CHAPTER 2

LITERATURE REVIEW

2.1 INTRODUCTION

In this chapter, the published literature on functional finishing of textiles, methods of functionalization, the concept and applications of nanotechnology in textiles, the concept and application of using metals and metal oxide nano-particles for functional finishing, the mechanism of photocatalytic oxidation, the methods of syntheses of TiO$_2$ and ZnO nano-particles and the desirable functions that can be imparted to the textiles by the nano-particles treatment are discussed.

The word textile finishing in its broad sense defines a series of processing operations applied to grey fabrics to enhance their appearance and hand properties and possible applications. In this thesis, the term finishing is used in the narrow definition to include all those processes that usually follow coloration and add useful qualities to the fabric, ranging from interesting appearance and fashion aspects to high performance properties for personal and industrial needs (Marsh 1947).

Though the terms finishing and functional finishing are similar and both play a fundamental role for the commercial excellence of textiles, there is a significant difference in the interpretation. The term finishing is more generic in nature whereas the term functional finishing is very specific to the special and specific performance enhancement. Depending upon the types of
textile substrate to be treated (woven, knitwear or non-wovens staple, yarn or fabric), functional finishing processes are carried out using different means. A review paper on functional finishing of textiles by the author of the thesis (Kathirvelu et al 2008) gives the details of functional finishing of textiles using traditional chemicals.

Usually several types of finishes are combined for economical reasons mostly in one bath (only one application and drying process). This is often the hardest challenge of chemical finishing.

- Some effects are similar or assist each other, for example silicone elastomers cause water repellency, softeners bring about antistatic effects and antistatic finishes can be softening.

- Some effects are obviously contradictory, for example hydrophobic finishes and hydrophilic antistatic finishes, or stiffening and elastomeric finishes, or stiffening and softening finishes.

The chemical structure of natural, artificial or synthetic fibres determines most of the properties that are naturally present in finished products. Some fibres (such as linen, hemp, silk, nylon, polyester) are stronger than others (wool, viscose, acrylic) according to more or less controlled distribution of macromolecules in the polymer mass, structure stiffness and any possible molecular interactions between the chains; other fibres tend to distort when stretched (cotton, viscose), and others recover their original shape after being distorted (wool); some others easily burn (cellulose), burn slowly and self-extinguish (wool, silk) or burn and melt (synthetic fibres). The above mentioned characteristics and many others make up the positive and negative properties of a textile material, which must be accurately considered in view of their final applications.
One of the great attributes of cotton is its ability to be imparted a wide variety of functional properties. Cotton and other natural cellulosic fibres are chemically reactive as are natural protein fibres such as wool. Most synthetic fibres are not very reactive, and some are considered inert. The reactive groups of the cotton molecule permit permanent attachment of these functional compounds. The surface of the fibre is polar and hydrophilic, which makes the fabric comfortable during wear and useful for absorbent applications such as towels. Furthermore, the fibre has a large surface area and is porous somewhat like a sponge (Miles 2003).

2.2 FUNCTIONALIZATION OF TEXTILES

Functionalization of textile materials can be defined as a process which imparts the desired functional properties to textile and clothing materials. In textile science, the approach to developing functional materials can be divided into three broad areas: 1. Use of novel fibres/yarns 2. Use of novel textile construction/production technology 3. Novel textile finishings. In each case, the objective is to develop specific properties which will enable these materials to perform a particular task in the final product in a better way. Functional textiles are high-tech products with additional novel functions. Many of the functional textiles in use are aimed to improve wear comfort, safety and health protection (Parachuru and Sawhney 2005).

The functional properties can be achieved in textiles either by: a. the use of specialized fibres which have the required characteristics for performing the special functions (characteristics of the polymer or additives before fibre spinning); yarn or fabric engineering (for instance, with different fibres or different layers); and b. textile finishing (Almedia 2005). The Figure 2.1 is a schematic diagram on functional textiles which is self explanatory.
2.3 FUNCTIONALISATION OF TEXTILES BY FINISHING

Many kinds of functional finishes are increasingly developed by the textile industries. The aim of these finishes is to produce textiles which are comfortable for the consumer. Such functional finishes are broadly divided into two categories, which are “Physically based technology” and “Chemically based technology”. Recently, the numbers of developments in physically based technology, which can harmonize the environment and production, have increased because the regulations on chemical substances have become stricter. At present, although chemically based technology is widely in use, its combination with physically based technology is steadily increasing.

The chemically based technology can be made by all the traditional finishing technologies, such as: exhaustion, padding, low add-on processes, foam application, printing, coating, etc. The innovative effects are assured by the application of specialty chemicals which can be applied by means of new alternatives, such as micro encapsulation, by using cyclodextrines. These alternatives are now very important for the application of several functional finishes, especially when a long term effect is intended, with controlled
release of chemicals. The emergence of the so-called “nanotechnologies” opens a wide range of new possibilities. In many cases, the functional properties involve a surface modification, which can be obtained by means of chemical modification, by the application of a surface layer or by more environmental friendly treatments such as the use of enzymes or physical modification (based namely on plasma technology).

The increasing demands for improved or even new properties of textiles, especially technical textiles as high performance products, can be observed worldwide. A broad overview of Applications of Nanotechnology in textile fabrics is given in Figure 2.2 (Singh and Parachuru 2006).

2.4 INTRODUCTION TO NANOTECHNOLOGY

Nanotechnology is increasingly attracting worldwide attention because it is widely perceived as offering huge potential in a wide range of end uses (nano means dwarf). The unique and new properties of nanomaterials have attracted not only scientists and researchers but also businesses, due to their huge economical potential. Nanotechnology is an emerging, highly interdisciplinary field, premised on the ability to manipulate structural materials on the level of individual atoms and molecules.

Nanotechnology is an umbrella term covering a wide range of technologies concerned with structures and processes on the nanometre scale (nanometre = nm, nm is one-billionth of a meter \(10^{-9}\)m). Nanotechnology can be considered as a ‘key’ technology and has revitalised material science and led to the development and evolution of a range of new improved materials through nano-structuring. Nanotechnology creates structures that have excellent properties by controlling atoms and molecules, functional materials, devices and systems on the nanometre scale by involving precise placement of individual atoms (Russel 2002).
Figure 2.2 A broad overview of applications of Nanotechnology in textile fabrics
Many nanotechnology based innovations have appeared in the literature, offering great promise for the future (Scientific American 2002; Gross 1999), although the meaning and the structure of the nanotechnology is very complex, it has already taken a great part in our daily life.

2.4.1 Size matters

Size effects constitute a fascinating aspect of nano-materials. In a pragmatic approach, one can use the following definition for nanotechnology: a) it deals with structures whose area is smaller than 100 nm at least in one dimension, b) it exploits characteristics and phenomena which occur in the transitional zone between the atomic and meso-scopic level and c) the technology describes deliberate manufacture and/or manipulation of individual nanostructures. Nanotechnology deals with the effect that properties of materials can change drastically when the particle size falls below 100 nm approximately. It may lead to novel and significantly improved physical, chemical, and biological properties, phenomena, and processes because of the particle size. Materials in the nanometre size range exhibit fundamentally new behaviour, as their size falls below the critical length associated with any given property. Intervention in the properties of materials at the nano-scale permits the creation of materials and devices with performance characteristics and functionality that are previously thought to be not possible. It marks a threshold where quantum physical effects increasingly play an important role and marks the interdisciplinary interaction of sciences (mostly chemistry and physics); therefore nanotechnology is called a convergent technology.

Nanoparticles or quantum dots are particles whose largest dimension is less than or equal to100nm. Nanoparticles may either be natural or incidental or engineered. They may also either be amorphous or crystalline or polymeric or composites. Their chemistries may be predominantly non-
metal (e.g., carbon), metallic (e.g., Au, Ag), semiconductor (e.g., CdSe), or a combination. Their shapes include spheres, tubes, rods, horns, and platelets. Their physical properties are related to their size and chemical composition. Their surface chemistries, including surface defects and impurities, contribute to their reactivity. Decreasing the size of particles to nano-scale dimensions fundamentally changes the properties of the material. For example, 50 kg of 1mm-size SiO$_2$ particles, with a surface of 120 m$^2$, when decreased to 1 nm would have a surface area of 120.000.000 m$^2$. In addition, as the particle size decreases the number of molecules in the surface relative to the bulk increases, giving new and unexpected properties. This has been illustrated schematically in Figure 2.3 (Parys 2006). There are two fundamental strategies for arriving at the nano-dimensions (Foster 2005). The underlying efforts responsible for nanotechnology-based advances can be largely divided into two seemingly divergent approaches: precision engineering (top-down) and structure-induced self-assembly (bottom-up).

2.4.2 The “top-down” approach

Starting from micro technology structures, the components are gradually miniaturised (primarily featured in physics and physical technology). Enlarging the surface and separation of the particles means an increase in free energy making the system less stable. Also, some work is lost due to friction effects.

2.4.3 The “bottom-up” approach

Increasingly complex structures are specifically assembled form atomic or molecular components. This approach is popular in chemistry and biology, where dealing with objects of the nanometer scale is a familiar practice. Colloidal particles can be produced by sol-gel technique. Stable
colloids guarantee that the particle size will be of nano size and no work is necessary to enlarge surface.

Figure 2.3  A schematic representation of particle size and surface area at nanoscale

2.4.4  Comparison of “top down” and “bottom up” approaches

In the “top down” approach of producing the nanoparticles, bigger particles are broken down into smaller particles. This method of nanoparticle production has the following disadvantages:

- Less precise
- Produces lots of waste and pollution
- Consumes lots of energy
On the other hand, the “bottom up” approach uses particles of sub-nano level to make the nanoparticles and hence it is a constructive process. Nanoparticles can be built precisely as tiny building blocks. Hence, it possesses the following advantages:

- Absolute precision (down to one single atom)
- Complete control of the process and hence no wastage
- Less energy is needed
- More eco-friendly

2.4.5 Relevance to textiles

As in the other fields, nanotechnology has a great role in textile industry (Kathiervelu 2003). Perhaps surprisingly the earliest commercialized applications of nanotechnology are seen in lifestyle applications. Textile and cosmetics are among the first products to use nanomaterials. Textile fabrics are one of the best platforms for deploying nanotechnology. Fibres make for optimal substrates where a large surface area is present for a given weight or volume of fabric. The synergy between nanotechnology and the textile industry judiciously exploits this property of large interfacial area and the drastic change of energetics experienced by macromolecules or supramolecular clusters in the vicinity of a fibre when going from a wet state to a dry state. Nanotechnology has real commercial potential for the textile industry (Sparkle News 2006). This 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 their functions after laundering or wearing. In contrast, 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 and leading to an increase in durability of the function (Wong et al 2006). In addition, a coating of nanoparticles on fabrics is less likely to affect physical and mechanical
properties such as hand, strength, air permeability and wetting, considerably (Carfagna 2005; Cientifica 2006; Xin 2006). The purposes of using nanotechnology in textile and apparel applications are low chemical usage; low energy costs. Different applications for nanotechnology based textiles are illustrated in Figure 2.4 (Parys 2006).

Therefore, the interest in using nanotechnologies in the textile industry is increasing. Current applications of the nanotechnology in the textile industry that have taken place in fibres, yarns, fabrics, nonwovens, finishing like dyeing and coating; electronic textiles, fibre modifications and those value added applications which are considered to be very important are discussed here (Ikilem 2006).

2.4.6  Applications in fibres, fabrics and dyeing

One of the applications of nanotechnology in textile industry is in polymeric materials for producing conventional fibres such as PES (Polyester), PA (Polyamide) and PP (Polypropylene) in nano scale. By nanotechnology, the electrical, thermal, mechanical and chemical properties of the fibres can be improved to enlarge the application fields of the fibres in the final use such as “breathable” laminates and super absorbency of fibres provided by the process of creating open-pore-structure in a variety of polymers. In medical textiles, high specific surface areas are required mostly. Polymeric nano-fibres are the right materials with nano-scaled diameters and long lengths.

For example, decreasing the fibre diameter reduces the contact angle between fibres; so that the final product made using these fibres have an excellent wetting behaviour (Huang 2005). In addition to these, the light weight fibres which are produced by nanotechnology gain phenomenal strength. Nano-fibres have multifunctional properties like high surface area, a
small fibre diameter, good filtration properties, thin layers and high permeability (Casey and Turney 2006; Nyati 2005).

Figure 2.4 General overview of nanotechnology in textile applications

It is proven that the addition of carbon nano-tubes to a common commercial polymer, polypropylene, leads to eliminate “die swell” effect, causes in swelling of polymers when passing through the capillary tube in electro-spinning process. This improvement enhances the strength of the fibres against the high voltage between capillary tube and the collector. So,
this composite polymer can be spun at high speed in production. Polyester is a textile fibre with very poor water absorption characteristic. Its hygroscopic properties have been increased by a factor of 30 by coating it with a special film of tens of nano-meter thick (50-nano-metre film - made up of 20 layers - on outside of fibre). Quup is a nylon filament yarn with the double moisture uptake of conventional yarn (Cookson and Wang 2007). In medical textiles, devices such as woven and knitted vascular grafts are used for replacing human arteries in by-pass surgery and in “scaffolding”-machine embroidered implants- for connecting nerves during reconstructive shoulder surgery. Dressings for wound healings are the most necessary health-care products for chronic wounds, warfare conflicts, traffic accidents etc. It facilitates the wound healing apart from covering the wounds from environmental infections. These new developments are the results of innovative use nanotechnology.

Nanotechnology has an important application area in dyeing process. Polypropylene is a wax like textile fibre and is the most difficult fibre to dye as it has no sites for the dye fixation. Nano-clays are used to create dye sites into PP fibres with modified quaternary ammonium salt. This lowers the cost of dyeing in apparel fibres. The nano-clay, montmorillonite, and some modified nano-clays can be used as sorbent for non-ionic, anionic, cationic dyes because nano-particles have small sizes that provide large surface area. To improve the dye sorption of polypropylene, the sorbent can be added physically into the polymer matrix for making a composite. Because of good dye sorption ability of the sorbent made from nano-clay, textiles made from that composite will have good dye ability, good colour fastness, less cost in dyeing and less problems in waste water treatment (Sparkle News 2006). Also, they have an added functionality to improve the properties of the textile material such as strength, modulus, UV absorbance and fire resistance. In a melting or dissolving process by using heat, organic sorbent and/or
mechanical blending nano-clays can be added to the polypropylene matrix. This gives the polymer structure the thermal and chemical stability and good mechanical properties (Fan et al 2002; Yang et al 2005).

### 2.4.7 Applications in finishing process

The most interesting application area of nanotechnology in textile industry is in the finishing process of textiles. The first work on nanotechnology in textiles was undertaken by Nano-Tex, a subsidiary of the US-based Burlington Industries (Russell 2002). Later, more and more textile companies began to invest in the development of nanotechnologies. Coating is a common technique used to apply nano-particles onto textiles. The coating compositions that can modify the surface of textiles are usually composed of nanoparticles, a surfactant, ingredients and a carrier medium (Cramer 2003). Several methods can apply coating onto fabrics, including spraying, transfer printing, washing, rinsing and padding. Of these methods, padding is the most commonly used (Anonymous 2003; Xing 2004; Yen et al 2003). The nanoparticles are attached to the fabrics with the use of a padder adjusted to suitable pressure and speed, followed by drying and curing. The properties imparted to textiles using nanotechnology include water repellence, soil resistance, wrinkle resistance, anti-bacteria, anti-static and UV-protection, flame retardation, improvement of dyeability and so on. Treating textiles with nanotechnology materials is a method to improve the properties of the textile, making it longer durable, have nicer colours etc. Nanotechnology can also be used to add new functionalities like energy storage and communications. The Figure 2.5 shows some of the opportunities offered by nanotechnology to improve the functionality of textiles. (Van Heeren 2005).

Focus has also been made on the finishes developed by Nano-Tex® and the application of TiO₂ nano-particles for textile finishing (Shulte 2005).
Nano-care® fabric protection imparts a revolutionary, carefree quality to wrinkle resistant fabric that minimizes stains, offers superior liquid repellence and maintains wrinkle resistance. Nano-dry® indicates enhanced fabrics able to move perspiration away from the body while drying quickly. Nano-fresh® is designed to capture body odour and finally Nano-pel® is designated for fabrics that breathes, yet remaining liquid and stain-repellent (Abbas 2007; Parsarpatet and Sonthisombat 2008).

2.4.8 The concept of Nano-Whisker Architecture: Nano-Care™ and Nano-Pel™

Nano-Pel is a water- and oil-repellent treatment that can be applied to all major apparel fabrics, including cotton, wool, polyester, nylon, rayon and blends. Nano-Care is a product for 100% cotton that imparts wrinkle resistance in addition to water and oil repellency. Since their introduction, Nano-Pel and Nano-Care have raised the bar on water- and stain-repellent performance (Lennox Kerr 2003).
Generally, copolymers exhibiting water and oil repellence are comprised of a (meth)acrylate monomer containing a per-fluoroalkyl group capable of directly giving water and oil repellence, a fluorine-free monomer capable of improving adhesiveness to fibres, and a monomer capable of ensuring durability through self cross-linking or reaction with reactive groups on the surface of the materials to be treated (Sahin 1996). However, when the fibrous substrate is treated with these copolymers, formaldehyde is produced, which is highly undesirable from an environmental and safety standpoint (Sello and Stevens 1984).

The architecture of the nano-whiskers is depicted in Figure 2.6, where oligomeric or polymeric side branches (brushes) are attached to a flexible spine. The brushes project outward from the surface, essentially forming a monomolecular layer to protect against future water or oil intrusion (Jain 2004).

Figure 2.6  Schematic representation of the transition of Nano-Whisker Architecture (Nano-Pel and Nano-Care Finishes)

Nano-Tex has patented a formulation containing a novel water- and oil-repellent agent capable of binding to fibrous substrates and other materials without the production of formaldehyde. This formulation can impart
formaldehyde-free wrinkle resistance and water and oil repellence when combined with a formaldehyde free resin such as dimethylurea glyoxal (DMUG) or butane tetra carboxylic acid (BTCA) (Banks et al 1994).

2.4.9 The concept of Nano-Dry™

A treatment that builds a three-dimensional molecular network surrounding a fibre (i.e. the Nano-Net architecture, Figure 2.7) is called Nano-Dry®. Nylon and polyester also often exhibit static cling and stain retention due to their hydrophobic nature. It is therefore desirable to find a way of imparting durable hydrophilic properties to nylon, polyester and other synthetic materials. The treatment durably attaches a hydrophilic network to a hydrophobic substrate without altering the other properties of the material, such as strength, colour fastness and hand (tactile feel).

Figure 2.7 The schematic representation of the 3-D molecular nano-net of Nano-Dry

The traditional treatments to impart hydrophilic properties for synthetic fabrics rely on film formation on the surface of the fabric and self-cross-linking properties of the chemical to achieve some level of durability to laundering. However, these treatments suffer from the conflicting refinements
of moisture absorbance and adhesion to a synthetic and inherently hydrophobic substrate. The Nano-Dry treatment achieves its durability not by film formation, but by the combination of covalent attachment to the fibre surface and the use of nano-molecules. A typical solids loading for Nano-Dry treatment onto the fabric surface is around 0.1–0.15% by weight of the fabric, compared to 0.8–4.0% by weight of fabric for conventional film-forming hydrophilic treatments (Jain 2004).

2.4.10 The concept of Nano-Touch®

Synthetic fibres will have static build-up problems even at much higher relative humidity (Adanur 1995). Nano-Tex has launched a project to develop fabrics that exhibit the positive qualities of cotton and synthetics but without their negative qualities. The Nano-Touch treatment has been developed to create a permanently attached carbohydrate sheath (carbohydrates have the desired properties of cotton, which is itself considered a carbohydrate) around each synthetic fibre of the web. This treatment endows the treated web with the most desirable characteristics of the synthetic core and most desirable characteristics of the natural, carbohydrate sheath. Figure 2.8 is the schematic diagram of the resulting architecture.

The Nano-Wrap architecture creates a permanent attachment of the carbohydrate sheath (Nano-Touch) around the fibre. Additionally, the hydrophilic nature of the wrap, the increased moisture regain, and the fact that this additional moisture content is localized to the surface of the fibre all cause Nano-Touch treatment to exhibit durable anti-static performance (Jain 2004).
2.5 FUNDAMENTAL CONCEPTS OF PHOTO-CATALYSIS

The word photo-catalysis is a composite word which is composed of two parts, “photo” and “catalysis”. The prefix “photo” means pertaining to light. Catalysis is the process where a substance participates in modifying the rate of a chemical transformation of the reactants without being altered or consumed in the end. This substance is known as the catalyst which increases the rate of a reaction by reducing the activation energy. Generally speaking, photo-catalysis is a reaction which uses light to activate a substance which modifies the rate of a chemical reaction without being involved itself (Fujishima and Honda 1972).

Solids that can promote reactions in the presence of light and are not consumed in the over all reactions referred to as photo-catalyst. Some metal oxide and sulphide semiconductors like zinc oxide (ZnO), Titanium dioxide (TiO2), zinc sulphide (ZnS), tungsten oxide (WO3), strontium titanate (SrTiO3), and hematite (Fe2O3) are proven to be dynamic photo-catalysts (Ullah and Dutta 2006).
2.5.1 Basic principles of heterogeneous photo-catalysis

A photo-catalyst decreases the activation energy of a given reaction. In the result of photo-induced processes, often particles with strong oxidation and reduction ability occur. A heterogeneous photo-catalytic system consists of semiconductor particles (photo-catalyst) which are in close contact with a liquid or gaseous reaction medium. Exposing the catalyst to light excited states are generated which are able to initiate subsequent processes like redox reactions and molecular transformations (Three Bond Co. Ltd. 2004).

Titanium dioxide is one of the basic materials in everyday life. It has been widely used as white pigment in paints, cosmetics and foodstuffs. TiO$_2$ exists in three crystalline modifications: rutile, anatase, and brookite. In 1972, Fujishima and Honda discovered the photo-catalytic splitting of water on TiO$_2$ electrodes (Nature 1972).

Although TiO$_2$ absorbs only approx. 5% of the solar light reaching the surface of the earth, it is the best investigated semiconductor in the field of chemical conversion and storage of solar energy. In recent years semiconductor photo-catalysis using TiO$_2$ has been applied to important problems of environmental interest like detoxification of water and of air. Generally, titanium dioxide is a semi conducting material which can be chemically activated by light (Teichner 2008).

Figure 2.9 shows the schematic diagram of operation of a photo-chemically excited TiO$_2$ particle. When the photo-catalyst titanium dioxide (TiO$_2$) absorbs Ultraviolet (UV) radiation from sunlight or illuminated light source (fluorescent lamps), it will produce pairs of electrons and holes. The electron of the valence band of titanium dioxide becomes excited when illuminated by light. The excess energy of this excited electron promoted the
electron to the conduction band of titanium dioxide therefore creating the negative-electron ($e^-$) and positive-hole ($h^+$) pair. This stage is referred as the semiconductor's 'photo-excitation' state. The energy difference between the valence band and the conduction band is known as the 'Band Gap'. Wavelength of the light necessary for photo-excitation is:

$$1240 \text{ (Planck's constant, h)} / 3.2 \text{ eV (band gap energy)} = 388 \text{ nm} \quad (2.1)$$

![Schematic diagram of operation of a photo-chemically excited TiO$_2$ particle](image)

**Figure 2.9** Schematic diagram of operation of a photo-chemically excited TiO$_2$ particle

The positive-hole of titanium dioxide breaks apart the water molecule to form hydrogen gas and hydroxyl radical. The negative-electron reacts with oxygen molecule to form super oxide anion. This cycle continues when light is available. Figure 2.10 shows the schematic diagrams showing the actions of a photo-catalyst (NanoTiO$_2$ -top) and the resultant benefits (bottom).
The band-edge positions of several semiconductors are presented in Figure 2.11 (Fujishima et al 1999).
The heterogeneous photo-catalytic oxidation with TiO$_2$ meets the following requirements what could make it competitive with respect to other processes oxidizing contaminants:

- A low-cost material is used as photo-catalyst.
- The reaction is quite fast at mild operating conditions (room temperature, atmospheric pressure).
- A wide spectrum of organic contaminants can be converted to water and CO$_2$.
- No chemical reactants must be used and no side reactions are produced. These aspects can be observed schematically in the Figures 2.12.

Figure 2.11 Band-edge energies of typical semiconductors
2.5.2 Applications of nano-TiO$_2$ in textile finishing

The application of nano-particles to textile materials has been the object of several studies aimed at producing finished fabrics with different performances. For example nano-Ag has been used for imparting antibacterial properties (Lee et al 2003) and ZnO nano-particles for antibacterial and UV-blocking properties (Xin et al 2004; Yadav et al 2006). Zinc oxide and titanium dioxide are non-toxic and chemically stable under exposure to both high temperatures and UV. Furthermore, nano-particles have a large surface area to-volume ratio that results in a significant increasing of the effectiveness in blocking UV radiation when compared to bulk materials. In this part, it will be relevant to discuss about Titania and functional mechanisms. TiO$_2$ is one of the most popular and promising materials in photo-catalytic application due to its strong oxidizing power of its holes, high photo-stability and redox selectivity (Colemana et al 2005). TiO$_2$ is commercially available and easy to prepare in the laboratory. Titania (TiO$_2$)
has three main polymorphs viz. anatase, rutile and brookite. Among the three kinds of crystal structure of TiO₂, commercially available anatase TiO₂ fine particles are the most active for photo-catalysis (Three Bond Technical News 2004). Production methods for nanoparticles can be loosely classified into three general categories: wet synthesis, dry synthesis, and milling. In both wet and dry synthesis, nanoparticles are generally produced in a bottom-up way from atomic precursors, whereas in the milling approach, nanoparticles are produced from the top down by mechanically breaking down larger particles. Wet approaches include sol-gel and precipitation methods, whereas dry approaches encompass combustion, furnace, and plasma synthesis of nanoparticles (Diess et al 1996).

In all cases, there are concerns about the narrowness of the size distribution of the nano-particles, and the degree of agglomeration. All processes for making nanoparticles lead to some spread in the particle size. The size distribution can be modified somewhat by adjusting the process parameters, or the size distribution can be tailored by removing the tails of the distribution through additional separation steps. This typically leads to lower process yield. With respect to agglomeration, nanoparticles have a high ratio of surface area to volume, and it is much more energetically favourable for them to reduce their surface area by coalescing together. Thus, materials that melt at high temperatures if they are in bulk form may fuse together at much lower temperatures if they are nanoparticles (Burniston and Bygott 2004).

There are three types of crystal structures in natural titanium oxide: the rutile type, the anatase type, and the brookite type. All three of these types are expressed using the same chemical formula (TiO₂); however, their crystal structures are different (Figure 2.13). Titanium oxide absorbs light having an energy level higher than that of the band gap, and causes electrons to jump to the conduction band to create positive holes in the valence band. Despite the
fact that the band gap value is 3.0 eV for the rutile type and 3.2 eV for the anatase type, they both absorb only ultraviolet rays. However, the rutile type can absorb the rays that are slightly closer to visible light rays (Daoud and Xin 2004).

As the rutile type can absorb light of a wider range, it seems logical to assume that the rutile type is more suitable for use as a photo-catalyst. However, in reality, the anatase type exhibits higher photo-catalytic activity. Due to the difference in the position of the conduction band, the anatase type exhibits higher overall photo-catalytic activity than the rutile type (Bozzi et al 2005).

![Schematic representation of the crystal structures of three polymorphs of TiO₂](image)

Figure 2.13 The schematic representation of the crystal structures of three polymorphs of TiO₂

2.6 TECHNOLOGY OF NANOPARTICLE SYNTHESIS

Novel methods of fabricating patterned nanostructures as well as new device concepts are being constantly discovered. The synthesis of
nanomaterials spans inorganic, organic, and biological systems on manipulation.

Nanostructured materials, particularly nanoparticles, have evolved as a separate class of materials over the past decade. The most remarkable feature has been the way in which completely disparate disciplines have come together with nanomaterials as the theme. The breadth of the field is enormous, ranging from the use of nanoparticles of zinc oxide in hygiene products, such as diapers (Saito 1993), to altering the characteristics of solid rocket propellants by the addition of nanoparticle fillers. The enthusiasm is justified for the most part, as the fundamental materials’ properties appear to be different at the nanoscale. For example, according to Qi and Wang (2003), when the ratio of the size of the atom to that of the particle becomes less than 0.01 to 0.1, the cohesive energy begins to decrease, which in turn reduces the melting point. In a related report, it has been shown that the surface energy of free nanoparticles is higher than that of embedded nanoparticles, and is substantially higher compared to that of the bulk. There is also ample evidence that nanoparticles display characteristics that are distinctly different from their microcrystalline counterparts. For example, Reddy et al (2004) have shown that nanoparticles of anatase TiO$_2$, synthesized by a precipitation technique, show direct band gap semiconductor behaviour, whereas microcrystalline TiO$_2$ is an indirect band gap material.

All particle synthesis techniques fall into one of the three categories: vapour-phase, solution precipitation, and solid-state processes. There are a handful of processes that combine aspects of one or more of these broad categories of processes. Although vapour-phase processes have been in vogue during the early days of nanoparticles development, the last of the three processes mentioned above is the most widely used in the industry for production of micron-sized particles, predominantly due to cost
considerations (Inaba et al 2006). One of the most established powder producers, Ferro Corporation, uses the solid-state synthesis method almost exclusively; hundreds of tons of lithium cobalt oxide, which is the commonly used cathode material in lithium-ion batteries, is produced using solid-state synthesis. In this literature survey, we will focus on the syntheses of TiO$_2$ and ZnO nanoparticles.

2.7 A REVIEW OF SYNTHESIS OF TiO$_2$ NANOPARTICLES

2.7.1 Introduction

Nanocrystalline materials are currently receiving much attention by virtue of their special chemical, physical and mechanical properties. For the purpose of the functionalization of the materials, their chemical and physical properties should be fully controlled. Titanium oxide (TiO$_2$) nanoparticles are important because of their outstanding chemical and physical properties, which are useful in many applications such as photovoltaic cell gas sensors catalysts, photo-catalysts and pigments etc. The titania particles must fulfil a wide range of requirements such as particle size, size distribution, morphology, crystallinity and phase, etc. (Lin et al 2005) so as to become useful in applications. The synthesis of nano-size TiO$_2$ particles with well-defined physical and chemical properties is a crucial step in nano technology area. A variety of methods have been developed for the synthesis of TiO$_2$ nanoparticles, for example, sol-gel process (Zhang et al 2004), hydrothermal methods (Wu et al 2006) solvothermal methods (Kim and kim 2003) and emulsion precipitation.

Many novel methodologies for synthesizing nanosized TiO$_2$ have been investigated, such as oxidation of titanium tetrachloride in a modified diffusion flame reactor, crystallization in reverse micelles or in supercritical CO$_2$, photo-assisted sol-gel method (Liu et al 2003) and polymer templating
method. The different synthetic processes usually result in the as-prepared nanosized TiO$_2$ with distinct physiochemical properties. Some of these novel methods using wet-chemistry have also been developed for the preparation of powders with spherical shape and uniform size. Sol-gel process, emulsion and pyrolysis have been used to prepare mono-dispersed spherical Titania powders (Arami et al. 2007). Although TiO$_2$ nano-particles have been prepared successfully via these methods, most of the nano-particles synthesized via traditional routes are poorly crystalline and/or exhibit a broad size distribution. For instance, sol-gel derived TiO$_2$ nano-particles are amorphous and further calcinations are generally required to induce crystallization. However, the heat treatment frequently leads to particle agglomeration and size change, which is harmful to their practical applications. Though preparation of nanosized TiO$_2$ is mainly by the sol-gel method, it has a main disadvantage that costly organic solvents are required. Several aqueous-based methods using metal salts as a precursor material, such as forced hydrolysis method and homogeneous precipitation method, have several shortcomings: the concentration of reacting species is too low and the reaction time is very long. For synthesis of anatase TiO$_2$ nanocrystalline, much attention has been paid to hydrothermal methods using amorphous TiO$_2$, TiCl$_4$ (Cheng et al. 1995), or TiOCl$_2$ aqueous solution (Deshpande et al. 2007), and sol-gel methods using titanium alkoxides (Hong et al. 2002; Lee et al. 2006; Ryu et al. 2006) TiO$_2$ can be also obtained by hydrolysis of titanium compounds, such as titanium tetrachloride or titanium alkoxides, in solution.

In this review paper, the recent developments in the synthesis of nano-size TiO$_2$ particles with well-defined physical and chemical properties will be discussed. In addition to that, the methods of syntheses of nano-size TiO$_2$ particles of rutile, anatase and brookite phases have also been discussed. As for anatase TiO$_2$ nanocrystalline, much attention has been paid to hydrothermal methods using amorphous TiO$_2$, TiCl$_4$, or TiOCl$_2$ aqueous solution (Fang and Chen 2003), and sol–gel methods using titanium
alkoxides, TiO$_2$ can be also obtained by hydrolysis of titanium compounds, such as titanium tetrachloride or titanium alkoxides in solution.

The different synthetic processes usually result in the as prepared nanosized TiO$_2$ with distinct physiochemical properties. Organic modifiers, such as hydroxyl group-containing, carboxylate group-containing, and amine group-containing organics are widely used in synthesis of nanosized TiO$_2$ to regulate their final morphology and hence their properties. The basis of such methods is the employment of organics with different types of functional groups to produce a desired product with the required shapes and interface structures of organic modifiers with crystal surface. A variety of methodologies for synthesizing nanosized TiO$_2$ have been investigated, such as oxidation of titanium tetrachloride in a modified diffusion flame reactor, crystallization in reverse micelles or in supercritical CO$_2$, photo-assisted sol-gel method polymer templating method, and hydrothermal method. Titanium iso-propoxide, titanium tetrachloride, titanium (IV) sulphate, and amorphous titanium dioxide are commonly used as starting materials in the above-mentioned synthetic processes. The different synthetic processes usually result in the as-prepared nanosized TiO$_2$ with distinct physiochemical properties.

The titania particles must fulfil a wide range of requirements such as particle size, size distribution, morphology, crystallinity and phase, etc. so as to become useful in applications. The synthesis of nano-size TiO$_2$ particles with well-defined physical and chemical properties is a crucial step in nano technology area (Tang et al 2006D). However, the next most important aspect is how to arrange them into well-defined assemblies/structures or porous aggregates possessing unique properties like pore size and its distribution, thermal stability of structures and their reproducibility, etc. In self-assembly processes, interactions between the primary building blocks are controlled in such a way that at ambient conditions, nanostructures with useful properties
are formed (Yang et al 2003). The additional advantage is that these structures have novel and unique properties that are not found in nano sized TiO₂ particles alone. A large number of reports are available on the synthesis of nano-particles of TiO₂-based materials (Sumio 2005).

2.7.2 Various Methods Syntheses of Nanoparticles of TiO₂

2.7.2.1 Sol-gel method

Sol-gel is one of the most successful techniques for preparing nanosized metallic oxide materials with high photo-catalytic activities. By tailoring the chemical structure of primary precursor and carefully controlling the processing variables, nanocrystalline products with very high level of chemical purity can be achieved. In sol–gel processes, TiO₂ is usually prepared by the reactions of hydrolysis and polycondensation of titanium alkoxides, Ti(OR)n to form oxopolymers, which are then transformed into an oxide network (Bessekhouad et al 2003).

It has been established that the photo-catalytic activity of TiO₂ strongly depends on its crystal structure. For instance, anatase-phase TiO₂ crystallites are generally found to be more active than rutile. Rutile phase has also been shown to be more active than anatase in few examples, such as photodecomposition of H₂S and photo-oxidation of H₂O with Fe₃⁺. Recently, it was found that anatase/rutile mixture (7/3) made the best photo-catalyst for the oxidation of organic materials in the wastewater treatment. Thus, the microstructure of the TiO₂ plays crucial role in determining its photo-catalytic activity (Ristic et al 2005).

A solution of titanium (IV) n-butoxide (Ti (O-Bu)₄,) in isopropyl alcohol (i-PrOH), was used as molecular precursor of TiO₂. In order to control the reaction kinetics, acetylacetone (acac) was used as a chemical additive to moderate the reaction rate. Water was deionized. The water used for
hydrolysis in solution with i-PrOH was added gradually under mechanical stirring. The reaction condition was carefully controlled to obtain white precipitate of titanium oxyhydroxide, which was then washed with water for several times. The molar ratio of these reactants was: Ti (OBu)$_4$: H$_2$O:i-PropOH:acac = 1:100:2:0.01. The final solution was peptized by adding HNO$_3$, followed by refluxing at 85 °C for 8 h to give a sol of pH ~2.5. During optimization of processing conditions in the early stage of this work, the important role of the pH value in the control of the size of the TiO$_2$ particles was revealed. A portion of as-prepared titania hydrosol was retained for further analysis and comparison. The other portion was gelled by drying at 100°C for 3 hours, then calcinated in vacuum oven at various temperatures (400–700°C) to give TiO$_2$ powder (Dhage et al 2004).

2.7.2.2 Flame Spray Pyrolysis

Flame-based methods are of potential commercial importance because of their high production rates and relatively low cost. Furthermore, they can be operated as continuous processes. Hence this technique has been used a lot to produce fine, pure and single-phase particles in the as-prepared state. Chang et al (2007) described a method to synthesise TiO$_2$ nanoparticles having different phase compositions and particle sizes were prepared by flame spray pyrolysis. Flame spray pyrolysis (FSP), a flame assisted liquid droplet to-particle conversion process, is an attractive method to obtain multicomponent nanoparticles. The precursor solution for the synthesis of TiO$_2$ nanoparticles was prepared by dissolving titanium tetraisopropoxide (TTIP).

The particles prepared by FSP exhibit high purity, controlled stoichiometry and clear crystallinity because the flame temperature can be maintained high enough to complete thermal decomposition through intense oxidation chemistries. Figure 2.14 shows a schematic diagram of the
experimental apparatus to synthesize TiO$_2$ nanoparticles. It consists of an ultrasonic atomizer, a diffusion flame burner, and a thermophoretic sampler.

The ultrasonic atomizer was operated at 1.7MHz to generate liquid droplets of precursor solution. The generated droplets were then carried by argon gas into the diffusion flame burner, in which the evaporation of solvent, the precipitation of solute, decomposition and oxidation occurred. Hydrogen gas was used as a fuel while oxygen and air were used as oxidants for the diffusion flame. The burner (36mm in outside diameter and 300mm in length) consisted of five concentric stainless tubes. Droplets were supplied to the high temperature flame zone through the central tube with an argon gas flow rate of 2 l/min.

In order to keep the straight pathway of the precursor droplets in the flame region, argon gas was flowed at 1 l/min through the second tube from central one. Hydrogen, oxygen, and air passed through the outer tubes with flow rate of 5, 6, and 15 l/min, respectively. A stainless tube of 50mm in diameter and 100mm in length was also installed at the burner exit to facilitate stable burning. Particles synthesized in the flame were thermo-phoretically collected on the surface of a cold glass tube (100mm in diameter and 300mm in length) which was installed at the location of 150mm above the burner exit and maintained at 12°C by flowing cooling water through the inside of the glass tube.
The average particle size was strongly dependent on the precursor concentration and flame temperature. From their results, they could suggest a mechanism for the particle formation and growth in FSP as shown in Figure 2.15.

2.7.2.3 One-component solution system

A novel one-pot synthesis route was proposed to prepare nanometric anatase TiO$_2$ using trichloroethylene as reaction medium, which may have a great advantage over multicomponent solution systems when TiO$_2$ is used as a reinforcing filler for polymers dissolved in trichloroethylene by Trunga and Ha (2004). Two millilitres of titanium isopropoxide was mixed with 60 ml of trichloroethylene with traces of water, under rigorous stirring, at
room temperature. Then the hydrolysis and condensation reactions occurred. The as-prepared powders were washed by ethanol and acetone for several times and dried at 100ºC in vacuum oven for 3 days, then heated at 400ºC for 10 h in air.

Figure 2.15 Suggested mechanisms for the generation and growth of TiO₂ nano-particles in the FSP

2.7.2.4 An improved continuous process

In general, the synthesis of particles has been developed by a batch or semi-batch process. In addition, Kim and Kim (2003) have already prepared TiO₂ nano-particles by hydrolysis of TEOT (tetraethylorthotitanate) in a semi-batch/batch two stages mixed process. However, on an industrial scale, the batch and semi-batch process are not suitable; a continuous process is required for mass production. Kim and Kim (2003) attempted an improved continuous process in which a small reactor for controlling the nucleation rate is connected in series with an aging tube for controlling the growth of
particles. The hydrolysis rate is controlled by the vaporization of H\textsubscript{2}O and the feed rate of TEOT (tetraethylorthotitanate) solution, respectively. In addition, by controlling the parameters affecting to the particle size in the aging tube, nano-particles can be obtained.

A schematic diagram of the continuous synthesis reactor system designed for this work is shown in Figure 2.16. The apparatus consists of the following sections; (1) small reactor (100 ml) for two feed reagents (vaporized water and TEOT) with an ethanol solvent, (2) a syringe pump (Kd scientific, Model 100) to supply the vaporized H\textsubscript{2}O/ Et(OH) solutions with a constant feed rate (0.040–0.306 ml/min) and a micro feed pump to supply the TEOT/ Et(OH) solutions with a constant feed rate (0.66–1.10 ml/min), (3) a heating tape for vaporizing the H\textsubscript{2}O, and (4) a long silicon tube (diameter: 3.0 mm) for aging of the particles. The aging tube is placed in a water bath at a constant temperature and can be changed for desired length and diameter. At the entrance of the aging tube, there is a valve to control the flow rate of solutions after mixing of TEOT and vaporized H\textsubscript{2}O. The two feeds are continuously supplied to the small reactor. Primary nuclei of titanium dioxide are generated by the polymerization of the hydrolysis product while passing through the small reactor. A part of them is grown to fine particles while passing through the aging tube (Hong et al 2003).

In this continuous reactor system, two methods for preparing nano-particles with narrow size distribution were used. One is the vaporized H\textsubscript{2}O/Et (OH) solution by which slower hydrolysis rate of TEOT is induced, resulting in prevention of agglomeration of particles. The other is intermittent flow in the aging tube described as shown in Figure 2.16. The possibility of an increase in particle size and agglomeration can be minimized by using this intermittent flow. The ways for changing the flow type in the aging tube are N\textsubscript{2} gas injection and valve handling. Firstly, at the entrance of the aging tube,
there is another inlet to feed the N₂ gas. So, the feed liquids and the injected N₂ gas form an intermittent flow in the aging tube. Secondly, the flow type of solution in the aging tube can be controlled by adjusting the valve placed in the middle of the small reactor and the entrance of the aging tube. By using these two methods, the continuous flow in the aging tube can be separated into small portions.

Figure 2.16 A schematic diagram of the continuous synthesis reactor system

Titanium dioxide (TiO₂) is a unique material that exhibits semi-conducting, piezoelectric, and pyroelectric multiple properties. Nanotechnology research into functional oxide-based, one-dimensional nanostructures has rapidly expanded because of their unique and novel applications in various fields. The various methods developed and tried by researchers have been reviewed. It can be seen that each of these methods has its own advantages and limitations. It can be concluded that the choice of
method and precursors will entirely depend on the end use requirements of the synthesised nano-particles. In future, the same could be fine tuned to improve the specific function of the nano-particles for which they are being developed (Bessekhouad et al 2003).

2.8 REVIEW OF DIFFERENT METHODS OF SYNTHESSES OF ZnO NANOPARTICLES

2.8.1 Introduction

Zinc oxide (ZnO) is an n-type, direct band gap, II-VI semiconductor material. ZnO nanostructures are used in a wide range of applications including field emission displays, nano-photonic devices, piezoelectric transducers, varistors, phosphors, and transparent conducting films. So far, various techniques have been used to synthesize ZnO nanoparticles including chemical or physical methods (Chen et al 2003). The former are thermal hydrolysis technique, hydrothermal processing and sol–gel method. The latter are spray pyrolysis vapour condensation method and thermo chemical decomposition of metal organic precursors. At present, the popular methods that are generally being used to obtain nano-sized ZnO powder are: vapour phase method and sol–gel method. For the vapour phase method, the resulting powders are agglomerates rather than separated powders because the reaction condition during the process is difficult to control. In addition, the method is time and energy-consuming. The sol–gel method produces uniform ZnO powders. However, strict control of the reaction condition is necessary because of its violent hydrolysis reaction in air during the synthesis. In addition, this method has high material costs, and so it is not commercialized but done only in small-scale laboratories. Therefore, the synthesis methods of nanocrystalline ZnO powders need to be improved. Nevertheless, the main problems of most methods have been the poor throughput efficiency and the difficulty in size control (Epibani 2007).
Diversified synthesis methods for ZnO nanoparticles were reported in recent years such as thermal decomposition, sol-gel techniques, supercritical precipitation and colloidal synthesis. The sizes of the zinc oxide particles were within micron or sub-micron scales. Ma et al (2008) reported a method for preparing mono dispersed ZnO nanoparticles by the thermolysis of Zinc Oxide propionate as a single molecular precursor and trioctylphosphine oxide, but high temperature (160°C) must be used to decompose the precursor. However, most methods employed organic solvents or required rigorous reaction conditions and complicated procedures. Therefore, it is important to identify and develop a process in which particles having controlled characteristics including size, morphology, and composition can be produced. The various methods of synthesising nano-size ZnO particles adopted and reported by researchers have been reviewed here below in three broad sub-sections namely, physical, thermal, novel and chemical methods (Guo et 2000).

2.8.2 Levitational gas condensation

The levitational gas condensation (LGC) method is one of the physical approaches to fabricate nano particles reported by Uhm et al (2004). It is a simple one step process for synthesizing nano particles with uniform size distribution. Uhm et al also reported about the Zinc oxide (ZnO) nano particles synthesized by the newly modified LGC and phase evolution (Uhm et al 2007). High-purity ZnO powders were synthesized by the LGC method shown in Figure 2.17. The apparatus consists of high frequency induction generator of 2.5kW, levitation and evaporation chamber, and oxygen concentration control unit. The wire feeding velocity (VZn) and mixed Ar and O$_2$ gas pressure in chamber was 50 mm/min and 18 kPa, respectively.
2.8.3 A novel combustion synthesis method

Hwang et al (2004) reported the Synthesis and characterization of nanocrystalline ZnO powders by a novel combustion synthesis method. The basis of this method is described in detail here: the mixtures composed of metal nitrates added with a suitable fuel powders in an appropriate ratio, are to be ignited and burnt to form ceramic oxides. In a sense, gunpowder can generate a lot of gases when burned. If such application is utilized in the synthesis of ceramic powders, a great deal of gases can be released via the combusting reactants. They are conducive to heat loss through convection, resulting in rapid reduction of product temperature. On a practical level, it is suggested that fine powders could be produced due to the prevention from both the growth of grains and the agglomeration of particles.

This study was done with glycine (NH$_2$CH$_2$COOH) as fuels since its price is inexpensive and its combustion heat (−3.24 kcal/g) is more negative when compared with urea (−2.98 kcal/g) or citric acid (−2.76 kcal/g).
On the other hand, zinc nitrate $[\text{Zn (NO}_3\text{)}_2\cdot6\text{H}_2\text{O}]$ is utilized in the present study because of its dual role of being the zinc source and the oxidant. The description of the experimental procedure is as given below. Analytic grade zinc nitrate and glycine were directly mixed at a desired molar ratio without adding water. From our experiment, it was found that zinc nitrate possesses hygroscopicity. The reactant mixture is easy to absorb moisture from the air and to become a transparent slurry matter.

Therefore, glycine and zinc nitrate can be mixed well by stirring, which makes them almost as homogeneous mixtures. This slurry mixture was heated using a hot-plate at 100°C to dehydrate. The dried mixture (hereafter termed as precursor) possesses the characteristic of combustion, which can be ignited to start combustion reaction by using mini gas burner. This is closely followed by combustion of the precursor with the evolution of a large volume of gases, producing a loose product. When comparing with other methods, it is a simple, quick, and inexpensive method involving a single-step reaction.

2.8.4 DC thermal plasma synthesis

Ko et al (2006) reported a rapid fabrication technique of ZnO nanopowders by dc thermal plasma synthesis with a high production rate. The growth rate and shapes of the ZnO nanopowders could be controlled by changing plasma gas combination and flow rate. In this study, ZnO nanopowders were synthesized in a novel dc plasma reactor operated at 70kW and atmospheric pressure as shown in Figure 2.18.
Figure 2.18 A schematic diagram of the dc plasma reactor

Commercial zinc powders containing impurities of Cr, Fe and Pb less than 50 ppm were used as the raw materials. The Zn powders were fed into plasma flame through nitrogen carrier gas and subsequently underwent vaporization, oxidation and quench processes. The ZnO nanopowders synthesis rate could be 1.2 kg/h (Lin et al 2007).

Zinc oxide (ZnO) is a unique material that exhibits semi conducting, piezoelectric, and pyroelectric multiple properties. Nanotechnology research into functional oxide-based, one-dimensional nanostructures has rapidly expanded because of their unique and novel applications in various fields. The various methods developed and tried by researchers have been compared reviewed for their merits and demerits. It can be seen that each of these methods has its own advantages and limitations. It can be concluded that the choice of method and precursors will entirely depend on the end use requirements of the synthesised nanoparticles (Fei et al 2006).
2.9 SIGNIFICANCE OF NANOPARTICLES

The significance of the nanoparticles can be summed up by their unique effects at quantum and surface levels. The quantum effects of the nanoparticles are due to the restriction of the space available to the electrons at the lower end of nanoscale. Thus, the properties of the nanoparticles are different from the bulk properties especially in electronic, optical and magnetic behaviour. The surface effects of the nanoparticles are due to the higher ratio of surface area to volume. This leads to an enhanced reactivity since the surface properties of the nanoparticles predominate in use. Moreover, nanoparticles are invisible and hence, do not cause any change in the visual appearance (Yamamoto et al 1998).

Thus, nanotechnology provides the ability to work on a nanoscale to create suitable molecular structures that have fundamentally different performance enhancing characteristics. Therefore, working on a nanoscale can allow us to build molecular architectures that can be specifically designed to create the desirable attributes in textiles (Kwon et al 2002).

2.10 CHARACTERIZATION OF NANOPARTICLES

The characterization of the nanoparticles can be done by the following tests (Wang 2000):

I. X-ray Powder Diffraction Method (XRD)
II. Fourier Transform Infrared Spectroscopy (FTIR)
III. Transmission Electron Microscope(TEM)
IV. Scanning Electron Microscopy (SEM)

The first three tests test the nanoparticles directly as particulate matter and the last test is used to characterize the nanoparticles deposited on to the fabric surface by the treatments.
2.10.1 X-ray powder diffraction method (XRD)

XRD is a very important experimental technique that has long been used to address all issues related to the crystal structure of solids, including lattice constants and geometry, identification of unknown materials, orientation of single crystals, preferred orientation of polycrystals, defects, stresses, etc. In XRD, a collimated beam of X-rays, with a wavelength typically ranging from 0.7 to 2 Å, is incident on a specimen and is diffracted by the crystalline phases in the specimen according to Bragg's law:

\[ A = 2d \sin \theta \]  

(2.2)

where \( d \) is the spacing between atomic planes in the crystalline phase and \( A \) is the X-ray wavelength. The intensity of the diffracted X-rays is measured as a function of the diffraction angle 2\( \theta \) and the specimen's orientation. This diffraction pattern is used to identify the specimen's crystalline phases and to measure its structural properties (Jenkins and Snyder 1996). The crystallite domain diameters (D) were obtained from XRD peaks according to the Scherrer’s equation (Jenkins and Snyder 1996):

\[ D = \frac{0.89 \times \lambda}{\Delta W \times \cos \theta} \]  

(2.3)

where \( \lambda \) is the wavelength of the incident X-ray beam, (1.54 Å for the Cu K\( \alpha \)), \( \theta \) is the Bragg’s diffraction angle, \( \Delta W \) is the full width of the X-ray pattern line at half peak-height in radians.

2.10.2 Fourier Transform Infrared Spectroscopy (FTIR)

FTIR is most useful for identifying chemicals that are either organic or inorganic. It can be utilized to quantify some components of an unknown mixture. It can be applied to the analysis of solids, liquids, and
gasses. By interpreting the infrared absorption spectrum, the chemical bonds in a molecule can be determined. FTIR spectra of pure compounds are generally so unique that they are like a molecular "fingerprint". While organic compounds have very rich, detailed spectra, inorganic compounds are usually much simpler (Smith 1996).

### 2.10.3 Transmission Electron Microscope (TEM)

The shape and size of the nanoparticles were obtained through TEM, using a JEM-100C X 11 apparatus operating at 80 kV (Williams and Carter 1996). The samples for TEM measurements were placed on carbon-coated copper grids. The samples for TEM measurements were prepared from much diluted dispersions of the particles in 2-propanol.

### 2.10.4 Characterization by Scanning Electron Microscopy (SEM)

SEM is one of the most widely used techniques used in characterization of nanomaterials and nanostructures. SEM provides the image of the morphology and microstructures of bulk and nanostructured materials and devices. The resolution of the SEM approaches a few nanometers, and the instruments can operate at magnifications that are easily adjusted from - 10 to over 300,000(Howard et al 1980). The nano-finished samples were mounted on a specimen stub with double-sided adhesive tape and coated with gold in a sputter coater and examined with a Scanning Electron Microscope (SEM) Jeol Model JSM-6360.

### 2.11 ENVIRONMENTAL AND HEALTH IMPACTS OF NANOPARTICLES

Nanotechnologies can represent a real innovation for human society and life. Nanomaterials are receiving growing attention as the result of their
increased use in engineering and biomedical industries. Like all technologies, nanoparticle technology will show its good and bad sides. The excessive deployment of nanoparticles has brought about a new environmental concern, that is, nanotoxicity. Despite the huge potential and benefits of nanoparticles and nanotechnology, there is little doubt, despite limited studies to date, that nanoparticles can pose severe threats to environmental health. On a mass basis, nanosized particles are more potent than fine particles in creating environmental and health stress (Sakthivel et al 2006).

It is also important to consider the ability of nanomaterials to affect elements with which they come in contact. TiO₂ and ZnO have long been used as fine powders in many sunscreens because of their ability to absorb or reflect UV radiation and reduce the amount of UV rays penetrating and damaging the deeper dermal layers of the skin. TiO₂ and ZnO have semiconductor and, consequently, photo-catalytic activity that can promote the transformation of organic molecules upon absorption of radiation. For this purpose, TiO₂ nanoparticles have been used to catalyze the photo-degradation of environmental contaminants. A point of consideration may be the toxicity of TiO₂-initiated photo-degradative reactions and any resulting products in the environment. It also remains to be seen whether the UV absorptive qualities of TiO₂ have the potential to disrupt food chains by competing for the UV energy on which marine and freshwater phytoplankton are dependent.

But, in order for nanoparticles to cause side effects or health problems in the human body, they first have to get into it. One large potential gateway, with an area of 2 m², is the skin. However, studies have shown that healthy, unbroken skin presents a reliable barrier. The gastro-intestinal tract (GIT) – the mouth, gullet and digestive apparatus, with its 2000 m², offers a vastly greater area, but the research literature contains no cases of inorganic nanoparticles being absorbed or allowed to pass through the walls of the GIT.
except when they were especially prepared for the purpose. The 140 m² active area of the lungs is currently regarded as the most important gateway for inorganic nanoparticles (Schulenburg 2008). Warheit et al (2007) investigated the lung toxicity of intratracheally instilled nano-TiO₂ particles using the pulmonary bioassay. The pulmonary toxicity of instilled rutile-type ultrafine-TiO₂ particles was compared with α-quartz (positive control), fine-TiO₂ particles (negative control), ultrafine uf-3 TiO₂ particle control, and vehicle controls. The results show that ultrafine-TiO₂ or fine-TiO₂ did not produce any adverse pulmonary effects in any of the end points (i.e., BAL inflammatory indicators, cell proliferation, or histopathology).

Recent European research projects have explored the possible risks of nanoparticles on human health, and their results are controversial. Some assert the safety of nanoparticles through in-vitro tests; others are more doubtful and less optimistic, while a few scientists have already presented clinical evidences of the presence of nanoparticles in pathological tissues (Gatti 2005). The inhalation or ingestion of those mainly metallic particles by humans and animals can bring about pathological effects (Nemmar et al 2002). It is easy to conclude that in more than one instance, the environment is already contaminated by nanosized particles. It may not be possible to eliminate nanoparticles from the environment, but, awareness of their possible adverse effects on human health is important. More research is needed to determine the safest procedures to handle them.

In summary, environmental fate depends on the chemistry of the specific nanomaterial and can be further influenced by environmental conditions such as physical binding or chemical reactivity with other compounds, water solubility, aggregation, and oxidation–reduction reactions. Modifications will greatly influence the behaviour of nanomaterials, including
their interaction with fauna and flora, accumulation in biological systems, and toxicity.

2.12 MULTIFUNCTIONAL TEXTILES

With the developments in science and technology, the living standard of mankind has improved considerably. This has in fact, multiplied the needs of the mankind towards still higher sophistication even in the traditional field of textiles. With faster paced life, customers need textiles with many additional functions which will perform well. The most commonly needed functions are: antibacterial activity, UV protection and stain release.

2.12.1 Antibacterial activity

Microbes-bacteria, virus fungi and yeast- are present almost everywhere. Whereas human beings have an immune system to protect against accumulation of micro-organisms, materials such as textiles can easily be colonised by high numbers of microbes or even decomposed by them. Textiles are carriers of micro-organisms such as pathogenic bacteria, odour-generating bacteria, mould and fungi. These micro-organisms can adhere to textile substrates. Additionally, the environmental conditions on textiles are favourable and thus support the bacteria growth. Indeed, micro-organisms are invisible and extremely adaptable. If the environment is favourable, certain bacteria grow in no time from single germ to millions. Given that sort of environment these germs develop rapidly via cell division they divide and multiply at an alarming rate, following the simple progression of 1, 2, 4, 8, 16, 32, 64 etc. And, because this can happen three times an hour, single bacteria can, theoretically, generate 4,800,000 per day. All of which goes to show why a measure of control is needed, particularly as our houses, working and leisure environments are becoming increasingly hermetic in terms of temperature and airflow. For their growth, especially humidity and as culture medium organic
material is required which they attack and digest with enzymes. Also dirt and sweat offer ideal environmental conditions for micro-organisms. Thriving micro-organisms in warm and damp conditions can cause stains, offensive odours, discolouration, the cross-infection or transmission of diseases etc., first indicators for infection, which can render an article unusable from the hygienic and aesthetic point of view.

At the same time, functional properties like tensile strength and water permeability are lost due to the fact that the fibres are degraded. Prone to hygienic problems caused by micro-organisms are fabrics which are in close contact to the body, like functional work, leisure, sports and military wear, mattresses, carpets, upholstery cushion, but also shower curtains and technical textiles such as outdoor textiles like tarpaulins, curtains, tents, geotextiles. Even chemicals can change properties (e.g. viscosity) due to the attack of micro-organisms. Also during finishing and wet storage, textiles are very sensitive to microbial attack (Ramachandran et al 2004).

The inherent properties of the textile fibres provide room for the growth of micro-organisms. Besides, the structure of the substrates and the chemical processes may induce the growth of microbes. Humid and warm environment still aggravate the problem. Infestation by microbes cause cross infection by pathogens and development odour where the fabric is worn next to skin. In addition to this, the staining and loss of the performance properties of textile substrates are the results of microbial attack. Basically, with a view to protect the wearer and the textile substrate itself antimicrobial finish is applied to textile materials.

It is a well known fact that the growth of bacteria and microorganisms in food or water is prevented when stored in silver vessels due to its antibacterial properties. The anti-bacterial properties of silver are now scientifically recognized. Silver ions have broad spectrum of anti
microbial activities. The method of producing durable silver containing antimicrobial finish is to encapsulate silver compound or nanoparticle with a fibre reactive polymer like poly (styrene co-maleic anhydride).

Neither natural nor synthetic textile fibres are resistant to bacterial or pathogenic fungi. Therefore, antibacterial disinfection and finishing techniques have been developed for many types of textiles including treatment of textile fibres by padding cotton and polyester fabrics with nano-sized silver, titanium dioxide and zinc oxide colloidal solutions (25-50 ppm). Metallic ions and metallic compounds display a certain degree of sterilizing effect.

It was seen that part of the oxygen in the air or water is turned into active oxygen by means of photo-catalysis with the metallic ion, thereby dissolving the organic substance to create a sterilizing effect. With the use of nano-sized particles, the number of particles per unit area is increased, and thus anti-bacterial effects can be maximized (Duran et al 2007).

With the general trend towards increasingly stringent hygiene standards, the consumers desire greater safety and better comfort by avoiding these inconvenient phenomena. These factors are the driving force behind the development of antibacterial materials.

2.12.2 UV protection

The most important functions performed by the garment are to protect the wearer from the weather. However it is also to protect the wearer from harmful rays of the sun. The rays in the wavelength region of 150 to 400nm are known as ultraviolet radiations. Exposure of human body to UV rays may cause severe damages. Long term exposure to UV light can result in acceleration of skin ageing, photo-dermatosis (acne), phototoxic reactions to
drugs, erythema (skin reddening), sunburn, increased risk of melanoma (skin cancer), eye damage (opacification of the cornea) and DNA damage. Numerous publications have appeared concerning the use of textiles to protect the wearer from these harmful effects; a selection is quoted (Hilfiker et al 1996). According to the U.S. National Institutes of Health, UV radiation from the sun has been the main cause of skin cancer. Protection from UV light can prevent skin cancers because 90% of all skin cancers happen due to lack of sun protection (Hatchb and Osterwalder 2006).

Clothing has the ability to protect the skin from incident solar radiation because the fabric from which it is made can reflect, absorb and scatter solar wavelengths. The UV-blocking property of a fabric is enhanced when a dye, pigment, delustrant, or ultraviolet absorber finish is present that absorbs ultraviolet radiation and blocks its transmission through a fabric to the skin.

Fabrics differ in their ability to attenuate light in this way because they differ in fibres composition and moisture content, as well as in type and concentration of dye, optical whiteners, or UV-absorbing finishes adsorbed to fibres. When radiation strikes a fibre surface, it can be reflected, absorbed, transmitted through the fibre or pass between fibres (Figure 2.19). The relative amounts of radiation reflected, absorbed or transmitted depend on many factors, including the fibre type, the fibre surface smoothness, the fabric cover factor (the fraction of the surface area of the fabric covered by yarns) and the presence or absence of fibre delustrants, dyes and UV absorbers. Fabric treated with UV absorbers ensures that the clothes deflect the harmful ultraviolet rays of the sun, reducing a persons UVR exposure and protecting the skin from potential damage. The extent of skin protection required by different types of human skin depends on UV radiation intensity and distribution in reference to geographical location, time of day, and season.
The actual damage to human skin from UV radiation is a function of the wavelength of the incident radiation, with the most damage done by radiation less than 300 nm.

If this erythemal effect is multiplied by the intensity of the incident solar light, as a function of wavelength, the wavelengths of maximum danger to skin are 305–310 nm (Hilfiker et al 1996). Therefore, to be useful in protecting the wearer from solar UV radiation, textiles must demonstrate effectiveness in the 300–320 nm range. To quantify the protective effect of textiles, the solar protection factor (SPF) is determined. The SPF is the ratio of the potential erythemal effect to the actual erythemal effect transmitted through the fabric by the radiation and can be calculated from spectroscopic measurements (Hilfiker et al 1996).

Figure 2.19 Schematic representation of the mechanism of UV protection

The larger the SPF, the more protective the fabric is to UV radiation. In Europe and Australia, the SPF is referred to as the ultraviolet protection factor (UPF). The SPF is also used with so-called ‘sun blocking’
skin creams, giving a relative measure of how much longer a person can be exposed to sunlight before skin damage occurs. Typically, a fabric with an SPF of > 40 is considered to provide excellent protection against UV radiation (according to AS/NZS 4399: Sun protective clothing – Evaluation and classification, Standards Australia, Sydney). It is possible to realise about 80% of the theoretical maximum of SPF 200 (Mentera and Hatchb 2003).

Since the most probable time for long-term solar exposure is in the summer, the most likely candidates for UV protective finishes are lightweight woven and knitted fabrics intended for producing shirts, blouses, T-shirts, swimwear, beachwear, sportswear, and the like. Industrial fabrics designed for awnings, canopies, tents and blinds may also benefit from a UV-protective treatment. The SPF value based UV protection classification is given in Table 2.1.

**Table 2.1 SPF value based UV protection classification**

<table>
<thead>
<tr>
<th>SPF</th>
<th>% UV transmission</th>
<th>UV Protection category</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 – 19.5</td>
<td>Very good</td>
<td>Poor</td>
</tr>
<tr>
<td>20 – 29.5</td>
<td>Good</td>
<td>Not good</td>
</tr>
<tr>
<td>30 – 49.5</td>
<td>Moderate</td>
<td>Good</td>
</tr>
<tr>
<td>50 &amp; above</td>
<td>Less than 2</td>
<td>Excellent</td>
</tr>
</tbody>
</table>

The SPF value of textile depends on fiber type, the fabric construction (Porosity and thickness), and the finish. It means that transmission, absorption and reflectance nature of textile influences SPF value. It provides vital Information about the fabric's sun protection ability. By using UV absorbers, exposure of the textile to UV Lights is reduced on the one hand as well as the intensity of the transmitted UV light on the other.
Good skin protection is achieved by the textile itself with a sufficient weight of fabric but the desired protective function is achieved by means of an additional finish. A UV absorber can be applied either during fiber manufacture or in the final textile finishes which also offers the same degree of protection.

The effect of fibre type on the SPF of undyed fabrics of similar construction is shown in the Table 2.2. Cotton and silk offer little protection to UV radiation since the radiation can pass through without markedly being absorbed. Wool and polyester, on the other hand, have significantly higher SPFs since these fibres will absorb UV radiation. Nylon falls in between these extremes. One factor influencing nylon and polyester absorbance is the presence of the delustrant TiO$_2$, a material that strongly absorbs UV radiation.

<table>
<thead>
<tr>
<th>Fabric description</th>
<th>Approximate SPF Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cotton tricot</td>
<td>4</td>
</tr>
<tr>
<td>Wool tricot</td>
<td>45</td>
</tr>
<tr>
<td>Silk twill</td>
<td>7</td>
</tr>
<tr>
<td>Polyester tricot</td>
<td>26</td>
</tr>
<tr>
<td>Nylon/Elastomer 80/20 tricot</td>
<td>12</td>
</tr>
</tbody>
</table>

If the fibres absorb all of the incident radiation, then the only source of transmitted rays is through the spacing between the yarns. By definition, the theoretical maximum SPF is the reciprocal of 1 minus the cover factor.

$$\text{SPF}_{\text{max}} = \frac{1}{1 - \text{cover factor}}$$ (2.4)
Figure 2.20 illustrates the relationship between the maximum SPF and the cover factor. Using a SPF value of 50 as the goal, a fabric with a cover factor of 0.98 and composed of fibres that absorb all of the non-reflected UV radiation will provide its wearer with excellent protection against solar UV radiation. Of course, tight micro-fibre fabrics will provide a better UV protection than fabrics made from normal sized fibres with the same specific weight and type of construction. Raleigh’s scattering theory states that the “scattering of light is inversely proportional to the fourth power of wavelength”. Based on this theory, the optimum particle size for scattering the radiation can be calculated as 20 to 40 nm (Burniston and Bygott 2004). This clearly illustrates the higher effectiveness of the nanoparticles in scattering of the UV rays than the bulk particles (Figure 2.21).

In addition to this, the metal oxides like TiO$_2$, ZnO as UV-blockers are more stable when compared to organic UV-blocking agents. Hence, nanoparticles of TiO$_2$ and ZnO will really enhance the UV-blocking property due to their increased surface area and intense absorption in the UV region (Xin and Daoud 2004).

2.12.3 Soil release finishing

Soil-release finishes on textiles facilitate the removal of soils during laundering under common household conditions. Removal of soils from fabrics has been attributed to several mechanisms (Kissa 1984; Cooke 1987). They are:

a. Adsorption of detergent and absorption of water leading to:
   - Penetration of soil-fibre interface by wash liquid
   - Solubilisation and emulsification of soils
   - Rollup of oily soil
b. Mechanical work leading to:
   - Hydrodynamic flow carrying away the removed soil
   - Fibre flexing to force soil between fibres
   - Surface abrasion to remove soil physically
   - Swelling of finish to reduces the inter-fibre spacing

Of these mechanisms, solublisation and emulsification of soils are controlled by detergent composition; hydrodynamic flow is controlled by washing machine design and fibre flexing is controlled by fabric construction.
2.21 Schematic illustration of light scattering by particles

The textile chemist can only influence the mechanisms that involve the fibre surface, i.e. rollup of oily soil, penetration of soil-fibre interface, surface abrasion and finish swelling. Finishes have been developed to provide
soil release performance by taking advantage of all these mechanisms. Particulate soil release is done by a two step process (Kissa 1984).

a. First a thin layer of wash liquid penetrates between the particle and the fibre surface enabling the surfactants to adsorb onto the particle surface (Figure 2.28). Then, the particle becomes solvated and is transported away from the fibre by mechanical action. Finishes that are hydrophilic (enhancing penetration of the fibre-soil interface) with low adhesion to soil under washing conditions should improve particulate soil release. Ablative or sacrificial finishes that leave the fabric surface during washing and take the soil particles along with them can also benefit particulate soil release.

![Schematic illustration of release of particulate soil](image)

**Figure 2.22 Schematic illustration of release of particulate soil**

b. For the most part, the removal of particulate soil is determined by the detergent composition and mechanical action.

- A low fibre-wash liquid interfacial energy is desired, i.e. a hydrophilic finish is preferred for spontaneous oil roll up.
- A high fibre-oil interfacial energy is desired, i.e. the finish should also be oleophobic.
A low interfacial tension between the oil and wash liquid will favour oily soil release.

The main factors affecting soil release are given in Table 2.3.

**Table 2.3  Main factors affecting soil release**

<table>
<thead>
<tr>
<th>Factor</th>
<th>Explanation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nature of the soil</td>
<td>Oily soil or particulate soil, hydrophobic or hydrophilic, liquid or solid</td>
</tr>
<tr>
<td>Kind of fibres</td>
<td>Type of the fibre, hydrophobic or hydrophilic, Smooth or porous fibre surface</td>
</tr>
<tr>
<td>Nature of textile</td>
<td>Textile construction; yarn 9staple or filament), fabric(knit, woven or nonwoven)</td>
</tr>
<tr>
<td>Effects of preparation</td>
<td>Residual waxes, warp sizes, or other hydrophobic materials</td>
</tr>
<tr>
<td>Effects of dyeing and printing</td>
<td>Difference in binder films, residual hydrophobic dyeing auxiliaries</td>
</tr>
<tr>
<td>Effects of other finishes</td>
<td>Compatible with antistatic finishes, easy-care finishes and other finishes not harmed by a hydrophilic surface. Not compatible with conventional repellent finishes and other finishes where hydphilicity is detrimental to finish performance</td>
</tr>
<tr>
<td>Washing conditions</td>
<td>Detergents, hydrodynamic flow in the washing machine.</td>
</tr>
</tbody>
</table>

Additional finish characteristics that should facilitate oily soil release include the ability of the finish to swell during the washing process and flexibility under mechanical action. As in particulate soil release, sacrificial finishes are expected to benefit oily soil release. The latest innovation in this area is the development of self-cleaning textiles. The term
self-cleaning textiles imply that the textiles are capable of being clean i.e. free from dirt and stains on their own. Such textiles do not need any chemicals and detergents required for cleaning them. The need for such textiles again, arises from the higher standard of living because of which consumers do not even have sufficient time to wash their clothes in a fast paced life.

2.13 METHODS OF FABRIC TREATMENT WITH THE NANOPARTICLES

In order to impart the sample fabrics with the multifunctionality, the sample fabrics can be treated with the nanoparticles using any one of the following three methods of applications of the nanoparticles to the fabric substrate (Mahltig et al 2003).

i. **Simple dip and dry method:** In this method, the known quantity of nanoparticles (usually a % of the dry fabric weight) to be applied on to the fabric is taken in a beaker where the nanoparticles are kept in colloidal state by means of a dispersing agent or peptizing agent. The fabric is simply dipped in this colloidal suspension for about 10 minutes by immersing it fully in the suspension. The treated fabric is then taken out and dried by any one of the three methods of drying namely, sun drying or hot air drying or microwave oven drying till the fabric is fully dry.

ii. **Pad-Dry-Cure method:** A padding mangle is used for the purpose of applying the nanoparticles from the suspension to the fabric surface. When the fabric is fed to the nip of the padding rollers, the pressure of the nip helps the nanoparticles to be pressed on to the fabric surface. The treated fabric is then dried and then cured at a high temperature to ensure the
fixation of the nanoparticles on to the fabric surface. This method invariably uses a binder chemical which is used for the binding of the nanoparticles on to the fabric surface. It is important to check the compatibility of the binder with that of the dispersing agent and the nanoparticles. This method also requires higher quantity of nanoparticles and liquor as it necessitates the use of a padding mangle.

iii. **Spraying with spray gun:** The two methods mentioned above are not ideally suited for this research work because of the possibility of the application of the nanoparticles on both sides of the fabric and also into the interstices of the fabric. The nanoparticles application method has to ensure the even application of the nanoparticles on to the fabric surface which is exposed to the sun since the concept of multifunctionality is based on the principle of photo-catalytic oxidation for antibacterial activity and soil release functions. In addition to that, they have to absorb the harmful UV rays of the sun light so as to offer UV protection. Though the dirt and bacteria can be from the either side of the garment, the nanoparticles have to be exposed to sun light so as to activate the photo-catalytic oxidation for achieving dual-functionality. Thus, it can be seen that it is advantageous to have the nanoparticles predominantly fixed on to the right side of the fabric. To ensure this and also to attain higher utilization efficiency of nanoparticles, it is preferable to use a hand held compressed air sprayer whose feed tank is filled with the colloidal suspension of the nanoparticles. Though there is a theoretical possibility of using the binder for the nanoparticles, it was not used for this research work as the nanoparticles have sufficient
energy to bind themselves with the fabric surface by virtue of their smaller size and large surface area. This method also ensures the uniform distribution of the nanoparticles on the fabric surface and proper utilization of the synthesized nanoparticles.

2.14 FUNCTIONAL TESTING OF FINISHED FABRIC SAMPLES

The sample fabrics treated with the nanoparticles are tested for the evaluation of the three special functions that were intended to be imparted to the fabrics by the treatments.

2.14.1 Evaluation of antimicrobial activity

To investigate the antibacterial activity of the woven and knitted fabric samples, the fabric samples were treated with zinc oxide and titanium dioxide nanoparticles separately. The evaluation of antibacterial activity was done by the Quantitative assessment method as per AATCC Test Method 100-2004(AATCC 2007). The test was carried out with Staphylococcus Aureus American type Culture collection No. 6538 (for Gram positive bacteria) and Klebsiella Pneumoniae, American Type Culture Collection No. 4352 (for Gram negative bacteria). The percentage reduction of bacteria by the 100% cotton and 45/55% polyester/cotton fabrics is reported as R,

\[ R = 100(B - A)/B \]  

where  

R - % reduction  

A - the number of bacteria recovered from the inoculated treated test specimen swatches in the jar incubated over 24 hours
B - the number of bacteria recovered from the inoculated treated test specimen swatches in the jar immediately after inoculation (at ‘0’ contact time).

2.14.2 Evaluation of UV absorption

This section describes the test method that is used to quantify the sunburn protection provided to skin by covering it with fabric. The in-vitro method, also called the instrumental method, is used for assessing the UV protection of the fabric. The evaluation of the UV protection offered by the fabric is done as per the AATCC Test Method 183 (AATCC 2005). It measures the transmittance or blocking of erythemally weighted UV radiation through fabrics by the use of an instrument called UV-Vis spectrophotometer. The two major steps in this procedure are transmittance testing and calculations based on the transmittance data collected. To obtain the transmittance data, a fabric swatch is placed in a spectrophotometer equipped with an integrating sphere. The procedure is to direct a beam of radiation composed of one wavelength in the UV light and of known quantity perpendicular to the surface of the fabric swatch and to measure the amount of radiation transmitted through the fabric. The sending of beams of radiation continues until all wavelengths in the UV range (or in some tests the wavelengths at 2 or 5 nm intervals) have been directed to the fabric face and transmittance data collected. Once the transmittance data have been collected (usually by measuring the UV transmittance of several swatches of the same fabric to take into account variation in fabric uniformity), they are used to calculate percent transmittance values (percent UVA, percent UVB, or a total percent transmittance value) and the fabric–ultraviolet protection factor (UPF) value.

The calculation of a UPF value is accomplished by combining the transmittance data with data collected that established the relative power of
UV wavelengths to cause the skin to redden. These latter data, data collected using human subjects, are given in the erythemal action spectra. The importance of using the erythemal action spectra data in a protection calculation is that fabrics that allow a greater portion of the most powerful skin reddening rays to be transmitted will receive a numerical value lower than a fabric that allows less of the powerful skin reddening rays through, even when both fabrics transmit the same amount of radiation. UPF can be calculated as in equation (2.10):

\[
UPF = \frac{\sum_{\lambda=280}^{400} E\lambda \times S \times \Delta\lambda}{\sum_{\lambda=280}^{400} E\lambda \times S \lambda \times T \lambda \times \Delta\lambda}
\] (2.6)

where \(E(\lambda)\) is the relative erythemal spectral effectiveness, \(S(\lambda)\) is the solar spectral irradiance, \(\Delta\lambda\) is measured wavelength interval (nm), and \(T(\lambda)\) is average spectral transmittance of the specimen. The definition of UPF is that it is the ratio of average effective UV radiation irradiance transmitted and calculated through air to the average effective UVR irradiance transmitted and calculated through fabric. The UPF value calculated therefore indicates how much longer a person can stay in the sun when fabric covers the skin as compared with the length of time in the sun without fabric covering to obtain same erythemal response.

### 2.14.3 Evaluation of soil release characteristic

The soil release properties of the treated fabrics were evaluated by the modified stain release test as we do not have a specific test method that can assess the soil release properties of the treated fabrics directly. The stain profiles of the untreated samples were compared to the ones collected from the same fabrics treated with the nanoparticles, and the effectiveness in soil
and stain release was compared with the AATCC ratings as per Test Method: 175: 2003 (AATCC 2007).

2.15 REVIEW OF RECENTLY REPORTED RESEARCH WORKS

Ki et al (2007) reported their study on multifunctional wool textiles treated with nano-sized silver. The purpose of this research was to study the characterization of novel nano-silver colloid and its application for wool textiles. Silver is one of non-toxic and safe antibacterial agents to the human body, and can kill many harmful microorganisms. The mechanism of antibacterial action of silver ions is closely related to their interaction with proteins, particularly at thiol (sulphydryl, –SH) groups, and are believed to bind protein molecules together by forming bridges along them. Since the proteins behaviour often like as enzymes, the cellular metabolism is inhibited and the microorganism dies. The nanosized silver particles are more effective in their antibacterial ability than the normal large sized silver particles. The wool textiles were prepared by a general padding method with the diluted SNSE colloidal solution. The SNSE was a new type of nano-silver colloid including a few sulphur compounds on nano-sized silver particles. The fibres were treated with nano-silver colloid by a conventional pad-dry-cure (PDC) method. The specimens were immersed in a fresh colloidal bath for 10 min and squeezed using a laboratory padder at the constant pressure. The samples were dried at room temperature for prevention of thermo-migration of metal particles for 30 min, and then the curing process of samples was performed at 120º C, for 5 min.

The wool textiles having nano-sized silver were investigated for their antibacterial, mothproofing, and electrical properties and surface observation with nano-particles. The antibacterial properties of wool specimens were quantitatively evaluated against Staphylococcus aureus
(S. aureus), ATCC 6538, a Gram-positive bacterium and Klebsiella pneumoniae (K. pneumoniae), ATCC 4352, a Gram-negative bacterium, according to the test method AATCC 100-1999. For the determination of the resistance to the larvae of certain insect, mothproofing test was conducted on the wool fibres according to assessment of the visible damage and fibre weight loss procedure established by the International Standardization Organization 3998-1977. The electrostatic propensity of prepared samples was conducted in compliance with the test method KSK 0555-1996 for woven or knitted fabrics. It was concluded that the manufactured wool textiles using the treated fibres with the silver particle were showed excellent antibacterial activity. The insect resistance evaluation test also showed that the weight loss of treated wool with 20 ppm silver significantly decreased compared with untreated fibres on a quantitative basis and the visual assessment of treated wool fibre for qualitative assessment on the whole was also excellent. Consequently, it was demonstrated that the finished wool fabrics with sulphur nanosilver colloid had various functionalities, such as mothproofing, antibiotic, and antistatic property. The noteworthy features of this study are its focus on wool fabrics, the non-usage of a binder for the nanoparticles and non-assessment of the washing fastness of the nano treatment.

Vigneshwaran et al (2006) reported on Functional finishing in cotton fabrics using zinc oxide nanoparticles. In this work, the ZnO nanoparticles were prepared by a novel aqueous method and applied onto cotton fabrics using acrylic binder. The UV-blocking property of these fabrics was evaluated. The zinc oxide (ZnO) nanoparticles were prepared by wet chemical method using zinc nitrate and sodium hydroxide as precursors and soluble starch as stabilizing agent. A fine-medium weight 100% cotton woven fabric (plain weave, 75×30 g/m2; ends, 75/inch; picks, 60/inch) was used for the application purpose. ZnO nanoparticles were applied on cotton using pad-dry-cure method. Simultaneously, bulk-ZnO coating was carried out for
comparison purposes. It was reported that the nano-ZnO coating on cotton fabrics resulted in uniform and very thin coating due to nano-size. It was claimed that the nano-ZnO coated cotton fabric is proved to have better strength properties, air permeability and UV-absorption property. This research work involved the use of a chemical binder for the nanoparticles application.

The synthesis and characterization of nanosized zinc oxide particles and their application on cotton and wool fabrics for UV shielding was reported by Nostro et al (2007). The study was about the peculiar property of ZnO nanoparticles as UV-absorbers which can be efficiently transferred to fabric materials through the application of ZnO nanoparticles on the surface of cotton and wool fabrics. The nanoparticles were produced in different conditions of temperature (90 or 150°C) and reacting medium (water or 1, 2-ethanediol). In both cases, the nanoparticles appear to be nearly spherical and with a quite narrow size range. Fourier transformed infrared spectroscopy (FTIR), transmission electron microscopy (TEM), and X-ray powder diffractometry (XRD) were used to characterize the nanoparticles composition, their shape, size and crystallinity. The specific surface area of the dry powders was also determined. ZnO nanoparticles were then applied to cotton and wool samples to impart sunscreen activity to the treated textiles. The effectiveness of the treatment was assessed through UV-Vis spectrophotometry and the calculation of the ultraviolet protection factor (UPF). The UV tests indicated a significant increment of the UV absorbing activity in the ZnO-treated fabrics. Such result can be exploited for the protection of the body against solar radiation and for other technological applications. The salient feature of this study was its focus on imparting the UV protection to the woven fabrics made of cotton and wool.
From the above literature survey, it can be seen that both TiO$_2$ and ZnO nanoparticles were used by researchers in the various investigations of functional finishing of textiles. However, a thorough and critical examination of this literature survey shows that the following aspects of the research works were not addressed by any of the researchers so far.

- Multifunctional finishing of textiles with a single treatment.
- Multifunctional finishing of textiles made of knitted fabrics and P/C blends.
- A comparative performance of functional finishing of TiO$_2$ and ZnO nanoparticles.

The plan of the research work will be suitably designed to cover these aspects in this research work.