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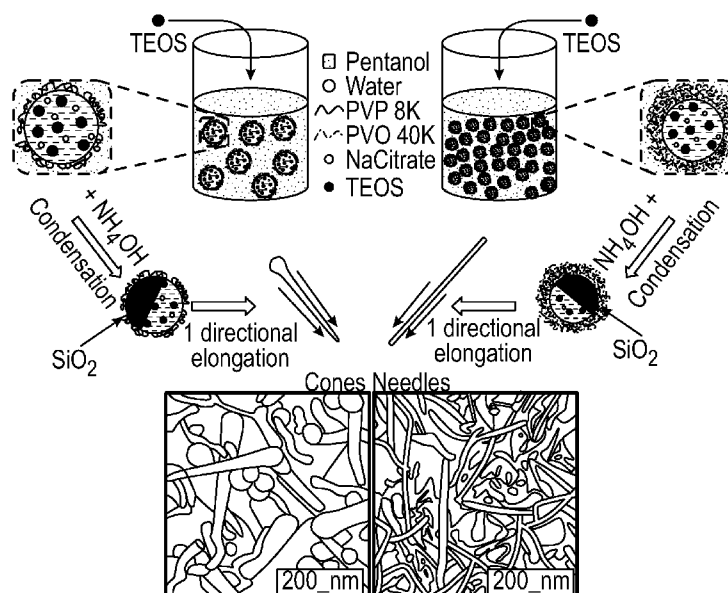


FIG. 1

(57) Abstract: Disclosed is a process for preparing a cellulosic fiber composition having a superhydrophobic surface involving: (a) synthesizing anisotropic particles of different shapes and covalently attaching them to a non-superhydrophobic cellulosic fiber, thereby yielding an intermediate cellulosic fiber composition having an altered surface; and (b) grafting long chain hydrocarbon lipids onto the altered surface of the intermediate cellulosic fiber composition, thereby lowering surface energy of the intermediate cellulosic fiber composition to yield a cellulosic fiber composition having a superhydrophobic surface. Cellulosic fiber compositions made from this process and products containing the cellulosic fiber compositions are also disclosed.



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CELLULOSIC FIBER COMPOSITIONS HAVING SUPERHYDROPHOBIC SURFACES AND GREEN PROCESSES FOR THEIR PRODUCTION

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application claims priority benefit of U.S. Provisional Patent Application Serial No. 62/846,570, filed May 10, 2019, the disclosure of which is hereby incorporated by reference herein in its entirety.

FIELD OF THE DISCLOSURE

[0002] The present invention generally provides, *inter alia*, environment-friendly superhydrophobic cellulosic fiber compositions, products made from the superhydrophobic cellulosic fiber compositions, and processes for their production.

BACKGROUND OF THE DISCLOSURE

[0003] Cotton fibers are made-up of cellulose, the most abundantly used natural polymer on earth. With worldwide efforts to curb the use of non-biodegradable petroleum-based products and replacing them with fully sustainable natural products, both government and industry have put increased emphasis on promoting the use of cellulosic products. As a result, the use of cellulose in the form of fabrics, non-woven mats, paper, micro- and nano-fibrillated cellulose, nano-crystalline cellulose, bacterial cellulose, etc., has been on the rise [1]. Apart from the conventional uses as apparel, footwear, bags, upholstery, automotive materials, food packaging, and filters, cellulose can now be found in many novel applications such as hydrogels, oil-water separation membranes, microfluidic devices and composite materials [2]. Some of the characteristics of products made using cellulose are light weight, flexible, portable and sustainable [3-12]. However, as a result of the enormous amount of hydroxyl groups present in cellulose the products made with it become hydrophilic. They absorb moisture causing them to swell and lose strength, a very undesirable characteristic in many applications. With significant increase in the use of cellulose over the past decade, engineering of superhydrophobic cellulosic surfaces has gained significant attention in the industrial arena as water-repellency can increase potential applications and durability of the cellulosic materials [13-16].

[0004] Superhydrophobic surfaces which exhibit water contact angles (WCAs) greater than 150° is a natural phenomenon found in many plant leaves, the most prominent example

being the lotus leaf, and some insects such as the water strider legs [17]. Decades of study of such naturally occurring surfaces have revealed that micro- and nano-scaled hierarchical structures along with the presence of low surface energy compounds make these surfaces inherently superhydrophobic [17]. Numerous strategies for mimicking nature's superhydrophobic surfaces on cotton fibers/fabrics have been put forward which are based on the principle of creating surface roughness using inorganic particles such as SiO₂, ZnO, TiO₂, Ag, Au, CeO₂, CuO, followed by chemical treatments to create hydrophobic surfaces using low surface energy fluorinated compounds such as Perfluorooctanoic acid (PFOA), fluoroalkylsilane and other fluorochemicals [14, 18-23]. Electrochemical deposition, layer-by-layer assembly, chemical vapor deposition, etching, templated nanopatterning, plasma, lithography and other such techniques have been used for creating superhydrophobic fabrics [16, 19].

[0005] Most of the techniques mentioned above do need expensive instrumentation or hazardous solvents such as tetrahydrofuran and N,N-dimethylformamide [24]. In recent years the use of fluorinated polymers has been restricted due to their bio-accumulative potential and toxicity to both humans and the environment [24, 25]. A major challenge in using inorganic particles in practical applications is their poor bonding to the fabrics. As most of them are physically deposited and use hydrogen bonding or ionic interactions as the primary mechanisms to stay on the fabric, these particles can easily leach out from the fabrics during washing or during use giving rise to significant environmental concerns. All these issues have hampered the scaling up of such techniques to create superhydrophobic cotton fabrics for commercial applications. At the same time, these issues have also generated calls for developing greener processes to obtain superhydrophobic cotton fabrics.

[0006] The present disclosure is directed to overcoming these and other deficiencies in the art.

SUMMARY

[0007] The present disclosure relates to, *inter alia*, environment-friendly processes based on 'green' chemistry principles to render durable superhydrophobicity (water repellency) to cellulosic fiber compositions and products and materials containing the cellulosic fiber compositions.

[0008] In one aspect, the present disclosure relates to a process for preparing a cellulosic fiber composition having a superhydrophobic surface. This process includes the steps of: (a) synthesizing anisotropic particles of different shapes and covalently attaching them to a non-superhydrophobic cellulosic fiber, thereby yielding an intermediate cellulosic fiber composition having an altered surface; and (b) grafting long chain hydrocarbon lipids onto the altered surface of the intermediate cellulosic fiber composition, thereby lowering surface energy of the intermediate cellulosic fiber composition to yield a cellulosic fiber composition having a superhydrophobic surface.

[0009] In another aspect, the present disclosure relates to a cellulosic fiber composition having a superhydrophobic surface, with the cellulosic fiber composition being produced by the process of described herein.

[0010] In another aspect, the present disclosure relates to a product comprising a cellulosic fiber composition as described herein.

[0011] In another aspect, the present disclosure relates to a cellulosic material having improved hydrophobicity, with the cellulosic material comprising a cellulosic fiber composition as described herein.

[0012] Various aspects of the present disclosure are also addressed by the following Paragraphs 1-48 and in the noted combinations thereof, as follows:

[0013] Paragraph 1: A process for preparing a cellulosic fiber composition having a superhydrophobic surface, said process comprising:

- (a) synthesizing anisotropic particles of different shapes and covalently attaching them to a non-superhydrophobic cellulosic fiber, thereby yielding an intermediate cellulosic fiber composition having an altered surface; and
- (b) grafting long chain hydrocarbon lipids onto the altered surface of the intermediate cellulosic fiber composition, thereby lowering surface energy of the intermediate cellulosic fiber composition to yield a cellulosic fiber composition having a superhydrophobic surface.

[0014] Paragraph 2: The process according to Paragraph 1, wherein the cellulosic fiber composition has a water contact angle (WCA) selected from the group consisting of at least 150°, 151°, 152°, 153°, 154°, 155°, 156°, 157°, 158°, 159°, and 160°.

[0015] Paragraph 3: The process according to Paragraph 1, wherein the cellulosic fiber composition has a durability characterized by a loss of water contact angle selected from the group consisting of less than 2 percent, less than 2.5 percent, less than 3 percent, less than 5 percent, less than 7 percent, and less than 8 percent, as confirmed by repeated standard laboratory laundry cycles.

[0016] Paragraph 4: The process according to Paragraph 3, wherein the repeated standard laboratory laundry cycles are selected from the group consisting of 2, 3, 4, 5, 6, 7, 8, 9, and 10 standard laboratory laundry cycles.

[0017] Paragraph 5: The process according to Paragraph 1, wherein the anisotropic particles are anisotropic silica particles.

[0018] Paragraph 6: The process according to Paragraph 1, wherein the anisotropic particles are selected from the group consisting of silicon oxides, silicon metal oxides, metal oxides, metal silicon oxides, halloysite nanotubes (HNTs), nanoclays, and polymers.

[0019] Paragraph 7: The process according to Paragraph 1, wherein the anisotropic particles are selected from the group consisting of nanoparticles and microparticles.

[0020] Paragraph 8: The process according to Paragraph 7, wherein the nanoparticles have a mean diameter in at least one dimension selected from the group consisting of between about 1 and 40 nanometers (nm), between about 40 and 100 nm, and between about 100 and 1000 nm.

[0021] Paragraph 9: The process according to Paragraph 7, wherein the microparticles have a mean diameter in at least one dimension selected from the group consisting of between about 1 and 2 microns (μm), between about 2 and 3 μm , and between about 3 and 4 μm .

[0022] Paragraph 10: The process according to Paragraph 1, wherein the anisotropic particles have a mean diameter in at least one dimension of between about 1 and 100 nm and in at least one other dimension of up to 2 μm .

[0023] Paragraph 11: The process according to Paragraph 1, wherein the anisotropic particles have different mean diameters in at least one dimension, said different mean diameters being selected from the group consisting of between about 40 nm and 100 nm, between about 100 nm and 2 μm , and between about 1 μm and 4 μm .

[0024] Paragraph 12: The process according to Paragraph 1, wherein the anisotropic particles are uniformly or substantially uniformly distributed on the superhydrophobic surface of the cellulosic fiber composition.

[0025] Paragraph 13: The process according to Paragraph 1, wherein the anisotropic particles cover a percentage of the superhydrophobic surface selected from the group consisting of at least 40 percent, at least 50 percent, at least 60 percent, at least 70 percent, at least 80 percent, and at least 90 percent.

[0026] Paragraph 14: The process according to Paragraph 1, wherein said anisotropic particles of different shapes comprise needle-shaped particles.

[0027] Paragraph 15: The process according to Paragraph 1, wherein said anisotropic particles of different shapes comprise cone-shaped particles.

[0028] Paragraph 16: The process according to Paragraph 15, wherein the cone-shaped particles have a mean or median an aspect ratio (length:diameter of base) selected from the group consisting of 2:1, 5:1, 10:1, 20:1, 40:1, and 100:1, or within ranges between any two choices from the group.

[0029] Paragraph 17: The process according to Paragraph 15, wherein the cone-shaped particles are oriented on the superhydrophobic surface vertex end upward, vertex end downward, or both vertex end upward and downward.

[0030] Paragraph 18: The process according to Paragraph 1, wherein said anisotropic particles of different shapes comprise spherical particles.

[0031] Paragraph 19: The process according to Paragraph 18, wherein said spherical particles have a diameter between about 40 nm and 4 μ m.

[0032] Paragraph 20: The process according to Paragraph 1, wherein said anisotropic particles comprise a combination of needle-shaped particles, cone-shaped particles, and/or spherical particles.

[0033] Paragraph 21: The process according to Paragraph 1, wherein said anisotropic particles of different shapes comprise elongated particles having a first width at a first end and a second width at a second end, the first width being greater than the second width, and having a length greater than the first width.

[0034] Paragraph 22: The process according to Paragraph 21, wherein said first width is at least 1.2 times the second width.

[0035] Paragraph 23: The process according to Paragraph 21, wherein said first width is at least 1.5 times the second width.

[0036] Paragraph 24: The process according to Paragraph 21, wherein said first width is at least 2.0 times the second width.

[0037] Paragraph 25: The process according to Paragraph 21, wherein a shape of the anisotropic particles at the first end is at least substantially spherical.

[0038] Paragraph 26: The process according to Paragraph 21, wherein at least some of the anisotropic particles are stacked upon one another.

[0039] Paragraph 27: The process according to Paragraph 26 further comprising spherical particles arranged around and/or mixed with the stacked anisotropic particles.

[0040] Paragraph 28: The process according to Paragraph 1, wherein the lipids are fatty acids.

[0041] Paragraph 29: The process according to Paragraph 28, wherein the fatty acids are aliphatic fatty acids.

[0042] Paragraph 30: The process according to Paragraph 29, wherein the aliphatic fatty acids comprise aliphatic fatty acid molecules have fatty chains of uniform or different lengths.

[0043] Paragraph 31: The process according to Paragraph 30, wherein the length of the fatty chain comprises between about 3 and about 38 carbon atoms.

[0044] Paragraph 32: The process according to Paragraph 1, wherein the cellulosic fiber is from cotton.

[0045] Paragraph 33: The process according to Paragraph 1, wherein the cellulosic fiber is from a source selected from the group consisting of rayon, viscose rayon, liquid crystalline cellulose, lyocell fibers (e.g., TENCEL[®]), bacterial cellulose, and all plant based fibers such as wood pulp based microfibrils and jute, kenaf, ramie, sisal, flax, pineapple, banana, henequen, curaua, bagasse, bamboo, hemp, and fibrils derived from them.

[0046] Paragraph 34: The process according to Paragraph 1, wherein the cellulosic fiber is in a form selected from the group consisting of fabric (woven, knitted, or nonwoven), yarn, fibers, filaments, microfibrils, and nanofibers.

[0047] Paragraph 35: The process according to Paragraph 1, wherein synthesizing the anisotropic particles comprises using a colloidal synthesis procedure with a surface stabilizer.

[0048] Paragraph 36: The process according to Paragraph 35, wherein the surface stabilizer comprises a mixture of one or more types of surface stabilizer of the same or different molecular weights.

[0049] Paragraph 37: The process according to Paragraph 35, wherein the surface stabilizer is an amphiphilic polymer having polar and non-polar sites.

[0050] Paragraph 38: The process according to Paragraph 35, wherein the amphiphilic polymer is a polyvinyl pyrrolidone (PVP) polymer.

[0051] Paragraph 39: The process according to Paragraph 1, wherein covalently attaching the anisotropic particles to the non-superhydrophobic cellulosic fiber comprises a crosslinking procedure effective to increase durability of the cellulosic fiber composition having a superhydrophobic surface.

[0052] Paragraph 40: The process according to Paragraph 39, wherein the crosslinking procedures uses a crosslinker selected from the group consisting of 1,2,3,4-butanetetracarboxylic acid (BTCA), citric acid, maleic acid, and other polycarboxylic acids.

[0053] Paragraph 41: The process according to Paragraph 39, wherein the crosslinking procedure is effective to produce crosslinking between the anisotropic particles and/or between the cellulosic fiber composition and the anisotropic particles.

[0054] Paragraph 42: The process according to Paragraph 39, wherein the crosslinking procedure further comprises crosslinking within cellulose molecules of the cellulosic fiber composition.

[0055] Paragraph 43: The process according to Paragraph 1, wherein the process is a fluorine-free process or a substantially fluorine-free process.

[0056] Paragraph 44: A cellulosic fiber composition having a superhydrophobic surface, said cellulosic fiber composition being produced by the process of any one of Paragraphs 1-43.

[0057] Paragraph 45: A product comprising a cellulosic fiber composition according to Paragraph 44.

[0058] Paragraph 46: The product according to Paragraph 45, wherein the cellulosic fiber composition is in a form selected from the group consisting of fabric (woven, knitted, or nonwoven), yarn, fibers, filaments, microfibrils, and nanofibers.

[0059] Paragraph 47: A cellulosic material having improved hydrophobicity, said cellulosic material comprising a cellulosic fiber composition according to Paragraph 44.

[0060] Paragraph 48: The cellulosic material according to Paragraph 47, wherein the cellulosic material is selected from the group consisting of viscose rayon, paper, liquid crystalline cellulose, cellulose acetate, lyocell fibers such as Tencel[®], bacterial cellulose and all plant based cellulosic fibers such as wood pulp based microfibrils and jute, kenaf, ramie, sisal, flax, pineapple, and banana, as well as yarns and fabrics made using them.

[0061] These and other objects, features, and advantages of this invention will become apparent from the following detailed description of the various aspects of the invention taken in conjunction with the accompanying drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

[0062] For the purpose of illustrating aspects of the present invention, there are depicted in the drawings certain embodiments of the invention. However, the invention is not limited to the precise arrangements and instrumentalities of the embodiments depicted in the drawings. Further, if provided, like reference numerals contained in the drawings are meant to identify similar or identical elements.

[0063] **Figure 1** is a schematic representation of the colloidal synthesis of anisotropic SiO₂ particles using two different molecular weights of PVP.

[0064] **Figure 2** is a schematic of the chemical reaction between cellulose and heptanoic anhydride via esterification.

[0065] **Figures 3A-3F** are SEM images of cones (Figures 3A-3C) and needles (Figures 3D-3F) at different reaction times (2h, 7h, and 18h).

[0066] **Figures 4A-4D** are cross-sectional TEM images of cones (Figures 4A-4B) and needles (Figures 4C-4D) at different magnifications.

[0067] **Figures 5A-5B** are ATR-FTIR spectra of cotton fabrics treated with (a) HA for 10, 20 and 30 min (Figure 5A) and (b) Control, PD-SiO₂, Xlink-SiO₂ and Xlink-SiO₂-HA fabrics treated for 30 min (Figure 5B).

[0068] **Figures 6A-6F** are SEM images of (a) control (Figure 6A); (b) HA (Figure 6B), (c) Xlink-SiO₂(cones)-HA (Figure 6C), (d) Xlink-SiO₂(needles)-HA fibers and digital photographs of the WCA (Figure 6D) for (e) Xlink-SiO₂(cones)-HA (Figure 6E) and (f) Xlink-SiO₂(needles)-HA (Figure 6F) fabrics.

[0069] **Figures 7A-7D** are SEM images of (a) PD-SiO₂(cones)-HA (Figure 7A), (b) Xlink-SiO₂(cones)-HA (Figure 7B), (c) PD-SiO₂(needles)-HA (Figure 7C), and (d) Xlink-SiO₂(needles)-HA fibers (Figure 7D) after 7 laundry cycles.

[0070] **Figures 8A-8B** are graphs illustrating the effect of superhydrophobic treatment on (a) stress (Figure 8A) and (b) strain (Figure 8B) of the fabrics.

DETAILED DESCRIPTION

[0071] The present invention generally provides, *inter alia*, environment-friendly cellulosic compositions, products, and processes for their production. The processes of the present invention involve the use of ‘green’ chemistry principles to improve hydrophobicity and/or surface roughness of cellulosic materials, thereby yielding modified cellulosic compositions having increased hydrophobicity and/or surface roughness. These modified cellulosic compositions are advantageous over prior art cellulosic compositions in that they are more durable in terms of their hydrophobicity and/or superhydrophobicity compared to cellulosic compositions not produced by the presently disclosed processes.

[0072] In one aspect, the present disclosure relates to a process for preparing a cellulosic fiber composition having a superhydrophobic surface. Generally, this process includes the steps of: (a) synthesizing anisotropic particles of different shapes and covalently attaching them to a non-superhydrophobic cellulosic fiber, thereby yielding an intermediate cellulosic fiber composition having an altered surface; and (b) grafting long chain hydrocarbon lipids onto the altered surface of the intermediate cellulosic fiber composition, thereby lowering surface energy of the intermediate cellulosic fiber composition to yield a cellulosic fiber composition having a superhydrophobic surface.

[0073] This process is an improvement over existing processes at least in that it is a ‘green’ process. For example, in certain embodiments, the process of the present disclosure is a fluorine-free process or a substantially fluorine-free process.

[0074] In certain embodiments of this process, synthesizing the anisotropic particles comprises using a colloidal synthesis procedure with a surface stabilizer. A suitable surface stabilizer for use in this process can include, without limitation, a mixture of one or more types of surface stabilizer of the same or different molecular weights. In one embodiment, the surface

stabilizer can include, without limitation, an amphiphilic polymer having polar and non-polar sites. In a particular embodiment, the amphiphilic polymer is a polyvinyl pyrrolidone (PVP) polymer.

[0075] In certain embodiments of this process, covalently attaching the anisotropic particles to the non-superhydrophobic cellulosic fiber involves the use of a crosslinking procedure effective to increase durability of the cellulosic fiber composition having a superhydrophobic surface. In certain embodiments, the crosslinking procedure is effective to produce crosslinking between the anisotropic particles and/or between the cellulosic fiber composition and the anisotropic particles. In certain other embodiments, the crosslinking procedure further involves crosslinking within cellulose molecules of the cellulosic fiber composition. Non-limiting examples of crosslinkers that can be used in the crosslinking procedure of this process can include, without limitation, 1,2,3,4-butanetetracarboxylic acid (BTCA), citric acid, maleic acid, other polycarboxylic acids, and the like.

[0076] In one aspect, the present disclosure relates to a cellulosic fiber composition having a superhydrophobic surface, with the cellulosic fiber composition being produced by the process described herein. In another aspect, the present disclosure provides a product comprising the cellulosic fiber composition as described herein.

[0077] As provided herein, the process of the present disclosure is effective to prepare a cellulosic fiber composition having a superhydrophobic surface. As used herein, the term “superhydrophobic” refers to a material having a water contact angle (WCA) of at least 150°. As provided herein, the term “superhydrophobic” is meant to also refer to a material that is “ultrahydrophobic.”

[0078] As used herein, a cellulosic fiber composition having a superhydrophobic surface is one that has a water contact angle of at least 150°, 151°, 152°, 153°, 154°, 155°, 156°, 157°, 158°, 159°, and 160°.

[0079] As used herein, the term “non-superhydrophobic cellulosic fiber” refers to any cellulosic fiber that does not have a water contact angle of at least 150°. More specifically, a “non-superhydrophobic cellulosic fiber” refers to a “hydrophilic cellulosic fiber.”

[0080] As described herein, a cellulosic fiber composition prepared by the process of the present disclosure has a superhydrophobic surface. In certain embodiments, as compared to non-superhydrophobic cellulosic fibers, the cellulosic fiber compositions prepared by the process of

the present disclosure have increased hydrophobicity durability. As used herein, durability of the superhydrophobic properties of the cellulosic fiber compositions of the present disclosure can be measured by a laundering durability test, such as the American Association of Textile Chemists and Colorists (AATCC) test method 61-2003.

[0081] In certain embodiments, the cellulosic fiber composition prepared according to the process of the present disclosure has a durability characterized by a loss of water contact angle selected from the group consisting of less than 2 percent, less than 2.5 percent, less than 3 percent, less than 5 percent, less than 7 percent, and less than 8 percent, as confirmed by repeated standard laboratory laundry cycles. For clarification, as used herein, one (1) “standard laboratory laundry cycle” corresponds to five (5) home washing cycles. In certain embodiments, the repeated standard laboratory laundry cycles can include, without limitation, 2, 3, 4, 5, 6, 7, 8, 9, and 10 standard laboratory laundry cycles.

[0082] In certain embodiments, the anisotropic particles synthesized in accordance with the process of the present disclosure include, without limitation, anisotropic particles such as silicon oxides, silicon metal oxides, metal oxides, metal silicon oxides, halloysite nanotubes (HNTs), nanoclays, and polymers.

[0083] In certain embodiments, the anisotropic particles synthesized in accordance with the process of the present disclosure include, without limitation, anisotropic silica particles.

[0084] In accordance with the process of the present disclosure, in certain embodiments, the anisotropic particles can include, without limitation, nanoparticles, microparticles, and/or mixtures thereof.

[0085] As used herein, non-limiting examples of nanoparticles include particles having a mean diameter in at least one dimension selected from the group consisting of between about 1 and 40 nanometers (nm), between about 40 and 100 nm, and between about 100 and 1000 nm.

[0086] As used herein, non-limiting examples of microparticles include particles having a mean diameter in at least one dimension selected from the group consisting of between about 1 and 2 microns (μm), between about 2 and 3 μm , and between about 3 and 4 μm .

[0087] In certain embodiments, the anisotropic particles can have, without limitation, a mean diameter in at least one dimension of between about 1 and 100 nm and in at least one other dimension of up to 2 μm .

[0088] In certain embodiments, the anisotropic particles can have, without limitation, different mean diameters in at least one dimension, with the different mean diameters being selected from the group consisting of between about 40 nm and 100 nm, between about 100 nm and 2 μ m, and between about 1 μ m and 4 μ m.

[0089] In certain embodiments, the anisotropic particles can be, without limitation, uniformly or substantially uniformly distributed on the superhydrophobic surface of the cellulosic fiber composition.

[0090] In certain embodiments, the anisotropic particles cover a percentage of the superhydrophobic surface. In certain non-limiting examples, the anisotropic particles can cover at least 40 percent, at least 50 percent, at least 60 percent, at least 70 percent, at least 80 percent, or at least 90 percent of the superhydrophobic surface of the cellulosic fiber composition according to the present disclosure.

[0091] In accordance with the present disclosure, the anisotropic particles can be of different shapes.

[0092] In certain embodiments, the anisotropic particles are needle-shaped particles.

[0093] In certain embodiments, the anisotropic particles are cone-shaped particles. In certain embodiments, the cone-shaped particles have a mean or median aspect ratio (length:diameter of base) such as, but not limited to, 2:1, 5:1, 10:1, 20:1, 40:1, and 100:1, or within ranges between any two choices from this group. In certain embodiments, the cone-shaped particles are oriented on the superhydrophobic surface with their vertex end upward or their vertex end downward. In certain embodiments, the cone-shaped particles are oriented on the superhydrophobic surface with some of the cone-shaped particles with their vertex end upward and some with their vertex end downward.

[0094] In certain embodiments, the anisotropic particles are spherical particles. In certain embodiments, the spherical particles have a diameter of between about 40 nm and 4 μ m.

[0095] In accordance with the present disclosure, the anisotropic particles can include a combination of needle-shaped particles, cone-shaped particles, and/or spherical particles.

[0096] In accordance with the present disclosure, the anisotropic particles of different shapes can include, without limitation, elongated particles having a first width at a first end and a second width at a second end, the first width being greater than the second width, and having a length greater than the first width. In certain embodiments, the first width is at least 1.2 times

the second width. In certain embodiments, the first width is at least 1.5 times the second width. In certain embodiments, the first width is at least 2.0 times the second width. In certain embodiments, the shape of the anisotropic particles at the first end is at least substantially spherical.

[0097] In certain embodiments, at least some of the anisotropic particles are stacked upon one another. In certain embodiments, the anisotropic particles are stacked upon one another can further include spherical particles arranged around and/or mixed with the stacked anisotropic particles.

[0098] In accordance with the process of the present disclosure, after yielding an intermediate cellulosic fiber composition having an altered surface, long chain hydrocarbon lipids are grafted onto the altered surface of the intermediate cellulosic fiber composition, thereby lowering surface energy of the intermediate cellulosic fiber composition to yield a cellulosic fiber composition having a superhydrophobic surface.

[0099] In certain embodiments, the lipids are fatty acids. More particularly, in certain embodiments, the fatty acids are aliphatic fatty acids. In certain embodiments, the aliphatic fatty acids can include aliphatic fatty acid molecules having fatty chains of uniform or different lengths.

[0100] While the lengths of the fatty chains of the fatty acids can be of any known length, particular embodiments can include fatty chains that comprise between about 3 and about 38 carbon atoms in length. More particularly, the fatty chains can correspond to the following fatty acids: propanoic acid, butanoic acid, pentanoic acid, hexanoic acid, heptanoic acid, octanoic acid, nonanoic acid, decanoic acid, undecanoic acid, dodecanoic acid, tridecanoic acid, tetradecanoic acid, pentadecanoic acid, hexadecanoic acid, heptadecanoic acid, octadecanoic acid, nonadecanoic acid, eicosanoic acid, heneicosanoic acid, docosanoic acid, tricosanoic acid, tetracosanoic acid, pentacosanoic acid, hexacosanoic acid, heptacosanoic acid, octacosanoic acid, nonacosanoic acid, triacontanoic acid, henatriacontanoic acid, dotriacontanoic acid, tritriacontanoic acid, tetratriacontanoic acid, pentatriacontanoic acid, hexatriacontanoic acid, heptatriacontanoic acid, and octatriacontanoic acid.

[0101] In accordance with the present disclosure, the cellulosic fiber, cellulosic fiber composition, product comprising the cellulosic fiber composition, and/or cellulosic material comprising the cellulosic fiber composition can be in various forms known in the art with respect

materials having a cellulosic surface. Suitable forms of the cellulosic fiber, cellulosic fiber composition, product comprising the cellulosic fiber composition, and/or cellulosic material comprising the cellulosic fiber composition of the present disclosure can include, without limitation, a form selected from the group consisting of fabric (woven, knitted, or nonwoven), yarn, fibers, filaments, microfibrils, and nanofibers.

[0102] In certain embodiments, the cellulosic fiber, cellulosic fiber composition, and/or cellulosic material is from cotton.

[0103] In certain embodiments, the cellulosic fiber, cellulosic fiber composition, and/or cellulosic material is from a source selected from the group consisting of rayon, viscose rayon, liquid crystalline cellulose, lyocell fibers (e.g., TENCEL[®]), bacterial cellulose, and all plant based fibers such as wood pulp based microfibrils and jute, kenaf, ramie, sisal, flax, pineapple, banana, henequen, curaua, bagasse, bamboo, hemp, and fibrils derived from them.

[0104] The product of the present invention can be any material or item that is used for protection, particularly as a water-repellant material. Suitable examples of such materials or items include, but are not limited to, any sort of apparel, outerwear, underwear, linens, blankets, coverings, banners, shoes, coats, jackets, sweaters, socks, headgear, tents, curtains, drapes, fabric, swimsuits, umbrellas, diapers, bandages for wounds, vehicle covers, awnings, and the like.

Additional Embodiments of the Present Disclosure

[0105] The present disclosure relates to, *inter alia*, a 'green' process for obtaining superhydrophobic cotton fabrics using anisotropic silica particles and lipids. In one aspect, the present disclosure provides a 'green' sustainable two-step process to create superhydrophobic cotton fabrics. In one embodiment, the disclosed process includes: (i) a first step in which anisotropic silica particles of different shapes are synthesized and covalently attached to the cotton fabrics; and (ii) a second step in which long chain hydrocarbon lipids are grafted to lower the surface energy to obtain superhydrophobic characteristics.

[0106] As described herein, the technology and processes of the present disclosure yield superior results over the current state of the art, including various improved properties of the processed cotton fabrics. For example, with respect to the improved resistance to washing, in

some embodiments of the present disclosure, the loss of water contact angle (WCA) after laboratory laundry cycles (e.g., 6, 7, 8, etc.) or home washing (e.g., 30, 35, 40, etc.) is less than 2%, less than 2.5%, less than 3%, less than 5%, less than 7%, or less than 8%, etc.

[0107] Furthermore, in accordance with the present disclosure, in certain embodiments, the process is effective to yield cotton fabrics having a water contact angle of at least 156°, at least 157°, and at least 158°.

[0108] Moreover, in accordance with the present disclosure, in certain embodiments, the process is effective to yield cotton fabrics exhibiting dramatic improvements over the state of the art. For example, the cotton fabrics produced according to the present disclosure exhibited much better resistance to wash due to the structural difference: cone shaped nanoparticle overlap with each other to form network with the round head of the cone protrude the surface of the fabric mimicking the lotus leaf structure vs. loose pure spherical nanoparticles covered the fabric. For example, in certain embodiments, the loss of WCA for the cotton fabrics of the present disclosure after 7 laundry cycle was only 2.55% (157° to 153°), while the loss of WCA for cotton fabrics made in accordance with other processes known in the art was shown to be almost 10%.

[0109] In one embodiment of a process of the present disclosure, in the first step, silica particles with different shapes were synthesized using water-in-alcohol emulsion and different molecular weights (MW) of polyvinyl pyrrolidone (PVP). Low MW PVP resulted in a combination of spherical and cone-shaped particles while high MW PVP resulted in needle-shaped particles. Particles were covalently bonded to the fabrics to create desired permanent surface roughness. In the second step, fabrics with altered-surfaces were grafted with fatty acid to lower the surface energy of fabrics. Covalent bonding of particles and grafting of fatty acids onto the fabrics was confirmed using ATR-FTIR. The combination of surface roughness obtained through silica particles and low surface energy of the fatty acid resulted in superhydrophobic cotton fabrics. In certain embodiments, fabrics grafted with spherical and cone-shaped particles, mimicking lotus leaf, showed water contact angle (WCA) of 157° whereas needle-shaped particles gave WCA of 153°. In certain embodiments, the durability of the superhydrophobic treatment was confirmed by repeated washing of the fabrics.

[0110] The ‘green’ process described herein can be scaled-up for other cellulosic materials such as viscose rayon, paper, etc., to expand their applications in self-cleaning surfaces, water-repellent protective coatings, packaging and others.

[0111] In one aspect, an objective of the present disclosure was to create superhydrophobic cotton fabrics using non-toxic and inexpensive methods and materials that are industrially scalable for practical applications. Colloidal syntheses of different shapes (spheres + cones and needles) of silica (SiO_2) particles were carried out using two different molecular weights of the emulsion stabilizer, PVP as shown in the schematic representation in Fig. 1.

[0112] The synthesized sphere + cone and needle-shaped silica particles were covalently bonded onto the cotton fabrics, separately, using a simple dip-cure method. The covalent bonding of the particles permanently altered the surface topography of the fabrics and increased the durability of the treatment. Seven-carbon aliphatic chains were then grafted on to the surface-altered fabrics using a simple dip-cure method via esterification as shown in the chemical reaction in Fig. 2.

[0113] The presence of SiO_2 particles on the surface creates micro-structured pockets that act as air-gaps between the fabric and the water droplet, enhancing the WCA of the fabrics. The combined effects of surface roughness created by two different types of SiO_2 particles and the low surface energy caused by the aliphatic chains on the hydrophobicity of the fabrics were studied.

[0114] In addition to improving hydrophobicity of cotton fabrics, it is contemplated that the technology and processes of the present disclosure may be suitable to improve the hydrophobicity of other cellulose fibers such as viscose rayon, liquid crystalline cellulose, cellulose derivatives such as cellulose acetate, lyocell fibers such as Tencel[®], bacterial cellulose and all plant based cellulosic fibers such as jute, kenaf, ramie, sisal, flax, pineapple, banana, and many others as well as yarns and fabrics made using them.

[0115] Various aspects, embodiments, techniques, and applications for use with the unique and improved technology, compositions, products, and processes of the present disclosure are described in US-2018/0119334-A1, entitled “Modified Cellulosic Compositions Having Increased Hydrophobicity and Processes for Their Production,” the disclosure of which is hereby incorporated by reference herein in its entirety.

EXAMPLES

[0116] The following examples are intended to illustrate particular embodiments of the present disclosure, but are by no means intended to limit the scope of the present disclosure.

Example 1

Bioinspired ‘Green’ Process Using Anisotropic Silica Particles and Fatty Acid for Superhydrophobic Cotton Fabrics

1. Abstract

[0117] Superhydrophobic cotton fabrics having lotus leaf-like dual scale roughness surface were prepared via a 2-step ‘green’ process. First, silica particles with different shapes were synthesized using a water-in-alcohol emulsion and polyvinyl pyrrolidone (PVP) of different molecular weights (MWs). Lower MW PVP resulted in a combination of spherical and cone-shaped particles while higher MW PVP resulted in needle-shaped particles. These anisotropic particles were covalently bonded to the fabrics to create desired permanent surface roughness. Second, fatty acid was grafted using a novel solvent-free grafting process of fatty acid to lower the surface energy of fabrics. Grafting of fatty acid and silica particles onto the fabric surface was confirmed using ATR-FTIR. The facile 2-step process consisting of obtaining surface roughness through silica particles and low surface energy through grafted fatty acid resulted in superhydrophobic cotton fabrics with water contact angles (WCA) above 150°. Fabrics with dual-shaped particles (spherical and cone-shaped) exhibited a higher WCA of 157° while fabrics with single-shaped (needles) particles showed a slightly lower WCA of 153°. Covalent bonding of both particles and fatty acid resulted in highly durable superhydrophobic characteristics. The ‘green’, fluorine-free process developed in this study can be easily scaled up for other cellulosic materials such as viscose rayon, paper, micro-fibrillated cellulose, etc., to expand their applications in self-cleaning surfaces, water-repellent protective coatings, packaging, polymer composites, electronics and others.

[0118] One aim of the research of this example was to create a fluorine-free and facile process to obtain superhydrophobic cotton fabrics that uses non-toxic and inexpensive materials and can be easily scaled up for industrial production. Colloidal syntheses of different shapes (spheres + cones and needles) of silica (SiO₂) particles were carried out using two different molecular weights (MWs) of the emulsion stabilizer, polyvinyl pyrrolidone (PVP) as shown in

the schematic representation in Fig. 1. The synthesized sphere + cone and needle-shaped silica particles were covalently bonded onto the cotton fabrics, separately, using a simple dip-cure method for the first time. The covalent bonding of the particles permanently altered the surface topography of the fabrics and increased the durability of the treatment. Seven-carbon aliphatic chains were then grafted on to the surface-altered fabrics using a simple dip-cure method via esterification as shown in the chemical reaction in Fig. 2. The presence of SiO₂ particles on the surface creates micro-structured pockets that act as air gaps at the interface between the fabric and the water droplet, enhancing the WCA of the fabrics. The combined effects of surface roughness created by two different types of SiO₂ particles and the low surface energy caused by the aliphatic chains on the hydrophobicity of the fabrics were studied.

2. Materials and Methods

[0119] 2.1 Materials. Desized and bleached plain weave cotton fabric (#400) was purchased from Testfabrics, Inc, PA. Tetraethyl orthosilicate, 98% (TEOS), Poly(vinylpyrrolidone) (PVP) with molecular weights (MW_n) of 8000 and 40,000 were purchased from Sigma Aldrich, Allentown, PA. 1-pentanol was purchased from Krackeler Scientific, Inc. Albany, NY. Heptanoic anhydride (HA) was purchased from TCI America, Philadelphia, PA. Ethanol (≥99.5% purity, absolute), sodium citrate, ammonium hydroxide (~28% NH₄OH), and butane tetra carboxylic acid (BTCA) were purchased from Sigma-Aldrich Chemical, Allentown, PA. Sodium hypophosphite monohydrate (SHP) was purchased from VWR international. Milli-Q deionized water (resistivity, 18.2 MΩ.cm, Millipore RiOs and Elix water purification systems, Millipore Corporation, MA) was used for hydrolysis of TEOS and deionized (DI) water was used for the measurement of WCA.

[0120] 2.2 Synthesis of anisotropic SiO₂ particles. Two g of PVP, both 8K and 40K were dissolved, separately, in 30 ml of 1-pentanol. The solutions were stirred continuously using magnetic stirrer at 300 rpm. Ethanol (3 ml) and 840 µl ultrapure water were added to the PVP solutions. Two hundred µl of 0.17 M sodium citrate was added to the water in oil (pentanol) emulsion. Both PVP and sodium citrate act as stabilizers for the water-in-pentanol emulsion. TEOS and NH₄OH, 300 µl and 500 µl, respectively, were added to the emulsions and left stirring at 300 rpm at room temperature for 18 h. At the end of 18 h, the emulsion was centrifuged at 20,000 rpm for 20 min and the supernatant was discarded. The precipitate was dissolved in

ethanol using vortex meter and centrifuged again at 20,000 rpm for 20 min. This process was repeated thrice to remove the surplus reactants.

[0121] 2.3 Hydrogen bonding vs. covalent bonding of anisotropic SiO₂ particles on to cotton fabrics. The SiO₂ particles were dispersed in ethanol by stirring at 1000 rpm for 30 min. Cotton fabric specimens (15 cm × 15 cm) were then dipped in 0.1% SiO₂ particle dispersion for 10 min and dried in an air-circulating oven at 130°C for 20 min to get SiO₂ particles immobilized on the fabrics based on hydrogen bonding. These hydrogen bonded fabrics are termed as physically deposited SiO₂ (PD-SiO₂). SiO₂ particles were covalently bonded to cotton fabric surface using BTCA. To obtain covalent bonding, cotton fabrics were immersed in 0.1% SiO₂ particle dispersion containing 3% BTCA and 1.5% SHP for 10 min and cured at 140°C for 20 min. These fabrics are termed as Xlink-SiO₂.

[0122] 2.3 Grafting of fatty acid onto cotton fabrics. Control fabrics as well as PD-SiO₂ and Xlink-SiO₂ fabrics were grafted with low surface energy molecules, on the surface. Cotton fabrics were dipped in HA and squeezed by hand to remove excess HA. They were further dipped and squeezed again and cured at 130°C in an air-circulating oven for required time. The fabrics were then rinsed with ethanol to remove the by-product, heptanoic acid and unreacted HA, if any. The fabrics were then dried at 50°C in an air-circulating oven to get rid of the treatment odor. The cotton fabrics with physically deposited sphere + cone-shaped and needle-shaped SiO₂ particles and treated with HA are termed as PD-SiO₂(cones)-HA fabrics and PD-SiO₂(needles)-HA fabrics, respectively. The covalently bonded sphere + cone-shaped and needle-shaped SiO₂ particles on cotton fabrics and further treated with HA are termed as Xlink-SiO₂(cones)-HA fabrics and Xlink-SiO₂(needles)-HA fabrics, respectively.

[0123] 2.4 Scanning electron microscopy (SEM). The surface morphologies of synthesized SiO₂ particles and the treated fibers were observed using a Zeiss Gemini 500 SEM (Germany) at 1 kV accelerating voltage. Image J software was used to analyze diameters and lengths of the particles. An average of 50 particles from 5 different images were reported. Images were taken from particles synthesized at two different times to ensure reproducibility of the results.

[0124] 2.5 Transmission electron microscopy (TEM). Cross-sections of the sphere + cone and needle-shaped particles were observed under FEI Tecnai T12 TEM (Thermo Fisher Scientific, Hillsboro, OR). The particles were dispersed in epoxy and cured. A thin slice of 70

nm thick was cut using an ultramicrotome fitted with a diamond knife to observe the cross-sections of the particles.

[0125] 2.6 Attenuated total reflectance Fourier-transform infrared spectroscopy

(ATR-FTIR). The ATR-FTIR spectra collected using Thermo Nicolet Magna-IR 560 spectrometer (Madison, WI) with a split pea accessory was used to confirm the grafting of both SiO₂ particles as well the aliphatic fatty chains onto the cotton fabrics. Each scan was an average of 300 scans from 4000 cm⁻¹ to 500 cm⁻¹ wavenumbers.

[0126] 2.7 Water contact angle (WCA). Contact angle analyzer CAA2, Imass Inc., (Accord, MA) was used to measure the contact angles of control and treated cotton fabrics. A DI water droplet (5 µL) was gently placed onto the specimen using a syringe and reading was taken after 30 s. Average of ten drops at different locations for each of the three specimens prepared at different times were recorded.

[0127] 2.8 Laundering durability. Laundry durability evaluation was carried out using a slightly modified version according to the American Association of Textile Chemists and Colorists (AATCC) Test Method 61–2003. The test was performed using a 500 mL flask containing 150 mL aqueous solution of Tide[®] laundry detergent (0.15%, w/w) and 50 stainless steel balls (diameter = 6 mm), the test was performed at 49°C, 40 rpm for 45 min. The size of the fabric specimens used in this test was 5 cm × 5 cm. Each laundry cycle in this study is considered to be equivalent to five home launderings.

[0128] 2.9 Tensile properties. Tensile strength of the fabrics was determined according to ASTM D5035 strip method. Fabrics having dimensions of 25 mm × 150 mm were cut and tested on Instron universal testing machine (model 5566, Canton, MA) at a gage length of 75 mm and crosshead speed of 300 mm/min (strain rate of 4min⁻¹). Six specimens each from different areas of the fabrics in both warp and weft directions were tested to obtain average values.

3. Results and Discussion

[0129] 3.1 Mechanistic insight into synthesis of anisotropic SiO₂ particles. Stöber process has been widely used since 1968 to create sphere-shaped silica particles [26]. However, apart from the conventional spherical particles, it has been possible to create anisotropic silica particles from an emulsion containing alcohol and water [27]. The biggest advantage of silica particles is the ease of chemical modifications of the particle surfaces due to presence of reactive

terminal Si-OH bonds [28]. In this study, two distinct anisotropic morphological silica particles (spheres + cones and needles), were obtained by using different molecular weights of PVP. For this, 8K and 40K PVP were dissolved in equal amount of pentanol, separately. Equal amounts of ethanol and water were added to the two different PVP solutions. PVP has both polar and non-polar binding sites and can act as an emulsion stabilizer by prohibiting the droplets from coalescing [29, 30]. When water is added to the high concentrated PVP solution (in pentanol), the water molecules bind to the PVP and water no longer acts only as a site for hydrolysis of TEOS, but also acts as a structure-directing agent due to bound PVP as shown earlier [31]. The ionic species induced after addition of sodium citrate creates inverse emulsion due to phase separation causing aqueous droplets to be dispersed in the pentanol-rich continuous phase [32]. The silica precursor, TEOS, when added to the emulsion, goes to the water phase and gets hydrolyzed [27]. Ethanol facilitates the hydrolysis of TEOS. Addition of NH_4OH at this stage causes condensation of TEOS and SiO_2 nucleation occurs at the interface of water droplet as shown in the schematic representation in Fig. 1. While condensation due to addition of NH_4OH causes nucleation, which attaches the head of the particles at the water-pentanol droplet interface, the reactive moieties in PVP cause growth in one direction leading to cone and needle shaped particles [27]. Fig. 3 shows the SEM images of the particles made using 8K and 40K PVP at different reaction times.

[0130] It was observed that 8K PVP resulted in cone-shaped SiO_2 particles along with some nanospheres whereas 40K PVP resulted in needle-shaped SiO_2 particles. As stated, 8K PVP resulted in a mixture of nanospheres and cones, as not all the spheres were elongated. It was observed that the shape and morphology of the cones did not change with the reaction time from 2 h to 18 h. However, it was observed that the suspension got cloudier and the particle yield increased with time. The average diameter of the head of the cone was found to be 240 nm and the average length of the cones after 18 h of reaction time was 2.2 μm . The average diameter of the needle-shaped particles was found to be 189 nm and the average length to be 3.8 μm after 18 h of reaction. It was observed that the diameter of the particles decreased, and the length increased when higher MW PVP was used. The 40K PVP has longer chain lengths and higher molecular entanglements as compared to 8K PVP. This may be a factor why 40K PVP resulted in smaller droplet size in the emulsion as shown the Fig. 1. As a result, the diameter of the needle-shaped particles was much lower as compared to that of cone shaped particles.

[0131] While some earlier studies have shown that the use of gold, silver or magnesium particles or precursors are the essential templates along with PVP for water-in-pentanol emulsions to create non-centrosymmetric or anisotropic SiO₂ particles such as rods, tubes or cones, this study has shown that the formation of anisotropic SiO₂ is independent of presence of such particles and the morphology of the SiO₂ particles is tunable using different MWs of PVP [28, 30, 31]. Overall, it was observed that keeping all other emulsion parameters (reactant ratios and stirring speed) constant and varying the molecular weight of PVP gave different shapes and sizes of SiO₂ particles. This suggests that factors such as initial droplet size, terminal droplet stability and the subsequent nucleation and growth of the SiO₂ particles are influenced by the molecular chain length and the resultant entanglements of PVP [33].

[0132] Fig. 4 shows TEM images of the cross sections of the sphere + cone and needle-shaped particles at different magnifications. From their cross-sectional views seen in these images it can be concluded that the synthesized particles are solid and not hollow, and no core-shell structure exists.

[0133] **3.2 Effect of heptanoic anhydride treatment on cotton fabrics.** Fig. 5 shows ATR-FTIR spectra of control and treated cotton fabrics. Fig. 5A shows ATR-FTIR spectra of the cotton fabric and the cotton fabrics treated with HA for 10, 20, and 30 min at 130°C. Control cotton fabrics show a broad peak between 3400 cm⁻¹ and 3200 cm⁻¹ which is due to the stretching of hydroxyl groups in cellulose as well as the absorbed moisture [34]. The peak at 2902 cm⁻¹ is due to the symmetric C-H and C-H₂ stretching vibrations and the peak around 1053 cm⁻¹ and 1030 cm⁻¹ is due to the C-O-C stretching absorption. These peaks are consistent with all the cellulosic materials [35]. As seen in Fig. 5A, a new peak at 1730 cm⁻¹ was observed in the HA treated fabrics which was found to grow stronger with the treatment time. This peak corresponds to the ester group formed due to the reaction between the hydroxyl groups on the cellulose and the anhydride groups from HA as shown in the chemical reaction in Fig. 2 [36]. The degree of substitution of the hydroxyl groups from cellulose increases with increase in treatment time as seen from the increasing intensity of the peak at 1730 cm⁻¹ in Fig. 5A. While the control fabrics can be quickly and completely wetted by water, WCAs of the fabrics treated with HA were found to be 112°, 120° and 127° after 10, 20, and 30 min of treatment time, respectively. The esterification results in the covalent attachment of the flexible seven-carbon planar zigzag aliphatic chains of HA which form a layer on the surface of the fibers in the fabric

making it hydrophobic. The surface polarity of the fabrics decreases as the hydroxyl groups from the cellulose are substituted by long aliphatic chains which have low surface energy. This lowers the surface energy of the fabrics without changing the surface topography of the fibers in the fabrics as seen in the SEM image in Fig. 6B. Dankovich and Hsieh grafted eighteen-carbon aliphatic chains onto cotton fabrics using stearic acid dissolved in ethanol to get a WCA of only 40° [37]. This is because fatty acids have extremely low reactivity towards the hydroxyl groups of the cellulose [37, 38]. On the other hand, anhydride groups are acylating agents known for their high reactivity as compared to carboxylic acids and thus, the use of heptanoic anhydride resulted in a significantly higher WCA of 127° in this research.

[0134] 3.3 Effect of SiO₂ particles and HA treatment on cotton fabrics. A

combination of surface roughness along with low surface energy is critical to create superhydrophobic surfaces (WCA above 150°) [39]. Two different shapes, cones + spheres and needles, of SiO₂ particles were physically deposited and covalently bonded, in separate processes, onto the cotton fabrics to change the surface topography. Fig. 5B shows ATR-FTIR spectra of PD-SiO₂ fabrics and Xlink-SiO₂ fabrics. As seen in Fig. 5B, an additional small peak is observed in both physically deposited and covalently bonded SiO₂ cotton fabrics at 800 cm^{-1} . This peak is the characteristic stretching vibration peak for Si-O-Si from the SiO₂ particles [40]. The intensity of the peak at 1053 cm^{-1} is lower than the intensity of the peak at 1030 cm^{-1} for the control cotton fabrics. The peak between 1015 cm^{-1} and 1060 cm^{-1} corresponds to C-O stretch in cellulose. The Si-O-Si asymmetric stretch overlaps with the C-O stretch in cellulose [34]. However, after the SiO₂ treatment, the intensity of peak at 1053 cm^{-1} increases (Fig. 5B). This is due to the presence of Si-O-Si from the SiO₂ particles. An additional peak at 1722 cm^{-1} is observed in the Xlink-SiO₂ fabrics. This peak is the result of the ester bonds formed by the co-condensation of Si-OH from the particles and the -COOH from BTCA as well as the reaction between -OH from cellulose and the -COOH from BTCA. Polycarboxylic acids such as BTCA are often used as heterogenous crosslinkers to improve the bonding between the inorganic-organic interfaces, especially between silica particles and cellulose [41-44]. BTCA has four carboxyl groups which can react with both, the SiO₂ particles as well as the cellulose from the fabric and act as a crosslink (bridge) between the two. This covalent bonding between SiO₂ particles and fabrics prevent these particles from leaving fabric during use and laundering and, thus, increases the washing durability. Physical deposition of the SiO₂ particles as well as

covalent bonding of SiO₂ particles on the fabrics are able to create new surface topography of the fabrics. However, the fabrics still remain hydrophilic. The HA treatment is necessary to lower the surface energy of the fabrics and increase the hydrophobicity to the desired level.

[0135] The WCA for Xlink-SiO₂(cones)-HA (8K PVP) fabrics was found to be 157° and Xlink-SiO₂(needles)-HA (40K PVP) fabrics was found to be 153°. Fig. 6 shows the SEM images of the fibers taken from control and treated fabrics along with the digital photographs of the WCA test. The surface of the control cotton fibers (Fig. 6A) is mostly smooth and flat with some convolutions and natural creases and does not change after the HA treatment (Fig. 6B). The Xlink-SiO₂(cones)-HA and Xlink-SiO₂(needles)-HA fibers (Figs. 6C and 6D) show that the surface of the fibers is coated with SiO₂ cones and needles, respectively. This changes the surface topography of the fabrics and creates a desired surface roughness. The combination of surface roughness created by the SiO₂ particles along with the low surface energy created by the grafting of HA results in a fabric surface that is superhydrophobic with significantly enhanced WCA, above 150°. Higher WCA was observed for the Xlink-SiO₂(cones)-HA as compared to Xlink-SiO₂(needles)-HA. This is perhaps because of the presence of nanospheres that are mixed with the micrometer size cone shaped SiO₂ particles that together create a dual surface roughness on the fabrics, closer to the lotus leaf. The dual size roughness creates air-pockets that can entrap a layer of air between SiO₂ particles and water droplet further enhancing the WCA [45].

[0136] The concentration of the SiO₂ particles used to treat the cotton fabrics was varied from 0.05% to 0.5%. Supplementary material shows the effect of SiO₂ concentration on WCA of the fabrics. It was observed that the WCA increased from 152° to 157° as the concentration of the sphere + cone shaped particles increased from 0.05% to 0.1%. However, further increasing the concentration of sphere + cone shaped particles to 0.3% or even 0.5% did not increase the WCA of the fabrics. Similar behavior was observed for the fabrics treated with needle shaped particles. Supplementary material shows the SEM images of Xlink-0.5% SiO₂(cones)-HA and Xlink-0.5% SiO₂(needles)-HA. Some particle clusters can be observed at 0.5% SiO₂ concentration in fabrics treated with both sphere + cone and needle-shaped particles.

[0137] **3.4 Laundry durability of the superhydrophobic fabrics.** Table 1 shows the effect of laundering (up to 7 laboratory laundry cycles) on the durability of the superhydrophobic treatment. The washings were carried out according to the modified AATCC Test Method 61–2003. Each laboratory laundry cycle, as mentioned earlier, corresponds to 5 home laundry

washes. As can be seen from data in Table 1, WCA decreased slightly with the number of laundry cycles. The decrease in the WCA was higher for the physically deposited particles as compared to the crosslinked particles as could be expected. The WCA decreased from 157° to 148° for the PD-SiO₂(cones)-HA samples after 7 laundry cycles (35 home washings) which was found to be statistically significant using unpaired t-test at a significance level of 0.05. The WCA decreased from 157° to 153° for the Xlink-SiO₂(cones)-HA samples which was statistically insignificant using unpaired t-test at a significance level of 0.05. Fig. 7 shows the SEM images of fibers after 7 laundry cycles. As seen in Fig. 7A and Fig. 7C, the surface of the physically deposited fibers is only partially covered with cone-shaped and needle-shaped particles, respectively as some of the particles are detached from the surface of the fibers during washing. Washing can remove physically deposited (PD) and loosely bonded particles from the surface of the fabrics. Earlier studies have shown that SiO₂ particles can be immobilized in the cotton fabrics by heat treatment [46]. However, crosslinking creates a covalent bond between fabrics and particles and can be expected to increase the durability of the treatment. This can be confirmed from images in Figs. 7B and 7D which show that majority of the fiber is still covered with the SiO₂ particles after 7 laundry cycles. Both, Xlink-SiO₂(cones)-HA and Xlink-SiO₂(needles)-HA fabrics maintained their superhydrophobicity, WCAs above 150°, after 7 laundry cycles which correspond to 35 home washings. The slight decrease in the WCA for the crosslinked fabrics could be due to the presence of cellulase enzyme in the detergent which can degrade and remove the top layer of the fibers during washing.

Table 1. Effect of laundry cycles on the WCA* of the fabrics.

Specimen	WCA (°)	WCA ₁ (°)	WCA ₃ (°)	WCA ₅ (°)	WCA ₇ (°)
HA	127 ± 2.1	126 ± 2.7	119 ± 1.3	120 ± 3.3	118 ± 3.3
PD-SiO ₂ (cones)-HA	157 ± 1.4	154 ± 2.2	150 ± 1.3	149 ± 2.1	148 ± 2.7
Xlink-SiO ₂ (cones)-HA	157 ± 1.2	156 ± 1.1	154 ± 3.2	153 ± 2.1	153 ± 1.3
PD-SiO ₂ (needles)-HA	152 ± 2.2	150 ± 2.2	147 ± 1.5	146 ± 2.9	147 ± 1.1
Xlink-SiO ₂ (needles)-HA	153 ± 2.4	154 ± 1.2	152 ± 2.4	150 ± 3.1	150 ± 1.3

[0138] 3.5 Tensile properties of the superhydrophobic fabrics. Fig. 8 shows the effect of superhydrophobic treatment on the tensile (fracture) stress and strain of the fabrics in both warp and weft directions. As seen in Fig. 8A, the tensile stress values for control and the HA treated fabrics in the warp direction are 56.8 MPa and 55.5 MPa, respectively. No change in the tensile stress was observed after grafting HA onto fabrics as it is simply a surface treatment and has no effect on the fiber morphology. Fig. 8B shows the effect superhydrophobic treatment on the tensile strain of the fabrics in both warp and weft directions. It was observed that the tensile strain of the HA treated fabrics increased slightly from 6% for control to 7.1% for the HA treated fabrics in the warp direction. The increase in the strain in the warp direction could be primarily due the relaxation of the built-up stress while weaving and finishing of the fabrics. It was observed that the tensile stress values of the PD-SiO₂-HA and Xlink-SiO₂-HA fabrics reduced to 50.2 MPa and 29 MPa, respectively. The slight reduction in the tensile stress of the PD-SiO₂-HA fabric could be due to the heat treatment. The reduction in tensile stress in the Xlink-SiO₂-HA fabrics as seen in Fig. 8A is a result of the crosslinking using BTCA which restricts the molecular movement causing a reduction in the stress as well the strain from 6% to 4.8% as seen in Fig. 8B. The acidic degradation of the cellulose chains due to BTCA is another reason for the loss in strength of the Xlink-SiO₂-HA fabrics [47]. Similar behavior was observed in the weft direction as can be seen in Fig. 8.

4. Applications and Conclusions

[0139] The superhydrophobic fabrics obtained in accordance with the research of this example are durable to laundry washings and can find applications in various areas such as outerwear, protective clothing, medical apparel and others. Supplementary material show that water beads up on the treated fabrics without wetting the surface. Also, when held at an angle, the water simply flows down without wetting the fabric. The superhydrophobic fabrics developed in this research support applications such as ‘easy-cleaning’ fabrics and water-repellent clothing. The treated fabrics are oil absorbent. Such materials can find applications in oil-absorbent wipes or even cleaning up oil-spills from oceans. The ‘green’ process developed in this research can be easily extended to other cellulose materials which can be used in developing biodegradable packaging films, microfluidic devices or oil-water separating membranes.

[0140] This study presents a bioinspired ‘green’ process to create superhydrophobic cotton fabrics using SiO₂ particles and HA. Different molecular weights of PVP were used which acted as emulsion stabilizer as well as directing agents for the 1 dimensional growth of SiO₂ particles. Higher molecular weight PVP (40K) produced smaller droplets in the emulsion and gave needle-shaped longer particles as compared to the lower molecular weight PVP (8K). Lower molecular weight PVP produced a mixture of spherical and cone-shaped particles. Spherical + cone-shaped and needle-shaped particles were covalently bonded onto the cotton fabrics, separately, to create a desired and permanent surface roughness and then treated with HA to lower the surface energy of the fabrics to get superhydrophobic fabrics. WCA of 157° was obtained using cone-shaped SiO₂ particles.

[0141] Anisotropic SiO₂ particles are crucial for creating desired dual size surface roughness or texture on the fabric surface which enhance their WCA as compared to spherical shaped particles which have been used to create surface roughness. The facile approach for synthesizing anisotropic SiO₂ particles used in this study is easily scalable for large scale commercial production. In addition, grafting of nontoxic fatty acid to lower the surface energy of the fabrics used in this study, compared to the current use of expensive fluoropolymers which are toxic in nature, creates a fully ‘green’ process to obtain superhydrophobic cotton fabrics. The ‘green’ process developed here can be easily scaled-up and applied to other cellulosic materials such as viscose rayon, paper and others to expand their applications for uses including self-cleaning surfaces, water-repellent protective coatings, medical apparel, packaging, electronics, composites, and many others.

REFERENCES

[0142] Citation of a reference herein shall not be construed as an admission that such reference is prior art to the present invention. All references cited herein are hereby incorporated by reference in their entirety. Below is a listing of various references cited with respect to this example:

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[0143] The terms “a,” “an,” “the” and similar referents used in the context of describing the invention (especially in the context of the following claims) are to be construed to cover both the singular and the plural, unless otherwise indicated herein or clearly contradicted by context. Recitation of ranges of values herein is merely intended to serve as a shorthand method of referring individually to each separate value falling within the range. Unless otherwise indicated herein, each individual value is incorporated into the specification as if it were individually recited herein. All methods described herein can be performed in any suitable order unless otherwise indicated herein or otherwise clearly contradicted by context. The use of any and all examples, or exemplary language (e.g., “such as”) provided herein is intended merely to better illuminate the invention and does not pose a limitation on the scope of the invention otherwise

claimed. No language in the specification should be construed as indicating any non-claimed element essential to the practice of the invention.

[0144] Groupings of alternative elements or embodiments of the invention disclosed herein are not to be construed as limitations. Each group member may be referred to and claimed individually or in any combination with other members of the group or other elements found herein. It is anticipated that one or more members of a group may be included in, or deleted from, a group for reasons of convenience and/or patentability. When any such inclusion or deletion occurs, the specification is deemed to contain the group as modified thus fulfilling the written description of all Markush groups used in the appended claims.

[0145] Certain embodiments of this invention are described herein, including the best mode known to the inventors for carrying out the invention. Of course, variations on these described embodiments will become apparent to those of ordinary skill in the art upon reading the foregoing description. The inventor expects skilled artisans to employ such variations as appropriate, and the inventors intend for the invention to be practiced otherwise than specifically described herein. Accordingly, this invention includes all modifications and equivalents of the subject matter recited in the claims appended hereto as permitted by applicable law. Moreover, any combination of the above-described elements in all possible variations thereof is encompassed by the invention unless otherwise indicated herein or otherwise clearly contradicted by context.

[0146] Furthermore, numerous references have been made to patents and printed publications throughout this specification. Citation of a reference herein shall not be construed as an admission that such reference is prior art to the present invention. All references cited herein are hereby incorporated by reference in their entirety.

[0147] In closing, it is to be understood that the embodiments of the invention disclosed herein are illustrative of the principles of the present invention. Other modifications that may be employed are within the scope of the invention. Thus, by way of example, but not of limitation, alternative configurations of the present invention may be utilized in accordance with the teachings herein. Accordingly, the present invention is not limited to that precisely as shown and described.

[0148] Illustrative embodiments of the processes, methods, and products of the present disclosure are described herein. It should be understood, however, that the description herein of

the specific embodiments is not intended to limit the present disclosure to the particular forms disclosed but, on the contrary, the intention is to cover all modifications, equivalents, and alternatives falling within the spirit and scope of the invention by the appended claims. Thus, although the present invention has been described for the purpose of illustration, it is understood that such detail is solely for that purpose and variations can be made by those skilled in the art without departing from the spirit and scope of the invention which is defined by the following claims.

WHAT IS CLAIMED IS:

1. A process for preparing a cellulosic fiber composition having a superhydrophobic surface, said process comprising:
 - a. synthesizing anisotropic particles of different shapes and covalently attaching them to a non-superhydrophobic cellulosic fiber, thereby yielding an intermediate cellulosic fiber composition having an altered surface; and
 - b. grafting long chain hydrocarbon lipids onto the altered surface of the intermediate cellulosic fiber composition, thereby lowering surface energy of the intermediate cellulosic fiber composition to yield a cellulosic fiber composition having a superhydrophobic surface.
2. The process according to claim 1, wherein the cellulosic fiber composition has a water contact angle (WCA) selected from the group consisting of at least 150°, 151°, 152°, 153°, 154°, 155°, 156°, 157°, 158°, 159°, and 160°.
3. The process according to claim 1, wherein the cellulosic fiber composition has a durability characterized by a loss of water contact angle selected from the group consisting of less than 2 percent, less than 2.5 percent, less than 3 percent, less than 5 percent, less than 7 percent, and less than 8 percent, as confirmed by repeated standard laboratory laundry cycles.
4. The process according to claim 3, wherein the repeated standard laboratory laundry cycles are selected from the group consisting of 2, 3, 4, 5, 6, 7, 8, 9, and 10 standard laboratory laundry cycles.
5. The process according to claim 1, wherein the anisotropic particles are anisotropic silica particles.

6. The process according to claim 1, wherein the anisotropic particles are selected from the group consisting of silicon oxides, silicon metal oxides, metal oxides, metal silicon oxides, halloysite nanotubes (HNTs), nanoclays, and polymers.
7. The process according to claim 1, wherein the anisotropic particles are selected from the group consisting of nanoparticles and microparticles.
8. The process according to claim 7, wherein the nanoparticles have a mean diameter in at least one dimension selected from the group consisting of between about 1 and 40 nanometers (nm), between about 40 and 100 nm, and between about 100 and 1000 nm.
9. The process according to claim 7, wherein the microparticles have a mean diameter in at least one dimension selected from the group consisting of between about 1 and 2 microns (μm), between about 2 and 3 μm , and between about 3 and 4 μm .
10. The process according to claim 1, wherein the anisotropic particles have a mean diameter in at least one dimension of between about 1 and 100 nm and in at least one other dimension of up to 2 μm .
11. The process according to claim 1, wherein the anisotropic particles have different mean diameters in at least one dimension, said different mean diameters being selected from the group consisting of between about 40 nm and 100 nm, between about 100 nm and 2 μm , and between about 1 μm and 4 μm .
12. The process according to claim 1, wherein the anisotropic particles are uniformly or substantially uniformly distributed on the superhydrophobic surface of the cellulosic fiber composition.
13. The process according to claim 1, wherein the anisotropic particles cover a percentage of the superhydrophobic surface selected from the group consisting of at least 40 percent, at

least 50 percent, at least 60 percent, at least 70 percent, at least 80 percent, and at least 90 percent.

14. The process according to claim 1, wherein said anisotropic particles of different shapes comprise needle-shaped particles.
15. The process according to claim 1, wherein said anisotropic particles of different shapes comprise cone-shaped particles.
16. The process according to claim 15, wherein the cone-shaped particles have a mean or median aspect ratio (length:diameter of base) selected from the group consisting of 2:1, 5:1, 10:1, 20:1, 40:1, and 100:1, or within ranges between any two choices from the group.
17. The process according to claim 15, wherein the cone-shaped particles are oriented on the superhydrophobic surface vertex end upward, vertex end downward, or both vertex end upward and downward.
18. The process according to claim 1, wherein said anisotropic particles of different shapes comprise spherical particles.
19. The process according to claim 18, wherein said spherical particles have a diameter between about 40 nm and 4 μ m.
20. The process according to claim 1, wherein said anisotropic particles comprise a combination of needle-shaped particles, cone-shaped particles, and/or spherical particles.
21. The process according to claim 1, wherein said anisotropic particles of different shapes comprise elongated particles having a first width at a first end and a second width at a second end, the first width being greater than the second width, and having a length greater than the first width.

22. The process according to claim 21, wherein said first width is at least 1.2 times the second width.
23. The process according to claim 21, wherein said first width is at least 1.5 times the second width.
24. The process according to claim 21, wherein said first width is at least 2.0 times the second width.
25. The process according to claim 21, wherein a shape of the anisotropic particles at the first end is at least substantially spherical.
26. The process according to claim 21, wherein at least some of the anisotropic particles are stacked upon one another.
27. The process according to claim 26 further comprising spherical particles arranged around and/or mixed with the stacked anisotropic particles.
28. The process according to claim 1, wherein the lipids are fatty acids.
29. The process according to claim 28, wherein the fatty acids are aliphatic fatty acids.
30. The process according to claim 29, wherein the aliphatic fatty acids comprise aliphatic fatty acid molecules have fatty chains of uniform or different lengths.
31. The process according to claim 30, wherein the length of the fatty chain comprises between about 3 and about 38 carbon atoms.
32. The process according to claim 1, wherein the cellulosic fiber is from cotton.

33. The process according to claim 1, wherein the cellulosic fiber is from a source selected from the group consisting of rayon, viscose rayon, liquid crystalline cellulose, lyocell fibers (e.g., TENCEL[®]), bacterial cellulose, and all plant based fibers such as wood pulp based microfibrils and jute, kenaf, ramie, sisal, flax, pineapple, banana, henequen, curaua, bagasse, bamboo, hemp, and fibrils derived from them.
34. The process according to claim 1, wherein the cellulosic fiber is in a form selected from the group consisting of fabric (woven, knitted, or nonwoven), yarn, fibers, filaments, microfibrils, and nanofibers.
35. The process according to claim 1, wherein synthesizing the anisotropic particles comprises using a colloidal synthesis procedure with a surface stabilizer.
36. The process according to claim 35, wherein the surface stabilizer comprises a mixture of one or more types of surface stabilizer of the same or different molecular weights.
37. The process according to claim 35, wherein the surface stabilizer is an amphiphilic polymer having polar and non-polar sites.
38. The process according to claim 35, wherein the amphiphilic polymer is a polyvinyl pyrrolidone (PVP) polymer.
39. The process according to claim 1, wherein covalently attaching the anisotropic particles to the non-superhydrophobic cellulosic fiber comprises a crosslinking procedure effective to increase durability of the cellulosic fiber composition having a superhydrophobic surface.
40. The process according to claim 39, wherein the crosslinking procedures uses a crosslinker selected from the group consisting of 1,2,3,4-butanetetracarboxylic acid (BTCA), citric acid, maleic acid, and other polycarboxylic acids.

41. The process according to claim 39, wherein the crosslinking procedure is effective to produce crosslinking between the anisotropic particles and/or between the cellulosic fiber composition and the anisotropic particles.
42. The process according to claim 39, wherein the crosslinking procedure further comprises crosslinking within cellulose molecules of the cellulosic fiber composition.
43. The process according to claim 1, wherein the process is a fluorine-free process or a substantially fluorine-free process.
44. A cellulosic fiber composition having a superhydrophobic surface, said cellulosic fiber composition being produced by the process of any one of claims 1-43.
45. A product comprising a cellulosic fiber composition according to claim 44.
46. The product according to claim 45, wherein the cellulosic fiber composition is in a form selected from the group consisting of fabric (woven, knitted, or nonwoven), yarn, fibers, filaments, microfibrils, and nanofibers.
47. A cellulosic material having improved hydrophobicity, said cellulosic material comprising a cellulosic fiber composition according to claim 44.
48. The cellulosic material according to claim 47, wherein the cellulosic material is selected from the group consisting of viscose rayon, paper, liquid crystalline cellulose, cellulose acetate, lyocell fibers such as Tencel[®], bacterial cellulose and all plant based cellulosic fibers such as wood pulp based microfibrils and jute, kenaf, ramie, sisal, flax, pineapple, and banana, as well as yarns and fabrics made using them.

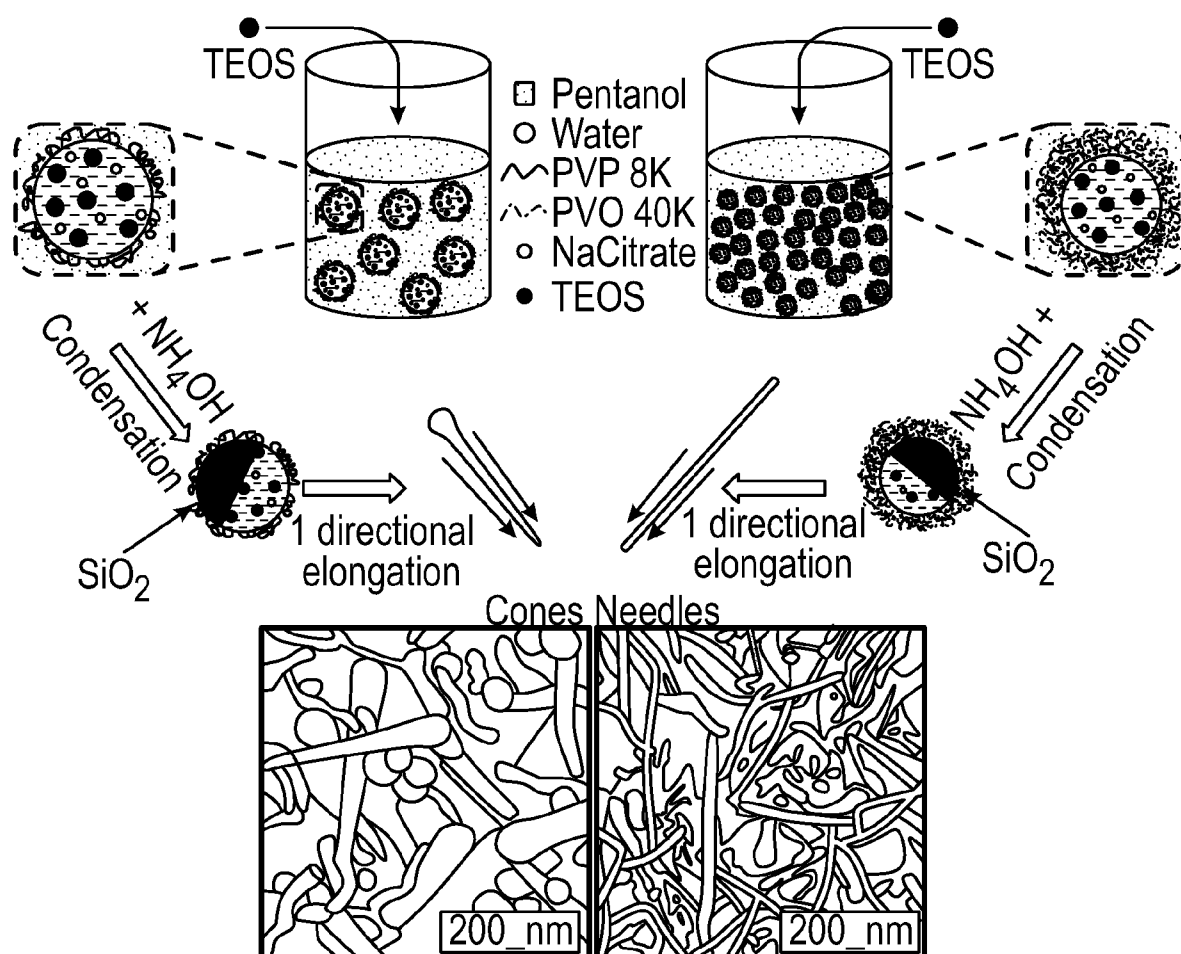


FIG. 1

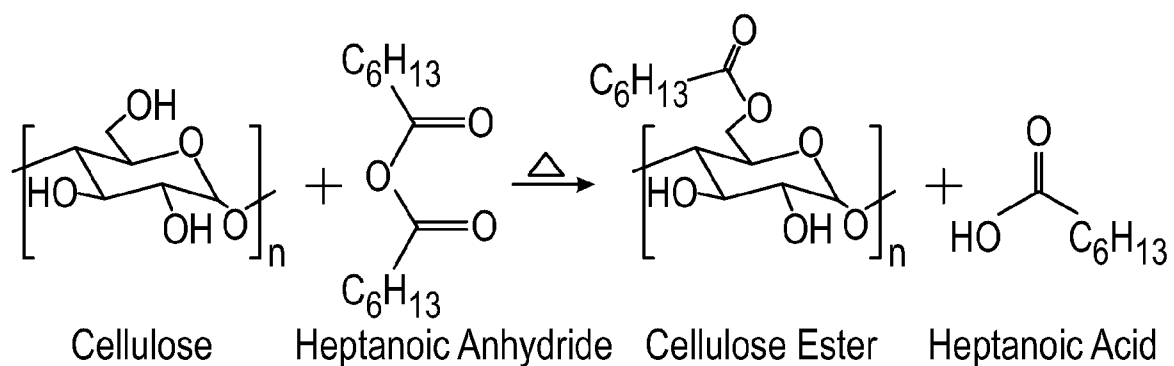
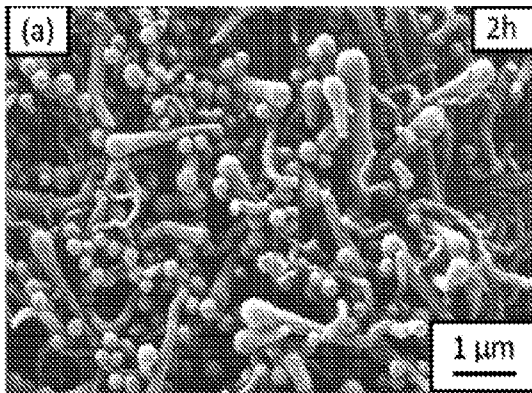
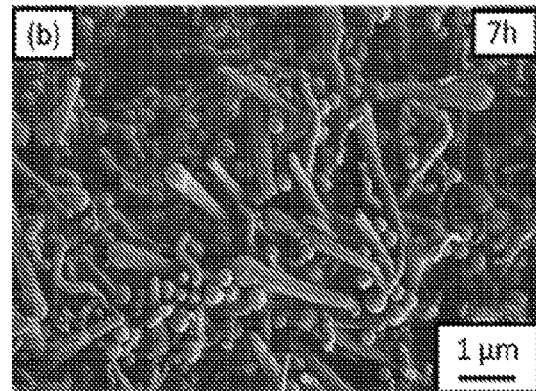
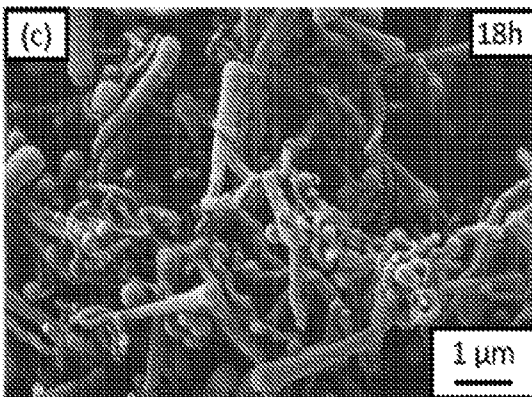
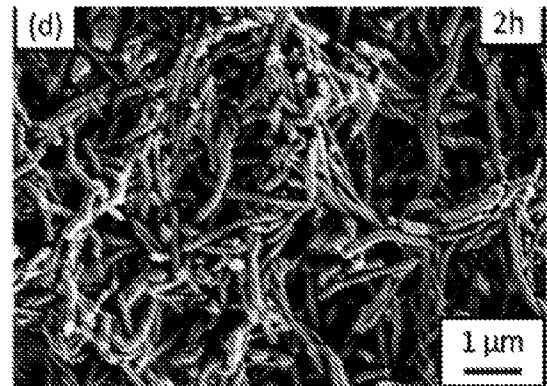
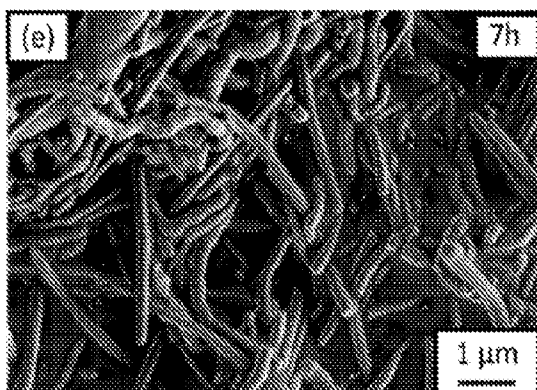
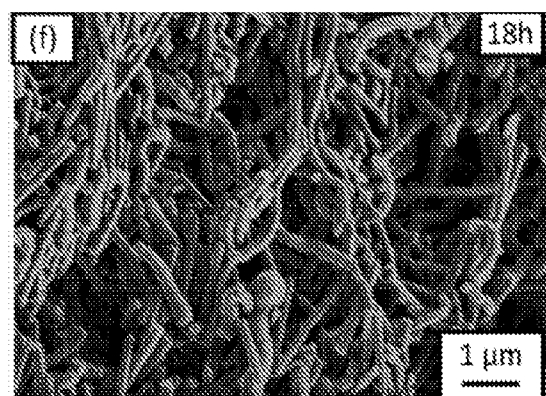
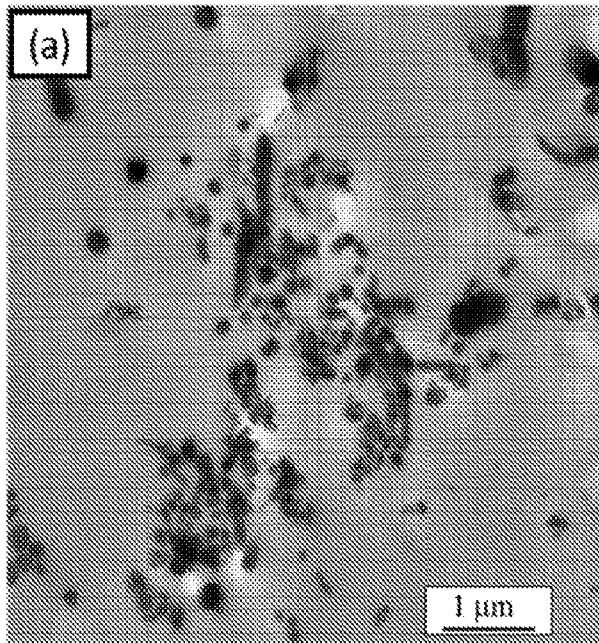
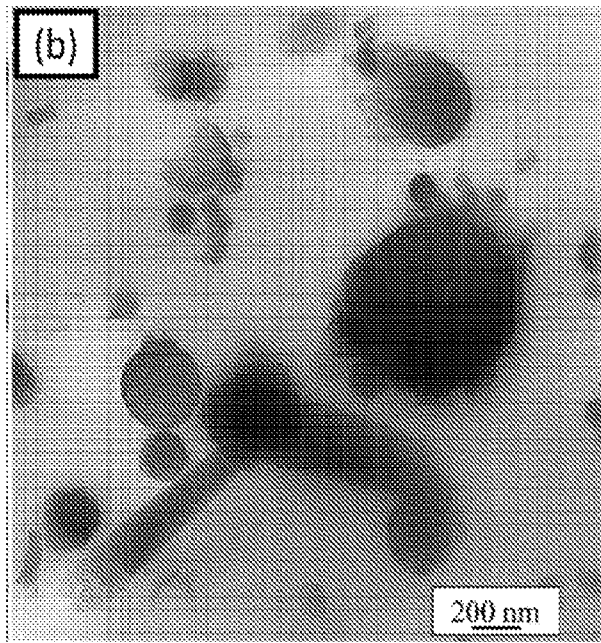
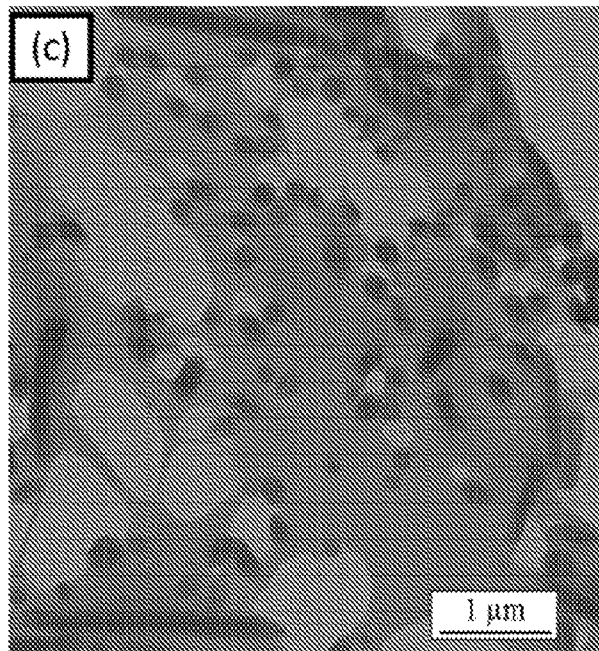
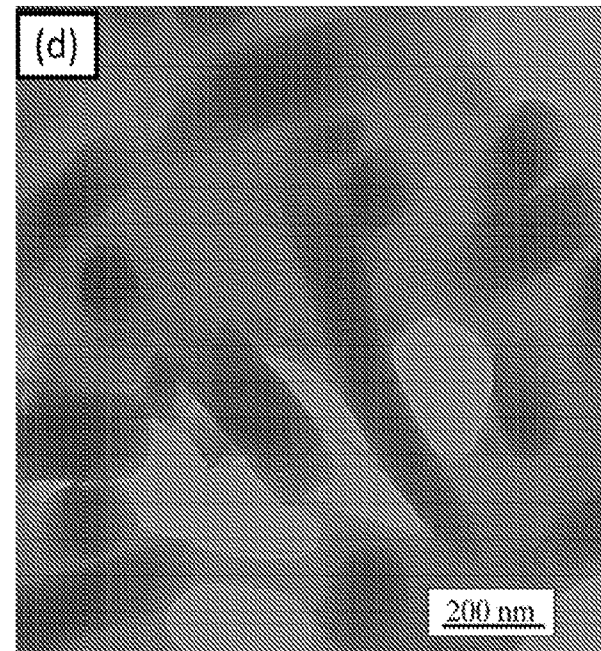
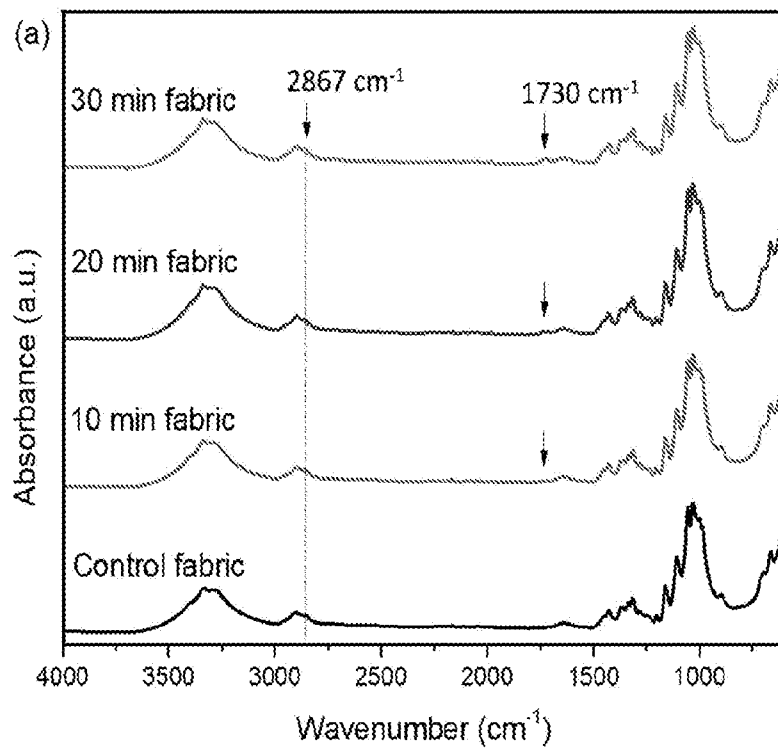
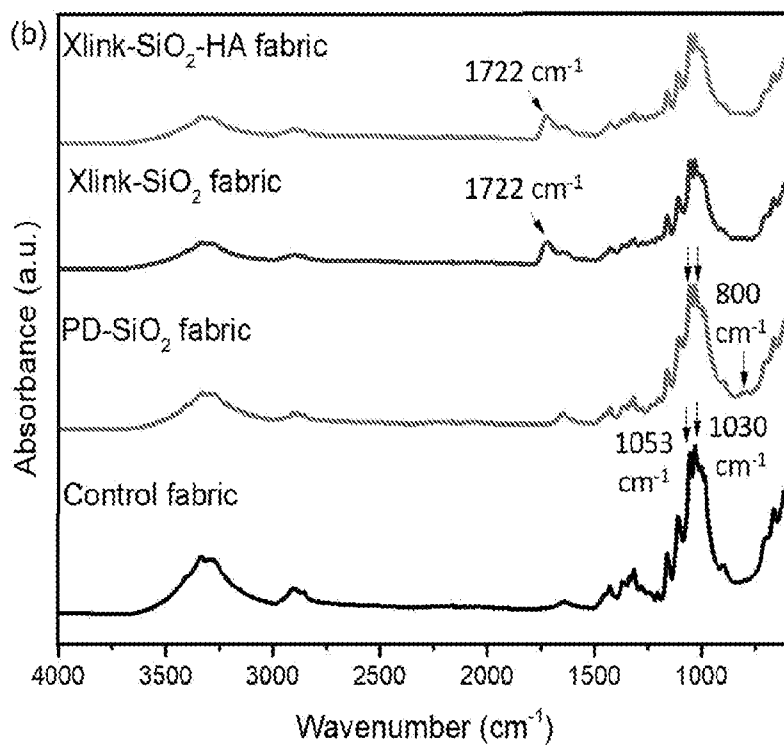
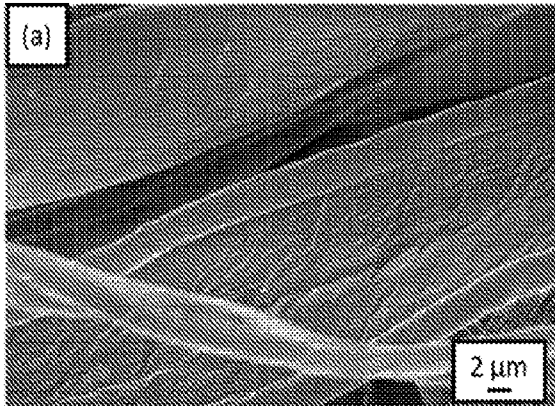
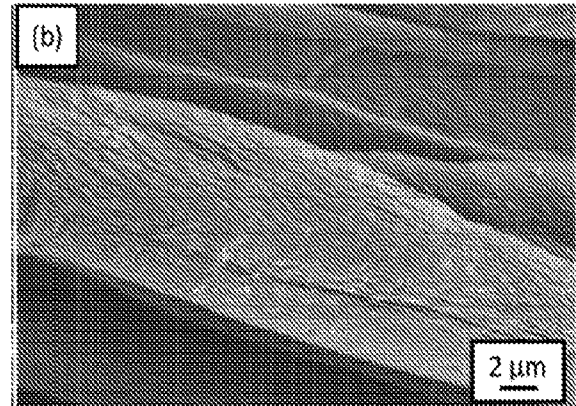
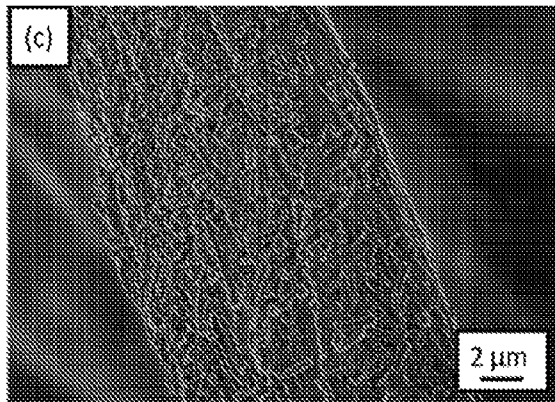
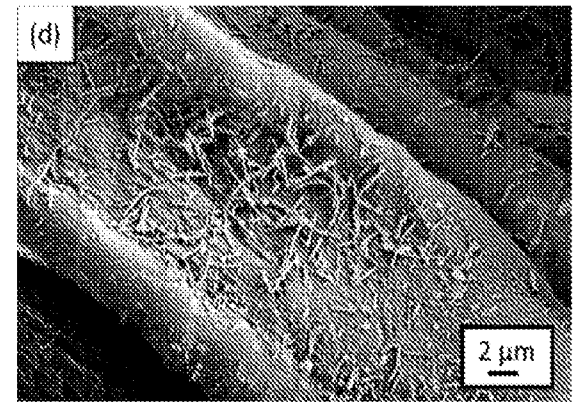
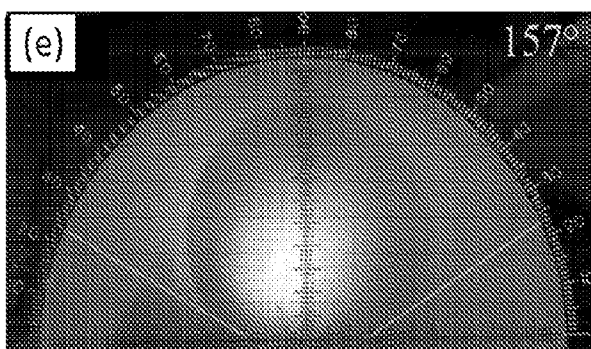
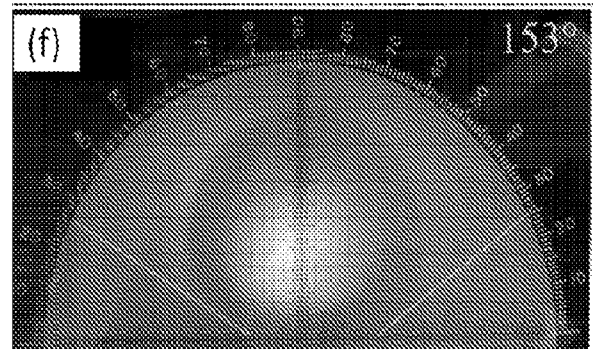


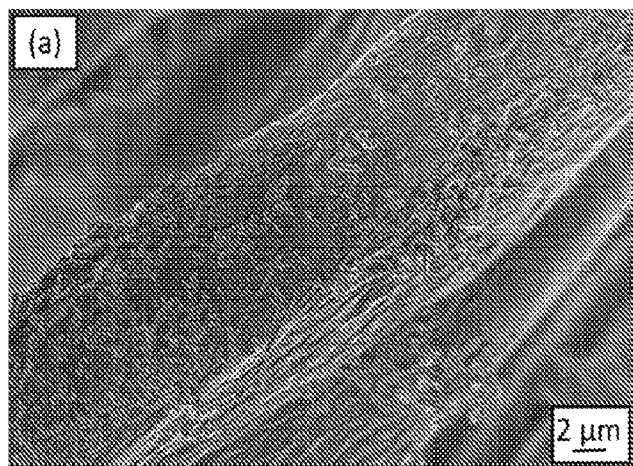
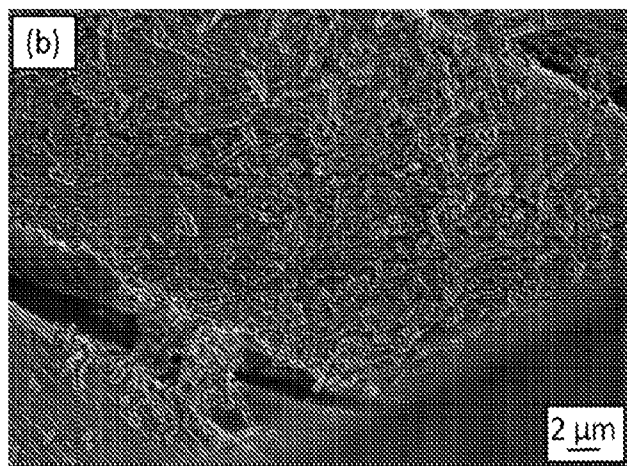
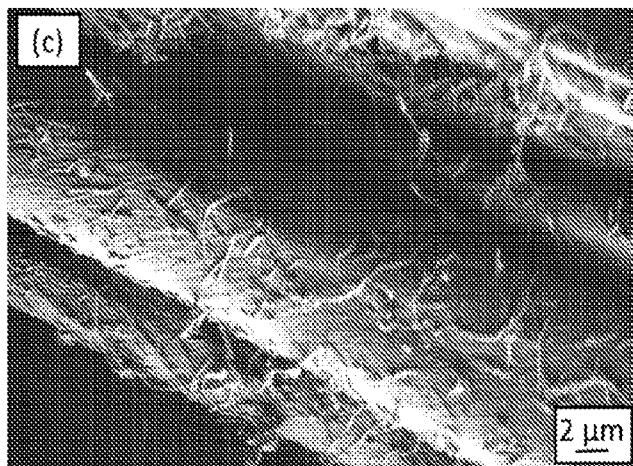
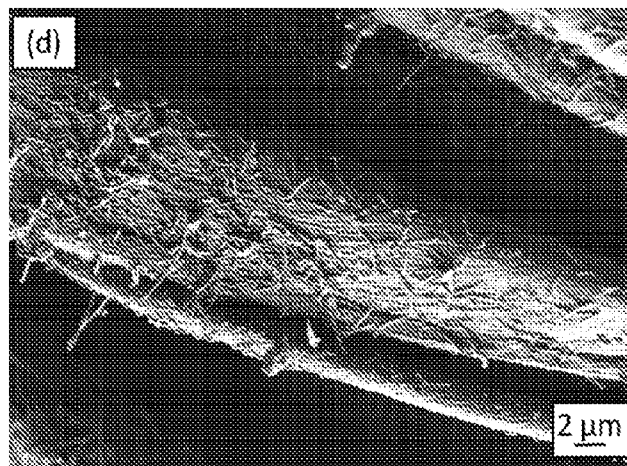
FIG. 2

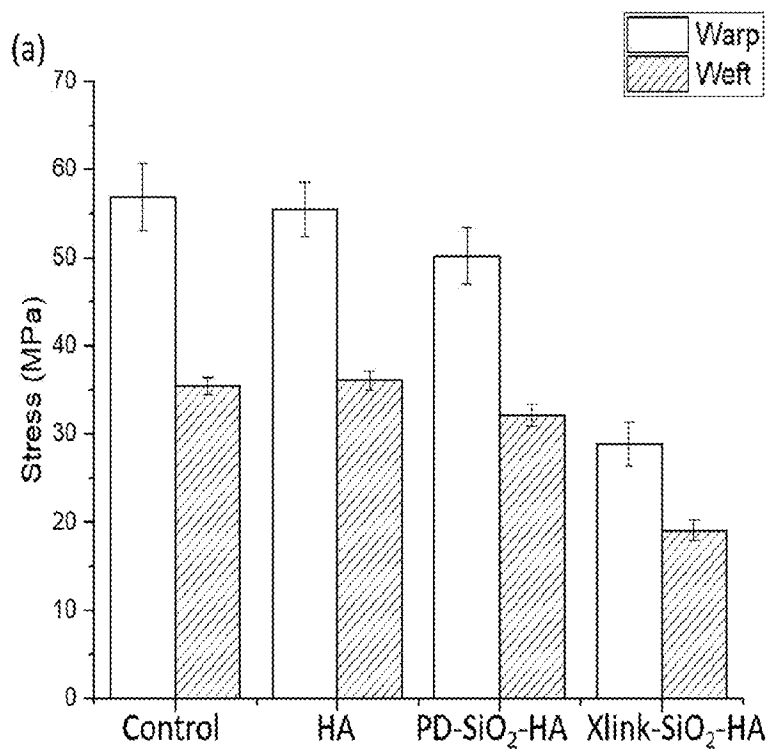
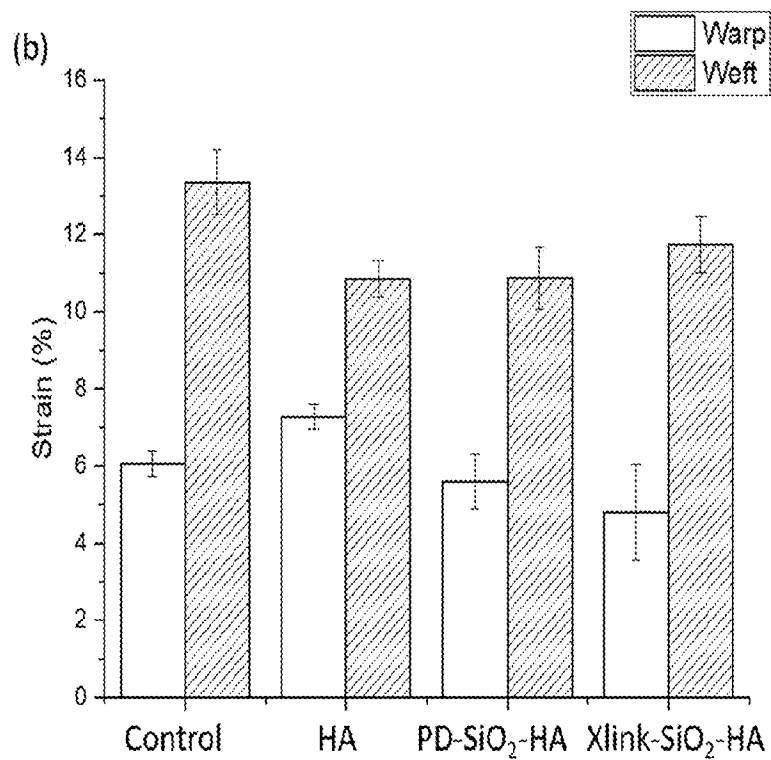
*FIG. 3A**FIG. 3B**FIG. 3C**FIG. 3D**FIG. 3E**FIG. 3F*

**FIG. 4A****FIG. 4B****FIG. 4C****FIG. 4D**

**FIG. 5A****FIG. 5B**

*FIG. 6A**FIG. 6B**FIG. 6C**FIG. 6D**FIG. 6E**FIG. 6F*

*FIG. 7A**FIG. 7B**FIG. 7C**FIG. 7D*

**FIG. 8A****FIG. 8B**

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 20/32279

A. CLASSIFICATION OF SUBJECT MATTER

IPC - B29C 70/12; C08L 1/08; C08L 67/04 (2020.01)

CPC - B29C 70/12; B42D 25/29; C08J 3/005; C08L 1/02

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.
Y	US 2018/0119334 A1 (Cornell University) 03 May 2018 (03.05.2018) para [0011], [0012], [0013], [0016], [0075], [0076], [0078], [0079], [0084], [0091], [0099], [0195], [0201], [0228], [0352], [0355], [0357], [0360], [0363]	1-48
Y	US 2019/0106611 A1 (The Trustees of the University of Pennsylvania) 11 April 2019 (11.04.2019) Abstract, para [0053], [0069]	1-48
Y	Yu et al., 'Synthesis of anisotropic silica colloids', RSC Adv., 2017, 7, 37542-37548, doi: 10.1039/C7RA02835K, Abstract	35-38
A	Xue et al., 'Superhydrophobic surfaces on cotton textiles by complex coating of silica nanoparticles and hydrophobization', Thin Solid Films, Vol: 517, Issue: 16, Page: 4593-4598, doi: 10.1016/j.tsf.2009.03.185, entire document	1-48
A	CN 101768856 A (Univ Shaanxi Science & Tech) 07 July 2010 (07.07.2010) entire document	1-48
X, E	Patil et al., 'Bioinspired process using anisotropic silica particles and fatty acid for superhydrophobic cotton fabrics', Cellulose 27, 545-559 (2020). doi: https://doi.org/10.1007/s10570-019-02811-4, entire document	1-48

☐ 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 "D" document cited by the applicant in the international application "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
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Date of the actual completion of the international search
27 July 2020

Date of mailing of the international search report
10 AUG 2020

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