Cellulose
https://doi.org/10.1007/s10570-019-02811-4

ORIGINAL RESEARCH

Bioinspired process using anisotropic silica particles and fatty acid for superhydrophobic cotton fabrics

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Received: 23 July 2019 / Accepted: 23 October 2019

Abstract Superhydrophobic cotton fabrics having lotus leaf-like dual scale surface roughness 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 high 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.

Keywords Anisotropic SiO_2 particles · Surface roughness · Durable superhydrophobic cotton fabrics · Polyvinyl pyrrolidone (PVP) · Fatty anhydride · Low surface energy

Introduction

Cotton fibers are made-up of cellulose, the most abundantly produced and 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 fibers, fabrics, non-woven mats, paper, micro- and nano-fibrillated cellulose, nano-crystalline cellulose, bacterial

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Electronic supplementary material The online version of this article (https://doi.org/10.1007/s10570-019-02811-4) contains supplementary material, which is available to authorized users.

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cellulose, etc., has been on the rise (Yasim-Anuar et al. 2019). 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 (Onur et al. 2019). Some common characteristics of the products made using cellulose are light weight, flexible, portable and sustainable (Jonoobi et al. 2010; Korhonen et al. 2011; Li et al. 2013, 2018; Mulyadi et al. 2016; Rodionova et al. 2011; Sai et al. 2015; Sehaqui et al. 2014; Shimizu et al. 2014; Song et al. 2014). However, as a result of the extensive amount of hydroxyl groups present in cellulose the products made with it are inherently hydrophilic. They absorb significant amount of moisture causing them to swell and lose their stiffness and strength, very undesirable characteristics 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 based materials (Afzal et al. 2014; Chen et al. 2019; Maity et al. 2010; Zhao et al. 2012).

Superhydrophobic surfaces which exhibit water contact angles (WCAs) greater than 150° are a natural phenomenon found in many plant leaves, the most prominent examples being lotus leaf, and some insects such as the water strider legs (Zimmermann et al. 2008). 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 (Zimmermann et al. 2008). 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 SiO_2, ZnO, TiO_2, Ag, Au, CeO_2, CuO, followed by chemical treatments to create hydrophobic surfaces using low surface energy fluorinated compounds such as Perfluorooctanoic acid (PFOA), fluoroalkylsilane and other fluorochemicals (Chen et al. 2019; Deng et al. 2010; Duan et al. 2011; Khalil-Abad and Yazdanshenas 2010; Molina et al. 2017; Wang et al. 2011; Yang et al. 2018b). 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 (Molina et al. 2017; Zhao et al. 2012).

Most of the techniques mentioned above do need expensive instrumentation or hazardous solvents such as tetrahydrofuran and N,N-dimethylformamide (Jiang et al. 2018). 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 (Jiang et al. 2018; Yang et al. 2018a). 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.

The main aim of the present research 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 (sphere + cone and needle) of silica (SiO_2) 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 SiO_2 particles on the surface creates micro-structured pockets that act as airgaps at the interface between the fabric and the water droplet, enhancing the WCA of the fabrics (Athauda and Ozer 2012; Hoefnagels et al. 2007). The combined effects of surface roughness created by two different types of

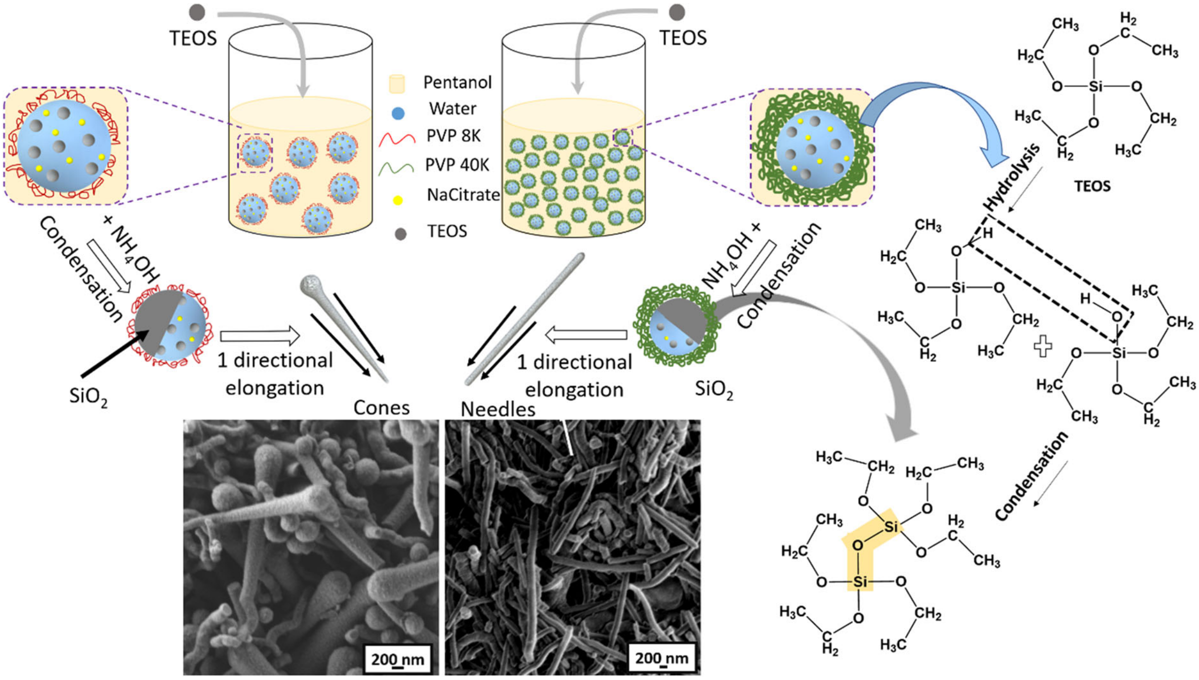

Fig. 1 Schematic representation of the colloidal syntheses of anisotropic SiO_2 particles using two different molecular weights of PVP

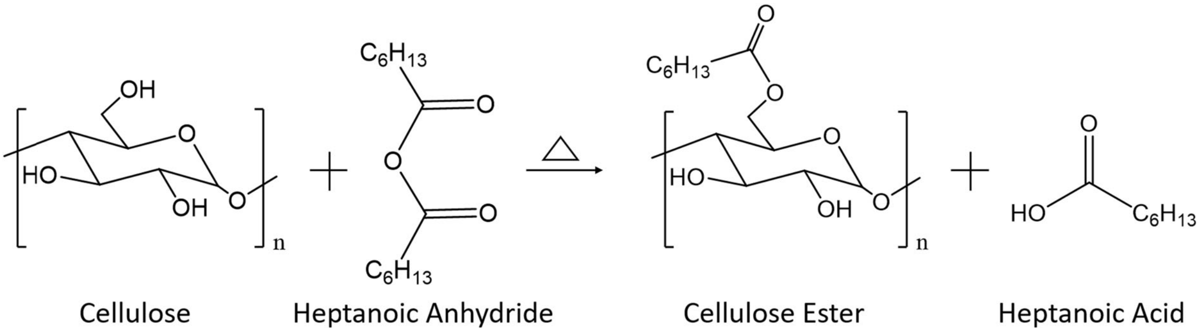

Fig. 2 Chemical reaction between cellulose and heptanoic anhydride via esterification

SiO_2 particles and the low surface energy caused by the aliphatic chains on the hydrophobicity of the fabrics were studied.

Experimental

Materials

Desized and bleached plain weave cotton fabric (#400) was purchased from Testfabrics, Inc, PA. Tetraethyl orthosilicate, 98% (TEOS), PVP (MW 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 ($\geq$ 99.5% purity, absolute), sodium citrate, ammonium hydroxide ($\sim$ 28% NH_4OH), 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.

Synthesis of anisotropic SiO_2 particles

Two g of PVP, both 8 K and 40 K 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 NH_4OH, 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.

Hydrogen bonding versus covalent bonding of anisotropic SiO_2 particles on to cotton fabrics

The SiO_2 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% SiO_2 particle dispersion for 10 min and dried in an air-circulating oven at 130 °C for 20 min to get SiO_2 particles immobilized on the fabrics based on hydrogen bonding. These hydrogen bonded fabrics are termed as physically deposited SiO_2 (PD-SiO_2). SiO_2 particles were covalently bonded to cotton fabric surface using BTCA. To obtain covalent bonding, cotton fabrics were immersed in 0.1% SiO_2 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-SiO_2.

Grafting of fatty acid onto cotton fabrics

Control fabrics as well as PD-SiO_2 and Xlink-SiO_2 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 SiO_2 particles and treated with HA are termed as PD-SiO_2(cones)-HA fabrics and PD-SiO_2(needles)-HA fabrics, respectively. The covalently bonded sphere + cone-shaped and needle-shaped SiO_2 particles on cotton fabrics and further treated with HA are termed as Xlink-SiO_2(cones)-HA fabrics and Xlink-SiO_2(needles)-HA fabrics, respectively.

Characterization

Scanning electron microscopy (SEM)

The surface morphologies of synthesized SiO_2 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.

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

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 SiO_2 particles as well the aliphatic fatty chains onto the cotton fabrics. Each scan was an average of 300 scans from 4000 to 500 cm^{-1} wavenumbers.

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.

Laundering durability

Laundry durability evaluation was carried out using a slightly modified version of 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.

Tensile properties

Tensile strength of the fabrics was determined according to ASTM D5035 strip method. Fabric specimens 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 4 min^{-1}). Six specimens each from different areas of the fabrics in both warp and weft directions were tested to obtain average values.

Results and discussion

Mechanistic insight into synthesis of anisotropic SiO_2 particles

Stöber process has been widely used since 1968 to create sphere-shaped silica particles (Wang et al. 2010). However, apart from the conventional spherical particles, it has been possible to create anisotropic silica particles from an emulsion containing alcohol and water (Brijitta et al. 2017). 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 (Longbottom et al. 2015). Anisotropic colloidal silica particles exhibit many advantages such as high surface area, biocompatibility, low toxicity, optical transparency and others (Chen et al. 2017). Due to such advantages, anisotropic silica particles have found applications in diverse fields that include catalysis, biomedical, photonic crystals, imaging sensors, coatings, electronics and many others (Guerrero-Martínez et al. 2010; Li et al. 2014; Yi et al. 2016). However, the use of anisotropic particles has been limited in the field of textiles. In this study, two distinct anisotropic morphological silica particles (sphere + cone and needle), were obtained by using different molecular weights of PVP. For this, 8 K and 40 K 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 (Kyrychenko et al. 2015; Maruthamuthu and Sobhana 1979). 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 by Zhang et al. (2008a). 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 (Wang and Lu 2016). The silica precursor, TEOS, when added to the emulsion, goes to the water phase and gets hydrolyzed (Brijitta et al. 2017). 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 (Brijitta et al. 2017). Figure 3 shows the SEM images of the particles made using 8 K and 40 K PVP after different reaction times. It was observed that 8 K PVP resulted in cone-shaped SiO_2 particles along with some nanospheres whereas 40 K PVP resulted in needle-shaped SiO_2 particles. As stated, 8 K PVP resulted in a

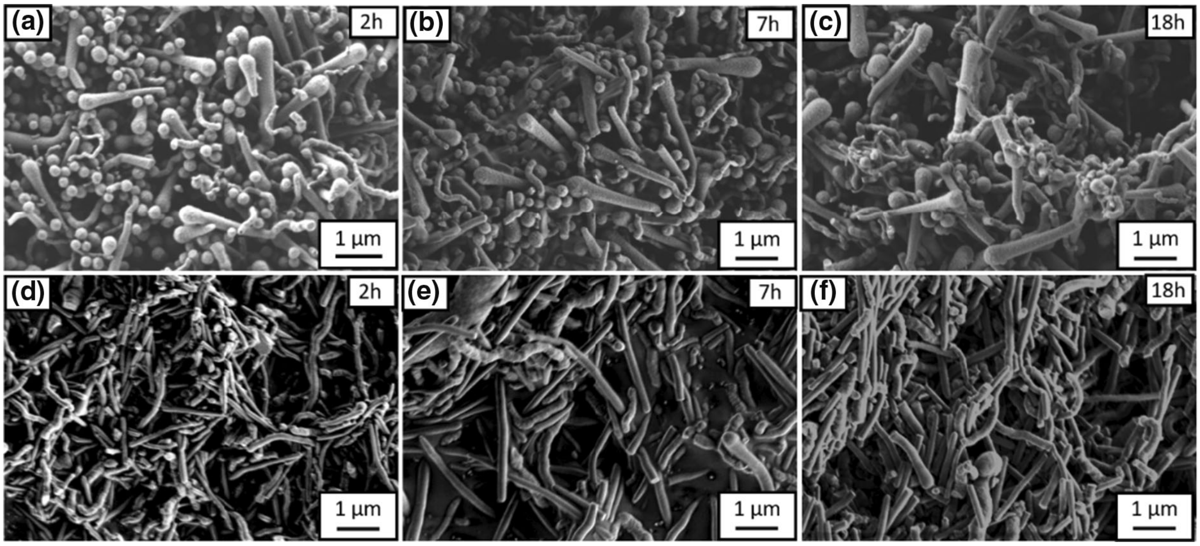

Fig. 3 SEM images of **a–c** sphere + cone and **d–f** needle-shaped particles after different reaction times (2 h, 7 h, and 18 h)

mixture of nanospheres and cones, as not all the spheres could elongate to form cones. At the end of 18 h, 40 K PVP resulted in all needle-shaped particles (no sphere-shaped particles observed) while 8 K PVP resulted in 86% cone-shaped particles and 14% sphere-shaped particles. It was observed that the shape and morphology of the sphere + cone or needle-shaped particles did not change with the reaction time from 2 to 18 h. However, it was observed that the particle yield increased with time and, as a result, the suspension got cloudier. 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 40 K PVP has longer chain lengths and higher molecular entanglements as compared to 8 K PVP. This may be a factor why 40 K 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.

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 SiO_2 particles such as rods, tubes or cones (Kyrychenko et al. 2015; Longbottom et al. 2015; Zhang et al. 2008a). The present study, however, clearly shows that the formation of anisotropic SiO_2 is independent of presence of such expensive particles and the morphology of the SiO_2 particles is tunable using different MWs of PVP (Kyrychenko et al. 2015; Longbottom et al. 2015; Zhang et al. 2008a). Overall, it was observed that keeping all other emulsion parameters (reactant ratios and stirring speed) constant and varying the MWs of PVP gave different shapes and sizes of SiO_2 particles. This suggests that factors such as initial droplet size, terminal droplet stability and the subsequent nucleation and growth of the SiO_2 particles are influenced by the molecular chain length and the resultant entanglements of PVP (Murphy et al. 2017).

Figure 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.

Effect of heptanoic anhydride treatment on cotton fabrics

Figure 5 shows ATR-FTIR spectra of control and treated cotton fabrics. Figure 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.

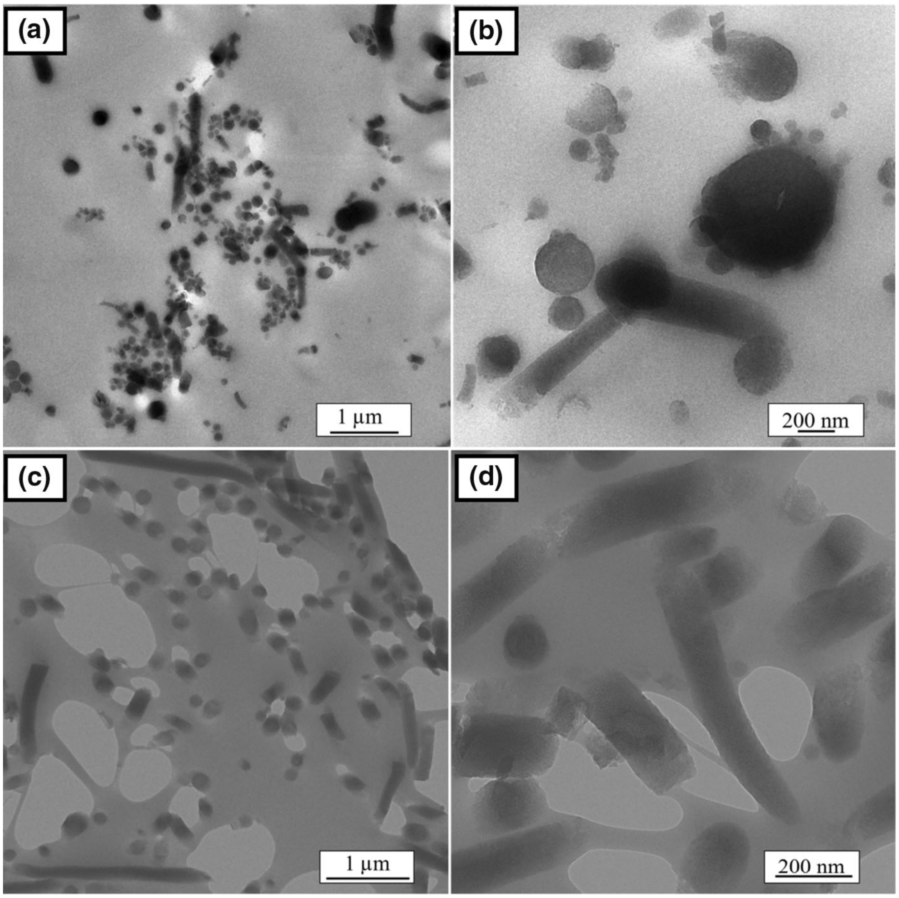

Fig. 4 Cross-sectional TEM images of **a**, **b** sphere + cone and **c**, **d** needle-shaped particles at different magnifications

Control cotton fabrics show a broad peak between 3400 and 3200 cm^{-1} which is due to the stretching of hydroxyl groups in cellulose as well as the absorbed moisture (Zhao et al. 2010). The peak at 2902 cm^{-1} is due to the symmetric C–H and C–H_2 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 cellulosic materials (Xue et al. 2008). 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 (David et al. 2019; Dankovich and Hsieh 2007; Zhong and Netravali 2016). 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 fabric 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. Dankovich and Hsieh grafted eighteen-carbon aliphatic chains onto cotton fabrics using stearic acid dissolved in ethanol to get a WCA of only 40° (Dankovich and Hsieh 2007). This is because fatty acids have extremely low reactivity towards the

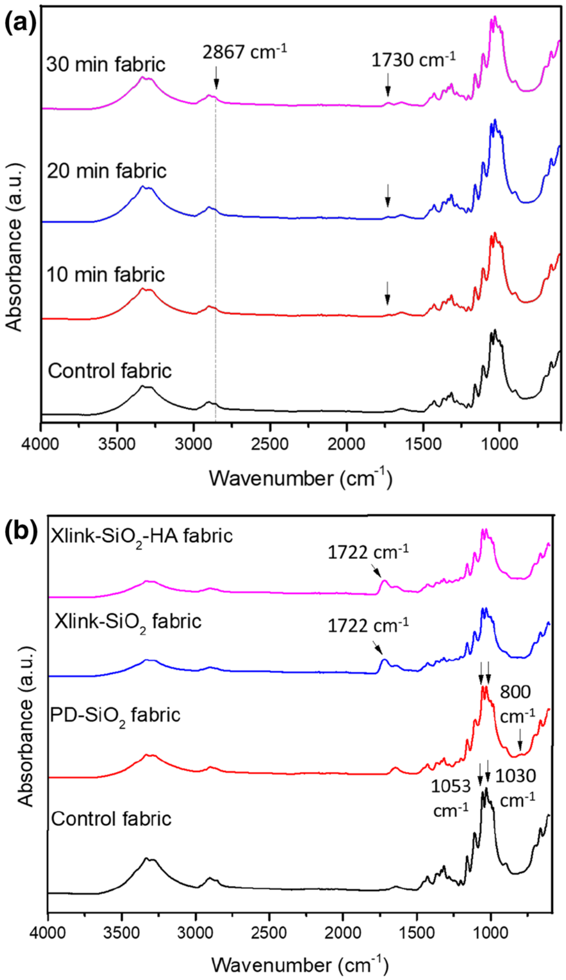

Fig. 5 ATR-FTIR spectra of cotton fabrics treated with **a** HA for 10, 20 and 30 min, **b** Control, PD-SiO_2, Xlink-SiO_2 and Xlink-SiO_2-HA fabrics treated for 30 min

hydroxyl groups of the cellulose (Dankovich and Hsieh 2007; Samyn et al. 2013). 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.

Effect of SiO_2 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°) (Zhang et al. 2008b). Two different shapes, cone + sphere or needle, of SiO_2 particles were physically deposited and covalently bonded, in separate processes, onto the cotton fabrics to change the surface topography. Figure 5b shows ATR-FTIR spectra of PD-SiO_2 fabrics and Xlink-SiO_2 fabrics. As seen in Fig. 5b, an additional small peak is observed in both physically deposited and covalently bonded SiO_2 cotton fabrics at 800 cm^{-1}. This peak is the characteristic stretching vibration peak for Si–O–Si from the SiO_2 particles as seen from the chemical structure in Fig. 1 (Lin et al. 2019; Singh and Singh 2017). 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 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 (Zhao et al. 2010). However, after the SiO_2 treatment, the intensity of peak at 1053 cm^{-1} increases (Fig. 5b). This peak is due to the presence of Si–O–Si from the SiO_2 particles. An additional peak at 1722 cm^{-1} is observed in the Xlink-SiO_2 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 (Gashti et al. 2012; Huang et al. 2010; Huang et al. 2011; Menaa et al. 2006). BTCA has four carboxylic acid groups which can react with the hydroxyl groups on both, SiO_2 particles as well as cellulose from the cotton fabric and act as a crosslink (bridge) between the two. This covalent bonding between SiO_2 particles and fabrics prevents these particles from leaving fabric during use and laundering and, thus, increases the washing durability. Physical deposition of the SiO_2 particles as well as covalent bonding of SiO_2 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.

The WCA for Xlink-SiO_2(cones)-HA (8 K PVP) fabrics was found to be 157° and Xlink-SiO_2(needles)-HA (40 K PVP) fabrics was found to be 153°. Figure 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

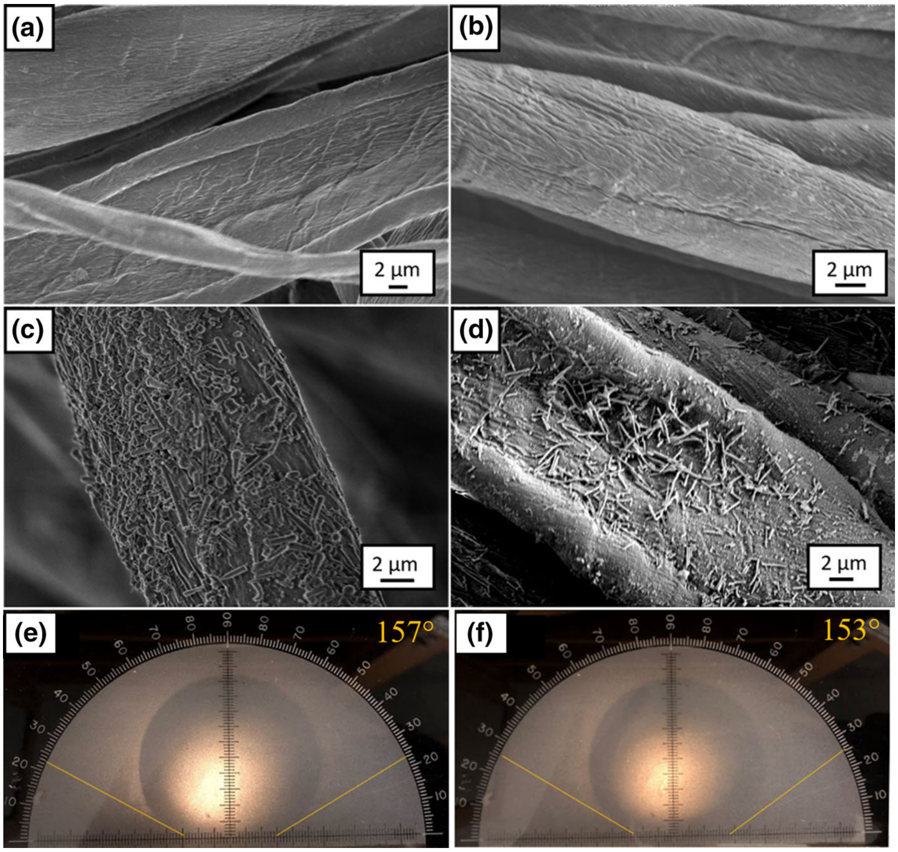

Fig. 6 SEM images of **a** control, **b** HA, **c** Xlink-SiO_2(cones)-HA, **d** Xlink-SiO_2(needles)-HA fibers and digital photographs of the WCA for **e** Xlink-SiO_2(cones)-HA, **f** Xlink-SiO_2(needles)-HA fabrics

convolutions and natural creases and does not change after the HA treatment (Fig. 6b). The Xlink-SiO_2(cones)-HA and Xlink-SiO_2(needles)-HA fibers (Fig. 6c, d) show that the surface of the fibers is coated with SiO_2 sphere + cone and needle-shaped particles, respectively. This changes the surface topography of the fabrics and creates a desired surface roughness. The combination of surface roughness created by the SiO_2 particles and 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-SiO_2(cones)-HA as compared to Xlink-SiO_2(needles)-HA. This is because of the presence of nanospheres that are mixed with the micrometer size cone-shaped SiO_2 particles which together create a dual surface roughness on the fabrics, creating a ‘petal effect’ explained by many researchers (Ebert and Bhushan 2012; Feng et al. 2008). The dual size roughness creates numerous air-pockets that entrap a layer of air between SiO_2 particles and water droplet further enhancing the WCA (Athauda and Ozer 2012; Hoefnagels et al. 2007; Patil and Netravali 2019).

The concentration of the SiO_2 particles used to treat the cotton fabrics was varied from 0.05% to 0.5%. Table S1 in the supplementary material shows the effect of SiO_2 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. Figure S1 in the supplementary material shows the SEM images of Xlink-0.5% SiO_2(cones)-HA and Xlink-0.5% SiO_2(needles)-HA. Some particle clusters can be observed at 0.5% SiO_2 concentration in fabrics treated with both sphere + cone and needle-shaped particles.

Lin et al. used O_2 plasma to activate cotton fabrics and then deposited irregular shaped ammonium polyphosphate particles via hydrogen bonding and further coated the fabrics with TEOS and polydimethylsiloxane (PDMS) to achieve WCA 162° (Lin et al. 2019). Bae et al. physically deposited spherical shaped SiO_2 particles of two different diameters (143 and 378 nm) to create dual size roughness followed by treatment with perfluoroacrylate-based commercial water-repellent agent to get WCA 130° (Bae et al. 2009). Wen et al. deposited iron stearate, copper stearate and zinc stearate onto paper to get yellow, blue and white colored superhydrophobic paper with WCA of 153°, 154° and 151° respectively (Wen et al. 2017). The process developed in this study obtains comparable WCAs using fully sustainable and 'green' raw materials.

Table 1 lists some state-of-the art methods of creating superhydrophobic surfaces using SiO_2 particles. As seen from Table 1, SiO_2 particles have been used earlier to create roughness on the desired surfaces such as cotton fabrics and others. SiO_2 particles are generally synthesized using TEOS as in this research. However, tetramethyl orthosilicate (TMOS) and sodium silicate have also been used to obtain SiO_2 particles by other researchers (Yang et al. 2014; Zulfiqar et al. 2016). NH_4OH has been commonly used for condensation of TEOS by other studies mentioned in Table 1 as well as in this study. However, the studies mentioned below only lead to sphere-shaped SiO_2 particles of different sizes. The use of PVP in this research facilitates elongation of spherical particles, thus producing different shapes such as cones and needles. As seen from Table 1, together with SiO_2 particles and the hydrophobic chemical agent, superhydrophobic surfaces with WCA of 150° can be achieved.

Laundry durability of the superhydrophobic fabrics

Table 2 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 2, 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 cross-linked particles as could be expected. The WCA decreased from 157° to 148° for the PD-SiO_2(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-SiO_2(cones)-HA samples which was statistically insignificant using unpaired t-test at a significance level of 0.05. Figure 7 shows the SEM images of fibers after 7 laundry cycles. As seen in Fig. 7a, the surface

Table 1 Comparison of different methods to achieve superhydrophobic surfaces using SiO_2 particles

Chemicals used for synthesis by modified Stöber method	Synthesis time (h)	SiO_2 particle shapes and size	Hydrophobic agent	Substrate	WCA (°)	References
2-propanol, TEOS, NH_4OH	1	Spherical 800 nm	Cyclohexane, methyl trichlorosilane	Cotton fabric	173	Dashairya et al. (2019)
TEOS, NH_4OH	2	Aggregated spherical 50 nm each	Dodecyltrimethoxysilane	Cotton fabric	159	Shang et al. (2018)
TMOS, HCl	6	Nano size coating	NA	Polypropylene membrane	Hydrophilic	Yang et al. (2014)
Sodium silicate, methanol,	2.5	Spherical 48 to 260 nm	Trimethylchlorosilane	Cotton fabric	158	Zulfiqar et al. (2016)
1-pentanol, TEOS, NH_4OH Sodium citrate PVP	18	Sphere + Cone and Needle-shaped	Heptanoic anhydride	Cotton fabric	157	This research

Table 2 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

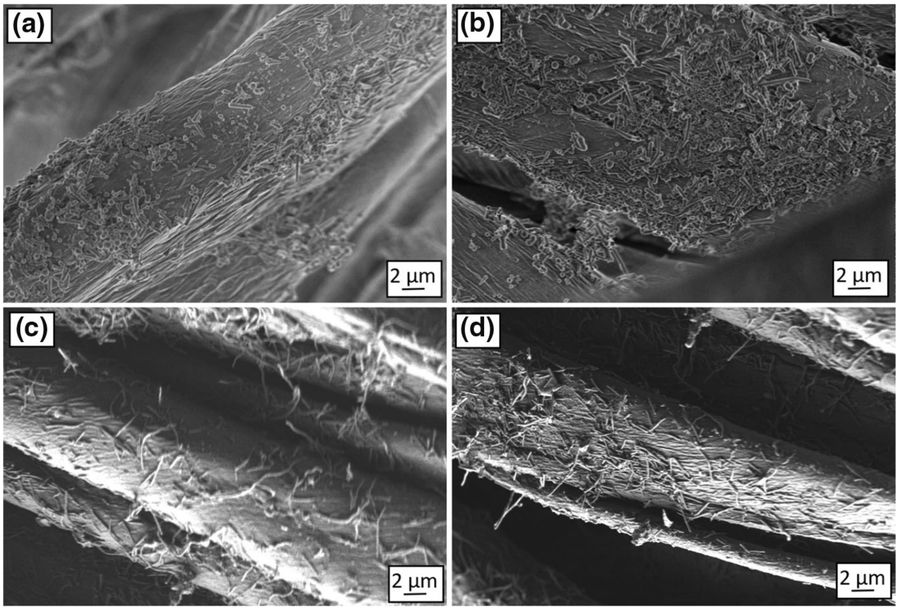

Fig. 7 SEM images of **a** PD-SiO_2(cones)-HA, **b** Xlink-SiO_2(cones)-HA, **c** PD-SiO_2(needles)-HA, and **d** Xlink-SiO_2(needles)-HA fibers after 7 laundry cycles

of the physically deposited fibers is only partially covered with cone-shaped particles 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 SiO_2 particles can be immobilized in the cotton fabrics by heat treatment (Bae et al. 2009). 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 the SEM image in Fig. 7b which shows that majority of the fiber is still covered with the SiO_2 particles after 7 laundry cycles. Similar effect was observed for the fabrics treated with needle-shaped particles as can be seen in the SEM images shown in Fig. 7c and d. Both, Xlink-SiO_2(cones)-HA and Xlink-SiO_2(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.

Tensile properties of the superhydrophobic fabrics

Figure 8 shows the effect of superhydrophobic treatment on the fracture (tensile) 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 the fabrics as it is simply a surface treatment and has no effect on the fiber morphology. Figure 8b shows the effect

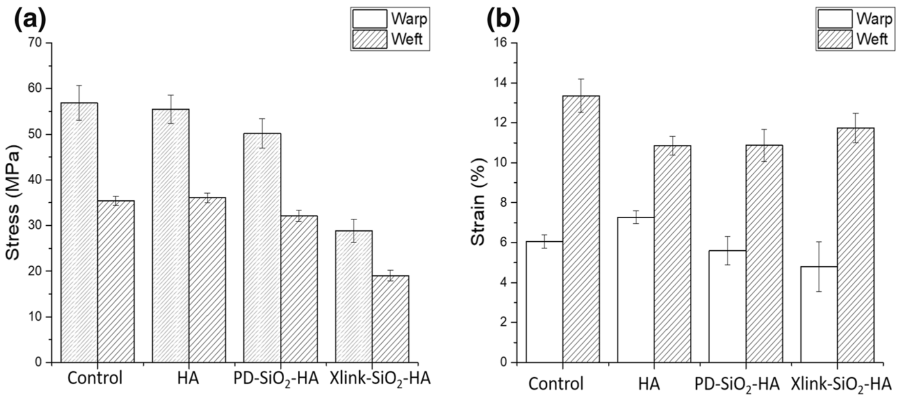

Fig. 8 Effect of Superhydrophobic treatment on **a** stress and **b** strain of the fabrics

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-SiO$_2$-HA and Xlink-SiO$_2$-HA fabrics reduced to 50.2 MPa and 29 MPa, respectively. The slight reduction in the tensile stress of the PD-SiO$_2$-HA fabric could be due to the heat treatment. The reduction in tensile stress in the Xlink-SiO$_2$-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-SiO$_2$-HA fabrics (Ji et al. 2016). Similar behavior was observed in the weft direction as can be seen in Fig. 8. The tensile stress of the fabrics reduced significantly (49% in warp direction and 44% in weft direction) only after using a crosslinker to bond the particles. The crosslinker also crosslinks cotton in the fabrics and reduces the strength of the fabrics. As a result, it has been a common practice to use softeners to combat the strength reduction or brittleness of the fabrics (Bao and Yun-Jun 2018; Tang et al. 2017). In applications where crosslinking of particles is important, a softener can be added to the finishing bath to retain the strength of fabrics. In this study no such softening was carried out.

Applications

The superhydrophobic characteristic of the fabrics obtained in this research is durable to laundry washings and can find applications in various areas such as outerwear, protective clothing, medical apparel and others. Videos S1, S2, S3 and S4 included in the supplementary material show that water beads up on the surface of the treated fabrics without wetting it. Also, when held at an angle, the water simply flows down without wetting the fabric. Unfortunately, in the present case, it is difficult to obtain the exact sliding angle because of the surface hairiness of the fabrics and the 'petal effect'. However, these superhydrophobic fabrics can support applications such as 'easy-cleaning' fabrics and water-repellent clothing as demonstrated in S1, S2, S3 and S4 videos in supplementary material. The video S5 presented in the supplementary material, clearly demonstrates that the treated fabrics are oleophilic or oil absorbent. As a result, such fabrics can find applications as 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.

Conclusions

This study has shown that anisotropic SiO$_2$ particles with distinct sphere + cone or needle shapes can be obtained using different molecular weights of PVP.

The sphere + cone shaped particles when covalently bonded onto the surface of the cotton fabrics created a durable lotus-leaf like dual size roughness on the fabric surface. Further grafting of fatty acid onto the fabric surface lowered their surface energy. The combination of dual surface roughness and low surface energy resulted in creating durable superhydrophobic fabrics with WCA of 157°.

Anisotropic SiO_2 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 in the past (Bae et al. 2009; Hoefnagels et al. 2007; Xue et al. 2009; Yu et al. 2007). Many researchers have also used expensive nanoparticles such as Au, metal oxides such as iron oxide or manganese oxide or chemical etching to form anisotropic silica particles (Hagemans et al. 2016; Longbottom et al. 2015; Panwar et al. 2015; Zhang et al. 2008a). However, the facile approach for synthesizing anisotropic SiO_2 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 (Bae et al. 2009). The 'green' process developed here can be easily applied to other cellulosic materials such as viscose rayon, paper and others to expand their applications including self-cleaning surfaces, water-repellent protective coatings, medical apparel, packaging, electronics, composites and many others.

Acknowledgments The authors would like to acknowledge the use of Cornell Center for Materials Research (CCMR) shared facilities supported through the NSF MRSEC program (DMR-1719875).

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