 4kV accelerating voltage, and 12 to 15 mm working distance.

## 4.4 Results and Discussions

### 4.4.1 Antibacterial Effectiveness of The Coated Fabrics

Antibacterial behaviors of raw and the coated samples against all E. coli and S. aureus bacteria after the stated contact period were calculated. The S. aureus bacterium is a pathogenic micro-organism that triggers multiple diseases such as toxic shock, purulence, abscess, coagulation of fibrins, and endocardia. In addition, it's immune to

rising antimicrobials. In addition, a common test organism is E. coli bacterium which causes urinary tract infections and wound infections (Dastjerdi and Montazer, 2010; Marambio-Jones and Hoek, 2010).

Electrospraying coating was used to cover the fabric surfaces with three specific concentrations of the prepared nanoparticle suspensions (bare $TiO_2$ and coated $TiO_2$@Au and $TiO_2$@Ag). For comparison, the well-known traditional process named pad-dry-cure was also used.

In the present study, untreated raw cotton/polyester fabric showed no antibacterial activity against both S. aureus and E. coli bacteria.

Firstly, treated fabrics with nano $TiO_2$@Au suspension at 0.1%, 0.5%, 0.9% concentration with the pad-dry-cure method were tested for comparison of antibacterial efficiency. The concentration effect was determined on the antibacterial test results. The results are given in Table 4.1. It can be concluded from Table 4.1 that the percent of antibacterial effect highly correlates with the concentration of coated nano-metal $TiO_2$@Au. Not only when the modified fabric with including metal nano $TiO_2$@Au suspensions reached a certain concentration, but the treated fabrics at three concentrations also exhibited obvious antibacterial property. Therefore, when the concentration of nano $TiO_2$@Au in the coating suspension exceeded 0.9% from 0.1% concentration the antibacterial efficiency was 99.44% for S. aureus bacteria. Our results are consistent with the previously published studies (Kale and Meena, 2012; Wang et al., 2014).

**Table 4.1** Concentration effect of nano $TiO_2$@Au suspensions on antibacterial efficiency

| **Percent decrease of bacteria (%)** | **Application Method** | **Concentration of nano $TiO_2$@Au (%)** | | |
|---|---|---|---|---|
| | | 0.1 | 0.5 | 0.9 |
| **Staphylococcus aureus** | Padding | 99.09 | 99.42 | 99.44 |
| **Escherichia coli** | Padding | 71.43 | 72.73 | 75.76 |

In order to improve the adhesion between nanoparticles and fabric surfaces, thiolated carboxylic acid was also used as a cross-linking agent. Obtaining thiol modified

surfaces was used to covalently bind metallic nanoparticles to the surface which provided for the attachment of metal nanoparticles (Au and Ag nanoparticle) to the surface via metal-sulphur bonding. After coating with $TiO_2$@Au nanoparticle suspension, thiol-modified coated fabrics containing strong metal-sulphur bonds with the nanoparticle and coated raw cotton/polyester fabric with nanoparticle were analyzed to compare antibacterial properties (Table 4.2). The thiol-modified fabrics showed a high antibacterial effect for both S. aureus and E. coli bacteria that have a strong covalent bond with containing metal nanoparticle suspension. Park et al. (2012) obtained strong antimicrobial activity against two representative bacteria with the metal coating with thiol-modified fabric. They succeeded with covalent bonds in the metal-cellulose which led to highly efficient deposition and durability of the nanoparticles compared to the metal/ cellulose without covalent bonds. Obtaining satisfactory antibacterial performance using thiol modified fabric in our study is supported (Park et al., 2012). The analysis was also determined using the electrospray coating method at a constant 0.5% concentration of used suspension. Bacteria reduction (%) of the coated fabrics with nanoparticle was 99.00% for S. aureus bacteria.

**Table 4.2** Thiol-modified fabric effect with obtained metal-sulphur bonds on antibacterial efficiency.

| **Percent decrease of bacteria (%)** | **Application Method** | **Fabric modified type with 0.5% $TiO_2$@Au nanosuspension** | |
|---|---|---|---|
| | | Cotton/polyester Fabric | Thiol-modified Cotton/polyester Fabric |
| **Staphylococcus aureus** | Padding | 99.42 | 98.97 |
| **Escherichia coli** | Padding | 72.73 | 76.01 |
| **Staphylococcus aureus** | Electrospraying | 98.40 | 99.00 |
| **Escherichia coli** | Electrospraying | 70.59 | 75.51 |

In Table 4.3, the antibacterial performances of the fabrics coated with $TiO_2$ nanoparticles using electrospraying and padding methods are given for comparison of the outcomes of these two methods. The antibacterial efficiency of the coated fabric with $TiO_2$ nanoparticles by the padding method shows higher than electrospraying method results for both two bacteria. The bacterial reduction of the treated fabrics by

padding method calculated 99.58% when the electrospraying method shows 99.13% ratio for against S. Aureus bacteria. This result changed against E. Coli bacteria as 81.82% for the padding method and 80.00% for the electrospraying method. This result can be explained by the weight gains of coated fabrics after using electrospraying and padding applications for coating. Because coated fabrics with electrospraying method have weight gains between 0.0005% and 0.002%, while padded fabrics have weight gains between 1.17% and 5.98% for coating $TiO_2$ nanoparticle suspension. On the other hand, the results showed that fabrics coated with bare $TiO_2$ nanoparticle suspension inhibited the growth of microorganisms in different rates with both electrospraying method and padding methods. In general, coated fabrics with $TiO_2$ nanoparticle have less antibacterial activity against E. coli and strongly inhibited the growth of the S. aureus (Palamutcu et al., 2011). Positive species of $TiO_2$ is the most scientifically justifiable explanation for $TiO_2$'s antimicrobial activity. $TiO_2$ produces positive species, particularly under UV rays which have a higher energy level than their bandgap. It gives rise to $TiO_2$'s photocatalytic existence, which responses at the cell surface of bacteria with negatively charged elements, contributing to intercellular material leakage. As a consequence, natural microorganism metabolism is disrupted which allows bacteria to die (Park et al., 2012; Wang et al., 2014; Zheng et al., 2008).

**Table 4.3** Application method effect on antibacterial efficiency

| **Percent decrease of bacteria (%)** | **Used application method for coating of cotton/polyester fabric with 0.5% $TiO_2$ nanosuspension** | |
|---|---|---|
| | Padding | Electrospraying |
| **Staphylococcus aureus** | 99.58 | 99.13 |
| **Escherichia coli** | 81.82 | 80.00 |

From Table 4.4, it can be concluded that treated fabrics with $TiO_2$@Au and $TiO_2$@Ag nanoparticle suspensions had a strong antibacterial effect on gram-positive S. aureus bacteria. The antibacterial efficiency was 100.00% for $TiO_2$@Ag nanoparticle suspensions for two bacteria. Compared with $TiO_2$@Au nanoparticle suspensions, treated fabrics had less antibacterial activity against E. coli and strongly inhibited the growth of the S. aureus. When thiol modified-fabric coated with metal $TiO_2$@Au

nanoparticles by electrospraying method, the antibacterial effect showed an increase from 70.56% to 75.51% against E. coli due to increased resistance of nanoparticle on the fabric surface via strong metal-sulphur bonding between metal nanoparticle with thiol-modified fabric.

**Table 4.4** Comparison of nanoparticle suspensions on antibacterial efficiency

| **Percent decrease of bacteria (%)** | **0.5% $TiO_2$@Au** | | **0.5% $TiO_2$@Ag** | |
|---|---|---|---|---|
| | Cotton/polyester Fabric | Thiol-modified Cotton/polyester Fabric | Cotton/polyester Fabric | Thiol-modified Cotton/polyester Fabric |
| **Staphylococcus aureus** | 98.40 | 99.00 | 100.00 | 100.00 |
| **Escherichia coli** | 70.59 | 75.51 | 100.00 | 100.00 |

The antibacterial effects of the coated fabric samples finished with bare $TiO_2$, $TiO_2$@Ag, and $TiO_2$@Au were also determined after washing and abrasion treatments. The results were given in Table 4.5 and 4.6 All fabric samples have more antibacterial property after the coating of thiol-modified fabric with the effect of metal-sulphur covalent bond in the electrospraying method, while all fabric samples washed with 10 cycles laundering have almost the same antibacterial effect results. These results were interpreted as a strong metal-sulphur chain that did not break between nanoparticle and fabric surface after 10 cycles washing.

Coating thiol-modified fabric samples treated with both prepared metal nanoparticle was subjected to abrasion testing for 10 cycles. After abrasion, antibacterial properties were observed to increase in contrast to a decrease. Because the nanoparticles on the surface didn't become distant in high quantity and shown the conglutination with each other by friction on the surface.

**Table 4.5** Washing and abrasion treatments effects of $TiO_2$@Au nanosuspensions coated fabric on antibacterial efficiency

| **Percent decrease of bacteria (%)** | | **0.5% $TiO_2$@Au nano suspension coating** | | |
|---|---|---|---|---|
| | | Electrospraying | | Padding |
| | | Cotton/polyester Fabric | Thiol-modified Cotton/polyester Fabric | Cotton/polyester Fabric |
| **Staphylococcus aureus** | | 98.40 | 99.00 | 99.42 |
| **Escherichia coli** | | 70.59 | 75.51 | 72.73 |
| **Staphylococcus aureus** | After washing | 98.33 | 99.50 | 99.52 |
| **Escherichia coli** | After washing | 70.00 | 75.00 | 71.43 |
| **Staphylococcus aureus** | After abrasion | 98.75 | 100.00 | 99.58 |
| **Escherichia coli** | After abrasion | 76.47 | 84.00 | 77.78 |

Table 4.6 pointed out that the treated sample with $TiO_2$@Ag nanoparticle has a strong antibacterial effect on both S. aureus and E. coli bacteria. Coated fabrics with $TiO_2$@Ag nanoparticle have 100% antibacterial efficiency. As is seen, coated with thiol-modified fabrics did not show any antibacterial results below 99.38% after 10 cycle laundering. Metal-sulphur bonding between metal nanoparticle with thiol-modified fabric preserved availability after washing due to strong antibacterial results of coated fabrics with $TiO_2$@Ag nanosuspensions. In addition, the coated fabric has not lost any antibacterial effect after abrasion, that showed also 100% efficiency. It has been reported that the photocatalytic activities of $TiO_2$ can be enhanced by adding metal ions such as Ag to the surface of $TiO_2$, due to the lower recombination rate of produced negative electrons and positive holes (Sung-Suh et al., 2004).

**Table 4.6** Washing and abrasion treatments effects of $TiO_2$@Ag nanosuspensions coated fabric on antibacterial efficiency

| **Percent decrease of bacteria (%)** | | **0.5% $TiO_2$@Ag nanosuspension coating** | | |
|---|---|---|---|---|
| | | Electrospraying | | Padding |
| | | Cotton/polyester Fabric | Thiol-modified Cotton/polyester Fabric | Cotton/polyester Fabric |
| **Staphylococcus aureus** | | 100.00 | 100.00 | 100.00 |
| **Escherichia coli** | | 100.00 | 100.00 | 100.00 |
| **Staphylococcus aureus** | After washing | 100.00 | 99.38 | 99.33 |
| **Escherichia coli** | After washing | 100.00 | 100.00 | 100.00 |
| **Staphylococcus aureus** | After abrasion | 100.00 | 100.00 | 100.00 |
| **Escherichia coli** | After abrasion | 100.00 | 100.00 | 100.00 |

The ten wash cycles didn't affect the antibacterial activity of samples too much (see Table 4.6). Compared inactivation results of S. aureus and E. coli on the treated fabrics with $TiO_2$ nanoparticle, S. aureus were inhibited more than E. coli (Palamutcu et al., 2011; Samal et al., 2015). The antibacterial effect of treated fabrics showed an important value for both $TiO_2$@Au and $TiO_2$@Ag nanosuspensions compared to the control fabric which has no antibacterial properties, whereas a significant difference in antibacterial efficiency was observed between $TiO_2$@Au and $TiO_2$@Ag nanoparticles. Metallic nanoparticles find use in many antibacterial applications due to they can cause cell lysis or inhibit cell transduction. Ag nanoparticles have the potential to attach and penetrate the bacterial cell wall and thus cause structural changes in the cell membrane, such as cell membrane permeability and cell death. There can be the formation of 'pits' on the cell surface, and an accumulation of the nanoparticles on the cell surface (Sondi and Salopek-Sondi, 2004; Wang et al., 2016). Recent studies results showed AuNPs have antibacterial activity, as well. Gold nanoparticles give heat to the environment when they are stimulated with light energy and Au NPs induced by radiation effect cause cell fractionation of the bacteria (Zhou et al., 2012). In this research, $TiO_2$@Ag and $TiO_2$@Au nanoparticles showed high antibacterial activity on S aureus bacteria. The cell wall of the type of bacteria of gram-negative E. coli is thicker than that of gram-positive S. aureus. Against E. coli bacteria,

$TiO_2$@Ag coated fabric has a more antibacterial effect than $TiO_2$@Au due to the antibacterial mechanism of them (Morales-Avila et al., 2017).

### 4.4.2 Determination of Comfort Properties of The Coated Fabric

In Figure 4.5, WVTRs of coated woven cotton/polyester fabrics before and after the applications were shown. WVTR of untreated fabric was performed to be about 700 $g.m^{-2}.24\ h^{-1}$. WVTR results were not conspicuously diminished after the coating process and found to be between 690-710 $g.m^{-2}.24\ h^{-1}$. A significant difference in WVTR results was not observed after coating with padding and electrospraying methods that demonstrated to keep the water vapor transmission and maintained fabric's comfort property. As the changing of WVTRs due to the coating of nanoparticle was minimal, coated fabrics were thought to have satisfying breathability to be applied as clothing materials (Gibson, 1993).

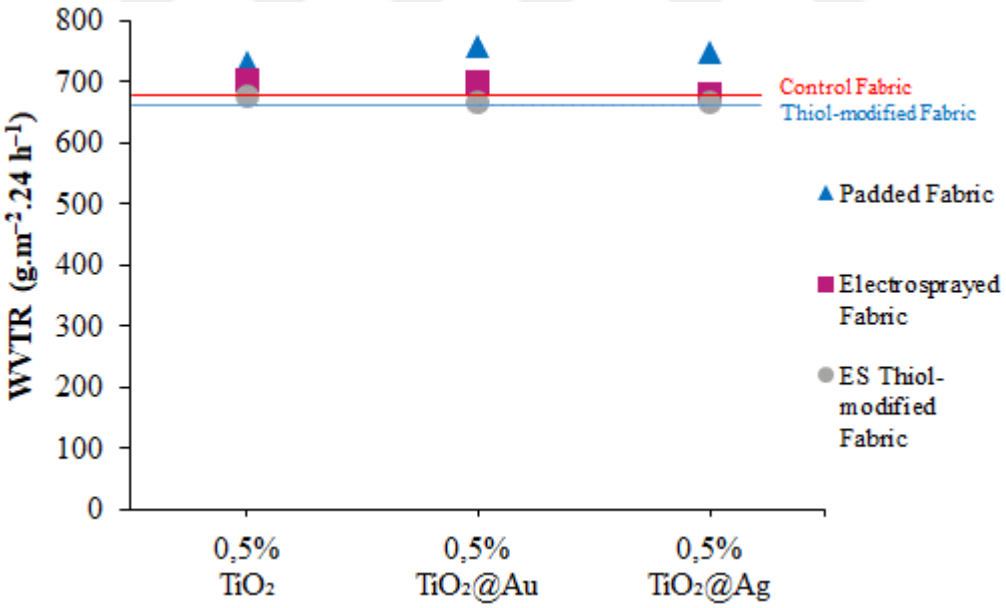



**Figure 4.5** Water vapor transmission rates (WVTR) of untreated, thiol-modified, padded, and electrosprayed fabrics

Air permeability is one of the important properties for comfort characteristics of the fabric, especially for medical textiles. As seen in Figure 4.6, air breathability values of coated fabric for the untreated woven cotton/polyester fabric was about 26 $cm^3.s^{-1}.cm^{-2}$, as to for padded and electrosprayed fabrics were between about 22 and 25 $cm^3.s^{-1}.cm^{-2}$. The coated fabric by padding method has lower air permeability compared to the electrospraying method. That was interpreted as higher nanoparticle weight gains of padded fabrics than electrosprayed fabric after coating, but a significant decrease was not observed for coating by the padding process. Results suggested that NPs adhered to the surface did not significantly influence the porosity of the coated fabrics. For these reasons, based on water vapor transmission and air permeability, padded and electrosprayed coated woven cotton/polyester fabrics show the almost same degree of breathability when compared with control fabrics. Similar supportive results were also obtained in the literature (Abbas et al., 2018; Kale et al., 2016).

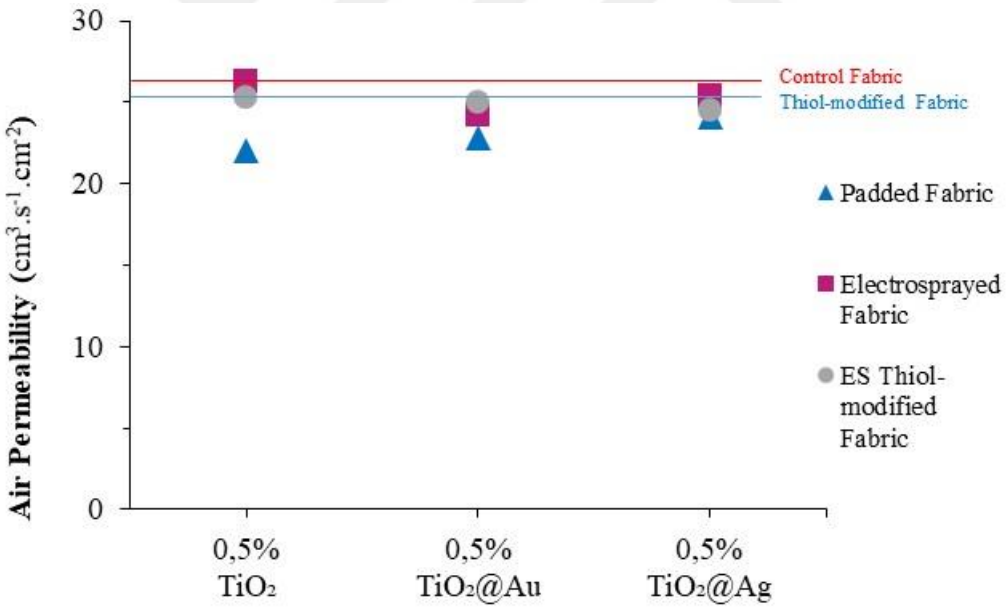



**Figure 4.6** Air permeability of untreated, thiol-modified, padded, and electrosprayed fabrics

### 4.4.3 Morphological Analysis of The Coated Surfaces

SEM images of thiol-modified fabrics treated with $TiO_2$@Ag and $TiO_2$@Au nanoparticle suspensions using the electrospraying method before and after the washing and abrasion treatments are given in Figure 4.7 and 4.8. Surfaces of fibers in all fabric samples contain nanoparticles dispersed well after the coating of thiol-modified fabric. After washing, $TiO_2$@Ag and $TiO_2$@Au nanoparticles as physically adhered to the fabric surface which removed from the fabric surface by 10 cycles laundering effect (see Figure 4.7(b) and 4.8(b)). But, completely removing of nanoparticles was not observed due to the metal-sulphur chain between nanoparticle and fabric surface. Figures 4.7(c) and 4.8(c) show SEM pictures of coated thiol-modified fabric with both nanoparticles after abrasion. It was observed that the nanoparticles on the surface were not physically removed after 10 repeated abrasion tests.

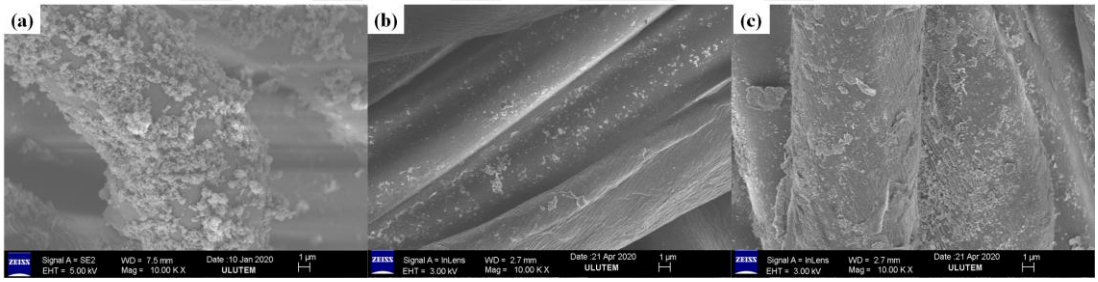



**Figure 4.7** SEM images of (a) thiol-modified fabric treated with 0.5% $TiO_2$@Ag nanoparticle suspensions by using electrospraying method; (b) after washing; (c) after abrasion

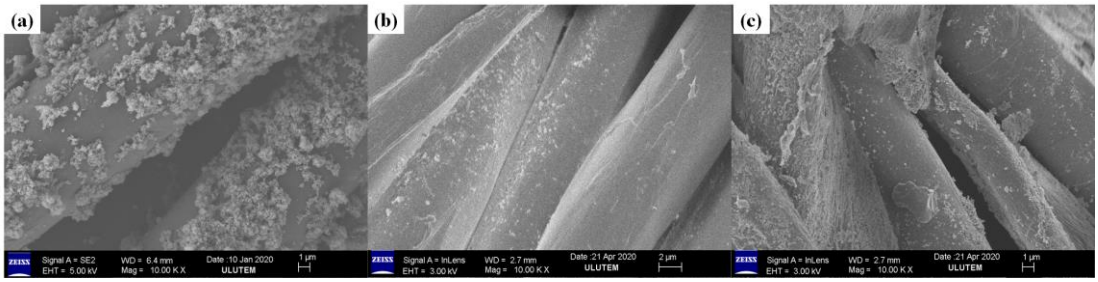



**Figure 4.8** SEM images of (a) thiol-modified fabric treated with 0.5% $TiO_2$@Au nanoparticle suspensions by using electrospraying method; (b) after washing; (c) after abrasion

Electrosprayed $TiO_2$@Au nanoparticles physically adhering to the fabric surface without metal-sulphur bonding were completely diminished from the cotton/polyester fabric surface after washing (see Figure 4.9). Figure 4.10 shows SEM pictures of the same coating by the padding method. Nanoparticle suspensions did not remove completely on the coated fabrics by padding method after washing. Our study revealed that weight gains of coated fabrics with padding method showed more nanoparticle amount than electrospraying method. Electrosprayed fabrics have 0.0020% weight gains, while padded fabrics have 2.6071% weight gains for coating with 0.5% $TiO_2$@Au nanoparticle suspensions. Therefore, it was expected to see some remained NPs after washing for padded fabrics. Figures 4.9(c) and 4.10(c) showed the same behavior on the surface with the electrospraying coating method and pad-dry-cure method due to the physical adhesion of nanoparticles after abrasion testing. Nanoparticles were not removed from the surface and showed a change of their form with the effect of force depending on the abrasion test. In addition, the antibacterial efficiency of fabrics treated with nanoparticle suspension by both the padding and electrospraying process did not significantly change after the washing and abrasion test.

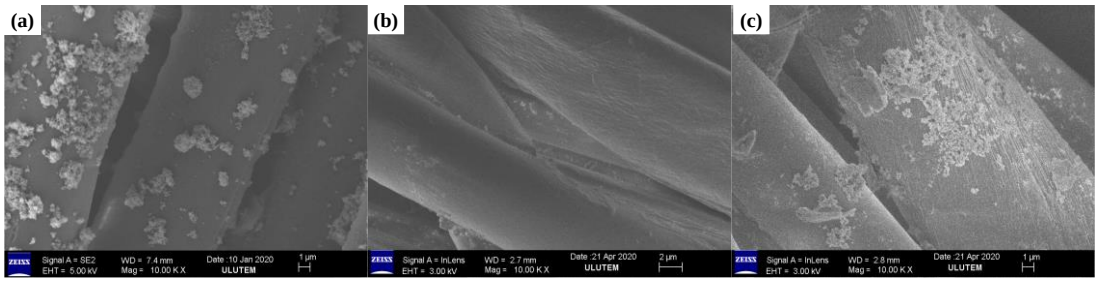



**Figure 4.9** SEM images of (a) raw fabric treated with 0.5% TiO2@Au nanoparticle suspensions by using electrospraying method; (b) after washing; (c) after abrasion

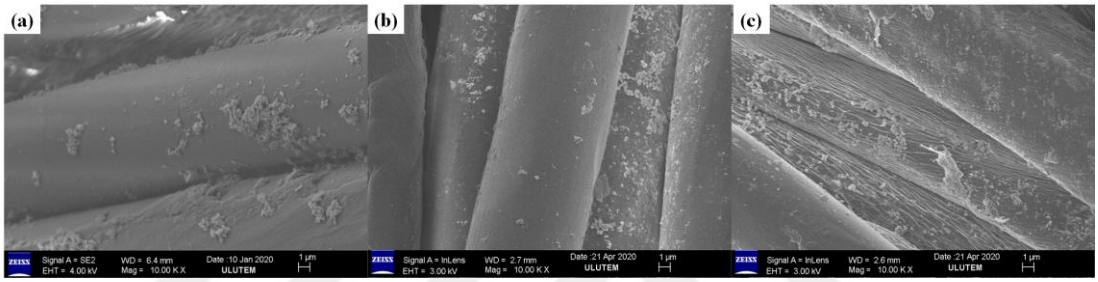



**Figure 4.10** SEM images of (a) raw fabric treated with 0.5% $TiO_2$@Au nanoparticle suspensions by using the pad-dry-cure method; (b) after washing; (c) after abrasion

# CHAPTER 5

# CONCLUSIONS

In this study, $TiO_2$@Ag and $TiO_2$@Au core/shell nanoparticles were prepared and coated on to textile surfaces for the modification of the textile surfaces to obtain superhydrophobic and self-cleaning characteristics on them. A conventional pad-dry-cure and novel electrospraying coating techniques were used for the coating of nanomaterials. Also, the bare fabric surface was modified with 12-mercaptododecanoic acid to not only increase the hydrophobicity of the surface but also enable metal-sulphur covalent bonding between fabric surface and metal coated nanoparticles. This study revealed that the electrospraying technique yielded almost one in a thousand nanoparticle usage compared to the conventional pad-dry-cure method for coating textile surfaces which is significant for the industrial applications to reduce the cost. Thiolation of the fabric surface both improved the water repellency due to its long hydrocarbon chain structure and enabled the covalent bonding of nanomaterials onto to textile surface via the sulphur-metal bond. $TiO_2$@Ag and $TiO_2$@Au core/shell nanoparticles provided an advanced photocatalytic effect in which $TiO_2$@Au nanoparticles performed the best in terms of degrading stains on the fabric. Coating these novel bicomponent nanomaterials on to textile surfaces greatly assisted us to change surface characteristics of hydrophilic textiles to the virtually superhydrophobic structure. Also, using the innovative electrospraying technique for coating enabled us to reach uniform and well-dispersed nanoparticle accumulation on the surface.

Also, we have successfully obtained antibacterial surfaces against two type bacteria (E. coli and S. aureus) by coating fabric surfaces with $TiO_2$, $TiO_2$@Au, $TiO_2$@Ag nanoparticle suspensions. Effect of different concentration ratios of nanoparticle suspensions and application methods on antibacterial efficiency were investigated. The antibacterial activity of all coated fabrics changed according to the concentration ratio of nanoparticle suspensions and the application method. Accordingly, weight

gain amount of chemical is effective on antibacterial property. Using thiol-modified fabric to create metal-sulphur bonding between nanoparticle suspension and fabric surface positively increased the antibacterial effect due to increased resistance of nanoparticles on the surface. It was deduced that the $TiO_2$@Ag nanoparticle coating was more successful for especially against E. coli bacteria than$TiO_2$@Au nanoparticle fabric coating. After the washing and abrasion treatments, the durability of nanoparticles on the coated fabric surface was evaluated with the antibacterial tests of coated fabrics. In addition, SEM images of the coated surfaces were given to evaluate the existence of the coating before and after the treatments. Antibacterial results did not show any significant decrease after washing. After abrasion, antibacterial results showed a small increase. With the friction effect, the nanoparticles did not remove away from the fabric surface, as well as they have settled in the free field in the woven fabric construction. Also, the physical adhesion of nanoparticles between each other on the fabric surface with a friction effect might cause an increase in antibacterial results. The comfort properties of the coated fabrics were also evaluated. Accordingly, WVTR and air permeability results did not show a significant change after the coating process. So, it can be said that the coated fabrics almost maintained breathability. The results implicated the potential of the coated textile as a clothing material. The nanoparticle coating significantly improved the value of fabrics and we anticipate that coated fabrics with functional properties produced may be promising for medical, hygiene, and environmental applications.

According to our research, our average cost of using nanoparticle was higher for the padding method than the electrospraying method. Prices of nanoparticles were 1.83 €/gr for TiO2, 4.20 €/gr for Ag, and 119.40 €/gr for Au (Sigma-Aldrich, June 2020). For each prepared nano chemical, unit prices were calculated according to used ratios of nano chemicals. When $TiO_2$ has 1.83 €/gr unit prices, the prepared nano $TiO_2$@Ag and $TiO_2$@Au have unit prices of 2.22 €/gr (83.33% $TiO_2$ + 16.66% Ag) and 21.42 €/gr (83.33% $TiO_2$ + 16.66% Au) respectively. As a result of calculations, the average cost of the electrosprayed $TiO_2$ coated fabrics was found to be 0.001 €/m², while the average cost of padded fabrics was 4.606 €/m² at 0.5% concentration ratio. The cost for TiO2@Ag nanoparticles was 0.006 €/m² for the electrosprayed fabric and it was 6,839 €/m² for the padded fabric. And for high-priced Au nanomaterials, the average cost was 0.049 €/m² for the electrosprayed fabrics and it was 59.998 €/m² for the

padded fabrics at 0.5% concentration ratio. Considering the relatively high price of Ag and Au nanoparticles and the promising application, we obtained a low amount of nanoparticle usage on the coating for electrospraying method which decreased the overall coating cost.

Consequently, electrospraying can be said to be a new, simple, and effective technique for textile surface modification. The key benefit of this method is much less energy consumption as this method needs no drying process. Thus, method costs with regard to traditional methods are considerably low. Another significant benefit is that this approach is ideal for the treatment of the fabric's single surface which protects the wearer from contact with chemical content. These advantages of the process of electrospraying, and the findings of this research, will illuminate the direction of future analysis. The application of the nanoparticle to produce versatile functional textiles will be more intensive in the near future to lots of industries.

Our suggestion for the future study is to investigate higher washing and abrasion cycles for testing the durability of the coated fabrics. When antibacterial results and SEM pictures of the coated fabrics were analyzed, ten abrasion and ten washing cycles demonstrated no noticeable effect on the durability of nanoparticles on the surface of the coated fabric. It would be better to investigate the durability of the nano chemical coatings at higher washing and abrasion cycles in the future studies.

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