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Perspective

Biological Chemicals as Sustainable Materials to Synthesize Metal and Metal Oxide Nanoparticles for Textile Surface Functionalization

Shahid ul Islam and Gang Sun*

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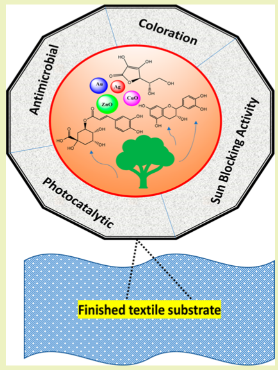
ABSTRACT: Tremendous progress has been made in developing highly efficient cutting-edge materials and textile surfaces by applying a wide range of nanostructures during the past few years. Due to their extraordinary and attractive features, metal and metal oxide nanoparticles (NPs) have introduced prominent novel antimicrobial, photocatalytic, stain repellence, fire retardant, and UV protective functions on textile surfaces. Unfortunately, their conventional syntheses based on physicochemical procedures often require energy-intensive processes and toxic chemicals, bringing environmental and human safety concerns. To address these issues, the latest approaches based on the biological production of NPs on polymeric material surfaces are currently being pursued. In this perspective, we present a systematic and comprehensive summary of the biological *in situ* and *ex situ* formation of metallic NPs on the surfaces of textiles and fibers. A detailed and insightful discussion on the *ex situ* and *in situ* mechanisms of nanoparticle formation from chemical compounds derived from plants and fungi is also provided. Finally, critical research gaps are identified, and prospects for efficient and sustainable nanofinishing technologies for textile surfaces using biological chemicals are provided.



KEYWORDS: *Nanostructures, Inorganic metal ions, Flavonoid compounds, Textile finishing, Antibacterial activity*

INTRODUCTION

Applications of nanotechnologies and nanomaterials have led to numerous innovations in all sectors, ranging from medicine, life science, physical science, chemical science, and material science.[1−4] Nanomaterials are the structural entities of inorganic and organic materials in the range of 1−100 nm, i.e., nanoparticles (NPs).[5,6] After several years of development, metallic NPs have found practical applications in the production of daily consumer products, including toothpaste, shampoos, detergents, cosmetics, and more.[7,8] Metallic NPs are promising candidates in the medical and healthcare sectors, chemical catalysis, sensing, and energy storage devices.[9,10] Recent introductions of nanotechnologies into the textile sector have created revolutions in functional textiles.[11−13] Opportunities are emerging from the incorporation of metallic NPs onto surfaces of fibers and textiles transforming them into advanced materials for use in different sectors such as sports, medicine, gaming, healthcare monitoring, defense and security, aerospace, and so on (Figure 1a).[14−18] The new trend, particularly since the spread of COVID-19, has drawn attention toward use of nanoparticles as antiviral agents for textile-based common personal protective equipment (PPE) like gowns, facemasks, gloves, and more (Figure 1b−d).[19−21] Research on their production using physical and chemical approaches, such as hydrothermal, sonochemical, solvothermal, sol−gel, and mechanical chemistries, has demonstrated new possibilities for the incorporation of NPs onto the surfaces of textiles and polymers.[22−26] While the physical agglomeration and chemical reduction of metal precursors to produce corresponding NPs on textiles are rising to an unprecedented height, they may be limited by complex setup restrictions and potential generation of toxic substances adversely affecting the environment.[27] Table 1 summarizes some of the research works carried out on applications of nanostructures formed onto textile surfaces by using so-called *in situ* or *ex situ* chemical processes. *Ex situ* formation of NPs on textiles is a two-step process, i.e., formation of NPs in separate processes and incorporation of NPS onto textiles by additional treatment steps, while the *in situ* formation of NPs can be achieved directly on surfaces of fibers during the treatments.

Most of the chemical formations of NPs usually require nonpolar solvents, use toxic substances (Table 1), and suffer from issues such as hazardous byproducts and toxicity to humans and the environment. On the contrary, biological methods based on biogenic and biochemical processes could produce NPs in the absence of any external reducing agents, which are therefore gaining scientific and academic interests and becoming an emerging alternative technology.[29] Biogenic synthesis of the NPs involves the direct use of microorganisms

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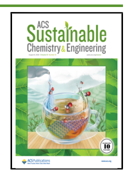

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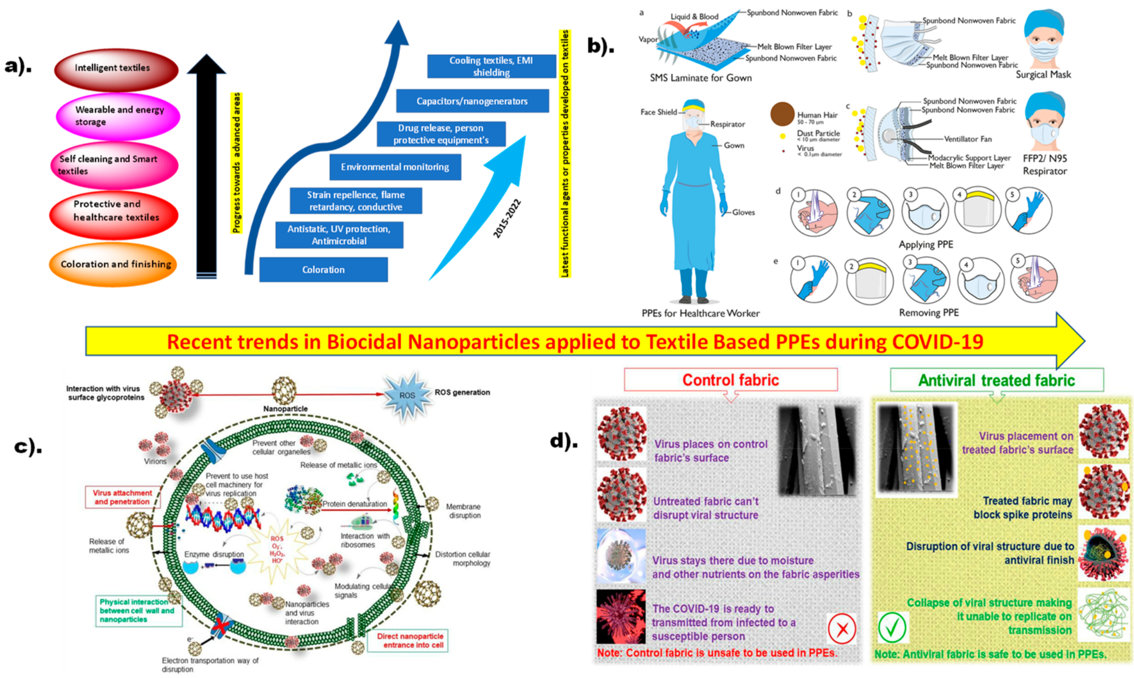

Figure 1. (a) Schematic illustration of the roadmap and latest innovations in textiles based on nanotechnological collaborations. (b) Commonly used textile substrate-based personal protection equipment. Reprinted from ref 28. Copyright 2020. American Chemical Society. (c) Example of a test nanoantiviral finish's efficacy and its possible application in PPE. (d) Antiviral protections offered by finished textiles. Reproduced with permission from ref 19. Copyright 2021, Taylor & Francis.

Table 1. Examples of Nanoparticles Formed on Textiles by Using Chemical Synthesis

authors	textile fabric	method	functionalities imparted	ref
Xue et al.	cotton	*In situ*: fabric immersed into $[Ag\ (NH3)_2]^+$ solution and glucose	conductive, antibacterial, and hydrophobic	51
Noorian et al.	cellulose	*In situ*: cotton fabric immersed in $ZnCl_2$ aqueous solution	UV protection and antibacterial	52
Rilda et al.	cotton	*In situ:* immersion of modified cotton in suspensions of $ZnO-SiO_2$ and chitosan	antibacterial	53
Borda d' Água et al.	cotton	*In situ*: immersion of cotton into aqueous solution of zinc acetate dihydrate	antibacterial	54
Montes-Hernandez et al.	cotton, wool, polyamide, and polyester	*In situ*: immersion of fabrics in $AgNO_3$ and then in $NaBH_4$	coloration and antimicrobial activity	55
El-Naggar et al.	cotton	*In situ*: immersion of plasma-coated cotton into silver carbamate solution	UV protection, antibacterial, self-cleaning, and photocatalytic	56
Tang et al.	cotton	*Ex situ*: aqueous solution of $AgNO_3$, trisodium citrate, and hydrogen peroxide mixed with $NaBH_4$; cotton fabrics immersed in prepared nanoparticles	dyeing effects	50

such as fungi and enzymes as reducing agents, while biochemical synthesis uses biological components extracted from plants. The biological synthesis of metal NPs has at least two steps in general, i.e., reduction of metal ions in the system to elements or formation of element oxides followed by their nucleation and growth into nanosized particles.[30,31] Both are determined and affected by the biological components, which can serve as reducing agents to metal ions and regulating agents to control the sizes and shapes of the formed NPs. Chemically speaking, biological materials are popular secondary metabolites isolated from different parts of various plant species containing primarily phenolic or carbonyl compounds that have the potential to reduce metal ions to metal elements and could assist agglomeration of metal oxides to nanoparticles during textile finishing processes.[32,33] Many of the chemicals may also absorb visible or UV light, due to the conjugated chemical structures, and are employed as colorants or UV absorbents. Interestingly, many of them could provide antimicrobial functions due to their chemical reactivities.[34−38]

Among the biosynthesis routes, plants and plant extracts have been ideal candidates for direct applications in functional textile treatments due to the easy production of NPs in different morphologies and the low costs of the processes, which have been called the green synthesis of NPs. Reviews on the green synthesis of nanoparticles have been published in the literature in recent years.[39−41] However, there is a lack of systemic discussion on the biological synthesis of metal NPs on textiles, especially on the *in situ* and *ex situ* formation of metal NPs on textile materials. Table 2 summarizes the latest literature on *ex situ* biological synthesis of NPs using plant extracts. Biologically formed NPs on textiles are playing pivotal roles due to their reliability, consistency, and robustness in the resulting functional products.[42,43] The NPs on the textiles formed by *in situ* and *ex situ* processes may affect certain properties and performances of the products. Most of the NPs

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Table 2. Newest Progresses on the Synthesis of NPs Using Biochemicals from Plant Parts

plant name	part used	types of nanoparticles	size (nm)	shape	reducing and stabilizing agents	ref
Melia azedarach	leaf	Ag	18−30 nm	spherical	tannic acid, flavonoid, and enzymes	71
Nycanthes arbor-tristis	leaf	Ag	10−50 nm	spherical	polyphenols, flavonoids, and tannins	72
Aerva lanata	flower	Ag	2−10 nm	spherical	carboxylic acids, proteins, and polyphenols	73
Annona squamosa	seed	Ag	22 nm	spherical	phenolic compounds	74
L. acapulcensis	−	Ag	5 nm	spherical, quasi-spherical	proteins and phenolic compounds	75
A. millefolium L	whole plant	Ag	14 nm	spherical, rectangular, cubical	proteins, flavonoids, and tannic acid	76
A. wilkesiana	leaf	Ag	10−30 nm	spherical	flavonoid, carbohydrates, and tannins	77
Eriobotrya japonica	leaf	Ag	−	quasi-spherical	polyphenols and terpenoids	78
Nigella sativa	seed	Ag	10−12 nm	spherical	flavonoids and proteins	79
Zingiber officinale	leaf	Ag	18 nm	spherical	flavonoid, phenolic, and carboxylic compounds	80
Tribulus terrestris	flower	Au	10−15 nm	spherical	polyphenols and carbonyl compounds	81
Mentha longifolia	leaf	Au	36 nm	spherical	phenolics and carbonyl compounds	82
Curcuma pseudomontana	rhizome	Au	20 nm	spherical	curcumin	83
Moringa oleifera	leaf	Au	35−51 nm	spherical, oval, hexagonal	phenolics and terpenoids	84
Celastrus paniculatus	leaf	Cu	2−10 nm	spherical	flavonoid and other phenolic compounds	85
Cardiospermum halicacabum	leaf	Cu	30−40 nm	hexagonal	phenolic and flavonoids	86
Hagenia abyssinica	leaf	Cu	34	spherical, hexagonal, triangular, cylindrical	polyphenols and tannins	87
Agaricus bisporus	leaf	Cu	2−10 nm	spherical	phenols, carboxylic acids, and polysaccharides	88
Cedrus deodara	leaf	CuO	−	spherical	phenols and carbonyl compounds	89
Curcuma longa	tuber	Cu	5−25 nm	spherical	curcumin	90
Phoenix dactylifera	fruit	ZnO	31 nm	spherical	polyols, tannins, anthocyanidins, flavonols, and amino acids	91
Ziziphus jujuba	leaf	ZnO	15 nm	spherical	polyphenols and carbohydrates	92
Melia azedarach	leaf	ZnO	33−96 nm	hexagonal, spherical	carbonyl compounds/proteins	93

are employed in the development of antimicrobial and healthcare textiles through textile finishing processes. Multifunctional textiles, including antimicrobial functions with additional UV protections or antistatic functions, could be achieved on textiles incorporated with selected metal NPs. In addition, antibacterial and antiviral functions provided by the NPs have significant potentials for personal protective clothing and smart medical materials to prevent transmission of diseases and reduce infections.[44,45] Novel metal NP-based antibacterial fibers have shown the functions of killing bacteria and viruses effectively.[26,46]

This perspective sets out to provide a systematic discussion toward recent advances in *ex situ* and *in situ* biological formations of metal and metal oxide NPs on textiles, as well as functional applications and potential concerns of the products. Due to similar chemistry in the formation of metal NPs, the synthesis processes of AgNPs will serve as models in the discussion. In the discussion of the formation of AgNPs, *ex situ* and *in situ* processes and their corresponding mechanisms and features are analyzed. Differences between biochemical and biogenic processes are illustrated. Other metal NPs and metal oxide NPs are additionally discussed afterward.

■ AGNPS COLORATION AND TEXTILE FUNCTIONALIZATION

Silver nanoparticles (AgNPs) are one of the most commercialized nanomaterials in the world, primarily due to their promising strong antimicrobial actions and historic human safety records.[47,48] AgNPs exhibit different colors due to their brilliant surface plasmon resonance property which is highly dependent upon their sizes and shapes, as shown in Figure 2a and b.[49] As indicated in Figure 2c−j, this property has inspired several textile and polymer chemists, and they have been increasingly applied in the textile industry as novel nanocolorants onto silk and cotton. Lately, AgNPs have been biologically produced and incorporated onto different textile substrates via both *ex situ* and *in situ* processes.[50]

■ *EX SITU* SYNTHESIS OF AGNPS

Examples of *Ex Situ* Synthesis. The *ex situ* preparation of NPs has been a major process in which the NPS of interest are first prepared separately, characterized, and then applied through various methods onto textile and polymer surfaces (Figure 2k−l).[59] The *ex situ* synthesis of NPs is more suitable to large-scale industrial applications. However, the lower diffusion rate and lack of interactions with polymers and difficulties in dispersion and applications of the NPs are major challenges with this approach.

The biochemical *ex situ* synthesis of AgNPs normally uses soluble silver nitrate and aqueous extracts of plants, such as *Curcuma longa* tuber,[60] leaves,[61] lemon leaves (*Citrus limon*),[62] tree leaves of *Eucalyptus citriodora* and *Ficus bengalensis*, *Xylocarpus granatum* bark, *Padina gymnospora*, tea stem wastes, honeysuckle, leaves of *Pluchea dioscoridis* (phenolic acids and flavonoids), mango leaves, neem and salep under varied concentrations of agents, and pH. The morphologies of the resulted AgNPs, including sizes and shapes, could be affected by the potential chemicals in the extracts, pH values, concentrations of silver ions in the systems, and conditions of the preparation processes, including use of ultrasound, microwave, and thermal methods.[63−67] The biological chemicals serving as effective reducing agents for silver ions are sugars, chebulinic acid, terpenes, citral, citronellal, phenolics, tannins, organic acids, alginic acids, hydroxycin-

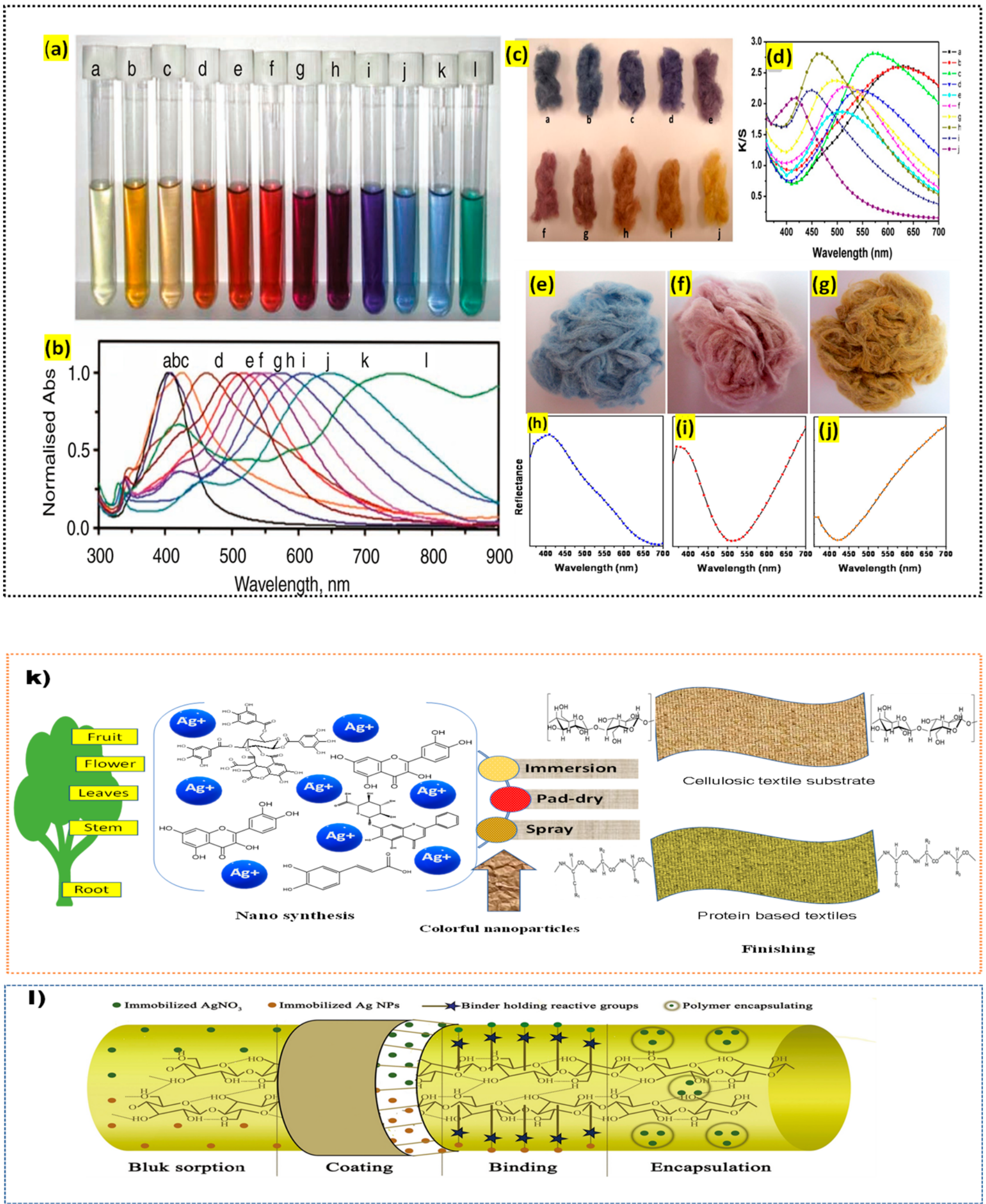

Figure 2. (a) Colorful AgNPs with different sizes and shapes and (b) UV−vis spectra of tunable rainbow colors. Reprinted with permission from ref 49. Copyright 2010, Royal Society of Chemistry. (c) Silk coloration with different colors of NPs. (d) Color strength curves of corresponding NP-dyed silk fibers. Reprinted with permission from ref 57. Copyright 2013. American Chemical Society. (e−g)Cotton fibers coloration with AgNPs. (h−j) Reflectance spectra of obtained shades. Reprinted with permission from ref 50. Copyright 2012, American Chemical Society. (k) Mechanism of *ex situ* NPs synthesis and their application for the coloration and functional finishing of textile substrates. (l) Representative example showing different modes of Ag interaction with cotton fabrics. Reprinted with permission from ref 58. Copyright 2021, Springer Nature.

namic acids, chlorogenic acid, ferulic acid, caffeic acid, and some of the structures are shown in Table 3. The common features of the compounds are that they have reducing potentials and chelating abilities to interact with silver ions and metals.[68−70]

The resulting AgNPs have been incorporated onto cotton, silk, and cotton/polyester blend fabrics by chemical finishing processes with the optional assistance of different chemicals. The resulting AgNPs have been incorporated onto cotton, silk, and cotton/polyester blend fabrics by chemical finishing processes with the optional assistance of different chemicals. Washing durability of *ex situ*-synthesized and finishing-incorporated AgNPs on textile fibers depends on interactions of AgNPs with fibers or the use of polymeric binders or cross-linking reactions.[94−96]

REACTION MECHANISMS OF *EX SITU* SYNTHESIS OF AGNP USING PLANT METABOLITES

Formation Mechanism. Formation of AgNPs from Ag^+ consists of two key steps: reduction of Ag^+ to Ag^o and nucleation and growth of Ag^o into AgNPs. The sizes and shapes of AgNPs are determined in the second step, while the reduction of Ag^+ is mainly affected by the nature and type of reducing agent and conditions in the system. Due to the complexity of natural components in the biological systems, the actual mechanisms of NP synthesis using plant extracts have not been specifically studied in detail so far. Several

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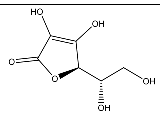
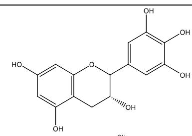
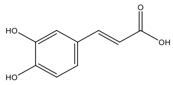
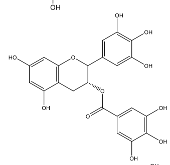
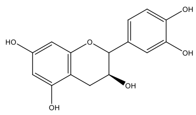
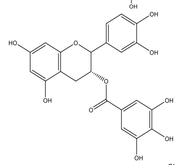
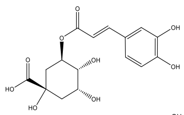
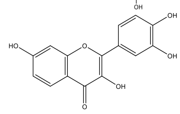
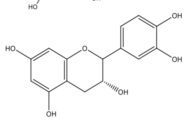
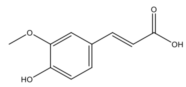
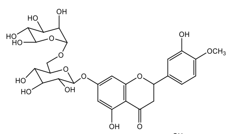
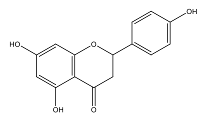
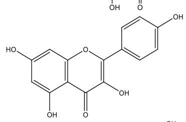
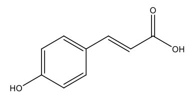
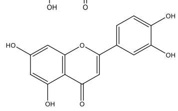
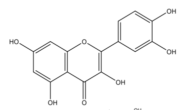
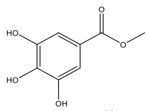
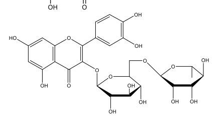
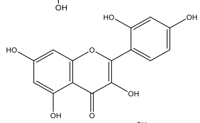
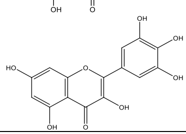
Table 3. Some Important Natural Polyphenolic Compounds Employed in Biological Synthesis of Nanoparticles onto Textiles and Their Reducing Potentials

Compound name	Structure	Reduction potential	Name	Structure	Reduction potential
Ascorbic acid		**0.19**	Epigallocatechin		**0.28**
Caffeic acid		**0.31**	Epigallocatechin gallate		**0.10**
Catechin		**0.28**	Epicatechin gallate		**0.09**
Chlorogenic acid		**0.39**	Fisetin		**0.30**
Epicatechin		**0.27**	Ferulic acid		**0.53**
Hesperidin		**0.72**	Naringenin		**0.76**
Kaempferol		**0.39**	p-coumaric acid		**0.59**
Luteolin		**0.41**	Quercetin		**0.29**
Methyl gallate		**0.56**	Rutin		**0.88**
Morin		**0.34**			
Myricetin		**0.20**			

hypotheses suggest that phenols, tannins, organic acids, flavonoids, terpenoids, vitamins, and/or saccharides are potential reducing agents to convert Ag^{1+} to Ag^{o}.[41,97] In the past few years, primary phytochemicals such as ketones, terpenoids, amides, flavones, carboxylic acids, and aldehydes with electron-rich groups (−OH, −HC═O, $-NH_2$, −SH) could donate electrons and form complex structures with Ag^+ ions.[98] The stability of formed NPs by plant-derived capping agents is another key factor affecting their shape. Most of the NPs formed by green synthesis are spherical compared to the different shapes produced by chemical stabilizing agents.[99] Analysis has proved that most of the stabilizing agents from plant extracts or biological sources have weaker interactions with the growing silver nanocrystals, leading to their isotropic growth and the formation of spherical shapes. On the other hand, chemical stabilizing agents such as cetyltrimethylammonium bromide produce anisotropy and yield different shapes.[100] The nature of the plant extract, the concentration and type of the precursor metallic salt used, and reaction parameters such as temperature, pH, and contact time have also demonstrated strong influences on the green synthesis, morphology, and characteristics of produced NPs.[101]

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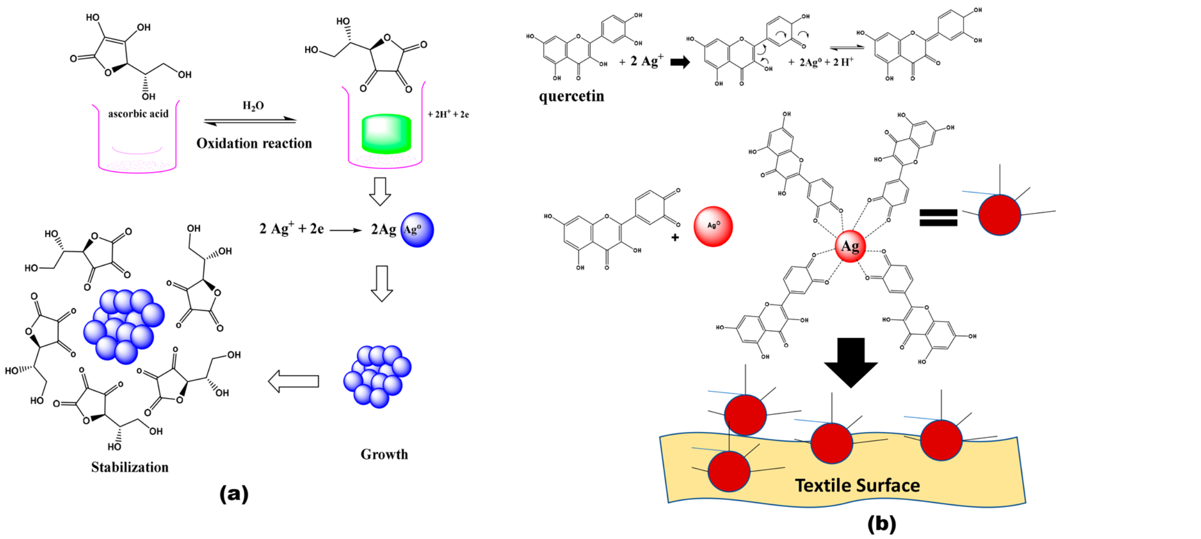

Figure 3. (a) Proposed reaction mechanism of AgNPs by ascorbic acid. Modified with permission from ref 102. Copyright 2021, Elsevier. (b) *Ex situ* formation, stabilization, and application of AgNPs onto textile surfaces produced by quercetin. Reduction mechanism data are based on Gecer et al. Modified with permission from ref 108. Copyright 2022, Taylor & Francis.

Examples of the proposed mechanisms are shown in Figure 3. Ascorbic acid isolated from *Morinda citrifolia* can chelate with silver ions and play an important role in its reduction to NPs, and subsequently, the oxidized forms of ascorbic acid were found to be responsible for capping and stabilization of Ag elements into AgNPs.[102] Amylose and amylopectin from hydrolyzed starch are also responsible for the formation of AgNPs.[103] AgNPs possess high surface energy and always undergo agglomeration during synthesis reactions.[104] The mechanical forces of ultrasound or microwave are reported to vary the sizes of AgNPs formed. Agglomeration is the main concern in NPs synthesis, and therefore, a supporting template is always necessary to produce well-defined NPs. Apart from several other natural biopolymers, the simultaneous stabilization of colloidal AgNPs is provided by most plant extracts and biomolecules. Consequently, a variety of different classes of natural compounds has recently been applied as stabilizing templates in reduction reactions of metal ions, and one such example is demonstrated by the oxidized forms of the quercetin molecule as shown in Figure 3b.[67,99] Furthermore, two natural flavonoids, quercetin, and rutin were also applied in the preparation of AgNPs on silk fabrics with the reaction mechanisms similar as proposed in Figure 3b.[105] As shown in the figure, the rutin flavonoid compound in fruit extract likewise dissipates two electrons and converts itself to a stable o-quinone structure.[106]

More importantly, the redox chemistries or reducing and stabilizing powers of natural polyphenolic and flavonoid compounds are associated with their reduction potentials, which further depend upon their structural peculiarities.[107] The reduction of metal ions by natural compounds is an electrochemical reaction, the driving power of which depends on the reduction potential of polyphenolic compounds. The arrangement of functional moieties, particularly hydroxyl groups, and conjugation in aromatic rings strongly influence their electrochemical profiles, which describe their electron or hydrogen donation abilities. The structure−activity relationship is a very important tool to choose the best natural reducing agents for the conversion of metal precursor salts into NPs.[109] However, little emphasis has been given to this area, and significant knowledge and literature gaps still exist when explaining the biological preparation of NP synthesis. Table 3 lists and summarizes the reduction potential of some commonly employed natural reducing compounds in volts which have already demonstrated success in biosynthesis and subsequent application on textiles. The lower the reduction potential value is, the better is the tendency to lose or donate electrons, implying a stronger reducing character. It is interesting to observe that many of the polyphenolic natural compounds have a reduction potential in the range of 0.2−0.8 V which is sufficient to reduce common noble metal ions, including Ag^{1+} (0.8 V), Cu^{2+} (+ 0.34 V), and Au^{3+} (1.50 V), to zerovalent forms.[109−113]

Incorporation onto Surfaces: Issues and Challenges. The application of biologically *ex situ*-produced NPs onto textile surfaces is typically done by several methods, such as pad-dry cure, spray, and immersion techniques.[114,115] Several research studies conducted in this area have shown that color and other functional properties are introduced to textiles after NP coating.[116] The incorporation of NPs includes the adsorption of NPs onto surfaces and the diffusion of the adsorbed NPs into fibers. The adsorption step could be controlled by the concentration of NPs, the pH of the system, and other components in the system. The diffusion of NPs into fibers may require elevated temperatures and the small sizes of NPs. For large NP particles, a binder may be necessary to improve the interaction of NPs with the textile surfaces and the washing fastness of the functions on the fabrics.[59,117] Such principles can be observed in these successful treatments of AgNPs on textiles, including curing the treated nonwoven fabrics at 120 °C for 5 min,[118] immersing fabrics in treatment solutions for 10 min,[119] reducing the size of AgNPs by using cationized cotton fabrics and dilution of AgNPs, or the addition of a binder (print fix binder MTBEG liquid), starch, or butyl acrylate.[114,120] The improvements in washing durability of the treated fabrics were not very impressive, especially the antimicrobial performance after 20 washing cycles.[94,116,121] Despite the prominent biological properties of AgNPs, lack of reactivity with fiber surfaces and diffusivity into

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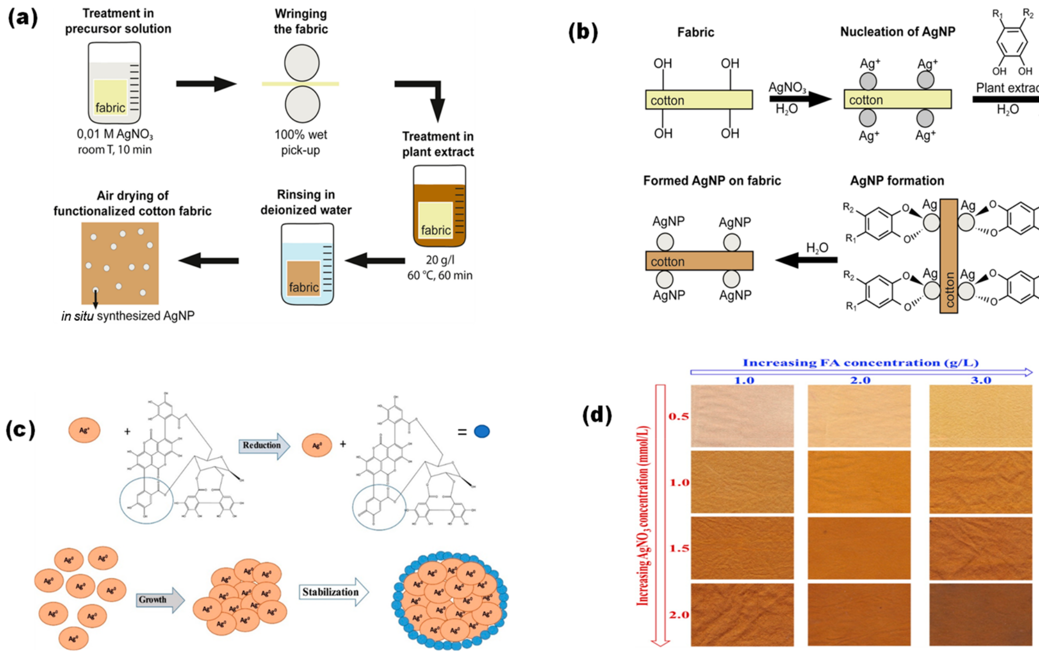

Figure 4. (a) Schematic representation of the *in situ* formation of AgNPs on cotton fibers. (b) Possible chemical reactions during AgNP development onto the cotton surface. Reproduced with permission from ref 137. Copyright 2021, Springer Nature. (c) Reduction, growth, and stabilization by tannin biomolecules from pomegranate extract. Reproduced with permission from ref 140. Copyright 2019, Elsevier. (d) Colorful hues produced on silk using ferulic acid as a bioreductant (FA). Reproduced with permission from ref 127. Copyright 2018, Elsevier.

textiles are key issues, leading to unsatisfactory washing durabilities of the claimed functionalities.[122]

Moreover, the poor binding ability of NPs causes their leaching from textile surfaces into water bodies, resulting in environmental concerns, as demonstrated by several recent studies conducted in this area.[115] To overcome these drawbacks, the use of binders or cross-linkers in the treatments has shown some potential. However, these strategies are not cost effective or easy to handle and may still involve the use of some toxic chemicals that limit their suitabilities for industrial production.[116] In this context, exploring novel and effective ways to promote stable and durable long-lasting interactions between *ex situ*-produced NPs and textile surfaces becomes a research direction in the functional modification of textiles. Fabric surfaces coated with polymers such as poly(acrylic acid) and starch, as well as cationized cellulose, have been explored.

■ *IN SITU* SYNTHESIS OF AGNPS

Examples of *In Situ* Synthesis of AgNP on Textiles. Biological *in situ* synthesis of metallic NPs on textiles has been explored as a simple and effective route to produce functional surfaces with improved durability. This is a more environmentally friendly approach, with only a one-step treatment to form NPs internally in fibers and materials.[55] This method allows facile and rapid generation and growth of metal and metal oxide NPs from corresponding precursor salts inside fibers or polymer substrates without employing binders.[123,124] NPs are formed and distributed more evenly without significant particle agglomeration on the treated textile, potentially offering improved washing durability. Thus, the *in situ* production of NPs on textiles has been receiving a great deal of attention from several research groups in recent years.

An interesting *in situ* synthesis of AgNPs on cotton was achieved by using *Seidlitzia rosmarinus* ashes, which are rich with sodium and potassium carbonates. The high alkaline condition increases the swelling of cellulose and improves the *in situ* formation of AgNPs on cotton, subsequently imparting excellent durable antibacterial activity against *Staphylococcus aureus* and *Escherichia coli*.[125] Anthraquinone derivatives and mannans in *Aloe vera* leaf extracts could reduce silver ions to Ag elements and promote the formation of AgNP in cellulose fibers.[126] A green pigment, ferulic acid, could reduce silver ions and form AgNPs in silk fabric with controlled morphology of AgNPs by changing the concentration of the precursor, ferulic acid, and pH of the solution. The AgNP formed in silk displayed strong antibacterial properties with a 99% reduction against *E. coli* and offered excellent protection against UV-A and UV-B radiations. The antibacterial properties of the fabrics were maintained even after 10 repeated washing cycles.[127] The depths and hues of the colored fabrics showed interesting patterns. Baicalin derived from *Scutellaria baicalensis* was able to *in situ* produce AgNPs on silk fabrics.[128] Caffeic acid also serves in the *in situ* synthesis of AgNPs insider silk fibers, showing an interesting golden yellow color, high durable antibacterial activity, and good fastness grades even after 10 washing cycles.[129] Extracts of *Allium cepa*, containing rich quercetin and sulfur-containing chemicals, could assist *in situ* fabrication of AgNPs in an average size of 36−98 nm in cotton with excellent antibacterial activity and good washing durability up to 50 cycles of home launderings, proving the potential and speculation of *in situ* synthesis of AgNPs in textiles.[130] Similarly, the aqueous extract from a pineapple crown top could also produce AgNPs on linen in the presence of chitosan polysaccharide.[131] Chitosan could assist the biological *in situ* formation of AgNPs on linen by using the aqueous seed extract of *Tamarindus indica* or direct reduction of silver ions and formation of AgNPs in linen samples.[132,133] Additionally, AgNPs were rapidly formed on wool fabrics with the existence of aqueous extracts of *A. tinctoria* leaves (5−30

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nm) (gall tannin, alkaloids), *T. chebula* fruits (3−5 nm), and *D. Regia* flowers (10−25 nm), respectively.[134]

Textile materials incorporated with biologically formed AgNPs may still contain certain flavonoids, anthraquinones, and other compounds from plants and microorganisms with highly conjugated aromatic systems. These compounds possess antioxidant, UV-adsorbing, and photosensitizing properties and colors, which could provide additional functions to the materials, apart from the functions of Ag or other NPs. Examples of antioxidant functions could be introduced by extracts from peanut shells[135] and skins,[136] green tea leaves, avocado seeds, pomegranate peels and Japanese knotweed rhizome, goldenrod flowers, and staghorn sumac fruit on cotton fabrics, together with antimicrobial AgNPs.[137] The antibacterial and UV protection properties of the loaded fabrics were affected by the nature of the extract from the different sources. In addition, anthocyanins in black rice aqueous extracts were responsible for the reduction and stabilization of the produced AgNPs on cotton surfaces.[138] The reduction of Ag^+ to Ag^o and formation of AgNPs were reported at pH 10 with the anthocyanin compounds present in the black rice extract.

REACTION MECHANISM OF *IN SITU* SYNTHESIS ON TEXTILE SUBSTRATES

AgNPs could form inside polymers if the metal ions and reducing agents can diffuse into the amorphous areas. Ag^+ ions and many natural phenolic compounds are water soluble and can diffuse into natural fibers.[139] The schematic setup for *in situ* preparation of AgNPs in cotton fabrics, including the mechanism of formation and shade development of the silk fabrics, is shown in Figure 4a−d. Results from the above-mentioned examples suggest that naphthoquinones, flavonoids, and polyphenolics were the main chemicals in the extracts of plants responsible for the *in situ* reduction of Ag^+ to Ag^o on natural fibers including cotton, silk, and wool.[126,129] In addition, carbohydrate polymers, such as mannans, starch, and chitosan, may also play important roles in reducing silver ions and formation of AgNPs. The chemical reactions are similar to the *ex situ* formation of AgNPs from silver ions. For example, tannin and punicalin in pomegranate ring and peel extract could provide direct reduction of silver ions and stabilization of AgNPs in fibers; the mechanism was proposed as shown in Figure 4c.[140] The coated AgNPs produced beautiful color hues with acceptable wash fastness and considerable antioxidant and antimicrobial properties, possibly due to the existence of polyphenolic compounds.[141]

In the case of the *in situ* fabrication of NPs on textiles, it is worth mentioning that the role of textile or polymer surfaces offers additional benefits and stronger interactions with the formed NPs. The polar and ionizable functional sites on textile surfaces first of all bind Ag^+ ions in water by electrostatic interactions, resulting in the formation of nucleation sites for metal ion reductions to proceed (Figure 4b).[137,142] The fabric acts as a template and aids in the inhibition of uncontrolled growth of produced NPs, thereby controlling their shapes and sizes.[143] In addition, another benefit of these textile fabrics is that sometimes, even without adding external reducing and stabilizing agents, reductions can be achieved by simply adjusting reaction conditions or the precursor salt composition. One such example is demonstrated by the reduction of silver/ammonia complex $[Ag(NH_3)_2]^+$ to AgNPs within polyamide fabrics by the functional groups of polyamide chains. The resulted fabrics demonstrated the formation of AgNPs in the size range of 20−150 nm with very good antibacterial functions and durability for 20 washing cycles.[144] Similar fabric-based reductions have been reported for cotton, but in all cases, $AgNO_3$ was first converted to Tollen's reagent.[145] Several researchers have demonstrated that if fabrics are left in the precursor $AgNO_3$ salt aqueous solutions for a few days, the NPs formation cannot take place and further emphasized that the introduction of additional −OH and −COOH groups from plant extracts are necessary to promote the *in situ* bioreductions.[142,146] More importantly, bigger AgNPs formed during *in situ* synthesis are entrapped inside fabrics and held by forces generated by the phytochemical layer over NPs, while smaller AgNPs could penetrate deep into fibers due to osmotic pressure and are more tightly held by the double layer of biomolecules. The *in situ* entrapping of AgNPs into polymer chains using biological agents has also been reported to reduce the cytotoxic effects of loaded fabrics.[147] In general, the *in situ* method is a promising technology to synthesize AgNPs on textile and clothing surfaces via green reducing agents without using harsh reaction conditions. As discussed above, the *in situ* method allows one-step preparation and deposition of NPs on textile substrates without using external stabilizing agents.[148] It is therefore an effective way of producing facile, spherical, smaller-sized NPs having higher surface areas, more stability, more durability on textiles, and hence lower environmental impact in comparison to the *ex situ* routes.

BIOGENIC SYNTHESIS OF NPS ON TEXTILE SURFACES

In contrast to the use of plant extracts in the production of noble AgNPs, biogenic synthesis uses microorganisms to produce NPs. Microorganisms such as fungi offer several advantages including having large surface areas and secretion of higher amounts of secondary metabolites.[149] Biogenic synthesis of NPs exploiting fungi is studied under myco-nanotechnology, and there is less information available on their use for NP synthesis on textiles. It is worth mentioning that fungal isolates are renewable sources of secondary metabolites, including proteins and enzymes having the ability to effectively chelate metal ions, donate electrons, and reduce them to nanoparticle form.[150,151] The literature shows that several fungi, particularly genus *Fusarium*-based species, have been preferred recently as biogenic routes to produce a variety of NPs with different morphologies.[23,152] Fungi are now becoming important reservoirs with the potential to fabricate NPs both intracellularly and extracellularly.[153] Many scientific efforts are underway to discover the mechanism of NPs formation under different microbial environments. It is widely accepted that cell wall proteins and enzymes, namely, α-NADPH-dependent nitrate reductase or hydrogenase secreted by *Fusarium* fungi, are mainly responsible for nanotransformation.[149,154] Apart from this, naphthoquinones and anthraquinones have been reported to act as electron shuttles to carry electrons generated by the reduction of nitrates to metal ions.[155] The produced NPs are stabilized by various fungal secretory components including nitrogenous biomacromolecules, peptides, and proteins.[149] Studies conducted on biogenic formation of AgNPs using *Lactobacillus fermentum* biomass have revealed that they could generate AgNPs with more robust antibacterial activity than chemically produced NPs. Likewise, *Fusarium oxysporum* fungi could generate AgNPs

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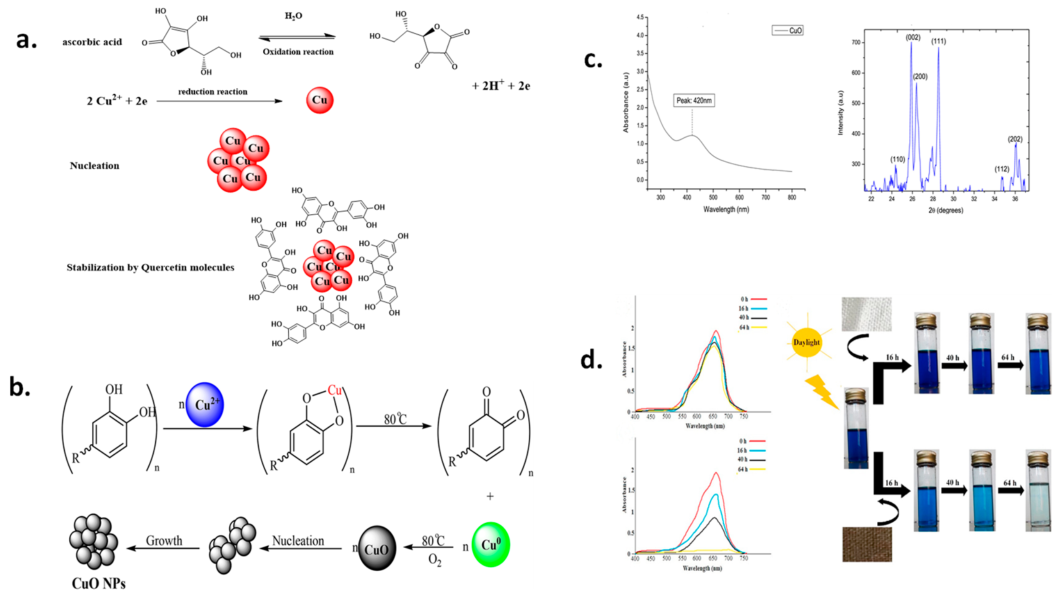

Figure 5. Proposed formation and stabilization reaction mechanism of Cu and CuO NPs by (a) Ascorbic acid and quercetin from RAFE or GJLE. Modified with permission from ref 32. Copyright 2022, Elsevier and (b) Flavonoid compounds. Reproduced with permission ref 170. Copyright 2021, Springer Nature. (c) UV−vis and XRD profile of CuO NPs formed by plant extract. Reproduced with permission from ref 171. Copyright 2022, American Chemical Society. (d) Photocatalytic dye discoloration by cotton-coated CuO NPs. Reproduced with permission from ref 181. Copyright 2018, Elsevier.

extracellularly in cotton cloth with demonstrated antimicrobial functions.[156,157]

Proteins present in these fungal isolates were reported to be responsible for the reduction of silver nitrate salt and stabilization of the generated NPs via cysteine residues and electrostatic interactions through carboxyl groups. The laundering durability of the antimicrobial functions of the biogenically treated cotton samples could survive more than 10 washing cycles.[158] Many fungi species have been employed in biogenic *in situ* and *ex situ* syntheses of AgNPs on textiles. Five different endophytic fungal strains were employed as possible reducing and stabilizing agents in both *in situ* and *ex situ* production of AgNPs on textiles.[159] Spherical and other shaped AgNPs with a mean size ranging from 5 to 30 nm were produced in *ex situ* processes, and incorporation of the AgNPs to cotton surface portrayed encouraging antimicrobial results against *S. aureus*, *E. coli*, *C. albicans*, and *A. niger* with good washing durability. Additional examples of biogenic syntheses of AgNPs include uses of *Streptomyces antimycotics* L-1192,[160] *Fusarium solani*,[161] *Aspergillus terreus* (Bios PTK 6)194,[162] *Aspergillus terrerus* MTCC632195,[163] *B. ochroleuca*,[164] *Streptomyces laurentii* (endophytic actinomycetes strain),[120] and *Alternaria alternata* in the *in situ* and *ex situ* formations of NPs in textiles.[116] The biogenically formed AgNPs are generally smaller in size than the biologically synthesized ones. Biomass filtrate of fungi *Alternaria alternata*-produced AgNPs on cotton samples in the system with encouraging protection results against soil microflora after 14 days of burring in moist soil, also confirmed by SEM results.

COPPER AND COPPER OXIDE NANOPARTICLES ON TEXTILE SURFACES

Copper nanoparticles (Cu NPs), due to their catalytic, optical, electrical, and antimicrobial applications, are widely used in different industrial applications such as photocatalysis magnetic recording media or microelectronics.[165,166] The Cu and CuO NPs have been *in situ* or *ex situ* fabricated and applied onto textile materials recently using several plant extract-derived biomolecules such as polyols, flavonoid, and terpenoids.[167] The reduction potential of Cu^{2+} to Cu is 0.34 V, which is lower than that of silver ions (0.8 V), indicating that Cu ions are relatively more difficult to reduce by many of the biological chemicals listed in Table 3. The phytochemicals from plants or microorganisms act as reducing agents of copper ions and stabilizing agents of Cu NPs and when applied onto textiles, which may then be oxidized to CuO NPs by air oxidation (Figure 5a, b).[32,168] The Cu NPs synthesis by ascorbic acid (reduction potential = 0.19 V) followed by the stabilizing powers of biomolecules isolated from *Rosa andeli* petals (RAFE) and *Gardenia jasminoides* leaves (GJLE) extracts are shown in Figure 5a.[32] Polyphenolic compounds, such as epigallocatechin gallate (0.153 V) and extract derived from *Stachys lavandulifolia* flower, have low reduction potentials that are capable of reducing copper ions to Cu, followed by oxidation to form CuO NPs.[169,170] The UV−vis peak at 420 nm and crystalline XRD pattens of typical CuO produced by seed extract of *B. monnieri* are displayed in Figure 5c.[171]

Cu NPs produced by *ex situ* and *in situ* synthetic routes for deposition on fabrics by using alkaloid and steroid-based compounds from plant extracts can be applied on fabrics to provide color, antibacterial, sensing, color discoloration, hydrophobic, or other important functions.[172] *Ex situ*-formed CuO NPs have been applied onto fabrics by using a printing process to increase the washing durability of the NPs and the antibacterial functions. For example, phenolic compounds present in *Cynomorium coccineum* extract and flavonoids and ascorbic acid from *Carica papaya* (saponins) extract have effectively produced CuO NPs from Cu^{2+}ions on cotton fabrics.[173,174] Due to the advantages including economic benefits, less time, and a one-step process, the *in situ* synthetic route represents a promising alternative and is more preferred by researchers. CuO NPs were formed and deposited via an *in*

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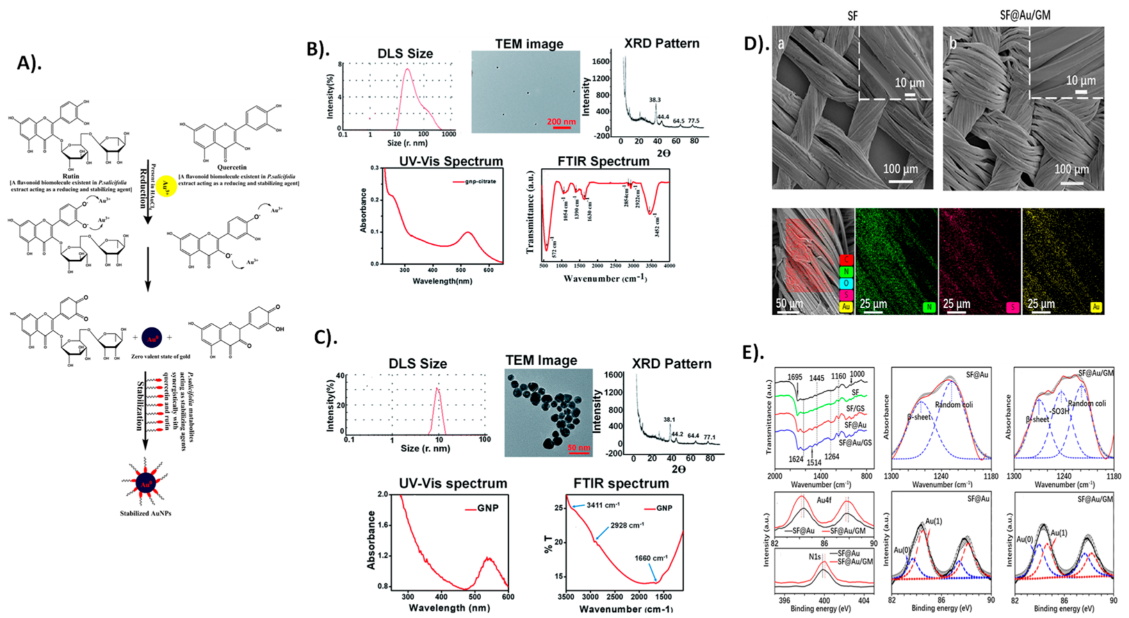

Figure 6. (A) Proposed mechanism for the reduction process and stabilization of AuNPs by *P. salicifolia* aqueous extract. Reproduced with permission from ref 191. Copyright 2021, Elsevier. (B, C) Formation and morphological characterizations of AuNPs synthesized by conventional citrate vs plant extract mediated. Reproduced with permission from ref 190. Copyright 2021, Royal Society of Chemistry. (D) SEM and EDX images showing uniform distributions of AuNPs produced using silk fibroin. (E) FT-IR and deconvolution spectra depicting chemical changes before and after silk fibrin fabric-generated AuNPs. Reproduced with permission from ref 192. Copyright 2019, Elsevier Ltd.

situ approach on or within cotton fibers through the help of a *Keliab* solution (a plant extract rich in potassium and sodium carbonate) which supplies hydroxyl ions and prepares cellulose chains as a source of the nucleation site for the reduction of copper precursor salt. The deposited Cu^{2+} ions on cellulose chains are further converted to copper hydroxide [$Cu\ (OH)_2$] due to the presence of OH groups and later transformed into CuO NPs upon heating. The fabrics deposited with these CuO NPs displayed multifunctional effects including self-cleaning and durable antibacterial properties and could be applied in colorimetric detection of inorganic and organic acids.[175]

In situ production of cupric oxide NPs (CuO NPs) on wool fibers was also accomplished using ashes from burned leaves and stems of the *Seidlitzia rosmarinus* plant, which provides an alkaline pH condition to aid in the formation of CuO NPs upon heating in fibers. CuO NPs could result in beautiful colored shades ranging from light to dark brown, with good to excellent washing fastness properties, excellent UV protection, and antibacterial results.[176] As predicted, the fabrics treated with CuO NPs were endowed with antibacterial properties (copper ion-induced toxicity) against *E. coli* and *S. aureus*.[177,178] Similarly, *Seidlitzia rosmarinus* ashes have produced cauliflower-shaped multifunctional CuO NPs on polyester fabrics.[179] Recently, CuNPs were *in situ* formed onto polyester fibers that were previously adsorbed with fatty acids with the help of ascorbic acid under alkaline conditions, and the fabrics showed both antimicrobial and hydrophobic functions. The preparation of nucleation sites on polyester/fatty acid was initiated by alkaline conditions provided by *Seidlitzia rosmarinus* ashes. It was reported that the presence of fatty acids on the polyester surface considerably reduced the CuNPs toxicity by increasing their colloidal stability.[180] Cotton fabrics containing green *in situ*-fabricated CuO NPs have also demonstrated the potential to be used as photocatalysts for the discoloration of methylene blue under solar light irradiation. The UV−vis peaks monitored at 663 nm showed a decrease in peak absorptions within 64 h of exposure time. It was shown that almost 97.41% of methylene blue is degraded after 64 h (Figure 5d).[181]

A biogenic formation of CuO NPs on cotton fabrics was reported by employing protein and enzyme secretions from the fungus *Aspergillus terreus* AF-1202. Depending on the use of various biological chemicals and methods, the produced CuO NPs were in varied shapes and sizes, with durable antibacterial functions and varied colors.[182]

GOLD NPS ON TEXTILE SURFACES (AUNPS)

Because of their promising optical, electronic, magnetic, and catalytic properties, gold nanoparticles (AuNPs) have recently emerged as attractive candidates for different application fields.[183] Gold NPs in the form of rods, sheets, and wires could be produced by biologically reducing Au^{3+} ions to Au°.[184] Like other metals, Au ions (Au^{1+} and Au^{3+}) have reduction potentials of 1.69 and 1.40 V, respectively, which can be reduced by all the biological agents shown in Table 3. Literature reveals that several polyphenolic and flavonoid chemicals, including caffeine, ferulic, catechin, quercetin, kaempferol, and gallic acid, have served as good reductants to Au ions with additional stabilizing powers.[103,185] It is interesting to note that phenolic compounds containing O—H groups chelate with Au ions together with binding abilities, reducing Au^{3+} to Au° atoms and themselves getting oxidized into relatively stable quinone methide forms.[186,187] The resultant Au atoms nucleate with other atoms followed by their growth and transformation into AuNPs, which are then stabilized and capped by oxidized products formed during the synthesis reaction. Figure 6A depicts the formation, growth, and capping of AuNPs using rutin and quercetin compounds isolated from plants.[188,189] The AuNPs produced by green *M. oleifera* extract have shown better properties than the ones produced by using the conventional citrate method, and their

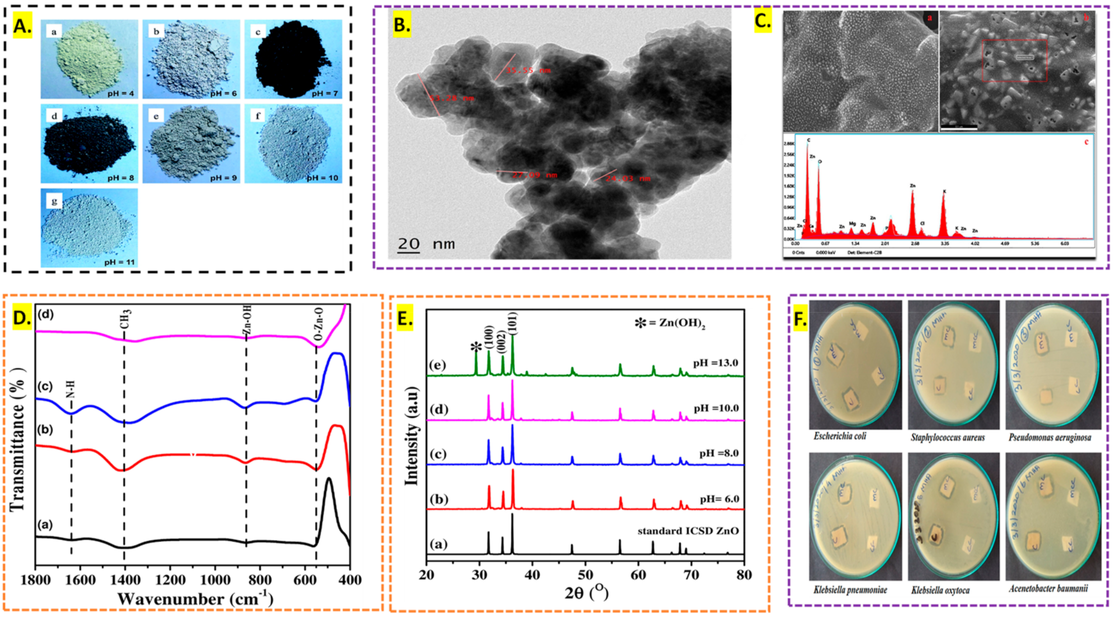

Figure 7. (A) Photographs of ZnO NP powders synthesized by orange peel extract biomolecules at different pH values (a−g). Reproduced with permission from ref 202. Copyright 2020, Royal Society of Chemistry. (B) TEM images of zinc oxide nanoparticles showing spherical morphology using *Pleurotus floridanus.* Reprinted with permission from ref 203. Copyright 2021, Elsevier. (C) SEM images (a, b) and SEM-EDX (c) spectrum of *Thymbra spicata* extract-mediated ZnONPs. Reproduced with permission from ref 217. Copyright 2022, Elsevier. (D) FTIR spectrum (a−d) and (E) XRD peaks originating from biosynthesis of ZnO at different pH values (a−e). Reproduced with permission from ref 218. Copyright 2022, Wiley-VCH GmbH. (F) Antibacterial activity showing zone of inhibition of biologically fabricated ZnO-treated cotton. Reproduced with permission from ref 219. Copyright 2021, Elsevier.

characterizations such as TEM, DLS, SEM, and FT-IR are depicted in Figure 6B and C. Both the methods have produced AuNPs with similar morphologies.[190]

Recently, AuNPs have been incorporated into different textile materials by using *in situ* or *ex situ* processes, including cotton, viscose, silk, and leather. The researchers used a variety of natural chemicals and processes to promote the reduction of Au^{3+} to the Au° element and the subsequent formation of AuNPs.[193−195] Also, it is interesting to mention that *in situ* green-fabricated AuNPs on silk fibroin (SF) could reduce the antibiotic gentamicin sulfate (GM) dosage for wound dressings. The SEM and FT-IR spectra confirm the formation AuNPs (Figure 6D, E). The SEM image reveals uniformly coated AuNPs on the fibers, and FT-IR and deconvolution peaks (Figure 6E) showed that no substantial chemical modification of fabric occurred after conservation of Au precursor salt into AuNPs.[192]

Bacterial isolates of *Streptomyces sp*. may aid in the biogenic formation of AuNPs from gold salt on plasma-modified cotton and viscose knitted fabrics.[196] Biogenic *in situ* synthesis of AuNPs on cotton, silk, and leather could be achieved by using extracts from *Ginkgo biloba* L. leaf powder (ginkgolides).[197] Overall, *in situ* formation of AuNPs can be easily achieved by using various biological chemicals or without using extra chemicals on cellulose due to the high reduction potential of Au ions. The *in situ*-generated AuNPs could impart color and also provide antibacterial activity with beautiful shades and acceptable washing and rubbing fastness properties.

■ ZINC/TITANIUM OXIDE AND OTHER NPS

Zinc and titanium ions have very low reduction potentials and exist in the forms of ZnO and TiO_2 NPs, which are photosensitizers and can provide photoinduced self-cleaning, UV-blocking, and antibacterial properties on various surfaces, including textiles.[198−200] A diverse class of plant biomolecules such as polyphenols, phytosterols, or saponins were reported to bind with zinc salts forming chelation complexes with zinc(II) ions from which zinc hydroxides are formed that are further calcinated to ZnO NPs.[201] The ZnO NPs produced by plant materials show different colors under different pH values, and their morphologies vary depending on several conditions including the nature of the extract (Figure 7A−E).[202,203] ZnO NPs, in particular, due to their excellent photosensitizing activity and UV-blocking properties, have been attached onto textile surfaces by employing different *ex situ* and *in situ* approaches and have been employed in producing protective, comfortable, and advanced textiles.[204,205] The photoantibacterial activity against different bacterial cultures by cotton fabrics coated with ZnO NPs formed in *A. calamus* extract is shown in Figure 7F.[206]

Ex situ preparations of ZnO NPs have been achieved by using biomolecules from aqueous extracts of *Nephelium lappaceum*, *Acalypha indica leaf* (phlorotannins), and *Phoenix dactylifera* seeds.[207−209] Subsequent coating and finishing procedures on cotton fabrics have incorporated these NPs onto the surfaces of the fibers. In addition to *ex situ* procedures, ZnO NPs can be formed on textile surfaces using more advantageous *in situ* procedures, which have shown better interactions between the particles and fiber surfaces and can enter into the inside of fibers resulting in improved washing and wearing durability.[210] Polyphenols, flavonoids, and other biomolecules that can improve the solubility of Zn^{2+} and stabilize ZnO should be able to show their efficacy in the *in situ* formation of ZnO on textiles. Several plant extracts such as aqueous peel extracts of pomegranate fruit and *Azadirachta indica* leaf have been successfully used to produce ZnO NPs on cotton surfaces.[179,211,212] A study showed that hexagonal ZnO NPs can be developed on cotton surfaces using an *in situ*

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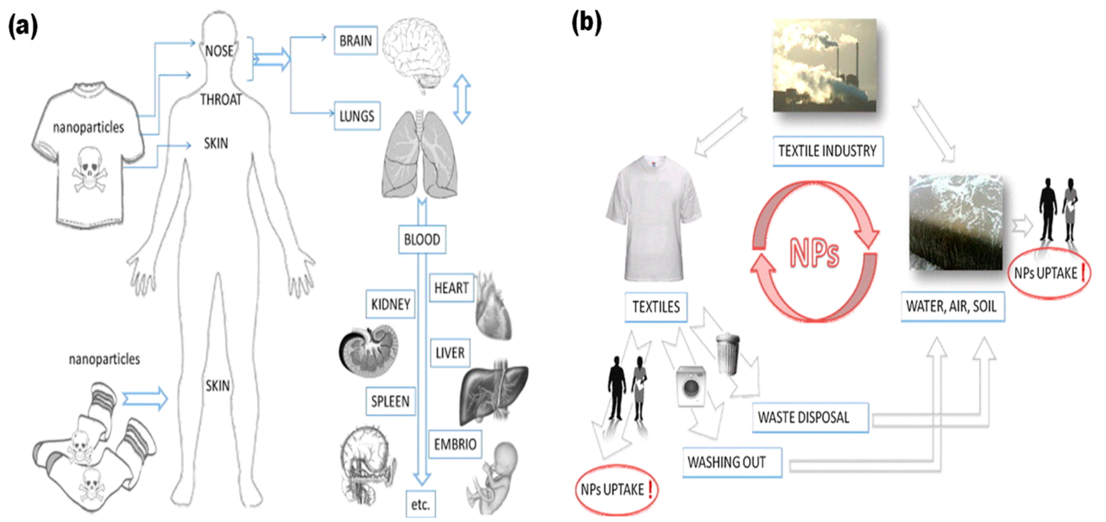

Figure 8. (a) Transport of NPs into the human body through different routes. (b) Release of NPs from textiles and their encounter with the human body. Reproduced with permission from ref 239. Copyright 2011, Elsevier.

synthesis process in a NaOH/urea solution of $ZnCl_2$.[213] When the impregnated fabric was placed in a steamer, $Zn(OH)_2$ produced on the cotton surfaces became dehydrated into ZnO NPs. A similar entrapment of Zn ions and formation of ZnO NPs on polyester and cotton fibers were achieved by using natural materials of corn silk/starch[214,215] and *Tragacanth gum*.[216] Lately, cotton oxidation by periodate followed by treatment with a 4-aminobenzoic acid ligand also has been shown to provide excellent nucleation sites for the growth of ZnO. These textiles have demonstrated multifunctional finishing properties.[52]

In recent years, biogenic formation of ZnO NPs was reported through extracellular and intracellular routes, involving reductive enzymes toward ZnO synthesis.[220] Extracellular route production of ZnO NPs offers advantage of easy recovery, becoming a common pathway.[153] In fact, proteins and amino acids in fungal isolates may assist formations and fixation of ZnO NPs on surfaces of textiles.[210,218,221]

Many other metal oxide nanoparticles have been prepared by *in situ* and *ex situ* ways on textiles, including TiO_2, FeO, and Fe_2O_3 NPs, due to the similar mechanisms of formation of ZnO NPs on surfaces of textiles.[222,223] These metal oxide NPs on the textile are not illustrated in this perspective.

■ ISSUES OF METAL NPS ON FUNCTIONAL TEXTILES

Textiles and fabrics are integral parts of human life, and nowadays, with the availability of nanotechnologies, they are being investigated intensively and transforming as there is growing consumer demand for high-tech advanced textile functions.[224] In this context, as discussed above, the biologically formed metals and their oxide NPs have delivered excellent results in comparison to those produced with conventional chemical formulations, which has stimulated research activities for upgrading chemical technologies and nanotechnology-based textiles.[225,226] Numerous NPs with photonic and electronic properties have been recently integrated into textiles for applications such as sensing, drug release, and other biomedical functions, making wearable technology one of the fastest developing areas in textile and materials science research.[11,227] However, despite these recent advances, it is important to understand that NPs compared to larger particles might pose higher human health and environmental risks because of their several physical, chemical, and biological attributes. Metal and metal oxide NPs on textiles could be released during wearing and washing cycles, and the amounts of NPs from certain textiles have been summarized by Yetisen et al.[228] NPs could enter human bodies through various routes as shown in Figure 8a and b, and released NPs from textiles may be able to use all three routes.[229−231] Metal and metal oxide NPs may lead to different mechanisms of toxicity to humans. For example, AgNPs can serve as a representative of NPs with lower toxicity concerns compared to other NPs, which could induce oxidative stress, DNA damage, and cytokine induction.[232] Results from *in vivo* studies have shown that exposure to AgNPs can result in effects in different major organs.[233] The sinks of nanotextiles are sewage sludge, wastewater, air, and soil, which contribute to environmental concerns.

Apart from other modes of release from textiles such as abrasion, physical degradation, or during their dumping in landfill sites, the major contributor toward their release is washing.[234] An adequate concentration of AgNPs has been found leached to sweat and distilled water from blankets and commercial socks containing Ag, respectively.[235,236] Although it is claimed that the leaching depends upon AgNPs concentrations and pH, the release process of NPs is certainly dependent on laundering behavior. Also, more recent cradle-to-grave life cycle assessments of functional t-shits and household textiles containing AgNPs indicate that the manufacturing and washing stages are two main hotspots and major contributors toward environmental degradation.[237,238]

Accordingly, some of the results from these life cycle assessments could expand our understanding of the pros and cons of green chemistry in synthesis of NPs and *in situ* formation with more durable NPs in materials. In addition, LCA studies recommend that reducing the silver content in textiles could subsequently reduce the associated toxicity of NPs.[234] Moreover, prevention of the release of NPs from textiles is a key that can reduce risks of the entrance of the NPs into human bodies. Therefore, *in situ* formed NPs on textile

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fibers may provide additional benefits versus the *ex situ*-formed and -incorporated NPS. While biologically produced NPs are mostly associated with natural polyphenolic compounds, which have inherent antimicrobial and other functional attributes, limited information on the functional attributes and no life cycle analysis data are available on such nanocoated textiles.[240] Additional and active research efforts are required to fill this knowledge gap, to explore the full potential of biological agents, and to ensure their impact on the environment and human health during different stages of practical biological production and applications of the NP-functionalized textiles.

■ CONCLUSIONS AND FUTURE OUTLOOK

The development of advanced nanotechnology-based textiles with antimicrobial activity, antioxidant activity, and UV protection has sparked interest in the sustainable preparation and application of metal and metal oxide NPs. As discussed, natural products with a huge diversity hold great promise to provide unlimited secondary metabolites with reducing and stabilizing power to generate nanoparticles by these *in situ* and *ex situ* processes. This perspective summarizes metal ions and promising components in natural products, as well as metal ion and metal element stabilization abilities of typical systems, which could represent principles for selecting different natural products in the development of eco-friendly multifunctional textiles. Even though the correlation between structures, the substitution of functional groups, and their influences on the redox chemistries of natural polyphenols have been studied in the literature, the in-depth analysis, particularly on the thermodynamics, kinetics, and electrochemical behaviors of these compounds for nanosynthesis, is still to be explored.

In general, secondary metabolites from natural products serve as the main reducing or binding agents to stabilize formed NPs and could also produce synergistic functional finishing effects after application. Nevertheless, the green chemistry methods for NP synthesis in the existing literature are largely limited to silver, which is only one of the candidates widely used in the textile and polymer functional industries, mostly due to its antimicrobial properties. Other important nanomaterials such as Cu, Zn, and AuNPs are excellent choices for creating novel and additional functional attributes on surfaces, and their synthetic protocols and fabrications onto textiles or polymer matrixes may aid in the development of textiles for smart and artificial intelligence applications. Even though natural product-mediated synthesis offers several benefits, the research on their use in textile and polymer modifications is still in its infancy, especially in scale-up and commercial production of NP-embedded textiles. In addition, cost-effective and life cycle assessments of the biological productions of NPs on textiles are still yet to be addressed. Apart from this, more intense research efforts should be directed toward elucidating the mechanisms of NP formation by using various extracts from plants and microorganisms and the factors influencing their growth and stability on textile and polymer surfaces, which will provide a means of achieving controlled synthesis and tailoring their well-defined properties. Complicated procedures and less control over natural resources are restricting the broad applications of many research results. Therefore, theoretical models and experimental verification by using representative phytochemicals of terpenoids, phenolic compounds, carbohydrates, and flavonoids from natural resources, as well as collaborations with environmental scientists, could break the barriers to the biological synthesis of NPs in commercial applications. In comparison to *ex situ* methods, *in situ* NP formation on textiles provides the advantages of one-step, facile, fast, and straightforward methods in textile finishing.

On the other hand, the recent use of fungal isolates in the so-called biogenic synthesis of NPs may bring in active enzymes and proteins as potential active components in the process. The extracellular synthesis of NPs for textile finishing holds great promise since fungal synthesis offers several advantages, such as large surface area, fewer steps to produce a large quantity of NPs, more production of secondary metabolites, lower costs involved in the production, and an easy to scale up technology. However, only a limited number of reports are available in this field, and thus, more new development in this area could appear in the future.

Nowadays, NPs in textile applications as novel colorants and finishing agents are highly influenced by surface area and surface plasmon resonance characteristics, which can be altered using different metal combinations and tuned by changing their compositions. We hope this perspective will provide researchers with the most recent progress in this area. Also, with a deep understanding of NP formation, we anticipate some novel NP structures with core−shell and multicomponent features showing up on textiles and polymers in the near future.

■ AUTHOR INFORMATION

Corresponding Author

Gang Sun − *Department of Biological and Agricultural Engineering, University of California, Davis, California 95616, United States;* orcid.org/0000-0002-6608-9971; Phone: +1 530 752 0840; Email: gysun@ucdavis.edu

Author

Shahid ul Islam − *Department of Biological and Agricultural Engineering, University of California, Davis, California 95616, United States;* orcid.org/0000-0001-9198-7530

Complete contact information is available at: https://pubs.acs.org/10.1021/acssuschemeng.2c03033

Notes

The authors declare no competing financial interest.

Biographies

Dr. Shahid ul Islam is a Fulbright Fellow at the University of California, Davis, USA. He is also a fellow of the International Society for Development and Sustainability (ISDS), Japan. He is currently working on the interface of materials science and textile technology, with a main emphasis on design and development of novel advanced light-activated antibacterial and antiviral materials, films, and nanofibrous membranes for biological protection and food coating applications.

Dr. Gang Sun is a professor in Biological and Agricultural Engineering at the University of California, Davis, USA, and has been conducting research on functional textiles, textile chemistry, and nanotechnologies since 1995.

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