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Nanotechnology in textiles

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Nanotechnology in Textiles

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Nanotechnology in Textiles

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KEYWORDS: Nanotechnology; fashion; fabrics; fibers; nanoparticles; carbon nanotubes; graphene; energy storage; fiber optics; nanotoxicity

VOCABULARY: **Wearables** - electronics, fiber optics, or nanomaterials embedded in clothing and accessories that offer improved mechanical, chemical, optical performance via sensing external stimuli and/or responding to the environment; **Warp** - to arrange threads in long lengths parallel to one another preparatory to further processing; **Weft** - threads widthways in a fabric as woven; **Finishing** - a process performed on yarn or fabric after weaving to improve the look, performance, or texture of the finished textile; **Lotus effect** - self-cleaning due to hydrophobicility induced by nano or microscale hierarchical structured surfaces; **Supercapacitor** - an electrochemical cell that allows storing electrical energy temporarily; **Photonic bandgap material** - a nano or microscale structure that controls the optical properties of incident light; **Electromagnetic shielding** - blocking the electromagnetic field by conductive or magnetic materials; **Bragg fiber** - fiber optics incorporating Bragg gratings to filter narrow-band light

ABSTRACT

Increasing customer demand for durable and functional apparels manufactured in a sustainable manner has created an opportunity for nanomaterials to be integrated into textile substrates. Nanomoieties can induce stain-repellence, wrinkle-freeness, static elimination, and electrical conductivity to fibers without compromising their comfort and flexibility. Nanomaterials also offer a wider application potential to create connected garments that can sense and respond to external stimuli via electrical, color, or physiological signals. This Review discusses electronic and photonic nonotechnologies that are integrated with textiles, and shows their applications in displays, sensing and drug release within the context of performance, durability, and connectivity. Risk factors including nanotoxicity, nanomaterial release during washing, and environmental impact of nanotextiles based on life cycle assessments have been evaluated. This Review also provides an analysis of nanotechnology consolidation in textiles market to evaluate global trends and patent coverage, supplemented by case studies of commercial products. Perceived limitations of nanotechnology in the textile industry and future directions are identified.

The concept of clothing is undergoing a transformation through innovation in wearable technologies. Intelligent clothing has increasing presence in prominent fashion weeks in New York, London, and Paris. Fashion designers are creating functional materials and integrating emerging, communication devices, flexible electronics and nanomaterials to garments and designer clothes. For example, Philips designed a dress (*Bubelle*) that can tune its colors based on the wearer's mood. Black Eyed Peas has also embraced technology at stage, for example, they used organic light-emitting diode (OLED) based clothing and adaptive materials in their performances. Fashion and technology company Studio XO has created "digital mermaid bra," whose crystals sparkled in time to Azealia Banks' real-time rapping. Recently, TechHaus, the technical division of Haus of Gaga, has created a series of performance dresses for Lady Gaga's ARTPOP campaign (2013). Gaga's featured artworks included a three-dimensional (3D)-printed bubble machine dress (*Anemone*), a Jeff Koons-inspired design called the Parametric Sculpture Dress, a piece with animated black mirrors (*Cipher*), and a flying drone-dress (*Volantis*). Singers, artists, designers, and fashion icons have directed their interest to new materials that can stand out in public events and media. The designers that have pioneered the use of technology in fashion include Ralph Lauren, Diane von Furstenberg, Hussein Chalayan, Zac Posen, Rebecca Minkoff, Richard Nicoll, and Iris van Herpen.

Cotton is a widely used fiber type that exhibits high absorbency, softness, and breathability. However, the use of cotton in non-classical applications is limited since its fibers have relatively low strength, low durability, easy creasing and soiling, and flammability.[2] Synthetic fibers can be antimicrobial, stain/crease-resistant, but generally lack comfort as compared to cotton. The development of new fiber types that combine the advantages of both natural and synthetic fibers,

as well as offering novel functions has been desirable since the 1940s.[3] Customer demand for improved appearance color, shape, texture, and functionality has also increased.[4] Flexible electronics and optical devices can be integrated into textiles.[2] The applications of the functionalized textiles include medical monitoring of body function and metabolism,[5, 6] rehabilitation,[7] and electronic devices integrated into clothes.[8] Furthermore, these technologies allow integrating sensors into textiles.[9]

A new frontier in clothing technology is nanoengineered functional textiles.[10-12] The advantage of nanomaterials concerns creating function without altering the comfort properties of the substrate.[13] Textile is an universal interface and ideal substrate for the integration of nanomaterials, electronics, and optical devices. Such integrated materials and technologies offer a platform that responds to mechanical, chemical, electrical, thermal, optical, or magnetic stimuli. Such wearable devices may include sensors, data transmission, and processing units. These engineered materials should seamlessly integrate into garments, and be flexible and comfortable while having no allergic reaction to the body. Additionally, such materials need to satisfy weight, performance, and appearance properties (color). A significant challenge in the textile industry is that conventional approaches to functionalize fabrics do not lead to permanent effects. For example, laundering decreases imparted functional effects. Hence, nanotechnology can play a part to introduce new and permanent functions to fabrics. Textiles can be nanoengineered to have specific functions including hydrophobicity, antibacterial properties, conductivity, antiwrinkle properties, antistatic behavior, and light guidance and scattering (Figure 1). Using nanotechnology, these properties can be achieved without affecting breathability or texture. Such materials may be in the form of surface coatings, voided patterns, fillers, or foams.

Figure 1. Applications of nanotechnology in textiles

NANOENGINEERED TEXTILES

Water and Oil Repellence. Water repellence can be imparted to textiles by forming nanowhiskers consisting of hydrocarbons that are three orders of magnitude smaller than a typical cotton fiber. Nanowhiskers are integrated within the fabric to create a peach fuzz effect.[14] Analogous to the Lotus effect, the spaces between individual whiskers are smaller than drop of water; however larger than water molecules, producing a high surface tension that allows the water to remain in the surface.[15, 16] The whiskers maintain breathability as they permeate gases. Water repellence can also be induced through creation of 3D surface structures on the fabric by adding gel-forming additives, or coating the textile by nanoparticulate film.[17] For example, audio frequency plasma of fluorocarbon derivatives can be applied to coat cotton fibers with

nanoparticulates.[18] By producing a roughness on the surface of the fabric, superhydrophobicity can be created without affecting abrasion resistance and softness of the fabric. Silica (SiO_2) nanoparticles (NPs) in combination with water-repellent agents can also be utilized to impart hydrophobicity to textiles.[19] SiO_2 NPs (143-378 nm) were synthesized via sol-gel process. Cotton fabrics treated with both SiO_2 NPs and water-repellent agent produced contact angles above 130°. SiO_2 NPs could be coated over cotton in the presence of perfluorooctylated quaternary ammonium silane coupling agent (PQASCA) to produce hydrophobicity.[20] While the SiO_2 NPs create roughness on the surface of cotton fibers, PQASCA lowered the surface energy. The resulting textiles exhibited water repellence with a water contact angle of 145°. Oil repellency of the fabric also improved showing a 131° contact angle for a diiodomethane (CH_2I_2) droplet on the fabric surface. In another study, amphiphilic Janus micro/NPs were chemically immobilized on textile surfaces.[21] While microparticles bound between fibers, NPs attached to fiber surface. Janus particle immobilized textiles showed water-repellence.

Bioinspired design has also motivated the investigation of water-repellent materials. For example, duck feathers consist of multiscale structures having preening oil to repel water. The microstructure of duck feathers were simulated by coating cotton and polyester textiles with chitosan using a surface solution precipitation method followed by modification with a silicone compound to achieve a low surface energy.[22] Figure 2a shows a scanning electron microscope (SEM) image of polyester and chitosan-treated polyester having nanosized roughness on the surface. Chitosan-treated polyester textiles provided flexibility and water repellence. Lotus leaf nanostructures also inspired biomimetic studies for application in textiles.[23] Cotton fibers were coated with pristine and surface-modified carbon nanotubes (CNTs) to mimic the nanostructure of lotus leaves. The resulting cotton fabrics had contact angles greater than 150°. Another study

that was inspired from lotus leaves involved the development of a nanocoating (20 nm) to create hydrophobic textiles.[24] The nanocoating consisted of epoxy-containing poly(glycidyl methacrylate) (PGMA) and SiO_2 NPs for the initial surface modification and generation of the primary reactive layer. Polymers with different functional groups (*e.g.*, carboxy, anhydride, amino and hydroxyl) could be grafted on the reactive layer.

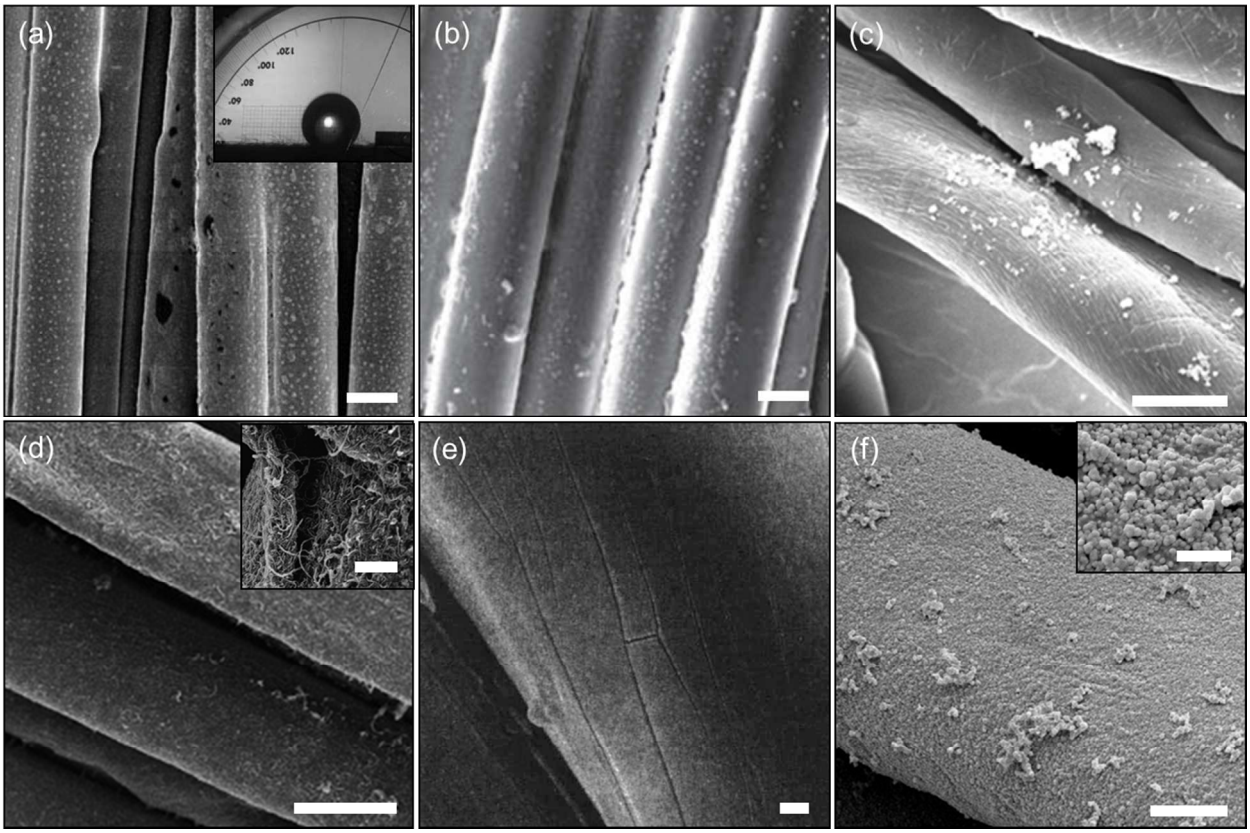

Figure 2. SEM images of nanoparticle functionalized fibers. (a) Water repellence: chitosan-treated polyester with nanoscale roughness on the surface. Scale bar = 10 μm. The inset shows the profile of a water droplet on the treated polyester fabric. Reprinted with permission from ref [22]. Copyright 2008 IOP Publishing. (b) Antistatic properties: polyester fiber surfaces treated with NPs and fluorine. Scale bar = 20 μm. Reprinted with permission from ref [25]. Copyright 2010 Sage Publications. (c) Wrinkle resistance: cotton fibers treated with 1,2,3,4-BCA and TiO_2 NPs. Scale bar = 10 μm. Reprinted with permission from ref [26]. Copyright 2010 Springer Publishing.

(d) Strength enhancement: CNT coated cotton fibers. Scale bar = 10 μm. Reprinted with permission from ref [27]. Copyright 2008 The Royal Society of Chemistry. The inset shows the magnified view of the fiber surface. Inset scale bar = 1 μm. (e) UV blocking: TiO_2 treated cotton fiber. Scale bar = 1 μm. Reprinted with permission from ref [28]. Copyright 2004 Sage Publications. (f) Antibacterial properties and odor control: cotton fibers treated with Ag NPs. Scale bar = 5 μm. The inset shows the magnified Ag NPs on the surface. Inset scale bar = 1 μm. Reprinted with permission from ref [29]. Copyright 2012 Elsevier.

Oil repellent textiles have been also produced. Polyester fabric could be coated with silicone nanofilaments and treated with plasma fluorination to impart superoleophobic properties.[30] The produced fabric samples had oil repellency grade of 8, and repelled alkanes. Hydrophobic and oleophobic properties could be simultaneously imparted to textiles. For example, cotton fibers were impregnated with SiO_2 particles to produce a dual-size surface roughness, followed by hydrophobization with poly(dimethylsiloxane) (PDMS), resulting in a static water contact angle of 155° for a droplet.[31] To induce oleophobicity, the SiO_2 particles on the fibers were treated with perfluoroalkyl chain, which was demonstrated by a static contact angle of 140° and a roll-off angle of 24° for oil droplets.

Antistatic Properties. Synthetic fibers such as polyester and nylon have high static charge as they are not hydrophilic. On the other hand, cellulosic fibers limit the static charges due to their high moisture content. TiO_2 NPs,[32] ZnO whiskers,[33] and antimony (Sb) doped tin oxide (SnO_2) particles[34] were utilized to impart antistatic properties to synthetic fibers. These materials are electrically conductive and dissipate the static charge accumulated on the textile. Additionally, silane nanosol enhances antistatic properties, as it absorbs moisture in the air through hydroxyl groups.[35] In commercial products, poly(tetrafluoroethylene) (PTFE) (W.L. Gore) developed an

antistatic membrane that consisted of electrically conductive NPs anchored in the fibrils of the membrane.[36] This membrane limited the formation of isolated chargeable areas and voltage peaks. This approach is advantageous over other antistatic agents since it does not wash off during laundry. Sol-gel coatings could be applied as a surface treatment to impart antistatic properties combined with hydrophobic properties.[37] Sol-gel composition consisted of hydrophobic compounds such as alkoxysilanes modified with alkyl chains and hydrophilic compounds including amino-functionalized alkoxysilanes. This combination allowed forming hydrophobic groups at the fiber-air interface while the deeper regions were hydrophilic. Sol-gel coated textiles had water repellence, but contained humidity in deeper regions of the coatings to produce antistatic properties. Antistatic charges with hydrophobicity could be achieved by treating polyester fabric with silver (Ag) NPs and fluorine water-repellent finish (Figure 2b).[25] After 10 washings, the polyester fabric had FTTS-FA-009 A grade antistatic property, and AATCC 22 spray rating 90 grade for its hydrophobic quality.

ZnO NPs have been utilized to produce antistatic properties.[38] ZnO NPs, prepared by direct precipitation using zinc chloride ($ZnCl_2$), were immobilized both on polyester fabrics through pad-dry-cure process with antistatic finishing agent. The charge density of polyester fabrics reduced from 58 to 0.95 (units in $\times 10^{-7}$ C m^{-2}). As the concentration of ZnO NPs increased in the finishing agent, the antistatic property of the fabric decreased due to reduced dispersion of NPs. Additionally, the addition of Ag NPs decreased the static voltage of polyester fabric by 60.4 %.[39] The combination of Ag, gold (Au) and Zn oxide particles decreased the static voltage by 77.7 %. In another study, Sb nanoparticle doped SnO_2 particles were utilized to impart antistatic properties to polyacrylonitrile (PAN) fibers.[40] These particles were dispersed in water using polyethyleneimine (PEIN), and this solution was added to the pre-heating bath during spinning

of PAN fibers. The particles diffused into the fibers create electrically conductive channels, which produced antistatic properties.

Wrinkle Resistance. Cellulose molecules in the cotton linearly organize themselves passing through the crystalline and amorphous sections of the fibers. Hydrogen bonds hold together cellulose molecules in their positions. Upon applying a force to the fibers, the cellulose chains displace from their original positions and hydrogen bonds reform at new locations. Nanocoatings that prevent crease while maintaining comfort is desirable in textile products. Traditionally, fabrics are impregnated with resin to impart wrinkle resistance to textiles. However, this approach decreases tensile strength of the fiber, abrasion resistance, and dyeability while inducing hydrophobicity. To impart wrinkle resistance, NPs have been applied to cotton and silk. TiO_2 NPs with carboxylic acid as a catalyst were utilized to form crosslinks between cellulose molecules and the acidic groups.[41, 42] The use of 1,2,3,4-butane tetracarboxylic acid (BCA) and succinic acid as crosslinking agents had the highest dry crease recovery angle and wet crease recover angles, respectively. Additionally, carboxylic acid treated fabrics with TiO_2 NPs were softer as compared to untreated fabric.[42] TiO_2 through its catalytic property can be used as a co-catalyst with sodium hypophosphite ($NaPO_2H_2$) to treat cotton with 1,2,3,4-BCA.[26, 43-45] Figure 2c shows SEM images of cotton fibers treated with BTCA and TiO_2 NPs. This increased the effectiveness of $NaPO_2H_2$, hence the wrinkle recovery of the cotton fabric. However, tear and tensile strength of the cotton fabric decreased due to the presence of TiO_2 NPs. *Bombyx mori* silk was also treated with TiO_2 NPs in chitosan by crosslinking reactions of citric acid and maleic anhydride.[46] Dry and wet delay-wrinkle recovery angles of the treated silk were 267° and 250° as compared to untreated fabric of 235° and 178°, respectively. Additionally, SiO_2 NPs and maleic anhydrate as a catalyst have been applied to silk to improve wrinkle resistance.[47]

Strength Enhancement. CNT reinforced polymer composite fibers have been developed to improve strength, toughness, and decrease weight. These composite fibers could be produced through melt-spinning of polypropylene and carbon particles.[48] Controlling the parameters in melt-spinning, the morphology, crystallinity and mechanical properties of nanostructured polycaprolactone non-woven mats were optimized.[49] Melt extrusion also produced a wide range of nanoadditive yarns with improved mechanical properties and various textures.[50]

Wet-dry spinning or jet melt spinning through spinnerets have been used to produce ordinary and fine denier textile fibers (1-100 μm in diameter). Nanoscale fibers require electrospinning, in which a solution is extruded though nanoscale spinnerets and the spun fibers are collected on a grounded plate. The fiber strength and conductivity can be increased by post-treatment approaches (*e.g.*, heat). Synthetic nanofibers can also be produced through coagulation-based CNT electrospinning by controlling the fiber diameter and increasing twist. Such composite fibers can consist of multiwalled CNTs (5-20). Highly twisted yarns have high strength, toughness, and energy damping capability for application in electronic textiles including actuators, electrostatic discharge protection, energy storage, heating, and radio and microwave absorption. The integration of CNTs into fibers has been shown to improve the strength and performance. For example, super-aligned arrays of CNTs have Young's modulus in the TPa scale, tensile strength of 200 GPa, breaking strain of 20 %, and elastic stain of 5 %.[51]

Dipping and coating method was also utilized to immobilize CNTs on cotton.[27] CNTs were modified with poly(butylacrylate) using surface grafting, and this composite was applied to cotton fabrics by dipping, drying, curing, and finishing. Figure 2d illustrates SEM images of CNT coated cotton fibers. The tensile strength of the CNT-coated cotton fabrics was improved along the weft and warp directions, showing enhancement in both the loading capability and

flexibility (displacement). For example, the tensile strength of the CNT coated cotton was 0.5 kN at 13.5 cm displacement as compared to 0.25 kN for untreated fabrics.[27]

UV Blocking. Inorganic UV blockers are non-toxic and chemically stable operating at high temperatures. Nanoscale semiconductor oxides such as TiO_2 and ZnO efficiently absorb and scatter UV radiation.[28, 52-54] Figure 2e shows a SEM image of a TiO_2 (~100 nm) treated cotton fiber. At nanoscale, scattering depends on the wavelength and the size of the NP, where the scattering is inversely proportional to the wavelength of the fourth power of the wavelength. For example, to scatter UV light (200-400 nm), the optimum particle size is 20-40 nm.[55] Sol-gel method can be used to form a thin layer of TiO_2 on the surface of the treated cotton. The UV-protection effect may be maintained up to 50 launderings.[56] Furthermore, ZnO nanorods (10-50 nm) have been incorporated in cotton to induce scattering at a high UV protective factor rating.[57] Additionally, ZnO NPs synthesized through sedimentation and peptization were immobilized on dyed polyester/cotton fabrics.[58, 59] The resulting fabric absorbed the light in the UV region.[58]

Antibacterial Properties. Ag, TiO_2 and ZnO NPs can be utilized to impart antibacterial and fungicidal properties to textiles.[53, 55, 60-62] Ag NPs have large surface areas that increase their contact with bacteria and fungi. The antiseptic mechanism of Ag NPs is based on reacting with proteins in these organisms and adversely affecting their cellular function and inhibiting cell growth. They also reduce respiration, limiting the activity of the basal metabolism of the electron transfer system, and substrate transport into the cell membrane. When Ag NPs contact with moisture or bacteria, they adhere to the cell wall and membrane.[63] While the Ag NPs in their metallic state are inert, they ionize in the presence of moisture. The Ag^+ ions are reactive and they diffuse through the cell wall and membrane into cytoplasm. Ag^+ ions bind to sulphur containing proteins on the cell membrane to structurally change the cell wall.[64] These structural

changes result in the release of the cellular components to extracellular fluid due to the changes in the osmotic pressure. Additionally, the Ag^+ ions bind to phosphate containing proteins to condense DNA, leading to a reaction with thiol group proteins to cause cell death. They also suppress the function of enzymes and inhibit the cell to produce ATP.[65] Ag NPs slow down the growth and multiplication of bacteria and fungi that are involved in odor creation and itchiness. Figure 2f shows cotton fibers treated with Ag NPs.[29] For example, Ag NPs can be applied to socks to prevent the growth of bacteria and fungi.

The antimicrobial efficacy of Ag additives depends on the concentration, surface area, and the release rate of the Ag^+ ions.[66-68] Ag-containing textiles can release dissolved and particulate Ag (20-30%) into washing liquid in the first cycle.[69-71] In fabrics comprising Ag metal, oxidation from Ag(0) to Ag(I) is required for releasing Ag^+ ions in solution.[70] Ion release from Ag NPs is a cooperative oxidation process involving dissolved oxygen and protons to produce peroxide intermediates and complete reactive dissolution. The presence of oxygen is essential for the release of dissolved Ag through the surface oxidation of Ag NPs. The ion release rates increase as the temperature is increased and as the pH is decreased.[72] For example, Ag NPs (2 mg L^{-1}) released 0.3 mg L^{-1} dissolved Ag after 24 h incubation in air-saturated solution (9.1 mg L^{-1} dissolved oxygen) at pH 5.68. The release of dissolved Ag was 0.6 and 0.1 mg L^{-1} at pH 4.0 and 8.0 after 24 h incubation, respectively.[72] Additionally, the change in ionic strength has negligible effect on the release kinetics.

TiO_2 NPs can also be utilized to impart textiles with antibacterial properties. Upon illumination with light with energy higher than its bandgap (3.2 eV), TiO_2 as a photocatalyst has the ability to have its electrons jump from the valence band to the conduction band. The electron and electric hole pairs form on the surface of the photocatalyst, where the electrons and oxygen

form O_2^- and the positive electric holes and water create hydroxyl radicals.[52] The unstable substances on the surface of the photocatalyst are oxidized into CO_2 and water. Through this mechanism, the photocatalyst decompose organic matters including odor molecules, bacteria, and viruses. The catalytic activity of TiO_2 NPs has been utilized in textiles to provide antibacterial properties.[56, 73] The photocatalytic activity might be improved by creating TiO_2/SiO_2 nanocomposites or Au-doped TiO_2 nanocomposites in cotton fabrics with self-cleaning properties.[74, 75] Furthermore, ZnO behaves similar to TiO_2 to produce antibacterial properties.[76] ZnO NPs (21-25 nm) have been synthesized in reverse micelle cores of polystyrene (PS) and polyacrylic acid.[77] ZnO NPs coated onto textiles showed self-cleaning properties in the presence of gram-negative *E. coli* and aerobic gram-positive *S. aureus*. Additionally, SiO_2 and Ag NPs with core-corona structure were electrostatically assembled onto cotton surfaces with high packing density to impart antibacterial properties to fabrics.[78] The coronas of NPs can be loaded with antibacterial moieties such as quaternary ammonia salts as well as metal coatings on cotton fabrics.[79] Discussions focusing on self-cleaning and antimicrobial nanomaterials in textiles can be found elsewhere.[17, 80, 81]

ELECTRONICS IN TEXTILES

Electrical Conductivity. Conducting polymers are attractive for creating textiles that enable the incorporation of sensors and actuators. For example, conducting polymers can change their resistivity and produce electrical signals in response to external stimuli. A range of dopants can be incorporated in these polymers. For example, polypyrrole (PPy) has high mechanical strength and is electroactive in organic and aqueous solutions. Another widely studied conductive polymer is polyaniline (PANI), which exist in three possible configurations: leucoemeraldine

base (fully reduced), emeraldine base (partly oxidized), and pernigraniline base (fully oxidized). In its oxidized form, the conductivity of PANI increases about 10 orders of magnitude. Additionally, polythiophene (PTs) and its derivatives can be in *p* or *n* type forms for application in field-effect transistors in flexible logic circuits. The low production costs, light weight and flexibility allow these materials to be easily integrated in textiles.

The surface structure of synthetic fibers can be modified to produce diverse functionalities.[82] SiO_2 NPs can be incorporated in polyimidoamide fibers through spinning. Incorporation of nanoparticles in PAN fibers can create electrically conductive channels with enhanced mechanical and antistatic properties.[40, 83] Fiber porosity, thermal and absorption characteristics can be controlled by chemically modifying the fibers. To improve thermal resistance and tenacity, the fibers can be coated with diamine (diaminodiphenyl methane), montmorillonite, and SiO_2 NPs.[84-86] Synthetic fibers can also be functionalized through chemical oxidative deposition, in which conducting electroactive polymers such as PANI, PPy, PTs are used to coat textiles for improving tensile strength and thermal stability.[87, 88] Furthermore, surface deposition of electroactive polymers increases conductivity of the fibers one order of magnitude.[89-91] Such composite fibers have application in the reduction of static electrical charge, microwave attenuation, and electromagnetic shielding.

Finding the balance between electrical conductivity, flexibility and comfort of the textile is a challenge. Coatings have been developed to impart electrical conductivity to cotton. One approach involved polyelectrolyte-based coating with multiwalled carbon nanotubes (MWCNTs).[92] Figure 3a shows SEM images of MWCNT-Nafion coated cotton threads. Charge transport through the network of nanotubes was 20 Ω cm^{-1}. Another strategy used a combination of metal NPs conformally coated around the heterogeneous contour of cotton fibers.[93] In-situ

polymerization was utilized to create polymeric bridges between the NPs. These flexible bridges allowed for the creation of coatings that were durable and resilient to mechanical deformation for application in cotton-based transistors. Figure 3b shows a Transmission Electron Microscope (TEM) image of cross-section of the conductive cotton fibers, showing uniform coating with Au NPs and poly(3,4-ethylenedioxithiophene) (PEDOT).

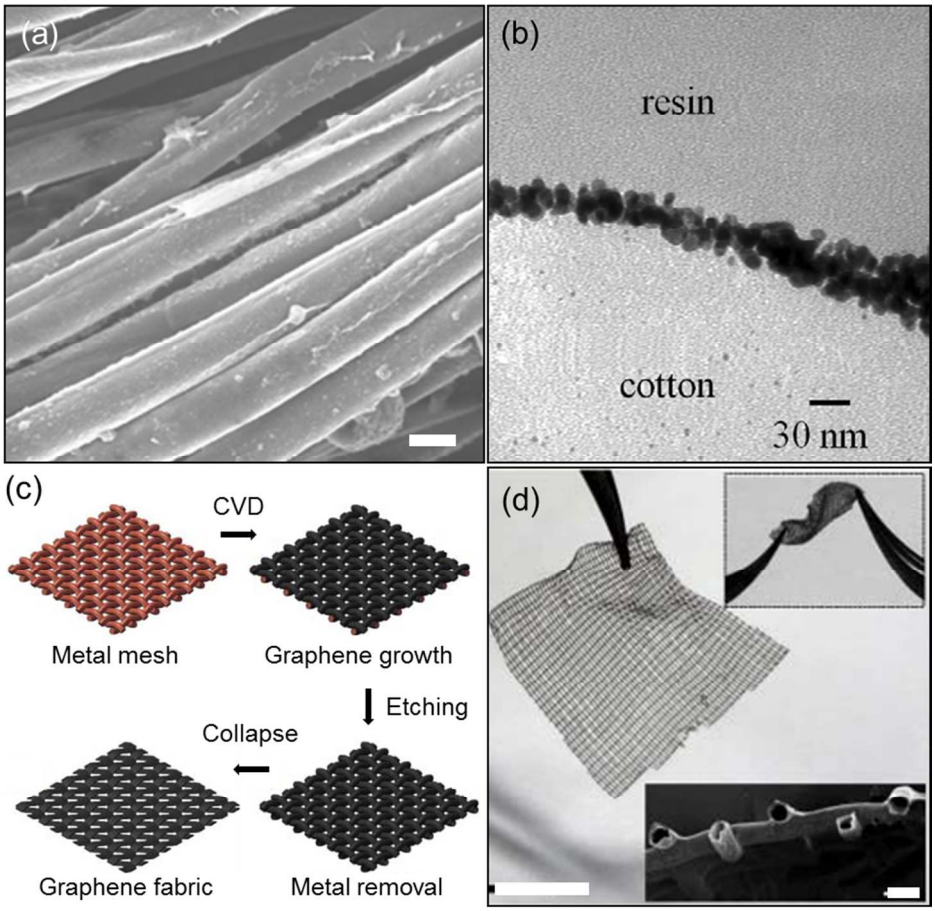

Figure 3. Conductive nanomaterials in textiles. (a) A SEM image of MWNT-Nafion coated thread. Scale bar = 10 μm. Reprinted with permission from ref [92]. Copyright 2008 American Chemical Society. (b) A TEM image of cross-section of the conductive Au NP and PEDOT coated cotton fibers. Reprinted with permission from ref [93]. Copyright 2011 Elsevier. (c) Fabrication of graphene woven fabric by CVD using copper (Cu) wire meshes as substrates.

Reprinted with permission from ref [94]. Copyright 2012 Nature Publishing Group. (d) Graphene woven fabric in PDMS. Scale bar = 5 mm. The top inset illustrates the twisted graphene fabric film. The bottom inset shows an SEM image of graphene fabric cross-section. Scale bar = 100 μm. Reprinted with permission from ref [94]. Copyright 2012 Nature Publishing Group.

Graphene-based woven fabrics have been prepared by interlacing two sets of graphene microribbons.[94] The resulting textile had dimensional stability in both the warp and the weft directions. The conductivity was optimized by tuning the ribbon packing density. Graphene woven fabrics were synthesized through atmospheric chemical vapor deposition (CVD) using Cu meshes consisting of wires with ~60 μm in diameter as substrates. The fabrication of the textiles involved growing graphene on the substrate, removing the Cu mesh wires, and subsequently collapsing the graphene to form double-layer microribbons (Figure 3c). Such polymers could be also embedded in PDMS or PET films (Figure 3d). The constructed fabric had a transparency of 1000 Ω sq^{-1}.[94] Conductive textiles could also be produced by immobilizing graphene via reduction from graphene oxide on cotton fabric by using a conventional dip and dry method.[95] The electrical conductivity of the fabric enhanced three orders of magnitude as the number of coating cycles was increased from 1 to 20. The surface conductivity of the resulting graphene depended on the reducing agent type and concentration. The electrical resistivity of the graphene immobilized cotton ranged from 10^3 to 10^6 kΩ cm^{-1}.[95]

Power Sources. Flexible and lightweight fabric supercapacitor electrodes have been designed for energy storage.[96] Activated carbon in poly(methyl methacrylate) (PMMA) and polyethylene glycol (PEG) were incorporated in woven cotton and polyester fabrics. The supercapacitor cells were assembled in a conventional symmetrical two electrode setup by screen printing on polyester microfibers. Electrodes coated with activated carbon had a gravimetric and

areal capacitance of 85 F g^{-1} at 0.25 A g^{-1} on cotton lawn and polyester microfiber.[96] Recently, a flexible supercapacitor textile consisting of CNTs/PANI composite fiber was developed.[97] The supercapacitor was integrated with a photoelectric conversion function to create a self-powering energy textile that converted solar energy into electrical energy and stored it in a stacked multilayer structure. The CNT array was synthesized by CVD. Aligned CNT sheets were dry-drawn from the array and stacked into a thicker film along the length direction, and twisted into an aligned fiber, which was woven into textiles. The resulting textiles were electrodeposited with PANI to create an electrode, followed by coating with a layer of gel electrolyte to create a supercapacitor. The resulting material had a capacitance of 272 F g^{-1} with 96% maintenance after 200 bending cycles.[97] Another study that aimed to improve the performance of textile-based supercapacitors involved embedding a metal wire (monofilament) in the center a CNT yarn.[98] One-step continuous spinning allowed forming a core/sheath structured CNT yarn architecture to create linear supercapacitors. CNTs formed a layer around the conductive metal filament core. The filament core acted as a current collector to transport charges. Foldable nanopatterned wearable triboelectric nanogenerators were also reported.[99] Figure 4a shows the device and its fabrication process using nanopatterned PDMS structure. Ag-coated textile and PDMS nanopatterns based on ZnO nanorod arrays were used as triboelectric materials. The nanopatterned structures produced 120 V (output) at 65 μA, and four-layered triboelectric nanogenerators produced 170 V (output) at 120 μA. No significant drift was observed after 120,000 cycles.[99] Another study reported the development of carbon-activated cotton threads on textile for energy generation.[100] The device harvested electrostatic energy from the environment through contact and friction electrifications. It was fabricated by treating carbon black NPs and encapsulating them with a thin layer of PDMS for stability. By rubbing and tapping with a PTFE

sheet, electrostatic charges were collected from the carbon-functionalized threads in textiles. The device had an open-circuit voltage of -60.9 V.[100] Piezoelectrocity via electrostatic forces were also utilized in textiles to create a nanogenerator.[101] ZnO nanowires and discharge films were incorporated into a textile to hybridize electrostatic and piezoelectric effects (Figure 4b). This nanogenerator had an output voltage of 8 V at 2.5 μA. The produced power source was utilized to power an OLED and a Liquid Crystal Displays (LCD) panel.[101] Recently, pristine soft conductive yarns were produced via a twist-bundle-drawing technique (Figure 4c).[102] Conductive yarns modified with reduced graphene oxide (rGO), MnO_2 nanosheets, and PPy films were used to produce weavable supercapacitors. The yarns had specific capacitances of 31 mF cm^{-1} and 411 mF cm^{-1} in solid-state two electrode cells with energy densities of 9.2 μWh cm^{-2} and 1.1 mWh cm^{-3}.[102]

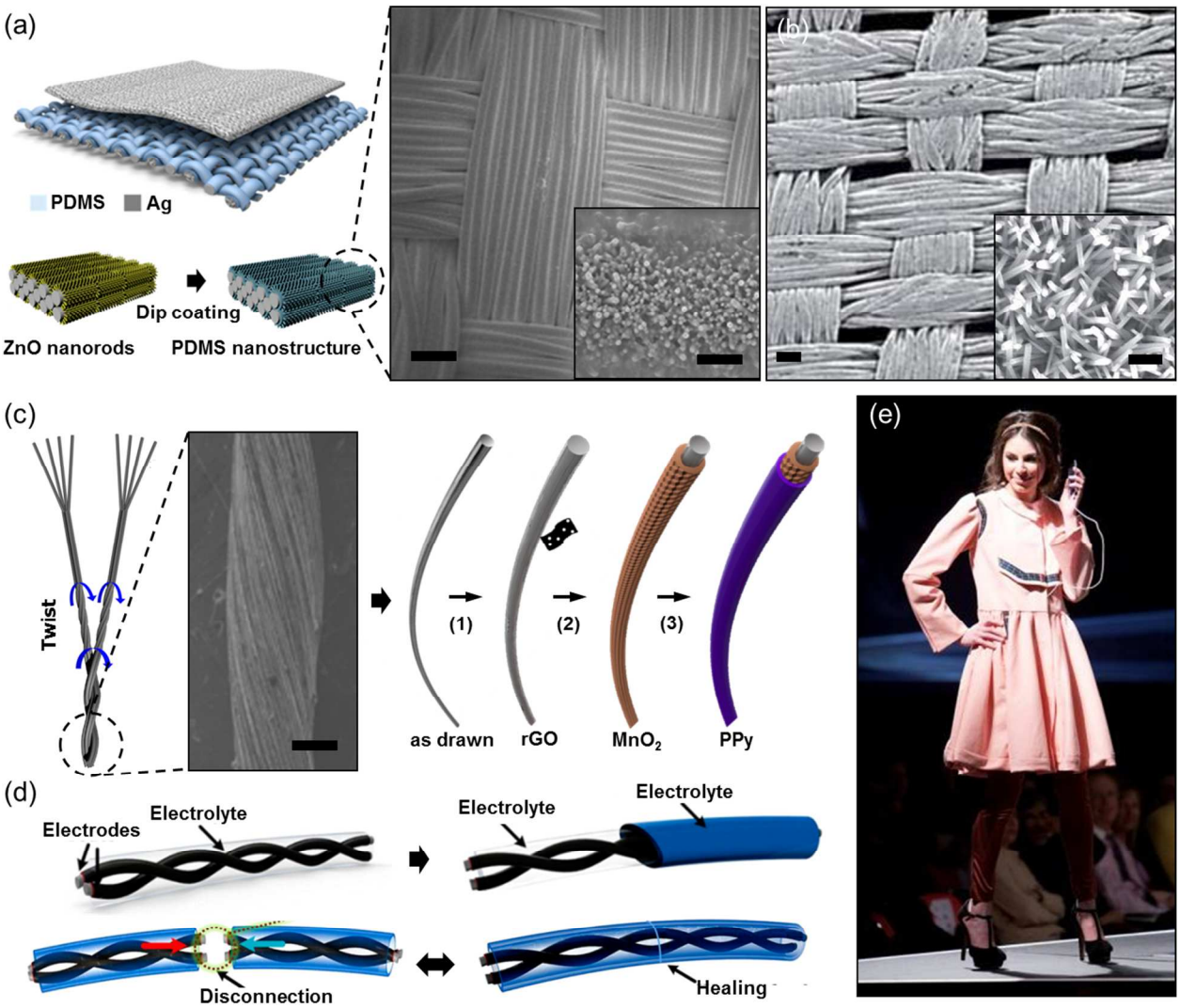

Figure 4. Energy generation and storage in textiles. (a) Fabrication of nanopatterned wearable triboelectric nanogenerator showing SEM images of ZnO nanorod-templated PDMS nanopatterns. The inset shows a magnified image of surface morphology. Scale bar = 500 μm, inset scale bar = 1 μm. Reprinted with permission from ref [99]. Copyright 2015 American Chemical Society. (b) SEM images of a textile electrostatic-piezoelectric hybrid nanogenerator containing ZnO nanowires. The inset shows magnified nanowires on the surface. Scale bar = 500 μm, inset scale bar = 1 μm. Reprinted with permission from ref [101]. Copyright 2012 The Royal Society of Chemistry. (c) Twisted yarn fabrication and illustration of the yarn functionalized by

rGO, MnO_2, and PPy. (1) Hydrothermal treatment (2-3) Electrodeposition. Reprinted with permission from ref [102]. Copyright 2015 American Chemical Society. (d) Fabrication and operation principle of magnetic-assisted, self-healable, yarn-based supercapacitors. Reprinted with permission from ref [103]. Copyright 2015 American Chemical Society. (e) A garment using cotton yarns coated with nanolayers of PEDOT-PSS. Copyright Abbey Liebman.

Stretchable PPy-based supercapacitors with cycling stability were also fabricated.[104] Electrochemical deposition of PPy on stretchable stainless steel meshes allowed producing solid state supercapacitors reaching 170 F g^{-1} at 0.5 A g^{-1}. Under 20% strain, the capacitance can be enhanced up to 214 F g^{-1}. These supercapacitors were operated at a scan rate of 10 V s^{-1}, which is a magnitude higher than PPy electrodes in aqueous solutions. These solid-state supercapacitors under no-strain and 20% strain had capacitance retentions 98% and 87% at 10 A g^{-1} after 10,000 cycles.[104]

In conventional planar or structures, the reconnection of the broken yarn electrode and the restoration of the electrical conductivity are challenging.[103] To improve the mechanical properties, yarns-based supercapacitors with self-healing properties have been developed. The electrodes fabricated by wrapping magnetic electrodes around a self-healing polymer shell (Figure 4d). The magnetic attraction reconnected broken fibers in the yarn electrodes to store electrical conductivity while polymer shell recovered mechanical strength and configuration integrity. The magnetic yarns allowed restoring the specific capacitance up to 71.8% after four breaking cycles by maintaining mechanical properties.[103]

Conductive fabrics have been incorporated in garments. Figure 4e shows a garment using cotton yarns coated with nanolayers of PEDOT- poly(styrenesulphonate) (PSS) deposited over an

array of Au NPs. These nanolayers allow the cotton yarns to become electrically conductive and transfer energy from solar cells attached to the exterior of the dress. A comprehensive discussion about energy storage technologies can be found elsewhere.[10]

Fabrication of multifunctional composite fibers has received attention due to their applications in conductive structures and batteries in the textile industry. Here "fiber" refers to wire-like composite structures produced via drawing techniques used in the production of fiber optics. Composite fibers can be fabricated through preform heating and drawing. A geometrically complex fiber preforms at a length of tens of centimeters is assembled by stacking of tubes, rods, multilayered films, or functional components within a hollow structured rod that serve as cladding.[105] The preform tip is then placed into the vertical furnace, where the temperature is increased above the softening or melting temperature of the preform materials. As a consequence, the preform tip melts, and then it is pulled downward, thus creating a slender rod that can be continuously pulled from the molten perform tip. Typically, a clamp tractor or a spooler is used to pull the fiber at a constant speed and tension. Geometry of the resultant fiber depends on parameters in the drawing process such as temperature distribution in a furnace, fiber drawing speed and preform feed velocity, pressurization of the preform, and electromagnetic fields.[106] This process creates both non-optical fiber and optical fibers. Fibers drawn from the macroscopic preform would generally retain the preform structure; however, sizes of the constituent structures (*e.g.*, layers, rods) will be reduced to micro- or nanoscale. Therefore, a geometrically complex, composite transverse structure could be realized within a fiber on a sub-micron scale by controlling the preform structure and optimizing the conditions of the fiber drawing process. This, generally, may not be accomplished by traditional yarn-spinning methods

such as melt-spinning,[107] wet-spinning,[108] or electro-spinning,[109, 110] which are typically utilized to produce fibers and yarns with simple structures in textile manufacturing. Moreover, materials including biofunctional polymers,[111-113] low-melting-temperature metal alloys,[114] optical plastics,[114-123] conductive polymers,[124-126] and electrochemical materials,[127-130] could be integrated into a composite fiber during drawing.

Flexible fiber or stripe batteries which can be directly weaved into a textile constitute a promising solution toward seamless integration with functional textiles. Flexible fiber batteries using both a simple inorganic chemistry[127, 128] as well as Li-ion chemistry[129, 130] have been proposed. The simplest fiber battery consisted of a microstructured low density polyethylene (LDPE) jacket with several intercommunicating channels running along the fiber. Aluminum (Al) and Cu wires were immobilized to produce a double stranded fiber as anode and cathode, respectively. The voids between these two channels were then filled with sodium hypochlorite (NaOCl) electrolyte. This fiber constituted a typical Al/air galvanic cell. To fabricate a fiber battery, the fiber jacket preform was prepared by drilling several interconnected channels throughout a LDPE rod. The two electrode wires (Al and Cu) were embedded into the two extreme channels of the fiber during production (*i.e.* drawing). Open cell voltage of a fiber battery was ~1.5 V with a linear capacity of 10^{-2}–10^{-1} mAh cm^{-1}. Flexible lithium (Li)-ion batteries could be built by from polyethylene oxide (PEO) as a thermoelastic polymer ionic electrolyte in all the electrodes and a separator layer. To assemble such a battery, solvent-casting method could be used to deposit an anode layer ($Li_4Ti_5O_{12}$ + PEO), a separator layer (PEO+LiI), and a cathode layer ($LiFePO_4$ + PEO) in sequence. The thermoelastic nature of PEO allows the production of such batteries in fiber drawing. This Li-ion battery could be cut into stripes that may be directly weaved into a textile.

Two prototypes of textiles based on fiber and stripe batteries have been demonstrated. The first prototype was fabricated by weaving fiber batteries into a wool textile matrix.[127] The maximum output power of a fiber battery textile could be achieved by optimizing series and parallel connections of the fiber batteries in the textile. Applications of this fiber battery integrated textile included lightning up a LED, driving a wireless mouse,[127] and actuating a shape-memory alloy.[127] The second prototype used flexible stripe Li-ion batteries.[129] The Li-ion battery stripes were weaved into a textile. Each stripe had an open cell voltage of ~0.3V. A textile battery made of eight battery stripes woven with wool threads and connected in series using Cu and Al wires were used to light up a 3V LED. The flexible fiber or stripe batteries constitute a promising technique toward the realization of on-garment power supply. In fashion industry, LEDs or electroluminescent wires are used as light emitting elements; and shape-memory alloys may be weaved into garments to provide kinetic features. The fiber and stripe batteries could be used as an efficient power source for these electronics.

Conductive fiber are widely used to interface with other electronic devices integrated into textiles. To fabricate conductive fiber, conductive fillers such as carbon black (CB)[125] or CNTs[131] are impregnated into plastic preform material. Fabrication of all-fiber electronic components is however a challenging task. The fabrication of a fiber electric capacitor using CB-impregnated LDPE films as compliant electrodes have been reported.[124-126] The fiber preform was fabricated by consecutive stacking of two conductive and two isolating LDPE layers and then turning the multilayer into a Swiss-roll configuration featuring a large central hole. A tension-adjustable reel was installed on the top of the fiber drawing tower that hosted a spool of Cu wires. These wires were then passed through the preform core, pulled down and embedded into the fiber center during drawing by collapsing the plastic cladding. The as-drawn fiber

capacitors featured one or two Cu wires as inner electrodes, and the outmost conductive LDPE layer constituted the outer electrode. The fiber capacitance was measured in the 60-100 nF m^{-1} range. The fiber capacitors were also demonstrated to build touch sensitive textiles.

Digital Components. OLEDs have been incorporated in soft fabrics.[132] OLEDs fabricated by thermal evaporation were mechanically stable over 1000 cycle bending test with a bending radius of 5 mm, an emission angle of 70°, and a current efficiency of ~8 cd A^{-1}.[132] Schottky diodes were also fabricated on textiles.[133] ZnO nanorods were grown on a Ag-coated textile fabric using a hydrothermal method, and Zn nitrate and hexamethylenetetramine were used to produce ZnO nanorods. The Schottky diode was prepared by applying photoresist and reactive plasma ion etching of the ZnO nanorods. A shadow mask was used to deposit Cu using thermal evaporation. The resulting diodes had performance comparable to glass-based diodes.[133] Schottky diode integrated textiles have potential applications in switched-mode power supplies, voltage clamping, and reverse current and discharge protection.

Polymer yarns/fibers that are twisted/embedded with metal wires have been used for production of electromagnetic shield garments and fabrics. These metal wires could be embedded into polymer rods during a drawing process. The metal components in such rods generally have a melting temperature similar to that of polymers. A polycarbonate cable containing arrays of the bismuth-tin ($Bi_{42}Sn_{58}$, melting temperature ~140 °C) micro/nanowires has been fabricated using the stack-and-draw technique.[114] For preform fabrication, molten $Bi_{42}Sn_{58}$ alloy was first filled into a polycarbonate tube to produce a preform that was subsequently drawn into cable. The resulting cable had a cross section featuring a metal core surrounded by a polycarbonate cladding. By stacking these cables within another polycarbonate tube, and by repeating the drawing process, metal wire arrays could be produced at smaller

dimensions. After several drawings, nanowires separated into NPs. Recently, the fabrication of polymer/wire composites containing indium,[134, 135] or tin-zinc[136-144] has been demonstrated based on the same drawing technique. While such polymer/metal wire composites are mainly used for electromagnetic shielding, they also have a potential for producing metamaterials and optical components.

PHOTONIC TECHNOLOGIES FOR TEXTILES

Integration of optical technologies into garments and apparels is desirable in the fashion industry. Photonic materials and devices including films, nanoadditives or optical fibers have been adopted in the fabrication of textiles and garments to not only enhance the aesthetic performance but also endow the garments with additional functionalities. The most distinctive and basic application of optical technologies on fabrics or garments is perhaps tuning their appearance by controlling the intensity, color, and pattern of light. For example, optical films made of periodical dielectric multilayers could be directly coated on fabrics, thus offering highly reflective colorful appearance and enabling different color perceptions depending on the angle of observation. Holographic films may also achieve similar functions and even provide a more complex 3D visual effect.[145, 146] Additionally, phosphorescent films can allow fabrics glow in the dark.[147] Optical additives such as thermochromic and photochromic inks could be applied to yarns or textile, thus enabling the change of a textile color in response to ambient heat or illumination.[148] Retro-reflective inks that could provide a high reflection directly toward a light source are widely used for security clothing.[145] Moreover, electroluminescent wires or optical fibers serving as light emitting elements could be seamlessly weaved into a textile or garment. Textiles based on electroluminescent wires,[149, 150] traditional single- or multi- mode optical

fibers,[151] fluorescent fibers[152] and photonic bandgap fibers[153] have been demonstrated. In addition to promoting aesthetics, multifunctional fibers could offer textiles with functionalities such as sensing of temperature,[154, 155] humidity,[156] strain,[157] bending,[158] and pressure,[159] optical displays,[160] data transfer and communication,[161] lasing,[162] and illumination.[160, 163]

Color-Tunable Optical Fibers. Bragg fibers, a subset of photonic bandgap fibers, have a hollow- or solid- core surrounded by periodic dielectric nanolayers with high- and low-refractive indexes (Figure 5a).[115-120] Recently, two methodologies have been reported for the fabrication of the all-polymer hollow-core Bragg fiber preforms.[123] One approach utilized consecutive deposition of layers of two different polymers by solvent evaporation inside a rotating polymer cladding tube. The other approach adopted co-rolling of two different polymer films inside a plastic tube. Solid-core Bragg fiber preforms were fabricated by co-rolling the multilayer around a rod.[155, 158, 159, 164] To fabricate Bragg reflectors, PMMA/PS or PVDF (polyvinylidene fluoride)/polycarbonate have been used. Solid-core Bragg fibers were manufactured by preform heating and drawing, while hollow-core fibers required core pressurization. Bragg fibers typically guide the light by the bandgap effect.[165] Bandgaps of Bragg fibers are defined as spectral regions of high diffraction efficiency caused by the interference effects inside a periodic multilayer. Upon launching spectrally broadband light into a Bragg fiber, only the spectral components within the reflector bandgaps would be strongly confined and thus guided in the optical fiber core (Figure 5b). For the wavelengths outside the reflector bandgap, the light penetrated deeply into the multilayer region exhibits high propagation loss due to scattering from the imperfections inside the multilayer structure. Therefore, narrow-band colors were observed at the output end of a Bragg fiber (Figure 5b inset). Spectral position of the bandgap was affected by the core refractive index and multilayer geometry. Thus, bandgap

guidance mechanism renders Bragg fibers suitable for application in spectral filtering,[118, 119] optical sensing,[117, 119-121, 166] and photonic textiles.[116, 122, 153]

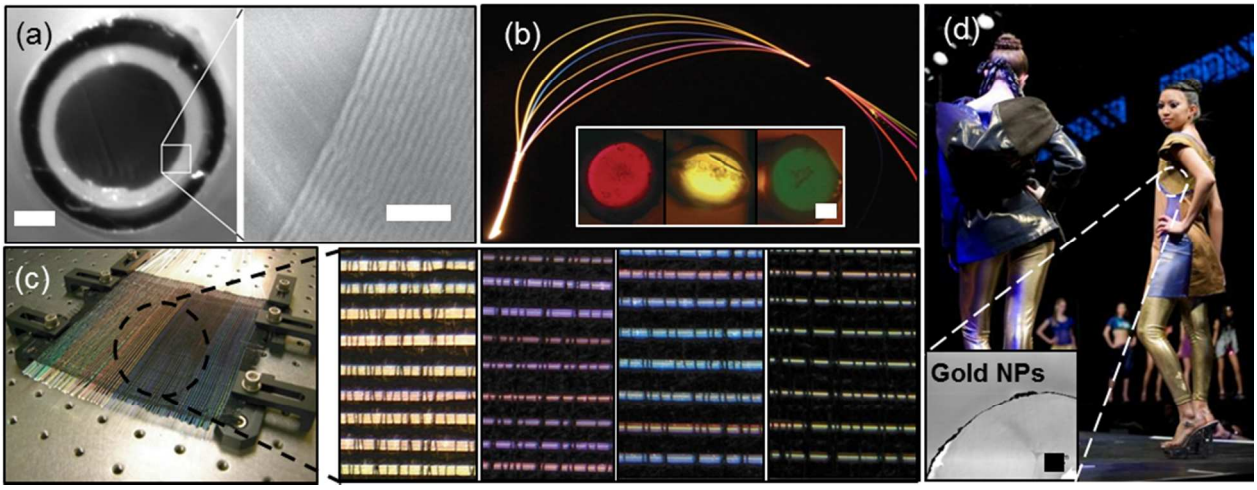

Figure 5. Fiber optic and plasmonic technologies for textiles. (a) Cross section of a solid-core Bragg fiber and its multilayer structure. Scale bar = 50 μm. Inset scale bar = 10 μm. Reprinted with permission from Ref. [116]. Copyright 2008 The Optical Society of America. (b) Light scattered from solid-core Bragg fibers. The inset shows Bragg fibers with different bandgaps. Scale bar = 200 μm. Reprinted with permission from Ref. [122]. Copyright 2008 CTT Group. (c) PBG Bragg fibers woven into a black silk textile. The inset shows color of the fibers tuned by mixing the emitted guided color with the diffracted color from ambient illumination. Reprinted with permission from ref [116]. Copyright 2008 The Optical Society of America (d) The use of plasmonic NPs in a garment. The inset shows an SEM image of Au NPs on the surface of a cotton fiber. Scale bar = 500 nm. Reprinted with permission from ref [167]. Copyright 2009 The American Chemical Society. Reprinted with permission from Olivia Ong.

The key feature of bandgap guidance of a Bragg fiber is wavelength filtering. When launching broadband light into a Bragg fiber, only a specific color defined by the spectral

position of the reflector bandgaps is guided. All the other colors are scattered out of the fiber after several centimeters of propagation. Moreover, due to the finite number of multilayers in the Bragg reflector, guided light partially leaks out from the fiber core. The leakage rate could be controlled by changing the number of multilayers. The spectral position of the reflector bandgaps, and hence the guided color, could be varied by changing the thicknesses of the reflector layers, with thicker layers shifting bandgaps to longer wavelengths. Layer thicknesses have been varied by drawing geometrically-similar preforms to optical fibers of different diameters.[116, 122, 153] Furthermore, under ambient (external) illumination, the Bragg fibers are colored depending on their diffraction properties. Therefore, the fiber color under ambient illumination is typically different from the fiber color due to emission of the guided light. This offers an opportunity to tune the overall fiber color by controlling the relative intensities of the ambient and propagating light. A ribbon of Bragg fiber diffracted green under ambient illumination while an emission of guided light diffracted red. In the far field (defocused view), the resultant color of a fiber ribbon was yellow.[116, 122]

Photonic Textiles Based on Bragg Fibers. A photonic textile based on solid-core Bragg fibers was hand woven on a Dobby loom.[116] The photonic textile showed colors when externally illuminated (Figure 5c). The textile exhibited colored bands made of optical fibers with similar diameters and coloration. Upon launching broadband light, the textile sample showed a number of brightly lit bands of distinct colors. Figure 6c inset shows textile samples under the ambient illumination. The textile sample had different colors depending on whether the textile was lit or not. This opens the possibility of controlling the resultant textile color by balancing the intensities of the guided and ambient light. When used in fashion industry, Bragg fibers and photonic textiles based on these optical fibers could be conveniently weaved into garments.

Compared to yarns or fabrics decorated by optical coatings or pigments, Bragg fiber-based textiles are resistant to mechanical abrasion and would not fade in color even under repeated washing.

Plasmonic Textiles. Cotton fabrics were also colored using arrays of plasmonic Ag, Au and Ru NPs.[167] The color in the fabrics originates from the closely packing of NPs, which were displayed on a garment (Figure 5d). TEM micrographs of the cotton fibers show the presence of conformal coatings of NPs assembled on the perimetries of the cotton fibers (Figure 5d inset).

SENSING AND DRUG RELEASE IN TEXTILES

Plasmonic bio/chemical optical fiber sensors can be fabricated via drawing techniques. Plasmonic sensors have been studied due to their high sensitivities for bio/chemical sensing.[168-170] In a plasmonic fiber sensor, a lossy surface plasmon mode propagating along a metal/dielectric interface could be excited at its resonance by an optical fiber core-guided mode *via* evanescent-wave coupling when the phase matching condition between the two modes is satisfied at certain frequency. The presence of such a plasmonic mode manifests itself as a spectral dip in the fiber transmission spectrum with its spectral location corresponding to the phase-matching frequency. Variations in the refractive index of an analyte adjacent to the metal layer could significantly modify the phase-matching condition, thus displacing the spectral dip in the optical fiber transmission spectrum. This constitutes the general sensing principle of a plasmonic fiber sensor. In the fabrication of a plasmonic sensor using conventional single- or multi-mode optic fibers, a series of modifications such as cladding etching or polishing followed by a subsequent deposition of several tens of metal nanolayer are generally required, in addition to the interfacing with a microfluidic system in the proximity of the fiber sensing head.[171-173]

These procedures bring challenges to the development of plasmonic fiber sensors. However, a complete plasmonic sensor fiber can be fabricated using stack-and-draw technique (Figure 6a). A fiber preform is first assembled at the microscale and it contains a plastic fiber core rod surrounded by the plastic tubes with one of them hosting a low melting temperature metal foil functionalized with a thermoplastic sensing layer. The inner channel of that tube is later used as a channel for analyte delivery. Next the preform assembly is drawn into fiber under pressure to keep the microfluidic channels in the fiber open. Finally, an additional wire can be passed through one of the tubes during drawing to be later used for active temperature control of the device. Additionally, high voltage supply can be connected to the wire and a foil to tune the distance between the fiber optic core and the plasmonic layer during drawing. Such fibers may contain multiscale features ranging from nano to macroscale, and consist of nano-additives for functionalization.

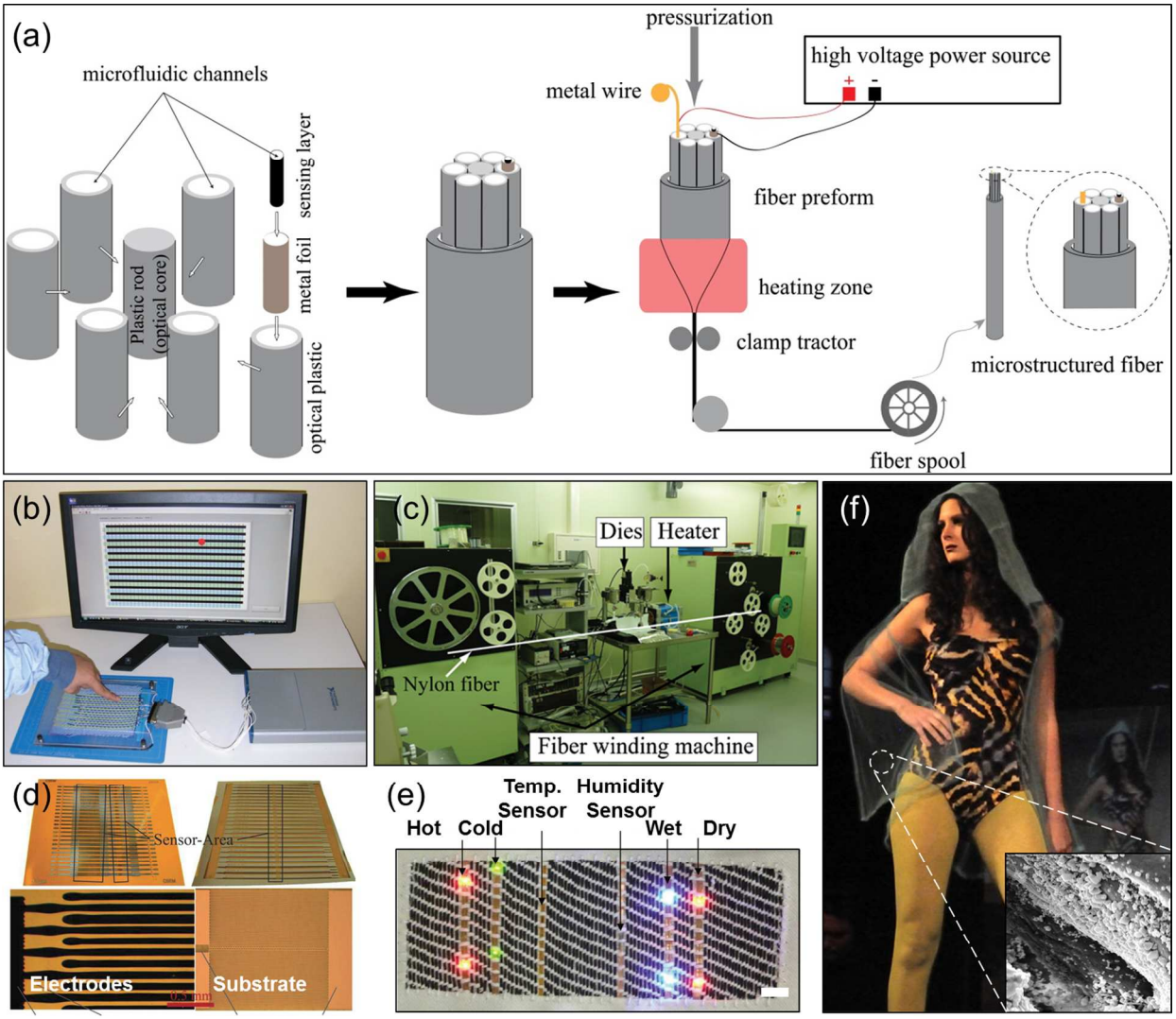

Figure 6. Sensors and insecticide-releasing textiles. (a) Fabrication of multifunctional fiber composites for sensing applications. Reprinted with permission from Ref. [105]. Copyright 2010 The International Society of Optics and Photonics. (b) Woven touchpad sensor with a 1D array of capacitor fibers connected to the ADC board to monitor an image of a textile with a reconstructed touch position. Reprinted with permission from ref [124]. Copyright 2012 IOP Publishing. (c) Die-coating system used in forming PEDOT:PSS and Cytop film on fibers. Reprinted with permission from ref [174]. Copyright 2012 Elsevier. (d) Fabrication of electrodes via photolithography for sensing applications. Reprinted with permission from ref [175]. Copyright

2013 IEEE. (e) Temperature and humidity sensors woven in a tablecloth. Scale bar=1 cm. Reprinted with permission from ref [175]. Copyright 2013 IEEE. (f) Permethrin-releasing textile net. Reprinted with permission from ref [176]. Copyright 2012 Springer. Reprinted with permission from Matilda Ceesay.

Using flexible fiber capacitors, touch sensor fabrics have been developed.[124, 125] Flexible and elastic fiber capacitors are well suited for a conventional weaving process. A Dobby loom was used to weave the capacitor fibers into a 1D sensor array integrated into a wool textile matrix. The touch sensor fabric consisted of 15 capacitor fibers (Figure 6b). The inner electrodes of all the fibers (Cu wires) were connected to the voltage source integrated into an Analog-to-Digital Converter (ADC) card. One end of the outer plastic electrode of each fiber was grounded, while the other end was connected to the individual channels of the ADC card to measure the voltage at the fiber endpoint. The human body could be approximated by an equivalent electrical circuit comprising a resistor connected in series to a capacitor. Touching a capacitor fiber with finger modified the local current flow and voltage distribution, thus sensing the measured voltage to touch. Moreover, a 1 cm spatial resolution was achieved with a single fiber, thus allowing the fabrication of 2D touch sensitive textiles with a 1D array of capacitor fibers. The fiber capacitors may also interface with other fiber electronics such as conductive fibers or battery fibers to constitute a functional on-garment electric circuit. Potential application of such on-garments electronics may include fashion, safety clothes as well as programmable and computing textiles.

Pressure-sensitive fabrics were also developed.[174] To fabricate the sensors, fibers were coated with organic conductive polymer poly(3,4-ethylenedioxythiophene) and poly(styrene sulfonate) and a dielectric film of perfluoropolymer using a die coating system (Figure 6c). The coated

fibers were woven as wefts and warps, and the rest of the matrix was filled with pristine nylon fibers. Capacitors were formed at the nodes, where the fibers intersected. When a pressure of 4.9 N cm^{-2} was applied on the fabric, capacitance increased from 0.22 to 0.63 pF with a sensitivity ranging from 0.98 to 9.80 N cm^{-2}.[174]

Temperature, humidity and pressure sensors have been incorporated in textiles.[177] These studies have utilized photolithography and inkjet printing to create the sensors woven into textiles (Figure 6d). Capacitive humidity and resistive temperature sensors were developed on flexible polymer foils and integrated into textiles.[175] To fabricate the sensors, metal films were deposited on polyimide sheets. In photolithography, a double metal layer of Cr/Au was electron beam evaporated under vacuum on polyimide sheets and patterned using a lift-off process. The sensing elements included an interdigitated thin-film capacitive transducer, and temperature sensitive thin-film meander-resistor. The inkjet printing of the sensors involved depositing Ag NP ink on the polyimide. Bus lines and interdigitated finger electrodes were printed in two separate printing steps (500-4000 dpi). The resulting line width and electrode gaps for resistors and capacitors were 80 μm, and the thickness of the printed layer was 400 nm. Sensing materials were encapsulated by laminating a photoresist film on the substrate. For the detection of humidity, cellulose acetate butyrate as the sensing medium was spray-coated on the capacitor through a stencil mask. In inkjet printing, the cellulose acetate butyrate in hexyl acetate was printed over the substrate to achieve a 5 μm film. The device was capped with a hydrophobic, gas permeable membrane. Subsequently, a commercial machine was used to weave the sensors into a textile band in weft direction with twill (1/8) pattern. Humidity and temperature sensors were inserted into the textile along the weft direction as replacement for weft yarn. Warp threads were replaced by conductive yarns to contact with the sensors inside the textile. The temperature

sensors operated from 10 to 80 °C with a sensitivity of 5 °C. Humidity sensors had a detection range from 25 to 85 % with 10 % sensitivity.[175] These textiles were combined with LEDs to give visual sensing information (Figure 6e).[178]

Metal-Organic Frameworks (MOF) built with rare earth elements and/or quantum nanorods have been immobilized on cotton fabrics at high concentrations.[179] These materials have shown the potential to be used as colorimetric sensors to detect the presence of toxic gases via the luminescence of the MOFs or the electrical conductivity of the nanorods.[180] These chemical sensors can be incorporated into uniforms, apparels or any textile substrate. A dress designed by Matilda Ceesay using cotton mesh coated with a Cu benzene tricarboxylic acid MOF-199 customized for capturing and controlled-release of permethrin (an insecticide) (Figure 6f). The designer aimed at functionalizing mosquito bed-nets commonly used as preventive measures in areas with high prevalence of malaria.[176]

TOXICITY OF NANOMATERIALS IN TEXTILES

The forms of NP released in washing liquid depend on the nanomaterial characteristics originally incorporated into the textile, the composition of the washing liquid, the washing procedure (*e.g.* rotation speed). Ag-containing textiles release significant amounts of dissolved and particulate Ag into washing liquid. The potential exposure to Ag NPs from a blanket has been evaluated. For a blanket containing 109.8±4.1 mg Ag kg^{-1}, 4.8 ± 0.3 mg Ag kg^{-1} was released into sweat in 1 h.[181] Commercial NP-impregnated socks (1360 μg-Ag g^{-1}) leached up to 650 μg of Ag in distilled water (500 mL) in 24 h.[71] However, other commercial socks containing large amounts of Ag (2105 μg and 31242 μg) released small percentages (1 wt%) of total Ag into the ultrapure wash water while some brands released ~100 wt% of the Ag after four consecutive

steps. These studies indicate that the manufacturing processes of these socks differ fundamentally. The socks released 155 μg and 15 μg of Ag into ultrapure water and tap water, respectively. Hence, tap water was less aggressive in stripping Ag from the textile than ultrapure water, which was attributed to differences in water corrosivity.[15] Artificial sweat was also used to test the concentration of the Ag released from fabrics.[182] The concentration of Ag released from Ag-impregnated fabrics was measured up to 322 mg kg^{-1} of fabric weight. The release rate depended on the concentration of the Ag in the fabric and pH of sweat. In another study, shirts and pants impregnated with TiO_2 NPs ranging from 2.9-8.5 g Ti kg^{-1} textile.[183] The release of TiO_2 into sweat per gram of textile after 30 min incubation in 120 mL of sweat was evaluated. Substances released into acidic sweat were 63 ± 13 μg $g^{-1}L^{-1}$ (particulate size<450 nm) and 725 ± 30 μg g^{-1} L^{-1} (particulate size >450 nm); whereas in alkaline sweat, the release amounts were 38 ± 13 μg g^{-1} L^{-1} (particulate size <450 nm) and 188 ± 213 μg g^{-1} L^{-1} (particulate size >450 nm).[19] External dermal exposure for TiO_2 was as maximal 11.6 μg kg^{-1} body weight for total (mainly particulate) TiO_2. When Ag was released from textiles, Ag-chloro complexes were the major dissolved species due to the presence of high chloride concentration in sweat. Figure 7 shows potential scenarios for Ag release from nanomatarial treated textiles.

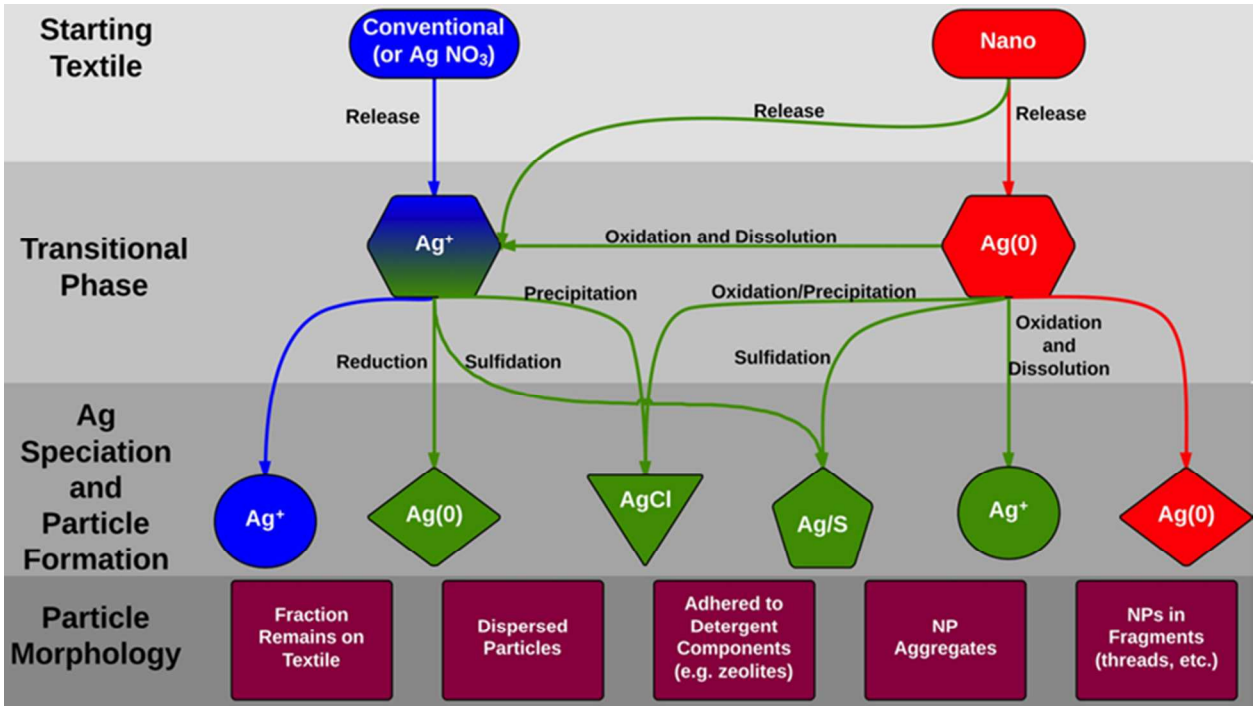

Figure 7. Scenarios for Ag release and subsequent transformation from nanomaterial-treated textiles. Blue shading indicate conventional materials or silver nitrate ($AgNO_3$) that persists through the transformation process, and red shading indicate pristine nanomaterials. Green shading show a transformation product. Reprinted with permission from ref [184]. Copyright 2014 American Chemical Society.

The release of NPs to the environment is a concern. Ag NPs are toxic to aquatic animals including fish, crayfish, and plankton.[185-188] Furthermore, the antibacterial properties of Ag NPs might disrupt the bacterial habitat in sewage treatment plants.[189] Nanowashing machines were shown to release Ag in effluent at a concentration of ~11 µg L^{-1}.[190] Recent life cycle assessments involved comparing environmental benefits and negative effects of nanoAg T-shirts with conventional textiles treated with triclosan (a biocide).[191] Figure 8 shows lifecycle stages of one T-shirt (1.56 m^2 textile, 130 g). The "cradle-to-gate" climate footprints of the manufacturing of

nanoAg T-shirt were 2.70 kg of CO_2-equiv for flame spray pyrolysis, and 7.67-166 kg of CO_2-equiv for plasma polymerization with Ag co-sputtering. However, conventional T-shirts produced by triclosan had emissions of 2.55 kg of CO_2-equiv. Additionally, the toxic releases from washing and disposal stages had minor relevance. However, the production phase holds importance due to toxic Ag emissions at mining sites. Overall, the use phase was the most important in terms of climate footprint in both nanoAg and triclosan cases. A limitation of these studies was that variation in Ag release rates was not taken into consideration. Also, current life cycle impact assessment methods do not distinguish colloidally bound phases of metals.[192, 193] Up to now, the life cycle assessments took into account only NP form. Considering other forms of nanomaterials such as ionic forms, agglomerated forms, and oxidized forms will provide improve life cycle assessments. While these assessments provide estimated effect of nanomaterials on the environment, public awareness holds importance in washing practices. For example, efficient washing procedures such as using tumblers less, and operating washing machine at lower temperatures with appropriate detergents may reduce the environmental impact. The increase in the awareness for recycling rate of NP embedded textiles may reduce the carbon footprint. Furthermore, exposure to NPs is a significant concern at workplace.[194] For example, spraying methods may result in exposure to inhalation of NPs.[195] The development of improved life cycle assessments will allow comparing nanoengineered textiles with conventional products in the market to prevent environmental consequences.

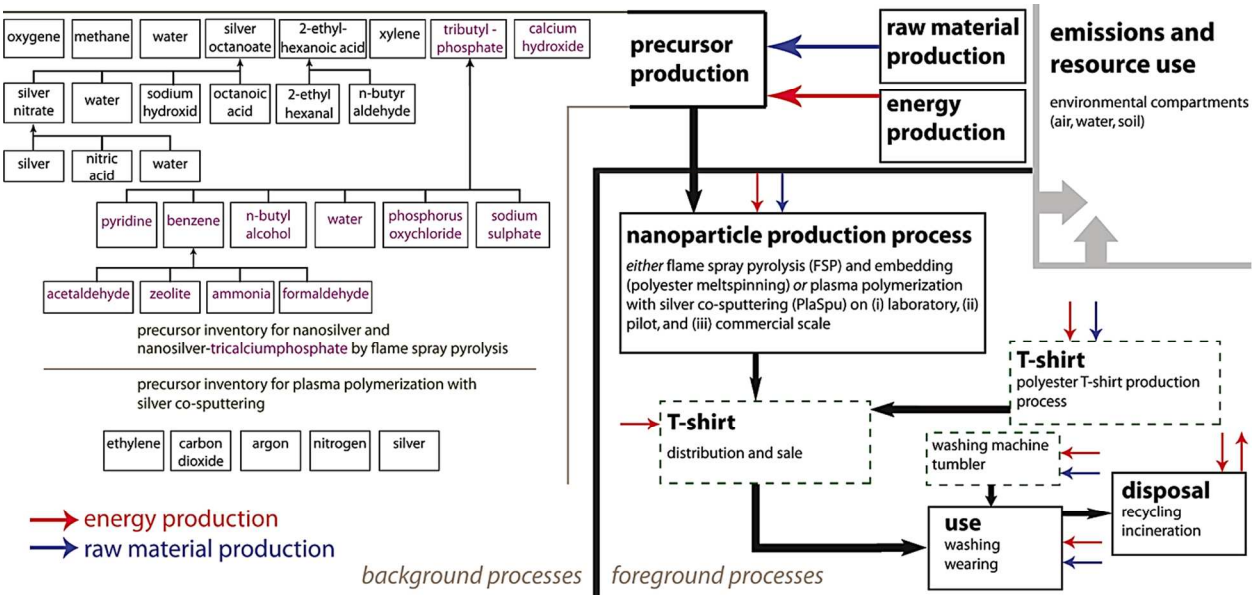

Figure 8. Lifecycle stages of one nanoAg T-shirt showing system boundaries (dashed boxes). Reprinted with permission from ref [191]. Copyright 2011 American Chemical Society.

CONSOLIDATION OF NANOTECHNOLOGY IN TEXTILES MARKET

Fashion and apparel industries were valued at $1.2 trillion globally in 2014, and the market size is expected to have a Compound Annual Growth Rate (CAGR) of 4.8% until 2025, mainly driven by emerging markets.[196,197] In the United States, 1.9 million people are employed, and $250 million is spent in fashion industry annually.[25] In 2014, the global smart textiles market was assessed as $795 million, which is anticipated to reach $4.72 billion by 2020 with a CAGR of 33%.[198] Major drivers for the smart textiles market are wearable electronics, increasing demand for devices with advanced functions, miniaturization of electronics, and rapid growth of low-cost wireless sensor networks. Military and security sectors have the largest shares of the smart textiles, accounting for about 27% of the total market. The market shares for the sports and fitness segments are expected to increase at a CAGR of 40% until 2020.[198] Americas was accounted for 41% of the global smart textiles market in 2014, followed by Europe (25%), and

Asia-Pacific (21%) in 2014 (Figure 9). However, Asia-Pacific market is expected to have highest CAGR (44%) in the next five years. The United States market is projected to grow at a CAGR of 31% until 2020.[198] High growth rates may be attributed to trends outside conventional apparels. This is because in the traditional apparels, there is more demand for cost reduction, as oppose to performance enhancement. In the case of innovative and functional applications of wearables, the customer motivation is opposite.[199] Furthermore, the market for nanofiber-based products is expected to reach over $1 billion by 2020.[200] However, this market is not limited to textile and apparel industry.[198, 201] With a demanding market for wearables and a growing trend for nano-fiber based products, the applications are diverse for the nanotextile products ranging from consumer apparels to medical wearables.[202]

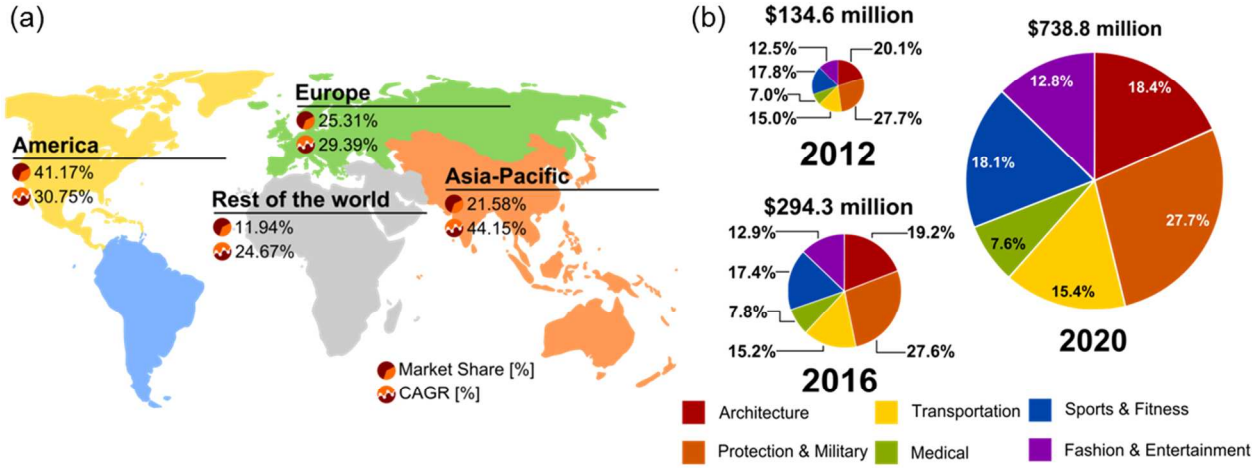

Figure 9. Smart textiles market. (a) Market shares and CAGRs by region in 2014[198]. (b) North America smart textiles market revenue by end-use, 2012–2020[198]

A driving force for the smart textiles industry is sensing technologies with Internet connection. This capability can be used to communicate data such as location, as well as physiological parameters (*e.g.* heart rate), which are important in healthcare, sports, and fitness. Therefore, this trend is expected to affect the market globally. For example, the use of functional

materials in textiles has led to electrophysical characteristics such as piezoresistive and conductivity. These technologies can aim to evaluate the patient's synoptic data. The process involves the development of smart textiles, communicating the data over the network, and using it to make informed decisions. One of the challenges facing the apparel industry in the use of such communication devices is ensuring simultaneous wearability, and functionality of efficient and portable power supplies.

In general, fashionable functional products transcending the traditional functions of fabric are highly desirable. Growth in the fashion and entertainment industry is expected to contribute to overall market growth. Additionally, the demand from the sports and fitness sector has increased due to growing awareness about healthy lifestyles. End users participating in extreme sports, running, skiing, have also contributed to the demand for smart textiles. To increase the competitiveness with respect to Asia, European Union has created initiatives for promoting incentives.[203] The European Commission has co-financed a number of projects such as Wealthy, MyHeart and Biotex. For example, Wealthy aims to create a wearable device for monitoring patient's vital signs.

To meet a wide range of end user needs, it is vital to market smart wearables that offer various levels of performance and comfort to wide customer base. The necessity for various levels of performance stems from global customers who are willing to pay a premium price for smart functional garments. However, in another market segment, the target customer may demand affordable functional textiles. One possible reason for the interest in innovation in textiles is that porous materials, synthetic microfibers and membranes used commercially over the past 30 years have been commodified. This may be attributed to the accessibility of blockbuster technologies due to patent expirations. The commodification subsequently reduced

profit margin and market share.[200] As a result, companies in the textile industry need to offer competitive advantage through innovation by either enhancing performance or reducing the production cost.

CASE STUDIES

Gore-Tex is a lightweight, waterproof, breathable fabric membrane comprising of expanded polytetrafluoroethylene (ePTFE) for application in medical devices, fabrics, and electronics.[44, 204] W. L. Gore & Associates (Newark, DE) invented ePTFE in the 1970s. Gore-Tex was originally a microporous structure that could be stretched up to 800% of its original length.[205] Gore-Tex is used in products manufactured by various enterprises including Patagonia, L.L. Bean, Oakley, Inc., Galvin Green, Marmot, Vasque, Arc'teryx, Haglöfs, and The North Face.[206,207] W. L. Gore & Associates holds more than 71 issued patents related to Gore-Tex or the use of PTFE, in which 18 patents are for use in garments. Although the basis for the Gore-Tex technology originated from microporous structures, the company has recently incorporated nanostructures into their products for the apparels market. For example, Nano and NanoPro jackets have been manufactured in conjunction with Marmot LLC.[208] Other nanotechnology-based examples could be seen in the company's patent portfolio. Examples include Nyagraph 351 (Nyacol Nano Technologies, Inc) for burn protective materials,[209] nanoemulsions of functionalized PTFE,[210] prefiltration layers comprising of nanofibers,[211] and NPs for improved insulated electrical conductors.[212] These cases serve to illustrate the importance of nanotechnology to a well-established innovative company in the apparel industry.

NanoSphere® marketed by Schoeller Textiles AG (Sevelen, Switzerland) is a finishing technology with hydrophobic surface properties that mimic the self-cleaning effect of lotus leafs.[39] Schoeller claims that NanoSphere® has improved water/oil and dirt repelling properties,

and washing performance as compared to traditional textile impregnation-based manufacturing. Furthermore, the protective function of NanoSphere® may be retained after frequent use and numerous washing cycles without affecting comfort, texture, and breathability. The textiles finished with NanoSphere® require less frequent washing at lower temperatures as compared to conventional textiles. Additionally, it has high abrasion resistance. The company's other products address a variety of applications ranging from stretch fabrics, sun reflectors, and temperature resistance, and bionic climate conditioning.[213] Their patent portfolio in nanotechnology includes PEIN NPs for antibacterial finishing of electrospinnable polymers,[214] NPs and CNTs for finishing of substrates,[215] and nanofibers having microbicidal properties.[216]

Aquapel, marketed by Nanotex LLC (Bloomfield Hills, MI), reproduces natural water-repellency of plant surfaces and animal coats.[179] Aquapel technology involves permanent attachment of hydrophobic 'whiskers' to individual fibers at the molecular level. Aquapel features a hydrocarbon polymer that is ecologically friendly and low-cost. Nanotex's portfolio consists of 28 WO patent applications and addresses textile sectors including repellency/stain resistance, moisture management, odor control, static elimination, and wrinkle resistance. In 2013, Nano-Tex products were on $280 million in branded products at retail.[10] In the same year, Nanotex was acquired by soft-surface technology company Crypton Inc.[217]

SmartSilver® is an antimicrobial yarn marked by NanoHorizons (Bellefonte, PA). It develops and manufactures Ag NP additives that provide antimicrobial characteristics to their products. The company markets Oeko-Tex® antimicrobial solution under the SmartSilver® brand.[218,219]

Nanosan, marketed by SNS-Nano Fiber Technology (Hudson, OH) and Schill & Seilacher (Germany), consists of spun polymers for application in filters and adsorbent fabrics.[220] SNS-

Nano Fiber Technology integrates microscale particles into the nanofiber structure at high-volume production. Nanosan fibers can be engineered to be function as high-strength, absorbent, or flexible material. Its product line consists of nanofiber matrixes with different absorption properties. The applications of Nanosan include filters, medical and military products and personal care products such as cosmetics. Its patent portfolio includes debris and particle absorbent materials.[221,222,223,224] The company is currently exploring the use of nanofibers for skin decontamination.

Wearable Motherboard™ (electronic shirt), marketed by Sarvint Technologies, Inc. (Atlanta, GA), uses engineered fibers to sense body signs, such as heart rate, temperature, skin conductivity, muscle exertion, blood pressure, and respiration rate.[164] Its patent portfolio includes the use of engineered fabric-based sensors (*e.g.* conductive fibers) for monitoring vital signs. Its technology comprises microporous elastic Spandex fiber, a polyester-polyurethane copolymer invented in 1958.[225-227] Table 1 shows the companies involved in smart textiles and wearables market.[228] Some of these companies use microtechnology as opposed to nanotechnology in apparels.

Table 1. Companies that have commercialized micro and nanotechnology-based apparels, their major products and applications.

Company	Year founded	Number of Pending patents /granted	Area (μ /Nano)	Technology & Products	Applications	Ref.
Auxetic Technologies Ltd (UK)	2004	3	μ/Nano	Auxetic materials (becomes thinner when stretched, and thicker when compressed)	Composite material, auxetic foams	229-231
Brandix Lanka	2002	N/A	Nano	Functional clothing	Fabric and garment accessories	N/A

Limited (Sri Lanka)						
Clothing Plus Ltd (Finland)	2001	2	μ	Heart rate sensing shirt (Combined textiles and electronics)	Comfortable biometric sensor electronics for sports and medical applications	232, 233
DuPont (US)	1802 (sold its textiles business to Koch Industries in 2004)	>100, out of which 32 is related to garment	μ/Nano	Lycra (spandex), a stretch fiber	Stretchable, compression and shaped garments, home furnishings	234-243
Exo2 (US)	2007	N/A	Nano	FabRoc™ and ThermoKnitt™ heating technology	Wireless heated outdoor clothing	N/A
FibeRio Technology Corporation (US)	2009	2	μ/Nano	Micro- and nanofibers	Apparel, filtration, healthcare, and electronics	244, 245
Fibretronic limited (Hong Kong)	2004	N/A	μ	Textile electronics	Wearable electronics and smart fabrics (sensors, heating and cooling elements)	N/A
Freudenberg Group (Germany)	1849	N/A	μ/Nano	Housewares and cleaning products, automobile parts, and textile	Nonwoven fabrics and textile materials	N/A
Gentherm Incorporated (US)	1960	18	μ	Heating and cooling comfort	Thermoelectrically heated and cooled seat system (automotive, medical, bedding)	246-255
Google Inc. (US)	1998, partnered with Levi Strauss & Co.	N/A	μ	Jacquard: a microfiber-woven textile	Textile with digital sensing microfibers	N/A
Hollingsworth and Vose (US)	1843	3	μ/Nano	Filtration and nonwoven materials	Composite materials, home furnishings, apparel	256-258
HeiQ (Switzerland)	2005	6	μ/Nano	Dynamic cooling, water and oil repellency on textiles	Outdoor products, medical implants	1259-264
Interactive Wear AG (Germany)	2005	2	μ	Functional textile products: textile cable, heating pads, interactive wearable solar energy source	Integrated textile systems	265, 266
International Fashion Machines, Inc. (US)	2002	2	μ	Electronically controllable flexible substrate	Electronic textiles, which behave as an electronic circuit or device	267, 268

Midé Technolog Corporation (US)	1989	11	µ	Piezo cooling, haptic actuators, energy harvesting, data logging)	General wearables	269-279
Nanohorizons (US)	2002	2	Nano	Ag NPs	NanoAg textiles	218, 219
Nanotex (US)	1998	22	Nano	Nanoengineered polymers	Moisture resistance, odor management	280-301
Ohmatex Aps (Denmark)	2004	N/A	µ	Elastic textile cables, conductive textiles, textile-based sensors	Textiles combined with IT technology	N/A
Peratech Ltd (UK)	1996	12	Nano	Electroactive polymeric material QTC (Quantum Tunnelling Composites)	Force and touch sensing within electronic circuits	302-313
Sarvint Technologies, Inc. (US)	2014	6	µ/Nano	Functional wearables	Garment with intelligence capability	226, 227, 314-317
Schoeller Textiles AG (Germany)	1967	9	µ/Nano	Stretchable fabrics, protection fabrics, soft shells, protective fabrics	NP-containing fibers	214-216, 318-323
Sensium Healthcare (UK)	2000	N/A	µ	SensiumVitals®, a lightweight patch reading of patients' heart rate, respiration and temperature	Wireless monitoring of vital signs	N/A
Sensoria Inc. (US)	2010	3	µ	Body -sensing wearable devices	Anklet and sensor infused socks and fitness bras and t-shirts with heart rate monitor	324-326
SNS Nano (US)	2007	4	Nano	Debris and particle absorbent materials	Textile composite material	221-224
Texas Instruments (US)	1951	>100	µ	Semiconductors, microcontrollers DLP Products & MEMS	Wearable displays, Bluetooth wearable watch	N/A
Textronics, Inc. (US)	2005	13	µ/Nano	NuMetrex, soft textile sensors	Health and fitness monitoring	327-332
Thermosoft International (US)	1996	6	µ	Flexible electric heaters	Heated fabric, conductive textile, heated bedding and clothing	333-344
VivoMetrics Inc (US)	2009	8	µ	Body worn sensors: Hexoskin (Sports Shirt), Nonin (Wrist worn Bluetooth pulse oximeter), Onyx (Finger clip Wireless pulse oximeter, LifeShirt (garment with embedded sensors)	Continuous ambulatory physiological monitoring sensor systems	345-352
Wearable Information Technologies (Weartech)	2007	1	µ	Smart fabrics and interactive textiles	Sports, fitness, health prevention, healthcare, and industrial safety	353

(Spain)						
W. L. Gore & Associates	1958	48 (Gore-Tex or PTFE): 13 in garments	μ/Nano	Gore-Tex is a waterproof, breathable fabric membrane	Widespread products, including fashion and apparel	205, 354-372

FUTURE DIRECTIONS

The integration of high-computing microprocessors and miniaturized computers can enable the capability to collect information throughout a garment. For example, the physiology of the body and posture data collection in garments could allow for correcting the unhealthy posture. Wearing high heels shifts the center of gravity forward, and this causes disturbances in the posture. This produces strains on the calf muscles and thigh muscles, and a forward tilt in the pelvis. These changes have negative implications in the body including misalignment of hips and spine and increase in the pressure on the forefoot, leading to degenerative arthritis in the knee. New wearable technologies can be incorporated in garments and shoes to measure the pressure and posture pattern and alert the user. Such technologies can be imparted to be active to loosen or stiffen the dress, or shoe based on the motion to prevent pain or sag. Weight loss is another potential area that can be explored with nanomaterials. For example, vibration motors can be integrated in textiles to promote blood circulation and weight loss. These devices may also achieve wireless powering of the internal or external electrical components. For example, self-winding mechanisms developed in automatic watches can be utilized to generate energy from the movement of the body. A significant area that nanotechnology-based energy sources can provide a solution is cooling. Highly-dense fabric batteries or solar cells need to be developed to power cooling without compromising comfort. Such powering mechanisms can be coupled with phase-change materials to cool the body in hot environments, or cool the electronic components in the textile.

Interactive garments in fashion will also evolve. Programmable visual components, LEDs and fiber optics in garments will find increasing use in fashion and entertainment industries. Incorporation of new approaches including structural colors, luminescence, plasmonics, metamaterials, holography, photonic crystals (PCs) and LED displays in textiles can create mesmerizing effects on garments. These dresses can be combined with pressure or motion sensors that can change the color of the dress based on touch, movement, temperature, light, electric field, or other external stimuli. The material may also include bioinspired patterns and chemical reactions with the environment.

In addition to serving as light emitting elements to enable the shinning and colorful appearance for fashion apparels, optical fibers offer more capabilities. For example, an array of fibers can be weaved into a garment to constitute a programmable fiber-optic display that is able to show dynamic graphics. Optical fibers can also be used as sensing components in multifunctional garments for sports and fashion. Recently, Cambridge Consultants has developed Xelflex fabric that was equipped with optical fiber sensors for tracking movements of human body.[373] Xelflex could be used in fitness and sports coaching as well as part of physiotherapy. Additionally, fiber sensor-based gloves and garments that can recognize postures of human hand and body have been demonstrated.[374] Physical or biological measurements may be detected by on-garment fiber sensors such as strain, pressure, temperature, humidity, and metabolites.[375] Thus, in the near future a fully functionalized sportswear based on fiber-optics sensors will be produced for monitoring of physiological conditions of human body including heart beating rate, blood pressure, sweating, body motions, temperature, and even potential disease risks. Such garments can also be used for increasing the interaction and connectivity of user with gaming consoles and virtual reality platforms.

Integration of optical displays into textiles or garments is desirable for many applications. Current textile displays are mostly based on LEDs. Although LEDs are low cost, small, and available in an array of different colors, they are not truly compatible with textiles due to their rigidity. Additionally, the resolution of the LED textile displays is typically low (LED pitch: 1-100 mm).[376] The LCDs that are commonly used in current smartphones, tablets and computers are usually inflexible.[377] Considering the flexibility and light weight required for textile displays, OLEDs composed of thin films of organic molecules constitute a potential candidate.[378] Another promising technology for the fabrication of textile displays is quantum-dot light emitting diode (QLED), which is similar to OLED in structure but have an additional active layer consisting of quantum dots.[379, 380] In textile displays, QLEDs could offer higher luminance efficiency and consume less energy than OLEDs. These technologies maybe combined with optical components such as diffraction gratings, diffusers, lenses, or microcavities.[381-384]

Photonic crystals are nanostructures in which the dielectric constant has a periodic variation in one, two or in all three orthogonal directions.[385-387] In such structures, one observes formation of the spectral photonic bandgaps, which are the spectral regions where photons are unable to propagate in the bulk of the periodic structure. Therefore, narrow-band colors could be seen in the light diffracted or transmited by PCs. They can be incorporated into flexible thin films that may be conveniently attached to a fabric or garment.[388, 389] These PC films may have their color changed when stimulated by external stimuli such as current, compression, stretch, or temperature and humidity. The structural parameters of PCs or the effective refractive index of PCs are modified by these stimuli, thus shifting the PC spectral bandgaps.[390, 391] This color-tuning property may be utilized for garments to not only promote the aesthetic performance, but also enable the garments for sensing applications.[392]

Combining holograms with garments and wearable devices is another potential research direction.[393, 394] A hologram is first produced by encoding interference information of an object on a recording medium. A 3D image of the recorded object could be reconstructed by illuminating the holographic film with a broadband light.[395, 396] To date, a variety of holographic films have been used as decorative coatings that are able to provide garments with iridescent appearances and 3D graphics.[145] Holograms may also be used in other wearable gadgets such as helmets and glasses for virtual-reality applications. In Hololens (Microsoft), holographic gears are equipped on a headset.[397] Thus, wearers of Hololens may appreciate a virtual life experience by visualizing and interacting with the environment on demand. Moreover, holographic sensors that are fabricated into thin films could also be integrated into garments for detecting metabolic function.[398-403]

Metamaterials are artificial structured substances made by assembling composite materials such as metals and plastics in periodic patterns at scales that are smaller than the wavelength of interest.[404] Metamaterials due to their extraordinary structures exhibit complex behavior to electromagnetic waves (*e.g.* negative refractive index). Many intriguing features could be offered by metamaterials when used in textiles and garments. For example, metamaterials have potential for the development of cloaking devices that are used to make a defined region invisibly isolated from the passing electromagnetic waves. While some progress on metamaterial-based cloaking devices was made at microwave[405] and THz frequencies,[406, 407] truly invisible garments may be realized in the visible spectral region. Moreover, many thin-film metamaterial sensors have been demonstrated.[408] These sensors could be potentially integrated into textiles and garments for monitoring physiological biomarkers.

Nanotextiles can be functionalized with molecular dyes and analyte-sensitive compounds. For example, microfluidics can be incorporated in thread-based channels for application in point-of-care diagnostics.[409-417] In the future, we expect many functional components being seamlessly integrated into textile architecture. Accordingly, production processes will also evolve to combine electronics, biomaterials, and optics into textile weaving. Applications in fashion and arts will also be realized.[418, 419] These sensing and display technologies may be controlled by smartphones.[420-422]

Another potential research area is to create green chemistries and fabrication approaches to synthesize nanomaterials that stay intact after laundering. For example, development of new covalent binding mechanics to attach nanomaterials to cotton or synthetic fibers is desirable. These nanomaterials may also require new surface finishing processes to ensure their immobilization in textiles and maintenance any environmental condition. Additionally, agglomeration of deposited nanomaterials is a major challenge and this requires the development of new nanoadditives and stabilizers in formulations and finishing treatments. These approaches may require functional surface-activated polymer or cotton composites to immobilize nanomaterials on textile without comprising their chemical, optical, and electrical properties. Furthermore, recycling of clothing is generally carried out by creating landfills. A significant concern about the nanomaterials is potential contamination of water or soil.[184] Hence, life cycle assessments should also focus on identifying risk factors for laundering, recycling and particle release after degradation while accounting different forms of nanoparticles and release rates. Effects of uncontrolled release of nanomaterials to the environment, and toxicity to humans, marine life needs to be evaluated before the introduction of nanoproducts to the market. Since these nanomaterial-based textiles are likely to be produced in the emerging economies, the safety

of the workers and exposure to nanomaterials warrant nanotoxicity analyses. The commercialization of nanotechnology-based textiles may be limited due to government regulations. For example, Biocidal textiles containing nanoAg are registered by the Environment Protection Agency (EPA) in the United States.[193] ISO catalogue enlists a number of standards for formulating and testing nanoproducts.[423]

CONCLUSIONS

The customer demand in improved appearance, functionality, and connectivity in fashion has motivated the development of nanotechnology-based textiles. Over the last two decades, numerous nanostructures and nanomaterials including NPs, CNTs, Bragg diffraction gratings, and nano-electronic components have been deposited or woven into textiles. The development of these nanomaterials also created new fabrication methods involving particle impregnation, spray coating, multifunctional composite fiber drawing, and direct weaving at industrial scale. The application of nanomaterials in the form of surface modifications, electronics and optics offers functionality as well as the potential of improved appearance. Realized nanotechnology applications in textiles include antibacterial properties, odor control, UV protection, water repellence, wrinkle resistance, antistatic properties, and strength enhancements. Advanced technologies included incorporation of moisture, temperature, pressure sensors, drug release, and fiber optics powered by textile-based batteries. With the emergence of nanomaterials, these technologies are transitioning from rigid to seamlessly integrated flexible substrates while offering light weight.

In parallel to the development of nanotextiles, life cycle assessments and toxicity of released nanomaterials from textiles are being critically evaluated. Nanotechnology-based products will

continue to emerge with new applications; however, manufacturers and regulatory agencies must ensure that these technologies will not have a negative effect on human health and the planet during their manufacture and life cycle. The textile industry is under scrutiny due its impact on climate change.[424] Today textiles and apparels account for ~10% of the total carbon emissions.[425] 17-20% of industrial water pollution originates from dyeing and finishing agents in textile industry, negatively affecting people inhabiting regions around textile production plants, particularly in the developing world.[426] The use of dyes and fixing agents (*e.g.*, chromium) in textile manufacturers and tanneries are major pollutants, particularly in Southeast Asia.[427] Hence, the effect of nanoproducts on the production dynamics and pollution remains questionable. Growing concerns among customers has begun forcing the manufacturers to reduce the environmental impact of their production methods, which will also involve the use of nanomaterials.[428, 429] Social awareness among customers has probed companies to invest in corporate social responsibility to offer environmentally sustainable products with reduced carbon footprints.[430-432] These trends in customer behavior and climate change will involve the use of nanotextiles, which need to be climate neutral and recyclable aimed at reducing greenhouse emissions. Nanotechnology will undoubtedly evolve textiles transcending style changes to shape the next big concept: the connected couture.

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Author Contributions

A.K.Y. designed the project. A.K.Y. and H.Q. wrote the article. A.M. contributed to Market and Case Studies sections. S.H.Y., A.K., H.B., J.H., and M.S. made intellectual contributions and edited the manuscript.

Notes

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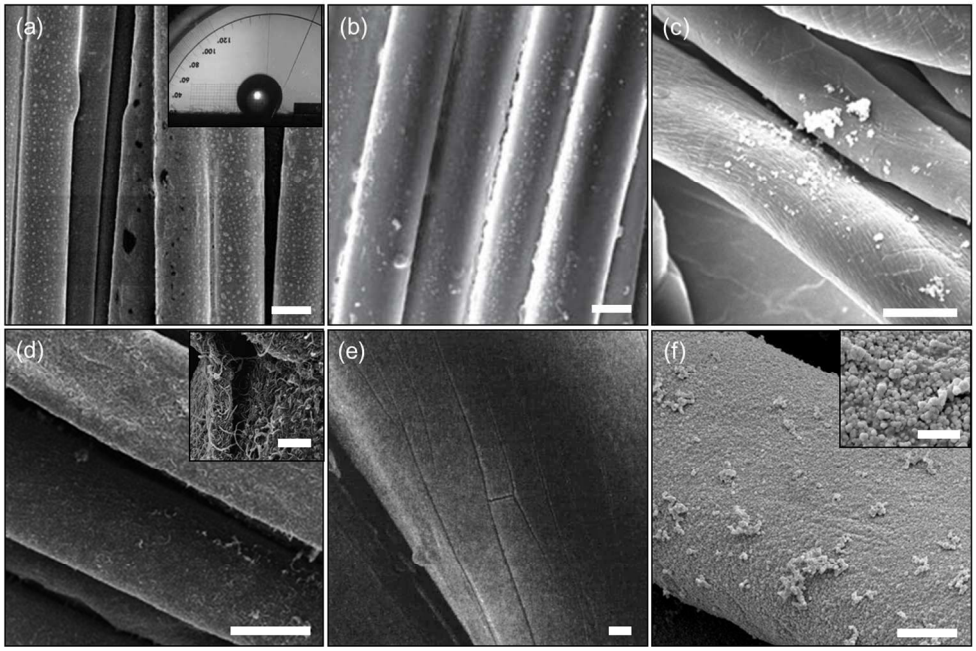
Table of Contents Graphic

Applications of nanotechnology in textiles
145x160mm (150 x 150 DPI)



SEM images of nanoparticle functionalized fibers
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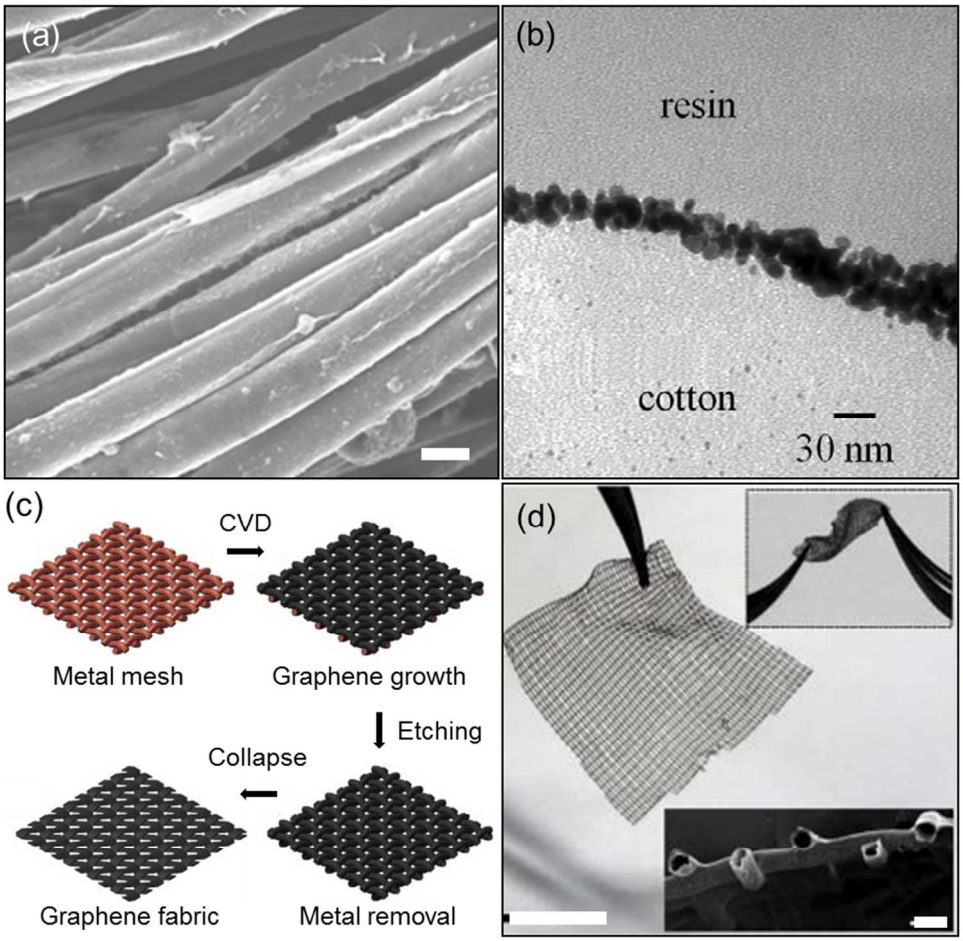

Conductive nanomaterials in textiles
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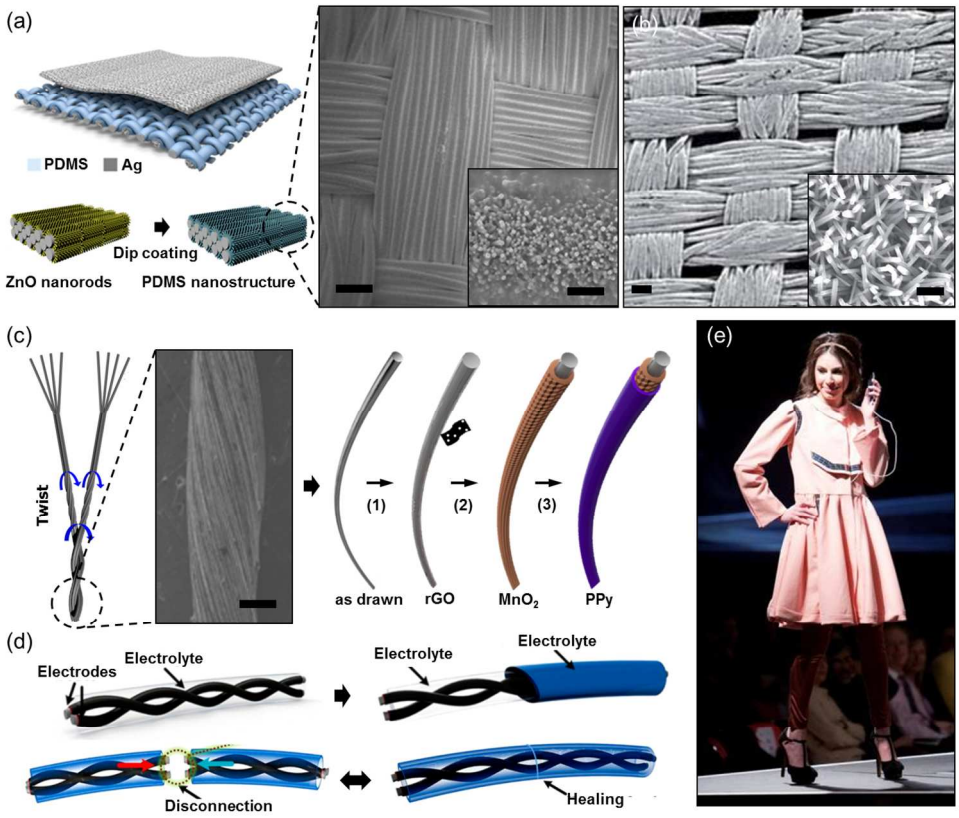

Energy generation and storage in textiles
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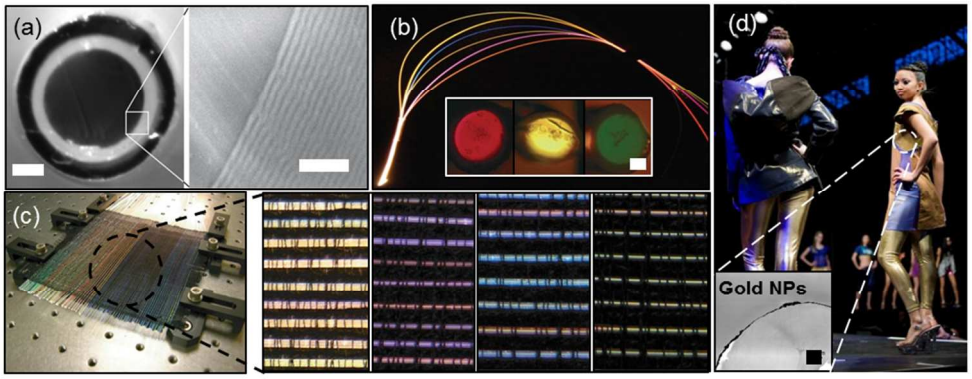

Fiber optic and plasmonic technologies for textiles
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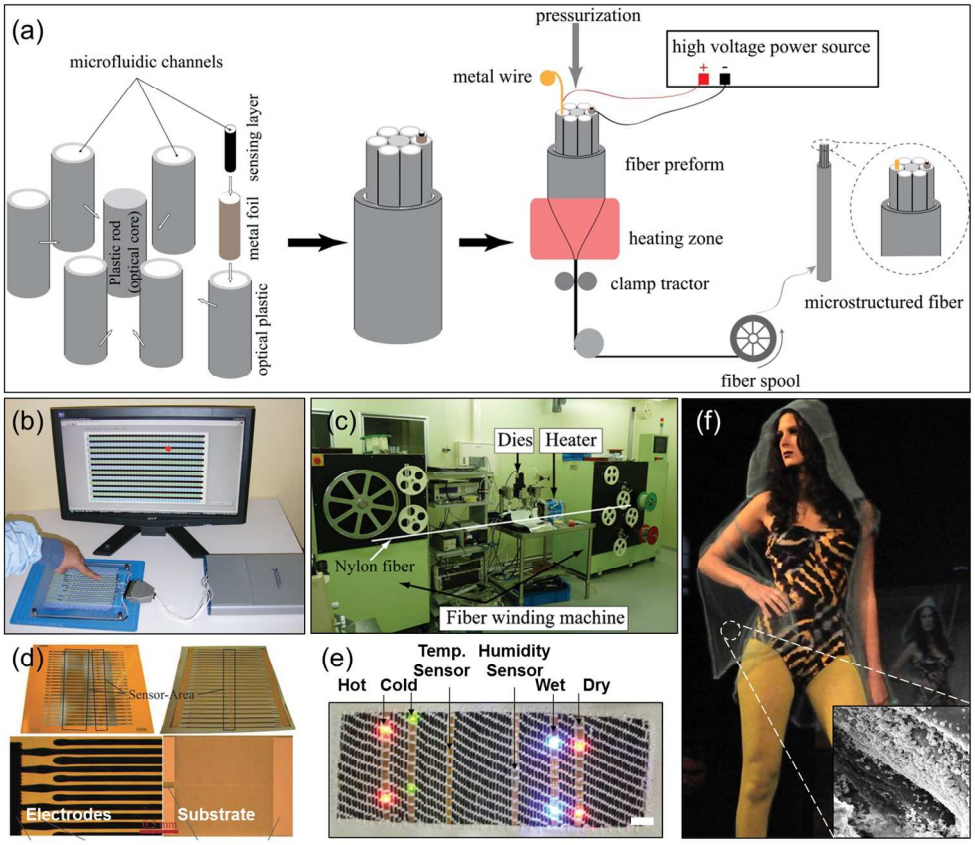

Sensors and insecticide-releasing textiles
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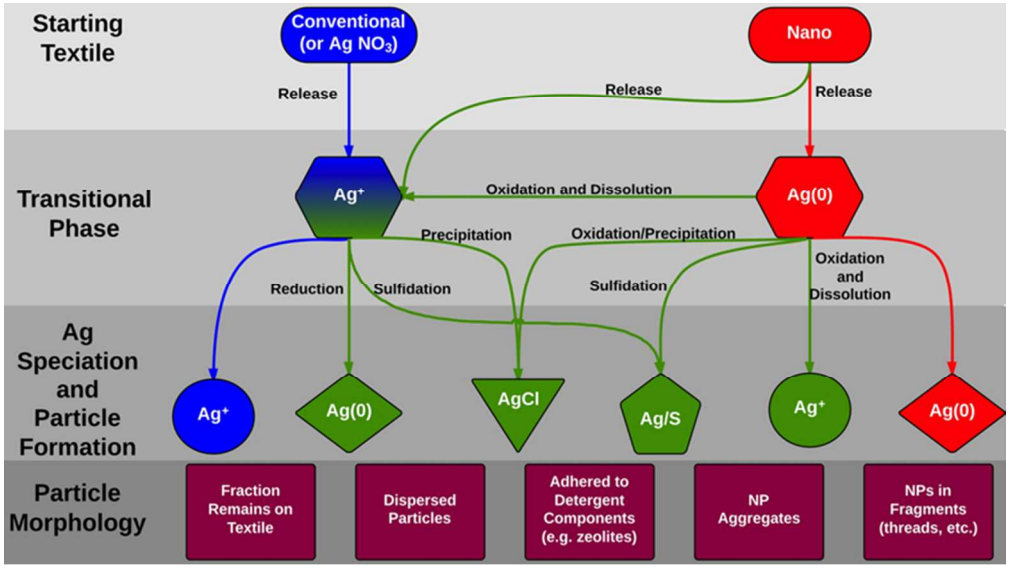

Scenarios for Ag release and subsequent transformation from nanomaterial-treated textiles
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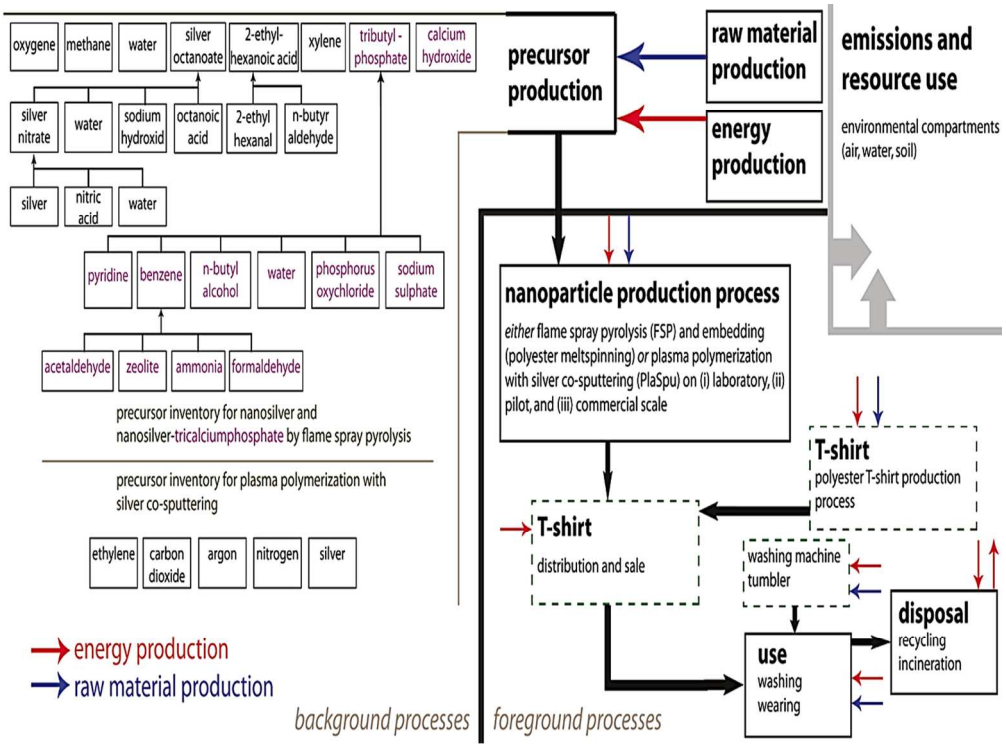

Lifecycle stages of one nanoAg T-shirt showing system boundaries
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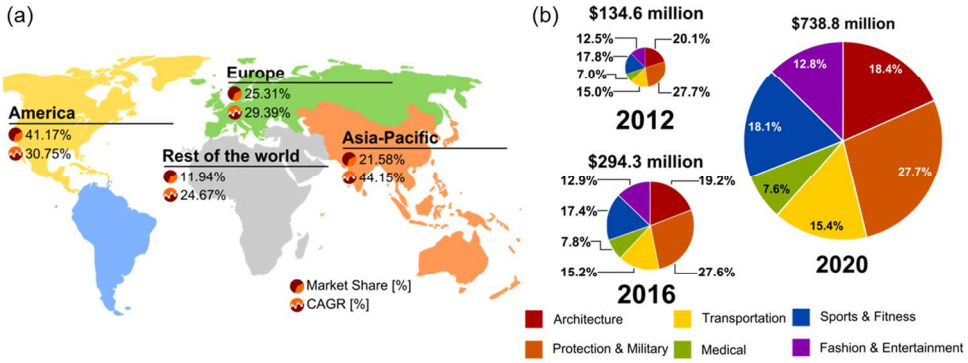

Smart textiles market
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