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Modification of textile surfaces using nanoparticles

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Abstract: The application of nanotechnology on textile materials could lead to the addition of several functional properties to the base substrate. Those functional properties are of the highest importance, giving noticeable improvements in the wear comfort and care. This chapter discusses various functional properties – for example, anti-microbial, easy-care, ultraviolet-protecting and flame-retardant finishes that could be achieved by the application of metal and metal oxide nanoparticles. In addition, novel applications of textile materials using nanotechnology in biological detection, decomposition of toxic gases, self-decontamination and military protection gear are discussed.

Key words: antimicrobial, dispersion, easy-care, functional finishes, Lotus-Effect®, nanoparticles, ultraviolet protection.

8.1 Introduction

Nanotechnology deals with materials having at least one dimension in the nanometre scale, and includes nanoparticles, nanorods, nanowires, thin films and bulk materials made of nanoscale building structures (Cao, 2004). A nanometre (nm) is one billionth of a metre, or $10^{-9}$ m. Nanotechnology is not simply the continuation of miniaturization from micrometre scale down to nanometre scale but also permits entirely different and improved functionalities. For example, crystals in the nanometre scale have a low melting point, reduced lattice constants, higher surface area and catalytic activity. The band gap of semiconductors can be engineered by varying their size in the nanometre range while super-paramagnetism will be observed in the case of magnetic materials. In the United States, nanotechnology has been defined as being ‘concerned with materials and systems whose structures and components exhibit novel and significantly improved physical, chemical and biological properties, phenomena and processes due to their nanoscale size’ (National Nanotechnology Initiative, 2000, www.nano.gov). Although nanotechnology is new, research in biology and colloidal science has been at a nanometre scale for centuries. The current enthusiasm for nanotechnology is driven by the availability of characterization
and manipulation techniques at nanometre level and the continued shrinking of
devices in the semiconductor industry, as predicted by Moore’s law.

One of the attractive applications of nanotechnology in medicine is the creation
of nanoscale devices, named nanorobots (Haberzettl, 2002) or simply nanobots,
having the potential to act as targeted drug delivery agents. Bandgap-engineered
quantum devices, such as lasers and heterojunction bipolar transistors, have been
developed with unusual electronic transport and optical effects (Capasso, 1987).
The invention of scanning tunnelling microscopy (STM) in the early 1980s
(Binnig et al., 1982) and subsequently atomic force microscopy (AFM) (Binnig et
al., 1986) have opened up new possibilities for the characterization, measurement
and manipulation of nanomaterials and their bulk structures.

Application of nanotechnology on textile materials could lead to the addition of
several functional properties to the base substrate. For example, deposition of
silver nanoparticles imparts antibacterial properties while gold nanoparticles
allow the use of molecular ligands so that the presence of biological compounds in
the surroundings is rapidly detected. Platinum and palladium nanoparticles impart
catalytic properties such as decomposition of harmful gases or toxic industrial
chemicals. More often, these nanomaterials are impregnated onto textile materials
without significantly affecting their texture or comfort. An additional benefit of the
use of metal nanoparticles is the presence of surface plasmons. These plasmons
have strong optical extinctions that can be tuned to different colours by varying
their size and shape. Silver nanoparticles can be used to create a shiny metallic
yellow to dark pink colour while simultaneously imparting antibacterial properties
to the textile materials.

Metal oxide nanoparticles – such as TiO₂, Al₂O₃, ZnO and MgO – possess
photocatalytic and antibacterial activity and ultraviolet (UV) absorption
properties. Textile materials treated with these nanoparticles have been proven to
impart antimicrobial, self-decontaminating and UV-blocking functions for both
military protection gear and civilian health products (Kim et al., 2002).

8.2 Nanoparticles synthesis and characterization

Owing to their extremely large surface areas, nanomaterials possess a huge surface
energy and hence are thermodynamically unstable. In addition to combining
individual nanostructures together to form large structures through sintering or
Ostwald ripening, agglomeration is another way to reduce the overall surface
energy. For practical applications, the formation of agglomerates should be
prevented as they are very difficult to separate. For the fabrication and processing
of nanomaterials, the following challenges must be met (Cao, 2004):

(a) overcoming the huge surface energy, a result of enormous surface area or
large surface to volume ratio;
(b) ensuring that all nanomaterials have the desired size, uniform size
distribution, morphology, crystallinity, chemical composition and micro-
structure that together result in the desired physical properties;

c) preventing nanomaterials from coarsening through either Ostwald ripening
or agglomeration as time passes.

The two common methods of preventing the formation of agglomerates are
electrostatic stabilization (due to surface charge density) and steric stabilization
(due to polymeric coating). The frequently used stabilizers are poly(vinyl
pyrrolidone), polyvinyl alcohol, sodium polyacrylate, polyethyleneimine, sodium
polyphosphate, starch, gelatine and proteins.

There are two main approaches for the synthesis and/or fabrication of
nanostructures: top-down and bottom-up. Milling and colloidal dispersion are
typical examples of top-down and bottom-up methods, respectively. The bottom-
up approach promises a better chance of obtaining nanostructures with fewer
defects and more homogeneous chemical composition, as it is mainly driven by the
reduction of Gibbs free energy leading to a state closer to thermodynamic
equilibrium. In contrast, the top-down approach is more likely to introduce internal
stress, in addition to surface defects and contaminations (Cao, 2004). A schematic
representation of the top-down and bottom-up approaches for the synthesis of
nanomaterials is given in Fig. 8.1.

For the synthesis of nanoparticles, apart from size, various parameters like
uniform size distribution, identical shape and chemical composition and complete
dispersion contribute largely to the quality of the final product. Figure 8.2 shows
the completely dispersed silver nanoparticles prepared in our laboratory. In
general, nanocrystals refer to single crystalline nanoparticles and quantum dots
refer to sufficiently small nanoparticles exhibiting quantum effects (in
semiconductors) and surface plasmon resonance (in metals). The synthesis of
metal nanoparticles, usually called colloids, can be traced back to Michael Faraday
in the mid nineteenth century. Even today it is a very convenient procedure to
generate gold colloids by Faraday’s method using the reduction of \([\text{AuCl}_4]^–\)
by citric acid. The particles formed are surrounded by an electric double layer arising
from adsorbed citrate and chloride ions and by the corresponding cations. The
resulting Coulomb repulsion between the particles prevents aggregation and
coalescence. Figure 8.3 illustrates the situation between two particles having
electric double layers. The Coulomb repulsion between the particles decays
approximately exponentially with the particle distance (Bradley, 1994).

Porel et al. (2007) demonstrated the synthesis of silver nanoparticles by the
8.3 Electrostatic stabilization of metal colloids. Van der Waals attraction and electrostatic repulsion compete with each other. $E$, Coulomb repulsion; $r$, particle distance.

well-known ‘polyol route’ and reported the following plausible mechanism for the reduction of silver nitrate by a secondary alcohol group:

$$R_2CHOH + AgNO_3 \rightarrow R_2CO + H_2O + NO_2 + Ag \quad [8.1]$$

In the case of metal oxide nanoparticles, a simple and novel aqueous route for the preparation of nanoparticles of ZnO from zinc nitrate hexahydrate without any requirement for high-temperature treatment has been reported recently (Wu et al., 2006). The possible reaction process is given as:

$$Zn(NO_3)_2 \cdot 6H_2O + 2NaOH = Zn(OH)_2 (gel) + 2NaNO_3 + 6H_2O \quad [8.2]$$

$$Zn(OH)_2 (gel) + 2H_2O = Zn^{2+} + 2OH^- + 2H_2O \quad [8.3]$$

$$= Zn(OH)^{3-} + 2H^+ \quad [8.4]$$

$$Zn(OH)^{2-} = ZnO + H_2O + 2OH^- \quad [8.5]$$

Here, with the increase of the reaction temperature, the morphology of the particles seems to change from a rod-like to a short prism-like form. Similarly, the reaction
process of sol-gel processing for the preparation of titania nanoparticles from titanium isopropoxide is:

\[
\text{Ti(OPr)}_4 + 4\text{EtOH} \rightarrow \text{Ti(OEt)}_4 + 4\text{PrOH} \quad \text{[8.6]}
\]

Hydrolysis

\[
\text{Ti(OEt)}_4 \text{ or Ti(OPr)}_4 + \text{H}_2\text{O} \rightarrow \text{Ti(OH)}_4 + 4\text{PrOH} \text{ or } 4\text{EtOH} \quad \text{[8.7]}
\]

Condensation

\[
\text{Ti(OH)}_4 \rightarrow \text{TiO}_2 + 2\text{H}_2\text{O} \quad \text{[8.8]}
\]

Hydrolysis and condensation reactions occur sequentially and in parallel. Condensation results in the formation of nanoscale clusters of metal oxides, often with organic groups embedded or attached to them. Wang et al. (2005) reported a unified approach to the synthesis of a large variety of nanocrystals with different chemistries and properties and with low dispersity; these included noble metal, magnetic/dielectric, semiconducting, rare-earth fluorescent, biomedical and conducting polymer nanoparticles. This strategy was based on a general phase transfer and separation mechanism occurring at the interfaces of the liquid, solid and solution (LSS) phases present during the synthesis.

Various physical and chemical techniques are being used to characterize the prepared nanomaterials. A brief account of the techniques used to analyze various parameters is given in Table 8.1.

### 8.3 Functional properties using nanoparticles

#### 8.3.1 Antimicrobial finishes

‘Silver’ has been used in jewellery and for food utensils. It is a well-known fact that the growth of bacteria and microorganisms in food or water is prevented when stored in silver vessels owing to the antibacterial properties of silver, which are now scientifically recognized. Silver ions have a broad spectrum of antimicrobial activities. They are believed to get bound to protein molecules, inhibiting the cellular metabolism and leading to the termination of the growth of microorganisms. An additional benefit to the use of metal nanoparticles is the presence of surface plasmons. These plasmons have strong optical extinctions that can be tuned to different colours by varying their size and shape. Silver nanoparticles can be used to create a shiny metallic yellow to dark pink colour while simultaneously imparting antibacterial properties to the textile materials. Scanning and transmission electron microscopy were used to study the biocidal action of this nanoscale material (Sondi and Salopek-Sondi, 2004). The results confirmed that the treated *Escherichia coli* cells were damaged, showing the formation of ‘pits’ in the cell wall of the bacteria, while the silver nanoparticles
**Table 8.1 Techniques for characterization of nanoparticles**

| Characterization techniques                                      | Parameters                                                                 |
|-----------------------------------------------------------------|---------------------------------------------------------------------------|
| **Structural characterization**                                  |                                                                           |
| X-ray diffraction (XRD)                                         | Crystal structures of nanoparticles and size of crystallites               |
| Small angle X-ray scattering                                    | Size of nanoparticles or their surface area per unit volume                |
| Scanning electron microscopy (SEM) with energy dispersive X-ray | Topographical information of nanomaterials and their chemical composition  |
| analysis (EDX)                                                   |                                                                           |
| Transmission electron microscopy (TEM) with EDX                 | Particle size and chemical composition                                    |
| Scanning probe microscopy (SPM)                                 | Three-dimensional real-space images                                        |
| Gas absorption                                                  | Surface area, particle size and porous structures                         |
| **Chemical characterization**                                    |                                                                           |
| Optical spectroscopy (UV and infrared absorption, fluorescence and Raman effect characteristics) | Bonding and chemical nature of the nanomaterials                           |
| Electron spectroscopy                                           | Chemical composition analysis                                             |
| Ionic spectrometry                                              | Thin-film characterization and elemental analysis                          |
| **Physical characterization**                                    |                                                                           |
| Melting point apparatus and XRD and TEM                        | Melting point and lattice constants                                        |
| Atomic force microscopy (AFM)                                   | Mechanical properties                                                     |
| Optical spectroscopy                                            | Surface plasmon resonance and quantum size effects                        |
| SPM                                                             | Electrical and magnetic properties                                         |

were found to accumulate in the bacterial membrane. A membrane with such morphology exhibits a significant increase in permeability, resulting in death of the cell.

On account of its non-toxic nature, nano-silver is biocompatible and can be used effectively to reduce bacterial counts on nonwoven materials such as air and water filters, medical clothing and textile woven fabrics that come into direct contact with human skin (Tiller et al., 2001). In our earlier report (Vigneshwaran et al., 2007), we reported on a novel, one-pot synthetic route for the preparation of silver nanoparticles, reduced and stabilized by starch on the surface of cotton fabrics. Thus-formed nanoparticles impart colour to the fabrics owing to the surface plasmon resonance. Figure 8.4 shows a scanning electron micrograph of silver nanoparticles deposited on the surface of cotton fabrics. It was also shown that
these silver nanoparticle-impregnated cotton fabrics showed excellent antibacterial activity against *Staphylococcus aureus* and bacteriostasis activity against *Klebsiella pneumoniae*.

Another research group from Hanyang University, Korea (Lee and Jeong, 2005) – in their work on the padding of colloidal silver solution onto textile fabrics made from cotton, polyester, cotton/polyester and cotton/spandex blended fabrics – have also reported efficient antibacterial activity against both *Staphylococcus aureus* and *Klebsiella pneumoniae* with good laundering durability (Lee et al., 2003). Jiang et al. (2006) applied a nanolayer of silver coating onto cotton and polyester fabrics by chemical silver plating and showed that these fabrics had improved properties, including antibacterial, ultraviolet (UV) light absorption, antistatic and light-fastness properties. These special properties are due to the fact that basic silver particles have higher shielding properties and better conductivity than the original fabrics.

### 8.3.2 Ultraviolet-protection finishes

Prolonged and repeated exposure to UV radiation from sunlight has been identified as the cause of an increase in the incidence of skin cancer in humans. Limiting the skin’s exposure to sunlight, especially during the hours of maximum intensity, is the best way to reduce risk. For a person who must work outdoors this is not feasible, well-designed clothing made from UV-blocking textiles is the best alternative. The various processes undergone by the incident UV light on a fabric material are represented in Fig. 8.5. The transmitted and scattered light will be the
8.5 UV-transmittance characteristics of a textile material.

8.6 Antibacterial finishing of cotton fabrics with nano-ZnO.

Focus here as it is this light that is actually responsible for sunburn. ZnO nanoparticles score better than other nanoparticles in terms of cost-effectiveness, whiteness and UV-blocking properties. The UV-blocking properties of a fabric are enhanced when a dye, pigment, delustrant or UV-absorbant finish is present that absorbs UV radiation and blocks its transmission through the fabric to the skin (Hustvedt and Crews, 2005). Metal oxides such as ZnO are more stable as UV blockers when compared with organic UV-blocking agents. Hence, the nano-form of ZnO will really enhance UV-blocking properties due to the increased surface area and intense absorption in the UV region. Our research (Vigneshwaran et al., 2006) has indicated excellent antibacterial activity against two representative bacteria, *Staphylococcus aureus* and *Klebsiella pneumoniae*, and promising protection against UV radiation for the nano-ZnO-impregnated cotton textiles. Figure 8.6 shows the steps in the process of coating cotton fabrics with nano-ZnO in our
8.7 Scanning electron micrograph of nano-ZnO (embedded inside starch granule) coated on cotton fibres.

laboratory and Fig. 8.7 shows a scanning electron micrograph of nano-ZnO (embedded inside starch granule)-coated cotton fibres.

The ultraviolet protection factor (UPF) was calculated using the following equation (AATCC Test Method 183–2006 (AATCC, 2006)):

$$\text{UPF} = \frac{\sum_{\lambda=280}^{400} E\lambda \times S\lambda \times \Delta \lambda}{\sum_{\lambda=280}^{400} E\lambda \times S\lambda \times T\lambda \times \Delta \lambda}$$

[8.9]

where $E\lambda$ is the relative erythermal spectral effectiveness, $S\lambda$ is the solar spectral irradiance, $T\lambda$ is the average spectral transmission of the specimen and $\Delta \lambda$ is the measured wavelength interval (nm). The UPF equation weighs the UV-B radiation more heavily than UV-A.

The UPF ratings are as follows:

- 50+, maximum achievable;
- 40–50, excellent protection;
- 25–39, very good protection;
- 15–24, good protection.

The nano-ZnO-impregnated fabrics were found to retain more than 80% efficiency of both antibacterial and UV-protection functions even after 25 hand-wash cycles. The wash fastness is generally studied by a standard test, AATCC Test Method 61–2006, where a single wash cycle corresponds to five typical careful
hand launderings. The loss and changes resulting from the detergent solution and the abrasive action of five typical hand launderings are roughly approximated by this 45 min test. The abrasive action is a result of the frictional effects of fabric against the canister, the low liquor ratio and the impact of the steel balls on the fabric. In yet another study (Vigneshwaran et al., 2007), nano-silver-coated fabrics exhibited better protection against UV radiation owing to the nano-silver absorption in the near-UV region. Gorensek and Recelj (2007) observed similar increases in UV absorption when they functionalized cotton fabric with commercial nano-silver.

8.3.3 Easy-care finishes

If the critical surface tension of a solid fabric is greater than or equal to the surface tension of a liquid, the liquid will wet the fabric. If the critical surface tension of the solid is less than surface tension of the liquid, the fabric will repel the liquid. In the case of solids ‘critical surface tension’ is used instead of ‘surface tension’. Thus, water repellency can be attained when the critical surface tension of the solid is smaller than surface tension of the liquid. For example, when a drop of water is dripped on a cotton fabric, it has been experimentally determined that the surface tension of water and the critical surface tension of cotton are, respectively, 72 dyne/cm and 200 dyne/cm, and, therefore, water readily wets the cotton fibre. However, once the cotton is treated with a fluorocarbon the water-repellency relation between them changes. The critical surface tension of water-repellent-finished cotton is less than the surface tension of water. Fluorocarbons are organic compounds consisting perfluorinated carbon chain. They tend to decrease the surface tension of the substrate (Zabicky, 2006).

The self-cleaning of super-hydrophobic micro- to nanostructured surfaces was observed to be a property of some plants — one of which is nasturtiums (Tropaeolum sp.). In 1975, the researcher Wilhelm Barthlott, then at the University of Heidelberg, elucidated this phenomenon. Only at the beginning of the 1990s was it possible for W. Barthlott, and his collaborator Christoph Neinhuis (later Zdenek Cerman and others) to harness this physico-chemical phenomenon technically. Barthlott coined the trade name Lotus-Effect® for the patented self-cleaning super-hydrophobic micro- to nanostructured products and copyrighted it in 1997 (http://www.lotus-effekt.de/en/faq/index.php). Over millions of years of evolution nature has developed surfaces — the ideal example being the leaves of the lotus (Nelumbo nucifera) — which, through a complicated micro- to nano-scale surface structure, repel dirt (see Fig. 8.8). The surfaces concerned are those that, owing to their chemistry, are water repellent (hydrophobic). These particular properties, however, are not only determined by the chemistry but also, in particular, the micro- to nanostructure: in the ideal case this is composed of a bulky structure (5–10 µm in diameter) and a fine structure (10 nm to 5 µm) layered on top. Adhesion of particles to these surfaces is minimal because they touch only the tips of the surface
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8.8 Scanning electron micrograph of lotus leaf.

8.9 Lotus-Effect® removing the dirt particles from super-hydrophobic surfaces.

structure. The particles are washed away by water droplets, which roll off. As a result, the surfaces stay dry even during a heavy shower. Furthermore, the droplets pick up small particles of dirt as they roll, and so the leaves of the lotus plant keep clean even during light rain. The technical expression of these basic ideas is patented as the Lotus-Effect®, and the surface acquired the aspect shown in Fig. 8.9; Fig. 8.10 shows a scanning electron micrograph of a super-hydrophobic textile material.
Nanocrystalline TiO$_2$ coatings have received much attention as photocatalysts in practical applications such as environmental purification, deodorization, sterilization, antifouling and self-cleaning glass, owing to their high oxidizing ability, non-toxicity, long-term stability and low cost. Among the different crystalline phases of titania, anatase is reported to have the best performance. Daoud and Xin (2004) successfully grew anatase nanocrystallites on cotton fabrics and these fabrics could be made into self-cleaning clothes that tackle dirt, environmental pollutants and harmful microorganisms. In addition, they have reported (Qi et al., 2006) on the application of a transparent thin layer of nanocrystalline titania coating on cotton textiles using a dip-pad–dry-cure process. These titania-coated cotton textiles possess significant photocatalytic self-cleaning properties, such as bactericidal activity, colourant stain decomposition and degradation of red wine and coffee stains. Figure 8.11 shows a schematic representation of the photocatalytic behaviour of titania nanoparticles; organic compounds are degraded on exposure to UV light.

Another study (Bozzi et al., 2005) reported on radiofrequency plasma (RF-plasma), microwave plasma (MW-plasma) and vacuum-UV light irradiation as pretreatments for synthetic textile surfaces, allowing the loading of TiO$_2$ by wet chemical techniques in the form of transparent coatings constituted of nanoparticles of diverse sizes. These loaded textiles show a significant photo-oxidative activity under visible light in air under mild conditions, which discolours and mineralizes persistent pigment stains contained in wine and coffee. The mineralization of stains on the textile loaded with TiO$_2$ was monitored quantitatively to assess the appropriate surface pretreatment in conjunction with the most suitable deposition
method for TiO$_2$ colloids, powders, or a combination of both; their photocatalytic activity allowed, in kinetically acceptable times, the almost complete discoloration of coffee and wine stains. The observed discoloration of coloured stains seems to involve visible light sensitization of the stain pigment on the TiO$_2$-loaded textile. The size of the particles obtained from colloidal precursors of TiO$_2$ varied between 5 and 25 nm.

The rate of super-hydrophobicity is measured by determining the so-called ‘repellent power’, which was first introduced by Dr Keller, BASF, Germany, via the determination of the dynamic roll-off angle. The static dynamic contact angle used for the characterization of even surfaces such as foils is applicable to textiles only in special cases. Recently, a water-repellent nanocoating – consisting of TiO$_2$ nanoparticles together with a hydrophobic fluoromethylic copolymer coating – was demonstrated on cement plate and cotton fabrics. Seven parameters – including the type of nanoparticle, solid ratio, dispersion time, fluoro-binder ratio, distance between nozzle and substrate, spray direction and layer number – were considered according to the construction analysis. The Taguchi method and the analysis of variance indicated that solid ratio had an important effect on the water repellency of the surface, i.e. it showed the highest contribution percentage of 48.2% (Lin et al., 2006).

In order to prove the super-hydrophobic and self-cleaning effects of textile products, ITV Denkendorf (Germany) issues the quality mark ‘self-cleaning – inspired by nature’; this quality mark is issued based on the results of conventional testing methods and scanning electron microscopy (SEM) examination.
8.3.4 Other functional finishes

New-generation medical textiles are an important and growing field, requiring functional properties such as bacteriostatic, antiviral, fungistatic, non-toxic, high absorbance, non-allergic, breathable, haemostatic and biocompatible properties. Therefore, in addition to metal and metal oxide nanomaterials, nanoscale biological materials such as enzymes and drugs are necessary to add specific functionality to medical textiles (Petrulyte, 2008). Specialized nanomaterials functionalized with ligands can be introduced on the surface of cotton textiles with the aim of absorbing odours, providing strong and durable antibacterial properties, easing pain and relieving irritation. In addition, such value-added textiles could be of immense use in tissue engineering, drug delivery and protective clothing.

Nyacol® Nano-technologies Inc. has been the world’s leading supplier of colloidal antimony pentoxide which is used for flame-retardant finishes on textiles. It supplies colloidal antimony pentoxide as a fine particle dispersion for use as a flame-retardant synergist with halogenated flame retardants. The ratio of halogen to antimony ranges from 5:1 to 2:1. Green-shield®, a nanotech firm from Taiwan, has created an underwear that aims to eliminate odour. The underwear textile material releases undetectable negative ions and infrared rays that destroy the odour-causing bacteria; also, the far-infrared rays are absorbed by cells causing all the individual atoms to vibrate at a higher frequency, which speeds up the

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8.12 Design and electricity-generating mechanism of the fibre-based nanogenerator driven by a low-frequency, external pulling force. (a) Schematic of the experimental set-up of the fibre-based nanogenerator. (b) An optical micrograph of a pair of entangled fibres, one of which is coated with Au (in darker contrast). (c) SEM image at the ‘teeth-to-teeth’ interface of two fibres covered by nanowires (NWs), with the top one coated with Au. The Au-coated nanowires at the top serve as the conductive ‘tips’ that deflect/bend the nanowires at the bottom. (d) Schematic illustration of the teeth-to-teeth contact between the two fibres covered by nanowires. (e) The piezoelectric potential created across nanowires I and II under the pulling of the top fibre by an external force. The side with positive piezoelectric potential does not allow the flow of current owing to the existence of a reverse-biased Schottky barrier. Once the nanowire is pushed to bend far enough to reach the other Au-coated nanowire, electrons in the external circuit will be driven to flow through the uncoated nanowire due to the forward-biased Schottky barrier at the interface. (f) When the top fibre is further pulled, the Au-coated nanowires may scrub across the uncoated nanowires. Once the two types of nanowires are in final contact, at the last moment, the interface is a forward-biased Schottky, resulting in further output of electric current, as indicated by arrowheads. The output current is the sum of all the contributions from all of the nanowires, while the output voltage is determined by one nanowire.
metabolism and the elimination of wastes. This nanofinish could eliminate up to 99.99% of bacteria, 90% of odour and 75% of sticky moisture within the cloth as well as contributing to the overall health of the wearer.

Recently, a simple, low-cost approach has been reported (Qin et al., 2008) that converts low-frequency vibration/friction energy into electricity using piezoelectric zinc oxide nanowires grown radially around textile fibres. By entangling two fibres and brushing the nanowires rooted on them with respect to each other, mechanical energy is converted into electricity owing to a coupled piezoelectric–semiconductor process. This work establishes a methodology for scavenging light-wind energy and body-movement energy using fabrics. Figure 8.12 shows the design and electricity-generating mechanism of the fibre-based nanogenerator driven by a low-frequency, external pulling force.

Apart from silver nanofinishing for an antimicrobial finish, nanoparticles consisting of a drug either surrounded by a synthetic, polymer shell or contained within a synthetic, three-dimensional polymer matrix, at scales ranging from micrometric to nanometric, can be used for drug delivery in medical textiles. Encapsulation can be achieved by several methods, e.g. interfacial polymerization, microemulsion polymerization, precipitation polymerization and diffusion. In general, the drug is brought into contact with a set of monomers, oligomers or polymers. These assemble around the payload; polymerization will give the final particles. An alternative method is to prepare the nanoparticle in the absence of the drugs, which are then absorbed by the nanoparticles following afterwards (Soane et al., 2001). Another MIT (Massachusetts Institute of Technology) investigation is a cloth linking nanoparticles of gold in solution with strands of DNA coded to change colour when exposed to the DNA of biological agents, so your shirt could detect low doses of chemicals in the air, for instance, or your dressing gown could diagnose viruses like flu or SARS (severe acute respiratory syndrome).

8.4 Commercialization of nanofinishing in textiles

The use of nanotechnology-based finishes to enhance the performance of textiles made from natural fibres (including cotton, wool and silk) and also from synthetic fibres (such as polyester and nylon) is growing fast. The Lotus Effect® has been emulated in textiles using nanotechnology. In the NANO-CARE® technology of Nano-Tex, LLC, USA, the textile is embedded with billions of nanowhiskers of 10 nm in length. These nanowhiskers cover the textile, making it so dense that liquids can hardly penetrate. In the NanoSphere® technology of Schoeller Textiles AG, Switzerland, a special three-dimensional surface structure of nanospheres 1–100 nm in size is created in textiles, limiting the available contact surface for dirt particles; the NanoSphere® finishing process renders fabric water and dirt repellant and anti-adhesive. Major companies involved in the nanofinishing of textiles include:
(a) Nano-Tex, LLC, USA;
(b) Texcote Technology Ltd, Sweden;
(c) Schoeller Textiles AG, Switzerland;
(d) Beijing Zhong-Shang Centennial Nano-Tech Co. Ltd, China.

To date, the world’s 20 largest textile mills have acquired licensing for Nano-Tex technology. Products provided by Nano-Tex are:

- NANO-CARE® for stain resistance, wrinkle resistance and liquid repellency on cotton;
- NANO-PEL™ for fabric that breathes, yet remains liquid- and stain-repellent;
- NANO-DRY® for enhanced fabrics able to move perspiration away from the body, while drying quickly;
- NANO-TOUCH™, which gives man-made fabrics the feel and comfort of natural fabrics;
- Another product designed to capture body odor, i.e. NANO-FRESH™.

Nanotechnology, although still very much in its infancy, is already proving to be a useful tool for improving the performance of textiles. With increased performance comes added value and additional revenue. One company to realize this has been the Burlington Industries subsidiary, Nano-Tex. Branded as one of the ‘coolest’ products in 2003 by Time Magazine, Nano-Tex is providing clothing manufacturers such as Levi’s, Eddie Bauer, Gap and Old Navy the means to make their products more durable, more water and oil repellent, and more stain resistant, while also reducing the need for washing – all without altering the feel of the fabric. Nano-Tex’s chemical formulation and application technology, which is easily adopted by existing textile mills, changes the fabric itself on a molecular level, embedding it with tiny, floppy, hair-like fibres that themselves are attached to a common spine. The ‘nanowhiskers’ in the chemical mix prevent stains from soaking into clothing. Nano-Tex is said to have plans to expand its product range to include stain-proof mattresses, boat covers and hotel bedding. Looking at the previously stated definition of nanotechnology it could be argued that Nano-Tex’s technology is not really nanotechnology but improved chemistry; however the company is realizing a profit while other ‘proper’ nanotechnology companies are still waiting and dreaming.

Toray Industries, Inc. developed a nanoscale processing technology that allows the molecular arrangement and molecular self-assembly that are necessary to bring about further advanced functionalities in textile processing. This technology is named ‘NanoMATRIX’, in which a functional nanoscale material coating is applied to each of the monofilaments that forms a woven or knitted fabric. Application of this technology is expected to lead to the development of new functionalities, the creation of complex functionalities, remarkable improvements in the existing functions (quality, durability, etc.) and expansion of usage in terms of materials/applications without losing the fabric’s texture.
8.5 **Strengths and weaknesses of nanotechnology for surface modification**

Microbes are developing an important role in manufacturing systems owing to their ability to synthesize and accumulate metal nanoparticles; they have been used experimentally to remove metal nanoparticles from effluent. The silver nanoparticles in the effluent from a cotton nanofinishing process could be removed efficiently by the use of *Chromobacterium violaceum* (Duran *et al.*, 2007), which is able to absorb, metabolize or store metal ions, and thus environmental damage will be avoided. With the onset of the Industrial Revolution, concerns relating to public health and safety and the environment have resulted in increasingly stringent environmental regulations (Theodore, 2006). Hence, there is a need for the development of fully-fledged norms and regulations for the use of nanomaterials and their disposal in the environment. In the case of textiles, it will be of great concern that both the finished product and the effluent will comply with these regulations. Since textile products have the closest interaction with our body, they must be evaluated for their toxicology and tolerance levels.

8.6 **Future trends**

Nanotechnology overcomes the limitations of conventional methods when imparting various functional properties to textile materials. Those functional properties are of the highest importance, and give noticeable improvements in the wear comfort and care. Despite great research effort into the nanofinishing of textiles, their commercial exploitation has only just begun. The main emphasis in the application of nanotechnologies to textiles will be to (Holme, 2005):

- improve the properties and performance of existing materials;
- develop smart and intelligent textiles with novel functions;
- greatly increase the use of fibres in technical textiles, biomedical textiles and healthcare applications;
- open up new opportunities for fibres as sensors.

8.7 **References**

AATCC (2006) Test Methods, 183-2006 and 61-2006, in *AATCC Technical Manual*, The American Association of Textile Chemists and Colorists, IHS, Englewood, Colorado.

Binnig G, Quate C F and Gerber C H (1986), ‘Atomic force microscope’, *Phys Rev Lett*, 56, 930–933.

Binnig G, Rohrer H, Gerber C and Weibel E (1982), ‘Surface studies by scanning tunneling microscopy’, *Phys Rev Lett*, 49, 57–61.

Bozzi A, Yuranova T and Kiwi J (2005), ‘Self-cleaning of wool-polyamide and polyester textiles by TiO$_2$-rutile modification under daylight irradiation at ambient temperature’, *J Photochem Photobiol A: Chem*, 172, 27–34.

Bradley J S (1994), in Schmid G (Ed.), *Clusters and Colloids: From Theory to Applications*, VCH, Weinheim, p. 459.
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CAO G (2004), *Nanostructures and Nanomaterials – Synthesis, Properties and Applications*, Imperial College Press, London.

CAPASSO F (1987), ‘Band-gap engineering: from physics and materials to new semiconductor devices’, *Science*, **235**, 172–176.

DAOUD W A and XIN J H (2004), ‘Synthesis of single phase anatase nanocrystalline at near room temperature’, *J Am Ceram Soc*, **87**, 953–955.

DURAN N, MARCATO P D, SOUZA G I H D, ALVES O L and ESPOSITO E (2007), ‘Antibacterial effect of silver nanoparticles produced by fungal process on textile fabrics and their effluent treatment’, *J Biomed Nanotechnol*, **3**, 203–208.

GORENSEK M and RECELI P (2007), ‘Nanosilver functionalized cotton fabric’, *Textile Res J*, **77**(3), 138–141.

HABERZETTL C A (2002), ‘Nanomedicine: destination or journey’, *Nanotechnology*, **13**, R9–R13.

HOLME I (2005), ‘Nanotechnologies for textiles, clothing, and footwear’, *Textiles Mag*, **1**, 7–11.

HUSTVEDT G and CREWS P C (2005), ‘The ultraviolet protection factor of naturally pigmented cotton’, *J Cotton Sci*, **9**, 47–55.

JIANG S Q, NEWTON E, YUEN C W M and KAN C W (2006), ‘Chemical silver plating on cotton and polyester fabrics and its application on fabric design’, *Textile Res J*, **76**(1), 57–65.

KIM Y K, RICE J M, LANGLEY K D, LEWIS A F, SEYAM A, PAWAR S and KUMBHANI M (2002), National Textile Center Annual Report MOOD08, http://www.ntcresearch.org/pdf-rpts/AnRp08/F08-MD01-A8.pdf.

LEE H J and JEONG S H (2005), ‘Bacteriostasis and skin innocuousness of nanosize silver colloids on textile fabrics’, *Textile Res J*, **75**(7), 551–556.

LEE H J, YEO S Y and JEONG S H (2003), ‘Antibacterial effect of nanosized silver colloidal solution on textile fabrics’, *J Mater Sci*, **38**, 2199–2204.

LIN T S, WU C F and HSIEH C T (2006), ‘Enhancement of water-repellent performance on functional coating by using the Taguchi method’, *Surface and Coat Technol*, **200**(18–19), 5253–5258.

PETRULYTE S (2008), ‘Advanced textile materials and biopolymers in wound management’, *Danish Med Bull*, **55**(1), 72–77.

POREL S, VENKATRAM N, RAO D N and RADHAKRISHNAN T P (2007), ‘In situ synthesis of metal nanoparticles in polymer matrix and their optical limiting applications’, *J Nanosci Nanotechnol*, **7**, 1887–1892.

QI K, DAOUD W A, XIN J H, MAK C L, TANG W and CHEUNG W P (2006), ‘Self-cleaning cotton’, *J Mater Chem*, **16**, 4567–4574.

QIN Y, WANG X and WANG Z L (2008), ‘Microfibre–nanowire hybrid structure for energy scavenging’, *Nature*, **451**, 809–813.

SOANE D S, OSFORD D A, WARE W JR, LINFORD M R, GREEN E and LAU R (2001) Worldwide Patent WO 0106054 A1.

SONDI I and SALOPEK-SONDI B (2004), ‘Silver nanoparticles as antimicrobial agent: a case study on E. coli as a model for Gram-negative bacteria’, *J Colloid Interface Sci*, **275**, 177–182.

THEODORE L (2006), Environmental regulations, in *Nanotechnology: Basic Calculations for Engineers and Scientists*, Chapter 21, Wiley-Interscience, USA, p. 333.

TILLER J C, LIAO C J, LEWIS K and KLIBANOV A M (2001), ‘Designing surfaces that kill bacteria on contact’, *Proc Natl Acad Sci USA*, **98**, 5981–5985.
VIGNESHWARAN N, KATHE A A, VARADARAJAN P V, NACHANE R P AND BALASUBRAMANYAR H (2007), ‘Functional finishing of cotton fabrics using silver nanoparticles’, *J Nanosci Nanotechnol*, 7, 1–5.

VIGNESHWARAN N, SAMPATH KUMAR T S, KATHE A A, VARADARAJAN P V, VIRENDRA PRASAD (2006), ‘Functional finishing of cotton fabrics using zinc oxide–soluble starch nanocomposites’, *Nanotechnology*, 17, 5087–5095.

WANG X, ZHUANG J, PENG Q AND LI Y (2005), ‘A general strategy for nanocrystal synthesis’, *Nature*, 437, 121–124.

WU C, QIAO X, CHEN J, WANG H, TAN F AND LI S (2006), ‘A novel chemical route to prepare ZnO nanoparticles’, *Mater Lett*, 60, 1828–1832.

ZABICKY J (2006), ‘Textiles stain repellency and self cleaning’, Advanced Materials Engineering, Zvi Reinstein, http://portal.jce.ac.il/courses/nano/Nanomaterials%20Projects/Self-cleaning%20textiles.pdf.