Review

A review on the application of inorganic nano-structured materials in the modification of textiles: Focus on anti-microbial properties

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Textiles can provide a suitable substrate to grow micro-organisms especially at appropriate humidity and temperature in contact to human body. Recently, increasing public concern about hygiene has been driving many investigations for anti-microbial modification of textiles. However, using many anti-microbial agents has been avoided because of their possible harmful or toxic effects. Application of inorganic nano-particles and their nano-composites would be a good alternative. This review paper has focused on the properties and applications of inorganic nano-structured materials with good anti-microbial activity potential for textile modification. The discussed nano-structured anti-microbial agents include TiO₂ nano-particles, metallic and non-metallic TiO₂ nano-composites, titania nanotubes (TNTs), silver nano-particles, silver-based nano-structured materials, gold nano-particles, zinc oxide nano-particles and nano-rods, copper nano-particles, carbon nanotubes (CNTs), nano-clay and its modified forms, gallium, liposomes loaded nano-particles, metallic and inorganic dendrimers nano-composite, nano-capsules and cyclodextrins containing nano-particles. This review is also concerned with the application methods for the modification of textiles using nano-structured materials.

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1. Introduction

Parallel to immediate improvement of human living, control of harmful effects of micro-organisms would be necessary. A broad range of micro-organisms coexists in a natural equilibrium with human body and living environments, but a rapid and uncontrolled fast thriving of microbes can lead to some serious problems [1–3]. Anti-microbial agents are used to prevent three undesirable effects in textiles. The first includes the degradation phenomena like coloring, staining and deterioration of fibers [4–6]. Because of their dye fastness in textiles. The second one produces unpleasant odor [8–10] and the third effect is the increase of potential health risks [11–13]. The conventional fibers and polymers not only show no resistance against micro-organisms and materials generated from their metabolism but also are most commonly prone to accumulation, multiplication and proliferation of micro-organisms into their surrounding environment. In fact, several factors such as suitable temperature and humidity, presence of dust, soil, spilled food and drink stains, skin dead cells, sweat and oil secretions of skin gland, also finishing materials on the textile surfaces can make textile optimal enrichment cultures for a rapid multiplication of micro-organisms [6,14]. Regarding to rapid improvement of hygienic living standard, controlling of aforementioned terrible effect is necessary. Therefore, many researches have focused on the anti-bacterial modification of textiles [15–50].

Recently, using natural material has been preferred for textile modification because of possible harmful or toxic effects of many chemical anti-microbial agents [51].

Application of inorganic nano-particles and their nano-composites would be a good alternative [52–54] and consequently, they can open up a new opportunity for anti-microbial and multi-functional modification of textiles. This review paper is concerned with properties and application methods of inorganic nano-structured materials with good potential of anti-microbial activity and their nano-composites for textile modification.

2. Classification of inorganic-based nano-structured materials

Nano-structured materials on the basis of inorganic active agents having good potential for anti-microbial activity on textile materials, can be categorized in two main groups (Fig. 1):

(1) Inorganic nano-structured materials and their nano-composites.

(2) Inorganic nano-structured loaded organic carriers.

The inorganic nano-structured materials include titanium dioxide, silver, zinc oxide, copper, gallium, gold nano-particles, carbon nanotubes, nano-layered clay, and their nano-composites.

The inorganic nano-structured loaded in organic materials include cyclodextrin loaded with inorganic materials, nano- and micro-capsules having inorganic nano-particles, metallic dendrimer nano-composites and inorganic nano-particles loaded in liposomes.

Note that categories such as loaded cyclodextrins, metallic dendrimer nano-composites and loaded liposome can be included in nano-capsules. However, each one has an especial concept, history, architecture and properties. Thus, in this review, they have been discussed in separate groups.

2.1. Inorganic nano-structured materials and their nano-composites

The most applicable inorganic nano-structured materials in this group can be classified as follows:


2.1.1. TiO₂ nano-particles

Currently, TiO₂ nano-particles have created a new approach for remarkable applications as an attractive multi-functional material. TiO₂ nano-particles have unique properties such as higher stability, long lasting, safe and broad-spectrum anti-biosis [55–58]. TiO₂ nano-particles have been especially the center of attention for their photo-catalytic activities [59–68]. This makes TiO₂ nano-particles applicable in many fields such as self-cleaning, anti-bacterial agent, UV protecting agent [69], environmental purification [70], water and air purifier [71,72], gas sensors, and high efficient solar cell [73–75]. The photo-activity property is strongly related to the structure, micro-structure and the powder purification [73–75].

Three famous crystalline structures for TiO₂ have been known as anatase (tетragonal, a = 0.3785 nm, c = 0.9514 nm, band gap = 3.2 eV which is equivalent to a wavelength of 388 nm), rutile (tetragonal, a = 0.4593 nm, c = 0.2959 nm, band gap = 3.02 eV) and brookite (orthorhombic, a = 0.9182 nm, b = 0.5456 nm, c = 0.5143 nm, band gap = 2.96 eV) [74,76–80].

Anatase is metastable at lower temperatures and is most applicable in catalysis and photo-catalysis because of its higher surface area [81]. The anatase form of titanium dioxide has a more photocatalytic activity than rutile [57]. Titanium dioxide irradiation by light with more energy compared to its band gaps generates electron–hole pairs that induce redox reactions at the surface of the titanium dioxide. Consequently, electrons in TiO₂ jump from the valence band to the conduction band, and the electron (e⁻) and electric hole (h⁺) pairs are formed on the surface of the photo-catalyst. The created negative electrons and oxygen will combine into O₂⁻, the positive electric holes and water will generate hydroxyl radicals. Ultimately, various highly active oxygen species can oxidize organic compounds of cell to carbon dioxide (CO₂) and water (H₂O). Thus, titanium dioxide can decompose common organic matters in the air such as odor molecules, bacteria and viruses [6,57,82].

The rutile is thermodynamically more stable than the anatase and brookite. At high temperature, the anatase and brookite are
converted to the rutile. Rutile has a direct band gap but anatase has an indirect band gap based on band structure calculation. Rutile is the mostly used form in the pigments industry. The band-gap energy of anatase is higher than that of rutile. However, a wide range of band-gap energies have been recorded for both anatase and rutile crystalline structure [74]. Addition of Zr$^{4+}$ and Si$^{4+}$ into the titania structure increases the anatase stability and the anatase to rutile transformation (ART) [81].

A number of techniques have been employed for production of TiO$_2$ nano-particles. One of the most common methods is the sol–gel processing [83]. Fu et al. have applied the sol–gel method to fabricate nano-particles of TiO$_2$ in its anatase form. The particle size is reported to be sensitive to solution pH and the rate of addition of isopropoxide [57].

Titanium dioxide nano-particles have been used to achieve anti-bacterial [57,84–86], self-cleaning [87–89], UV-protection [69], hydrophilic [90] or ultra-hydrophobic properties [91], dye degradation in textile effluent [92] and as a nano-catalyst for cross-linking cellulose with poly carboxylic acids [93–96].

2.1.1.1. Metallic TiO$_2$ nano-composites. Since TiO$_2$ has a relatively high energy band gap (3.2 eV), TiO$_2$ nano-particles can only be excited by high energy UV irradiation with a wavelength shorter than 387.5 nm. Many investigations confirm that the addition of noble metals such as gold and silver increases the photo-catalytic activities of titanium dioxide by extending the light absorption range of TiO$_2$ from UV to visible light [57,97–99]. As an example, Ag can act as the electron traps aiding electron–hole separation, and also facilitates electron excitation by creating a local electric field [100]. When the achievements of anti-bacterial activity are considered, surface coating of nano-silver on titanium dioxide also maximizes the number of silver nano-particle per unit area on the surface compared to using equal mass fraction of pure silver (Fig. 2) [101,102]. Moreover many researchers have tried to increase the attainable surface activation sites by either using nano-crystalline materials or making porous micro-structure. Thus, the photo-catalytic performance can be enhanced [103].

Kim et al. employed hydrazine hydrate as a reducing agent for deposition of Ag nano-particles via chemical reduction on the surface of TiO$_2$ nano-particles. Silver with a particle size of 5 nm had been formed on the TiO$_2$ surfaces. By increasing the Ag fraction, the UV–vis absorption spectrum shifted to long wavelengths (>400 nm) resulting from the interaction of Ag and TiO$_2$ particles. Enhancement of anti-bacterial activity under radiation using a fluorescent lamp in the Ag-deposited TiO$_2$ nano-particles compared to pure TiO$_2$ nano-particles and Ag-coated TiO$_2$ particles has been confirmed [103].

The TiO$_2$ zeta potential has not been affected by silver modification. The point of zero charge for TiO$_2$ and TiO$_2$/Ag is the same and is fixed at pH of 5.6. Consequently, electrostatic properties and interaction with other materials on their surfaces should not be affected. Maximum photo-catalytic activity has been reported at pH 3.5 [65].

2.1.1.2. Non-metallic TiO$_2$ nano-composites. Zhao et al. have reported that adding an optimum weight ratio of hydroxyl propyl cellulose (HPC) to TiO$_2$ nano-particles can improve the photo-induced hydrophilicity and the photo-catalytic activity of the TiO$_2$ film [95]. Anti-UV and other physical properties of TiO$_2$/chitosan nano-composite have been reported by Hsieh et al. [105].

The production of Pt/TiO$_2$ [100], TiO$_2$/chitosan nano-composites [105], TiO$_2$/SiO$_2$ [106], CNTs–TiO$_2$ composites [107–109], TiO$_2$–hydroxyapatite [110] and many others has also been reported.

2.1.1.3. Titania nanotubes (TNTs). Nanotubues have a large surface area. Titania nanotubes (TNTs) have large surface area and particular tubular structure. In addition, their potential breakthrough in high efficient dye-sensitized solar cells has been mentioned [111]. The decomposition of gases [63], effects of electronic field on optical properties of nano-TiO$_2$ [93], their structural and optical properties [74], effects of UV irradiation on hydrophilicity of TiO$_2$ treated fabric [90], anti-creasing of cellulose with multi-functional organic acid (carboxylic acids) using catalytic effects of TiO$_2$ under UV irradiation [93] and UV protecting effect of TiO$_2$ for fabric [69] have been explored.

2.1.2. Silver nano-particles

Since ancient times among various anti-microbial agents, silver has been most extensively studied and used to fight against infections and prevent spoilage [112]. At present, many researchers have focused on anti-bacterial and multi-functional properties of silver nano-particles [112–115]. Various methods have been employed for nano-silver production. Photo-catalytic reduction [97], chemical reduction process [116] photo-chemical or radiation–chemical reduction, metallic wire explosion, sono-chemical, polyols [113], matrix chemistry [117], photo-reduction [118], reverse micelle-based methods [119] and even biological synthesized [120–124], have been applied for the preparation of silver nano-particles. Silver is a safer anti-microbial agents in comparison with some organic anti-microbial agents [6] that have been avoided because of the risk of their harmful effects on the human body [51]. Silver has been described as being ‘oligo-dynamic’ because of its ability to exert a bactericidal effect on products containing silver, principally due to its anti-microbial activities and low toxicity to human cells [102]. Its therapeutic property has been proven against a broad range of micro-organisms [125,126], over 650 disease-causing organisms in the body even at low concentrations [114]. The ability of silver to prevent bio-film formation has also been proven [127]. Similar mechanism has been quoted for silver ions and nano particles [125].

Silver nano-particles are a non-toxic and non-tolerant disinfectant [128–130]. Using silver nano-particles leads to increase in number of particles per unit area and, thus, anti-bacterial effects can be maximized [131]. The brief explanation of its anti-microbial mechanism can be explained as follows: Generally, metal ions destroy or pass through the cell membrane, and bond to the –SH group of cellular enzymes [132]. The consequent critical decrease of enzymatic activity causes micro-organism metabolisms change and inhibits their growth, up to the cell’s death. The metal ions also catalyze the production of oxygen radicals that oxidize molecular struc-
ture of bacteria. The formation of active oxygen occurs according to chemical reaction (1)

\[ H_2O + \frac{1}{2}O_2^{\text{Metal ion}} \rightarrow H_2O_2 \rightarrow H_2O + (O) \] (1)

Such a mechanism does not need any direct contact between anti-microbial agent and bacteria, because the produced active oxygen diffuses from fiber to the surrounding environment. Therefore, metal ions inhibit the multiplication of micro-organisms. Bacteria are not permanently exposed to oxygen radicals and, thus, the ionic additive does not seem to facilitate the selection of resistant strains [6,133].

Silver ions can lead to denaturing of protein and cell death because of their reaction with nucleophilic amino acid residues in proteins, and attach to sulphydryl, amino, imidazole, phosphate and carboxyl groups of membrane or enzyme proteins [134]. Respiration blocking and cell death also may be caused by forming R–S–S–R bonds [135,120]. Kumar et al. have proposed these bonds may be formed via reaction between silver in oxidic form and sulphydryl (–S–H) groups [135]. Silver is also known to inhibit a number of oxidative enzymes such as yeast alcohol dehydrogenase, the uptake of succinate by membrane vesicles and the respiratory chain of Escherichia coli, causing metabolite efflux and interfering with DNA replication [136]. Silver can associate with the cell wall [137], cytoplasm and the cell envelope [138]. Attachment of Ag ions or nano-particles to the bacteria because of electrostatic interaction with negative charge of bacterial cell wall is known as one of the mechanisms of cell death by Ag via rupturing cell membrane [120,125]. Generally, low concentrations of Ag⁺ induce a massive proton leakage through the bacterial membrane and cell death [5,6,139]. Moreover, nanomolar concentration of silver nano-particles can be efficient while Ag ions are needed at the micromolecular level [125]. Recently Kim et al. suggested that the anti-microbial mechanism of Ag nano-particles is related to the formation of free radicals and subsequent free radical-induced membrane damage. They confirmed that the anti-microbial activity of Ag nano-particles and silver nitrate was influenced by NAC (N-acetylcysteine). They have also suggested that free radicals that might have been derived from the surface of Ag nano-particles were responsible for the anti-microbial activity through ESR (electron spin resonance) [133].

Investigation of bio-innocuousness of silver revealed that smaller-sized silver particles are less toxic to skin than larger ones at the same level of concentration. Although a small irritation has been reported by applying the colloidal silver with 30 nm particle size, the colloidal silver with 2–3 nm particle size has been known to be innocuous [140].

Pape et al. developed an activated carbon fibre after-treated with nano-silver [141]. Yeo et al. applied silver nano-particles to produce anti-bacterial as-spun mono-filament yarns [115].

da Silva Paula et al. have reported the influence of nano-silver introduction into poly(styrene-co-acrylic acid) copolymer on anti-bacterial activity. They believe that the carboxylic groups of acrylic acid lead to increased ionic mobility in the copolymer responsible for the enhanced antibacterial surface activity of the copolymer [142]. Fernández et al. have developed the silver nano-particles on cellulose fibers used as the absorbent pad. They immersed fluff pulp and nano-structured lyocell fibers in silver nitrate and subsequent transformation to silver nano-particles have been done by physical (thermal or UV) or chemical (sodium borohydride) methods [143].

The effect of silver [144] and silver nano-particles on the electrical conductivity of polymeric matrices [145–149], improvement of UV protection properties [146] and the effect of dyeing on the ultra-violet protection factor (UPF) [150] have also been investigated. Producing silver nano-wires has been expanded by Sun et al. [151].}

llic et al. have described the anti-fungal efficiency of pretreated polyester and polyamide fabrics treated with Ag nano-particles [152].

2.1.2.1. Silver-based -nano-structured materials. In addition to silver, silver-based anti-bacterial agents are of interest to the researchers. Silver chloride nano-crystals have been synthesized on silk fibers by sequential dipping in AgNO₃ and NaCl. Anti-bacterial properties of AgCl crystal have been pointed [153].

Nano-sized Ag/PVP composite has also received considerable attention because of having the best protecting properties of poly (N-vinyl pyrrolidone) [151,154–157]. The N and O atoms of its amide group probably have a strong affinity for the silver ions and metallic silver [155]. Many advantages such as non-toxicity, biocompatibility, high hydrophilicity, good complexity, anti-microbial activity [16], acceptable solubility in water and most organic solvents and good processability have made it suitable for a wide variety of applications especially in bio-medical fields and hold great promises as a protective agent for silver nano-particles [158,159]. Anti-bacterial efficiency Ag/SiO₂ grafted on wool has been investigated by Wang et al. [160]. Oh et al. have also prepared Ag/SiO₂ and investigated its antibacterial and antifungal effectiveness [161]. Fu et al. have produced multi-layer composite films from heparin/chitosan/nano-silver for bio-medical applications [162].

Twu et al. extended a method on the basis of using a basic chitosan suspension with simultaneous stabilizing and reducing effect to synthesize silver/chitosan nano-composites from an aqueous AgNO₃ solution [163]. Jeong et al. applied an Ag–sulfur composition and observed that addition of sulfur enhances the anti-bacterial properties and the stability of Ag ions. They emphasized that the Ag–sulfur composite is non-toxic though sulfur is a toxic agent [126]. Silver nano-silver colloidal solution (SNS), having Ag/S complex has also been used by Kim et al. for functionalization of wool [164]. Silver/sodium carboxy methyl cellulose has been designed for burn wound bandages [165].

Considering large surface and strong adsorption properties of hydroxyapatite nano-ribbon to adsorb bacteria and high bioactivity of silver nano-particles, the hydroxyl apatite nano-ribbon spheres containing nano-silver have been successfully prepared by Liu et al. [166]. Hydroxyapatite/silver composite coating has been designed particularly for reducing bacterial infections after implant placement [167]. Bio-activity, dissolution range, and sorption properties, which are close to those of natural bones, have presented hydroxyapatite and its composites as good candidates for wide applications in coating artificial joints and tooth roots [166].

Silver nano-particle loaded poly(methyl methacrylate) microspheres have also been produced [168]. Kim et al. used in situ deposition of silver onto porous poly (ethylene glycol dimethacrylate) microspheres. Hydroxy groups of poly (EGDMA) microspheres play a key role in controlling the degree of deposition of colloidal silver [169].

2.1.3. ZnO nano-particles and nano-rods

Recently, ZnO has been found highly attractive because of its remarkable application potential in solar cells, sensors, displays, gas sensors, varistors, piezoelectric devices, electro-acoustic transducers, photo-diodes and UV light emitting devices, sun-screens, gas sensors, UV absorbers, anti-reflection coatings, photo-catalysis and catalyst [170–181]. Potentiality of ZnO for removing dye from textile effluent under UVC light has been proved by Behnajady et al. [173].

ZnO is an n-type semi-conductor as well as TiO₂. Only these two metal oxides, among the 3d transition metal oxide semi-conductor series, have sufficient stability on photo-excitation state. The band gap energy of ZnO is 3.37 eV. Their stability can be justified with
decreasing the possibility of electron–hole re-combination. This phenomenon is related to dissimilar parity of produced photo-excited electron–hole pair under UV irradiation [179].

ZnO nano-particles have some advantages, compared to silver nano-particle, such as lower cost, white appearance [179] and UV-blocking property [180]. ZnO powders can absorb infra-red light and infra-red electromagnetic wave with 5–16.68 dB in the range of 2.45–18 GHz [179]. ZnO is also used to reinforce polymeric nano-composites [179]. They also appeared for enhancement wear resistant phase and anti-sliding phase in composites as a consequence of their high elastic modulus and strength [181]. Li and colleagues have investigated the durability of anti-bacterial activity of nano-ZnO functionalized cotton fabric to sweat. They have treated cotton fabrics at a concentration of 11 g/L ZnO and padded them to 100% wet pick-up. The durability of anti-bacterial activity of the finished fabric in alkaline, acidic and inorganic salt artificial sweat solution has been evaluated. Results showed better salt and alkaline resistances than acid resistances for the treated fabrics [182]. A negative surface charge has been deduced for ZnO nanoparticles and illumination can increase anti-bacterial performance compared to normal conditions [182].

Tetrapod-like nano-particle ZnO was also used for producing acrylic composite resin [181]. ZnO nano-belts, nanowires, nanotubes and nanocages have also been produced by Pan et al. [170, 176–178]. Xu and Cai [183] have grown ZnO nano-rod on cotton fabric samples through the dip-pad-cure process [183]. However, the control mechanism of nano-rod growth has not been described. They have tried to cover the prepared nano-rod with a super hydrophobic agent to produce a cotton fabric with super hydrophobic properties based on the Cassie and Baxter theory (Eq. (2))

\[
\cos \theta = \frac{f_1 \cos \theta_1 - f_2 \cos \theta_2}{f_1 + f_2}\n\]

where \(f_1\) is the fraction of fluid area in contact with the substance, and \(f_2\) is the fraction of the fluid area in contact with air. \(\theta\) indicates the contact angle at a surface composed of solid and air. \(\theta_1\) and \(\theta_2\) are the corresponding water contact angles on smooth solid surface and vapor surface. The equation can be used for hydrophobic surfaces that trap air in the hollows of the rough surface and the liquid–air contact angle \((\theta_1)\) is 180° [183, 184].

2.1.4. Copper nano-particles

Copper nano-particles were embedded into submicron particles of Sepiolite (MgsSi2O3(OH)2(H2O)2·8H2O) and their anti-bacterial properties were compared with triclosan [185]. Cubillo et al. reported strong bactericidal properties for both composites and triclosan [185]. However, the observation of Pape et al. confirmed that copper nano-particles anti-bacterial activity is clearly less than that of silver nano-particles [141].

Magnetron sputter deposition of Cu nano-particles on the poly propylene (PP) nonwoven was used for the improvement of UV protection properties [186]. Wel et al. also found significant enhancement in electrical conductivity after Cu coating on the fabrics [186].

2.1.5. Nano-clay and its modified species

Many investigations are concerned with clay/polymer nano-composites. Outstanding advantages of polymeric clay nano-composites are derived from many researches. In this interesting field such as the increase of tensile strength, modulus, HDT, gas barrier property, transparency, flame retardancy and dimensional stability [187–212].

Anti-bacterial efficiency, sterilizing effect, adsorption of toxins and membrane coating are pointed out as some practical potential bio-medical applications of nano-clay [213].

The first research on the medicinal application of clay was recorded by Romanes in 60 BC. Clay was used as poultice in wound plaster. The physical absorption of water, toxic bacteria, viruses and organic matter are among the mainly known reasons for healing the properties of clay on the wound plaster. Metal elements such as silver, copper, manganese, zinc, iron as well as metal oxides such as titanium dioxide can also be associated with anti-bacterial properties of mineral clay. However, the mechanism of chemical interaction between clay and bacteria is not clearly known. The healing effect of French clay is confirmed in numerous case studies [214]. Williams et al. observed the complete sterilization of E. coli by Agricure clay [214].

Application of clay mineral was known from aboriginal antibiotic-susceptible and antibiotic-resistant pathogenic bacteria by Haydel et al. They used two iron-rich clay minerals to assess the feasibility of clay minerals treatment as therapeutic agents [215].

Seckin et al. extended a clay–poly vinyl pyridinium matrix for the removal of bacterial cells from water [216]. Hu et al. investigated the anti-bacterial effect of ion exchanged montmorillonite with Cu ions [217]. XNa groups of montmorillonite are known as the binding sites for ion exchange reaction [218]. Magâna et al. produced silver-modified montmorillonites via ion exchange with silver and assessed the anti-bacterial properties of the modified clay [219]. Zhou et al. synthesized polymer/silver-chitosan/clay nano-composite and evaluated the bacterio-static properties [220].

Mlynarcikova et al. and Pavlikova et al. successfully produced clay containing poly propylene fiber [191, 192]. An interesting observed phenomenon reported by Pavlikova et al. is that clay nano-layers are oriented parallel with fiber axes on the fiber surface without any polymer coverage [192]. Consequently, they can play as an anti-bacterial agent. However, the anti-bacterial properties of nano-layer structured organo-clay–loaded fiber matrix have not been reported.

2.1.6. CNT and its nano-composites

Extraordinary properties of CNTs have consistently attracted massive research interests [221, 222]. In fact, many special properties such as good electrical conductivity [223, 224], fire retardancy [221], UV protection [225], increasing garment comfort [225] high stiffness and high strength by using low content of CNTs in polymeric nano-composites have already been reported [221, 226, 227]. Noncovalent adsorption of organic dyes on the sidewalls of carbon nanotubes was investigated by Liu and co-workers [228].

The first evidence of the anti-microbial activity of CNT was reported for single-walled carbon nanotubes (SWNT) against E. coli by Kang et al. Cell membrane damage, caused by direct contact of bacteria cells and CNTs, is known as the CNT antibacterial mechanism [229]. On the basis of their next observation that involved compression of SWNT and multi-walled carbon nanotubes (MWNs), highly stronger anti-bacterial efficiency of SWNT compare to MWN against E. coli is emphasized [230].

The preparation of carbon nanotubes (CNT)/TiO2 nano-composites has also been reported [107–109]. A synergistic anti-bacterial effect using CNT/TiO2 nano-composites is expected. Unique architecture, high aspect ratio, and electrical properties of CNT have proposed it as an excellent photo-generated electron scavenging because of the multiple graphene layers where electrons can flow through, while contacting with a photo-catalyst. The work function of MCNT, required energy to transfer an electron can flow through, while contacting with a photo-catalyst. The work function of MCNT, required energy to transfer an electron to a point at infinite distance away outside, is approximately 5 eV, which is bigger than TiO2. Consequently, the photo excited electrons of TiO2 conduction band can be scavenged through CNT. Moreover, a high specific interfacial area, resulted by a high aspect ratio of CNT, causes an enhancement of electron trapping efficiency [108]. In addition, Oh et al. have claimed that this composite may gain quicker entry into cells and thereby pro-
2.1.7. Gold nano-particles

Gold nano-particles are known as a novel biomedical application. Their potent antibacterial effectiveness against acne or scurf and no tolerance to the antibiotic have caused their commercial usage in soap and cosmetic industries. They can remove waste materials from the skin and control sebum [233–236].

Zhang et al. have proposed the inhibit growth and multipli-
cations of different microbes with Au nano-particles efficiently against gram positive, gram negative and fungi [236].

Yonezawa and Kunitake have produced gold nano-particle sta-
bilized with sodium (3-mercaptopropionate) (MPA) via reduction of HAuCl₄ [234]. Grace and Pandian have used gold nano-particles as a carrier core coated antibiotics like streptomycin, gentamycin and neomycin. Their result proved that gold nano-composites have an intense antibacterial efficiency against various gram negative and gram positive bacteria, viz. *E. coli*, *Pseudomonas aeruginosa*, *Staphylococcus aureus* and *Micrococcus luteus*. They concluded that metal nano-particles may change the metabolite pathway and the release mechanism of bacterial cells. Therefore, a better antibac-
terial efficiency can be obtained as a result of the strong efficiency of the Au/drug nano-composites [235]. Park et al. loaded gold nano-particles inside the liposome [233]. They found that a lot of gold nano-particles filled in liposomes and existed in their edge. Loading nano-sized gold particles into the structure of liposomes lead to an increase in the fluidity and permeability of barrier of the lipid and provide a kind of thermally sensitive liposome. Consequently, these systems have potentially been suggested for controlled release delivery system at particular temperatures [233].

2.1.8. Anti-bacterial agents based on gallium

Valappil et al. [237] investigated the anti-bacterial properties of quaternary Ga₂O₃-doped PBGs with various concentrations. They reported that a concentration of 1 mol% Ga₂O₃ could provide a sufficient antibacterial efficiency and had a good potential promising therapeutic agent for pathogenic bacteria including MRSA and *Clostridium difficile*. Since ionic radius of Ga³⁺ is very similar to Fe³⁺, biological systems cannot distinguish these two ions. Therefore, Ga³⁺ can arrive to the cell as a substitute of Fe³⁺. However, Ga⁺⁺ is not able to play a key role as Fe⁺⁺ in cell metabolism. This phenomenon causes cell death [237].

A brief list of important characteristics of inorganic nano-
structured materials on the textile substrates is summarized in Table 1.

2.2. Inorganic nano-structured loaded organic carriers

Metallic and inorganic nano-structured materials can be loaded into different organic carriers, viz. liposomes, cyclodextrins, nano-
and micro-capsules and dendrimers.

2.2.1. Liposomes

Vesicle like self-assembled amphiphrile lipid dispersed in water is called liposome. Because of their amphiphilic structures, they can trap and carry both hydrophobic and hydrophilic materials. Liposomes have been used in drug-delivery systems (DDS) as a container for storage, transfer and controllable release of agents [238,239]. Liposomes are used for dyeing with several types of dyes and fibers for the reduction of processing temperature and saving energy [240–242]. Recently, the application of liposomes in textile processing has been reported by Barani and Montazer [241]. The size of liposomes changes in the range of nanometers to micrometers [240].

Park and co-workers have increased the fluidity and permeabil-
ity of the barrier of lipid via loading nano-sized silver and gold particles into the structure of liposomes. They emphasized that the silver nano-particles affect the release rate of some biological agents used in DDS from these thermally sensitive liposomes containing nano-particles [233,243].

It seems that loading inorganic nano-structured material into liposomes present an active agent that can act via control release mechanism for textile modification. However, in the case of applying this method, some practical cases should be mentioned. Thermal and mechanical stability of liposomes as well as the release of nano-structured materials should be determined. The liposomes should also have an active group to attach to textile substrate or stabilized on the fabric surface using different types of stabilizers. The purpose of using liposomes in textile industry is normally to carry different compounds towards textile substrate. Therefore, the resistance of liposomes against thermal, mechanical and chemical textile processing is necessary during some stages of production and usage. Synthesizing liposomes based on applying amino functionalized stabilizer has not been suggested for textile usage. The stability of liposome in alkaline condition of laundering should also be evaluated. On the other hand, the key factor required in this case is controlled release which needs to be approved. In the case of anti-
bacterial modification, phospholipid layers can act as a fertilizing agent to increase bacterial growth and, in this way exert a negative effect on anti-bacterial efficiency. However, this can be overcome by anti-bacterial effects of nano-silver [244]. Thermal stability of matrix and stabilizer in the autoclave condition (121 °C for 30 min), especially for medical usages of anti-microbial textiles should be dealt with.

2.2.2. Dendrimers

Dendrimers are a novel class of regularly branched 3D, man-made molecules produced by an unusual synthetic route incorporat-
ing repetitive branching sequences to create a unique novel architecture by an unusual and high level of uniformity of control the size [245–247]. Dendrimers can act as nano-reactors with the ability of pre-organization of metallic elements [248,249]. Atomic/molecular dispersion of the guest in a dendrimer host has created unique physical as well as chemical properties. The dendrimer carboxylate salts can carry high local concentrations of
silver as a result of a large number of active surface groups on dendrimers. Therefore, nanoscopic delivery vehicle can be provided via loading variable concentrations of bioactive materials such as metals and metal ions into dendrimers. The bio-compatibility of dendrimer conjugates has been confirmed by in vitro and in vivo experiments [247,249]. Metals can serve different position of dendritic architectures as terminal units, branching centers, building blocks, structural auxiliaries and connectors [250].

2.2.3. Nano-capsules

Nano- and micro-capsules as well as liposomes and dendrimers can be used for storage, carrying and delivery of active agents in different goals [251]. An innovative nano-encapsulation technology to achieve permanent anti-microbial efficiency on cotton fabrics has been presented by the Ciba Company. The commercial products based on this concept are now available under the label of Ciba Tinosan CEL [252].

In general, capsules are composed of a shell made up of natural or synthetic polymers and a core including appropriate materials such as different active agents, catalysts, vitamins, drugs, bioactive materials, proteins, deodorants and phase change materials (PCMs). The loaded agent may be dispersed at the core of the capsule or aggregated in its central part. In the case of PCM capsule, the shell should be resistant to surface pressure varieties resulted from volume changes of PCMs during phase changing. However, releasable capsules, utilized for carrying, delivering and controlled release of required active agents, should release loaded active agent via a repeatable controlled release mechanism. Recent groups should have a sensitive shell that can be excited for the release of required materials by changing the surrounding agents such as light, pressure and temperature [253,254]. It seems that decreasing the capsule sizes to nanocapsules can help mechanically the increase of the shell resistance to the pressure changes in encapsulated PCMs, and simultaneously intensify shell sensitivity of releasable capsules because of their effective surface enhancement. Moreover, nanocapsules are preferred for textile modification due to their smaller effect on the textile handles. Applying a high vigorous stirring or ultra-sonication can be helpful to achieve nano-sized emulsion [255]. Zhang et al. have found that the size and size distribution of capsules decrease with the increase of stirring rate (from 3000 to 9000 rpm) and content of emulsifier during encapsulation of n-octadecane. They emphasized on the effect of diameter on the crystallization behavior of PCMs [256].

Shim et al. have successfully encapsulated zinc oxide (ZnO) nano-particles in poly(methyl methacrylate) (PMMA) [257]. Oku et al. succeeded to synthesize encapsulated nano-silver via chemical reduction of silver nitrate with the aim of achieving at special electronic properties [258]. However, they did not report the evaluation of anti-bacterial efficiency of encapsulated nano-silver or nano-ZnO.

2.2.4. Cyclodextrin

Cyclodextrins (CDs) are a family of cyclic oligosaccharides composed of α-1,4-linked glucopyranose subunits. They are used as molecular complexation agents [259]. They are produced during the destruction process of starch by enzymatic degradation [260]. CDs are of three types: α-CD, β-CD and γ-CD composed of six, seven and eight α-1,4-linked glycosyl units, respectively. β-CD is the most accessible and useful one with lower price. The β-CD molecule is in the form of a horn or sugar loaf with a molecular weight of 1135 and a height of 750–800 pm. The internal diameter of the holes of these molecules is between 600 and 680 pm and their external diameter is 1530 pm [261,262]. The volume of holes is 260–263 Å³ and their dissolution is 1.85 g per 100 ml. water [260–263]. The internal section is hydrophobic and the external section is hydrophilic in nature [260]. The most notable feature of CDs is their ability to form molecular complexation with a wide range of solid, liquid and gaseous compounds (host–guest). They can be used in controlled release of perfumed materials and guest molecules from the cavity as a retarding effect in dyeing and finishing baths and as an absorbent of smell as well as a drug release in the textile industry [261–282]. Since fabrics are in direct contact with human skin, toxic specification of cyclodextrin has been studied [260]. Results indicate that they may be harmful to human body in very high concentrations [260]. Since November 13, 2000, β-CD has been introduced as a food additive in Germany. With respect to OECD experiments, this compound has shown no allergic impact [268–270].

Szejtli et al. reported the grafting of CDs onto cellulose fibers using epichlorohydrin as a cross-linking agent [273]. It has been claimed that incorporation of CDs into natural or synthetic materials by a physical means or by chemical paths involving CD derivatives carrying aliphatic and aromatic groups, chloro carboxylic acids, chloro amino and di methylol bifunctional compounds as linking agents. Besides, monochlorotriadanyl β-CD derivative is fixed onto different polymer materials including cotton fibers [274,275]. Furthermore, in a recent study, the possibility of permanently fixed CDs to cotton and wool fibers using poly carboxylic acids (PCA) as binding and cross-linking agents has been proposed [276]. Martel et al. [272] concluded that grafting occurred through the formation of a cross-linked copolymer between PCA and CDs. This copolymer was not covalently fixed to the fibers, but physically adhered or entangled into the fibrous network. They remarked that grafting was resistant to washing [272]. The polyester spacer fabric has been modified by β-CD and stabilized with citric acid [283]. Montazer et al. also loaded β-CD with sodium diclofenac for wound dressing purposes [282]. Moreover, CD has the potentiality of being loaded with nano-inorganic materials for carrying these nano-particles to textile materials through different processings and making them stabilized on the fabric surfaces using different cross-linking agents.

3. Textile modification methods

Considering special advantages and high potentialities of the application of nano-structured materials in textile industry, especially for producing high performance textiles, this paper reviews the application of nano-structured materials for anti-bacterial modification of textile and polymeric materials.

Modification of textiles via producing polymeric nano-composites and also surface modification of textiles with metallic and inorganic nano-structured materials are developed due to their unique properties. Considering the fact that fiber and film processing are the most difficult procedures of molding polymeric materials, bulk modification of continuous multi-filament yarns is an extremely sensitive process. However, achieving optimum process conditions will present an economical technique. Our previous researches have conducted the bulk modification of filament yarns with various concentrations of nano-composite fillers via melt mixing of the two different silver-based nano-composite fillers (silver/zinc and Ag/ TiO₂), and polymer powder in three different mixing methods (single and twin screw extruder as well as master batch preparation) that have been performed on a pilot plant scale and has a remarkable potentiality for mass production [6,101,102,284,285]. This technique is a high-quality, environmental-friendly and easily adjustable industrial modification method. However, it is limited to synthetic fiber and particles situated in the central part of the filaments not incorporated in the antibacterial performance. Although the production of core–shell bi-component fiber can be helpful to remove this disadvantage, the required systems are not common. The similar problem is also
noticeable in the case of reduction of metallic salts to nano-particles in the bulk polymeric matrix.

Different methods have been used for surface modifications of textiles. Meierert et al. have used poly carboxylic acids as spacers for attaching TiO₂ nano-particles to the fabrics [88]. Plasma pre-treatment has been used for the generation of active groups on the surface to be combined with TiO₂ nano-particles [87,286]. Wang et al. have used argon plasma grafting nano-particles on wool surface [160]. The radical groups on the surface have also been generated using irradiation of the textile surfaces with UV light to bond the nano-particles [287]. Yuranova et al. have deposited nano-particles from their metallic salt solution on the surface pretreated with RF-plasma and vacuum-UV [288]. Won et al. have produced nano-particles in the polymeric matrix via reducing metallic salts under the irradiation with UV light [289].

Sol–gel processing [68,84,290–293], loading nano-particles into liposomes [233,243], using nanoporous structure of cellulose fiber as a nano-reactor for in situ synthesis of metal nano-particles [99], sputtering of nano-particles during plasma polymerization [294], adding ion exchange functionalized surfactants in polymerization process [295] and conventional pad-dry-cure system (process) for the treatment of fabric with nano-sized colloidal particles [296] are among other used methods for the modification of polymeric substrates.

Potiyaraj et al. have designed a process to grow silver nano-particles via successive treatment of AgNO₃ and AgCl [153]. Perkas et al. have synthesized (incorporated) nano-particles into the PA66 chips via the reduction of AgNO₃ solution using ultrasound irradiation under Ar purge [297]. Jiang et al. used chemical pleating for functionalization of fabrics with nano-particles [146,147]. Goresek and Recelj have used a jet dyeing machine to exhaust nano-particles [150]. Dyeing process has also been applied as a simple way to exhaust CNTs [223]. Li and Sun used chemical oxidation for compatibilization nano-particles before the exhaustion procedure [298]. Graffiti organic compounds on the nano-particles has been applied for the compatibilization of inorganic nano-particles for mixing with the polymeric matrix [299]. Yuranova et al. used SiO₂ as a binder for TiO₂ cotton surfaces modification [106].

Mondal and Hu have coated fabrics with functionalized and dispersed CNTs in hydrophilic polyurethane (HPU) solution [225]. Perelstein et al. have reduced the silver ions to metallic silver on the fabrics under sonication and called sonochemical coating [36]. Jiang et al. prepared plasma aldehyde functional surfaces with the reduction ability of the silver ion to Ag nano-particles [300]. Poly electrolyte self-assembled multi-layers have been designed on the basis of interaction between oppositely charged sequential layers via layer-by-layer coatings [162,301–303]. Functionalization resin with metallic ion via ion exchange and then reduction of ion embedded in the matrix to the nano-particles has been presented by Maria et al. [304]. Montazer et al. also prepared the photo-stabilized wool fabric using nano-TiO₂ [305].

However, conventional surface modification of textiles with inorganic nano-particles is not permanent especially against washing. Most presented methods for stabilization of inorganic nano-structured materials on the textile surfaces need several preparatory steps including functionalization, neutralization, washing, drying, curing, final treatment and other processes. These processes are costly and very time-consuming for large-scale manufacturing and/or are hazardous for the environment because of the application of many chemicals or organic solvents. Most of them cause a reduction in tensile properties, softness, abrasion resistance, appearance and other practical properties of textiles even color changing. As an example, a method such as the irradiation of textile surfaces with UV light has been used to generate some radical groups on the surface that can bond with nano-particles [287]. Irradiation with UV light has also been applied to reduce metallic salts to nano-particles in the polymeric matrix [289]. Overlooking, economical disadvantages such as being costly and time-consuming, remaining of free radicals that can migrate to the surface during usage on clothing, leads to some health risks for people. Applying acrylic binder for fixation of zinc oxide/soluble starch nanoComposite particles on the cotton fabrics [179] reduces the comfort of the cloth and decreases the abrasion resistance. Moreover, possible decomposition of soluble starch or acrylic binder resin during autoclaving process should be put into consideration. Sufficient thermal stability in the autoclave condition (121 °C for 30 min) is an important factor, especially for medical usages of anti-microbial textiles. Most of the organic materials are limited to this property. Processes on the base of using ultra-sonication are accompanied with irritating sound pollution, heat risk and high level of energy consumption. To overcome these problems and develop an affordable method, we have proposed a new method for the stabilization of nano-structures on the textile surfaces. This technique is the embedding of silver nano-particles in a cross-linkable polysiloxane layer in combination with or after nano-finishing process. Polysiloxane treatment can create a polymeric layer on the fabric surfaces. This layer is stable against light, heat, chemical and microbial attacks. In this way, a dramatic control will be obtained in the rate of nano-structured release from the coating. Consequently, the long-term activity especially against home laundering is expected. Considering the metal ions (such as silver, zinc and nano-titanium dioxide) catalyzing the production of oxygen radicals that oxidize the molecular structure of bacteria, the protective layer applied for the stabilization of aforementioned nano-particles should be resistant to active oxygen [5]. Polysiloxane not only has such good resistance against oxygen radicals but also has many unique properties such as blood and biocompatibility, environmental friendliness, transparency, air permeability, comfort, softness, good releasability, flexibility, dimension stability, water repellency, tear resistance improvement, good durability against domestic laundering and dry cleaning as well as water and fire retardancy and anti-pilling [5,306–313]. These functional coatings are prone to major key promotion in performance and durability for technical and multi-functional textiles by applying the optimum mixture of nano-structured material. Cross-linkable polysiloxane treatment can be applied to all textiles and each nano-structure types. It is also adaptable to any substrate constructions. These special characteristics make the presented idea more valuable. For example, in a newer approach, we have designed an incorporated system for simultaneous texturing and yarn surfacing modification using nano-sized colloidal particles. We are developing this system to achieve permanent multi-functional textiles via applying the appropriate formulations of nano-structures and polysiloxane mixtures in designed two or three linked baths before the feeding rolls of the texturing machine [314] and following the aim of linking this system to the weaving and knitting machines. Consequently, this method has a remarkable potentiality for manufacturing scale-up production of all types of natural, synthetic and blended textiles systems.

4. Potentiality of health and environmental risks of nano-structured materials

Nano-particles have been introduced as the materials with good potentiality to be extensively used in biological and medical applications. They may be used as contrast agents for medical imaging, therapeutic drug delivery, labeling of cells, elimination of tumors, etc. [315,316]. Some evidence proved the safety of application of nano-structured materials. Some examples can be pointed out as follows: Skin-innoxiousness of nano-silver colloidal solution especially in the case of smaller nano-particles has been demonstrated
via the skin irritation test performed on the rabbits [140]. Non-toxicity of the interaction of nano-silver and the membrane surface has been proved by growing human fibroblasts on various concentrations of silver nano-particles [128]. Silver is mentioned as an almost non-toxic to mammalian systems [317] Incubation of astrocyte primary cultures with magnetic iron oxide nano-particles has also demonstrated that the particles do not induce any acute damage to these brain cells [316].

On the other hand, recently, with increasing the public knowledge about health care in the world, people are increasingly concerned about the rise of possible subsequent diseases caused by new technologies including nanotechnology and application of nano-materials especially inhalation during manufacturing or usage. About 30 organizations from different countries are investigating the potential risks of nano-structured materials with the aim of developing appropriate test methods to assess their possible side-effects on the human health and the environment. The toxic effect of inhalation CNT has been proved by in vivo testing [318]. Potential CNT health hazards, because of its similarity to asbestos fibers, have been also warned [319].

High dosage of inhalation nano-TiO2 can act as a pulmonary inflammation agent and be harmful for body tissues [316]. Although blood flow has been pointed out [318], skin contact of dermal titanium inflammation agent and be harmful for body tissues [316]. Although, they cannot reach the blood [318]. The pro-inflammatory effect of silver and inhaled TiO2, toxicity of inhaled silver, and also the possibility of allergic effects of TiO2 [319,320] should be also cautioned.

5. Remarks and outlooks

Inorganic and metallic-based nano-structured materials have created a new interesting field in all sciences for the continuous investigations due to their undeniable unique properties. Their applications have already led to the development of new practical productions. Considering the indubitable role of textiles in human life, these new fields in textile industry have been increasingly welcomed. However, designing new applicable and affordable techniques for manufacturing scale-up production will not only create a new field of study, but meet the expanding human requirements.

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