CHARACTERISATION OF NANO-TREATED MATERIALS USING ADVANCED INSTRUMENTAL TECHNIQUES

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By

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Certificate of Originality

I hereby declare that this thesis is my own work and that, to the best of my knowledge and belief, it reproduces no material previously published or written, nor material that has been accepted for the award of any other degree of diploma, except where due acknowledgment has been made in the text.

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January, 2006

Abstract

The thesis is concerned with the development of systematic procedures to characterise the nano-treated anti-bacterial and UV-protective cotton fabrics using both the instrumental techniques and extraction method. In addition, the performance of the nano-treated cotton fabrics was evaluated, and the systematic evaluation procedure for nano-treated textile product was proposed.

Two commercial nano-suspensions with unknown content were used for imparting UV-protective and anti-bacterial properties respectively onto cotton fabrics. The particle size distribution of these two nano-suspensions was determined using a particle size analyser. The types and concentration of metal in each nano-suspension were identified using the Inductively Coupled Plasma Optical Emission Spectrophotometer (ICP-OES) screening. The organic compositions of each suspension were determined by the Gas Chromatography/Mass Spectrum (GC/MS). The study showed that both anti-bacterial nano-suspension and UV-protective nano-suspension contained titanium, zinc and silver elements. These two nano-suspensions also contained other anti-bacterial agents and several kinds of nonionic detergents.

Nano-treated anti-bacterial and UV-protective cotton fabrics were prepared by padding their respective nano-suspensions on the cotton fabrics. The washing fastness and performance of the nano-treated cotton fabrics were evaluated according to the international standards. The test results showed that these two different nano-treated cotton fabrics possessed their specific functional properties effectively. The washing fastness of the nano-treated cotton fabrics was also confirmed to be satisfactory.

The dispersion of nano-particles on fabric substrate was investigated by the Field Emission Scanning Electron Microscopy (FE-SEM). X-ray Photoelectron Spectrometer (XPS) and X-ray Diffraction (XRD) were used to examine the elemental composition of the nano-materials present on the surface of nano-treated fabric. FE-SEM images showed the presence of nano-particles on both nano-treated anti-bacterial and UV-protective cotton fabrics. The size of the nano-particles was inhomogeneous. XPS and XRD analysis only showed the presence of zinc oxide on two different nano-treated cotton fabrics but not the titanium dioxide and silver as their amounts were too small to be detected by these two instruments.

The particle size distribution and the metal content of nano-particles present on the nano-treated cotton fabrics were further characterised with the aid of extraction method. Titanium, zinc and silver were extracted from two different nano-treated fabrics processed in water medium. Based on the analytical results of extraction, it was confirmed that pH 4 or pH 7 and 21^0C were the essential parameters that could help extract the highest amount of nano-particles from both the nano-treated anti-bacterial cotton fabric and UV-protective cotton fabric with less aggregation of nano-particles. By combining both instrumental analysis and extraction method, a clear picture of the particle size distribution and elemental composition of the nano-treated cotton fabric could be obtained.

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Publications

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3. Y. W. H. Wong, C. W. M. Yuen, M. Y. S. Leung, S. K. A. Ku, **Characterization of nano-treated textiles**, May 2005, The Fiber Society 2005 Spring Conference, p.73.
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Chapter 1

Introduction

1.1 Background

The concept of nanotechnology is not new as it has been started over forty years. The timeline of nanotechnology history began with a talk given in 1959 by a physicist named Richard Feynman, and the title was “There's Plenty of Room at the Bottom”. The next milestone came in 1981 when a graduate student named K. Eric Drexler of the Massachusetts Institute of Technology (MIT), who was inspired by Feynman, published an article called “Protein design as a pathway to molecular manufacturing”. This was followed by Drexler's definitive 1986 book, “Engines of Creation”. The first publicised application of nanotechnology was in mechanical engineering, producing micro-machines such as pumps that could be placed in human veins to assist the heart’s action [1].

Nanotechnology, according to the National Nanotechnology Initiative (NNI), is defined as utilisation of structures with at least one dimension of nanometre size for the construction of materials, devices or systems with novel or significantly improved properties due to their nano-size. Apart from producing small structures, nanotechnology is also regarded as a manufacturing technology by inexpensive control of the structure of material. Nanotechnology can be described as the activities at the level of atoms and molecules that have applications in the real world. It refers to the ability to manipulate individual atoms and molecules, making it possible to build machines using molecular blocks, or create materials and structures from the bottom upwards. It relates to materials, devices or systems that operate at the nano-level, that is 10^{-9} m [1]. It is a science that creates structures with improved molecular organisation. Nano-particle is a solid particle with size ranging from 1 to 1000nm that can be non-crystalline, an aggregate of crystallites, or a single crystallite. Nano-particles commonly used in commercial products are in the range of 1 to 100nm. A nanometre is one ten thousandth of the diameter of a human hair, or a billionth of a metre. The nano-size comparisons are shown in Figure 1.1.

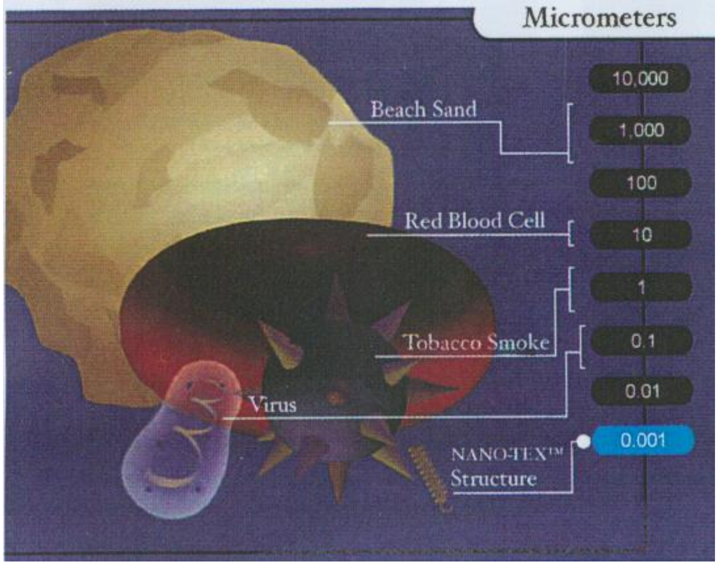


Figure 1.1 Nano-size comparisons [2]

The concept of nanotechnology comprises more than just producing small structures. Recent nanotechnology research primarily focuses on molecular manufacturing such as creation of tools, materials and machines that will eventually enable us to snap together the fundamental building blocks of nature easily, inexpensively and in most of the ways permitted by the laws of physics. Researchers hope to design and programme nano-machines that build large-scale objects atom by atom. With such self-replicating assemblies, objects of any size and in any quantity can be manufactured using common materials like dirt, sand and water. Computers might be 1000 times faster and cheaper than current devices. Biological nano-robots might be applied to fix cancerous cells. On the other hand, towers, bridges, and roads can be made of unbreakable diamond strands. Furthermore, buildings that can repair themselves or change shape on command might be the future implications of nanotechnology [1].

Nanotechnology is increasingly attracting worldwide attention because it is widely perceived as offering huge potential in wide range of end uses. The unique and new properties of nano-materials have attracted not only scientists and researchers but also the businesses due to their huge economical potential. Nanotechnology has been applied to different areas. For example, it is now possible to produce new solid state medicines by simply manufacturing them in nano-particle form. The high surface areas of these small particles allow them to be solubilised into the bloodstream where normal micro-particles or larger particles cannot [1, 3]. Another example is that nano-particulate metals exhibit unusual surface hardness when compressed into solid objects, sometimes as high as five times that of the normal micro-crystalline metal [3]. Apart from the examples mentioned above, there are innumerable potential benefits of using nanotechnologies for society and the environment, such as application in solar cells, water purification and optical computers.

Nanotechnology also presents a real commercial potential for textile industry. It is mainly due to the fact that conventional methods used to impart different properties to fabrics often do not lead to permanent effects and will lose the functions after laundering or wearing. Nanotechnology can provide high durability for fabrics because nano-particles have a large surface area to volume ratio and high surface energy, thus presenting better affinity for fabrics leading to the increase in the durability of the function. In addition, coating of nano-particles on fabrics will not affect the breathability and hand feel. Therefore, the interest of using nanotechnology in textile industry is increasing.

The first work on nanotechnology in textiles has been undertaken by Nano-Tex, a subsidiary of the US-based Burlington Industries [2]. Later on, more and more textile companies are investing on the development of nanotechnology. The properties imparted to textiles using nanotechnology include water repellency, soil resistance, wrinkle resistance, anti-bacteria, anti-static, UV-protection, flame retardancy, improvement of dyeability and so on.

For textile and clothing industries, there are numerous well-known organisations such as the International Standards Organisation (ISO), American Society for Testing and Materials (ASTM) and American Association of Textile Chemists and Colorists (AATCC) which develop standard test methods for evaluating and predicting the performance of textile products. Although the exploration of nanotechnology has been contributed in a great extent to textile and clothing industry, standard testing methods used for evaluating nano-treated textile materials have not yet been developed. This leads to the query concerning the quality of nano-products. There are many textile products claimed to be nano-treated in the market without any evidence provided. Customers feel confusing about whether such nano-treated products are really nano-treated. In fact, some textile products claimed to be nano-treated are just simply treated by the conventional methods. Hence, it is necessary to develop testing methods for identifying the nano-treated textiles in order to provide assurance for the customers about the quality and reliability of the nano-treated textile products.

1.2 Objectives

This thesis is aimed at developing a series of new systematic testing procedures for the nano-coated textiles. The objectives of the thesis are summarised as follows:

(i) To characterise the surface properties of nano-materials by means of advanced instrumental techniques.

(ii) To standardise the testing methods for the identification and size measurement of adhered nano-particles on the surface of fibre/fabric.

(iii) To study the functional effects of different types of nano-particles such as anti-bacterial and UV absorbency properties.

1.3 Project Significance and Value

The benefits obtained from the present study are summarised as follows:

(i) Successful development of a series of new systematic testing procedures to identify whether the textile product is nano-treated or not;

(ii) Assurance of the quality and reliability of the nano-treated textile products can be provided for the end-buyers.

As for the academic study, this study will lead to:

(i) An exploration of the functional effects of different types of nano-particles;

(ii) A better understanding of how nanotechnology can be applied onto textiles.

1.4 Methodology

In order to achieve the objectives, the following research methodologies have been employed.

(i) Literature review was conducted to gain the background knowledge and recent development in the relevant areas.

(ii) UV-protective suspension and anti-bacterial suspension claimed to be nano-suspensions with unknown content were bought from Sino Canada Holdings Ltd.. The particle size distribution of these two suspensions was evaluated using the Particle Size Analyser aiming to check the presence of nano-particles in the suspensions. Their contents were determined using the Inductively Coupled Plasma Optical Emission Spectrophotometer and Gas Chromatography/Mass Spectrum.

(iii) The fabric samples were prepared by padding the nano-suspensions on the woven cotton fabric. The padding conditions including the pressure of padder, rate of padder rotation, processing time and curing temperature were maintained constant.

(iv) The performance of the nano-treated cotton fabrics was evaluated using the international standards. The UV-protective and anti-bacterial properties of the nano-treated cotton fabrics were tested according to Australia-New

Zealand standard AS/NZS 4399:1996 and AATCC Test Method 100-1999, respectively. The washing fastness of these two nano-treated cotton fabrics was tested using the AATCC 135-2003 test method.

(v) Several advanced instrumental techniques including Field Emission Scanning Electron Microscopy, X-ray Photoelectron Spectrometry and X-ray Diffraction were used to investigate the surface morphology and examine the elemental composition of the nano-treated cotton samples.

(vi) Extraction technique was employed to help characterise the nano-treated cotton fabric. The nano-treated materials present on the fabric were extracted at different pH and temperatures using different extraction solutions. The presence of nano-particles in the extracts was investigated by means of the Particle Size Analyser. The contents and amount of the extracted materials were checked and quantified using the Inductively Coupled Plasma Optical Emission Spectrophotometer. The essential parameters for extracting the nano-treated materials from fabric were determined by studying the particle size distribution and content of the extracted materials under different conditions.

1.5 Outline of Thesis

The thesis consists of 7 chapters with details as follows:

Chapter 1 introduces the background information of the study, objectives, project significance and value, methodology and outline of the thesis.

In Chapter 2, literature review was conducted on the common application of nanotechnology in textiles, methods used for fabrication of nano-treated textiles, instruments used for the characterisation of nano-treated materials, and determination of particle size distribution and compositions of colloidal solution.

In Chapter 3, the particle size distribution and the materials present in the commercial UV-protective and anti-bacterial nano-suspensions were examined. The presence of nano-particles in the suspensions was checked using the Particle Size Analyser while the content was determined using the Inductively Coupled Plasma Optical Emission Spectrophotometer and Gas Chromatography/Mass Spectrum.

In Chapter 4, nano-treated cotton fabrics were fabricated by padding method using the UV-protective and anti-bacterial nano-suspensions. The performance and washing fastness of the nano-treated cotton fabric were evaluated according to the international standards.

In Chapter 5, the nano-treated UV-protective and anti-bacterial cotton fabrics were characterised by means of a series of analytical methods including the Field Emission Scanning Electron Microscopy, X-ray Photoelectron Spectrometry and X-ray Diffraction.

In Chapter 6, the nano-treated UV-protective and anti-bacterial cotton fabrics were processed by extraction method. The essential parameters for extracting materials from the nano-treated cotton fabric were determined by studying the particle size distribution and content of the nano-materials which were extracted at different pH and temperatures.

In Chapter 7, a series of systematic evaluation procedures were proposed for characterising the claimed nano-treated anti-bacterial or UV-protective textile product by combining the overall investigation results obtained from the instrumental techniques and extraction method.

Chapter 8 summarised the results and findings of the present work and drew the final conclusions. The possible future research work was recommended.

Chapter 2

Literature Review

2.1 Common Application of Nanotechnology in Textiles

The exploitation of nanotechnology in textile industry has increased rapidly due to its unique and valuable properties. The properties imparted to textiles using nanotechnology include water repellency, soil resistance, wrinkle resistance, anti-bacteria, anti-static, UV-protection, flame retardancy, improvement of dyeability and so on. As there are so many various potential applications of nanotechnology in textile industry, only the present status of some well-known properties imparted by nano-treatment is reviewed with an emphasis on the improvement of various properties of textiles.

2.1.1 UV-protection

In order to prevent the UV radiation from reaching the bulk of the polymer, or from penetrating the coating and reaching a UV-sensitive substrate such as human skin, organic and inorganic UV absorbers have been used in textiles for about 15 years. Most of the commercially used UV absorbers are based on one of the five chromophores which are benzophenone, benzotriazola, triazine, oxanilide and cyanoacrylate. Generally, there are two application methods of UV radiation absorber. The first method is resin coating formulation that contains UV radiation absorbers. The other method is to apply them during the exhaustion or pad-batch process. Apart from the UV absorbers mentioned above, inorganic particles have been used as optical opacifiers and whiteners in commercial products for a long time to provide the high degree of optical light scattering. Inorganic UV blockers are more preferable than organic UV blockers as they are non-toxic and chemically stable under both high temperature and UV exposure. Inorganic UV blockers are usually certain semi-conductor oxides such as TiO_2, ZnO, SiO_2 and Al_2O_3 [3-5].

When the semi-conductors are reduced to the nano-scale, it was discovered that the efficiency of UV-blocking activity could be greatly increased. Among the semi-conductor oxides, nano-titanium dioxide [4, 6-8] and nano-zinc oxide [9, 10] are commonly used. It was determined that nano-sized titanium dioxide and zinc oxide were more efficient in absorbing and scattering UV radiation than the conventional size and thus having a better ability of UV blocking [7, 9]. It is due to the fact that nano-particles have larger surface area per unit mass and volume than the conventional materials, leading to the increase of the effectiveness of blocking UV radiation. For small particles, light scattering predominates at approximately one tenth of the wavelength of the scattered light. Rayleigh scattering theory stated that the scattering was strongly dependent upon the wavelength, where the scattering was inversely proportional to the wavelength to the fourth power. This theory predicted that in order to scatter UV radiation between 200 and 400nm, the optimum particle size was between 20 and 40nm [6].

Various research works on the application of UV-blocking treatment to fabric using nanotechnology were conducted. UV-blocking treatment of cotton fabrics was developed using the sol-gel method. A thin layer of titanium dioxide was formed on the surface of the treated cotton fabric which provided excellent UV-protection, and the effect could be maintained after 50 home launderings [7, 11]. Apart from titanium dioxide, zinc oxide nano-rods with 10 to 50 nm were applied onto cotton fabric to provide UV-protective property [12]. According to the study of the UV-blocking effect, the fabric treated with zinc oxide nano-rods demonstrated excellent UV protective factor (UPF) rating.

2.1.2 Anti-bacteria

The use of anti-bacterial agent should be traced back to 1900. At that time, the commonly used anti-bacterial agent was quaternary ammonium compounds. These compounds are still used nowadays. In addition, many chlorinated organic compounds and organometallic compounds containing copper, silver, iron, manganese or zinc also make fabrics resist growth of bacteria [13, 14]. Silver has been used for the treatment of medical ailments for over 100 years due to its natural anti-bacterial and anti-fungal properties.

For imparting anti-bacterial property by nanotechnology, nano-sized silver [15-17], titanium dioxide [6, 7, 11, 18] and zinc oxide [9] are used. Metallic ion and metallic compound have some degree of sterilising effect. It is considered that part of the oxygen in the air or water is turned into active oxygen by means of catalysis by the metallic ion, thereby dissolving organic substance to create sterilising effect [9]. With the use of nano-sized particles, the number of particles per unit area is increased and thus anti-bacterial effect can be maximised.

Nano-silver particles have extremely large relative surface area, thus increasing their contact with bacteria or fungi, and vastly improving its bactericidal and fungicidal effectiveness. The nano-silver is very reactive with proteins. When contacting with bacteria and fungus, it will adversely affect cellular metabolism and inhibit cell growth. It also suppresses respiration, basal metabolism of electron transfer system, and transport of substrate in the microbial cell membrane. Furthermore, it inhibits multiplication and growth of those bacteria and fungi which cause infection, odour, itchiness and sores. Hence, nano-silver particles are widely applied to socks for prohibiting the growth of bacteria. In addition, nano-silver can be applied to a range of other healthcare products such as dressings for burns, scald, skin donor and recipient sites [15, 19, 20].

For titanium dioxide which is a photocatalyst, once it is illuminated by light with energy higher than its band gaps, the electrons in TiO_2 will jump from the valence band to the conduction band, and the electron (e^-) and electric hole (h^+) pairs will form on the surface of photocatalyst. The negative electrons and oxygen will combine into O_2^-; while the positive electric holes and water will generate hydroxyl radicals. Since both are unstable chemical substances, thus when the organic compound falls on the surface of photocatalyst, it will combine with O_2^- and OH- respectively and turn into carbon dioxide (CO_2) and water (H_2O). This cascade reaction is called “Oxidation-Reduction” [8] and the mechanism is shown in Figure 2.1. Through the reaction, photocatalyst is able to decompose common organic matters in the air such as odour molecules, bacteria and viruses.

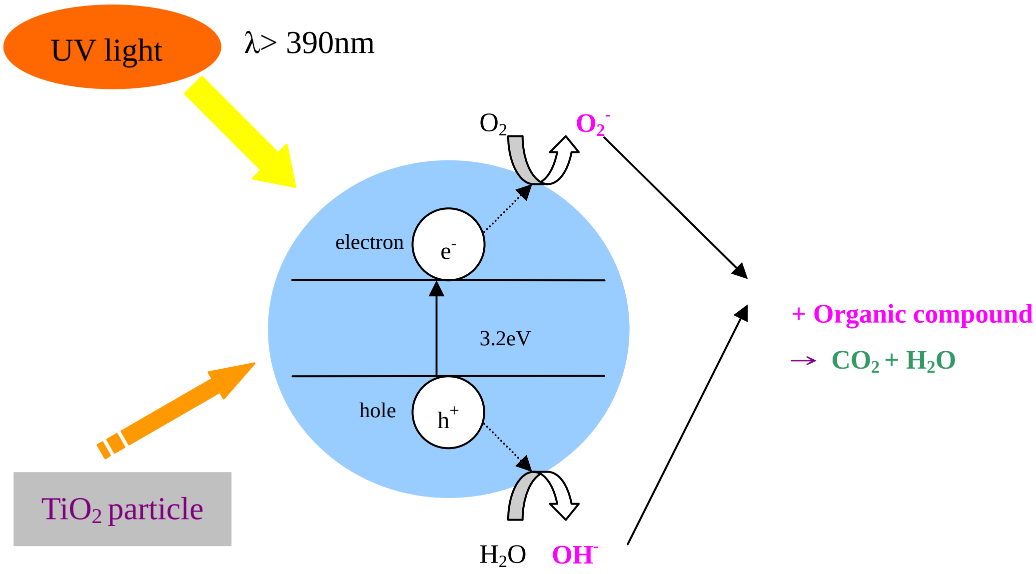


Figure 2.1 Photocatalysis mechanism of titanium dioxide

Several papers have discussed the use of photocatalytic property of TiO_2 in textile area [11, 18, 21]. It was determined that the fabric treated with nano-TiO_2 could provide effective anti-bacterial property and discolouration of stains due to the photocatalytic activity of nano-TiO_2. On the other hand, zinc oxide is also a photocatalyst and the photocatalysis mechanism is similar to that of titanium dioxide, only the bandgap (ZnO: 3.37eV, TiO_2: 3.2eV) is different from titanium dioxide. Nano-ZnO provides effective photocatalytic property once it is illuminated by light and thus it is employed to provide anti-bacterial property for textiles [22-24].

2.1.3 Water Repellency

Water repellent finish modifies the surface of fibres and does not block the interstices. Hence, the fabric permits air and water vapour to pass through. Early water repellent coatings were easily removed by dry cleaning or laundering. The first durable water repellent finish was introduced over 60 years ago. It was based on the use of quaternary ammonium compounds. Nowadays, wax emulsions, pyridinium compounds, N-methylol compounds, silicones and fluorochemicals are used to impart water repellency to various natural and synthetic fibres [13, 14].

Nano-Tex improves water-repellent property of fabric by creating nano-whiskers, which are hydrocarbons and 1/1000 of the size of a typical cotton fibre, that are added to the fabric to create a peach fuzz effect without lowering the strength of cotton. The spaces between the whiskers on the fabric are smaller than the typical drop of water, but still larger than water molecules, thus water remains on the top of the whiskers and above the surface of the fabric [1, 2, 25]. However, liquid can still pass through the fabric if pressure is applied. The performance is permanent while maintaining breathability.

Apart from Nano-Tex, a Swiss-based textile company called Schoeller developed NanoSphere to make water-repellent fabrics. NanoSphere impregnation involves a three-dimensional surface structure with gel-forming additives which repel water and prevent dirt particles from attaching themselves. The mechanism is similar to the lotus effect occurred in nature as demonstrated in Figure 2.2. Lotus plants have superhydrophobic surfaces because of their rough and textured surfaces. Once water droplets falling onto them, water droplets bead up and, if the surface slopes slightly, will roll off. As a result, the surfaces stay dry even during a heavy shower. Furthermore, the droplets pick up small particles of dirt as they roll, therefore, the leaves of the lotus plant keep clean even by light rain [2].

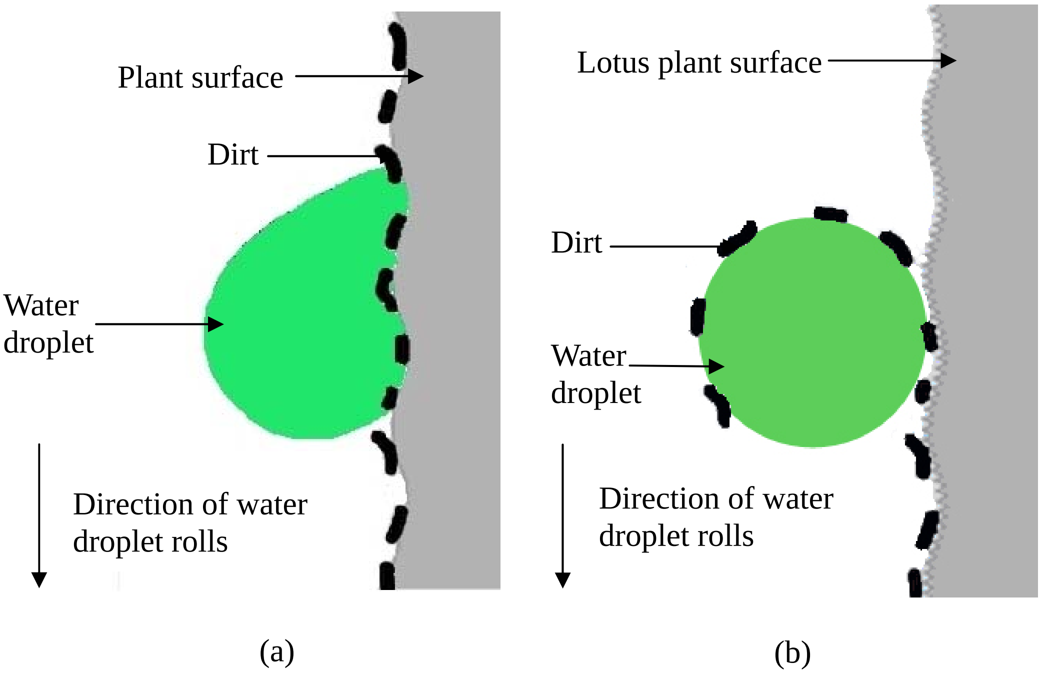


Figure 2.2 Mechanism of NanoSphere on textiles applied by NanoSphere technology (a) water droplet rolls down a plant, (b) water droplet rolls down a lotus plant

On the other hand, hydrophobic property can be imparted to cotton fabric by coating with a thin nano-particulate plasma film [26]. The audio frequency plasma of some kinds of fluorocarbon chemical was applied to deposit a nano-particulate hydrophobic film onto a cotton fabric surface to improve its water repellent property. The superhydrophobicity was obtained due the roughness of the fabric surface without affecting the softness and abrasion resistance of cotton fabric.

2.1.4 Wrinkle Resistance

Wrinkling occurs when the fibre is severely creased. When the fibre or fabric is bent, hydrogen bonds between the molecular chains in the amorphous regions break and allow the chains to slip past one another. The bonds reform in new places and the fibre or fabric is held in the creased configuration. Before 1920, the coating of starch was the only method to minimise the wrinkles of cellulose fabric. Later, resin finishing was applied to improve wrinkle resistance. The mechanism was that the cross-linkages were produced between molecular chains in the amorphous regions of fibre. This minimised the mobility of amorphous regions and decreased the chain slippage. The aminoplast resin was firstly used, however, chlorine retention occurred and high degree of formaldehyde was released. Later, dimethylol ethylene urea (DMEU) and dimethylol dihydroxy ethylene urea (DMDHEU) were made to reduce the release of chlorine and formaldehyde to trace level. However, there are limitations of applying resin including the decrease in tensile strength of fibre, abrasion resistance, water absorbency, dyeability, as well as breathability. [13, 14]

To overcome the limitations of using resin, researchers employed nano-titanium dioxide [27, 28] and nano-silica [29] to improve wrinkle resistance of cotton and silk respectively. Nano-titanium dioxide was employed with carboxylic acid as a catalyst under UV irradiation to catalyse the crosslinking reaction between the cellulose molecule and the acid. On the other hand, nano-silica was applied as a catalyst with maleic anhydride and the results showed that the application of nano-silica with maleic anhydride could successfully improve the wrinkle resistance of silk [29].

2.1.5 Anti-static

Static usually builds up in synthetic fibres such as nylon and polyester because they absorb little water. Cellulosic fibres have higher moisture content to carry away static charges, thus static charge will not accumulate. In conventional method, non-ionic surfactants are used to spread the small amount of moisture on the surface of fibres so as to cause the charge to leak away. In particular, the surfactant containing N-methylol compounds can improve the durability since N-methylol compounds can chemically bond the surfactant to the fibres [13, 14].

As synthetic fibres provide poor anti-static property, a lot of research works concerning the improvement of anti-static property of textile using nanotechnology were conducted. It was determined that the nano-sized titanium dioxide [30], zinc oxide whisker [31], nano antimony-doped tin oxide (ATO) [32] and silane nanosol [33] could impart anti-static property to synthetic fibres. TiO_2, ZnO and ATO provide anti-static effect due to the fact that they are electrically conductive materials. Such material helps to dissipate the static charge built-up on the fabric effectively. On the other hand, silane nanosol improves the anti-static property as the silane gel particles on fibre absorb water and moisture in the air by means of amino and hydroxyl groups and bound water.

Nanotechnology has been applied to clothing industries to produce garments with anti-static property. W.L. Gore and Associates GmbH used nanotechnology and polytetrafluroethylene (PTEE-DupPont's Teflon®) to develop an anti-static membrane for protective clothing. Gore-Tex® I Workwear protects wearer from electrostatic discharges. Electrically conductive nano-particles are durably anchored in the fibrils of the Gore-Tex® I membrane of Teflon, creating an electrically conductive network that prevents the formation of isolated chargeable areas and voltage peaks commonly found in conventional anti-static materials. This method can overcome the limitation of conventional method such that the anti-static agent is easily washed off after a few laundry cycles [34].

2.2 Methods Used for Fabrication of Nano-treated Textiles

To fabricate nano-treated textiles, several methods have been developed. Coating is the most common technique used to apply nano-particles or nano-materials onto textiles. The coating compositions that can modify the surface of textiles are usually composed of nano-particles, surfactant, ingredients and carrier medium [35]. Inorganic nano-particles are more commonly used than organic nano-particles. One of the commonly used techniques is to apply coating by padding the colloidal solution containing nano-particles onto textiles. The nano-particles are attached to the fabrics with the use of padder adjusted by suitable pressure and speed followed by drying and curing [7, 36, 37]. For example, titanium dioxide thin film was padded onto cotton fabric to impart UV-protective function [7, 12]. On the other hand, cold plasma technology can be used to apply coating containing nano-particles or nano-materials onto textiles for enhancing functional properties[26, 38, 39]. Plasma technology is an alternative to conventional wet chemical processes and provides efficient surface treatment opportunities. Plasma sputtering is a vacuum process which allows the direct application of coating containing nano-particles or nano-materials onto fabrics. Research on the application of audio frequency plasma of fluorocarbon chemical to deposit a nano-particulate hydrophobic film onto a cotton fabric surface has been conducted [26].

Apart from coating techniques, nano-treated textiles can be fabricated by melt spinning [37, 40, 41]. Nano-particles can be dispersed into polymer melts like pigments, and nano-composite can be spun using current polymersation and extrusion equipment. Nano-particles such as nano-clays modified with quaternary ammonium salts were infused into polypropylene fibres to create dye sites for lower cost dyeing in apparel fibres [40]. Another example is that of bicomponent fibres produced by general melt spinning method with polypropylene chips and silver nano-particles. Fibres with added silver in the sheath part exhibited excellent anti-microbial effects [37].

2.3 Instrumental Analysis of Nano-treated Materials

To characterise the morphology and chemical composition of nano-treated materials, the use of sophisticated analytical instruments becomes essential. There are numerous advanced techniques and instruments that can be employed to determine the presence of nano-particles and their structures, thus applicable methods should be selected.

2.3.1 Investigation of Surface Morphology

2.3.1.1 Scanning Electron Microscopy (SEM)

Scanning Electron Microscopy (SEM) has been widely employed to obtain information regarding the morphology of nano-treated materials. By means of SEM, it is easy to determine the change in the surface morphology of the sample before and after nano-treatment.

SEM can be employed for measuring three dimensions of both conductive and non-conductive samples. The resolution of the instrument can be down to one nanometre. By employing SEM, a simple and fast sample preparation is allowed for investigating the size, shape and distribution of features attached on the sample surface. When observing the non-conductive sample such as fabric, a conductive coating has to be applied prior to investigation in order to avoid electron accumulation on the sample surface which may cause the deterioration of image quality. Another advantage of using SEM is that a large area view of the variation in surface structure can be acquired all at once.

The principle of SEM is to apply a voltage to filament, resulting in electron emission from the filament to the conductive sample. This occurs in a vacuum environment ranging from 10^{-4} to 10^{-10} Torr. The electrons interact with the sample within a few nanometres to several microns of the surface. Electrons are emitted from the sample primarily as either backscattered electrons or secondary electrons, and secondary electrons are the most common signal used for the investigation of surface morphology. SEM image is formed as a result of the intensity of the secondary electron emitted from the sample at each x and y data point during the rastering of the electron beam across the surface [42]. The schematic sectional view of a scanning electron microscope (JEOL JSM-840) is shown in Figure 2.3.

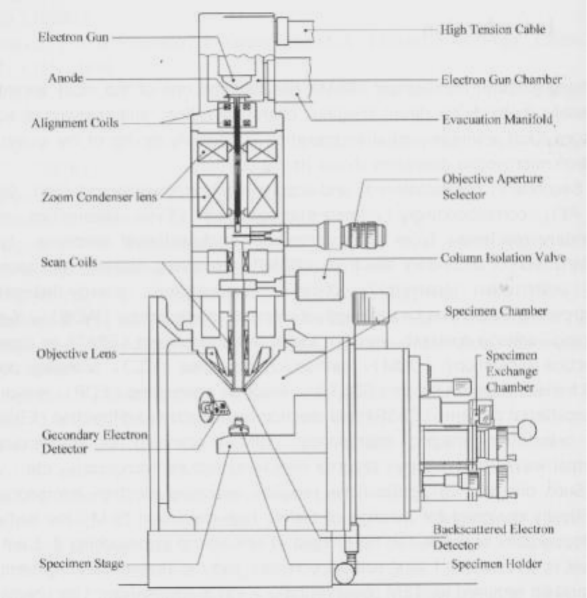


Figure 2.3 Schematic sectional view of a conventional type scanning electron microscope (JEOL JSM-840) [43]

SEM is a common technique used for investigating the surface morphology of nano-level coating on polymer materials. Review of literature indicated that most researchers employed SEM for surface characterisation, such as nano-structured poly(ε-caprolactone) non-woven mats [44] and poly(vinylidenefluoride-co-hexafluoropropylene)-based polymer electrolyte filled with TiO_2 nano-particles [45]. In addition, SEM had been employed to investigate the dispersion of nano-sized silver [15] and average size of particles of nano-titania coating on textile fabrics [15, 46].

2.3.1.2 Atomic Force Microscopy (AFM)

Atomic Force Microscopy (AFM) provides three dimensional surface topography at nanometre in lateral and subangstrom vertical resolution on both insulators and conductors. Figure 2.4 demonstrates the schematic diagram of an atomic force microscope. AFM utilises a sharp probe moving over the surface of a sample in a raster scan. The probe is a tip on the end of a cantilever which bends in response to the force between the tip and sample. The interaction between the tip and sample is monitored by reflecting a laser of the back of the cantilever into a split photodiode detector. By measuring the deflection of the cantilever, the surface topography of the sample with atomic resolution can be mapped out [42, 47].

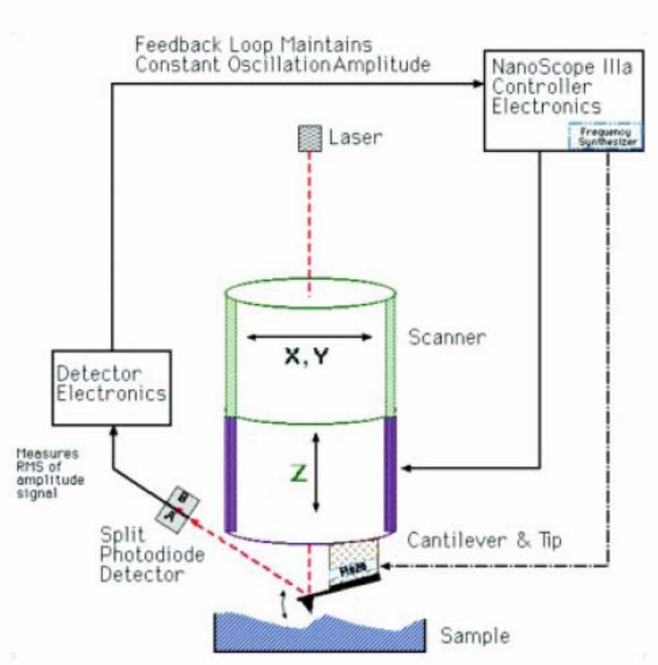


Figure 2.4 Schematic of the major components of an atomic force microscope [42]

AFM provides three dimensional image of the nano-particles attached on the surface of the samples, such as nano-silica on polyurethane [48] and poly(ethylene terephthalate) [49].

However, it will be very time consuming by employing AFM to obtain good image of the topography of nano-treated fabric. This is due to the fact that the fibrils and hairs on the fabric surface act as the barriers for the tip to tap or oscillate on the surface. As a result, the tip is difficult to probe features on a sample accurately. It is suitable for investigating thin film as its surface is flat. In addition, the imaging time is long due to slow scanning speed. If a large surface area of nano-treated textile materials is investigated, AFM may not be a good choice.

2.3.1.3 Transmission Electron Microscopy (TEM)

Transmission Electron Microscopy (TEM) provides real space imaging at a resolution of 1-2Å, and acts as an analytical tool for quantitative structure and chemical analysis. TEM is unique because it can provide a real space image on the atom distribution in the nano-crystal and on its surface. It can obtain full morphology, e.g. gain size, grain boundary and interface, crystallographic, atomic structure and microanalysis such as chemical composition at nanometre scale, atomic bonding and electronic structure. It composes of an illumination system, specimen stage, objective lens system, magnification system, data recording system and chemical analysis system [50]. The sample viewed by TEM is under vacuum environment. Figure 2.5 shows the schematic structure of a transmission electron microscope.

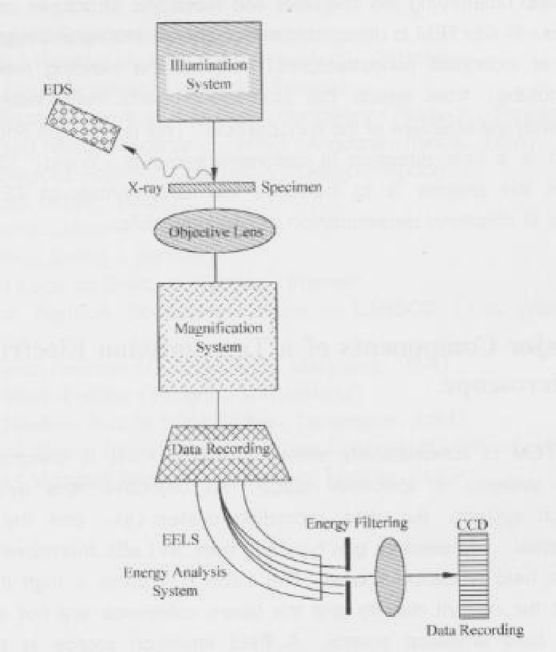


Figure 2.5 Schematic structure of a transmission electron microscope [43]

Images in TEM are usually dominated by three types of contrast. Firstly, diffraction contrast is produced due to a local distortion in the orientation of the crystal. This image is suitable for imaging defects and dislocations. For nano-crystals, most of the grains are defect-free in volume, while a high density of defect is localised at the surface or grain boundary. Diffraction contrast can be useful for capturing strain distribution in nano-crystals whose sizes are larger than 15nm. The second type is phase contrast which is produced by the phase modulation of the incident electron wave when transmitting through a crystal potential. This type of contrast is sensitive to the atom distribution in the specimen and it is the basis of high-resolution TEM. The third type is mass-thickness or atomic number produced contrast. Atoms with different atomic numbers exhibit different powers of scattering. If the image is formed by collecting the electrons scattered to high-angles, the image contrast will be sensitive to the average atomic number along the beam direction [43, 50].

TEM has been widely used for investigating the morphology of nano-treated materials such as poly(butylmethacrylate)/SiO_2 [51] and BAO-ODPA polyimide/TiO_2 nano hybrid film [52]. It had been employed to observe the shape, size and distribution of nano-sized silver particles [15]. In addition, it had been used to characterise the particle size of titania cluster on textile surface [18].

However, the sample thickness affects the quality of the image formed. The sample should be very thin, usually less than 100nm in order to obtain better electron beam penetration. Therefore, skillful technique is required for specimen preparation and the preparation time will be long.

2.3.2 Chemical Composition Analysis

2.3.2.1 X-ray Photoelectron Spectroscopy (XPS)

X-ray Photoelectron Spectroscopy (XPS) is a powerful technique for the analysis of surfaces. XPS has reliable sensitivity of about 0.1 atomic percentage and provides topmost 5 to 10nm surface analysis. As it is sensitive to surface composition, thus it is reliable for chemical composition analysis of nano-coating.

In the basic experiment conducted by XPS, the sample surface is irradiated by a source of X-ray under ultra-high vacuum condition. Photoionisation takes place on the sample surface and the resulting photoelectrons will have kinetic energy escaped from the surface of the sample. The kinetic energy of the emitted electrons is measured by the following equation:

$$KE = hv - BE - \phi_{spec}$$

where hv is the energy of the photons, BE is the binding energy which is equal to the energy of final state minus the energy of initial state, and ϕ_{spec} is the spectrometer work function.

XPS provides a spectrum consisting of a plot of the number of emitted electrons per energy interval versus their binding energy. Elements have unique electron binding energies. Hence, knowing the electron binding energy allows the identification of various elements. XPS is thus able to detect all elements except hydrogen. Furthermore, the electron binding energy is also sensitive to the electronic environment of the atom. When an atom is bonded to another atom of an element having a different electronegativity, the electron binding energy may increase or decrease. This change in binding energy is called the chemical shift, which can be used to provide chemical information of a molecule or compound [53]. Figure 2.6 shows the schematic arrangement of the basic elements of an X-ray photoelectron spectrometer.

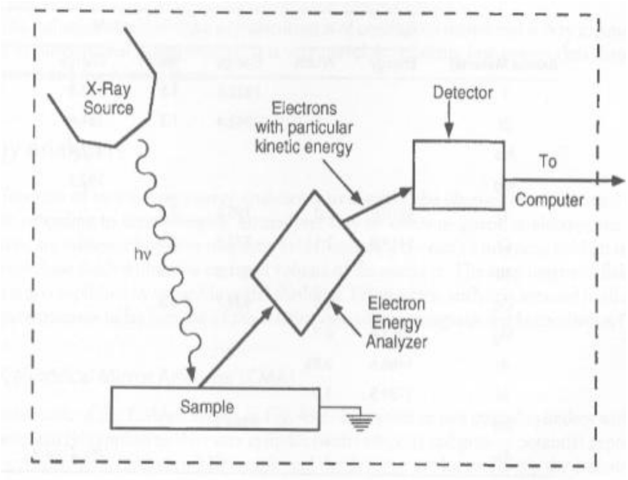


Figure 2.6 Schematic arrangement of the basic elements of an X-ray photoelectron spectrometer [53]

Both conductive and insulating materials can be analysed by XPS, for example, the chemical composition of poly(butylmethacrylate)/SiO_2 [51], BAO-ODPA polyimide/TiO_2 nano hybrid film [52] and nano-zinc oxide on copolymer [54] were investigated by XPS. However, the samples to be analysed must be vacuum compatible since XPS experiments are carried out under ultra-high vacuum.

2.3.2.2 Auger Electron Spectroscopy (AES)

Auger Electron Spectroscopy (AES) is one of the commonly employed surface analytical techniques for investigating the elemental composition of surface layer of a sample. The basic elements of an Auger electron spectrometer are quite similar to that of an X-ray photoelectron spectrometer except the excitation source is different. AES has reliable sensitivity of about 0.1 atomic percentage and provides topmost 0.5 to 10nm surface analysis. As it is sensitive to surface composition, thus it is reliable for chemical composition analysis of nano-coating. However, it can just be employed for examining conductive sample as it uses the electron beam as excitation source. The electron beam causes discharging effect on non-conductive sample which is due to the difference between the number of electrons arriving and leaving the sample.

The Auger process starts with the removal of an inner shell atomic electron to form a vacancy by an electron beam. The inner shell vacancy is filled by a second electron from an outer shell. The energy released kicks a third electron, the Auger electron, out of the atom. The energy of the Auger electron, specific to the atom from which is originated, is detected and measured with an electron spectrometer and thus the type and concentration of the detected material can be determined [53].

2.3.2.3 Energy Dispersive Spectroscopy (EDS)

In most of the modern Energy Dispersive Spectroscopy (EDS) system, a semi-conductor detector is used for measuring the energy of the X-ray photon emitted from the specimen. The X-ray energy is displayed as a histogram of number of photons versus energy [42].

The detection limit of EDS is about 1000ppm. When there is insufficient amount of an element attached on the surface, the signal generated will not be strong enough and the percentage of such element attached on the surface calculated by EDS may not be accurate. On the other hand, EDS provides topmost (up to 1μm) surface analysis. Hence, the signal generated from the surface layer may be blocked or covered by other signals and the results are affected by the substrate. As a result, EDS is not suitable for analysing and determining nano-coating.

2.3.3 Crystallite Size Analysis

X-ray diffraction spectroscopy (XRD) is an analytical technique used for examining crystalline solids. When a beam of X-ray strikes a single crystal, diffraction takes place. The operative equation in XRD diffraction is the Bragg equation:

$$n\lambda = 2d\sin\theta$$

where n is the order of a reflection, λ is the wavelength, d is the distance between parallel lattice planes, and θ is the angle between the incident beam and a lattice plane.

XRD has been commonly employed to measure the crystallite size [12, 55, 56]. By measuring the full width at half maximum (FWHM) of reflected X-ray from crystal, crystallite size can be measured. The crystallite size is determined by applying Scherrer equation to XRD data:

$$\beta(2\theta) = K\lambda/L\cos\theta,$$

where $\beta(2\theta)$ is the FWHM, K is constant which is about 1, λ is the wavelength (usually 1.54056 Å for Cu Kα radiation), L is crystallite size and θ is the peak position.

On the other hand, XRD had been applied to determine the phase of nano-titanium dioxide on textile [18] and the presence of nano-sized silver on polypropylene fibre [57].

2.3.4 Determination of Particle Size Distribution and Composition of Colloidal Solution

2.3.4.1 Particle Size Analysis

The most feasible way of determining the presence of nano-size materials in colloidal solution is to employ particle size analyser. It applies scattering of light, which is one of the most widely used technique, for measuring the size distribution of particles. The basis of the method is simple. A laser light source is used to illuminate particulates usually contained within a suitable sample cell. The light scattered by the particles is then detected by silicon photo-detectors. The intensity of light on each detector measured as a function of angle is then subjected to mathematical analysis using a complex inversion matrix algorithm. The result is a particle size distribution displayed as volume percentage or number of particle in discrete size classes. Figure 2.7 shows the schematic diagram of a particle size analyser. It allows determining the size of dry, aqueous and non-aqueous samples. It measures particle size ranging from 40nm to 2,000µm in aqueous or non-aqueous samples.

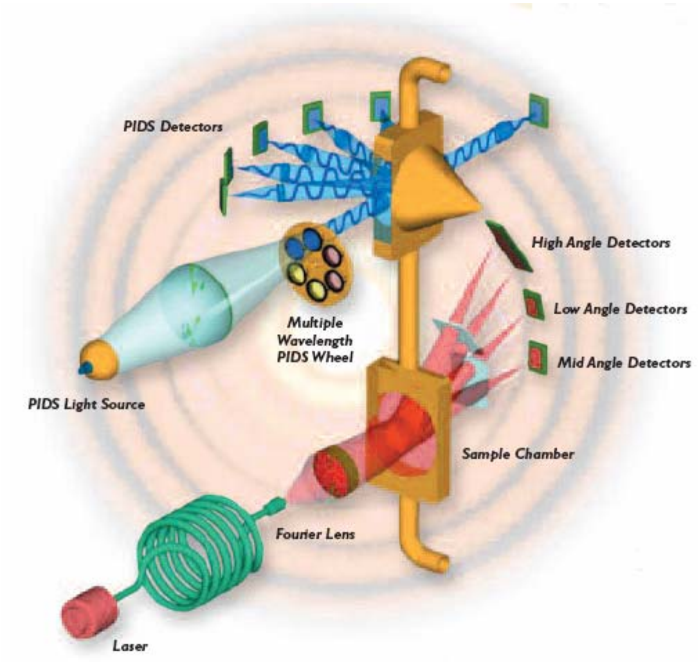


Figure 2.7 Schematic diagram of a particle size analyser (Beckman Coulter LS13320 series) [58]

Particle size analyser had been used to determine particle size distribution of colloidal solution such as nano-titanium dioxide dispersed in water [8], nano-silver dispersed in aqueous solution [16] and silica nano-particles dispersed in toluene [59].

2.3.4.2 Inductively Coupled Plasma Optical Emission Spectrophotometer (ICP-OES)

As various kinds of colloidal solution used for coating contains metallic nano-particles, it is necessary to examine the metal composition of colloidal solution in order to determine what kinds of nano-particles are present in the solution. Inductively Coupled Plasma Optical Emission Spectrophotometer

(ICP-OES) is an analytical instrument which can determine the type and concentration of metals present in colloidal solution. It measures the light emitted by the elements in a sample introduced into an ICP source. The measured emission intensities are then compared with the intensities of standards with known concentration to obtain the elemental concentrations of the unknown sample. Its detection limit is from sub ppb to ppm [53].

2.3.4.3 Gas Chromatography/Mass Spectrum (GC/MS)

To investigate organic compositions of colloidal solution, Gas Chromatography/Mass Spectrum (GCMS) can be employed. The sample is injected into a heated block and is then vapourised and swept as a plug of vapour by the carrier gas into the column. Separation is accomplished based on the mass-to-charge (m/e) ratios of the ions. The sample is automatically detected as it emerges from the column. By comparing the peak of the spectrum with that of standard pure substance, the organic compositions in the sample can be identified [60].

2.4 Analysis of Nano-coating

Since coating is commonly used for applying nano-materials onto fabrics, extraction method seems to be the most practical way to remove nano-materials from the fabrics. Soxhlet extraction is a widely used method for extracting materials from fabric. In this method, the fabric is placed in a Soxhlet thimble which is a disposable porous container made of stiffened filter paper. The thimble is placed in the Soxhlet apparatus where refluxing extraction solvent condenses into the thimble and leaches out the soluble components. The Soxhlet apparatus is designed to siphon the solvent with extracted components once the inner chamber holding the thimble fills up with solution to a certain volume. The siphoned solution containing the dissolved analyte then returns to the boiling flask and the process is repeated until the analyte is successfully removed from the solid sample [53]. To remove the analyte effectively, a solvent or solvent mixture that has a high affinity for the analyte and a low affinity for the solid sample matrix should be applied.

Soxhlet extraction has been applied as standard test method for identifying and determining the amount of finishes in textiles [61, 62]. Suitable solvent is applied to remove the finishing chemicals which are organic in nature. To determine the amount of extractable harmful metals present on textiles, the extraction method used is by shaking according to the Öko-Tex Standard 100. The solvents used are artificial saliva or sweat. The extraction is carried out in a liquor to goods ratio of 20:1 at 40°C for one hour, and the metal concentration is determined by means of Atomic Absorption Spectroscopy (AAS) [63].

Extraction method has never been employed for extracting nano-coating materials from nano-treated fabric. According to the principle of extraction method, it can easily remove nano-coating.

Chapter 3

Analysis of Nano-suspension

3.1 Introduction

Colloidal solutions containing nano-titanium dioxide [4, 6-8] or nano-zinc oxide [9, 10] are widely used as coating for imparting UV-protective property to textiles. On the other hand, the colloidal solutions containing nano-silver [15-17], nano-titanium dioxide [6, 7, 11, 18] or nano-zinc oxide [9, 22, 23] are also found to be effective in anti-bacterial activity.

To prepare nano-treated textiles for experiment, two different functional nano-suspensions having the UV-protective property and anti-bacterial property respectively were obtained from the Sino Canada Holdings Ltd.. These two suspensions were applied directly onto textile materials by padding method. Prior to padding, the particle size distribution of the suspensions was checked in order to ensure that they were nano-suspension. In addition, the content of the suspensions was studied aiming to determine how these two suspensions could provide the fabrics with certain specific properties.

3.2 Experimental Procedures

Two commercially available nano-suspensions with unknown content were used for imparting UV-protective and anti-bacterial properties respectively to fabrics. The particle size distribution of these two nano-suspensions was determined using a particle size analyzer (Beckman Coulter, LS 13320 series). The types and concentration of metal in each functional nano-suspension were identified using the Inductively Coupled Plasma Optical Emission Spectrophotometer (ICP-OES). 71 different kinds of metals were screened by ICP-OES as shown in Table 3.1. The measured emission intensities of samples were compared with those of the standards of known concentration to obtain the elemental concentration. The organic compositions of each suspension were determined using the Gas Chromatography/Mass Spectrum (GC/MS).

Table 3.1 Metals screened by ICP-OES

	Element	Symbol		Element	Symbol		Element	Symbol
1.	Titanium	Ti	**25.**	Palladium	Pd	**49.**	Platinum	Pt
2.	Silver	Ag	**26.**	Selenium	Se	**50.**	Plutonium	Pu
3.	Silicon	Si	**27.**	Tin	Sn	**51.**	Potassium	K
4.	Zinc	Zn	**28.**	Vanadium	V	**52.**	Praseodymium	Pr
5.	Aluminium	Al	**29.**	Beryllium	Be	**53.**	Rhenium	Re
6.	Tungsten	W	**30.**	Boron	B	**54.**	Rhodium	Rh
7.	Antimony	Sb	**31.**	Cerium	Ce	**55.**	Rubidium	Rb
8.	Manganese	Mn	**32.**	Cesium	Cs	**56.**	Ruthenium	Ru
9.	Barium	Ba	**33.**	Dysprosium	Dy	**57.**	Samarium	Sm
10.	Bismuth	Bi	**34.**	Erbium	Er	**58.**	Scandium	Sc
11.	Cadmium	Cd	**35.**	Europium	Eu	**59.**	Sodium	Na
12.	Calcium	Ca	**36.**	Gadolinium	Gd	**60.**	Strontium	Sr
13.	Chromium	Cr	**37.**	Gallium	Ga	**61.**	Sulphur	S
14.	Cobalt	Co	**38.**	Germanium	Ge	**62.**	Tantalum	Ta
15.	Copper	Cu	**39.**	Hafnium	Hf	**63.**	Tellurium	Te
16.	Gold	Au	**40.**	Holmium	Ho	**64.**	Terbium	Tb
17.	Indium	In	**41.**	Iridium	Ir	**65.**	Thallium	Tl
18.	Iron	Fe	**42.**	Lanthanum	La	**66.**	Thorium	Th
19.	Lead	Pb	**43.**	Lithium	Li	**67.**	Thulium	Tm
20.	Magnesium	Mg	**44.**	Lutetium	Lu	**68.**	Uranium	U
21.	Arsenic	As	**45.**	Neodymium	Nd	**69.**	Ytterbium	Yb
22.	Mercury	Hg	**46.**	Niobium	Nb	**70.**	Yttrium	Y
23.	Molybdum	Mo	**47.**	Osmium	Os	**71.**	Zirconium	Zr
24.	Nickel	Ni	**48.**	Phosphorus	P			

3.3 Results and Discussions

3.3.1 Particle Size Distribution and Content of Anti-bacterial Nano-suspension

In general, particle can be claimed as nano-particle when its size is smaller than 100nm. The result of particle size analysis of the anti-bacterial nano-suspension indicated that the particles present in it were actually not nano-particles as shown in Figure 3.1. Most of the particles fell into the range between 400 nm to 640 nm.

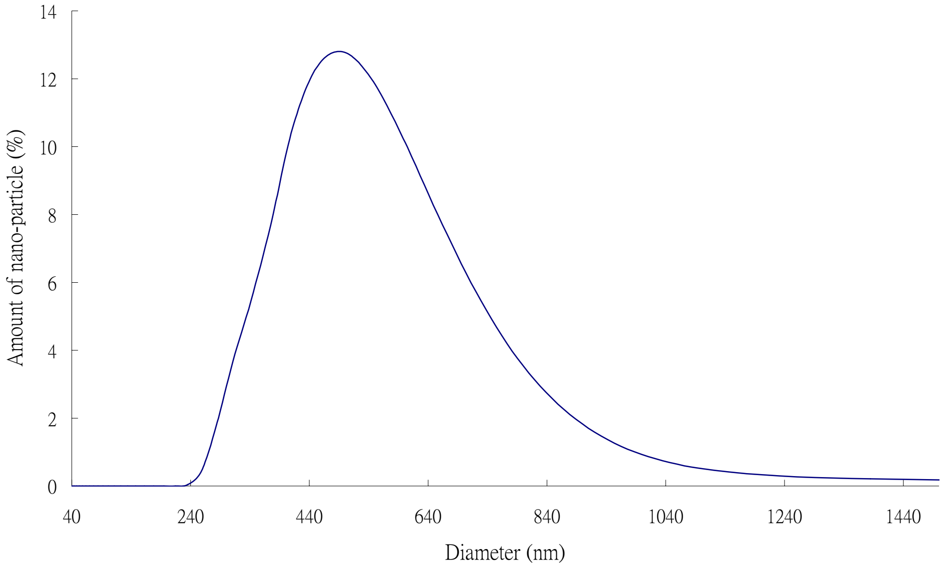


Figure 3.1 Particle size distribution curve of anti-bacterial nano-suspension

Since the result of particle size obtained was bigger than 100nm which might be due to aggregation problem, thus the anti-bacterial nano-suspension was processed again by ultrasonic method aiming to break down the size of particles before the fabrication of fabric. The particle size distribution curves of anti-bacterial nano-suspension before and after processing by ultrasonic method are shown in Figure 3.2. The curves clearly showed that the original size of large particles was greatly decreased by ultrasonic method. The majority of the particles size was smaller than 100 nm implying that the particles present inside the suspension were successfully broken down to nano-particles by ultrasonic method.

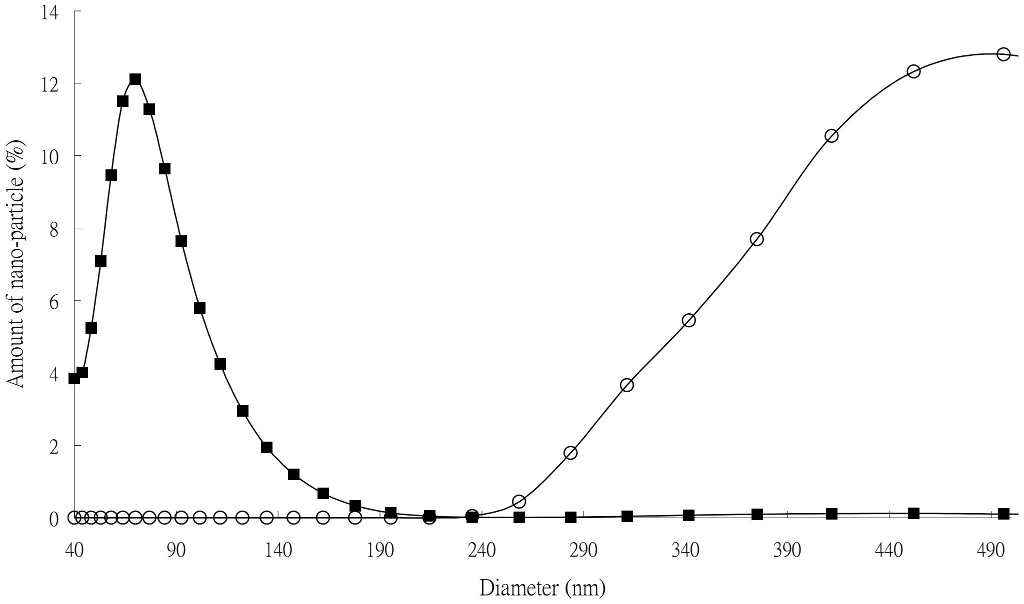


Figure 3.2 Particle size distribution curves of anti-bacterial nano-suspension before and after processing by ultrasonic method: ○ before, ■ after

The results of ICP-OES showed that the anti-bacterial nano-suspension contained various concentrations of titanium, zinc and silver as shown in Table 3.1.

According to the literature review [4, 6, 9, 15-17, 19, 36, 64], it was revealed that titanium dioxide (TiO_2), zinc oxide (ZnO) and silver could provide the fabric with anti-bacterial property effectively. This is due to the fact that these metallic compounds can catalyse part of the oxygen in the air or water and turn it into active oxygen, thus dissolving all the bacteria which are organic in nature. Hence, it was believed that the titanium present in the anti-bacterial nano-suspension most probably would be in the form of titanium dioxide while zinc most probably would be in the form of zinc oxide. When comparing the concentration of these three different kinds of metal, the amount of zinc was found to be much more than the other two metals.

Table 3.2 Concentration of different kinds of metal present in anti-bacterial nano-suspension

Suspension	Conc. mg/L		
	Ag	Ti	Zn
Anti-bacterial	42.40	0.80	11831.00

By using GC/MS, it was found that triclosan ($C_{12}H_7Cl_3O_2$) did exist in the anti-bacterial nano-suspension. Figure 3.3 shows the chemical structure of triclosan which is an anti-bacterial agent against a wide range of both gram-negative and gram-positive bacteria. It is popularly used in many products including textiles as it can provide them with anti-bacterial properties. Triclosan can easily penetrate into cell membranes. Once it is inside the cell, it poisons a specific enzyme that many bacteria and fungi need for survival [65]. Triclosan blocks the active site of an enzyme called enoyl-acyl carrier-protein reductase (ENR) thereby preventing the bacteria from manufacturing fatty acids that are needed for building up cell membranes and other vital functions. One molecule of triclosan permanently disables an ENR molecule and so this is the main reason to explain why triclosan can render powerful antibiotic action even at very low concentration. Furthermore, an anti-bacterial agent called 2, 7-dichlorodibenzo-p-dioxin ($C_{12}H_6C_{l2}O_2$) was also found in the anti-bacterial nano-suspension. It has been reported to have anti-bacterial, fungicidal and insecticidal properties [66], and its chemical structure is shown in Figure 3.4.

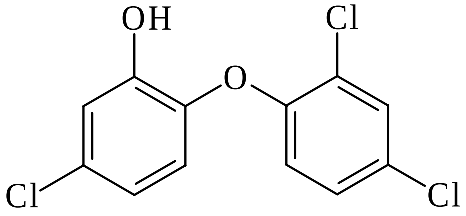


Figure 3.3 Chemical structure of triclosan ($C_{12}H_7Cl_3O_2$)

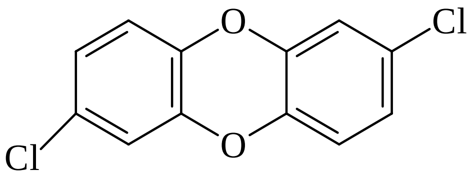


Figure 3.4 Chemical structure of 2, 7-dichlorodibenzo-p-dioxin ($C_{12}H_6C_{l2}O_2$)

In addition, several kinds of nonionic detergents namely ethanol 2-(dodecyloxy)-($C_{14}H_{30}O_2$) [67], diethylene glycol monododecyl ether ($C_{16}H_{34}O_3$) [68], triethylene glycol lauryl ether ($C_{18}H_{38}O_4$) [69], pentaethylene glycol dodecyl ether ($C_{22}H_{46}O_6$) [70], hexaethylene glycol dodecyl ether ($C_{24}H_{50}O_7$) [71] and tetraethylene glycol dodecyl ether ($C_{20}H_{42}O_5$) [72] were identified in the anti-bacterial nano-suspension. All the nonionic detergents present contained ethylene oxide group (CH_2- CH_2-O) which could provide hydrophilic property to the surfactant [73].

Nonionic surfactants have head groups containing no ionisable species. In water, nonionic surfactants are less sensitive to the presence of electrolytes than are ionic surfactants, and so are good for applications with hard water [74]. The most important function of surfactant is to lower interfacial tensions [75]. Surfactant lowers the equilibrium interfacial tension between the medium in which it is dissolved and any other contacting fluid. Since dispersing any material to colloidal size scales generates an enormous amount of interface, thus the ability of surfactant to reduce interfacial tensions is critical to the applications such as the preparation of emulsions and the wetting and dispersal of powders in liquids [74].

Liquid can be considered as colloid when the liquid droplets or solid particles present in it have the size in diameter between one nanometre (nm) and one micrometer (μm) [76]. Therefore, the anti-bacterial nano-suspension is a colloid. Inside the colloid, the unprotected particles in the form of dispersion will rapidly aggregate if they are not provided with a potential energy barrier to prevent it [76], especially for nano-particles as they have high surface energy and tend to aggregate more rapidly. Nonionic detergent can stablise and provide better dispersion of the particles in colloid [76, 77]. Literature review also indicated the use of detergent or surfactant for better dispersion and stablisation of metallic nano-particles in colloid [78, 79]. Non-aggregate zinc oxide nano-particles were prepared with the use of surfactant. As the surface of nano-particles was covered by surfactant, thus the nano-particles repelled each other [80]. For textile finishing, the application of nano-particles will normally be through media such as emulsions or dispersions in liquids [38]. Hence, the existence of nonionic detergent in anti-bacterial nano-suspension can prevent aggregation of nano-particles and thus provide better dispersion of nano-particles in the suspension. On the other hand, a mixture of surfactants is commonly used for stablising purpose as surfactant mixtures have many advantages over simply using a single surfactant [69]. This is the reason why several kinds of nonionic surfactants were determined in the anti-bacterial nano-suspension.

3.3.2 Particle Size Distribution and Content of UV-protective Nano-suspension

The particle size distribution curve of UV-protective nano-suspension is shown in Figure 3.5. Almost all the particles evaluated were smaller than 200 nm. Over 80% of the particles present in the UV-protective nano-suspension were smaller than 100nm. The size of most of the nano-particles was confirmed to be between 60 nm to 80nm indicating that the UV-protective nano-suspension contained nano-particles.

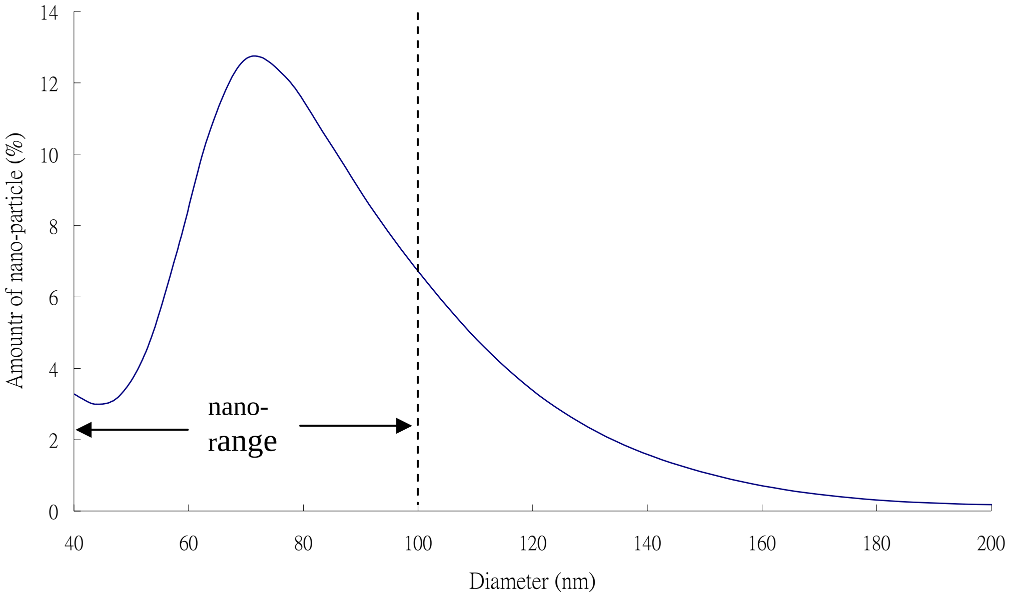


Figure 3.5 Particle size distribution curve of UV-protective nano-suspension

The results of ICP-OES demonstrated that the UV-protective nano-suspension contained various concentrations of titanium, zinc and silver as shown in Table 2. Literature review [4, 6-10] indicated that titanium dioxide (TiO_2) and zinc oxide (ZnO) were commonly applied onto textiles to give UV-protective function effectively by absorbing and scattering UV radiation. Hence, it was believed that titanium present in the UV-protective nano-suspension would probably be in the form of titanium dioxide while zinc would probably be in the form of zinc oxide. When comparing the concentration of these three different kinds of metal, the amount of zinc was found to be much more than the other two metals. By using GC/MS, it was found that the anti-bacterial agents, triclosan ($C_{12}H_7Cl_3O_2$) and 2, 7-dichlorodibenzo-p-dioxin ($C_{12}H_6C_{l2}O_2$), did exist in UV-protective nano-suspension. On the other hand, several kinds of nonionic detergents including ethanol 2-(dodecyloxy)- ($C_{14}H_{30}O_2$), diethylene glycol monododecyl ether ($C_{16}H_{34}O_3$), triethylene glycol lauryl ether ($C_{18}H_{38}O_4$), pentaethylene glycol dodecyl ether ($C_{22}H_{46}O_6$) and hexaethylene glycol dodecyl ether ($C_{24} H_{50}O_7$) were found in the nano-suspension which were similar to those existed in the anti-bacterial nano-suspension. However, tetraethylene glycol dodecyl ether ($C_{20}H_{42}O_5$) did not exist in the UV-protective nano-suspension. Furthermore, a new nonionic detergent call p-Octylphenol ethoxylate ($C_{22}H_{38}O_5$) [81] was found only in the UV-protective nano-suspension but was not present in the anti-bacterial nano-suspension.

Table 3.3 Concentration of different kinds of metal present in UV-protective nano-suspension

Suspension	Conc. mg/L		
	Ag	Ti	Zn
UV protective	12.40	0.50	7197.00

In order to determine whether the nano-particles present in the UV-protective nano-suspension were metal-oxide, the organic removal test using C18 column was conducted to trap the organic compounds existed in the nano-suspension. C18 column is a silica based column which belongs to solid-phase extraction product. Solid-phase extraction (SPE) is a common and effective technique for extracting analytes from the complex samples. It is a sample preparation tool used for the elimination of matrix interferences and undesired compounds prior to chromatographic injection. SPE prepares multiple samples in parallel and uses relatively low quantities of solvents, and the procedures can be readily automated. Commercially available phases for SPE based on silica and bonded silicas have been used for a wide range of analytes [82].

1ml of UV-protective nano-suspension was diluted to 10ml with deionised water. The diluted suspension was then added to a C18 column which was activated with methanol and washed with deionised water. The extract was collected by passing toluene through the C18 column and this extract was classified as Extract A. After that, the C18 column was eluted with hexane and the extract collected was classified as Extract B. The organic contents of Extract A and Extract B were studied by means of Gas Chromatography/Mass Spectrum (GC/MS) aiming to identify the types of organic compounds that could be removed by C18 column. The particle size distribution of Extract A was then investigated using particle size analyser to examine whether the nano-particles could be removed by C18 column.

It was determined that both Extract A and Extract B contained triclosan and 2, 7-dichlorodibenzo-p-dioxin, but the concentration of these organic compounds in sample A was only about 1/10 of that in sample B. This implied that certain amount of organic compounds was removed by C18 column. Extract A and nano-UV-protective suspension were then examined separately by the particle size analyser. Figure 3.6 demonstrates the particle size distribution of both Extract A and UV-protective nano-suspension.

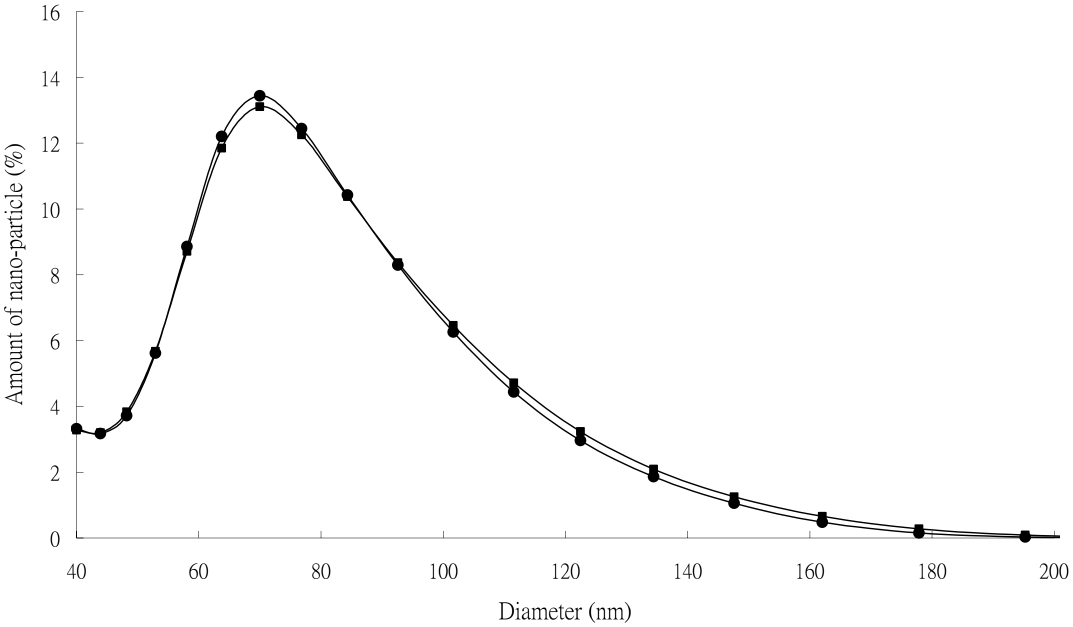


Figure 3.6 Particle size distribution of Extract A and UV-protective nano-suspension: ■ Extract A, ● UV-protective nano-suspension

Although certain amount of organic compounds was removed by C18 column, the particle size distribution curves of Extract A and UV-protective nano-suspension were still very similar. This implied that the nano-particles present in the UV-protective nano-suspension should belong to metallic types.

3.4 Conclusion

The study showed that although the nano-suspension purchased from the commercial market was claimed to be in nano-scale, the size of particles present in it was still larger than 100 nm. The metal contents of both anti-bacterial nano-suspension and UV-protective nano-suspension were quite similar as they all contained titanium, zinc and silver. Apart from containing metals, these two different nano-suspensions also contained anti-bacterial agents namely triclosan and 2, 7-dichlorodibenzo-p-dioxin ($C_{12}H_6C_{l2}O_2$). Several kinds of nonionic detergents found inside in these two nano-suspensions were used for the purpose of better dispersion of nano-particles. The amount of zinc present in both nano-suspensions was the highest among these three kinds of metal. In addition, the amount of titanium, zinc and silver present in anti-bacterial nano-suspension was higher than that of the UV-protective nano-suspension. This implied that more titanium, zinc and silver were needed to provide the fabric with anti-bacterial property.

Chapter 4

Fabrication and Evaluation of Nano-treated Cotton Fabric

4.1 Introduction

Nano-treated fabric is efficient in providing corresponding function with good durability [2, 7, 11]. This is due to the fact that nano-particles have a large surface area to volume ratio and high surface energy, thus presenting better affinity for fabrics leading to the increase in the durability of the function. Many nano-treated textiles are claimed to be withstanding over 20 washing cycles without losing or weakening the corresponding function.

In order to study the performance and washing fastness of nano-treated fabric and see whether the nano-suspensions examined in Chapter 3 can provide the claimed property, the nano-treated anti-bacterial fabric and UV-protective fabric were prepared separately by applying the respective nano-suspension onto cotton fabrics. After the fabrication of nano-treated cotton fabrics, their performance and washing fastness were evaluated according to the international standard.

4.2 Experimental Procedures

4.2.1 Fabrication of Nano-treated Anti-bacterial Cotton Fabric and UV-protective Cotton Fabric

The respective nano-suspension was diluted with deionised water at room temperature and the mixture was stirred prior to coating. A Z-twill semi-bleached cotton fabric was then padded with the mixture using an automatic padder with 60% pickup. The padded substrate was dried at 80^{o}C for 1 minute in a pre-heated oven followed by curing at 170^{o}C for 3 minutes in a pre-heated curing oven.

4.2.2 Evaluation of the Nano-treated Anti-bacterial Cotton Fabric

Anti-bacterial tests are generally classified into two methods namely quantitative analysis and qualitative analysis. In this study, the cotton fabric treated with anti-bacterial nano-suspension was quantitatively evaluated against Staphylococcus aureus according to the AATCC 100-1999 test method. 1ml of bacterial inoculum was added separately to the untreated and nano-treated cotton fabrics which were placed in two 250ml containers. The specimens were allowed to contact with the bacteria for 24 hours. After the contact period, 100ml of 0.85% sodium chloride solution was poured into the vessel and vigorously shaken. The solution was then plated on a nutrient agar and incubated for 24 hours at 37^{o}C. Washing fastness of the nano-treated cotton fabric was tested based on the AATCC 135-2003 test method using the AATCC standard washing machine and detergent.

4.2.3 Evaluation of the Nano-treated UV-protective Cotton Fabric

The performance of the fabric treated with UV-protective suspension was studied according to the Australia-New Zealand standard AS/NZS 4399:1996 using Varian Cary 300 UV spectrophotometer. Washing fastness of nano-treated fabric was tested based on the AATCC 135-2003 test method using AATCC standard washing machine and detergent.

4.3 Results and Discussions

4.3.1 Performance of Nano-treated Anti-bacterial Cotton Fabric

The anti-bacterial properties of both the untreated cotton fabric and nano-treated anti-bacterial cotton fabric before and after washing were quantitatively evaluated against the Staphylococcus aureus according to the AATCC 100. The reduction in number of bacteria was calculated using the following equation:

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

where R is the reduction rate, A is the number of bacteria recovered from the inoculated nano-treated fabric placed in the jar and incubated over 24 hours, and B is the number of bacteria recovered from the inoculated nano-treated fabric placed in the jar immediately after inoculation, i.e. at “0” contact time

Table 4.1 shows the reduction rate of the samples whereas Figure 4.1 indicates the comparison of the anti-bacterial activity of both the untreated and nano-treated cotton fabrics. Figure 4.1b reveals the complete killing of bacteria by the nano-treated anti-bacterial cotton fabric while Figure 4.1a shows the continuous growth of bacteria. It was confirmed that the nano-treated anti-bacterial cotton fabric provided 100% reduction of bacteria and had excellent anti-bacterial property. As mentioned in Chapter 3, the anti-bacterial nano-suspension contained nano-zinc oxide, nano-titanium dioxide and nano-silver. The results agreed very well with the previous studies which demonstrated that metal nano-particles including silver, titanium dioxide and zinc oxide could kill and inhibit the growth of bacteria effectively. On the other hand, as the anti-bacterial nano-suspension also contained anti-bacterial agents triclosan and 2,7-dichlorodibenzo-p-dioxin, the anti-bacterial effect might be induced or enhanced by these two agents. The reduction rate of bacteria was slightly decreased after 5 washing cycles. The nano-treated cotton fabric still maintained fairly good anti-bacterial effect even after 20 washing cycles, implying that the attachment of the nano-particles to fabric substrate was quite well.

Table 4.1 Anti-bacterial effect of untreated cotton fabric and nano-treated anti-bacterial cotton fabric before and after washing

Sample	Bacterial concentration (cfu/sample)		Reduction rate of bacteria (%)*
	0 hour	24 hours	
Untreated cotton fabric	5,000,000	5,100,000,000	+1019
Nano-treated anti-bacterial cotton fabric without washing	3,000,000	0	-100
Nano-treated anti-bacterial cotton fabric with 5 washing cycles	3,000,000	300,000	-90
Nano-treated anti-bacterial cotton fabric with 10 washing cycles	580,000	190,000	-67.2
Nano-treated anti-bacterial cotton fabric with 20 washing cycles	3,000,000	1,210,000	-60

“+” represents growth of bacteria, “-” represents reduction of bacteria

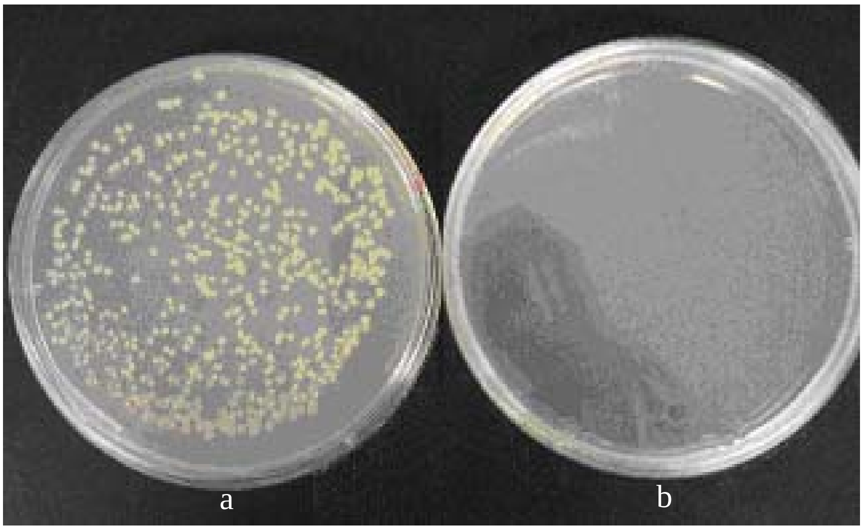


Figure 4.1 Anti-bacterial activity of (a) untreated cotton fabric (b) nano-treated anti-bacterial cotton fabric

4.3.2 Performance of Nano-treated UV-protective Cotton Fabric

Australian/New Zealand Standard AS/NZS 4399:1996 describes the standard laboratory procedures used for measuring the ultraviolet protection factor (UPF) of fabrics and for labelling UPF rated clothing. Fabrics are assigned a UPF rating number and a protection category depending on how much UV radiation that they can block. Table 4.2 shows the rating system.

Table 4.2 Rating system of Australian/New Zealand Standard AS/NZS 4399:1996

UPF Rating	Protection Category	% UVR Blocked
15 - 24	Good	93.3 - 95.9
25 - 39	Very Good	96.0 - 97.4
40 and over	Excellent	97.5 or more

The test standard states that the highest UPF rating that the garments may be labelled with is 50. Garments made from fabrics with ratings higher than 50 are labelled as UPF 50+.

According to the Australian/New Zealand Standard AS/NZS 4399:1996, the UV protection performance of fabric was evaluated and expressed in terms of ultraviolet protection factor (UPF). UPF value represents how long a human being wearing clothing can be exposed to UV, versus not wearing it, until the skin develops reddening [83]. UPF is calculated according to the following equation:

$$UPF = \frac{\int_{290}^{400} E_\lambda S_\lambda d\lambda}{\int_{290}^{400} E_\lambda S_\lambda \cdot \tau_\lambda d\lambda}$$

where λ represents the wavelength in nm, E_λ is the relative erythemal effective, S_λ is the solar UV spectral irradiance in W m-2nm-1, τ_λ is the spectral transmittance of the specimen, and dλ is the wavelength increment in nm.

Ultraviolet radiation is ranging from 100 to 400 nm and is conventionally subdivided into UVA (315 to 400 nm), UVB (280 to 315 nm) and UVC (100 to

280 nm). Only UVA and part of UVB reach the earth as UVC and some UVB are absorbed by the stratospheric ozone in the atmosphere.

The UPF rating and transmittance results of the untreated cotton fabric and nano-treated cotton fabric before and after washing are shown in Table 4.3 and Figure 4.2 respectively.

Table 4.3 UPF rating of untreated cotton fabric and nano-treated cotton fabric before and after washing

Sample	UPF rating
Untreated cotton fabric	5
Nano-treated UV-protective cotton fabric before washing	50+
Nano-treated UV-protective cotton fabric after 5 washing cycles	45
Nano-treated UV-protective cotton fabric after 10 washing cycles	35
Nano-treated UV-protective cotton fabric after 20 washing cycles	30

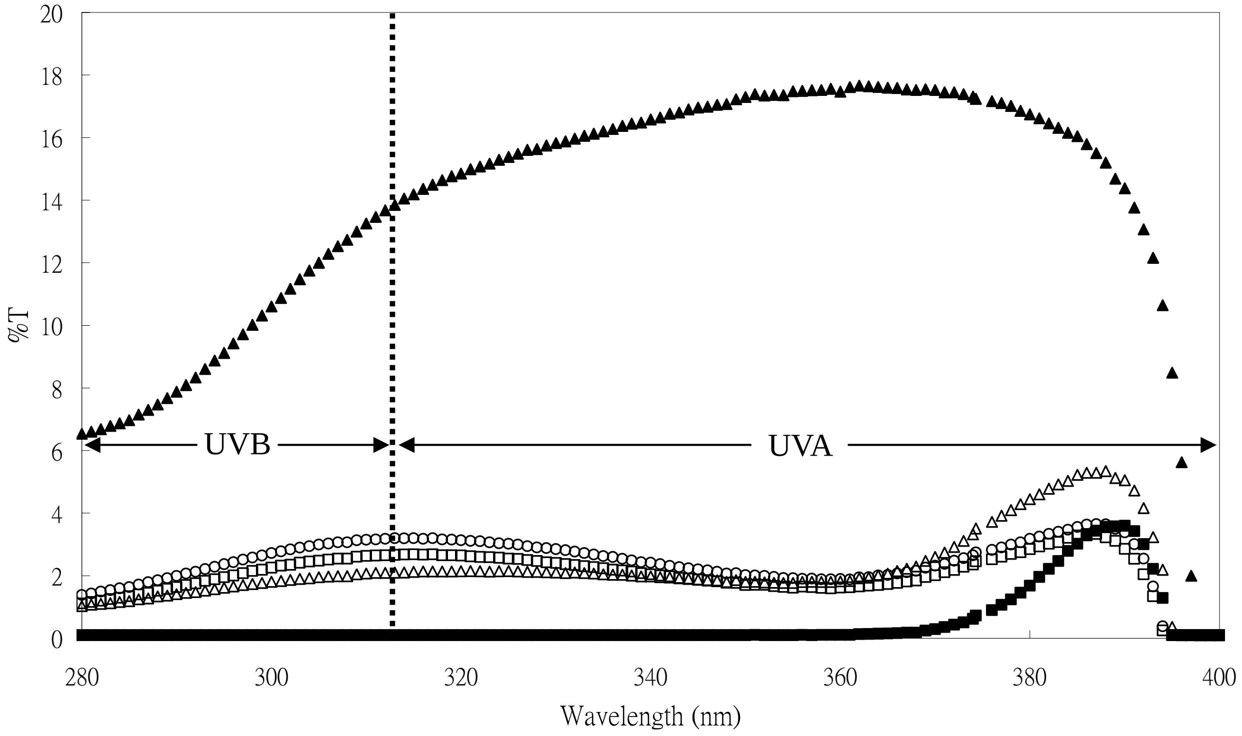


Figure 4.2 UPF investigation of untreated cotton fabric and nano-treated UV-protective cotton fabric before and after washing ▲untreated cotton fabric, ■ nano-treated cotton fabric without washing, Δ nano-treated cotton fabric with 5 washing cycles, □nano-treated cotton fabric with 10 washing cycles, ○ nano-treated cotton fabric with 20 washing cycles

The results showed that the nano-treated UV-protective cotton fabric without washing exhibited the UPF rating of 50+ according to the testing standard, implying that it could provide excellent protection from ultra-violet. On the other hand, the UPF rating of the untreated cotton fabric was 5 which was classified as non-ratable. The UV transmittance of the nano-treated cotton fabric was much lower than that of the untreated cotton fabric. When compared, the nano-treated UV-protective cotton fabric demonstrated zero transmittance of UVB and 3% transmittance of UVA. The UV-protective fabric absorbed UVB better than UVA.

Since the UV-protective nano-suspension contained nano-zinc oxide and nano-titanium dioxide as mentioned in Chapter 3, thus this showed that nano-zinc oxide and nano-titanium dioxide could provide better UVB screening than UVA screening which agreed well with the literature review [8, 84]. However, UVA screening is more important than UVB screening as UVA rays can penetrate deeper into the skin and are implicated in premature ageing and wrinkling as well as skin allergies and rashes, while UVB rays are responsible for sun burn effects and production of vitamin D [85]. There was a slight decrease in the UPF rating of nano-treated cotton fabric after 5, 10 and 20 washing cycles, but the fabric could still maintain very good protection against UV. The transmittance was only increased slightly, i.e. about 2 %, after 20 washing cycles. This showed that the bonding existed between the nano-metal particles and cotton fabric was quite strong.

4.4 Conclusion

Both nano-suspensions indeed provided the claimed function effectively. The nano-treated anti-bacterial cotton fabric rendered 100% reduction of bacteria. The anti-bacterial property was imparted by the metallic nano-particles (titanium dioxide, zinc oxide and silver) and organic anti-bacterial agents (triclosan and 2, 7-dichlorodibenzo-p-dioxin). On the other hand, the nano-treated UV-protective cotton fabric exhibited the UPF rating of 50+. It demonstrated zero transmittance of UVB and almost zero transmittance of UVA. The UV-protective property of the cotton fabric treated with UV-protective nano-suspension was imparted by the nano-titanium dioxide and nano-zinc oxide. The washing fastness of the nano-treated samples was satisfactory demonstrating that the attachment of nano-particles on the fabric was quite strong.

Chapter 5

Characterisation of Nano-treated Cotton Fabric using Instrumental Techniques

5.1 Introduction

Characterisation of the nano-treated fabric plays an important role in nanotechnologies. The unique properties and the improved performance of nano-treated materials are determined according to their size, surface morphology and inter-particle interaction. It is known that the properties of nano-structures depend strongly on their size and shape [50]. In order to fully understand the impact of nano-treated materials, the concern on the surface characterisation of the nano-treated materials is raising rapidly. Characterisation of nano-particles and nano-treated materials is indispensable to understand their behaviour and properties.

One of the characteristics of nano-particles is that they tend to aggregate [7, 48, 86, 87]. When the surface area of nano-particles increases, their surface energy will increase making the nano-particles become unstable. Therefore, nano-particles aggregate easily during the fabrication of nano-treated fabric. In order to study the quality of nano-coating as well as the attachment and dispersion of nano-particles on fabric substrate, advanced measurement techniques must be involved. Scanning electron microscopy (SEM) can be applied to observe the surface morphology and the extent of aggregation of nano-particles [7, 44, 45]. To investigate whether the elemental composition of the nano-coating of the nano-treated fabric is the same as that of the original nano-suspension, X-ray photoelectron spectrometer (XPS) can be used. Some literatures indicate that XPS is always employed for the characterisation of nano-materials [7, 51, 52, 88]. In addition, X-ray Diffraction (XRD) can be applied to study the elemental composition and crystallite size of different material.

5.2 Experimental Procedures

5.2.1 Field Emission Scanning Electron Microscopy (FE-SEM)

The quality of nano-coating as well as the attachment and dispersion of nano-particles on fabric substrate was observed by the FE-SEM (Jeol JSM-6335F). Prior to the FE-SEM investigation, the fabric specimens were gold coated to create a conductive surface and prevent charging defects. FE-SEM was used due to the voltage applied was just 3kV. Usually low voltage was more suitable for polymeric specimens as it could ensure adequate image resolution with the lowest damage to specimen surface. The magnification employed was up to 30,000.

5.2.2 X-ray Photoelectron Spectroscopy (XPS)

The elemental composition of the nano-coating of the nano-treated fabric was investigated by the XPS (Phi Quantum 2000) using Al K-alpha line as excitation source. The X-ray spot size was 100 micron in diameter and the number of sweep was 10. The sample was analysed without sputtering. XPS was employed since its detection depth was less than 10nm

5.2.3 X-ray Diffraction Spectroscopy (XRD)

The component of the nano-coating attached to the nano-treated fabric was studied by the X-ray diffraction spectroscopy (XRD) using the Philips Xpert XRD System operating at 30 kV in θ-2θ configuration. The sample was scanned from 5^0 to 60^0.

5.3 Results and Discussions

5.3.1 Nano-treated Anti-bacterial Cotton Fabric

5.3.1.1 Surface Morphology

According to the result of previous investigation mentioned in Section 3.3.1, the particles present in the anti-bacterial nano-suspension were larger than 100nm. Therefore, the nano-suspension had to be processed by ultrasonic method in order to break down the size of particles before fabricating the anti-bacterial fabric. The surface morphology of untreated and nano-treated anti-bacterial cotton fabrics is shown in Figure 5.1. The results showed that the particles present on the fabric coated with anti-bacterial nano-suspension were larger than 100nm. As for the fabric coated with ultrasonic processed anti-bacterial suspension, the particles observed had various sizes and most of them are smaller than 100nm. The presence of particles larger than 100nm was probably due to (1) the aggregation of nano-particles during fabrication process as particles in nano-size generally possessed a higher surface energy, and (2) the existence of attractive interaction forces between the nano-particles [57]. On the whole, the results of FE-SEM were confirmed to be consistent with the results of particle size analysis of the nano-suspension.

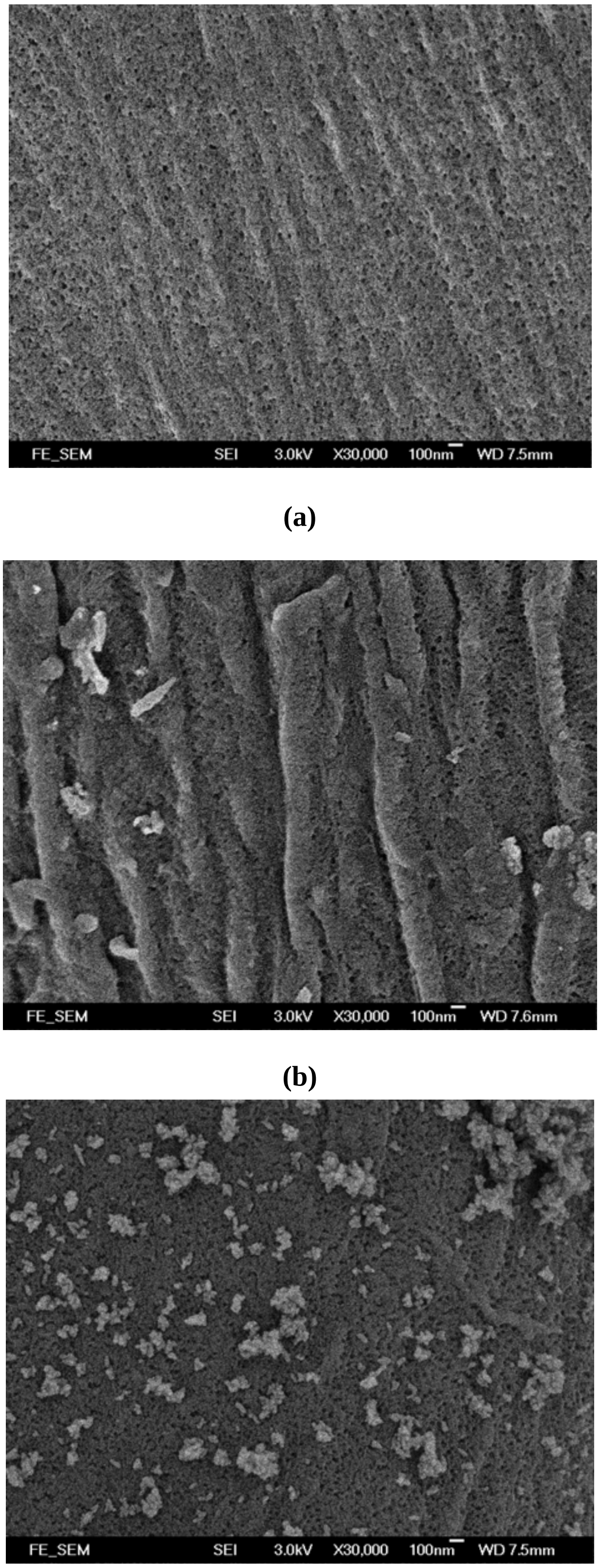


Figure 5.1 FE-SEM images of (a) untreated cotton fibre, (b) cotton fibre treated with anti-bacterial nano-suspension, (c) cotton fibre treated with ultrasonic-processed anti-bacterial nano-suspension

5.3.1.2 Elemental Composition

Figures 5.2 and 5.3 demonstrate the XPS spectra of pure cotton fabric and nano-treated anti-bacterial cotton fabric respectively. Table 5.1 summarises the major elemental composition of both the untreated and nano-treated cotton fabrics obtained by XPS.

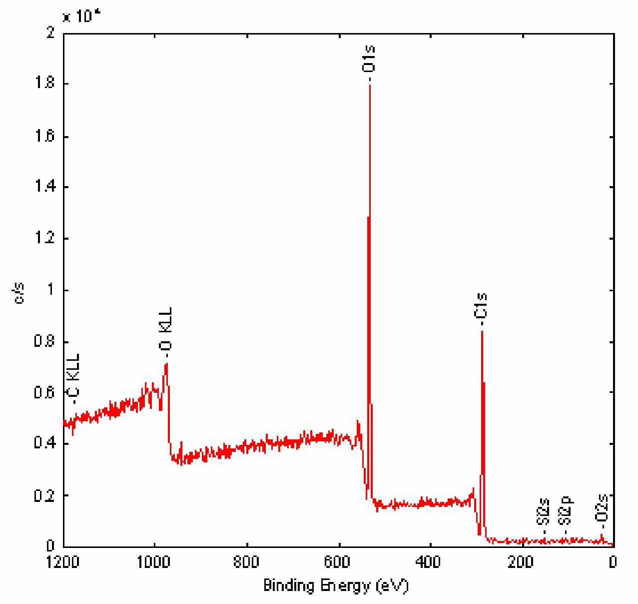


Figure 5.2 XPS spectrum of pure cotton fabric

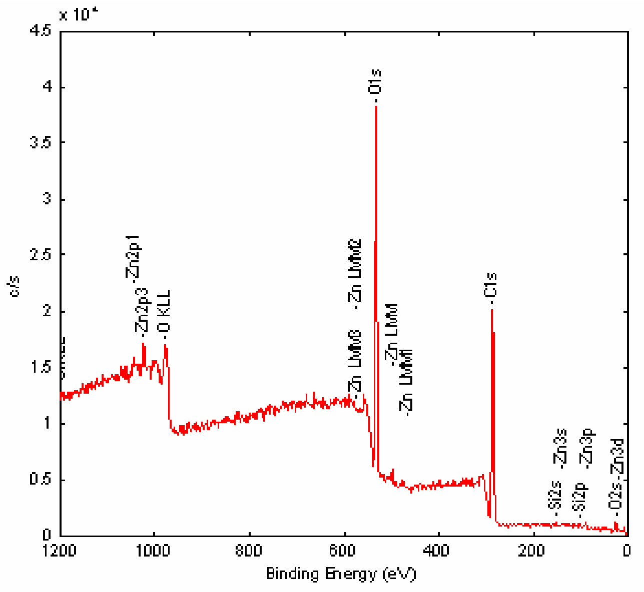


Figure 5.3 XPS spectrum of nano-treated anti-bacterial cotton fabric

Table 5.1 Elemental composition of untreated cotton fabric and nano-treated anti-bacterial cotton fabric in atomic percentage

	Elemental Composition (Atomic %)			
Sample	**C**	**O**	**Zn**	**Si**
Untreated cotton fabric	59.1	40.4	-	0.2
Nano-treated anti-bacteria cotton fabric	61.0	36.8	0.6	0.8

Based on the XPS investigation, the main compositions of the untreated cotton fabric were oxygen and carbon which represented the chemical structure of cotton. A small amount of silicon was also present on the fabric indicating that silicon-based softener was added on the fabric during finishing process.

The XPS result indicated that besides oxygen and carbon, the nano-treated anti-bacterial cotton fabric also contained 0.6% zinc element which evidenced the successful attachment of nano-zinc oxide on the fabric substrate when compared with the untreated cotton fabric.

On the other hand, the XPS results did not indicate the presence of titanium and silver on the nano-treated anti-bacterial cotton fabric although titanium and silver were actually present in the nano-suspension. It was believed that the detection limit of XPS was larger than 0.1 atomic percentage. If the percentage of the element being studied was too little when comparing with the other elements, it would be very difficult to be detected by XPS. In addition, the X-ray spot with very small size (about 100 micron in diameter) would randomly struck on the specimen surface, in such a way that it could not completely cover the whole fabric surface. As the percentage of titanium and silver was so small, the X-ray spot might not easily strike these two elements. As a result, the presence of titanium and silver could not be found.

The component of the nano-coating attached onto the anti-bacterial cotton fabric was examined by XRD. The XRD curve of pure cotton fabric and mamp-treated anti-bacterial cotton fabric is shown in Figure 5.4. When comparing the XRD curve of pure cotton fabric with that of the anti-bacterial cotton fabric, it was discovered that most of the X-ray signal generated from the nano-treated anti-bacterial cotton fabric was originated from the cotton substrate. Diffraction peaks at 32^0 and 37^0 were observed in a small magnitude as shown Figure 5.4. According to literature review [46, 56, 89], XRD curve of TiO_2 showed the peak at 32^0 while XRD curve of ZnO showed the peaks at 32^0 and 37^0 as shown in Figure 5.5. As the amount of ZnO present in the anti-bacterial nano-suspension was much more than TiO_2, thus it was expected that the amount of ZnO attached onto the cotton fabric should be much more than TiO_2. Figure 5.4 shows that the peak signal generated at 32^0 and 37^0 should come from ZnO present on the nano-treated anti-bacterial cotton fabric. The XRD results agreed very well with the investigation results of anti-bacterial nano-suspension conducted by ICP-OES. The XRD results provided more evidence and information about the component of the nano-treated anti-bacterial cotton fabric.

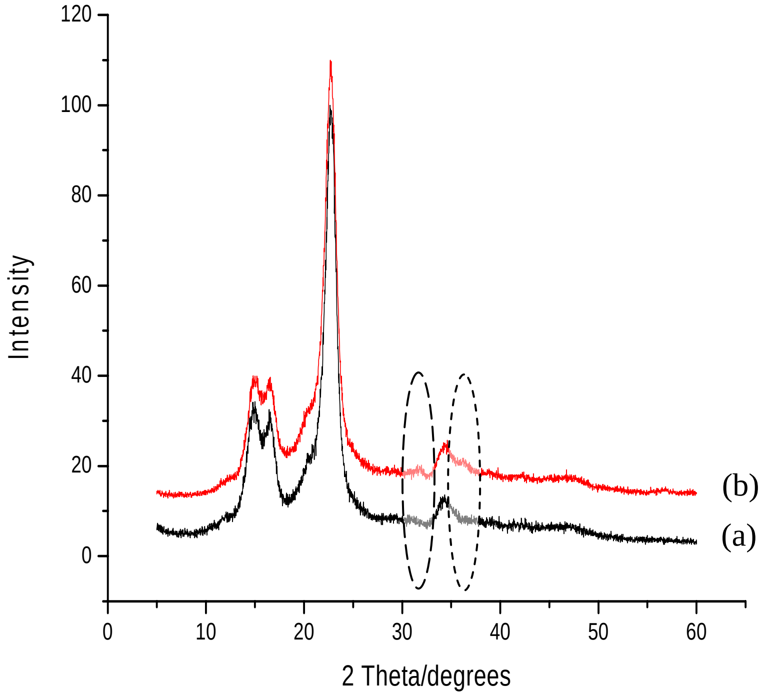
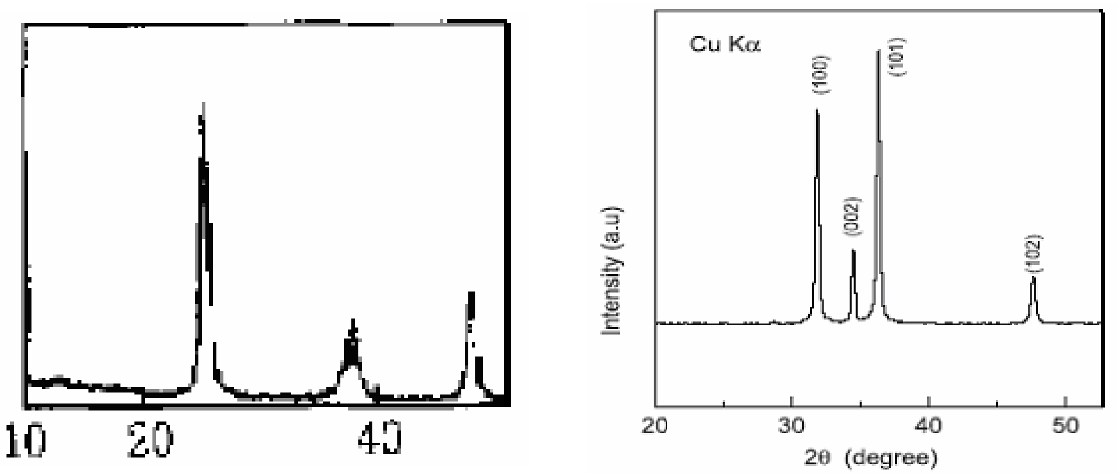


Figure 5.4 XRD patterns of (a) pure cotton and (b) cotton coated with anti-bacterial nano-suspension



(a) **(b)**

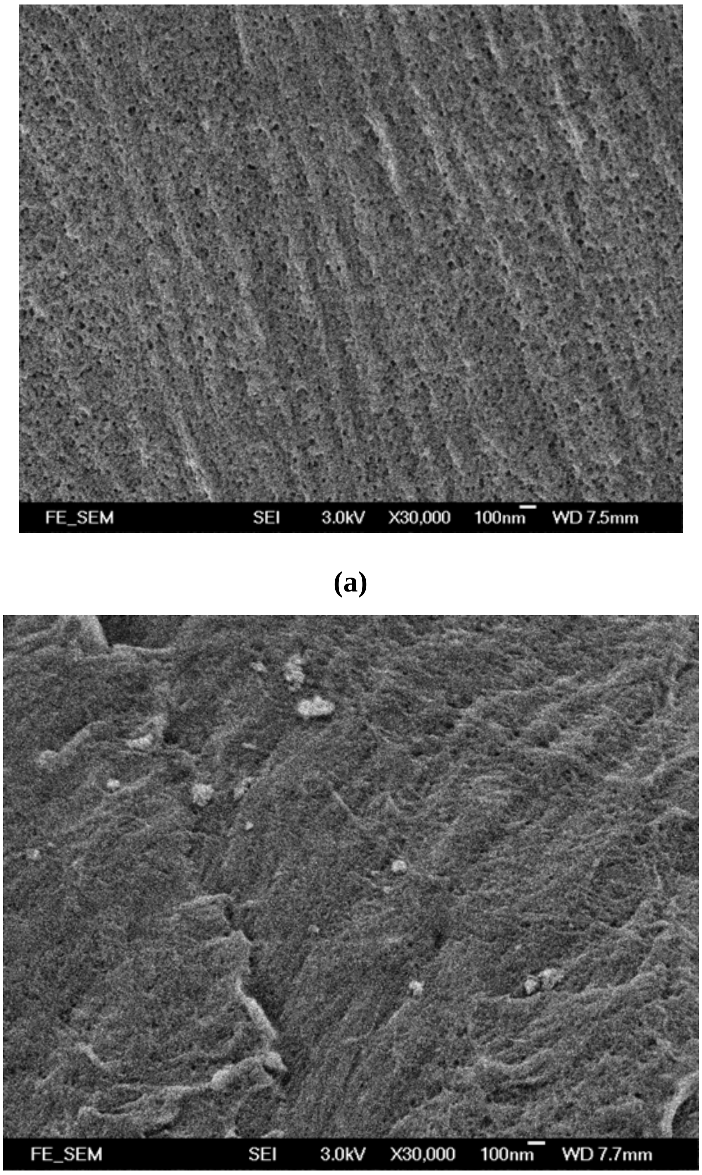
Figure 5.5 XRD patterns of (a) TiO_2 and (b) ZnO [56, 89]

XRD had been applied to determine the particle size of chemical compounds present on cotton fabric using Scherrer equation [90]. However, the magnitude of peaks at 32^0 and 37^0 shown in Figure 5.4 was too small that it was not appropriate to apply Scherrer equation to determine the crystallite size. As a result, XRD could only be applied in the present study to examine the presence of materials coated on fabric because the signal of the coating was usually masked by the signal of substrate unless the amount of coating material was sufficient.

5.3.2 Nano-treated UV-protective Cotton Fabric

5.3.2.1 Surface Morphology

The surface morphologies of both the untreated and nano-treated cotton fabrics are shown in Figure 5.6. It was obvious that no nano-particles could be observed from the untreated cotton fabric. For the fabric treated with UV-protective nano-suspension, a few nano-particles with the dimension below 100 nm could be observed on the fabric surface and their shape was quite spherical. It was interesting to see that some large particles with different sizes were observed on the surface of nano-treated cotton fibres as a result of the aggregation of nano-particles. Particles in nano-size generally possessed a higher surface energy resulting in the enhancement of their aggregation during fabrication process. Some small cracks appeared on the surface of untreated and nano-treated cotton fibre was believed to be caused by the electron beam of FE-SEM hitting on the fabric.



(a)

(b)

Figure 5.6 FE-SEM images of (a) untreated cotton fibre, (b) cotton fibre treated with UV-protective nano-suspension

5.3.2.2 Elemental Composition

Figures 5.7 and 5.8 demonstrate the XPS spectra of pure cotton fabric and nano-treated UV-protective cotton fabric respectively. Table 5.2 summarises the major elemental composition of both the untreated and nano-treated cotton fabrics obtained by XPS.

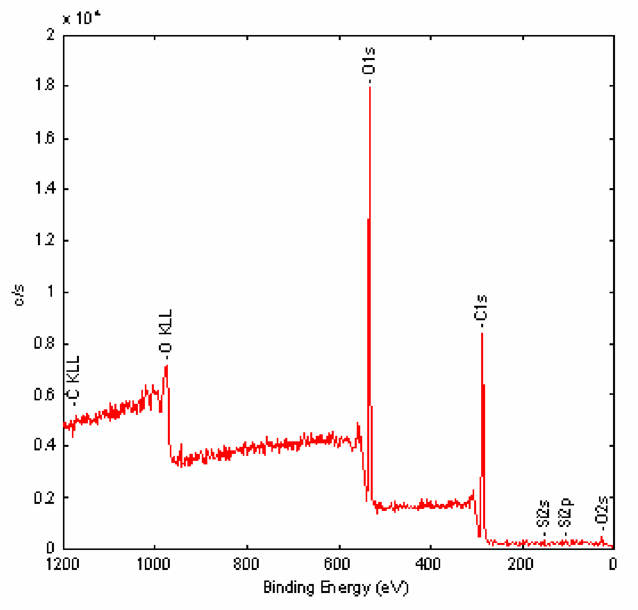


Figure 5.7 XPS spectrum of pure cotton fabric

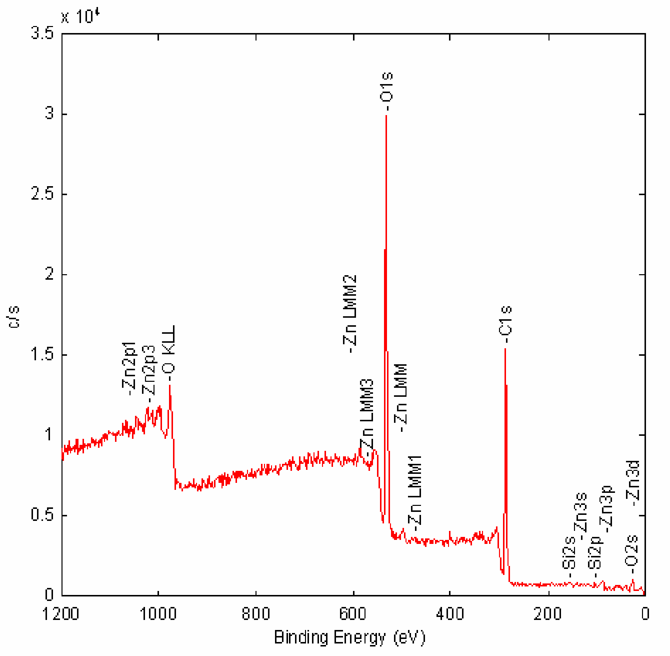


Figure 5.8 XPS spectrum of nano-treated UV-protective cotton fabric

Table 5.2 Elemental composition of untreated cotton fabric and nano-treated UV-protective cotton fabric in atomic percentage

	Elemental Composition (Atomic %)			
Sample	**C**	**O**	**Zn**	**Si**
Untreated cotton fabric	59.1	40.4	-	0.2
Nano-treated UV-protective cotton fabric	61.6	36.7	0.4	0.9

Similar to the previous results of the XPS investigation in Section 5.3.1.2, the main compositions of the untreated cotton fabric were oxygen and carbon which represented the chemical structure of cotton.

The XPS result indicated that besides oxygen and carbon, the nano-treated UV-protective cotton fabric also contained 0.4% zinc element which evidenced the successful attachment of nano-zinc oxide on the fabric substrate when compared with the untreated cotton fabric.

The XPS results also did not indicate the presence of titanium and silver on the nano-treated UV-protective cotton fabric although these metals were originally present in the nano-suspension. It was probably due to the detection limit of XPS. As explained previously, if the percentage of the element being studied was too little when comparing with the other elements, it would be very difficult to be detected by XPS. On the other hand, the percentage of titanium and silver was so small that the X-ray spot might not easily strike these two elements. As a result, the presence of titanium and silver could not be found.

The component of the nano-coating attached onto the nano-treated UV-protective cotton fabric was examined by XRD. Most of the X-ray signals generated were originated from cotton substrate. Diffraction peaks at 32^0 and 37^0 were observed in a small magnitude as shown in Figure 5.9. As mentioned previously in Section 5.3.2.1, these peaks demonstrated the presence of TiO_2 and ZnO. Since the amount of ZnO present in the UV-protective nano-suspension was much more than TiO_2, thus it was expected that the amount of ZnO attached onto the cotton fabric should be much more than TiO_2. Figure 5.9 shows that the peak signal generated at 32^0 and 37^0 should come from the ZnO present on the UV-protective cotton fabric. This agreed very well with the investigation results of UV-protective nano-suspension conducted by ICP-OES. The results further confirmed the attachment of nano-zinc oxide particles on the nano-treated UV-protective cotton fabric.

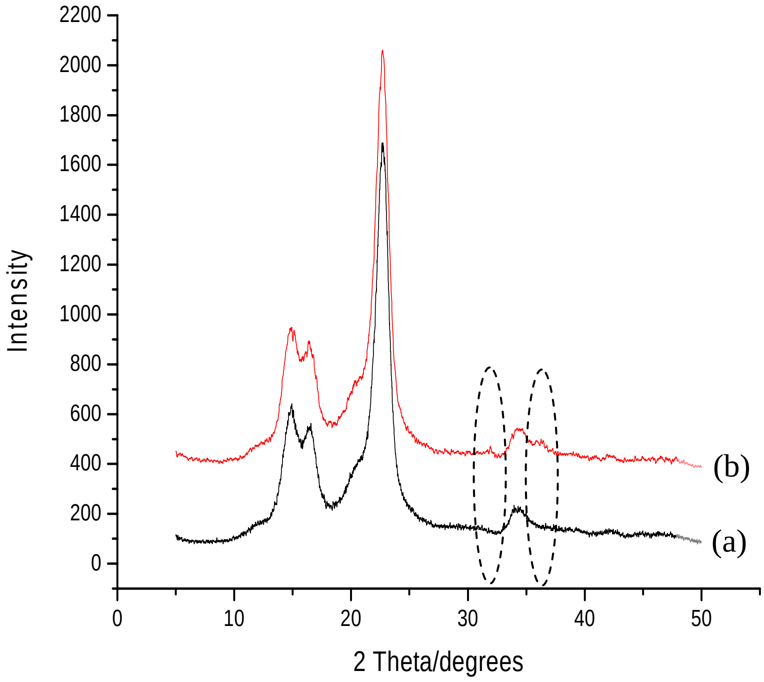


Figure 5.9 XRD patterns of (a) pure cotton and (b) cotton treated with UV-protective nano-suspension

Similar to the nano-treated anti-bacterial fabric, it was not appropriate to apply Scherrer equation to determine the crystallite size of nano-particles attached on the nano-treated UV-protective cotton fabric as the peak magnitude was very small.

5.4 Conclusion

FE-SEM images showed the presence of nano-particles on both the nano-treated anti-bacterial and UV-protective cotton fabrics. The size of nano-particles were inhomogeneous. Although FE-SEM could not show the size distribution of nano-particles coated on the cotton fabric, yet it could preliminarily examine whether the fabric was nano-treated or not.

XPS analysis showed the presence of zinc on these two nano-treated cotton fabrics. The amount of zinc present on the nano-treated anti-bacterial cotton fabric was confirmed to be higher than that of the nano-treated UV-protective fabric. However, XPS did not indicate the presence of titanium and silver on the nano-treated cotton fabrics as the percentage amount of these two elements was too little. Since XPS could examine the elemental composition of the nano-coating quite accurately, thus it was employed to check the components of nano-chemicals that had been applied onto the fabric.

XRD investigation could not determine the crystalline size of particles attached onto the nano-treated anti-bacterial and UV-protective cotton fabrics as the peak magnitude was too small. However, XRD could show the presence of zinc oxide on these two nano-treated cotton fabrics. The results obtained by XRD agreed well with XPS analysis. On the other hand, both XPS and XRD results could not reveal the complete elemental composition of these two nano-treated cotton fabrics as the existence of titanium and silver on the nano-treated fabrics were not indicated by XPS and XRD.

Chapter 6

Characterisation of Nano-materials Extracted from the Nano-treated Fabric

6.1 Introduction

Instrumental techniques are commonly employed for characterising the nano-treated fabric. However, there are no standard analytical methods so far that can provide the highest accuracy for characterising the nano-treated fabric. This may be due to the complicated composition of nano-materials as well as the possibility of aggregation of the nano-particles.

The instrumental analysis of the extracted nano-materials attaching on the fibre surface is a feasible way to provide more precise information about the nano-coating materials adhered on fabric. The nano-particles are attached to the fabrics with the use of padder adjusted by suitable pressure and speed followed by drying and curing [4, 7, 37, 86]. Coating refers to the application of a semi-liquid material to one or both sides of a textile material. Once the coating has been dried and cured, it forms a bond with the fabric [91].

Extraction method can be applied to remove the coating by breaking the bonding between the coating and the fabric substrate. Acidic medium is frequently used in the conventional extraction methods for extracting metals particles from fabric. According to the AATCC test method 94-2002 [62], hydrochloric acid is employed to extract metals from the finished fabric in order to identify the types of finishes coated on the fabric surface. The extract can be investigated by means of the atomic absorption spectrometry (AAS) or inductively coupled plasma emission spectrometry (ICP-AES). On the other hand, artificial acidic sweat solution can be applied to extract metal from textiles based on the Öko-Tex Standard 100. The solution is prepared using L-histidine monohydrochloric, sodium chloride and disodium hydrogen orthophosphate. The solution is adjusted to pH 5.5 using sodium hydroxide [92, 93]. The fabric sample and the solution are transferred to a beaker and agitated by a magnetic stirrer. The amount of extracted metal can be measured by AAS or ICP-AES [92]. On the other hand, TEGEWA study group [94] developed a new method to extract metals from fabric using Morapex S instrument. Acid mixture containing formic acid and amidosulphuric acid was employed as the extraction medium. The extraction process included 3 extraction cycles, i.e. 2 extractions with 5 ml of the acid mixture in each case plus 1 extraction with 5 ml of distilled water. The total extraction time was 90 seconds. Apart from using Morapex S instrument, TEGEWA study group also preformed extraction using shaking water bath and the result was also significant. Titration method was then used to determine the quantity of extracted metal.

The pH, temperature and types of extraction solution were selected to be the essential parameters that affect the efficiency of extraction of metallic nano-particles. The general approach used for an experiment study is to select few parameters and then vary one parameter at a time while keeping the rest of the parameters as constant. However, the validity of the results may be affected by the interaction effect of the parameters. The full factorial design was employed in this study to determine the effect of individual parameter, the main effects as well as the interaction effect of respective parameters [95]. In a full factorial design all k parameters are taken into account at two levels, namely low level and high level. Therefore, the number of experiments required is 2^k [96].

6.2 Experimental Procedures

6.2.1 Extraction Procedures

The nano-particles present on the nano-treated cotton fabric were extracted by different types of solutions using the shaking method. Untreated cotton fabric used as control was also extracted. Extraction solution and nano-treated cotton fabric were added together into a conical flask which was then put in a shaking water bath. The liquor ratio of fabric to extraction solution was 1:8 and the extraction time was 10 minutes. Metal content and particle size distribution of the extracts were examined by the Inductively Coupled Plasma Optical Emission Spectrophotometer (ICP-OES) and particle size analyser respectively.

6.2.2 Full Factorial Design

Two-level full factorial design was used to explore the effect of a number of parameters on the extraction of metallic nano-particle from the nano-treated anti-bacterial cotton fabric and UV-protective cotton fabric. The response of the design was determined by the amount of nano-particle existed in the extracts. As the extraction solutions employed at pH 4 and 5 were different from those at pH 6 and 7, thus two full factorial designs were employed for each type of nano-treated fabric. The parameters and the corresponding levels of two designs are listed in Tables 6.1 and 6.2 respectively.

Table 6.1 Parameters and respective levels in the factorial design for pH 4 and 5

Parameter	Level	
	(-)	(+)
pH	4	5
Temperature (^0C)	21	95
Extraction solution	HCl	HNO_3

Table 6.2 Parameters and respective levels in the factorial design for pH 6 and 7

Parameter	Level	
	(-)	(+)
pH	6	7
Temperature (^0C)	21	95
Extraction solution	$NaHCO_3$	Na_2CO_3

The design matrix was generated according to the 2^3 full factorial design. For each type of nano-treated fabric, 2 replicates were conducted. Hence, 16 trials were conducted for two pH pairs (pH 4 and 5, pH 6 and 7) separately, i.e. a total of 32 trials for each type of nano-treated fabric. The design matrices shown in Tables 6.3 to 6.6 were defined as design matrix A, B, C and D respectively. The extraction conditions for the trials number 9 to 16 were the replicate of trials number 1 to 8 respectively while the extraction conditions for trials number 25 to

32 were the replicate of trials number 17 to 24 respectively.

Table 6.3 2^3 full factorial design matrix for nano-treated anti-bacterial cotton fabric extracted at pH 4 and pH 5

Trial*	Parameter		
	pH	Temperature (^{0}C)	Extraction solution
AB1	-	-	-
AB2	-	+	-
AB3	-	-	+
AB4	-	+	+
AB5	+	-	-
AB6	+	+	-
AB7	+	-	+
AB8	+	+	+
AB9	-	-	-
AB10	-	+	-
AB11	-	-	+
AB12	-	+	+
AB13	+	-	-
AB14	+	+	-
AB15	+	-	+
AB16	+	+	+

***AB represents the extract obtained from the nano-treated anti-bacterial cotton fabric**

Table 6.4 2^3 full factorial design matrix for nano-treated anti-bacterial cotton fabric extracted at pH 6 and pH 7

Trial*	Parameter		
	pH	Temperature (^{0}C)	Extraction solution
AB17	-	-	-
AB18	-	+	-
AB19	-	-	+
AB20	-	+	+
AB21	+	-	-

AB22	+	+	-
AB23	+	-	+
AB24	+	+	+
AB25	-	-	-
AB26	-	+	-
AB27	-	-	+
AB28	-	+	+
AB29	+	-	-
AB30	+	+	-
AB31	+	-	+
AB32	+	+	+

***AB represents the extract obtained from the nano-treated anti-bacterial cotton fabric**

Table 6.5 2^3 full factorial design matrix for nano-treated UV-protective cotton fabric extracted at pH 4 and pH 5

Trial*	Parameter		
	pH	Temperature (^{0}C)	Extraction solution
UVP1	-	-	-
UVP 2	-	+	-
UVP 3	-	-	+
UVP 4	-	+	+
UVP 5	+	-	-
UVP 6	+	+	-
UVP 7	+	-	+
UVP 8	+	+	+
UVP 9	-	-	-
UVP 10	-	+	-
UVP 11	-	-	+
UVP 12	-	+	+
UVP 13	+	-	-
UVP 14	+	+	-
UVP 15	+	-	+
UVP 16	+	+	+

***UVP represents the extract obtained from nano-treated UV-protective cotton fabric**

Table 6.6 2^3 full factorial design matrix for nano-treated UV-protective cotton fabric extracted at pH 6 and pH 7

Trial*	Parameter		
	pH	Temperature (^{0}C)	Extraction solution
UVP17	-	-	-
UVP 18	-	+	-
UVP 19	-	-	+
UVP 20	-	+	+
UVP 21	+	-	-
UVP 22	+	+	-
UVP 23	+	-	+
UVP 24	+	+	+
UVP 25	-	-	-
UVP 26	-	+	-
UVP 27	-	-	+
UVP 28	-	+	+
UVP 29	+	-	-
UVP 30	+	+	-
UVP 31	+	-	+
UVP 32	+	+	+

***UVP represents the extract obtained from nano-treated UV-protective cotton fabric**

6.3 Results and Discussions

6.3.1 Extraction of Nano-treated Anti-bacterial Cotton Fabric

6.3.1.1 Metal Content of the Extract

According to the results stated in Chapters 3 to 5, the nano-particles attached on the nano-treated anti-bacterial cotton fabric were metallic type. Literature review

[62, 92-94] showed that the pH range investigated for the extraction of metal from textile material was selected between pH 4 and pH 7. Based on the analysis of anti-bacterial and UV-protective nano-suspensions stated in Chapter 3, it was shown that both detergents and anti-bacterial agents did exist in these two nano-suspensions. As the drying temperature (80^oC) and curing temperature (170^oC) was lower than the boiling points of the detergents and anti-bacterial agents as shown in Table 6.7, these organic compounds would not vapourise after drying and curing processes and were still attached on the nano-treated cotton fabrics. Since the detergents were nonionic type, thus they were not affected by the change of pH. As a result, the detergents attached on the nano-treated cotton fabrics would not affect the result of extraction irrespective of the change of pH. In general, extremely acidic or alkaline medium favours the extraction of metal. The studied pH range was selected between 4 to 7 due to the fact that triclosan and 2,7-dichlorodibenzo-p-dioxin were found in the anti-bacterial nano-suspension and UV-protective nano-suspension. The structure of these two organic compounds is stable at pH 4 to pH 7 and will not have any chemical change. However, these two organic compounds are not stable in alkaline medium or extremely acidic condition and thus they will probably degrade. There is the possibility that the degraded organic compounds might react with the metallic nano-particles and affect the detachment of metallic nano-particle from fabric and leading to poor results of extraction.

Table 6.7 Boiling point of organic compounds existed in two functional nano-suspensions

Organic compounds existed in anti-bacterial and UV-protective nano-suspension	Boiling point (^{0}C)
Triclosan ($C_{12}H_7Cl_3O_2$)	344.6
2, 7-dichlorodibenzo-p-dioxin ($C_{12}H_6C_{l2}O_2$)	350.2
Ethanol, 2-(dodecyloxy)- ($C_{14}H_{20}O_2$)	304.4
Triethylene glycol lauryl ether ($C_{18}H_{38}O_4$)	412.0
Pentaethylene glycol dodecyl ether ($C_{22}H_{46}O_6$)	486.6
Hexaethylene glycol dodecyl ether ($C_{24}H_{50}O_7$)	521.0
Tetraethylene glycol dodecyl ether ($C_{20}H_{42}O_5$)	450.3
P-Octylphenol ethoxylate ($C_{22}H_{38}O_5$)	478.0

Based on the extraction procedures provided by TEGEWA study group, the extraction time of the experiment was set at 10 minutes. Both the fabric sample and extraction solution were put in a shaking water bath during extraction in order to provide mechanical force for enhancing the detachment of nano-particles from the nano-treated cotton fabric.

Selection criteria of extraction solution are based on the reactivity between the metallic nano-particles of titanium dioxide, silver and zinc oxide. The selected extraction solutions should not react with these nano-particles, otherwise the particle size distribution of the extracted nano-particles cannot be obtained. According to the structure, titanium dioxide can be divided into three types including anatase, rutile and brookite. The stability of brookite is not good and so it is rarely used. Since rutile type with higher reflective index is more thermally and chemically stable than anatase type, thus it is more suitable to be used as a UV blocker. When compared, the band gap of rutile is narrower than that of anatase. This implies that rutile has much higher excited electron-hole recombination probability and substantially lower light-catalysing activity than those of anatase. As a result, anatase is more suitable to be used as a light catalyser [8, 97]. Anatase and rutile type titanium dioxide are both chemically inert. These types of titanium dioxide are resistant to acids and alkaline [97]. On the other hand, silver is insoluble in hydrochloric acid, sulphuric acid or dilute nitric acid for it only dissolves in concentrated nitric acid or hot, concentrated sulphuric acid [98]. Although there is lack of information concerning the reactivity of nano-sized titanium dioxide and silver in acid medium, yet they can be predicted to be stable in acid medium similar to that of the non nano-sized titanium dioxide and silver [97, 98]. For nano-zinc oxide, there is also lack of information to tell whether it dissolves in acid or not. Since nano-zinc oxide aggregates easily, surface modification may be applied to nano-zinc oxide to reduce the phenomenon of aggregation [99]. However, the properties of nano-zinc oxide will be changed after surface modification, thus it is hardly to predict whether the nano-sized zinc oxide is stable in acid or not. It is known that acids and bases typically react with the surface of metal oxide powders resulting in surface modification. For example, in the case of photoactive anatase, the treatment of TiO_2 particles with sulphuric acid can improve the activity of this photocatalyst without changing the crystalline structure of particles [100]. After summarising the literature review relating to the extraction of metals from textile and the properties of titanium dioxide, silver and zinc oxide, the HCl, HNO_3, Na_2CO_3 and $NaHCO_3$ were finally chosen as extraction solutions for extracting the nano-particles.

After analysing the experimental results obtained from the extraction of nano-treated anti-bacterial cotton fabric using ICP-OES, it was confirmed that zinc, titanium and silver were present in all extracts as shown in Table 6.8.

Table 6.8 Concentration of metals present in different extracts obtained from the extraction of nano-treated anti-bacterial cotton fabric

Extraction condition			Concentration (mg/l)		
pH	Temperature (^{0}C)	Solution	Titanium	Zinc	Silver
4	21	HCl	0.049	141.910	0.647
	95	HCl	0.051	**142.860**	1.207
	21	HNO_3	0.032	141.850	0.533
	95	HNO_3	0.036	132.930	0.970
5	21	HCl	**0.189**	141.810	0.370
	95	HCl	0.072	142.840	0.793
	21	HNO_3	0.023	142.760	0.308
	95	HNO_3	0.051	142.180	1.090
6	21	$NaHCO_3$	0.018	142.140	0.435
	95	$NaHCO_3$	0.019	71.589	1.001
	21	Na_2CO_3	0.001	97.554	0.433
	95	Na_2CO_3	0.006	28.853	**2.062**
7	21	$NaHCO_3$	0.032	141.980	1.368
	95	$NaHCO_3$	0.023	83.975	1.671
	21	Na_2CO_3	0.009	136.680	0.700
	95	Na_2CO_3	0.013	62.257	1.256

*** The bolded value represents the highest concentration of the extracted metal**

It was obvious that titanium, zinc and silver could be extracted under different extraction conditions as shown in Table 6.8. However, these metals did not exist in the extract obtained from the untreated cotton fabric. This implied that all the extraction conditions being studied could be employed to extract titanium, zinc and silver from the nano-treated anti-bacterial cotton fabric. The amount of zinc extracted was much more than that of titanium and silver under each extraction condition being studied. It was probably due to the fact that the amount of zinc oxide attached on the nano-treated anti-bacterial cotton fabric was much more than the other two metals as stated in Chapter 5.

When compared with the other extraction conditions, the one conducted at pH 5 at 21^{0}C using HCl solution could contribute a higher concentration of titanium, and so it is considered to be the most suitable one for extracting titanium from the nano-treated anti-bacterial cotton fabric.

In Table 6.8, the results also showed that the extraction solutions at pH 4 or pH 5 were more favourable as over 140 mg/l of zinc could be extracted from the nano-treated anti-bacterial cotton fabric irrespective of the extraction temperature. On the other hand, the results demonstrated that at pH 6 or pH 7, 21^{0}C was a more suitable extraction temperature than 95^{0}C. In general, increasing the extraction temperature can enhance the extraction process. However, the results obtained in Table 6.8 showed the opposite phenomenon at higher temperature. It might be due to the fact that when extraction took place at higher temperature (95^0C) under pH 6 and pH 7 condition, HCO_3^- and CO_3^- released from the $NaHCO_3$ and Na_2CO_3 respectively might react with the H^+ ion of OH bonding of triclosan while Zn^+ of zinc oxide particles would react with O^- of OH bonding of triclosan. Therefore, the amount of extracted zinc decreased at 95^0C when comparing with those extracted at 21^0C.

Of all the studied parameters, the parameters of Na_2CO_3, pH 6 and 95^0C were found to be the most essential parameters to extract silver. When compared, 95^0C was a more suitable condition to extract silver irrespective of pH. As silver was not soluble in the extraction solution, thus it would not react with the O^- of triclosan. Therefore, increasing the temperature increased the amount of extracted silver. This explained why the extraction condition suitable for extracting silver nano-particles from nano-treated anti-bacterial cotton fabric was different from that of extracting zinc oxide nano-particles.

6.3.1.2 Full Factorial Design Used for Analysing the Dominant Parameters Affecting the Amount of Nano-particle Present in the Extract

After studying the amount of metals extracted under different extraction conditions, the particle size distribution of each extract was investigated. The particle size distribution curves of design matrices A and B are shown in Figures 6.1 and 6.2 respectively, and the amount of nano-particles present in each extract is shown in Tables 6.9 and 6.10 respectively. As the concentration of particles present in the Extracts AB20 and AB28 was not high enough to obtain accurate particle size distribution curve, thus Figure 6.2 did not show the curve of this extract.

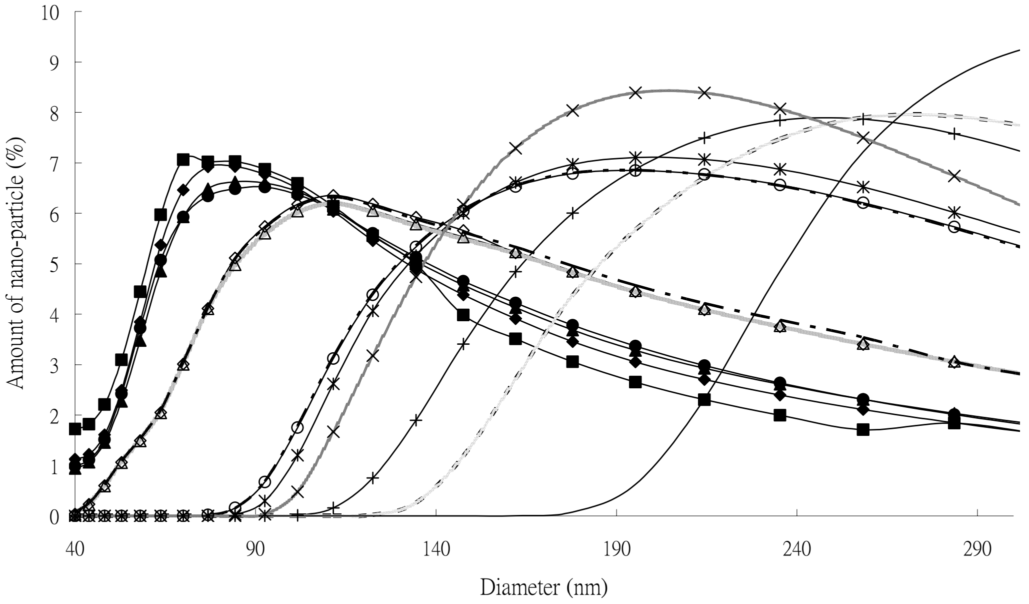


Figure 6.1 Particle size distribution curves of design matrix A —▲— AB1, —○— AB2, —◆—AB3, – – – AB4, —△— AB5, - - - -AB6, ▒▒▒AB7, ·········AB8, —●—AB9, —✳—AB10, —■—AB11, ∿∿∿AB12, —◇— AB13, —+—AB14, ━ ━AB15 and ——AB16

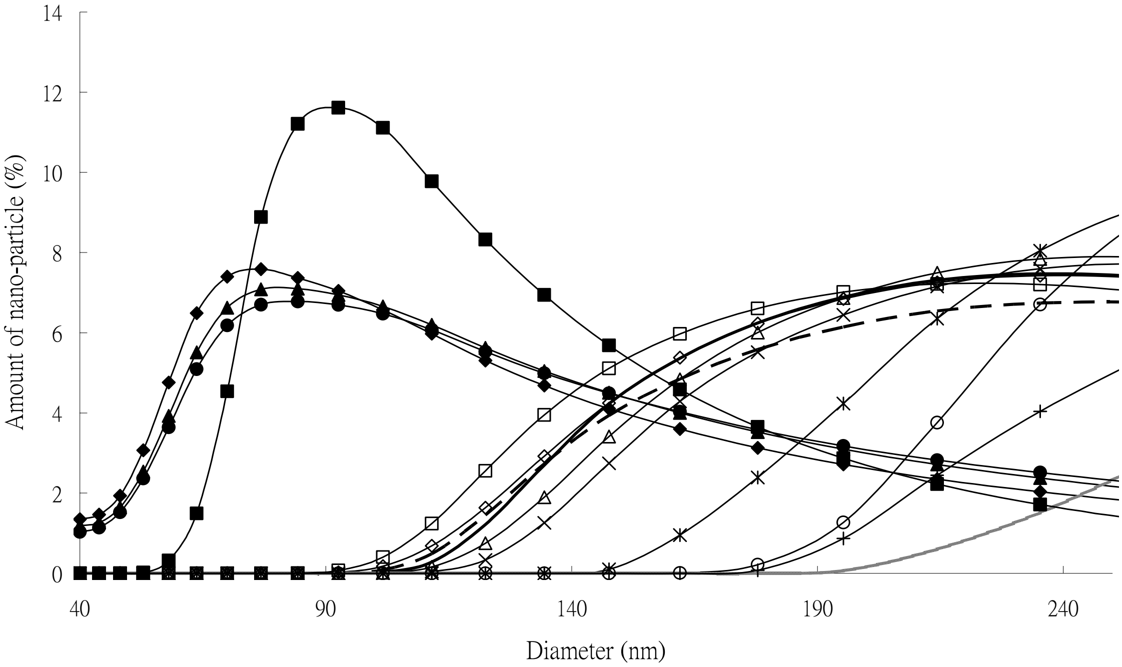


Figure 6.2 Particle size distribution curves of design matrix B - - - AB17, —×— AB18, —◇— AB19, —▲— AB21, —— AB22, —●— AB23, —□— AB24, —△— AB25, —○— AB26, —✳— AB27, —◆— AB29, ~~~~ AB30, —■— AB31 and —+— AB32

Table 6.9 Amount of nano-particle present in the extracts of design matrix A

Trial	Extraction condition			Amount of nano-particle (%) (within 40nm – 100nm)
	pH	Temperature (^{0}C)	Solution	
AB1	4	21	HCl	46.14
AB2		95	HCl	2.60
AB3		21	HNO_3	49.23
AB4		95	HNO_3	2.64
AB5	5	21	HCl	29.18
AB6		95	HCl	0
AB7		21	HNO_3	29.31

AB8		95	HNO_3	0
AB9	4	21	HCl	46.48
AB10		95	HCl	1.53
AB11		21	HNO_3	53.83
AB12		95	HNO_3	0.51
AB13	5	21	HCl	29.63
AB14		95	HCl	0.01
AB15		21	HNO_3	29.82
AB16		95	HNO_3	0

Table 6.10 Amount of nano-particle present in the extracts of design matrix B

Trial	Extraction condition			Amount of nano-particle (%) (within 40nm – 100nm)
	pH	Temperature (^{0}C)	Solution	
AB17	6	21	$NaHCO_3$	0.09
AB18		95	$NaHCO_3$	0
AB19		21	Na_2CO_3	0. 2
AB20		95	Na_2CO_3	-----
AB21	7	21	$NaHCO_3$	50.48
AB22		95	$NaHCO_3$	0
AB23		21	Na_2CO_3	47.63
AB24		95	Na_2CO_3	0.48
AB25	6	21	$NaHCO_3$	0.01
AB26		95	$NaHCO_3$	0
AB27		21	Na_2CO_3	0

AB28		95	Na_2CO_3	-----
AB29	7	21	$NaHCO_3$	55.03
AB30		95	$NaHCO_3$	0
AB31		21	Na_2CO_3	49.19
AB32		95	Na_2CO_3	0

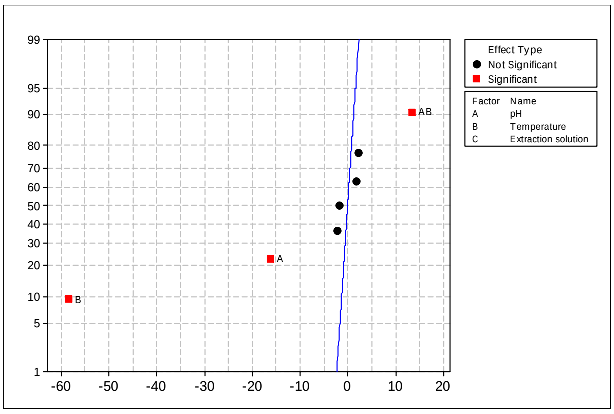
According to the results of ICP-OES shown in Section 6.3.1.1, the amount of extracted titanium and silver was very little when comparing with zinc. This confirmed that the amount of zinc oxide particles in the extracts was much higher than that of the titanium dioxide and silver particles. The difference in the amount of extracted nano-particles under different extraction conditions was probably due to different concentrations of nano-zinc oxide particles present in the extracts.

The concentration of particles present in the Extracts AB20 and AB28 was not high enough to generate particle size distribution curve. The results fully agreed well with those obtained by ICP-OES as such extraction condition would normally extract less zinc when compared with other extraction conditions.

By computing the amount of nano-particles of each trial using Minitab programme package software, the dominant parameters in the extraction process were generated by the normal probability plot, pareto chart and main effect plot. The interaction effects between the parameters were presented in the interaction plot while the relationship between the response and parameters was demonstrated in the surface plot.

6.3.1.2.1 Normal Probability Plot

Normal probability plot is employed to judge effect significance. It is assumed that the effects are normally distributed with the means equal to the effects. Under the null hypothesis, all the effects are zero. The resulting normal probability of the effects will be a straight line. If the effect is non-zero, such effect will fall off the straight line and is defined as significant effect [101]. The normal probability plots of design matrices A and B are shown in Figures 6.3 and 6.4 respectively.



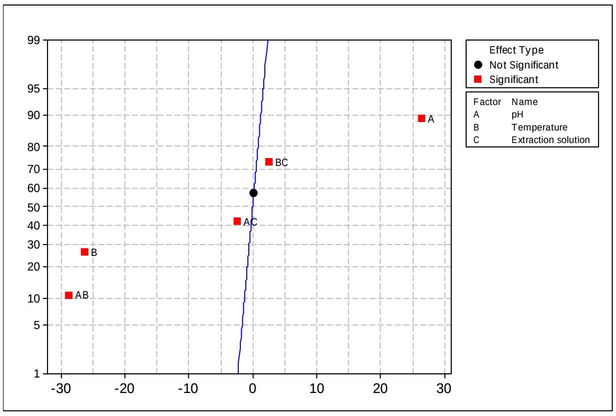


Figure 6.3 Normal probability plot of design matrix A

Figure 6.4 Normal probability plot of design matrix B

According to the results of normal probability plots, the pH, temperature and the interaction between pH and temperature were confirmed as significant parameters in response to the amount of nano-particles present in the extract as these parameters fell off the straight line for both pH pairs, i.e. pH 4 and pH 5, pH 6 and pH 7. The priority of the importance of parameters could be obtained by measuring the distance between the parameter and the straight line. The parameter would be considered as the most important one if the distance between such factor and the straight line was the longest. Therefore, temperature and the interaction between temperature and pH were the dominant parameters with respect to the response of design matrices A and B respectively.

6.3.1.2.2 Pareto Chart

Pareto chart can be employed to determine the most significant factor by examining the quality data. It places the highest cause of effect to the highest position and places the lowest cause of effect to the lowest position [101]. The pareto charts of the design matrices A and B are shown in Figures 6.5 and 6.6.

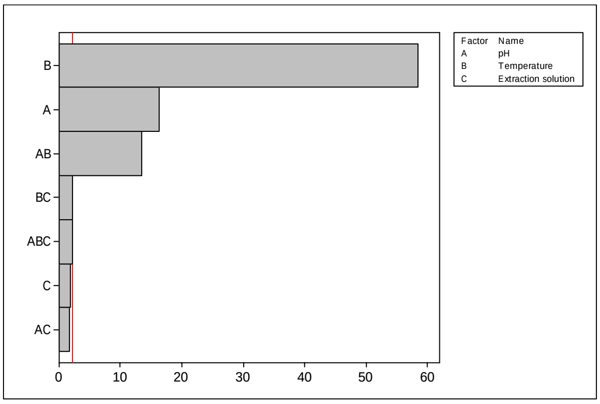


Figure 6.5 Pareto chart of design matrix A

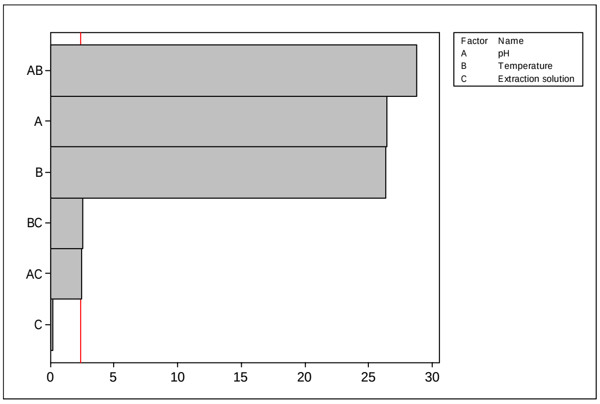


Figure 6.6 Pareto chart of design matrix B

The pareto chart of matrix A showed that temperature was located at the highest position when compared with the other parameters. This implied that temperature was the most significant parameter affected the amount of nano-particles in design matrix A while for design matrix B, the effect of pH, temperature and interaction between pH and temperature also affected the response. The pareto chart further confirmed the importance of these parameters.

6.3.1.2.3 Main Effect Plot

The main effect plot is used to show the averages of all the observations at each level of the parameter and the averages are connected by a line. The vertical height of the line is the main effect. The greater the gradient of the slope of the line, the more the importance of the parameter will be [101]. The main effect plots of the design matrices A and B are shown in Figures 6.7 and 6.8 respectively.

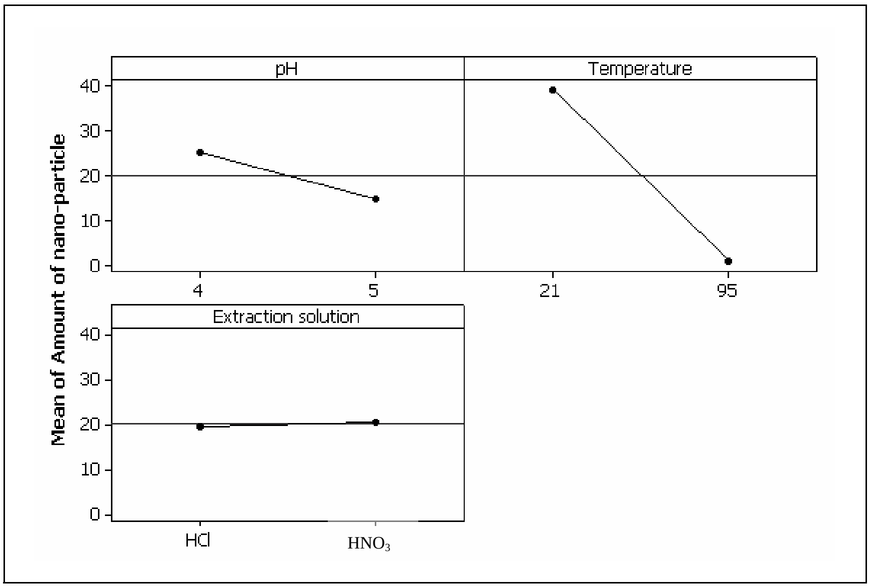


Figure 6.7 Main effect plot of design matrix A

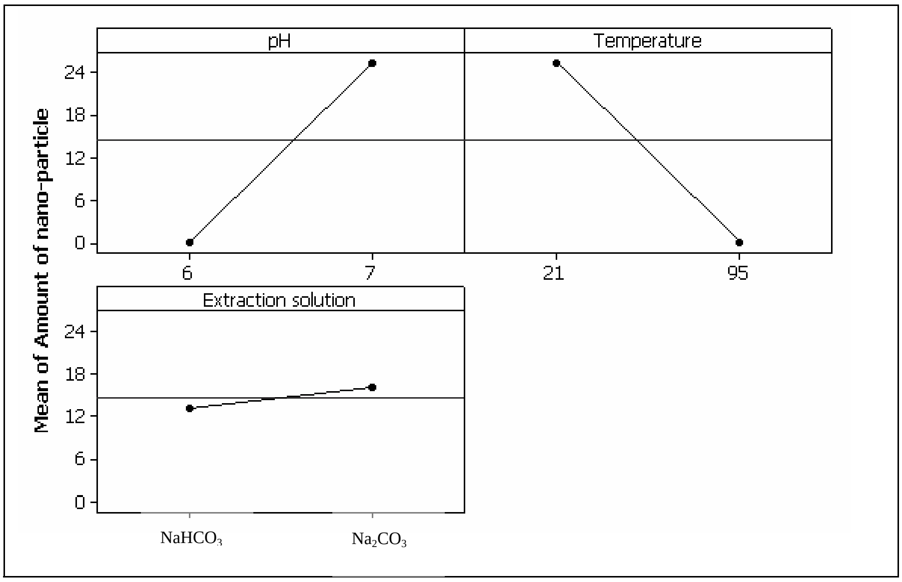


Figure 6.8 Main effect plot of design matrix B

The main effect plot demonstrated that for design matrix A, lower temperature together with pH 4 contributed the highest amount of nano-particles present in the extract. Temperature was a more dominant parameter than pH as the gradient of the temperature line was greater than that of pH. For design matrix B, lower temperature together with pH 7 contributed the highest amount of nano-particles. On the other hand, the types of extraction solution very slightly affected the response of both the design matrices A and B.

6.3.1.2.4 Interaction Plot

The interaction plots illustrating the interaction between the three parameters for the design matrices A and B are shown in Figures 6.9 and 6.10 respectively.

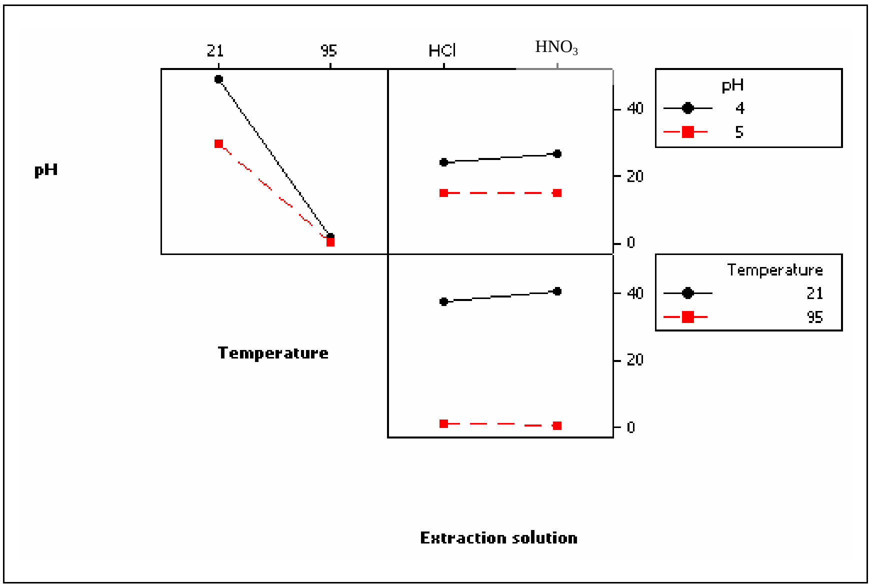


Figure 6.9 Interaction plot of design matrix A

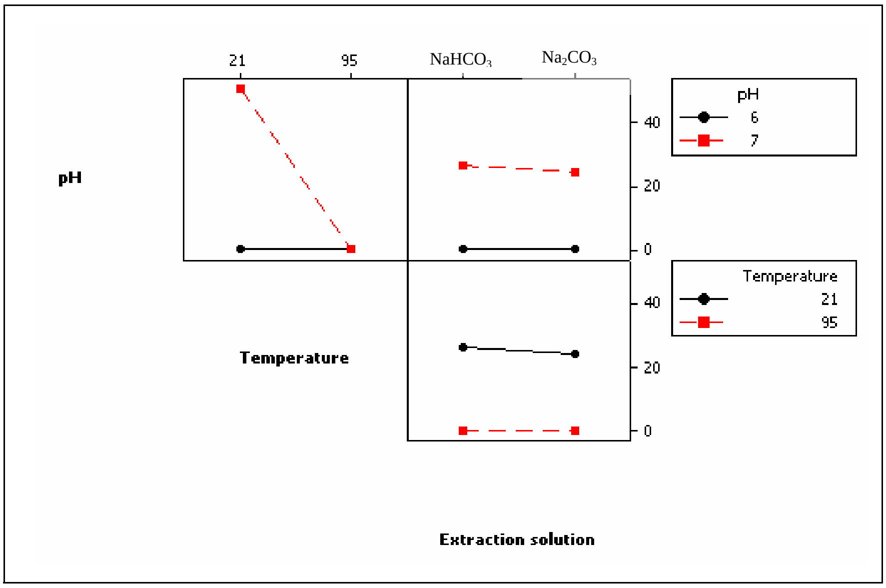


Figure 6.10 Interaction plot of design matrix B

The interaction plot further confirmed that for design matrix A, pH 4 together with 21^{0}C could enhance the extraction of nano-particles from the nano-treated anti-bacterial cotton fabric. As for design matrix B, pH 7 together with 21^{0}C contributed higher efficiency of extraction process. On the other hand, the types of extraction solution very slightly affected the response of two design matrices.

6.3.1.2.5 Surface Plot

Surface plot provides a clear picture of the relationship between the parameters and the response. Two surface plots were generated for design matrices A and B separately by comparing the response in two kinds of extraction solutions. The surface plots presenting the relationship between two parameters (temperature and pH) and the response in each extraction solution are shown in Figures 6.11 to

6.14.

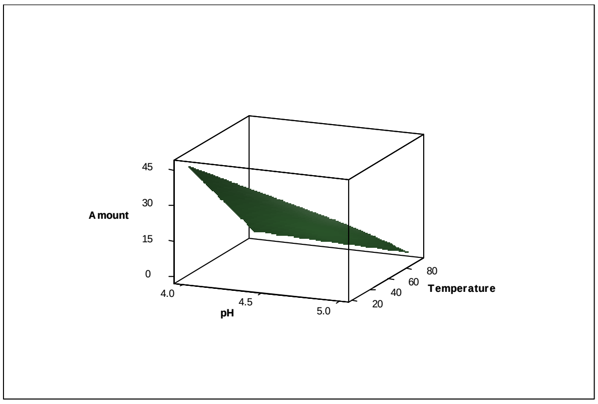


Figure 6.11 Surface plot of amount of nano-particles versus temperature and pH using HCl as extraction solution

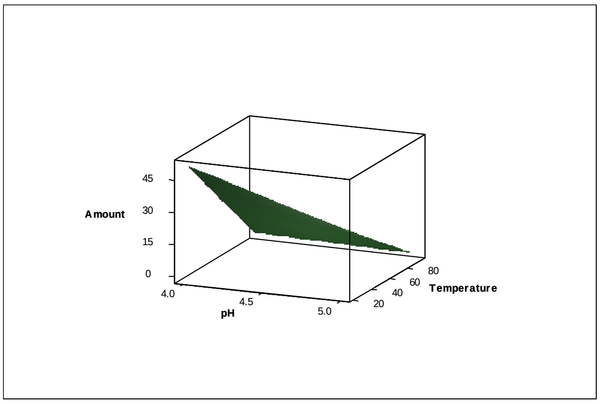


Figure 6.12 Surface plot of amount of nano-particles versus temperature and pH using HNO_3 as extraction solution

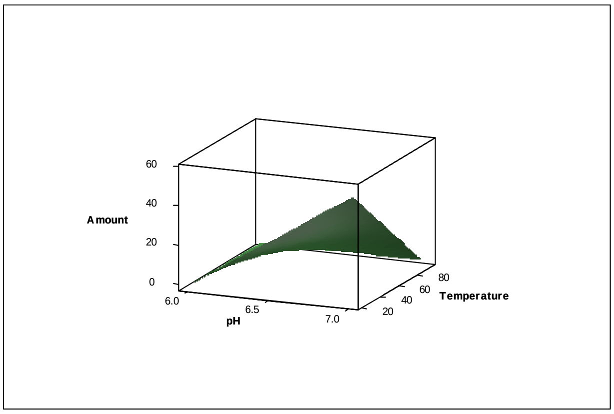


Figure 6.13 Surface plot of amount of nano-particles versus temperature and pH using $NaHCO_3$ as extraction solution

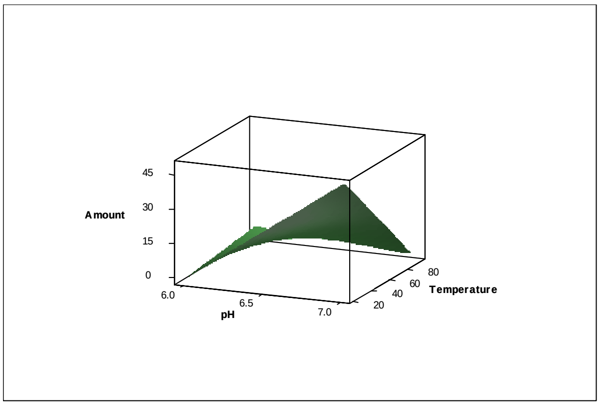


Figure 6.14 Surface plot of amount of nano-particles versus temperature and pH using Na_2CO_3 as extraction solution

The surface plots further confirmed that the type of extraction solution was not a significant parameter with respect to the response of two design matrices as the surface plots of HCl and HNO_3 solutions as well as $NaHCO_3$ and Na_2CO_3

solutions were similar. The surface plots demonstrated that extraction took place at 21^0C using extraction solution together with pH 4 or pH 7 could provide the highest response.

Based on the graphical results, it was determined that temperature was a significant parameter affecting the amount of nano-particle present in the extract. According to the results of ICP-OES, all the extracts contained a significant amount of zinc oxide particles. However, the extracts obtained from the extraction process at 95^0C contained very little amount of nano-zinc oxide particles when comparing with that of the extracts obtained at 21^0C. The particles present in the extracts obtained at 95^0C were much larger than that of the extracts obtained at 21^0C. This implied that the heat energy applied during extraction process might favour the aggregation of nano-zinc oxide particles.

On the other hand, pH also played an important role in the extraction process. In Figures 6.1 and 6.2 as well as Tables 6.9 and 6.10, the results showed that the amount of nano-particles extracted from the extraction solution at both pH 4 and pH 7 was higher than that extracted from the extraction solution at both pH 5 and pH 6. This implied that nano-zinc oxide particles were not stable in the extraction solution at pH 5 and pH 6, and had the tendency to aggregate.

For design matrix B, the interaction between pH and temperature was also another importance parameter affecting the response. This meant that when design matrix B was employed for extraction, not only the change of pH and temperature affected the response, but also the interaction between pH and temperature should be considered. When compared, design matrix A was more preferable as fewer parameters have to be considered.

6.3.2 Extraction of Nano-treated UV-protective Cotton Fabric

6.3.2.1 Metal Content of the Extract

According to the results stated in Chapter 3, the contents of UV-protective nano-suspension were similar to that of the anti-bacterial nano-suspension. Therefore, the same extraction conditions applied to the nano-treated anti-bacterial cotton fabric were also employed to extract metallic nano-particles from the nano-treated UV-protective fabric. After analysing the extracts obtained from the extraction of nano-treated UV-protective fabric using ICP-OES, it was confirmed that different amounts of zinc, titanium and silver were present in the extracts as shown in Table 6.11.

Table 6.11 Concentration of metals present in different extracts obtained from the extraction of nano-treated UV-protective cotton fabric

Extraction condition			Concentration (mg/l)		
pH	Temperature (^{0}C)	Solution	Titanium	Zinc	Silver
4	21	HCl	0.016	74.558	1.048
	95	HCl	0.028	46.431	1.608
	21	HNO_3	0.012	65.400	0.639
	95	HNO_3	0.023	44.780	1.499
5	21	HCl	0.024	**75.419**	0.631
	95	HCl	0.002	16.490	1.924
	21	HNO_3	0.010	56.458	0.561
	95	HNO_3	0.025	47.107	1.425
6	21	$NaHCO_3$	0.027	52.068	0.589
	95	$NaHCO_3$	0.033	48.606	1.645
	21	Na_2CO_3	0.008	42.303	0.312
	95	Na_2CO_3	0.020	37.004	1.880
7	21	$NaHCO_3$	0.021	52.015	0.604
	95	$NaHCO_3$	0.011	26.554	**2.239**
	21	Na_2CO_3	0.007	57.809	0.372
	95	Na_2CO_3	**0.047**	30.461	1.578

*** The bolded value represents the highest concentration of the extracted metal**

It was obvious that titanium, zinc and silver could be extracted under various extraction conditions as shown in Table 6.11. However, these metals did not exist in the extract obtained from the untreated cotton fabric This implied that all the extraction conditions being studied could be employed to extract titanium, zinc and silver from the nano-treated UV-protective cotton fabric.

Since the amount of titanium extracted from the nano-treated UV-protective cotton fabric under different extraction conditions was quite similar, i.e. less than 0.1mg/l, thus the extraction results could not indicate which extraction condition would be the most suitable one for extracting titanium from the nano-treated UV-protective cotton fabric.

To extract zinc from the nano-treated UV-protective cotton fabric, the extraction solution at pH 4 or pH 5 and 21^0C was found to be more suitable among all the studied parameters. By comparing the amount of zinc extracted at 21^0C with that at 95^0C irrespective of pH, it was discovered that 21^0C was a more suitable temperature and the reason was similar to the explanation mentioned in Section 6.3.1.1 covering the extraction of zinc from the nano-treated anti-bacterial cotton fabric.

Of all the studied parameters, the parameter of $NaHCO_3$, pH 7 and 95^0C were found to be the most essential parameters to extract silver. When compared, 95^0C was a more suitable temperature to extract silver and the reason was similar to the explanation mentioned in Section 6.3.1.1 covering the extraction of silver from the nano-treated anti-bacterial cotton fabric.

6.3.2.2 Full Factorial Design Used for Analysing the Dominant Parameters Affecting the Amount of Nano-particle Present in the Extract

After studying the amount of metals extracted under different extraction conditions, the particle size distribution of each extract was studied. The particle size distribution curves of design matrices C and D are shown in Figures 6.15 and 6.16 respectively, and the amount of nano-particles in each extract is shown in Tables 6.12 and 6.13 respectively. As the concentration of particles present in the Extracts of UVP6, UVP8, UVP14, UVP16, UVP17, UVP18, UVP19, UVP20, UVP22, UVP24, UVP25, UVP26, UVP27, UVP28, UVP30 and UVP32 was not high enough to obtain accurate particle size distribution curve, thus Figures 6.15 and 6.16 do not show the curves of these extracts.

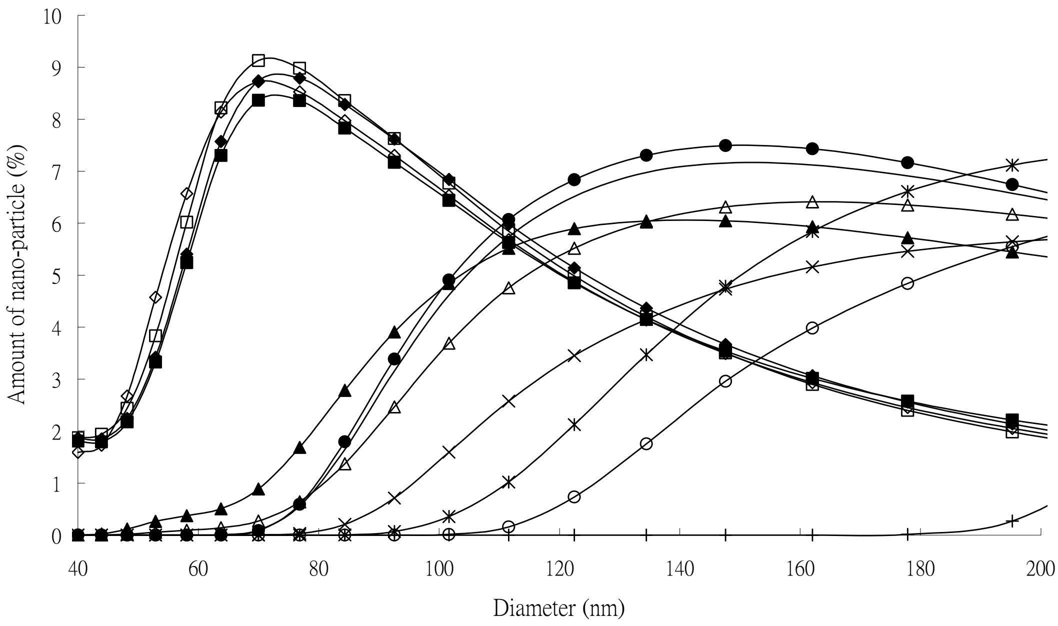


Figure 6.15 Particle size distribution curves of design matrix C: —◆—UV1, —◆—UV2, —■—UV3, —○—UV4, —△—UV5, —×—UV7, —▲—UV9, —□—UV10 —◇—UV11, —+—UV12, ——UV13 and —✳—UV15

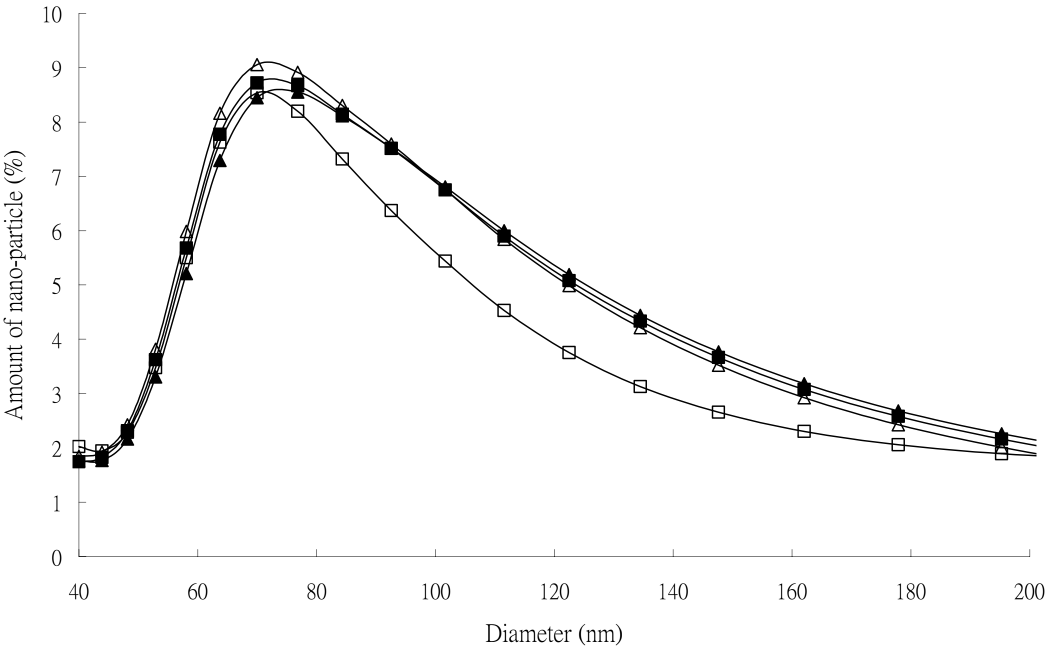


Figure 6.16 Particle size distribution curves design matrix D: —△—UV21, —□—UV23, —▲—UV29 and —■—UV31

Table 6.12 Amount of nano-particle present in the extracts of design matrix C

Trial	Extraction condition			Amount of nano-particle (%) (within 40nm – 100nm)
	pH	Temperature (^{0}C)	Solution	
UVP1	4	21	HCl	62.63
UVP2		95	HCl	15.38
UVP3		21	HNO_3	59.80
UVP4		95	HNO_3	0.01
UVP5	5	21	HCl	8.75
UVP6		95	HCl	-----
UVP7		21	HNO_3	2.55
UVP8		95	HNO_3	-----
UVP9	4	21	HCl	65.18
UVP10		95	HCl	10.77
UVP11		21	HNO_3	64.33
UVP12		95	HNO_3	0
UVP13	5	21	HCl	10.08
UVP14		95	HCl	-----
UVP15		21	HNO_3	0.43
UVP16		95	HNO_3	-----

Table 6.13 Amount of nano-particle present in the extracts of design matrix D

Trial	Extraction condition			Amount of nano-particle (%) (within 40nm – 100nm)
	pH	Temperature (^{0}C)	Solution	
UVP17	6	21	$NaHCO_3$	-----
UVP18		95	$NaHCO_3$	-----
UVP19		21	Na_2CO_3	-----
UVP20		95	Na_2CO_3	-----
UVP21	7	21	$NaHCO_3$	60.94
UVP22		95	$NaHCO_3$	-----
UVP23		21	Na_2CO_3	58.72
UVP24		95	Na_2CO_3	-----
UVP25	6	21	$NaHCO_3$	-----
UVP26		95	$NaHCO_3$	-----
UVP27		21	Na_2CO_3	-----
UVP28		95	Na_2CO_3	-----
UVP29	7	21	$NaHCO_3$	64.77
UVP30		95	$NaHCO_3$	-----
UVP31		21	Na_2CO_3	58.72
UVP32		95	Na_2CO_3	-----

The results of ICP-OES shown in Section 6.3.2.1 demonstrated that the amount of extracted titanium and silver was very little when comparing with zinc. This confirmed that the amount of zinc oxide particles present in the extracts was much higher than that of the titanium dioxide and silver particles. The difference in the amount of extracted nano-particle under different extraction conditions was probably due to the various concentration of nano-zinc oxide particles present in the extracts.

The concentration of particles present in the Extracts UVP6, UVP8, UVP14, UVP16, UVP17, UVP18, UVP19, UVP20, UVP22, UVP24, UVP25, UVP26, UVP27, UVP28, UVP30 and UVP32 was not high enough to generate particle size distribution curve. The results fully agreed with those obtained by ICP-OES as the amount of zinc extracted under these conditions was less than the other extraction conditions.

The amount of nano-particles of each trial was computed using Minitab programme package software. Details concerning the dominant factors, interaction effects between the factors as well as the relationship between the response and factors could be found in Section 6.3.1.2. With regard to the design matrix D, only the Trials UVP13 and UVP 15 could extract certain amount of nano-particles which the other trials could not obtained anything as the concentration of nano-particles present in these extracts was very little. Therefore, the dominant factors, interaction effects between the factors as well as the relationship between the response and factors for the pair of pH 6 and pH 7 could not be analysed using Minitab programme package. As a result, Minitab programme package was only employed for analysing the design matrix C.

Based on the results of the Trials UVP 17 to UVP 32, it was concluded that the extraction conditions used for Trials UVP21/29 and UVP23/31 could be employed for extracting sufficient amount of nano-zinc oxide particles from the nano-treated UV-protective cotton fabric. In addition, it was discovered a large amount of extracted nano-particles could maintain the size smaller than 100nm.

6.3.2.2.1 Normal Probability Plot

The basic theory of normal probability plot has been discussed in Section 6.3.1.2.1 and the normal probability plot of design matrix C is shown in Figure 6.17.

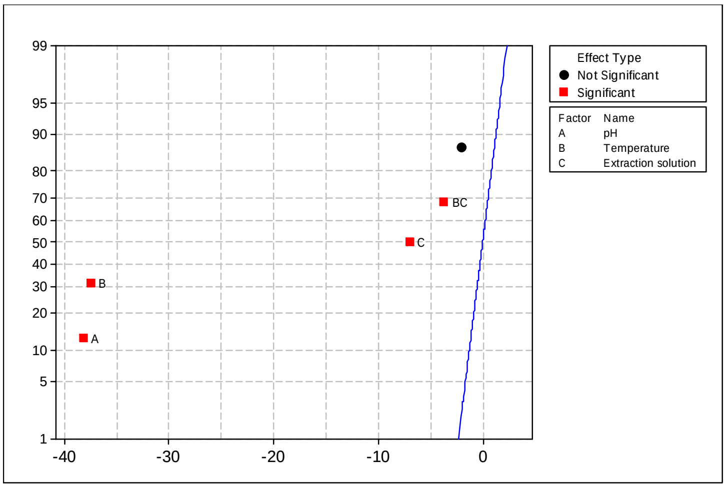


Figure 6.17 Normal probability plot of design matrix C

According to the results of normal probability plot, both pH and temperature were confirmed as the significant parameters in response to the amount of nano-particles present in the extract as these parameters fell of the straight line. Based on the distance between the factor and the straight line, it was determined that the parameters, i.e. pH and temperature, had similar effect of response.

6.3.2.2.2 Pareto Chart

The basic theory of pareto chart has been discussed in Section 6.3.1.2.2 and the pareto chart of design matrix C is shown in Figure 6.18.

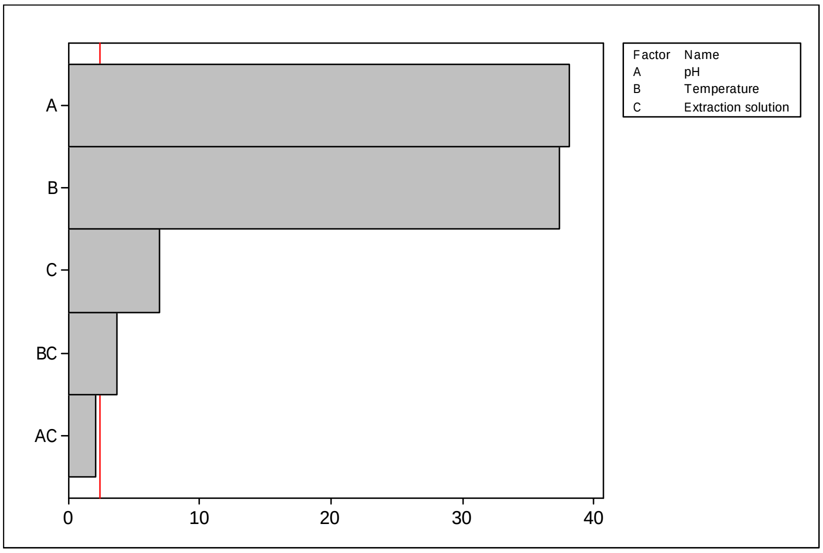


Figure 6.18 Pareto chart of design matrix C

The pareto chart of design matrix C demonstrated that both pH and temperature were located at the higher position when comparing with the other parameters. It further confirmed the importance of these parameters with similar effect of response.

6.3.2.2.3 Main effect plot

The basic theory of main effect plot has been discussed in Section 6.3.1.2.3 and the main effect plot of design matrix C is shown in Figure 6.19.

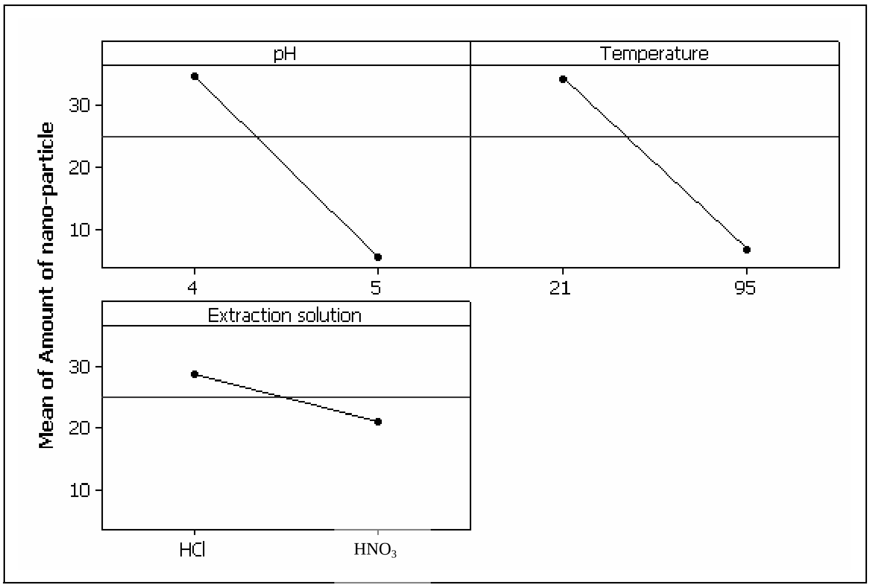


Figure 6.19 Main effect plot of design matrix C

The main effect plot illustrated that for design matrix C, lower temperature together with pH 4 contributed the highest amount of nano-particles present in the extract. When compared, the type of extraction solution very slightly affected the response as the gradient of the slope was smaller than the other two parameters.

6.3.2.2.4 Interaction Plot

The interaction plot presenting the interaction between the three parameters for design matrix C is shown in Figure 6.20.

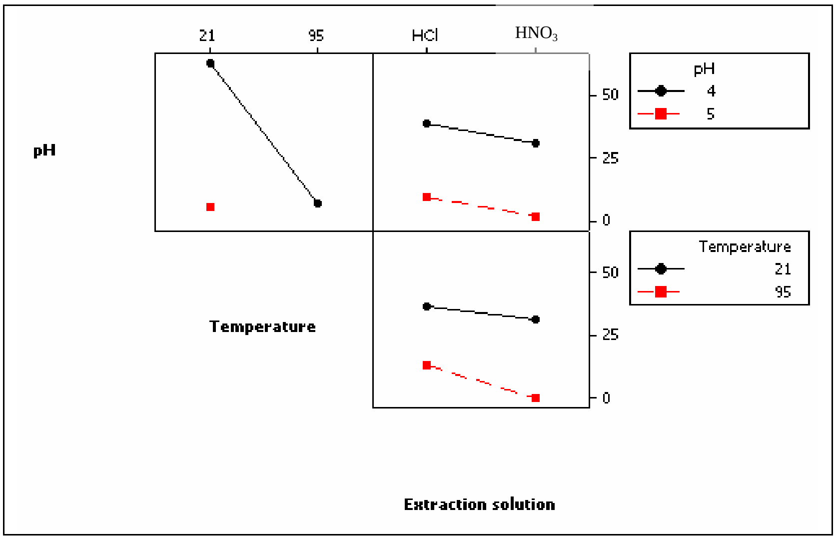


Figure 6.20 Interaction plot of design matrix C

The interaction plot further confirmed that pH 4 together with 21^{0}C could enhance the extraction of nano-particles from the nano-treated UV-protective cotton fabric. On the contrary, the types of extraction solution did not contribute much to the response.

6.3.2.2.5 Surface plot

The surface plots demonstrating the relationship between two parameters (temperature and pH) and the response in two extraction solutions (HCl and HNO_3) are shown in Figures 6.21 and 6.22 respectively.

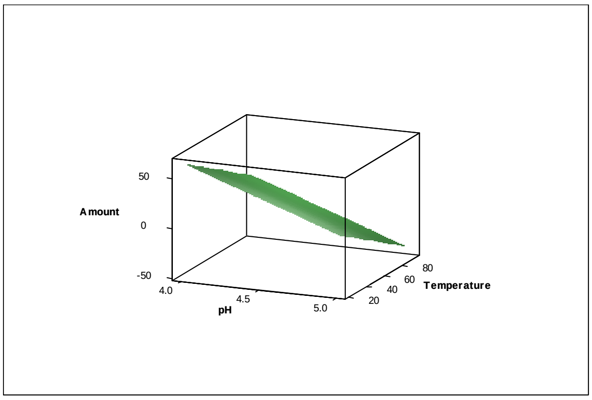


Figure 6.21 Surface plot of amount of nano-particles versus temperature and pH using HCl as extraction solution

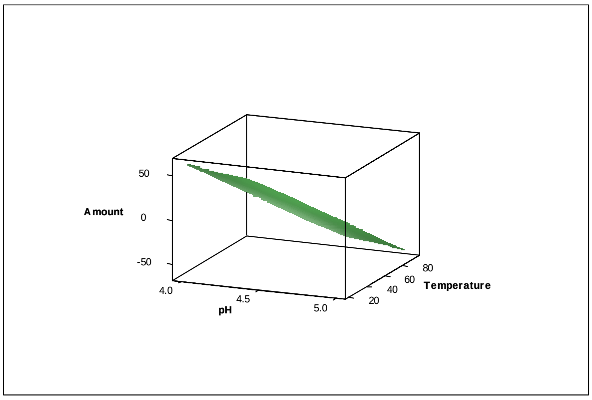


Figure 6.22 Surface plot of amount of nano-particles versus temperature and pH using HNO_3 as extraction solution

The surface plots further confirmed that the type of extraction solution was not a significant parameter with respect to the response as the surface plots of HCl and HNO_3 solutions were similar. The surface plots demonstrated that the extraction pH should be set at 4 and extraction temperature should be set at 21^0C in order to obtain the highest response..

Based on the graphical results, it was determined that temperature was a significant parameter affecting the amount of nano-particle present in the extract for design matrix C. The amount of nano-particles extracted from the Trials UVP1, UVP2, UVP3 and UVP4 showed that when the extraction temperature was increased, the amount of nano-particle would decrease. Although there was a considerable amount of zinc oxide particles present in the Trials UVP2 and

UVP4, yet only few of them were actually nano-particles when comparing with those of Trials UVP1 and UVP3.

On the other hand, pH was also an important factor affecting the response of design matrix C. In Figure 6.14 and Table 6.12, the results illustrated that the amount of nano-particles present at pH 4 was higher than that at pH 5. This implied that nano-zinc oxide particles were not stable in the extraction solution at pH 5 and had the tendency to aggregate.

With regard to the design matrix D, the results showed that the extraction conditions, i.e. at pH 7 and 21^0C, of the Trials UVP21/29 and UVP23/31 could be employed for extracting sufficient amount of ano-zinc oxide particles from the nano-treated UV-protective cotton fabric. At the same time, it was found that a large amount of extracted nano-particles could maintain the size smaller than 100nm.

6.4 Conclusion

Different types of metallic nano-particles present on the nano-treated fabric could be further revealed by extraction method. Analysis of metal content of the extracts showed that titanium, zinc and silver presented on both the nano-treated anti-bacterial cotton fabric and UV-protective cotton fabric.

By using Minitab programme package, it was found that pH and temperature were the two most significant parameters affecting the amount of nano-particles extracted from the nano-treated anti-bacterial cotton fabric and UV-protective cotton fabric. When compared, pH 4 and 21^0C were found to be the most essential parameters among all the studied parameters to extract the highest percentage of nano-particle from these two kinds of nano-treated cotton fabrics.

Chapter 7

Proposed Systematic Evaluation Procedures for Nano-treated Textile Product

7.1 Introduction

As mentioned in Chapter 1, the standard testing methods used for evaluating nano-treated textile materials have not yet been developed. This will lead to a lot of query and argument concerning the genuine quality of nano-products. Since some textile products claimed to be nano-treated are just simply treated by the conventional methods, thus it is necessary to develop standard testing methods with accurate and consistent results for identifying the nano-treated textiles in order to provide assurance for the customers.

In this Chapter, a series of systematic evaluation procedures were developed to characterise the claimed nano-treated anti-bacterial and UV-protective cotton fabrics based on the overall investigation results of previous chapters.

7.2 Proposed Evaluation Procedures for the Commercially Claimed Nano-treated Anti-bacterial and UV-protective Textile Product

According to the results stated in Chapters 3 to 6, the performance, surface morphology and elemental composition of the cotton fabrics treated with anti-bacterial and UV-protective nano-suspensions as well as the particle size distribution of the nano-materials attached on the fabrics were successfully examined using various advanced instrumental techniques and extraction method. After analysing and summarising all the results of Chapter 3 to Chapter 6, a series of systematic characterisation evaluation used for characterising a claimed nano-treated anti-bacterial or UV-protective textile product were developed. The proposed evaluation procedures are divided into six steps as shown in Figure 7.1.

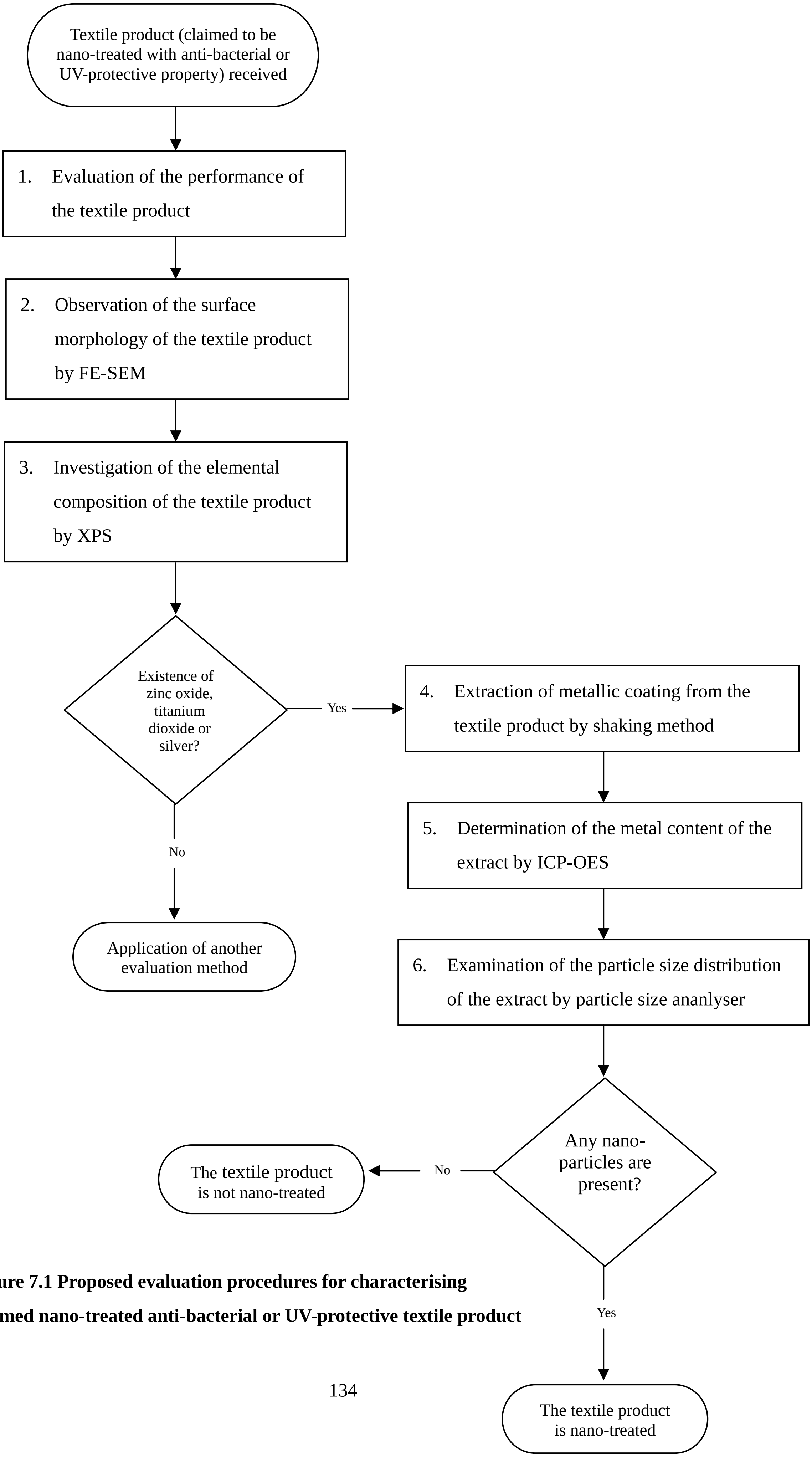


Figure 7.1 Proposed evaluation procedures for characterising claimed nano-treated anti-bacterial or UV-protective textile product

The elaboration and explanation of the proposed evaluation procedure are summarised as follows.

Step 1: Evaluation of the performance of the textile product

This step is aimed to examine whether the performance of the textile product can fulfil the requirements according to the international standards.

Step 2: Observation of the surface morphology of the textile product by FE-SEM

The textile product can be preliminarily evaluated to see whether it is nano-treated by examining the presence of nano-particles on the fabric surface.

Step 3: Investigation of the elemental composition of the textile product by XPS

The types of elements attaching on the fabric surface are examined. If the textile product can provide anti-bacterial or UV-protective function, normally titanium dioxide, zinc oxide or silver should be found on it. Once these metals are found, the textile product can be further characterised by means of shaking extraction method. If nothing can be found, another method should be employed.

Step 4: Extraction of metallic coating from the textile product by shaking method

In this step, shaking method is employed to completely remove the metallic coating from the textile product. Extraction is conducted at 21^{0}C using pH 4 solution.

Step 5: Determination of the metal content of the extract by ICP-OES

The types of metal attaching on the surface of the textile product are further studied as some metals may not be revealed by XPS due to the detection limit.

Step 6: Examination of the particle size distribution of the extract by particle size analyser

The final step is to study the particle size distribution of the particles attaching on the textile product in order to determine whether the textile product is nano-treated.

By combining both instrumental analysis and extraction method, a clear picture of the particle size distribution and elemental composition of the textile product can be obtained. Based on the overall results of systematical analysis, textile product can be affirmatively identified to be nano-treated or not.

Chapter 8

Conclusions

The thesis is mainly focused on providing a new concept of applying instrumental techniques and extraction method for identifying the nano-treated fabric. A series of advanced characterisation techniques and analytical instruments were used to investigate the properties of the nano-treated cotton fabric and the extract obtained from the extraction of nano-treated cotton fabric, aiming to develop a series of systematic evaluation procedures for characterising the nano-treated fabric.

8.1 Analysis of Nano-suspension

The analytical results of particle size distribution and contents of anti-bacterial nano-suspension and UV-protective nano-suspension showed that the majority of particles existed in the UV-protective nano-suspension was smaller than 100nm while all the particles existed in the anti-bacterial nano-suspension were larger than 100nm. The metal contents of both anti-bacterial nano-suspension and UV-protective nano-suspension were quite similar as they all contained the elements of titanium, zinc and silver. Apart from containing metals, these two different nano-suspensions also contained anti-bacterial agents namely triclosan and 2, 7-dichlorodibenzo-p-dioxin. In addition, several kinds of nonionic detergents were found in these two nano-suspensions. When compared, the amount of titanium, zinc and silver present in the anti-bacterial nano-suspension was higher than that of the UV-protective nano-suspension, implying that more titanium, zinc and silver were needed to provide the fabric with anti-bacterial property.

8.2 Fabrication and Evaluation of Nano-treated Cotton Fabric

The nano-treated anti-bacterial cotton fabric and UV-protective cotton fabric were prepared separately by applying the respective nano-suspension onto cotton fabrics using padding method. The results demonstrated both nano-treated cotton fabrics indeed provided the claimed function effectively. The anti-bacterial property was imparted by metallic nano-particles (titanium dioxide, zinc oxide and silver) and organic anti-bacterial agents (triclosan and 2, 7-dichlorodibenzo-p-dioxin), while the UV-protective property of the fabric was imparted by the presence of nano-titanium dioxide and nano-zinc oxide. The washing fastness of the nano-treated samples was confirmed to be satisfactory implying that the attachment of nano-particles on the fabric was quite well.

8.3 Characterisation of Nano-treated Cotton Fabric using Instrumental Techniques

The attachment and dispersion of nano-particles on fabric substrate were examined using FE-SEM. The elemental composition of the untreated cotton fabric and two kinds of nano-treated cotton fabrics was investigated by XPS and XRD. There was a significant change in surface morphology and elemental composition when comparing the untreated cotton fabric with the nano-treated cotton fabric. FE-SEM images showed the presence of nano-particles on both the nano-treated anti-bacterial and UV-protective cotton fabrics. The size of nano-particles were confirmed to be inhomogeneous. XPS and XRD analysis also showed the presence of zinc on both the nano-treated cotton fabrics. The amount of zinc present on the nano-treated anti-bacterial cotton fabric was confirmed to be higher than that of the nano-treated UV-protective cotton fabric. However, both XPS and XRD results could not reveal the presence of titanium and silver on the nano-treated fabrics as their concentration were too small to be detected by the two concerned instruments.

8.4 Characterisation of Nano-materials Extracted from the Nano-treated Fabric

A new trial used for studying the nano-treated cotton fabric was conducted by means of extraction method. The nano-coating was successfully extracted by this method and the extract was examined using ICP-OES and particle size analyser aiming to investigate the metal content and particle size distribution respectively. ICP-OES results demonstrated that titanium, zinc and silver were successfully extracted under the extraction conditions being studied, which confirmed the attachment of these elements onto the two different nano-treated cotton fabrics. The dominant factors and suitable conditions employed for extracting metallic nano-particles from the nano-treated anti-bacterial and UV-protective cotton fabrics were determined by analysing the results obtained from the particle size analyser using the statistical method called full factorial design. The dominant factors of the extraction process were found to be pH and temperature.

8.5 Proposed Systematic Evaluation Procedures for Nano-treated Textile Product

By combining the overall investigation results obtained from the instrumental techniques and extraction method, a series of systematic evaluation procedures proposed for characterising the claimed nano-treated anti-bacterial or UV-protective cotton fabric were successfully developed. Surface morphology and elemental composition were investigated by FE-SEM and XPS respectively to study the change of the characteristics of both the untreated cotton fabric and nano-treated cotton fabric. After instrumental analysis, extraction method was employed to further study the metal content and particle size distribution of particles attached on the nano-treated cotton fabric. Based on the overall results of systematical analysis, fabric can be affirmatively identified to be nano-treated or not in the future.

8.6 Recommendations for Future Work

In order to improve the accuracy and consistency of evaluation procedures, further study and investigation are therefore necessary. The following recommendations are made with reference to the findings obtained from the experimental works.

i) The effect of temperature should be further studied in order to determine the optimum extraction condition. Any temperatures between 21^0C and 95^0C can be selected to extract nano-particles from the nano-treated cotton fabric in order to obtain more information concerning the relationship between the temperature and the percentage of nano-particles present in the extract.

ii) Since numerous types of nano-functional treatments are widely applied to textile products such as water resistance and anti-static, thus it is essential to modify the existing extraction process in order to evaluate different kinds of nano-treated textile products.

iii) Various kinds of finishing treatments are imparted onto the nano-treated textile materials before being launched commercially, for example, dyeing and raising. These treatments may affect the characterisation of the nano-treated fabric. Hence, it is recommended to further investigate the effect of finishing treatments on the proposed systematic evaluation procedures in order to get a clear picture about the properties of the commercial nano-treated textile materials.

iv) As the nano-suspensions were obtained from the commercial market, thus the actual content of the nano-suspensions is unknown. This leads to the difficulty of fully understanding how the change of extraction parameters affects the extraction process. Hence, it is recommended to use more advanced analytical instruments to analyse the content of nano-suspensions.

v) The proposed systematic evaluation procedure is only suitable for characterising the nano-treated anti-bacterial or UV-protective cotton fabric which is fabricated by padding method. For characterisating different nano-treated fabrics fabricated by other methods, the existing extraction process has to be further studied and modified.

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