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### Nanotechnology in textiles

Yetisen, Ali; Qu, Hang; Manbachi, Amir; Butt, Haider; Dokmeci, Mehmet R; Hinestroza, Juan P; Skorobogatiy, Maksim; Khademhosseini, Ali; Yun, Seok Hyun

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## Nanotechnology in Textiles

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# Nanotechnology in Textiles

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7 KEYWORDS: Nanotechnology; fashion; fabrics; fibers; nanoparticles; carbon nanotubes;  
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9 graphene; energy storage; fiber optics; nanotoxicity  
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15 VOCABULARY: **Wearables** - electronics, fiber optics, or nanomaterials embedded in clothing  
16 and accessories that offer improved mechanical, chemical, optical performance via sensing  
17 external stimuli and/or responding to the environment; **Warp** - to arrange threads in long lengths  
18 parallel to one another preparatory to further processing; **Weft** - threads widthways in a fabric as  
19 woven; **Finishing** - a process performed on yarn or fabric after weaving to improve the look,  
20 performance, or texture of the finished textile; **Lotus effect** - self-cleaning due to  
21 hydrophobicity induced by nano or microscale hierarchical structured surfaces;  
22  
23 **Supercapacitor** - an electrochemical cell that allows storing electrical energy temporarily;  
24  
25 **Photonic bandgap material** - a nano or microscale structure that controls the optical properties  
26 of incident light; **Electromagnetic shielding** - blocking the electromagnetic field by conductive  
27 or magnetic materials; **Bragg fiber** - fiber optics incorporating Bragg gratings to filter narrow-  
28 band light  
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7 ABSTRACT  
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11 Increasing customer demand for durable and functional apparels manufactured in a sustainable  
12 manner has created an opportunity for nanomaterials to be integrated into textile substrates.  
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14 Nanomaterials can induce stain-repellence, wrinkle-freeness, static elimination, and electrical  
15 conductivity to fibers without compromising their comfort and flexibility. Nanomaterials also  
16 offer a wider application potential to create connected garments that can sense and respond to  
17 external stimuli via electrical, color, or physiological signals. This Review discusses electronic  
18 and photonic nanotechnologies that are integrated with textiles, and shows their applications in  
19 displays, sensing and drug release within the context of performance, durability, and  
20 connectivity. Risk factors including nanotoxicity, nanomaterial release during washing, and  
21 environmental impact of nanotextiles based on life cycle assessments have been evaluated. This  
22 Review also provides an analysis of nanotechnology consolidation in textiles market to evaluate  
23 global trends and patent coverage, supplemented by case studies of commercial products.  
24 Perceived limitations of nanotechnology in the textile industry and future directions are  
25 identified.  
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6 The concept of clothing is undergoing a transformation through innovation in wearable  
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8 technologies. Intelligent clothing has increasing presence in prominent fashion weeks in New  
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10 York, London, and Paris. Fashion designers are creating functional materials and integrating  
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12 emerging, communication devices, flexible electronics and nanomaterials to garments and  
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14 designer clothes. For example, Philips designed a dress (*Bubelle*) that can tune its colors based  
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16 on the wearer's mood. Black Eyed Peas has also embraced technology at stage, for example, they  
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18 used organic light-emitting diode (OLED) based clothing and adaptive materials in their  
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20 performances. Fashion and technology company Studio XO has created "digital mermaid bra,"  
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22 whose crystals sparkled in time to Azealia Banks' real-time rapping. Recently, TechHaus, the  
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24 technical division of Haus of Gaga, has created a series of performance dresses for Lady Gaga's  
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26 ARTPOP campaign (2013). Gaga's featured artworks included a three-dimensional (3D)-printed  
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28 bubble machine dress (*Anemone*), a Jeff Koons-inspired design called the Parametric Sculpture  
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30 Dress, a piece with animated black mirrors (*Cipher*), and a flying drone-dress (*Volantis*).  
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32 Singers, artists, designers, and fashion icons have directed their interest to new materials that can  
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34 stand out in public events and media. The designers that have pioneered the use of technology in  
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36 fashion include Ralph Lauren, Diane von Furstenberg, Hussein Chalayan, Zac Posen, Rebecca  
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38 Minkoff, Richard Nicoll, and Iris van Herpen.  
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46 Cotton is a widely used fiber type that exhibits high absorbency, softness, and breathability.  
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48 However, the use of cotton in non-classical applications is limited since its fibers have relatively  
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50 low strength, low durability, easy creasing and soiling, and flammability.<sup>2</sup> Synthetic fibers can be  
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52 antimicrobial, stain/crease-resistant, but generally lack comfort as compared to cotton. The  
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54 development of new fiber types that combine the advantages of both natural and synthetic fibers,  
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3 as well as offering novel functions has been desirable since the 1940s.<sup>3</sup> Customer demand for  
4 improved appearance color, shape, texture, and functionality has also increased.<sup>4</sup> Flexible  
5 electronics and optical devices can be integrated into textiles.<sup>2</sup> The applications of the  
6 functionalized textiles include medical monitoring of body function and metabolism,<sup>5, 6</sup>  
7 rehabilitation,<sup>7</sup> and electronic devices integrated into clothes.<sup>8</sup> Furthermore, these technologies  
8 allow integrating sensors into textiles.<sup>9</sup>

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



**Figure 1.** Applications of nanotechnology in textiles

## NANOENGINEERED TEXTILES

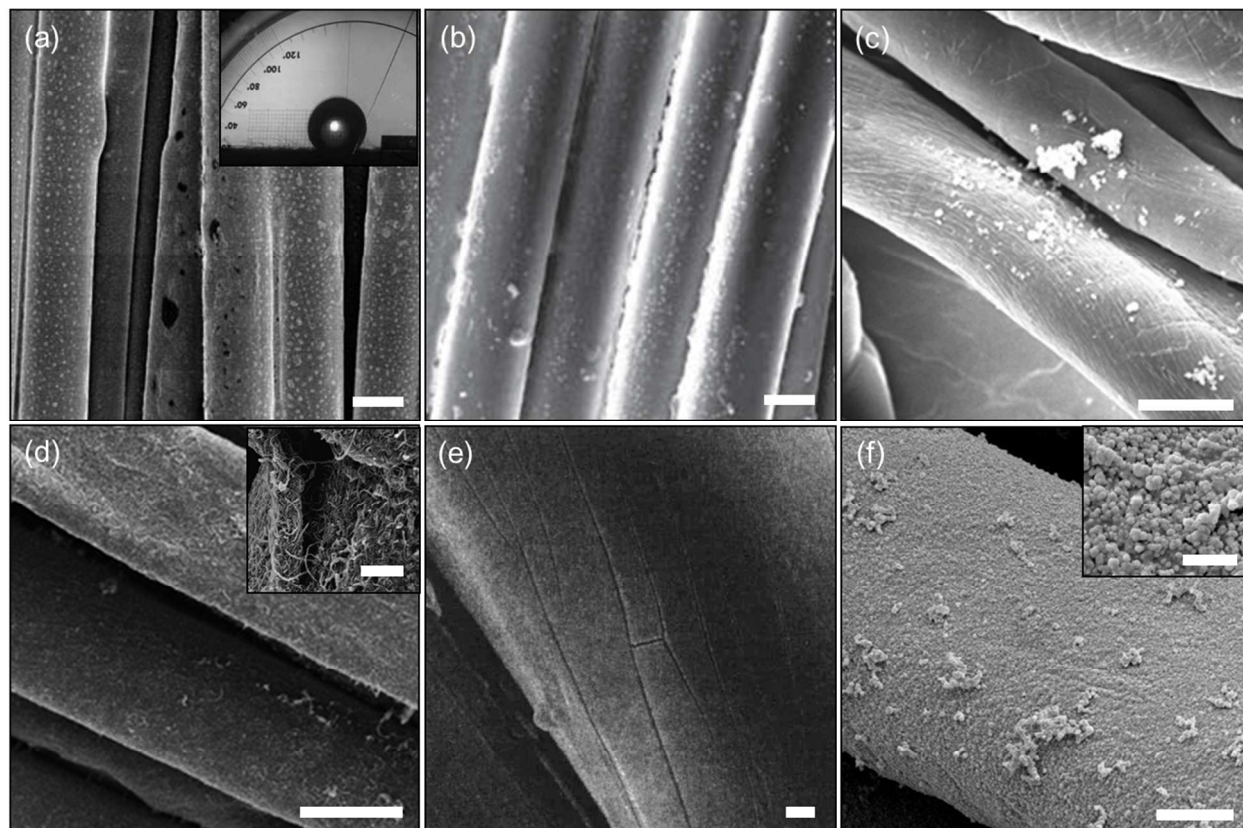
**Water and Oil Repellence.** Water repellence can be imparted to textiles by forming nanowhiskers consisting of hydrocarbons that are three orders of magnitude smaller than a typical cotton fiber. Nanowhiskers are integrated within the fabric to create a peach fuzz effect.<sup>14</sup> Analogous to 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.<sup>15, 16</sup> 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.<sup>17</sup> For example, audio frequency plasma of fluorocarbon derivatives can be applied to coat cotton fibers with



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3 nanoparticulates.<sup>18</sup> By producing a roughness on the surface of the fabric, superhydrophobicity  
4 can be created without affecting abrasion resistance and softness of the fabric. Silica (SiO<sub>2</sub>)  
5 nanoparticles (NPs) in combination with water-repellent agents can also be utilized to impart  
6 hydrophobicity to textiles.<sup>19</sup> SiO<sub>2</sub> NPs (143-378 nm) were synthesized via sol-gel process.  
7 Cotton fabrics treated with both SiO<sub>2</sub> NPs and water-repellent agent produced contact angles  
8 above 130°. SiO<sub>2</sub> NPs could be coated over cotton in the presence of perfluorooctylated  
9 quaternary ammonium silane coupling agent (PQASCA) to produce hydrophobicity.<sup>20</sup> While the  
10 SiO<sub>2</sub> NPs create roughness on the surface of cotton fibers, PQASCA lowered the surface energy.  
11 The resulting textiles exhibited water repellence with a water contact angle of 145°. Oil  
12 repellency of the fabric also improved showing a 131° contact angle for a diiodomethane (CH<sub>2</sub>I<sub>2</sub>)  
13 droplet on the fabric surface. In another study, amphiphilic Janus micro/NPs were chemically  
14 immobilized on textile surfaces.<sup>21</sup> While microparticles bound between fibers, NPs attached to  
15 fiber surface. Janus particle immobilized textiles showed water-repellence.  
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34 Bioinspired design has also motivated the investigation of water-repellent materials. For  
35 example, duck feathers consist of multiscale structures having preening oil to repel water. The  
36 microstructure of duck feathers were simulated by coating cotton and polyester textiles with  
37 chitosan using a surface solution precipitation method followed by modification with a silicone  
38 compound to achieve a low surface energy.<sup>22</sup> Figure 2a shows a scanning electron microscope  
39 (SEM) image of polyester and chitosan-treated polyester having nanosized roughness on the  
40 surface. Chitosan-treated polyester textiles provided flexibility and water repellence. Lotus leaf  
41 nanostructures also inspired biomimetic studies for application in textiles.<sup>23</sup> Cotton fibers were  
42 coated with pristine and surface-modified carbon nanotubes (CNTs) to mimic the nanostructure  
43 of lotus leaves. The resulting cotton fabrics had contact angles greater than 150°. Another study  
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3 that was inspired from lotus leaves involved the development of a nanocoating (20 nm) to create  
4 hydrophobic textiles.<sup>24</sup> The nanocoating consisted of epoxy-containing poly(glycidyl  
5 methacrylate) (PGMA) and SiO<sub>2</sub> NPs for the initial surface modification and generation of the  
6 primary reactive layer. Polymers with different functional groups (*e.g.*, carboxy, anhydride,  
7 amino and hydroxyl) could be grafted on the reactive layer.  
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43 **Figure 2.** SEM images of nanoparticle functionalized fibers. (a) Water repellence: chitosan-  
44 treated polyester with nanoscale roughness on the surface. Scale bar = 10 μm. The inset shows  
45 the profile of a water droplet on the treated polyester fabric. Reprinted with permission from ref  
46 <sup>22</sup>. Copyright 2008 IOP Publishing. (b) Antistatic properties: polyester fiber surfaces treated with  
47 NPs and fluorine. Scale bar = 20 μm. Reprinted with permission from ref <sup>25</sup>. Copyright 2010  
48 Sage Publications. (c) Wrinkle resistance: cotton fibers treated with 1,2,3,4-BCA and TiO<sub>2</sub> NPs.  
49 Scale bar = 10 μm. Reprinted with permission from ref <sup>26</sup>. Copyright 2010 Springer Publishing.  
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3 (d) Strength enhancement: CNT coated cotton fibers. Scale bar = 10  $\mu\text{m}$ . Reprinted with  
4 permission from ref <sup>27</sup>. Copyright 2008 The Royal Society of Chemistry. The inset shows the  
5 magnified view of the fiber surface. Inset scale bar = 1  $\mu\text{m}$ . (e) UV blocking: TiO<sub>2</sub> treated cotton  
6 fiber. Scale bar = 1  $\mu\text{m}$ . Reprinted with permission from ref <sup>28</sup>. Copyright 2004 Sage  
7 Publications. (f) Antibacterial properties and odor control: cotton fibers treated with Ag NPs.  
8 Scale bar = 5  $\mu\text{m}$ . The inset shows the magnified Ag NPs on the surface. Inset scale bar = 1  $\mu\text{m}$ .  
9 Reprinted with permission from ref <sup>29</sup>. Copyright 2012 Elsevier.

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21 Oil repellent textiles have been also produced. Polyester fabric could be coated with silicone  
22 nanofilaments and treated with plasma fluorination to impart superoleophobic properties.<sup>30</sup> The  
23 produced fabric samples had oil repellency grade of 8, and repelled alkanes. Hydrophobic and  
24 oleophobic properties could be simultaneously imparted to textiles. For example, cotton fibers  
25 were impregnated with SiO<sub>2</sub> particles to produce a dual-size surface roughness, followed by  
26 hydrophobization with poly(dimethylsiloxane) (PDMS), resulting in a static water contact angle  
27 of 155° for a droplet.<sup>31</sup> To induce oleophobicity, the SiO<sub>2</sub> particles on the fibers were treated  
28 with perfluoroalkyl chain, which was demonstrated by a static contact angle of 140° and a roll-  
29 off angle of 24° for oil droplets.

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42 **Antistatic Properties.** Synthetic fibers such as polyester and nylon have high static charge as  
43 they are not hydrophilic. On the other hand, cellulosic fibers limit the static charges due to their  
44 high moisture content. TiO<sub>2</sub> NPs,<sup>32</sup> ZnO whiskers,<sup>33</sup> and antimony (Sb) doped tin oxide (SnO<sub>2</sub>)  
45 particles<sup>34</sup> were utilized to impart antistatic properties to synthetic fibers. These materials are  
46 electrically conductive and dissipate the static charge accumulated on the textile. Additionally,  
47 silane nanosol enhances antistatic properties, as it absorbs moisture in the air through hydroxyl  
48 groups.<sup>35</sup> In commercial products, poly(tetrafluoroethylene) (PTFE) (W.L. Gore) developed an  
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3 antistatic membrane that consisted of electrically conductive NPs anchored in the fibrils of the  
4 membrane.<sup>36</sup> This membrane limited the formation of isolated chargeable areas and voltage  
5 peaks. This approach is advantageous over other antistatic agents since it does not wash off  
6 during laundry. Sol-gel coatings could be applied as a surface treatment to impart antistatic  
7 properties combined with hydrophobic properties.<sup>37</sup> Sol-gel composition consisted of  
8 hydrophobic compounds such as alkoxy silanes modified with alkyl chains and hydrophilic  
9 compounds including amino-functionalized alkoxy silanes. This combination allowed forming  
10 hydrophobic groups at the fiber-air interface while the deeper regions were hydrophilic. Sol-gel  
11 coated textiles had water repellence, but contained humidity in deeper regions of the coatings to  
12 produce antistatic properties. Antistatic charges with hydrophobicity could be achieved by  
13 treating polyester fabric with silver (Ag) NPs and fluorine water-repellent finish (Figure 2b).<sup>25</sup>  
14 After 10 washings, the polyester fabric had FTTS-FA-009 A grade antistatic property, and  
15 AATCC 22 spray rating 90 grade for its hydrophobic quality.

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34 ZnO NPs have been utilized to produce antistatic properties.<sup>38</sup> ZnO NPs, prepared by direct  
35 precipitation using zinc chloride ( $\text{ZnCl}_2$ ), were immobilized both on polyester fabrics through  
36 pad-dry-cure process with antistatic finishing agent. The charge density of polyester fabrics  
37 reduced from 58 to 0.95 (units in  $\times 10^{-7} \text{ C m}^{-2}$ ). As the concentration of ZnO NPs increased in the  
38 finishing agent, the antistatic property of the fabric decreased due to reduced dispersion of NPs.  
39 Additionally, the addition of Ag NPs decreased the static voltage of polyester fabric by 60.4 %.<sup>39</sup>  
40 The combination of Ag, gold (Au) and Zn oxide particles decreased the static voltage by 77.7 %.  
41 In another study, Sb nanoparticle doped  $\text{SnO}_2$  particles were utilized to impart antistatic  
42 properties to polyacrylonitrile (PAN) fibers.<sup>40</sup> These particles were dispersed in water using  
43 polyethyleneimine (PEIN), and this solution was added to the pre-heating bath during spinning  
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3 of PAN fibers. The particles diffused into the fibers create electrically conductive channels,  
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5 which produced antistatic properties.  
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8 **Wrinkle Resistance.** Cellulose molecules in the cotton linearly organize themselves passing  
9 through the crystalline and amorphous sections of the fibers. Hydrogen bonds hold together  
10 cellulose molecules in their positions. Upon applying a force to the fibers, the cellulose chains  
11 displace from their original positions and hydrogen bonds reform at new locations. Nanocoatings  
12 that prevent crease while maintaining comfort is desirable in textile products. Traditionally,  
13 fabrics are impregnated with resin to impart wrinkle resistance to textiles. However, this  
14 approach decreases tensile strength of the fiber, abrasion resistance, and dyeability while  
15 inducing hydrophobicity. To impart wrinkle resistance, NPs have been applied to cotton and silk.  
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17 TiO<sub>2</sub> NPs with carboxylic acid as a catalyst were utilized to form crosslinks between cellulose  
18 molecules and the acidic groups.<sup>41, 42</sup> The use of 1,2,3,4-butane tetracarboxylic acid (BCA) and  
19 succinic acid as crosslinking agents had the highest dry crease recovery angle and wet crease  
20 recover angles, respectively. Additionally, carboxylic acid treated fabrics with TiO<sub>2</sub> NPs were  
21 softer as compared to untreated fabric.<sup>42</sup> TiO<sub>2</sub> through its catalytic property can be used as a co-  
22 catalyst with sodium hypophosphite (NaPO<sub>2</sub>H<sub>2</sub>) to treat cotton with 1,2,3,4-BCA.<sup>26, 43-45</sup> Figure  
23 2c shows SEM images of cotton fibers treated with BTCA and TiO<sub>2</sub> NPs. This increased the  
24 effectiveness of NaPO<sub>2</sub>H<sub>2</sub>, hence the wrinkle recovery of the cotton fabric. However, tear and  
25 tensile strength of the cotton fabric decreased due to the presence of TiO<sub>2</sub> NPs. *Bombyx mori* silk  
26 was also treated with TiO<sub>2</sub> NPs in chitosan by crosslinking reactions of citric acid and maleic  
27 anhydride.<sup>46</sup> Dry and wet delay-wrinkle recovery angles of the treated silk were 267° and 250° as  
28 compared to untreated fabric of 235° and 178°, respectively. Additionally, SiO<sub>2</sub> NPs and maleic  
29 anhydrate as a catalyst have been applied to silk to improve wrinkle resistance.<sup>47</sup>  
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4     **Strength Enhancement.** CNT reinforced polymer composite fibers have been developed to  
5 improve strength, toughness, and decrease weight. These composite fibers could be produced  
6 through melt-spinning of polypropylene and carbon particles.<sup>48</sup> Controlling the parameters in  
7 melt-spinning, the morphology, crystallinity and mechanical properties of nanostructured  
8 polycaprolactone non-woven mats were optimized.<sup>49</sup> Melt extrusion also produced a wide range  
9 of nanoadditive yarns with improved mechanical properties and various textures.<sup>50</sup>

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

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45     Dipping and coating method was also utilized to immobilize CNTs on cotton.<sup>27</sup> CNTs were  
46 modified with poly(butylacrylate) using surface grafting, and this composite was applied to  
47 cotton fabrics by dipping, drying, curing, and finishing. Figure 2d illustrates SEM images of  
48 CNT coated cotton fibers. The tensile strength of the CNT-coated cotton fabrics was improved  
49 along the weft and warp directions, showing enhancement in both the loading capability and  
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3 flexibility (displacement). For example, the tensile strength of the CNT coated cotton was 0.5 kN  
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5 at 13.5 cm displacement as compared to 0.25 kN for untreated fabrics.<sup>27</sup>  
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8 **UV Blocking.** Inorganic UV blockers are non-toxic and chemically stable operating at high  
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10 temperatures. Nanoscale semiconductor oxides such as TiO<sub>2</sub> and ZnO efficiently absorb and  
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12 scatter UV radiation.<sup>28, 52-54</sup> Figure 2e shows a SEM image of a TiO<sub>2</sub> (~100 nm) treated cotton  
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14 fiber. At nanoscale, scattering depends on the wavelength and the size of the NP, where the  
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16 scattering is inversely proportional to the wavelength of the fourth power of the wavelength. For  
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18 example, to scatter UV light (200-400 nm), the optimum particle size is 20-40 nm.<sup>55</sup> Sol-gel  
19  
20 method can be used to form a thin layer of TiO<sub>2</sub> on the surface of the treated cotton. The UV-  
21  
22 protection effect may be maintained up to 50 launderings.<sup>56</sup> Furthermore, ZnO nanorods (10-50  
23  
24 nm) have been incorporated in cotton to induce scattering at a high UV protective factor rating.<sup>57</sup>  
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26 Additionally, ZnO NPs synthesized through sedimentation and peptization were immobilized on  
27  
28 dyed polyester/cotton fabrics.<sup>58, 59</sup> The resulting fabric absorbed the light in the UV region.<sup>58</sup>  
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34 **Antibacterial Properties.** Ag, TiO<sub>2</sub> and ZnO NPs can be utilized to impart antibacterial and  
35  
36 fungicidal properties to textiles.<sup>53, 55, 60-62</sup> Ag NPs have large surface areas that increase their  
37  
38 contact with bacteria and fungi. The antiseptic mechanism of Ag NPs is based on reacting with  
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40 proteins in these organisms and adversely affecting their cellular function and inhibiting cell  
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42 growth. They also reduce respiration, limiting the activity of the basal metabolism of the electron  
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44 transfer system, and substrate transport into the cell membrane. When Ag NPs contact with  
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46 moisture or bacteria, they adhere to the cell wall and membrane.<sup>63</sup> While the Ag NPs in their  
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48 metallic state are inert, they ionize in the presence of moisture. The Ag<sup>+</sup> ions are reactive and  
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50 they diffuse through the cell wall and membrane into cytoplasm. Ag<sup>+</sup> ions bind to sulphur  
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52 containing proteins on the cell membrane to structurally change the cell wall.<sup>64</sup> These structural  
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3 changes result in the release of the cellular components to extracellular fluid due to the changes  
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5 in the osmotic pressure. Additionally, the  $\text{Ag}^+$  ions bind to phosphate containing proteins to  
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8 condense DNA, leading to a reaction with thiol group proteins to cause cell death. They also  
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10 suppress the function of enzymes and inhibit the cell to produce ATP.<sup>65</sup> Ag NPs slow down the  
11  
12 growth and multiplication of bacteria and fungi that are involved in odor creation and itchiness.  
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14 Figure 2f shows cotton fibers treated with Ag NPs.<sup>29</sup> For example, Ag NPs can be applied to  
15  
16 socks to prevent the growth of bacteria and fungi.  
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20 The antimicrobial efficacy of Ag additives depends on the concentration, surface area, and  
21  
22 the release rate of the  $\text{Ag}^+$  ions.<sup>66-68</sup> Ag-containing textiles can release dissolved and particulate  
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24 Ag (20-30%) into washing liquid in the first cycle.<sup>69-71</sup> In fabrics comprising Ag metal, oxidation  
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26 from Ag(0) to Ag(I) is required for releasing  $\text{Ag}^+$  ions in solution.<sup>70</sup> Ion release from Ag NPs is a  
27  
28 cooperative oxidation process involving dissolved oxygen and protons to produce peroxide  
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30 intermediates and complete reactive dissolution. The presence of oxygen is essential for the  
31  
32 release of dissolved Ag through the surface oxidation of Ag NPs. The ion release rates increase  
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34 as the temperature is increased and as the pH is decreased.<sup>72</sup> For example, Ag NPs ( $2 \text{ mg L}^{-1}$ )  
35  
36 released  $0.3 \text{ mg L}^{-1}$  dissolved Ag after 24 h incubation in air-saturated solution ( $9.1 \text{ mg L}^{-1}$   
37  
38 dissolved oxygen) at pH 5.68. The release of dissolved Ag was 0.6 and  $0.1 \text{ mg L}^{-1}$  at pH 4.0 and  
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40 8.0 after 24 h incubation, respectively.<sup>72</sup> Additionally, the change in ionic strength has negligible  
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42 effect on the release kinetics.  
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49  $\text{TiO}_2$  NPs can also be utilized to impart textiles with antibacterial properties. Upon  
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51 illumination with light with energy higher than its bandgap (3.2 eV),  $\text{TiO}_2$  as a photocatalyst has  
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53 the ability to have its electrons jump from the valence band to the conduction band. The electron  
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55 and electric hole pairs form on the surface of the photocatalyst, where the electrons and oxygen  
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3 form  $O_2^-$  and the positive electric holes and water create hydroxyl radicals.<sup>52</sup> The unstable  
4 substances on the surface of the photocatalyst are oxidized into  $CO_2$  and water. Through this  
5 mechanism, the photocatalyst decompose organic matters including odor molecules, bacteria,  
6 and viruses. The catalytic activity of  $TiO_2$  NPs has been utilized in textiles to provide  
7 antibacterial properties.<sup>56, 73</sup> The photocatalytic activity might be improved by creating  
8  $TiO_2/SiO_2$  nanocomposites or Au-doped  $TiO_2$  nanocomposites in cotton fabrics with self-  
9 cleaning properties.<sup>74, 75</sup> Furthermore, ZnO behaves similar to  $TiO_2$  to produce antibacterial  
10 properties.<sup>76</sup> ZnO NPs (21-25 nm) have been synthesized in reverse micelle cores of polystyrene  
11 (PS) and polyacrylic acid.<sup>77</sup> ZnO NPs coated onto textiles showed self-cleaning properties in the  
12 presence of gram-negative *E. coli* and aerobic gram-positive *S. aureus*. Additionally,  $SiO_2$  and  
13 Ag NPs with core-corona structure were electrostatically assembled onto cotton surfaces with  
14 high packing density to impart antibacterial properties to fabrics.<sup>78</sup> The coronas of NPs can be  
15 loaded with antibacterial moieties such as quaternary ammonia salts as well as metal coatings on  
16 cotton fabrics.<sup>79</sup> Discussions focusing on self-cleaning and antimicrobial nanomaterials in  
17 textiles can be found elsewhere.<sup>17, 80, 81</sup>

## 41 ELECTRONICS IN TEXTILES

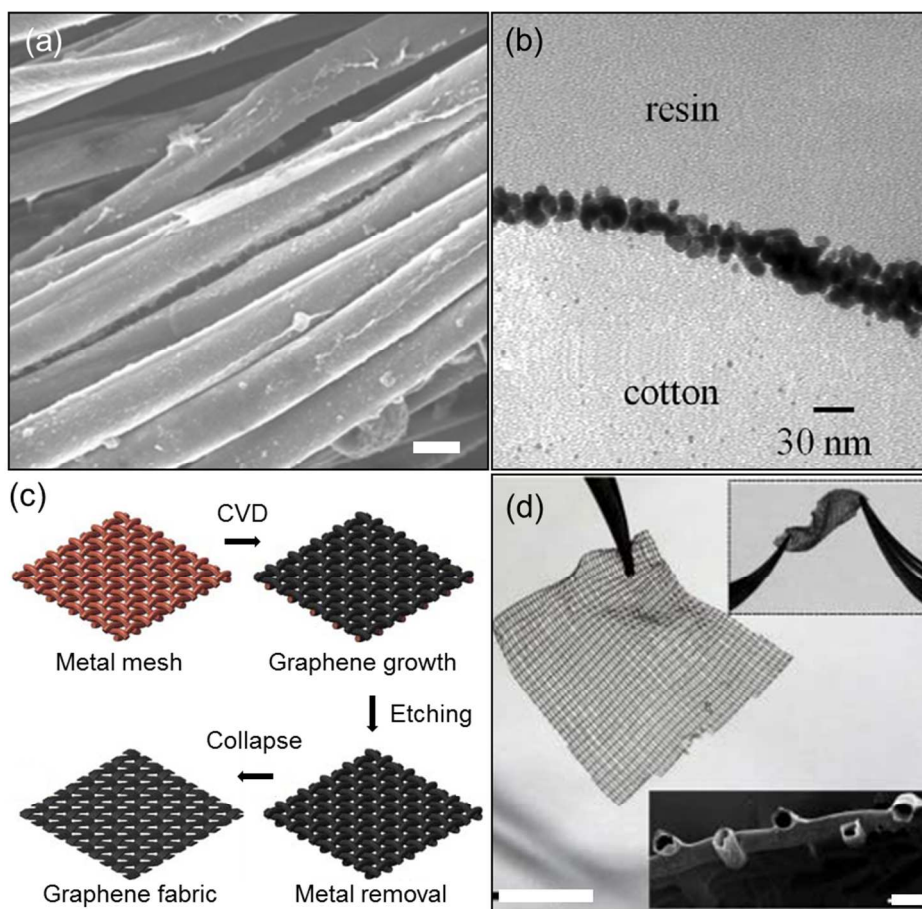
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43 **Electrical Conductivity.** Conducting polymers are attractive for creating textiles that enable  
44 the incorporation of sensors and actuators. For example, conducting polymers can change their  
45 resistivity and produce electrical signals in response to external stimuli. A range of dopants can  
46 be incorporated in these polymers. For example, polypyrrole (PPy) has high mechanical strength  
47 and is electroactive in organic and aqueous solutions. Another widely studied conductive  
48 polymer is polyaniline (PANI), which exist in three possible configurations: leucoemeraldine  
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3 base (fully reduced), emeraldine base (partly oxidized), and pernigraniline base (fully oxidized).  
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5 In its oxidized form, the conductivity of PANI increases about 10 orders of magnitude.  
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8 Additionally, polythiophene (PTs) and its derivatives can be in *p* or *n* type forms for application  
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10 in field-effect transistors in flexible logic circuits. The low production costs, light weight and  
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12 flexibility allow these materials to be easily integrated in textiles.  
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15 The surface structure of synthetic fibers can be modified to produce diverse functionalities.<sup>82</sup>  
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17 SiO<sub>2</sub> NPs can be incorporated in polyimidoamide fibers through spinning. Incorporation of  
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19 nanoparticles in PAN fibers can create electrically conductive channels with enhanced  
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21 mechanical and antistatic properties.<sup>40, 83</sup> Fiber porosity, thermal and absorption characteristics  
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23 can be controlled by chemically modifying the fibers. To improve thermal resistance and  
24  
25 tenacity, the fibers can be coated with diamine (diaminodiphenyl methane), montmorillonite, and  
26  
27 SiO<sub>2</sub> NPs.<sup>84-86</sup> Synthetic fibers can also be functionalized through chemical oxidative deposition,  
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29 in which conducting electroactive polymers such as PANI, PPy, PTs are used to coat textiles for  
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31 improving tensile strength and thermal stability.<sup>87, 88</sup> Furthermore, surface deposition of  
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33 electroactive polymers increases conductivity of the fibers one order of magnitude.<sup>89-91</sup> Such  
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35 composite fibers have application in the reduction of static electrical charge, microwave  
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37 attenuation, and electromagnetic shielding.  
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43 Finding the balance between electrical conductivity, flexibility and comfort of the textile is a  
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45 challenge. Coatings have been developed to impart electrical conductivity to cotton. One  
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47 approach involved polyelectrolyte-based coating with multiwalled carbon nanotubes  
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49 (MWCNTs).<sup>92</sup> Figure 3a shows SEM images of MWCNT-Nafion coated cotton threads. Charge  
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51 transport through the network of nanotubes was 20 Ω cm<sup>-1</sup>. Another strategy used a combination  
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53 of metal NPs conformally coated around the heterogeneous contour of cotton fibers.<sup>93</sup> In-situ  
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3 polymerization was utilized to create polymeric bridges between the NPs. These flexible bridges  
4 allowed for the creation of coatings that were durable and resilient to mechanical deformation for  
5 application in cotton-based transistors. Figure 3b shows a Transmission Electron Microscope  
6 (TEM) image of cross-section of the conductive cotton fibers, showing uniform coating with Au  
7 NPs and poly(3,4-ethylenedioxihiophene) (PEDOT).  
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48 **Figure 3.** Conductive nanomaterials in textiles. (a) A SEM image of MWNT-Nafion coated  
49 thread. Scale bar = 10 μm. Reprinted with permission from ref <sup>92</sup>. Copyright 2008 American  
50 Chemical Society. (b) A TEM image of cross-section of the conductive Au NP and PEDOT  
51 coated cotton fibers. Reprinted with permission from ref <sup>93</sup>. Copyright 2011 Elsevier. (c)  
52 Fabrication of graphene woven fabric by CVD using copper (Cu) wire meshes as substrates.  
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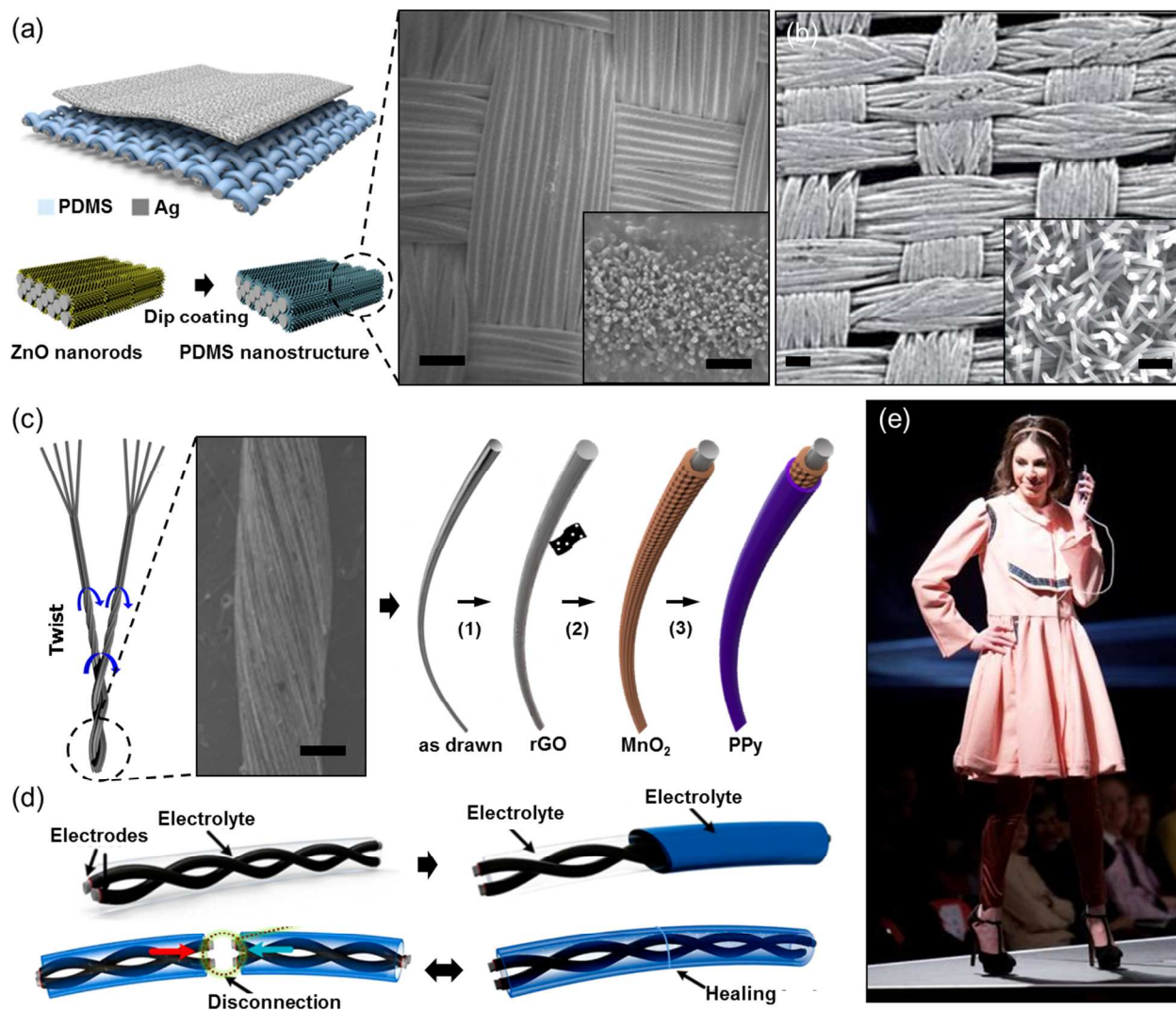
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3 Reprinted with permission from ref<sup>94</sup>. Copyright 2012 Nature Publishing Group. (d) Graphene  
4 woven fabric in PDMS. Scale bar = 5 mm. The top inset illustrates the twisted graphene fabric  
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8 film. The bottom inset shows an SEM image of graphene fabric cross-section. Scale bar = 100  
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10  $\mu\text{m}$ . Reprinted with permission from ref<sup>94</sup>. Copyright 2012 Nature Publishing Group.  
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14 Graphene-based woven fabrics have been prepared by interlacing two sets of graphene  
15 microribbons.<sup>94</sup> The resulting textile had dimensional stability in both the warp and the weft  
16 directions. The conductivity was optimized by tuning the ribbon packing density. Graphene  
17 woven fabrics were synthesized through atmospheric chemical vapor deposition (CVD) using Cu  
18 meshes consisting of wires with  $\sim 60 \mu\text{m}$  in diameter as substrates. The fabrication of the textiles  
19 involved growing graphene on the substrate, removing the Cu mesh wires, and subsequently  
20 collapsing the graphene to form double-layer microribbons (Figure 3c). Such polymers could be  
21 also embedded in PDMS or PET films (Figure 3d). The constructed fabric had a transparency of  
22  $1000 \Omega \text{ sq}^{-1}$ .<sup>94</sup> Conductive textiles could also be produced by immobilizing graphene via  
23 reduction from graphene oxide on cotton fabric by using a conventional dip and dry method.<sup>95</sup>  
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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  $10^6 \text{ k}\Omega \text{ cm}^{-1}$ .<sup>95</sup>

**Power Sources.** Flexible and lightweight fabric supercapacitor electrodes have been  
designed for energy storage.<sup>96</sup> 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

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3 areal capacitance of  $85 \text{ F g}^{-1}$  at  $0.25 \text{ A g}^{-1}$  on cotton lawn and polyester microfiber.<sup>96</sup> Recently, a  
4 flexible supercapacitor textile consisting of CNTs/PANI composite fiber was developed.<sup>97</sup> The  
5 supercapacitor was integrated with a photoelectric conversion function to create a self-powering  
6 energy textile that converted solar energy into electrical energy and stored it in a stacked  
7 multilayer structure. The CNT array was synthesized by CVD. Aligned CNT sheets were dry-  
8 drawn from the array and stacked into a thicker film along the length direction, and twisted into  
9 an aligned fiber, which was woven into textiles. The resulting textiles were electrodeposited with  
10 PANI to create an electrode, followed by coating with a layer of gel electrolyte to create a  
11 supercapacitor. The resulting material had a capacitance of  $272 \text{ F g}^{-1}$  with 96% maintenance after  
12 200 bending cycles.<sup>97</sup> Another study that aimed to improve the performance of textile-based  
13 supercapacitors involved embedding a metal wire (monofilament) in the center a CNT yarn.<sup>98</sup>  
14 One-step continuous spinning allowed forming a core/sheath structured CNT yarn architecture to  
15 create linear supercapacitors. CNTs formed a layer around the conductive metal filament core.  
16 The filament core acted as a current collector to transport charges. Foldable nanopatterned  
17 wearable triboelectric nanogenerators were also reported.<sup>99</sup> Figure 4a shows the device and its  
18 fabrication process using nanopatterned PDMS structure. Ag-coated textile and PDMS  
19 nanopatterns based on ZnO nanorod arrays were used as triboelectric materials. The  
20 nanopatterned structures produced 120 V (output) at  $65 \mu\text{A}$ , and four-layered triboelectric  
21 nanogenerators produced 170 V (output) at  $120 \mu\text{A}$ . No significant drift was observed after  
22 120,000 cycles.<sup>99</sup> Another study reported the development of carbon-activated cotton threads on  
23 textile for energy generation.<sup>100</sup> The device harvested electrostatic energy from the environment  
24 through contact and friction electrifications. It was fabricated by treating carbon black NPs and  
25 encapsulating them with a thin layer of PDMS for stability. By rubbing and tapping with a PTFE  
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3 sheet, electrostatic charges were collected from the carbon-functionalized threads in textiles. The  
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5 device had an open-circuit voltage of -60.9 V.<sup>100</sup> Piezoelectricity via electrostatic forces were  
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7 also utilized in textiles to create a nanogenerator.<sup>101</sup> ZnO nanowires and discharge films were  
8  
9 incorporated into a textile to hybridize electrostatic and piezoelectric effects (Figure 4b). This  
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11 nanogenerator had an output voltage of 8 V at 2.5  $\mu$ A. The produced power source was utilized  
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13 to power an OLED and a Liquid Crystal Displays (LCD) panel.<sup>101</sup> Recently, pristine soft  
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15 conductive yarns were produced via a twist-bundle-drawing technique (Figure 4c).<sup>102</sup> Conductive  
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17 yarns modified with reduced graphene oxide (rGO), MnO<sub>2</sub> nanosheets, and PPy films were used  
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19 to produce weavable supercapacitors. The yarns had specific capacitances of 31 mF cm<sup>-1</sup> and 411  
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21 mF cm<sup>-1</sup> in solid-state two electrode cells with energy densities of 9.2  $\mu$ Wh cm<sup>-2</sup> and 1.1 mWh  
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23 cm<sup>-3</sup>.<sup>102</sup>  
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**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  $\mu\text{m}$ , inset scale bar = 1  $\mu\text{m}$ . Reprinted with permission from ref <sup>99</sup>. 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  $\mu\text{m}$ , inset scale bar = 1  $\mu\text{m}$ . Reprinted with permission from ref <sup>101</sup>. Copyright 2012 The Royal Society of Chemistry. (c) Twisted yarn fabrication and illustration of the yarn functionalized by

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3 rGO, MnO<sub>2</sub>, and PPy. (1) Hydrothermal treatment (2-3) Electrodeposition. Reprinted with  
4 permission from ref <sup>102</sup>. Copyright 2015 American Chemical Society. (d) Fabrication and  
5 operation principle of magnetic-assisted, self-healable, yarn-based supercapacitors. Reprinted  
6 with permission from ref <sup>103</sup>. Copyright 2015 American Chemical Society. (e) A garment using  
7 cotton yarns coated with nanolayers of PEDOT-PSS. Copyright Abbey Liebman.  
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18         Stretchable PPy-based supercapacitors with cycling stability were also fabricated.<sup>104</sup>  
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20 Electrochemical deposition of PPy on stretchable stainless steel meshes allowed producing solid  
21 state supercapacitors reaching 170 F g<sup>-1</sup> at 0.5 A g<sup>-1</sup>. Under 20% strain, the capacitance can be  
22 enhanced up to 214 F g<sup>-1</sup>. These supercapacitors were operated at a scan rate of 10 V s<sup>-1</sup>, which is  
23 a magnitude higher than PPy electrodes in aqueous solutions. These solid-state supercapacitors  
24 under no-strain and 20% strain had capacitance retentions 98% and 87% at 10 A g<sup>-1</sup> after 10,000  
25 cycles.<sup>104</sup>  
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35         In conventional planar or structures, the reconnection of the broken yarn electrode and the  
36 restoration of the electrical conductivity are challenging.<sup>103</sup> To improve the mechanical  
37 properties, yarns-based supercapacitors with self-healing properties have been developed. The  
38 electrodes fabricated by wrapping magnetic electrodes around a self-healing polymer shell  
39 (Figure 4d). The magnetic attraction reconnected broken fibers in the yarn electrodes to store  
40 electrical conductivity while polymer shell recovered mechanical strength and configuration  
41 integrity. The magnetic yarns allowed restoring the specific capacitance up to 71.8% after four  
42 breaking cycles by maintaining mechanical properties.<sup>103</sup>  
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53         Conductive fabrics have been incorporated in garments. Figure 4e shows a garment using  
54 cotton yarns coated with nanolayers of PEDOT-poly(styrenesulphonate) (PSS) deposited over an  
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3 array of Au NPs. These nanolayers allow the cotton yarns to become electrically conductive and  
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5 transfer energy from solar cells attached to the exterior of the dress. A comprehensive discussion  
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7 about energy storage technologies can be found elsewhere.<sup>10</sup>  
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12 Fabrication of multifunctional composite fibers has received attention due to their  
13 applications in conductive structures and batteries in the textile industry. Here “fiber” refers to  
14 wire-like composite structures produced via drawing techniques used in the production of fiber  
15 optics. Composite fibers can be fabricated through preform heating and drawing. A  
16 geometrically complex fiber preforms at a length of tens of centimeters is assembled by stacking  
17 of tubes, rods, multilayered films, or functional components within a hollow structured rod that  
18 serve as cladding.<sup>105</sup> The preform tip is then placed into the vertical furnace, where the  
19 temperature is increased above the softening or melting temperature of the preform materials. As  
20 a consequence, the preform tip melts, and then it is pulled downward, thus creating a slender rod  
21 that can be continuously pulled from the molten preform tip. Typically, a clamp tractor or a  
22 spooler is used to pull the fiber at a constant speed and tension. Geometry of the resultant fiber  
23 depends on parameters in the drawing process such as temperature distribution in a furnace, fiber  
24 drawing speed and preform feed velocity, pressurization of the preform, and electromagnetic  
25 fields.<sup>106</sup> This process creates both non-optical fiber and optical fibers. Fibers drawn from the  
26 macroscopic preform would generally retain the preform structure; however, sizes of the  
27 constituent structures (*e.g.*, layers, rods) will be reduced to micro- or nanoscale. Therefore, a  
28 geometrically complex, composite transverse structure could be realized within a fiber on a sub-  
29 micron scale by controlling the preform structure and optimizing the conditions of the fiber  
30 drawing process. This, generally, may not be accomplished by traditional yarn-spinning methods  
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3 such as melt-spinning,<sup>107</sup> wet-spinning,<sup>108</sup> or electro-spinning,<sup>109, 110</sup> which are typically utilized  
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5 to produce fibers and yarns with simple structures in textile manufacturing. Moreover, materials  
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7 including biofunctional polymers,<sup>111-113</sup> low-melting-temperature metal alloys,<sup>114</sup> optical  
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9 plastics,<sup>114-123</sup> conductive polymers,<sup>124-126</sup> and electrochemical materials,<sup>127-130</sup> could be  
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11 integrated into a composite fiber during drawing.  
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15 Flexible fiber or stripe batteries which can be directly weaved into a textile constitute a  
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17 promising solution toward seamless integration with functional textiles. Flexible fiber batteries  
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19 using both a simple inorganic chemistry<sup>127, 128</sup> as well as Li-ion chemistry<sup>129, 130</sup> have been  
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21 proposed. The simplest fiber battery consisted of a microstructured low density polyethylene  
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23 (LDPE) jacket with several intercommunicating channels running along the fiber. Aluminum  
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25 (Al) and Cu wires were immobilized to produce a double stranded fiber as anode and cathode,  
26  
27 respectively. The voids between these two channels were then filled with sodium hypochlorite  
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29 (NaOCl) electrolyte. This fiber constituted a typical Al/air galvanic cell. To fabricate a fiber  
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31 battery, the fiber jacket preform was prepared by drilling several interconnected channels  
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33 throughout a LDPE rod. The two electrode wires (Al and Cu) were embedded into the two  
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35 extreme channels of the fiber during production (*i.e.* drawing). Open cell voltage of a fiber  
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37 battery was ~1.5 V with a linear capacity of  $10^{-2}$ – $10^{-1}$  mAh cm<sup>-1</sup>. Flexible lithium (Li)-ion  
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39 batteries could be built by from polyethylene oxide (PEO) as a thermoelastic polymer ionic  
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41 electrolyte in all the electrodes and a separator layer. To assemble such a battery, solvent-casting  
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43 method could be used to deposit an anode layer (Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> + PEO), a separator layer (PEO+LiI),  
44  
45 and a cathode layer (LiFePO<sub>4</sub> + PEO) in sequence. The thermoelastic nature of PEO allows the  
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47 production of such batteries in fiber drawing. This Li-ion battery could be cut into stripes that  
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49 may be directly weaved into a textile.  
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3 Two prototypes of textiles based on fiber and stripe batteries have been demonstrated. The  
4 first prototype was fabricated by weaving fiber batteries into a wool textile matrix.<sup>127</sup> The  
5 maximum output power of a fiber battery textile could be achieved by optimizing series and  
6 parallel connections of the fiber batteries in the textile. Applications of this fiber battery  
7 integrated textile included lighting up a LED, driving a wireless mouse,<sup>127</sup> and actuating a  
8 shape-memory alloy.<sup>127</sup> The second prototype used flexible stripe Li-ion batteries.<sup>129</sup> The Li-ion  
9 battery stripes were woven into a textile. Each stripe had an open cell voltage of ~0.3V. A  
10 textile battery made of eight battery stripes woven with wool threads and connected in series  
11 using Cu and Al wires were used to light up a 3V LED. The flexible fiber or stripe batteries  
12 constitute a promising technique toward the realization of on-garment power supply. In fashion  
13 industry, LEDs or electroluminescent wires are used as light emitting elements; and shape-  
14 memory alloys may be woven into garments to provide kinetic features. The fiber and stripe  
15 batteries could be used as an efficient power source for these electronics.  
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34 Conductive fiber are widely used to interface with other electronic devices integrated into  
35 textiles. To fabricate conductive fiber, conductive fillers such as carbon black (CB)<sup>125</sup> or  
36 CNTs<sup>131</sup> are impregnated into plastic preform material. Fabrication of all-fiber electronic  
37 components is however a challenging task. The fabrication of a fiber electric capacitor using CB-  
38 impregnated LDPE films as compliant electrodes have been reported.<sup>124-126</sup> The fiber preform  
39 was fabricated by consecutive stacking of two conductive and two isolating LDPE layers and  
40 then turning the multilayer into a Swiss-roll configuration featuring a large central hole. A  
41 tension-adjustable reel was installed on the top of the fiber drawing tower that hosted a spool of  
42 Cu wires. These wires were then passed through the preform core, pulled down and embedded  
43 into the fiber center during drawing by collapsing the plastic cladding. The as-drawn fiber  
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3 capacitors featured one or two Cu wires as inner electrodes, and the outmost conductive LDPE  
4 layer constituted the outer electrode. The fiber capacitance was measured in the 60-100 nF m<sup>-1</sup>  
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6 range. The fiber capacitors were also demonstrated to build touch sensitive textiles.  
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10 **Digital Components.** OLEDs have been incorporated in soft fabrics.<sup>132</sup> OLEDs fabricated by  
11 thermal evaporation were mechanically stable over 1000 cycle bending test with a bending  
12 radius of 5 mm, an emission angle of 70°, and a current efficiency of ~8 cd A<sup>-1</sup>.<sup>132</sup> Schottky  
13 diodes were also fabricated on textiles.<sup>133</sup> ZnO nanorods were grown on a Ag-coated textile  
14 fabric using a hydrothermal method, and Zn nitrate and hexamethylenetetramine were used to  
15 produce ZnO nanorods. The Schottky diode was prepared by applying photoresist and reactive  
16 plasma ion etching of the ZnO nanorods. A shadow mask was used to deposit Cu using thermal  
17 evaporation. The resulting diodes had performance comparable to glass-based diodes.<sup>133</sup>  
18 Schottky diode integrated textiles have potential applications in switched-mode power supplies,  
19 voltage clamping, and reverse current and discharge protection.  
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34 Polymer yarns/fibers that are twisted/embedded with metal wires have been used for  
35 production of electromagnetic shield garments and fabrics. These metal wires could be  
36 embedded into polymer rods during a drawing process. The metal components in such rods  
37 generally have a melting temperature similar to that of polymers. A polycarbonate cable  
38 containing arrays of the bismuth-tin (Bi<sub>42</sub>Sn<sub>58</sub>, melting temperature ~140 °C) micro/nanowires  
39 has been fabricated using the stack-and-draw technique.<sup>114</sup> For preform fabrication, molten  
40 Bi<sub>42</sub>Sn<sub>58</sub> alloy was first filled into a polycarbonate tube to produce a preform that was  
41 subsequently drawn into cable. The resulting cable had a cross section featuring a metal core  
42 surrounded by a polycarbonate cladding. By stacking these cables within another polycarbonate  
43 tube, and by repeating the drawing process, metal wire arrays could be produced at smaller  
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3 dimensions. After several drawings, nanowires separated into NPs. Recently, the fabrication of  
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5 polymer/wire composites containing indium,<sup>134, 135</sup> or tin-zinc<sup>136-144</sup> has been demonstrated based  
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8 on the same drawing technique. While such polymer/metal wire composites are mainly used for  
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10 electromagnetic shielding, they also have a potential for producing metamaterials and optical  
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12 components.  
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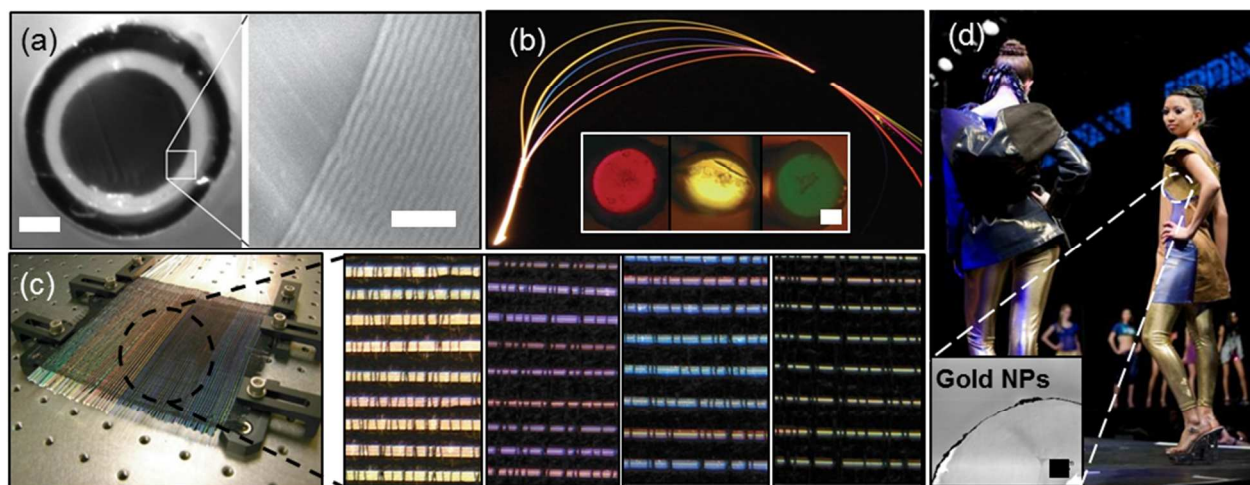
## 14 15 16 17 18 **PHOTONIC TECHNOLOGIES FOR TEXTILES**

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

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3 fibers,<sup>151</sup> fluorescent fibers<sup>152</sup> and photonic bandgap fibers<sup>153</sup> have been demonstrated. In  
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5 addition to promoting aesthetics, multifunctional fibers could offer textiles with functionalities  
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7 such as sensing of temperature,<sup>154, 155</sup> humidity,<sup>156</sup> strain,<sup>157</sup> bending,<sup>158</sup> and pressure,<sup>159</sup> optical  
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9 displays,<sup>160</sup> data transfer and communication,<sup>161</sup> lasing,<sup>162</sup> and illumination.<sup>160, 163</sup>  
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13 **Color-Tunable Optical Fibers.** Bragg fibers, a subset of photonic bandgap fibers, have a  
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15 hollow- or solid- core surrounded by periodic dielectric nanolayers with high- and low-  
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17 refractive indexes (Figure 5a).<sup>115-120</sup> Recently, two methodologies have been reported for the  
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19 fabrication of the all-polymer hollow-core Bragg fiber preforms.<sup>123</sup> One approach utilized  
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21 consecutive deposition of layers of two different polymers by solvent evaporation inside a  
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23 rotating polymer cladding tube. The other approach adopted co-rolling of two different polymer  
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25 films inside a plastic tube. Solid-core Bragg fiber preforms were fabricated by co-rolling the  
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27 multilayer around a rod.<sup>155, 158, 159, 164</sup> To fabricate Bragg reflectors, PMMA/PS or PVDF  
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29 (polyvinylidene fluoride)/polycarbonate have been used. Solid-core Bragg fibers were  
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31 manufactured by preform heating and drawing, while hollow-core fibers required core  
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33 pressurization. Bragg fibers typically guide the light by the bandgap effect.<sup>165</sup> Bandgaps of Bragg  
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35 fibers are defined as spectral regions of high diffraction efficiency caused by the interference  
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37 effects inside a periodic multilayer. Upon launching spectrally broadband light into a Bragg  
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39 fiber, only the spectral components within the reflector bandgaps would be strongly confined and  
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41 thus guided in the optical fiber core (Figure 5b). For the wavelengths outside the reflector  
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43 bandgap, the light penetrated deeply into the multilayer region exhibits high propagation loss due  
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45 to scattering from the imperfections inside the multilayer structure. Therefore, narrow-band  
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47 colors were observed at the output end of a Bragg fiber (Figure 5b inset). Spectral position of the  
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49 bandgap was affected by the core refractive index and multilayer geometry. Thus, bandgap  
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3 guidance mechanism renders Bragg fibers suitable for application in spectral filtering,<sup>118, 119</sup>  
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5 optical sensing,<sup>117, 119-121, 166</sup> and photonic textiles.<sup>116, 122, 153</sup>  
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25 **Figure 5.** Fiber optic and plasmonic technologies for textiles. (a) Cross section of a solid-core  
26 Bragg fiber and its multilayer structure. Scale bar = 50  $\mu\text{m}$ . Inset scale bar = 10  $\mu\text{m}$ . Reprinted  
27 with permission from Ref. <sup>116</sup>. Copyright 2008 The Optical Society of America. (b) Light  
28 scattered from solid-core Bragg fibers. The inset shows Bragg fibers with different bandgaps.  
29 Scale bar = 200  $\mu\text{m}$ . Reprinted with permission from Ref. <sup>122</sup>. Copyright 2008 CTT Group. (c)  
30 PBG Bragg fibers woven into a black silk textile. The inset shows color of the fibers tuned by  
31 mixing the emitted guided color with the diffracted color from ambient illumination. Reprinted  
32 with permission from ref <sup>116</sup>. Copyright 2008 The Optical Society of America (d) The use of  
33 plasmonic NPs in a garment. The inset shows an SEM image of Au NPs on the surface of a  
34 cotton fiber. Scale bar = 500 nm. Reprinted with permission from ref <sup>167</sup>. Copyright 2009 The  
35 American Chemical Society. Reprinted with permission from Olivia Ong.  
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54 The key feature of bandgap guidance of a Bragg fiber is wavelength filtering. When  
55 launching broadband light into a Bragg fiber, only a specific color defined by the spectral  
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3 position of the reflector bandgaps is guided. All the other colors are scattered out of the fiber  
4 after several centimeters of propagation. Moreover, due to the finite number of multilayers in the  
5 Bragg reflector, guided light partially leaks out from the fiber core. The leakage rate could be  
6 controlled by changing the number of multilayers. The spectral position of the reflector  
7 bandgaps, and hence the guided color, could be varied by changing the thicknesses of the  
8 reflector layers, with thicker layers shifting bandgaps to longer wavelengths. Layer thicknesses  
9 have been varied by drawing geometrically-similar preforms to optical fibers of different  
10 diameters.<sup>116, 122, 153</sup> Furthermore, under ambient (external) illumination, the Bragg fibers are  
11 colored depending on their diffraction properties. Therefore, the fiber color under ambient  
12 illumination is typically different from the fiber color due to emission of the guided light. This  
13 offers an opportunity to tune the overall fiber color by controlling the relative intensities of the  
14 ambient and propagating light. A ribbon of Bragg fiber diffracted green under ambient  
15 illumination while an emission of guided light diffracted red. In the far field (defocused view),  
16 the resultant color of a fiber ribbon was yellow.<sup>116, 122</sup>

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



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3 Compared to yarns or fabrics decorated by optical coatings or pigments, Bragg fiber-based  
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5 textiles are resistant to mechanical abrasion and would not fade in color even under repeated  
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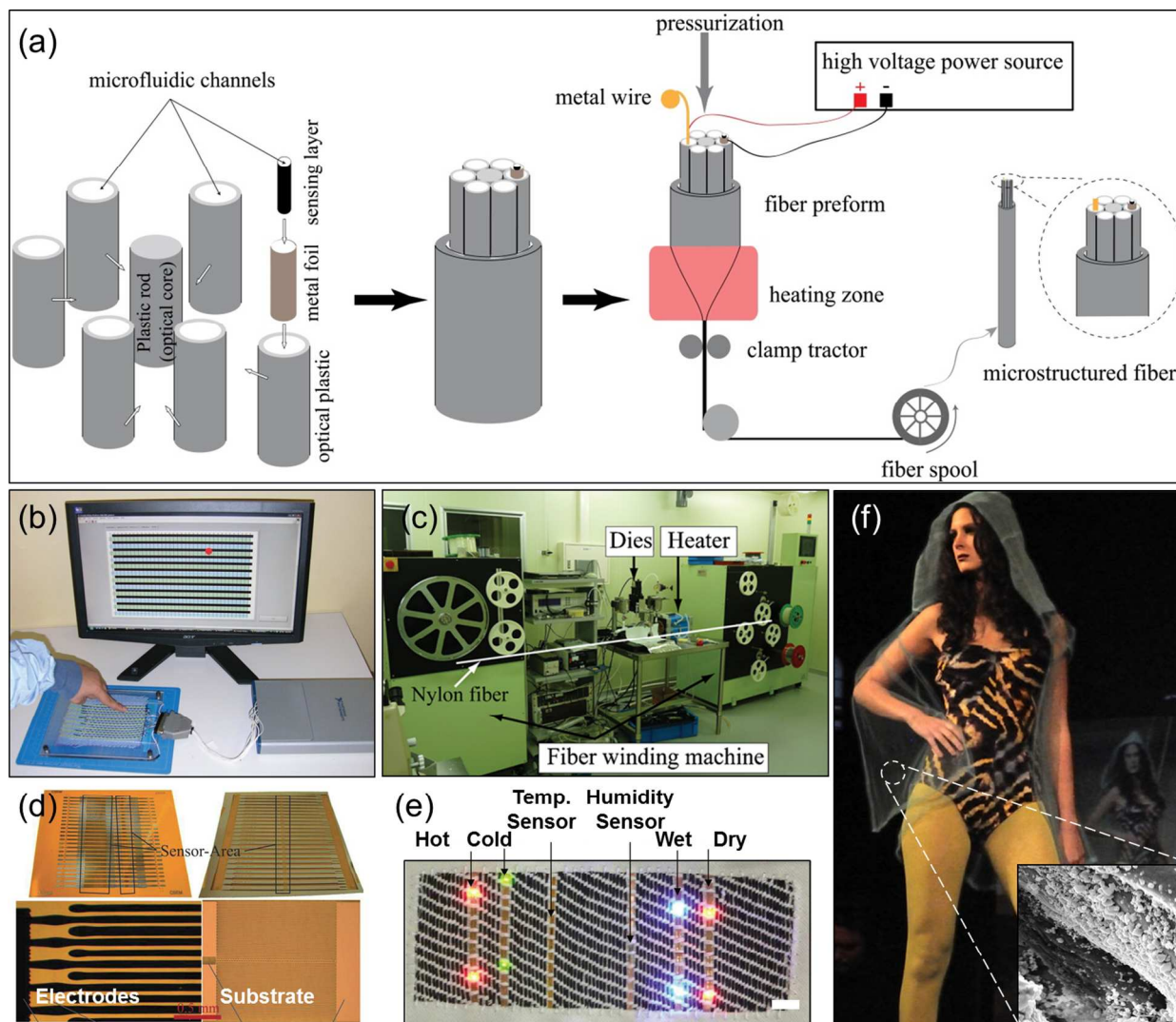
10 **Plasmonic Textiles.** Cotton fabrics were also colored using arrays of plasmonic Ag, Au and  
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12 Ru NPs.<sup>167</sup> The color in the fabrics originates from the closely packing of NPs, which were  
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14 displayed on a garment (Figure 5d). TEM micrographs of the cotton fibers show the presence of  
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16 conformal coatings of NPs assembled on the perimetries of the cotton fibers (Figure 5d inset).  
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## 22 SENSING AND DRUG RELEASE IN TEXTILES

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24 Plasmonic bio/chemical optical fiber sensors can be fabricated via drawing techniques.  
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26 Plasmonic sensors have been studied due to their high sensitivities for bio/chemical sensing.<sup>168-</sup>  
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28 <sup>170</sup> In a plasmonic fiber sensor, a lossy surface plasmon mode propagating along a  
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30 metal/dielectric interface could be excited at its resonance by an optical fiber core-guided mode  
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32 *via* evanescent-wave coupling when the phase matching condition between the two modes is  
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34 satisfied at certain frequency. The presence of such a plasmonic mode manifests itself as a  
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36 spectral dip in the fiber transmission spectrum with its spectral location corresponding to the  
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38 phase-matching frequency. Variations in the refractive index of an analyte adjacent to the metal  
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40 layer could significantly modify the phase-matching condition, thus displacing the spectral dip in  
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42 the optical fiber transmission spectrum. This constitutes the general sensing principle of a  
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44 plasmonic fiber sensor. In the fabrication of a plasmonic sensor using conventional single- or  
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46 multi-mode optic fibers, a series of modifications such as cladding etching or polishing followed  
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48 by a subsequent deposition of several tens of metal nanolayer are generally required, in addition  
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50 to the interfacing with a microfluidic system in the proximity of the fiber sensing head.<sup>171-173</sup>  
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3 These procedures bring challenges to the development of plasmonic fiber sensors. However, a  
4 complete plasmonic sensor fiber can be fabricated using stack-and-draw technique (Figure 6a). A  
5 fiber preform is first assembled at the microscale and it contains a plastic fiber core rod  
6 surrounded by the plastic tubes with one of them hosting a low melting temperature metal foil  
7 functionalized with a thermoplastic sensing layer. The inner channel of that tube is later used as a  
8 channel for analyte delivery. Next the preform assembly is drawn into fiber under pressure to  
9 keep the microfluidic channels in the fiber open. Finally, an additional wire can be passed  
10 through one of the tubes during drawing to be later used for active temperature control of the  
11 device. Additionally, high voltage supply can be connected to the wire and a foil to tune the  
12 distance between the fiber optic core and the plasmonic layer during drawing. Such fibers may  
13 contain multiscale features ranging from nano to macroscale, and consist of nano-additives for  
14 functionalization.  
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**Figure 6.** Sensors and insecticide-releasing textiles. (a) Fabrication of multifunctional fiber composites for sensing applications. Reprinted with permission from Ref. <sup>105</sup>. 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 <sup>124</sup>. Copyright 2012 IOP Publishing. (c) Die-coating system used in forming PEDOT:PSS and Cytop film on fibers. Reprinted with permission from ref <sup>174</sup>. Copyright 2012 Elsevier. (d) Fabrication of electrodes via photolithography for sensing applications. Reprinted with permission from ref <sup>175</sup>. Copyright

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3 2013 IEEE. (e) Temperature and humidity sensors woven in a tablecloth. Scale bar=1 cm.  
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5 Reprinted with permission from ref <sup>175</sup>. Copyright 2013 IEEE. (f) Permethrin-releasing textile  
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7 net. Reprinted with permission from ref <sup>176</sup>. Copyright 2012 Springer. Reprinted with permission  
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9 from Matilda Ceesay.  
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15 Using flexible fiber capacitors, touch sensor fabrics have been developed.<sup>124, 125</sup> Flexible and  
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17 elastic fiber capacitors are well suited for a conventional weaving process. A Dobby loom was  
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19 used to weave the capacitor fibers into a 1D sensor array integrated into a wool textile matrix.  
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21 The touch sensor fabric consisted of 15 capacitor fibers (Figure 6b). The inner electrodes of all  
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23 the fibers (Cu wires) were connected to the voltage source integrated into an Analog-to-Digital  
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25 Converter (ADC) card. One end of the outer plastic electrode of each fiber was grounded, while  
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27 the other end was connected to the individual channels of the ADC card to measure the voltage  
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29 at the fiber endpoint. The human body could be approximated by an equivalent electrical circuit  
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31 comprising a resistor connected in series to a capacitor. Touching a capacitor fiber with finger  
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33 modified the local current flow and voltage distribution, thus sensing the measured voltage to  
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35 touch. Moreover, a 1 cm spatial resolution was achieved with a single fiber, thus allowing the  
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37 fabrication of 2D touch sensitive textiles with a 1D array of capacitor fibers. The fiber capacitors  
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39 may also interface with other fiber electronics such as conductive fibers or battery fibers to  
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41 constitute a functional on-garment electric circuit. Potential application of such on-garments  
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43 electronics may include fashion, safety clothes as well as programmable and computing textiles.  
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50 Pressure-sensitive fabrics were also developed.<sup>174</sup> To fabricate the sensors, fibers were coated  
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52 with organic conductive polymer poly(3,4-ethylenedioxythiophene) and poly(styrene sulfonate)  
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54 and a dielectric film of perfluoropolymer using a die coating system (Figure 6c). The coated  
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3 fibers were woven as wefts and warps, and the rest of the matrix was filled with pristine nylon  
4 fibers. Capacitors were formed at the nodes, where the fibers intersected. When a pressure of 4.9  
5 N cm<sup>-2</sup> was applied on the fabric, capacitance increased from 0.22 to 0.63 pF with a sensitivity  
6 ranging from 0.98 to 9.80 N cm<sup>-2</sup>.<sup>174</sup>  
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12 Temperature, humidity and pressure sensors have been incorporated in textiles.<sup>177</sup> These  
13 studies have utilized photolithography and inkjet printing to create the sensors woven into  
14 textiles (Figure 6d). Capacitive humidity and resistive temperature sensors were developed on  
15 flexible polymer foils and integrated into textiles.<sup>175</sup> To fabricate the sensors, metal films were  
16 deposited on polyimide sheets. In photolithography, a double metal layer of Cr/Au was electron  
17 beam evaporated under vacuum on polyimide sheets and patterned using a lift-off process. The  
18 sensing elements included an interdigitated thin-film capacitive transducer, and temperature  
19 sensitive thin-film meander-resistor. The inkjet printing of the sensors involved depositing Ag  
20 NP ink on the polyimide. Bus lines and interdigitated finger electrodes were printed in two  
21 separate printing steps (500-4000 dpi). The resulting line width and electrode gaps for resistors  
22 and capacitors were 80 μm, and the thickness of the printed layer was 400 nm. Sensing materials  
23 were encapsulated by laminating a photoresist film on the substrate. For the detection of  
24 humidity, cellulose acetate butyrate as the sensing medium was spray-coated on the capacitor  
25 through a stencil mask. In inkjet printing, the cellulose acetate butyrate in hexyl acetate was  
26 printed over the substrate to achieve a 5 μm film. The device was capped with a hydrophobic,  
27 gas permeable membrane. Subsequently, a commercial machine was used to weave the sensors  
28 into a textile band in weft direction with twill (1/8) pattern. Humidity and temperature sensors  
29 were inserted into the textile along the weft direction as replacement for weft yarn. Warp threads  
30 were replaced by conductive yarns to contact with the sensors inside the textile. The temperature  
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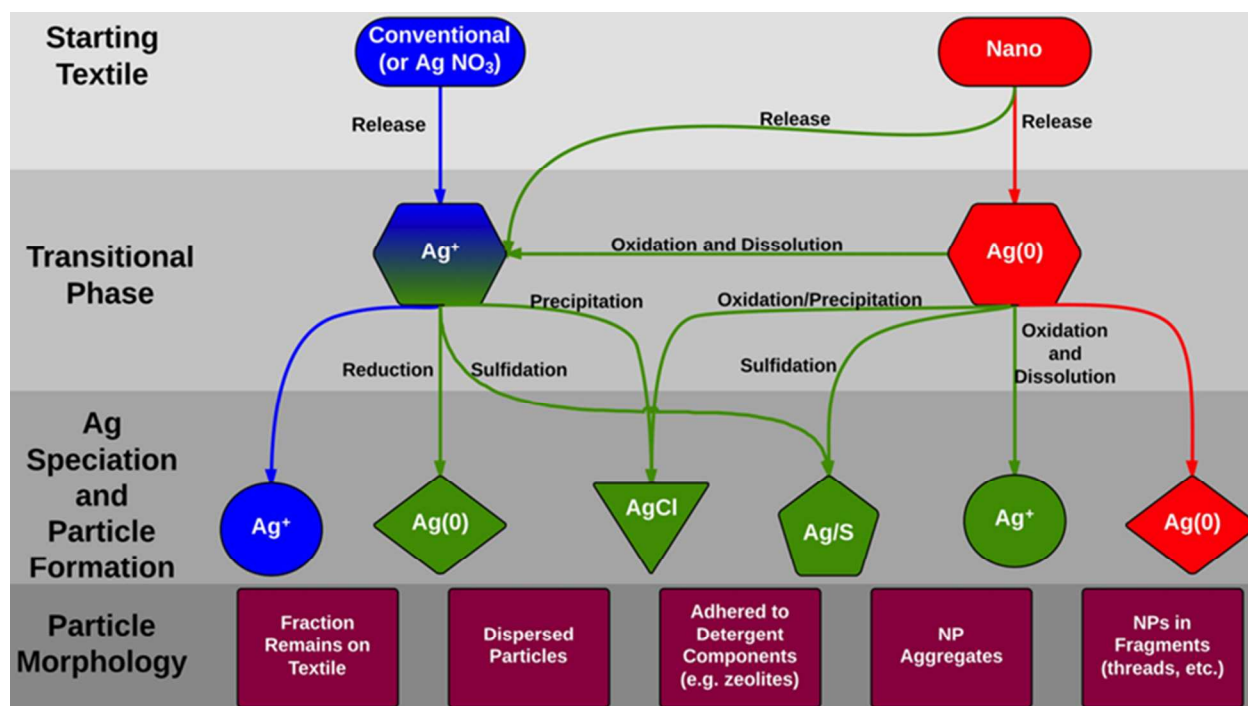
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3 sensors operated from 10 to 80 °C with a sensitivity of 5 °C. Humidity sensors had a detection  
4 range from 25 to 85 % with 10 % sensitivity.<sup>175</sup> These textiles were combined with LEDs to give  
5 visual sensing information (Figure 6e).<sup>178</sup>  
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10 Metal-Organic Frameworks (MOF) built with rare earth elements and/or quantum nanorods  
11 have been immobilized on cotton fabrics at high concentrations.<sup>179</sup> These materials have shown  
12 the potential to be used as colorimetric sensors to detect the presence of toxic gases via the  
13 luminescence of the MOFs or the electrical conductivity of the nanorods.<sup>180</sup> These chemical  
14 sensors can be incorporated into uniforms, apparels or any textile substrate. A dress designed by  
15 Matilda Ceesay using cotton mesh coated with a Cu benzene tricarboxylic acid MOF-199  
16 customized for capturing and controlled-release of permethrin (an insecticide) (Figure 6f). The  
17 designer aimed at functionalizing mosquito bed-nets commonly used as preventive measures in  
18 areas with high prevalence of malaria.<sup>176</sup>  
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### 34 TOXICITY OF NANOMATERIALS IN TEXTILES

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36 The forms of NP released in washing liquid depend on the nanomaterial characteristics  
37 originally incorporated into the textile, the composition of the washing liquid, the washing  
38 procedure (*e.g.* rotation speed). Ag-containing textiles release significant amounts of dissolved  
39 and particulate Ag into washing liquid. The potential exposure to Ag NPs from a blanket has  
40 been evaluated. For a blanket containing 109.8±4.1 mg Ag kg<sup>-1</sup>, 4.8 ± 0.3 mg Ag kg<sup>-1</sup> was  
41 released into sweat in 1 h.<sup>181</sup> Commercial NP-impregnated socks (1360 µg-Ag g<sup>-1</sup>) leached up to  
42 650 µg of Ag in distilled water (500 mL) in 24 h.<sup>71</sup> However, other commercial socks containing  
43 large amounts of Ag (2105 µg and 31242 µg) released small percentages (1 wt%) of total Ag into  
44 the ultrapure wash water while some brands released ~100 wt% of the Ag after four consecutive  
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3 steps. These studies indicate that the manufacturing processes of these socks differ  
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5 fundamentally. The socks released 155  $\mu\text{g}$  and 15  $\mu\text{g}$  of Ag into ultrapure water and tap water,  
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7 respectively. Hence, tap water was less aggressive in stripping Ag from the textile than ultrapure  
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9 water, which was attributed to differences in water corrosivity.<sup>15</sup> Artificial sweat was also used to  
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11 test the concentration of the Ag released from fabrics.<sup>182</sup> The concentration of Ag released from  
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13 Ag-impregnated fabrics was measured up to 322  $\text{mg kg}^{-1}$  of fabric weight. The release rate  
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15 depended on the concentration of the Ag in the fabric and pH of sweat. In another study, shirts  
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17 and pants impregnated with  $\text{TiO}_2$  NPs ranging from 2.9-8.5  $\text{g Ti kg}^{-1}$  textile.<sup>183</sup> The release of  
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19  $\text{TiO}_2$  into sweat per gram of textile after 30 min incubation in 120 mL of sweat was evaluated.  
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21 Substances released into acidic sweat were  $63 \pm 13 \mu\text{g g}^{-1}\text{L}^{-1}$  (particulate size <450 nm) and  $725 \pm$   
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23  $30 \mu\text{g g}^{-1}\text{L}^{-1}$  (particulate size >450 nm); whereas in alkaline sweat, the release amounts were  $38$   
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25  $\pm 13 \mu\text{g g}^{-1}\text{L}^{-1}$  (particulate size <450 nm) and  $188 \pm 213 \mu\text{g g}^{-1}\text{L}^{-1}$  (particulate size >450 nm).<sup>19</sup>  
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27 External dermal exposure for  $\text{TiO}_2$  was as maximal 11.6  $\mu\text{g kg}^{-1}$  body weight for total (mainly  
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29 particulate)  $\text{TiO}_2$ . When Ag was released from textiles, Ag-chloro complexes were the major  
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31 dissolved species due to the presence of high chloride concentration in sweat. Figure 7 shows  
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33 potential scenarios for Ag release from nanomaterial treated textiles.  
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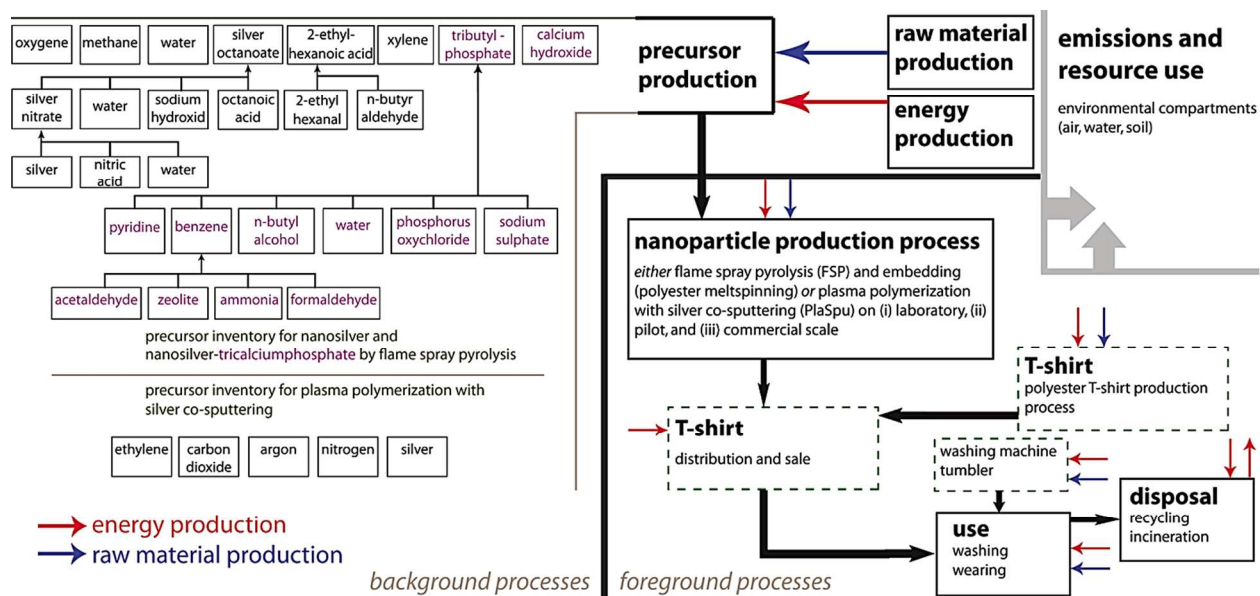


**Figure 7.** Scenarios for Ag release and subsequent transformation from nanomaterial-treated textiles. Blue shading indicate conventional materials or silver nitrate ( $\text{AgNO}_3$ ) that persists through the transformation process, and red shading indicate pristine nanomaterials. Green shading show a transformation product. Reprinted with permission from ref<sup>184</sup>. 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.<sup>185-188</sup> Furthermore, the antibacterial properties of Ag NPs might disrupt the bacterial habitat in sewage treatment plants.<sup>189</sup> Nanowashing machines were shown to release Ag in effluent at a concentration of  $\sim 11 \mu\text{g L}^{-1}$ .<sup>190</sup> Recent life cycle assessments involved comparing environmental benefits and negative effects of nanoAg T-shirts with conventional textiles treated with triclosan (a biocide).<sup>191</sup> Figure 8 shows lifecycle stages of one T-shirt ( $1.56 \text{ m}^2$  textile, 130 g). The “cradle-to-gate” climate footprints of the manufacturing of



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3 nanoAg T-shirt were 2.70 kg of CO<sub>2</sub>-equiv for flame spray pyrolysis, and 7.67-166 kg of CO<sub>2</sub>-  
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5 equiv for plasma polymerization with Ag co-sputtering. However, conventional T-shirts  
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7 produced by triclosan had emissions of 2.55 kg of CO<sub>2</sub>-equiv. Additionally, the toxic releases  
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9 from washing and disposal stages had minor relevance. However, the production phase holds  
10  
11 importance due to toxic Ag emissions at mining sites. Overall, the use phase was the most  
12  
13 important in terms of climate footprint in both nanoAg and triclosan cases. A limitation of these  
14  
15 studies was that variation in Ag release rates was not taken into consideration. Also, current life  
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17 cycle impact assessment methods do not distinguish colloiddally bound phases of metals.<sup>192, 193</sup>  
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19 Up to now, the life cycle assessments took into account only NP form. Considering other forms  
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21 of nanomaterials such as ionic forms, agglomerated forms, and oxidized forms will provide  
22  
23 improve life cycle assessments. While these assessments provide estimated effect of  
24  
25 nanomaterials on the environment, public awareness holds importance in washing practices. For  
26  
27 example, efficient washing procedures such as using tumblers less, and operating washing  
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29 machine at lower temperatures with appropriate detergents may reduce the environmental  
30  
31 impact. The increase in the awareness for recycling rate of NP embedded textiles may reduce the  
32  
33 carbon footprint. Furthermore, exposure to NPs is a significant concern at workplace.<sup>194</sup> For  
34  
35 example, spraying methods may result in exposure to inhalation of NPs.<sup>195</sup> The development of  
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37 improved life cycle assessments will allow comparing nanoengineered textiles with conventional  
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39 products in the market to prevent environmental consequences.  
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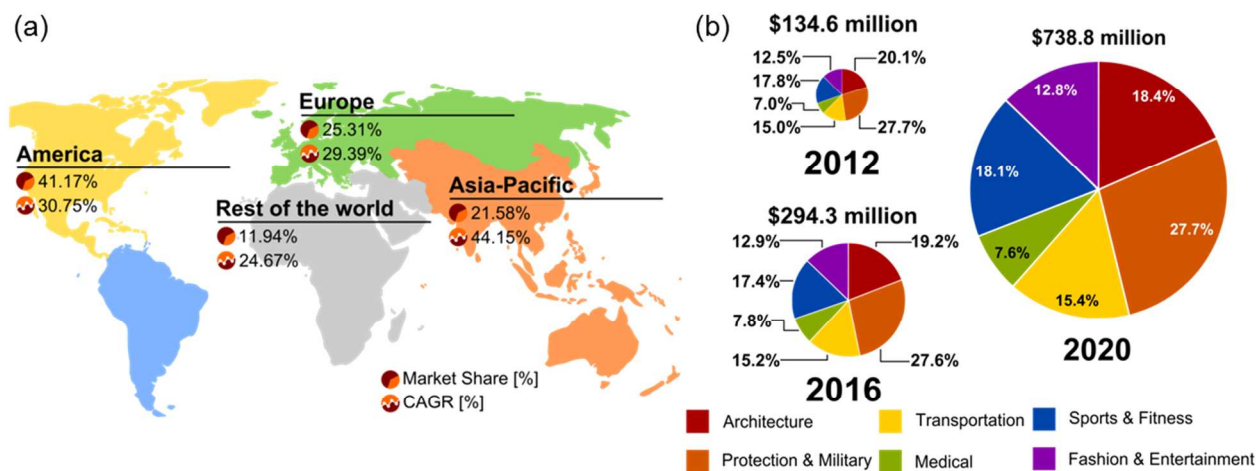
**Figure 8.** Lifecycle stages of one nanoAg T-shirt showing system boundaries (dashed boxes).

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## 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.<sup>196,197</sup> In the United States, 1.9 million people are employed, and \$250 million is spent in fashion industry annually.<sup>25</sup> 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%.<sup>198</sup> 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.<sup>198</sup> Americas was accounted for 41% of the global smart textiles market in 2014, followed by Europe (25%), and

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3 Asia-Pacific (21%) in 2014 (Figure 9). However, Asia-Pacific market is expected to have highest  
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5 CAGR (44%) in the next five years. The United States market is projected to grow at a CAGR of  
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7 31% until 2020.<sup>198</sup> High growth rates may be attributed to trends outside conventional apparels.  
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9 This is because in the traditional apparels, there is more demand for cost reduction, as oppose to  
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11 performance enhancement. In the case of innovative and functional applications of wearables,  
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13 the customer motivation is opposite.<sup>199</sup> Furthermore, the market for nanofiber-based products is  
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15 expected to reach over \$1 billion by 2020.<sup>200</sup> However, this market is not limited to textile and  
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17 apparel industry.<sup>198, 201</sup> With a demanding market for wearables and a growing trend for nano-  
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19 fiber based products, the applications are diverse for the nanotextile products ranging from  
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21 consumer apparels to medical wearables.<sup>202</sup>



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

48 A driving force for the smart textiles industry is sensing technologies with Internet  
49 connection. This capability can be used to communicate data such as location, as well as  
50 physiological parameters (*e.g.* heart rate), which are important in healthcare, sports, and fitness.  
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52 Therefore, this trend is expected to affect the market globally. For example, the use of functional  
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3 materials in textiles has led to electrophysical characteristics such as piezoresistive and  
4 conductivity. These technologies can aim to evaluate the patient's synoptic data. The process  
5 involves the development of smart textiles, communicating the data over the network, and using  
6 it to make informed decisions. One of the challenges facing the apparel industry in the use of  
7 such communication devices is ensuring simultaneous wearability, and functionality of efficient  
8 and portable power supplies.  
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17 In general, fashionable functional products transcending the traditional functions of fabric are  
18 highly desirable. Growth in the fashion and entertainment industry is expected to contribute to  
19 overall market growth. Additionally, the demand from the sports and fitness sector has increased  
20 due to growing awareness about healthy lifestyles. End users participating in extreme sports,  
21 running, skiing, have also contributed to the demand for smart textiles. To increase the  
22 competitiveness with respect to Asia, European Union has created initiatives for promoting  
23 incentives.<sup>203</sup> The European Commission has co-financed a number of projects such as Wealthy,  
24 MyHeart and Biotex. For example, Wealthy aims to create a wearable device for monitoring  
25 patient's vital signs.  
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39 To meet a wide range of end user needs, it is vital to market smart wearables that offer  
40 various levels of performance and comfort to wide customer base. The necessity for various  
41 levels of performance stems from global customers who are willing to pay a premium price for  
42 smart functional garments. However, in another market segment, the target customer may  
43 demand affordable functional textiles. One possible reason for the interest in innovation in  
44 textiles is that porous materials, synthetic microfibers and membranes used commercially over  
45 the past 30 years have been commodified. This may be attributed to the accessibility of  
46 blockbuster technologies due to patent expirations. The commodification subsequently reduced  
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3 profit margin and market share.<sup>200</sup> As a result, companies in the textile industry need to offer  
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5 competitive advantage through innovation by either enhancing performance or reducing the  
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7 production cost.  
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## 10 11 **CASE STUDIES**

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14 **Gore-Tex** is a lightweight, waterproof, breathable fabric membrane comprising of expanded  
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16 polytetrafluoroethylene (ePTFE) for application in medical devices, fabrics, and electronics.<sup>44, 204</sup>  
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18 W. L. Gore & Associates (Newark, DE) invented ePTFE in the 1970s. Gore-Tex was originally a  
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20 microporous structure that could be stretched up to 800% of its original length.<sup>205</sup> Gore-Tex is  
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22 used in products manufactured by various enterprises including Patagonia, L.L. Bean, Oakley,  
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24 Inc., Galvin Green, Marmot, Vasque, Arc'teryx, Haglöfs, and The North Face.<sup>206,207</sup> W. L. Gore  
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26 & Associates holds more than 71 issued patents related to Gore-Tex or the use of PTFE, in which  
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28 18 patents are for use in garments. Although the basis for the Gore-Tex technology originated  
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30 from microporous structures, the company has recently incorporated nanostructures into their  
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32 products for the apparels market. For example, Nano and NanoPro jackets have been  
33  
34 manufactured in conjunction with Marmot LLC.<sup>208</sup> Other nanotechnology-based examples could  
35  
36 be seen in the company's patent portfolio. Examples include Nyagraph 351 (Nyacol Nano  
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38 Technologies, Inc) for burn protective materials,<sup>209</sup> nanoemulsions of functionalized PTFE,<sup>210</sup>  
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40 prefiltration layers comprising of nanofibers,<sup>211</sup> and NPs for improved insulated electrical  
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42 conductors.<sup>212</sup> These cases serve to illustrate the importance of nanotechnology to a well-  
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44 established innovative company in the apparel industry.  
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52 **NanoSphere®** marketed by Schoeller Textiles AG (Sevelen, Switzerland) is a finishing  
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54 technology with hydrophobic surface properties that mimic the self-cleaning effect of lotus  
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56 leaves.<sup>39</sup> Schoeller claims that NanoSphere® has improved water/oil and dirt repelling properties,  
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3 and washing performance as compared to traditional textile impregnation-based manufacturing.  
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5 Furthermore, the protective function of NanoSphere® may be retained after frequent use and  
6  
7 numerous washing cycles without affecting comfort, texture, and breathability. The textiles  
8  
9 finished with NanoSphere® require less frequent washing at lower temperatures as compared to  
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11 conventional textiles. Additionally, it has high abrasion resistance. The company's other  
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13 products address a variety of applications ranging from stretch fabrics, sun reflectors, and  
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15 temperature resistance, and bionic climate conditioning.<sup>213</sup> Their patent portfolio in  
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17 nanotechnology includes PEIN NPs for antibacterial finishing of electrospinnable polymers,<sup>214</sup>  
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19 NPs and CNTs for finishing of substrates,<sup>215</sup> and nanofibers having microbicidal properties.<sup>216</sup>  
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24 **Aquapel**, marketed by Nanotex LLC (Bloomfield Hills, MI), reproduces natural water-  
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26 repellency of plant surfaces and animal coats.<sup>179</sup> Aquapel technology involves permanent  
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28 attachment of hydrophobic 'whiskers' to individual fibers at the molecular level. Aquapel  
29  
30 features a hydrocarbon polymer that is ecologically friendly and low-cost. Nanotex's portfolio  
31  
32 consists of 28 WO patent applications and addresses textile sectors including repellency/stain  
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34 resistance, moisture management, odor control, static elimination, and wrinkle resistance. In  
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36 2013, Nano-Tex products were on \$280 million in branded products at retail.<sup>10</sup> In the same year,  
37  
38 Nanotex was acquired by soft-surface technology company Crypton Inc.<sup>217</sup>  
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43 **SmartSilver**® is an antimicrobial yarn marked by NanoHorizons (Bellefonte, PA). It  
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45 develops and manufactures Ag NP additives that provide antimicrobial characteristics to their  
46  
47 products. The company markets Oeko-Tex® antimicrobial solution under the SmartSilver®  
48  
49 brand.<sup>218,219</sup>  
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53 **Nanosan**, marketed by SNS-Nano Fiber Technology (Hudson, OH) and Schill & Seilacher  
54  
55 (Germany), consists of spun polymers for application in filters and adsorbent fabrics.<sup>220</sup> SNS-  
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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.<sup>221,222,223,224</sup> 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.<sup>164</sup> 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.<sup>225-227</sup> Table 1 shows the companies involved in smart textiles and wearables market.<sup>228</sup> 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 ( $\mu$ /Nano)	Technology & Products	Applications	Ref.
Auxetic Technologies Ltd (UK)	2004	3	$\mu$ /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	$\mu$	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	$\mu$ /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	$\mu$ /Nano	Micro- and nanofibers	Apparel, filtration, healthcare, and electronics	244, 245
Fibretronic limited (Hong Kong)	2004	N/A	$\mu$	Textile electronics	Wearable electronics and smart fabrics (sensors, heating and cooling elements)	N/A
Freudenberg Group (Germany)	1849	N/A	$\mu$ /Nano	Housewares and cleaning products, automobile parts, and textile	Nonwoven fabrics and textile materials	N/A
Gentherm Incorporated (US)	1960	18	$\mu$	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	$\mu$	Jacquard: a microfiber-woven textile	Textile with digital sensing microfibers	N/A
Hollingsworth and Vose (US)	1843	3	$\mu$ /Nano	Filtration and nonwoven materials	Composite materials, home furnishings, apparel	256-258
HeiQ (Switzerland)	2005	6	$\mu$ /Nano	Dynamic cooling, water and oil repellency on textiles	Outdoor products, medical implants	1259-264
Interactive Wear AG (Germany)	2005	2	$\mu$	Functional textile products: textile cable, heating pads, interactive wearable solar energy source	Integrated textile systems	265, 266
International Fashion Machines, Inc. (US)	2002	2	$\mu$	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	$\mu$ /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.

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3 Interactive garments in fashion will also evolve. Programmable visual components, LEDs  
4 and fiber optics in garments will find increasing use in fashion and entertainment industries.  
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6 Incorporation of new approaches including structural colors, luminescence, plasmonics,  
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8 metamaterials, holography, photonic crystals (PCs) and LED displays in textiles can create  
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10 mesmerizing effects on garments. These dresses can be combined with pressure or motion  
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12 sensors that can change the color of the dress based on touch, movement, temperature, light,  
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14 electric field, or other external stimuli. The material may also include bioinspired patterns and  
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16 chemical reactions with the environment.  
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22 In addition to serving as light emitting elements to enable the shinning and colorful  
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24 appearance for fashion apparels, optical fibers offer more capabilities. For example, an array of  
25  
26 fibers can be weaved into a garment to constitute a programmable fiber-optic display that is able  
27  
28 to show dynamic graphics. Optical fibers can also be used as sensing components in  
29  
30 multifunctional garments for sports and fashion. Recently, Cambridge Consultants has developed  
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32 Xelflex fabric that was equipped with optical fiber sensors for tracking movements of human  
33  
34 body.<sup>373</sup> Xelflex could be used in fitness and sports coaching as well as part of physiotherapy.  
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36 Additionally, fiber sensor-based gloves and garments that can recognize postures of human hand  
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38 and body have been demonstrated.<sup>374</sup> Physical or biological measurements may be detected by  
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40 on-garment fiber sensors such as strain, pressure, temperature, humidity, and metabolites.<sup>375</sup>  
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42 Thus, in the near future a fully functionalized sportswear based on fiber-optics sensors will be  
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44 produced for monitoring of physiological conditions of human body including heart beating rate,  
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46 blood pressure, sweating, body motions, temperature, and even potential disease risks. Such  
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48 garments can also be used for increasing the interaction and connectivity of user with gaming  
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50 consoles and virtual reality platforms.  
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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).<sup>376</sup> The LCDs that are commonly used in current smartphones, tablets and computers are usually inflexible.<sup>377</sup> Considering the flexibility and light weight required for textile displays, OLEDs composed of thin films of organic molecules constitute a potential candidate.<sup>378</sup> 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.<sup>379, 380</sup> 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.<sup>381-384</sup>

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Photonic crystals are nanostructures in which the dielectric constant has a periodic variation in one, two or in all three orthogonal directions.<sup>385-387</sup> 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 transmitted by PCs. They can be incorporated into flexible thin films that may be conveniently attached to a fabric or garment.<sup>388, 389</sup> 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.<sup>390, 391</sup> This color-tuning property may be utilized for garments to not only promote the aesthetic performance, but also enable the garments for sensing applications.<sup>392</sup>

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4 Combining holograms with garments and wearable devices is another potential research  
5 direction.<sup>393, 394</sup> A hologram is first produced by encoding interference information of an object  
6 on a recording medium. A 3D image of the recorded object could be reconstructed by  
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8 illuminating the holographic film with a broadband light.<sup>395, 396</sup> To date, a variety of holographic  
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10 films have been used as decorative coatings that are able to provide garments with iridescent  
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12 appearances and 3D graphics.<sup>145</sup> Holograms may also be used in other wearable gadgets such as  
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14 helmets and glasses for virtual-reality applications. In Hololens (Microsoft), holographic gears  
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16 are equipped on a headset.<sup>397</sup> Thus, wearers of Hololens may appreciate a virtual life experience  
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18 by visualizing and interacting with the environment on demand. Moreover, holographic sensors  
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20 that are fabricated into thin films could also be integrated into garments for detecting metabolic  
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22 function.<sup>398-403</sup>  
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30 Metamaterials are artificial structured substances made by assembling composite materials  
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32 such as metals and plastics in periodic patterns at scales that are smaller than the wavelength of  
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34 interest.<sup>404</sup> Metamaterials due to their extraordinary structures exhibit complex behavior to  
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36 electromagnetic waves (*e.g.* negative refractive index). Many intriguing features could be offered  
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38 by metamaterials when used in textiles and garments. For example, metamaterials have potential  
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40 for the development of cloaking devices that are used to make a defined region invisibly isolated  
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42 from the passing electromagnetic waves. While some progress on metamaterial-based cloaking  
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44 devices was made at microwave<sup>405</sup> and THz frequencies,<sup>406, 407</sup> truly invisible garments may be  
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46 realized in the visible spectral region. Moreover, many thin-film metamaterial sensors have been  
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48 demonstrated.<sup>408</sup> These sensors could be potentially integrated into textiles and garments for  
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50 monitoring physiological biomarkers.  
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3 Nanotextiles can be functionalized with molecular dyes and analyte-sensitive compounds.  
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5 For example, microfluidics can be incorporated in thread-based channels for application in point-  
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7 of-care diagnostics.<sup>409-417</sup> In the future, we expect many functional components being seamlessly  
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9 integrated into textile architecture. Accordingly, production processes will also evolve to  
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11 combine electronics, biomaterials, and optics into textile weaving. Applications in fashion and  
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13 arts will also be realized.<sup>418, 419</sup> These sensing and display technologies may be controlled by  
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15 smartphones.<sup>420-422</sup>  
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20 Another potential research area is to create green chemistries and fabrication approaches to  
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22 synthesize nanomaterials that stay intact after laundering. For example, development of new  
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24 covalent binding mechanics to attach nanomaterials to cotton or synthetic fibers is desirable.  
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26 These nanomaterials may also require new surface finishing processes to ensure their  
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28 immobilization in textiles and maintenance any environmental condition. Additionally,  
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30 agglomeration of deposited nanomaterials is a major challenge and this requires the development  
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32 of new nanoadditives and stabilizers in formulations and finishing treatments. These approaches  
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34 may require functional surface-activated polymer or cotton composites to immobilize  
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36 nanomaterials on textile without comprising their chemical, optical, and electrical properties.  
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38 Furthermore, recycling of clothing is generally carried out by creating landfills. A significant  
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40 concern about the nanomaterials is potential contamination of water or soil.<sup>184</sup> Hence, life cycle  
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42 assessments should also focus on identifying risk factors for laundering, recycling and particle  
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44 release after degradation while accounting different forms of nanoparticles and release rates.  
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46 Effects of uncontrolled release of nanomaterials to the environment, and toxicity to humans,  
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48 marine life needs to be evaluated before the introduction of nanoproducts to the market. Since  
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50 these nanomaterial-based textiles are likely to be produced in the emerging economies, the safety  
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3 of the workers and exposure to nanomaterials warrant nanotoxicity analyses. The  
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5 commercialization of nanotechnology-based textiles may be limited due to government  
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7 regulations. For example, Biocidal textiles containing nanoAg are registered by the Environment  
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9 Protection Agency (EPA) in the United States.<sup>193</sup> ISO catalogue enlists a number of standards for  
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11 formulating and testing nanoproducts.<sup>423</sup>  
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## 17 CONCLUSIONS

19 The customer demand in improved appearance, functionality, and connectivity in fashion has  
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21 motivated the development of nanotechnology-based textiles. Over the last two decades,  
22  
23 numerous nanostructures and nanomaterials including NPs, CNTs, Bragg diffraction gratings,  
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25 and nano-electronic components have been deposited or woven into textiles. The development of  
26  
27 these nanomaterials also created new fabrication methods involving particle impregnation, spray  
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29 coating, multifunctional composite fiber drawing, and direct weaving at industrial scale. The  
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31 application of nanomaterials in the form of surface modifications, electronics and optics offers  
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33 functionality as well as the potential of improved appearance. Realized nanotechnology  
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35 applications in textiles include antibacterial properties, odor control, UV protection, water  
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37 repellence, wrinkle resistance, antistatic properties, and strength enhancements. Advanced  
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39 technologies included incorporation of moisture, temperature, pressure sensors, drug release, and  
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41 fiber optics powered by textile-based batteries. With the emergence of nanomaterials, these  
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43 technologies are transitioning from rigid to seamlessly integrated flexible substrates while  
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45 offering light weight.  
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52 In parallel to the development of nanotextiles, life cycle assessments and toxicity of released  
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54 nanomaterials from textiles are being critically evaluated. Nanotechnology-based products will  
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3 continue to emerge with new applications; however, manufacturers and regulatory agencies must  
4 ensure that these technologies will not have a negative effect on human health and the planet  
5 during their manufacture and life cycle. The textile industry is under scrutiny due its impact on  
6 climate change.<sup>424</sup> Today textiles and apparels account for ~10% of the total carbon emissions.<sup>425</sup>  
7  
8 17-20% of industrial water pollution originates from dyeing and finishing agents in textile  
9 industry, negatively affecting people inhabiting regions around textile production plants,  
10 particularly in the developing world.<sup>426</sup> The use of dyes and fixing agents (*e.g.*, chromium) in  
11 textile manufacturers and tanneries are major pollutants, particularly in Southeast Asia.<sup>427</sup> Hence,  
12 the effect of nanoproducts on the production dynamics and pollution remains questionable.  
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14 Growing concerns among customers has begun forcing the manufacturers to reduce the  
15 environmental impact of their production methods, which will also involve the use of  
16 nanomaterials.<sup>428, 429</sup> Social awareness among customers has probed companies to invest in  
17 corporate social responsibility to offer environmentally sustainable products with reduced carbon  
18 footprints.<sup>430-432</sup> These trends in customer behavior and climate change will involve the use of  
19 nanotextiles, which need to be climate neutral and recyclable aimed at reducing greenhouse  
20 emissions. Nanotechnology will undoubtedly evolve textiles transcending style changes to shape  
21 the next big concept: the connected couture.  
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## 45 AUTHOR INFORMATION

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### 51 52 53 54 **Author Contributions**



1  
2  
3 A.K.Y. designed the project. A.K.Y. and H.Q. wrote the article. A.M. contributed to Market and  
4  
5 Case Studies sections. S.H.Y., A.K., H.B., J.H., and M.S. made intellectual contributions and  
6  
7 edited the manuscript.  
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## 10 11 Notes

12  
13 The authors declare no competing financial interests.  
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Table of Contents Graphic



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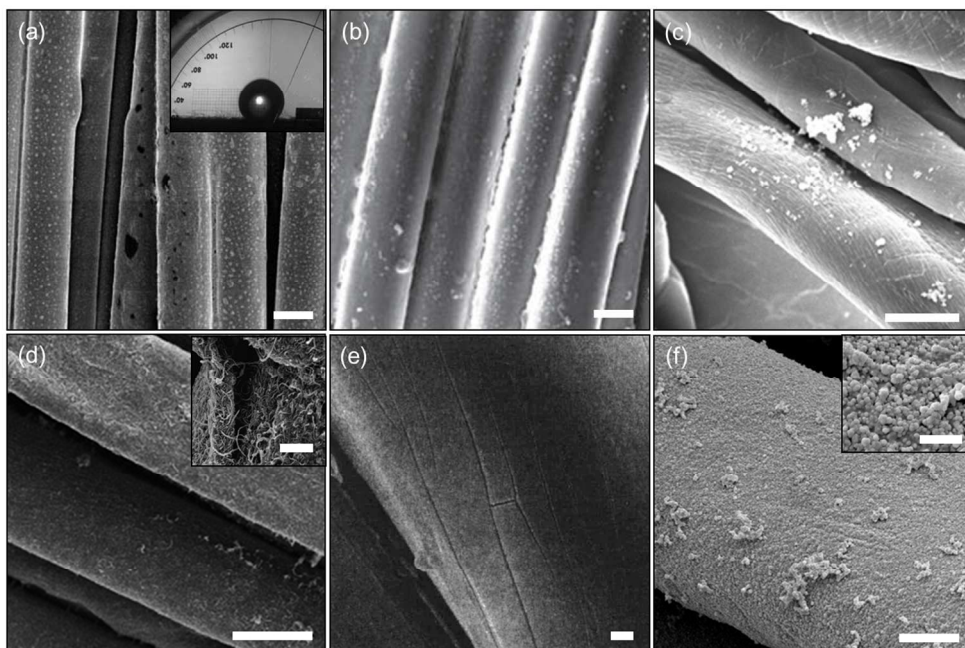
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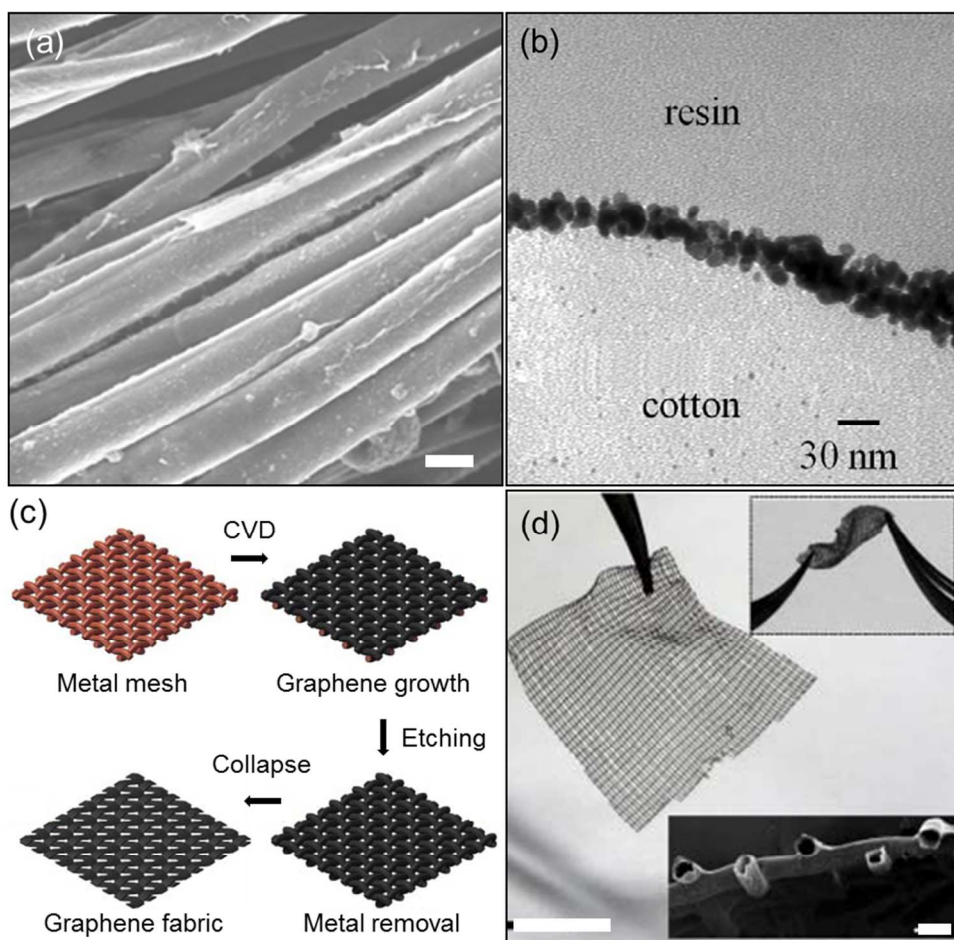
Applications of nanotechnology in textiles  
145x160mm (150 x 150 DPI)



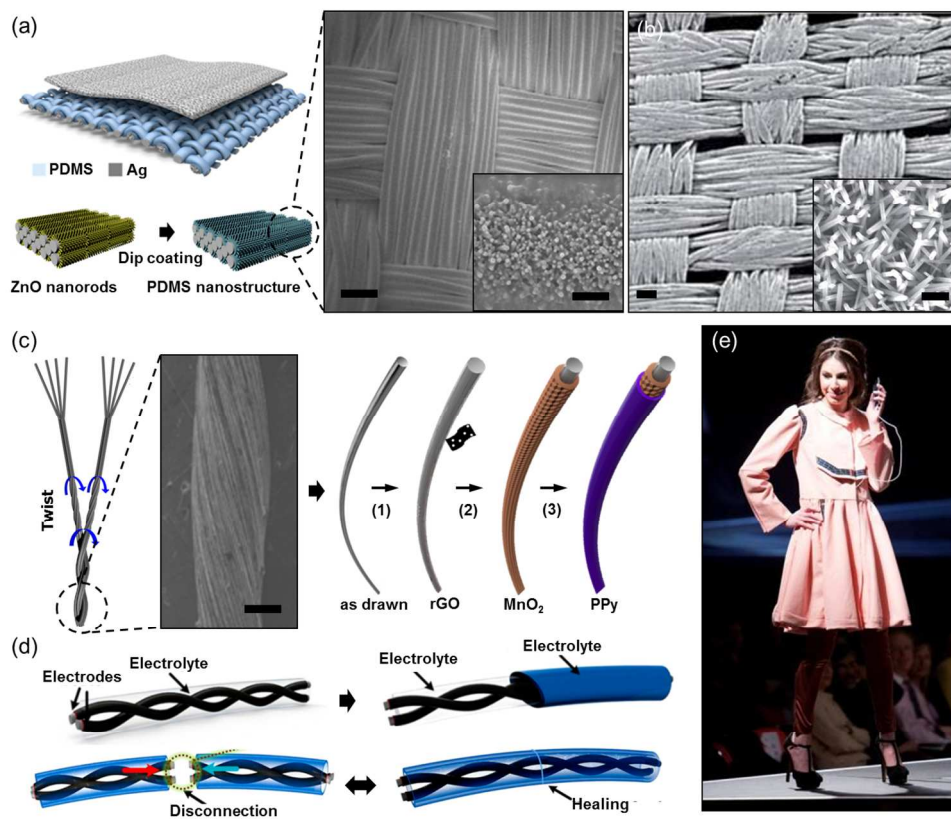
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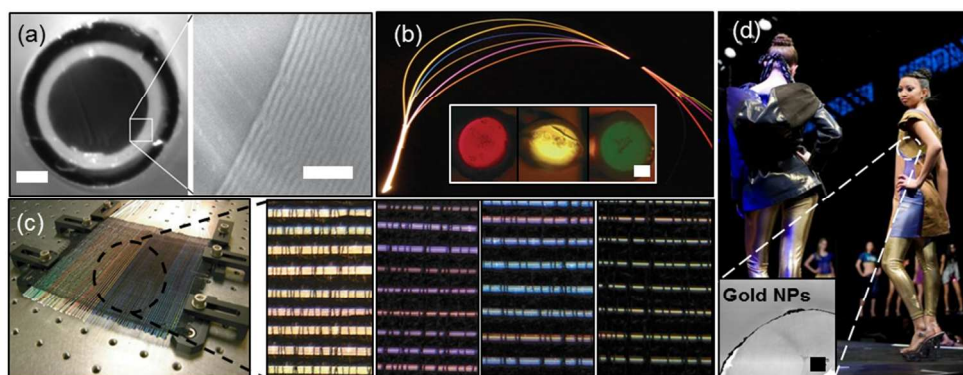
SEM images of nanoparticle functionalized fibers  
239x160mm (150 x 150 DPI)



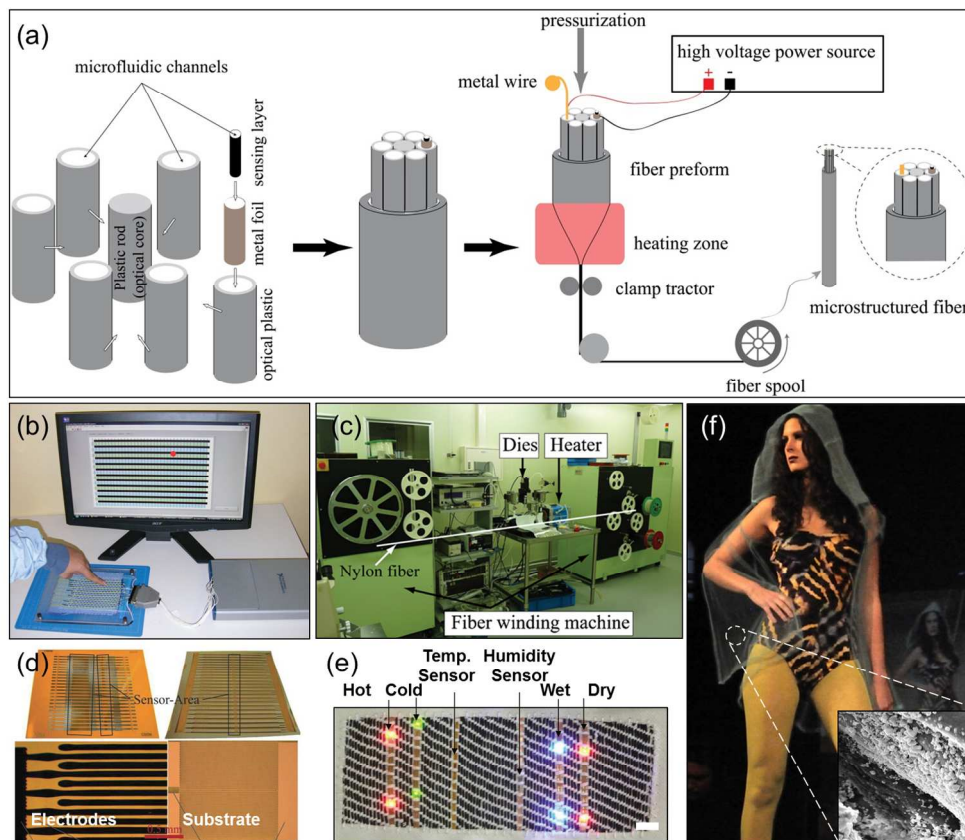
Conductive nanomaterials in textiles  
168x163mm (150 x 150 DPI)



Energy generation and storage in textiles  
253x213mm (150 x 150 DPI)

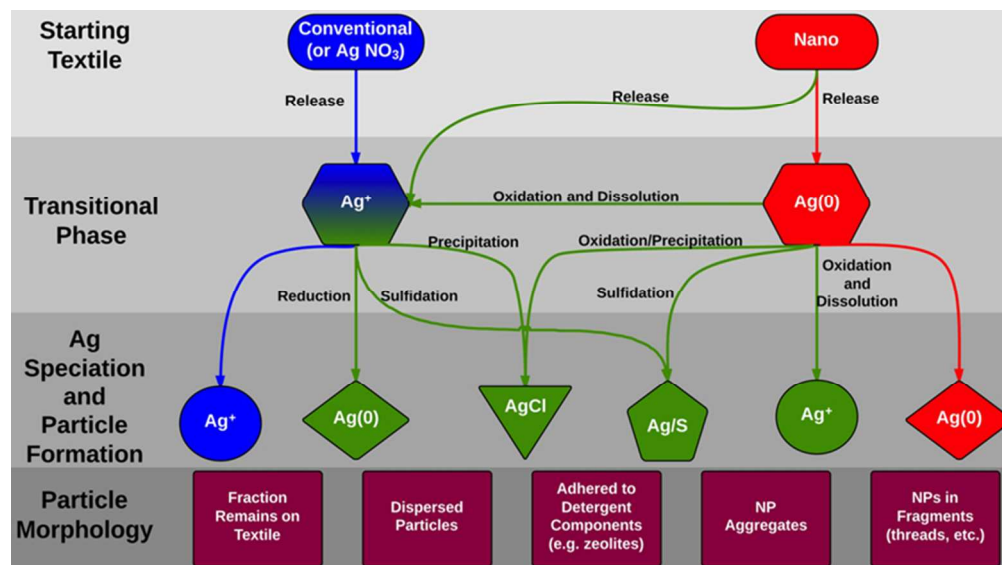


Fiber optic and plasmonic technologies for textiles  
177x71mm (150 x 150 DPI)

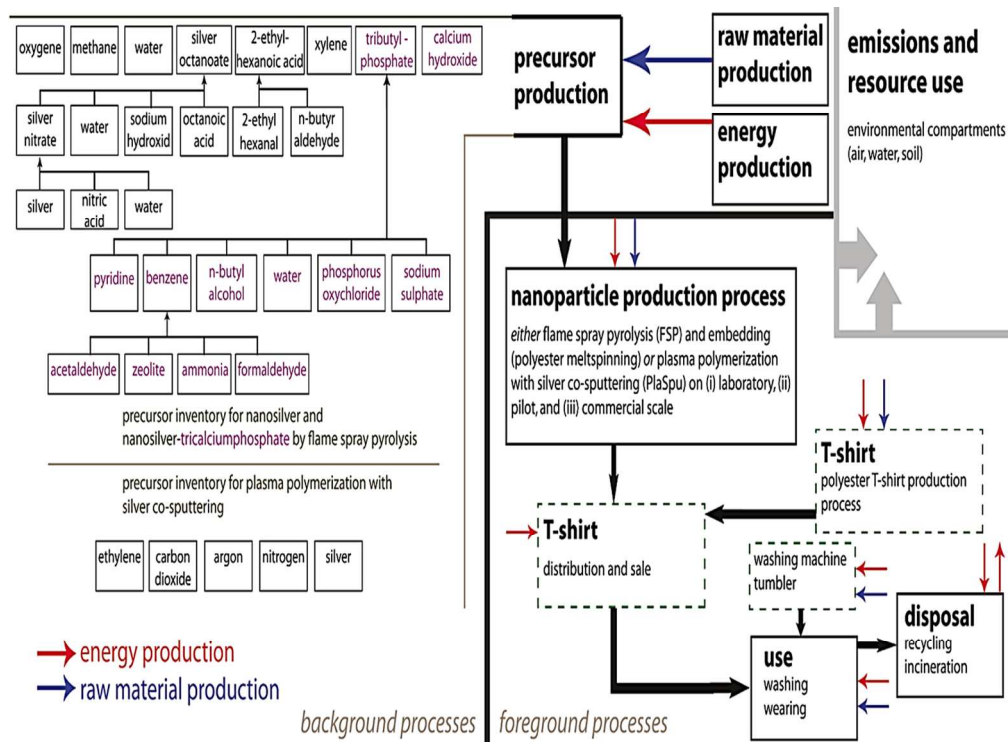


Sensors and insecticide-releasing textiles  
292x251mm (150 x 150 DPI)



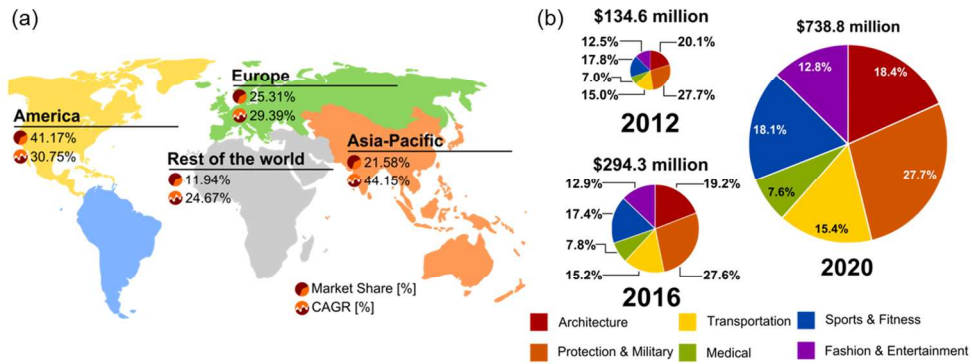


Scenarios for Ag release and subsequent transformation from nanomaterial-treated textiles  
147x82mm (150 x 150 DPI)



Lifecycle stages of one nanoAg T-shirt showing system boundaries  
 457x214mm (95 x 150 DPI)

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Smart textiles market  
224x88mm (150 x 150 DPI)