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(54) Title: COTTON RECYCLING

(57) Abstract: Cellulose materials and methods of making the cellulose materials are described herein. The method can include contacting a cotton fabric with an oxidizing system to obtain an oxidized cotton material and processing the oxidized cotton material to form the cellulose material. The oxidizing system can include an aqueous mixture of a *N*-oxyl compound and a hypochlorite compound. During oxidation, the pH of the aqueous mixture can be maintained at from 8.5 to 11. Cellulose products can be formed from the cellulose materials. For example, the cellulose products can be used to form a packaging material, a biomedical device or implant, a drug delivery material, a fiber, a textile material, a template for electronic components, or a separation membrane. Methods of making the cellulose product include dissolving or suspending an active ingredient in a medium comprising the cellulose material.

COTTON RECYCLING

FIELD OF THE DISCLOSURE

This disclosure relates generally to recycling cotton fibers, more particularly, to recycling cotton fabrics to provide functional cellulose materials.

BACKGROUND OF THE DISCLOSURE

Barrier properties of materials are important in reducing the penetration of moisture, oxygen, grease, aromas and, in some cases, bacteria. For example, exclusion of oxygen and moisture from packaged foods retards product spoilage. In certain applications, such as packaging of detergents, cleaners, fertilizers and the like, it is important that the packaging material prevents the odors from spreading outside. In other applications, such as juices, wines, pretzels and biscuits it is sought to protect the contents against acquisition of undesirable flavors from the outside. Therefore, film structures which provide a barrier to oxygen, flavor/odor, grease/oil and moisture are highly desirable food packaging materials.

There is an ongoing trend to coat paper products with metalized films such as aluminum to provide moisture vapor and oxygen barrier protection. However, while these films provide good barrier properties, they limit the recyclability of the paper product. Development of low-carbon-footprint high barrier film materials in place of foil is increasingly needed.

To address this need, polymer-based film products such as ethylene vinyl alcohol, poly(vinyl) alcohol, and nylon prepared from m-xylene diamine are being used in today's food packaging market. These polymers possess high oxygen barrier properties but they have poor moisture barrier properties. In view of the foregoing limitations of known barrier films, there remains a need for barrier compositions which exhibit sufficient barrier properties in reducing the penetration of moisture and oxygen. The compositions and methods disclosed herein address these and other needs.

SUMMARY

Cellulose materials and methods of preparing the cellulose materials are disclosed herein. The cellulose material can be derived from a cotton fiber such as a cotton fabric, including post-consumer waste cotton fabrics. The method of preparing the cellulose material can include contacting the cotton fiber or fabric with an oxidizing system to obtain an oxidized cotton

material. The cotton fabric may be decolored, mechanically shredded, milled, or a combination thereof, prior to contacting it with the oxidizing system.

Any suitable oxidizing system can be used for oxidizing the cotton fiber. In some examples, the oxidizing system can include an *N*-oxyl compound. Exemplary *N*-oxyl compounds include 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO), 4-hydroxy-2,2,6,6-tetramethylpiperidine-1-oxyl (4-hydroxy TEMPO), a 4-hydroxy TEMPO derivative obtained by etherification or esterification of a hydroxyl group of 4-hydroxy TEMPO, a phthalimide-*N*-oxyl (PINO) radical, an aza-adamantane type nitroxy radical, or a mixture thereof. The oxidizing system can further include a secondary oxidant, such as a hypochlorite compound. In some embodiments, the oxidizing system can include an aqueous mixture of the *N*-oxyl compound and a hypochlorite compound. During oxidation of the cotton fiber, the pH of the aqueous mixture can be maintained at from 8.5 to 11, such as at pH 10.

The method of preparing the cellulose materials can include processing the oxidized cotton material to form the cellulose material. Processing the oxidized cotton material can include filtering, neutralizing, evaporating, distilling, rinsing, casting, extruding, spinning, or a combination thereof.

Cellulose products can be formed from the cellulose materials described herein. For example, an active ingredient can be incorporated into the cellulose material to confer a suitable property to the cellulose material. In some examples, the cellulose product can be a packaging material, a biomedical device or implant, a drug delivery material, a fiber, a textile material, a template for electronic components, or a separation membrane. Methods of preparing the cellulose product can include dissolving or suspending an active ingredient in the cellulose material to form the cellulose product. The active ingredient can be selected from an inorganic nanoparticle, a therapeutic agent, and a combination thereof. The active ingredient can be present in an amount of from 0.01% to 20% by weight, based on the weight of the cellulose product.

In some examples, the cellulose product can be a food packaging material. The food packaging material can include the cellulose material and a nanoparticle active ingredient. In some cases, the nanoparticle active ingredient can exhibit moisture barrier properties, oxidation barrier properties, or a combination thereof. Examples of suitable nanoparticle active ingredient can include a silicon oxide nanoparticle, a silver nanoparticle, a cerium oxide nanoparticle, a zinc oxide nanoparticle, a poly(vinyl) alcohol nanoparticle, or a combination thereof. The food

packaging material can have a moisture vapor transmission rate (MVTR) of 1.0 g/m^2 per 24 hours when measured at 38°C and 90RH%. Additionally, the food packaging material coated with the cellulose product can have an oxygen transmission rate (OTR) of 10 cm^3/m^2 per 24 hours when measured at 23°C, 0% RH, and 1 atm.

In some examples, the cellulose product can be a textile material. The textile material can include the cellulose material and nanoparticles that can impart a functionality selected from insulating finishing, electrical conductivity, hydrophobic finishing, waterproof finishing, soil repellent finishing, fire resistance finishing, wrinkle free finishing, anti-UV finishing, antimicrobial finishing, antistatic finishing, coloration, reflective finishing, sunblock finishing, fragrance finishing, fabric softening finishing, anti-oxidant finishing, or combinations thereof. Examples of suitable nanoparticles for use in the textile material can include nanoparticles as described herein, such as a silicon oxide nanoparticle, a silver nanoparticle, a cerium oxide nanoparticle, a zinc oxide nanoparticle, a poly(vinyl) alcohol nanoparticle, or a combination thereof.

Cellulose articles can be prepared from the cellulose materials described herein. Methods for recovering a cellulose article from the cellulose material can include casting, extruding, or spinning the cellulose material to form the cellulose article.

DETAILED DESCRIPTION

Provided herein are compositions and articles comprising cellulose materials. The compositions and articles comprising the cellulose materials can also include an active ingredient. Methods of making and using the compositions and articles are also described herein.

The compositions, articles, and methods described herein can be understood more readily by reference to the following detailed description of specific aspects of the disclosed subject matter and the Example included therein. However, before the present compositions and methods are disclosed and described, it is to be understood that the aspects described below are not limited to specific synthetic methods or specific reagents, as such may, of course, vary. It is also to be understood that the terminology used herein is for the purpose of describing particular aspects only and is not intended to be limiting.

General Definitions

In this specification and in the claims that follow, reference will be made to a number of terms, which shall be defined to have the following meanings:

The term "fabric" as used herein refers to a web having a structure of individual fibers or threads which are interlaid by weaving (woven), knitting, braiding, or in an irregular, non-repetitive manner (non-woven). A nonwoven fabric or web can be formed from for example, melt-blowing processes, spun-bonding processes, and bonded carded web processes.

Throughout this specification the word "comprise" and other forms of the word, such as "comprising" and "comprises," means including but not limited to, and is not intended to exclude, for example, other additives, components, integers, or steps. The term "include" and other forms of "include" has the same meaning as "comprise" and its other forms.

The singular forms "a," "an," and "the" include plural referents unless the context clearly dictates otherwise. Thus, for example, reference to "a composition" includes mixtures of two or more such compositions and reference to "the compound" includes mixtures of two or more such compounds, and the like.

"Optional" or "optionally" means that the subsequently described event or circumstance can or cannot occur, and that the description includes instances where the event or circumstance occurs and instances where it does not.

A weight percent (wt%) of a component, unless specifically stated to the contrary, is based on the total weight of the formulation or composition in which the component is included.

Reference will now be made in detail to specific aspects of the disclosed materials, compounds, compositions, articles, and methods, examples of which are illustrated in the accompanying Example.

Compositions

Provided herein are compositions and articles comprising cellulose materials. The cellulose materials can be derived from a natural cotton fiber or a cotton fabric. Cotton fabrics are known in the art and can include denim, terry, corduroy, flannel, canvas, and twill. In some cases, the cotton fabric can be derived from a pre-consumer or post-consumer cotton waste such as jeans or towels. Pre-consumer jeans manufacturing clippings or rags are available from the "jeans industry," the jeans comprising long cotton fibers, the length of which are in the range of 20 to 50 mm and the fineness of which are in the range of 10 to 20 μm.

The cellulose material can be formed into cellulose products. The cellulose products can include the cellulose material and an active ingredient that confers a suitable property to the

cellulose product. For example, the cellulose product can include an active ingredient selected from an inorganic nanoparticle, a therapeutic agent, or a combination thereof. In some embodiments, the cellulose product can be a packaging material, a biomedical device or implant, a drug delivery material, a fiber, a textile material, a template for electronic components, or a separation membrane.

The active ingredient can be present in the cellulose product in an amount of 0.01% or greater by weight of the cellulose product. For example, the cellulose product can comprise 0.1% or greater, 0.1% or greater, 0.1% or greater, 0.2% or greater, 0.5% or greater, 1% or greater, 1.5% or greater, 2% or greater, 3% or greater, 4% or greater, 5% or greater, 6% or greater, 7% or greater, 8% or greater, 9% or greater, 10% or greater, 12% or greater, 15% or greater, 20% or greater, or 25% or greater of the active ingredient, based on the weight of the cellulose product. In some examples, the cellulose product can comprise 25% or less, 20% or less, 15% or less, 12% or less, 10% or less, 9% or less, 8% or less, 7% or less, 6% or less, 5% or less, 4% or less, 3% or less, 2.5% or less, 2% or less, 1.5% or less, 1% or less, 0.5% or less by weight active ingredient, based on the weight of the cellulose product. The amount of active ingredient in the cellulose product can range from any of the minimum values described above to any of the maximum values described above. For example, the amount of active ingredient in the cellulose product can range from 0.01% to 25%, 0.01% to 20%, 0.01% to 15%, 0.01% to 10%, 0.01% to 5%, 0.5% to 10%, 0.5% to 5%, 0.5% to 2.5%, 1% to 10%, or 1% to 5% by weight, based on the weight of the cellulose product.

Suitable examples of active ingredients useful in the cellulose products disclosed herein include an insulating material, an electrically conductive material (such as an antistatic material), a hydrophobic material, a fire retardant or suppressant, a water repellent material, a soil repellent material, a reflective material (such as a metallic reflector), a magnetic material, a thermochromic material, a bioactive agent (such as an anti-microbial agent, anti-fungal agent, or an insect repellent), a sunblock agent, a dye, a pigment, a fragrance, an insect repellent, a fabric softener, an anti-wrinkle material, a UV-protective material, an oxidation resistant material, or a combination thereof.

In some embodiments, the active ingredient can include a nanoparticle. The term "nanoparticle" as used herein, refers to any structure with one or more nanosized features. A nanosized feature can be any feature with at least one dimension less than 1 μm in size. The nanoparticle can have any of a wide variety of shapes including for example, spheroidal and

elongated nanostructures. Thus, the term nanoparticle includes nanowires, nanotubes, spheroidal nanoparticles, and the like, or combinations thereof. The nanoparticles used herein can have an average diameter of 900 nanometers (nm) or less. In some embodiments, the average diameter of the nanoparticle can be 800 nm or less, 700 nm or less, 600 nm or less, 500 nm or less, 450 nm or less, 400 nm or less, 350 nm or less, 300 nm or less, 250 nm or less, 200 nm or less, 150 nm or less, 100 nm or less, or 50 nm or less. In some embodiments, the average diameter of the nanoparticle can be 5 nm or greater, 50 nm or greater, 100 nm or greater, 150 nm or greater, 200 nm or greater, 250 nm or greater, 300 nm or greater, 350 nm or greater, 400 nm or greater, 450 nm or greater, 500 nm or greater, 600 nm or greater, 700 nm or greater, 800 nm or greater, or 900 nm or greater. The average diameter of the nanoparticle can range from any of the minimum values described above to any of the maximum values described above. For example, the average diameter of the nanoparticle can range from 5 nm to 700 nm, from 5 nm to 500 nm, from 50 nm to 500 nm, or from 50 nm to 250 nm.

Examples of suitable nanoparticles for use in the cellulose product can include aluminum, iron, silver, cerium, zinc, gold, copper, cobalt, nickel, platinum, manganese, rhodium, ruthenium, palladium, titanium, vanadium, chromium, molybdenum, cadmium, mercury, calcium, zirconium, iridium, silicon, an oxide thereof, zeolite, graphite, carbon nanotubes, or a combination thereof. Specific examples can include silicon oxide nanoparticles, silver nanoparticles, cerium oxide nanoparticles, zinc oxide nanoparticles, polyvinyl alcohol nanoparticles, or combinations thereof. The nanoparticles described herein can be encapsulated within the cellulose material, dispersed throughout the cellulose material, or form a layer/coating on the cellulose material.

In some embodiments, the cellulose product can be a food packing material. In these embodiments, a nanoparticle that can exhibit moisture barrier properties, oxygen barrier properties, or a combination thereof, can be included in the cellulose material. In some examples, the cellulose product can be a textile material. The textile material can include any one of the active ingredients described herein.

Methods

Methods of making the cellulose materials and compositions containing the cellulose materials are also described herein. As described herein, the cellulose material may be derived from a cotton fiber or cotton fabr10046ic. The method can include cutting, mechanically

shredding, and/or milling the cotton fabric to provided finely divided cotton fabrics. Any suitable device can be used to cut, shred, and/or mill the cotton fabric.

The method of making the cellulose material can include contacting the cotton fabric with an oxidizing system to obtain an oxidized cotton material. The oxidizing system can include an *N*-oxyl compound. Suitable *N*-oxyl compounds include 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO), 4-hydroxy-2,2,6,6-tetramethylpiperidine-1-oxyl (4-hydroxy TEMPO), a 4-hydroxy TEMPO derivative obtained by etherification or esterification of a hydroxyl group of 4-hydroxy TEMPO, a phthalimide-*N*-oxyl (PINO) radical, an aza-adamantane type nitroxy radical, or a mixture thereof. Other suitable *N*-oxyl compounds include 4-oxo-2,2,6,6-tetramethyl-1-piperidinyloxy (4-oxo-TEMPO), 4-amino-2,2,6,6-tetramethylpiperidine-1-oxyl (4-amino-TEMPO), 4-acetamido-2,2,6,6-tetramethylpiperidine-1-oxyl (4-acetamido-TEMPO), 4-benzyloxy-2,2,6,6-tetramethylpiperidine-1-oxyl (4-benzyloxy-TEMPO), and 4-acetoxy -2,2,6,6-tetramethylpiperidine-1-oxyl (4-acetoxy-TEMPO), 4-phosphonooxy-TEMPO, *N*-hydroxybenzotriazole, or a mixture thereof.

The N-oxyl compound in the oxidizing system can be present in an amount of at least 0.1 mmol per gram of the cotton fabric. In some embodiments, the N-oxyl compound can be present in an amount of 0.15 mmol or greater or 0.2 mmol or greater per gram of the cotton fabric. In some embodiments, the N-oxyl compound can be present in an amount of 0.25 mmol or less, 0.2 mmol or less, or 0.15 mmol or less per gram of the cotton fabric. In some embodiments, the N-oxyl compound can be present in an amount of from 0.1 mmol to 0.25 mmol or from 0.15 mmol to 0.20 mmol per gram of the cotton fabric. In some embodiments, the N-oxyl compound can be present in a catalytic amount for oxidation of the cotton fabric.

The oxidizing system can include a secondary oxidant. Suitable secondary oxidants can include a hypochlorite compound such as sodium hypochlorite or tert-butyl hypochlorite, sodium chlorite, (diacetoxyiodo)benzene, meta-chloroperoxybenzoic acid, calcium chlorite, sodium bromite, chlorine, bromine, trichloroisocyanuric acid, or a combination thereof.

The secondary oxidant, such as sodium hypochlorite can be present in an amount of at least 3 mmol per gram of the cotton fabric. In some embodiments, the secondary oxidant can be present in an amount of 4 mmol or greater, 5 mmol or greater, 6 mmol or greater, 7 mmol or greater, 8 mmol or greater, 9 mmol or greater, 10 mmol or greater, 15 mmol or greater, or 20 mmol or greater per gram of the cotton fabric. In some embodiments, the secondary oxidant can be present in an amount of 25 mmol or less, 20 mmol or less, 15 mmol or less, 10 mmol or less,

9 mmol or less, 8 mmol or less, 7 mmol or less, 6 mmol or less, 5 mmol or less, or 4 mmol or less per gram of the cotton fabric. In some embodiments, the secondary oxidant can be present in an amount of from 3 mmol to 25 mmol or from 5 mmol to 15 mmol per gram of the cotton fabric.

In some embodiments, the oxidizing system can include an aqueous mixture of the *N*-oxyl compound and the secondary oxidant. For example, the oxidizing system can include an aqueous mixture of 4-hydroxy TEMPO, sodium hypochlorite, and sodium bromide.

The cotton fabric can be present in an amount of 50% or less by weight of the aqueous mixture. For example, the cotton fabric can be present in an amount of 35% by less, 25% by less, 10% by less, 5% by less, 3% by less, or 2% by less by weight of the aqueous mixture.

Oxidation of the cotton fabric can be controlled by maintaining the pH of the aqueous mixture from 8.5 to 11. In some cases, the pH of the aqueous mixture can be maintained at 10. Any suitable compound can be used to adjust the pH of the aqueous mixture. In some embodiments, the pH can be adjusted using a base such as sodium hydroxide. Oxidation of the cotton fabric can also be controlled by heating the mixture comprising the cotton fabric and the oxidizing system.

In some cases, the method can include decoloring the cotton fabric prior to contacting the fabric with the oxidizing system. For example, where the cotton fabric is a post-consumer waste, such as a jeans, the method can include decoloring the cotton fabric prior to oxidation. In some embodiments, the method does not include decoloring the cotton fabric prior to contacting the fabric with the oxidizing system. In these embodiments, the cotton fabric can be decolored during oxidization of the cotton fabric.

Decoloring the cotton fabric can include contacting the cotton fabric with an oxidizing or reducing agent. Suitable oxidizing agents for decoloring the cotton fabric can include hypochlorite (for e.g. sodium hypochlorite), peroxide (such as hydrogen peroxide or benzoyl peroxide), sodium chlorite, potassium permanganate, or ozone. Suitable reducing agents for decoloring the cotton fabric can include sulfur dioxide, thiourea dioxide, sodium hydrosulfite, sodium hydroxymethanesulfinate, zinc formaldehyde sulfoxylate, calcium formaldehyde sulfoxylate, sodium sulfite, sodium bisulfite, and tin (II) chloride.

The oxidized cotton material can be processed to form the cellulose materials described herein. Processing the oxidized cotton material can include filtering (for example to separate insoluble cotton fabric), neutralizing, evaporating, distilling, rinsing/washing, casting, extruding,

spinning, or a combination thereof, the mixture comprising the oxidized cotton material. In some embodiments, processing the oxidized cotton material can include neutralizing the aqueous mixture to a pH of about 7. For example, the method can include rinsing the oxidized cotton material with a solvent, such as water until the filtrate solution is neutral.

As described herein, the cellulose material can be used to form a cellulose product. The method of forming the cellulose product can include dispersing, such as by homogenizing the cellulose material into a medium comprising a solvent. The solvent can include be any suitable solvent such as water, an alcohol, or an ionic liquid. Optionally, the medium can be filtered to remove insoluble fractions of cellulose material. The method can further include dissolving and/or suspending one or more active ingredients in the medium comprising the cellulose material. The mixture of the cellulose material and active ingredient can be homogenized to form a viscous mixture. The homogenized mixture can be casted into a film by pouring into a container and drying at low temperature for example about 40°C. In some embodiments, the cellulose product can be obtained from extruding, spinning, or a combination thereof. For example, a cellulose product can be prepared from a spinning process such as a gap/dry-wet spinning process or by a wet-wet spinning process.

As described herein, the cellulose product can be a food packing material. The food packaging material can exhibit moisture barrier and oxygen barrier properties. The liquid-water and water-vapor resistance of the food packaging material comprising the cellulose material can be tested with the Cobb method, described by TAPPI T 441 (2001), which is incorporated by reference herein in its entirety. This method determines the amount of liquid water or moisture vapor absorbed by the cellulose material in a specified time under standardized conditions. In some embodiments, the food packaging product comprising the cellulose material described herein would pass the water resistance test set forth in this test method.

In some embodiments, the food packaging material comprising the cellulose material can exhibit a Cobb value of 0.01 g/m^2 to 25 g/m^2 (e.g., 25 g/m^2 or less, 20 g/m^2 or less, 15 g/m^2 or less, 10 g/m^2 or less, or 5 g/m^2 or less). In some embodiments, the food packaging material can exhibit a moisture vapor transmission rate (MVTR) of 1 g/m^2 or less per 24 hours when measured at 38°C and 90RH%. For example, the food packaging material can exhibit a moisture vapor transmission rate of 0.5 g/m^2 or less or 0.3 g/m^2 or less. In some embodiments, the food packaging material comprising the cellulose material can exhibit an oxygen transmission rate (OTR) of 10 cm^3/m^2 or less per 24 hours when measured at 23°C, 0RH%, and 1 atm. For

example, the food packaging material can exhibit an oxygen transmission rate of 8 cm^3/m^2 or less, 6 cm^3/m^2 or less, 5 cm^3/m^2 or less, 4 cm^3/m^2 or less, 3 cm^3/m^2 or less, 2 cm^3/m^2 or less, or 1 cm^3/m^2 or less per 24 hours when measured at 23°C, 0RH%, and 1 atm. The moisture vapor transmission rate (MVTR) can be determined as described in ASTM E398, ASTM F1249 or TAPPI T448-M49. In some examples, the moisture vapor transmission rate (MVTR) can be determined as described in ASTM E398. The oxygen transmission rate (OTR) can be determined as described in ASTM D3985 or ASTM F1927. In some examples, the oxygen transmission rate (OTR) can be determined as described in ASTM D3985.

In some examples, the cellulose product can be a textile material. The textile material can include an active ingredient such that it can exhibit an insulating property, an electrically conductive property (such as an antistatic property), a hydrophobic property, a fire retardant or suppressant property, a water repellent property, a soil repellent property, a reflective property, a magnetic property, a thermochromic property, a bioactive property, a sunblock property, a fragrance, an insect repellent property, a fabric softening property, an anti-wrinkle property, a UV-protective property, an oxidation resistant property, or a combination thereof. In some examples, the textile material can be thermally insulating. The basis weight of the textile material can be 20 g/m^2 or greater. For example, the basis weight of the textile material can be 25 g/m^2 or greater, 30 g/m^2 or greater, 35 g/m^2 or greater, 40 g/m^2 or greater, 45 g/m^2 or greater, 50 g/m^2 or greater, 55 g/m^2 or greater, 60 g/m^2 or greater, 65 g/m^2 or greater, 70 g/m^2 or greater, 80 g/m^2 or greater, 90 g/m^2 or greater, 100 g/m^2 or greater, 110 g/m^2 or greater, 140 g/m^2 or greater, 150 g/m^2 or greater, 170 g/m^2 or greater, 180 g/m^2 or greater, 190 g/m^2 or greater, or 200 g/m^2 or greater. In some examples, the basis weight of the textile material can be 200 g/m^2 or less. For example, the basis weight of the fabric can be 190 g/m^2 or less, 180 g/m^2 or less, 160 g/m^2 or less, 150 g/m^2 or less, 130 g/m^2 or less, 110 g/m^2 or less, 100 g/m^2 or less, 90 g/m^2 or less, 80 g/m^2 or less, 70 g/m^2 or less, 65 g/m^2 or less, 60 g/m^2 or less, 55 g/m^2 or less, 50 g/m^2 or less, 45 g/m^2 or less, 40 g/m^2 or less, 35 g/m^2 or less, 30 g/m^2 or less, or 25 g/m^2 or less. The basis weight of the textile material can range from any of the minimum values described above to any of the maximum values described above. For example, the basis weight of the textile material can range from 25 g/m^2 to 200 g/m^2, from 50 g/m^2 to 200 g/m^2, or from 50 g/m^2 to 170 g/m^2. The textile material can be made into textiles including jackets, coats, skirts, pants, suits, slacks, vests, gloves, and the like. The fabrics can also be made into use in non-apparel applications such as furniture and carpets.

EXAMPLES

Example 1: Preparation of recycled cotton nanofiber film

A piece of towel fabric (0.5 g) was cut, ground, and suspended in a solution system containing water (25mL), 4-hydroxyl-TEMPO (0.008 g, 0.04 mmol), and sodium bromide (0.05 g, 0.5 mmol). TEMPO-mediated oxidation of the fabric slurry was started by adding 5% NaClO solution (10 mmol of NaClO per gram of cellulose) dropwise with gentle agitation at room temperature. The oxidation was controlled by maintaining the pH value at 10 by adding 0.5 M NaOH. When no more decrease in pH was observed, the reaction was taken as finished. The NaClO-oxidized cellulose (NOC) was thoroughly washed with distill water until the filtrate solution was neutral.

To make cellulose nanofibers, 0.2 g NOC was dispersed in 200 mL water (0.1 wt% of NOC concentrations) at room temperature and mechanically agitated for 10 minutes using a planetary mixer at a low rotation rate. The insoluble fractions were removed from the dispersion by filtration. The cellulose dispersion was homogenized for 3 h in the mixer with a high rotation rate to produce a viscous NOC nanofiber suspension, by adding 1 wt% SiO_2 nanoparticle. A NOC nanofiber film was formed by a casting method. The nano-dispersion was poured into a 4 x 4 inch plastic dish for drying for 24 h at 40°C.

It will be apparent to those skilled in the art that various modifications and variations can be made in the present disclosure without departing from the scope or spirit of the invention. Other embodiments of the disclosure will be apparent to those skilled in the art from consideration of the specification and practice of the methods disclosed herein. It is intended that the specification and examples be considered as exemplary only, with a true scope and spirit of the invention being indicated by the following claims.

What is claimed is:

1. A cellulose material prepared by a process comprising:
   a. contacting a cotton fabric with an oxidizing system to obtain an oxidized cotton material; and
   b. processing the oxidized cotton material to form the cellulose material.

2. The cellulose material of claim 1, wherein the cotton fabric is derived from a post-consumer cotton waste.

3. The cellulose material of claim 1 or 2, wherein the oxidizing system comprises an *N*-oxyl compound.

4. The cellulose material of claim 3, wherein the *N*-oxyl compound is selected from 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO), 4-hydroxy-2,2,6,6-tetramethylpiperidine-1-oxyl (4-hydroxy TEMPO), a 4-hydroxy TEMPO derivative obtained by etherification or esterification of a hydroxyl group of 4-hydroxy TEMPO, a phthalimide-*N*-oxyl (PINO) radical, an aza-adamantane type nitroxy radical, or a mixture thereof.

5. The cellulose material of claim 3 or 4, wherein the oxidizing system comprises an aqueous mixture of the *N*-oxyl compound and a hypochlorite compound.

6. The cellulose material of any one of claims 1-5, wherein processing the oxidized cotton material comprises filtering, neutralizing, evaporating, distilling, rinsing, casting, extruding, spinning, or a combination thereof.

7. A cellulose product prepared from the cellulose material according to any one of claims 1-6.

8. The cellulose product of claim 7, further comprising an active ingredient.

9. The cellulose product of claim 8, wherein the active ingredient is selected from an inorganic nanoparticle, a therapeutic agent, and a combination thereof.

10. The cellulose product of claim 8 or 9, wherein the active ingredient includes a nanoparticle having moisture barrier properties, oxidation barrier properties, or a combination thereof.

11. The cellulose product of any one of claims 8-10, wherein the active ingredient includes a silicon oxide nanoparticle, a silver nanoparticle, a cerium oxide nanoparticle, a zinc oxide nanoparticle a polyvinyl alcohol nanoparticle, or a combination thereof.

12. The cellulose product of any one of claims 8-11, wherein the active ingredient is present in an amount of from 0.01% to 20% by weight, based on the weight of the cellulose product.

13. The cellulose product of any one of claims 7-12, wherein the cellulose product is a packaging material, a biomedical device or implant, a drug delivery material, a fiber, a textile material, a template for electronic components, or a separation membrane.

14. The cellulose product of claim 13, wherein the cellulose product is a food packaging material.

15. The cellulose product of claim 13, wherein the cellulose product is a textile material.

16. The cellulose product of claim 15, wherein the textile material comprises nanoparticles dispersed throughout the textile that impart a functionality selected from insulating finishing, electrical conductivity, hydrophobic finishing, waterproof finishing, soil repellent finishing, fire resistance finishing, wrinkle free finishing,

anti-UV finishing, antimicrobial finishing, antistatic finishing, coloration, reflective finishing, sunblock finishing, fragrance finishing, fabric softening finishing, anti-oxidant finishing, or combinations thereof.

17. A method of making a cellulose material from a cotton fabric, the method comprising:
    a. contacting the cotton fabric with an oxidizing system to obtain an oxidized cotton material, and
    b. processing the oxidized cotton material to form the cellulose material.

18. The method of claim 17, wherein the cotton fabric is derived from a post-consumer cotton waste.

19. The method of claim 17 or 18, wherein the cotton fabric is mechanically shredded, milled, or a combination thereof, prior to the step of contacting the cotton fabric with an oxidizing system.

20. The method of any one of claims 17-19, wherein the oxidizing system comprises an *N*-oxyl compound.

21. The method of claim 20, wherein the *N*-oxyl compound is selected from 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO), 4-hydroxy-2,2,6,6-tetramethylpiperidine-1-oxyl (4-hydroxy TEMPO), a 4-hydroxy TEMPO derivative obtained by etherification or esterification of a hydroxyl group of 4-hydroxy TEMPO, a phthalimide-*N*-oxyl (PINO) radical, an aza-adamantane type nitroxy radical, or a mixture thereof.

22. The method of claim 20 or 21, wherein the oxidizing system comprises an aqueous mixture of the *N*-oxyl compound and a hypochlorite compound.

23. The method of claim 22, wherein the pH of the aqueous mixture is maintained at from 8.5 to 11.

24. The method of any one of claims 17-23, further comprising decoloring the cotton fabric prior to the step of contacting the cotton fiber with an oxidizing system.

25. The method of any one of claims 17-24, wherein processing the oxidized cotton material comprises filtering, neutralizing, evaporating, distilling, rinsing, casting, extruding, spinning, or a combination thereof.

26. The method of any one of claims 17-25, wherein the method further comprises dissolving or suspending an active ingredient in the cellulose material.

27. The method of 26, wherein the active ingredient is selected from an inorganic nanoparticle, a therapeutic agent, and a combination thereof.

28. The method of claim 27, wherein the active ingredient comprises nanoparticles that impart a functionality selected from insulating finishing, electrical conductivity, hydrophobic finishing, waterproof finishing, gas barrier, soil repellent finishing, fire resistance finishing, wrinkle free finishing, anti-UV finishing, antimicrobial finishing, antistatic finishing, coloration, reflective finishing, sunblock finishing, fragrance finishing, fabric softening finishing, anti-oxidant finishing, or combinations thereof.

29. The method of any one of claims 26-28, wherein the active ingredient includes a silicon oxide nanoparticle, a silver nanoparticle, a cerium oxide nanoparticle, a zinc oxide nanoparticle a polyvinyl alcohol nanoparticle, or a combination thereof.

30. The method of any one of claims 26-29, wherein the active ingredient includes a silicon oxide nanoparticle.

31. The method of any one of claims 26-30, wherein the active ingredient is present in an amount of from 0.01% to 20% by weight, based on the weight of the cellulose product.

32. A method of making a cellulose product from a cotton fiber, the method comprising:
    a. contacting the cotton fiber with an oxidizing system to obtain an oxidized cotton material;
    b. recovering a cellulose material from the oxidized cotton material; and
    c. dissolving or suspending an active ingredient in the cellulose material to form the cellulose product.

33. The method of claim 32, wherein the cotton fiber is derived from a post-consumer cotton waste.

34. The method of claim 32 or 33, wherein the method further comprises step (e) casting, extruding, or spinning the cellulose product.

35. A cellulose article prepared according to a method of any one of claims 32-34.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 17/36695

A. CLASSIFICATION OF SUBJECT MATTER
IPC(8) - D21H 11/20, A61L 15/28, D21H 27/00 (2017.01)
CPC - D21H 27/007, D21H 11/20, A61L 2300/80, A61L 15/28, D21H 5/141, D21H 13/04

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
See Search History Document

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
See Search History Document

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
See Search History Document

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X -- Y	WO 2015/077807 A1 (LENZING AG) 04 June 2015 (04.06.2015), pg 1 ln 13-15, pg 7 ln 16, pg 7 ln 22-23, pg 8 ln 6-15, pg 8 ln 20-27, pg 15 ln 4-20.	1-2, 17-19 --- 3(2), 4, 32-34
X -- Y	US 9,296,829 B2 (ISOGAI et al) 29 March 2016 (29.03.2016), col 2 ln 3-5, col 12 ln 28-45, col 13 ln 58-67, col 15 ln 56-62.	1, 3(1) --- 3(2), 4
X	CN 101,307,563 B (SUZHOU UNIVERSITY) 15 September 2010 (15.09.2010) pg 5 para 10 - pg 6 para 2.	32
Y	US 7,709,089 B2 (FUSHITANI et al) 04 May 2010 (04.05.2010), col 2 ln 22, col 6 ln 53-58, col 7 ln 29-30.	32-34
X,P	US 2016/0369456 A1 (EVRNU), 22 December 2016 (22.12.2016), entire document	1-2, 17-19

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
07 August 2017	06 SEP 2017
Name and mailing address of the ISA/US Mail Stop PCT, Attn: ISA/US, Commissioner for Patents P.O. Box 1450, Alexandria, Virginia 22313-1450 Facsimile No. 571-273-8300	Authorized officer: Lee W. Young PCT Helpdesk: 571-272-4300 PCT OSP: 571-272-7774

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 17/36695

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☒ Claims Nos.: 5-16, 20-31, 35
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.

☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.

☐ No protest accompanied the payment of additional search fees.