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ARTICLE

Organic Solvent-Free Fabrication of Durable and Multifunctional Superhydrophobic Paper from Waterborne Fluorinated Cellulose Nanofiber Building Blocks

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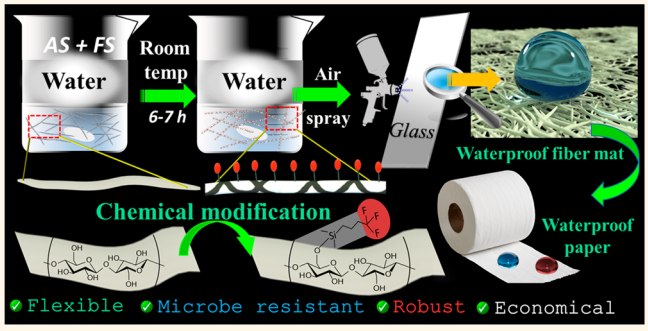
Supporting Information

ABSTRACT: In view of a great demand for paper-based technologies, nonwettable fibrous substrates with excellent durability have drawn much attention in recent years. In this context, the use of cellulose nanofibers (CNFs), the smallest unit of cellulosic substrates (5−20 nm wide and 500 nm to several microns in length), to design waterproof paper can be an economical and smart approach. In this study, an eco-friendly and facile methodology to develop a multifunctional waterproof paper *via* the fabrication of fluoroalkyl functionalized CNFs in the aqueous medium is presented. This strategy avoids the need for organic solvents, thereby minimizing cost as well as reducing safety and environmental concerns. Besides, it widens the applicability of such materials as nanocellulose-based aqueous coatings on hard and soft substrates including paper, in large areas. Water droplets showed a contact angle of 160° (±2°) over these surfaces and rolled off easily. While native CNFs are extremely hydrophilic and can be dispersed in water easily, these waterborne fluorinated CNFs allow the fabrication of a superhydrophobic film that does not redisperse upon submersion in water. Incorporated chemical functionalities provide excellent durability toward mechanochemical damages of relevance to daily use such as knife scratch, sand abrasion, spillage of organic solvents, *etc.* Mechanical flexibility of the chemically modified CNF composed paper remains intact despite its enhanced mechanical strength, without additives. Superhydrophobicity induced excellent microbial resistance of the waterproof paper which expands its utility in various paper-based technologies. This includes waterproof electronics, currency, books, *etc.*, where the integrity of the fibers, as demonstrated here, is a much-needed criterion.



KEYWORDS: *cellulose nanofibers, superhydrophobicity, durability, waterproof paper, antimicrobial material*

As a convenient way to tune the characteristic properties of various materials, surface engineering has become one of the most important research areas of recent decades. Various techniques such as plasma deposition,[1] chemical vapor deposition (CVD),[2] atomic layer deposition (ALD),[3] nanoparticle deposition,[4] and sol−gel methods[5] have been developed to create micro/nanoscale coatings that essentially control the properties of materials by introducing functionalities on the surface. Among these, developing materials with tunable surface wettability is one such interesting research direction that expanded to several potential applications such as self-cleaning,[6−8] anticorrosion,[9] water−oil separation,[10−12] anti-icing,[13−15] drag reduction,[16,17] sensing,[18,19] atmospheric water capture,[20,21] construction materi-

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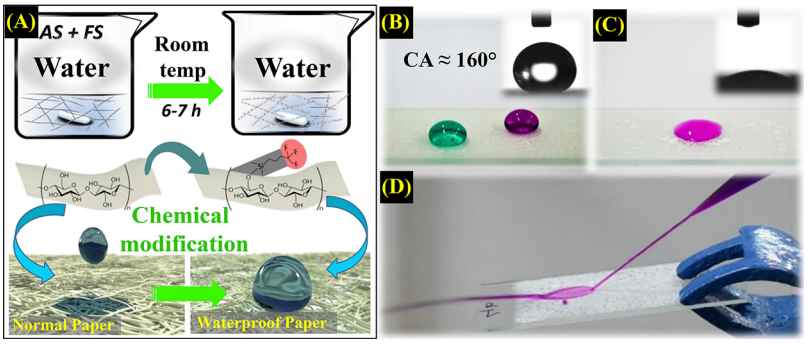

Figure 1. (A) Schematic representation of CNF-based waterborne superhydrophobic material, the building block of waterproof paper. (B and C). Water droplet on modified and native CNF-coated surface. (Inset) The static contact angle of the water droplet. (D) Continuous jet flow on coated glass. $KMnO_4$ and $NiSO_4$ aqueous solutions were used in B–D, respectively, instead of pure water to have color contrast.

als,[22] microfluidic devices,[23] smart windows,[24] *etc.* Surfaces with low surface energy also minimize bacterial adhesion which essentially prevents the growth of biofilms, known as biofouling.[25−29] Mother nature is bestowed with such surfaces which are characteristic of several species of plants, insects, animals, and birds, *etc.*[30−32] In this account, lotus leaves,[33] water striders,[31] and rose petals[32] have already been studied in great detail. Surface roughness (nano/microscale) and controlled chemical functionalities are the underlying reason for such phenomena.[34] While different approaches have been introduced,[1,23,35−39] in most of the cases, surface compatibility, complicated manufacturing processes, cost, and limitation of large-scale production restrict the use of such surfaces in real-life applications.[40] Meanwhile, availability of different chemically functionalizable materials has enhanced the interest to design such materials by wet-chemical techniques[41,42] that are applicable on various substrates of nonidentical surface morphology through easily accessible coating processes. Clays,[43] polymers,[44] oxide nanoparticles,[45] cellulosic materials,[46,47] *etc.* are often used as templates for the same. Yet, stability, strength, and adhesion of such coatings are the limiting factors.[48] For instance, small mechanical perturbations like gentle touch with tissue paper or finger wiping can damage these surfaces permanently.[49−52] The nano and/or microscale structures that support the trapped air layer get damaged easily by mechanical abrasion, leading to failure of the Cassie state of wetting. Therefore, there is a need to design a material that provides superhydrophobic films of sufficiently robust nature for real-life applications.

Cellulose-based materials being economical, green, sustainable, and biodegradable, they are increasingly investigated both in research and industry.[23,53−55] Even though the presence of a large number of functionalizable hydroxyl groups makes it hydrophilic, different forms of cellulose fibers such as napkins, papers, cotton, *etc.* are developed to exhibit nonwettable properties.[11,35,37,43,46,47,56] Recently, Zhang and co-workers and Li and co-workers have developed hydrophobic/lipophobic paper-based sensors where fibrous substrates were treated with different fluoroalkyl silane compounds to demonstrate nonwettability.[18,23] However, such surfaces have not been built starting from cellulose nanofibers (CNFs), the smallest subunit of cellulosic materials. In addition, for such materials to be industrially viable, synthesis in the aqueous medium is needed. Though a few reports on waterborne superhydrophobic materials are known,[41,43,57,58] in most of the cases, organic solvents are used extensively as the primary solvent medium[45,59,60] which limit the dispersibility of hydrophilic CNFs. In addition, use of organic solvents also raises a concern regarding the safety, environmental pollution, and cost of production. Therefore, fabrication of waterborne superhydrophobic materials starting from CNFs is desirable.

Here, an easy strategy to develop a multifunctional flexible waterproof paper through the chemical modification of hydrophilic native CNFs in water is reported. As a well-dispersed liquid material, it was also used for creating superhydrophobic coatings over various substrates. While coated surfaces show excellent durability upon various chemical and mechanical damages, incorporated functionality induces enhanced strength and integrity of the waterproof paper upon exposure to water for extensive periods. This material also exhibits inhibition to both bacterial and fungal growth in the cellulosic material. Being synthesized in water at room temperature and at neutral pH, environmental concerns are eliminated. We also demonstrated the extent of water resistivity and enhanced integrity of the waterproof paper for use in paper-based flexible electronics, the publishing industry, and currency printing. The science presented here is useful in converting waste to wealth in the form of superhydrophobic paints, packaging materials, affordable sensors, *etc.*

RESULTS AND DISCUSSION

Figure 1A illustrates the synthesis of chemically modified/fluorinated CNFs in water that forms excellent water repelling thin films upon coating over various substrates. Briefly, native hydrophilic CNFs were chemically functionalized with two different functional silanes, 1*H*,1*H*,2*H*,2*H*-perfluorooctyltriethoxysilane (FS) and 3-(2-aminoethylamino)-propyltrimethoxysilane (AS) by a wet chemical process in water at room temperature and spray coated both on hard (glass) and soft (paper) substrates. Though nanoscale cellulose fibers impart surface roughness (Figure S1), an important parameter to achieve nonwetting property, the hydroxyl groups present on such surfaces make them hydrophilic. However, these active functional groups also facilitate the covalent attachment between CNFs and silane molecules, FS and AS. Thus, a complete reversal of the hydrophilic property of cellulose not only increases the wetting resistance of the coating but also forces water to sit as a droplet (Figure 1B). This minimizes the air−water−solid interaction energy on the superhydrophobic surface, unlike unmodified CNFs-coated surface where water spreads easily (Figure 1C). The extent of the water repelling property of the coated surface was also demonstrated by rolling off or jet motion of water drops on the modified CNFs-coated substrate (Figure 1D, Video S1). This

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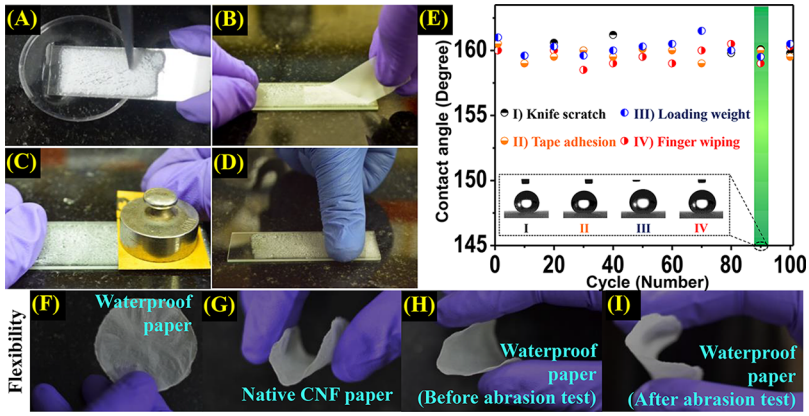

Figure 2. Mechanical damages induced on modified CNF-coated glass surface. (A) Scratching with a knife, (B) tape adhesion test, (C) sand paper abrasion with 50 g of load, and (D) finger wiping. (E) Durability test for the water repelling surface. Change in CA of water droplet during multiple abrasion cycles. One experiment consists of 10 complete abrasion cycles. (Inset) Photograph showing static contact angle of water on mechanically tested surfaces (after the 9th experiment, *i.e.*, 90th cycle). (F–I) Physical appearance and flexibility of waterproof paper before and after abrasion tests.

was further studied with a droplet drag experiment where water droplet (~2 μL) attached with a needle was dragged back and forth over the coated surface by 5 cm. Deformed shape of the water droplet during the experiment can be related to contact angle hysteresis (CAH) which is the result of fibrous structure induced macroscale roughness of the prepared film (Figure S2, Video S2). This was also observed during the roll off angle measurement. Water droplet having a volume $\geq$10 μL rolls off easily with a roll-off angle <10° (±2°). However, for smaller volume droplets, they did not either roll off or stick to the surface and immediately flew off with a gentle blow of air. Excellent water repellent property of the material was also evaluated with a vertical drop adhesion test for multiple cycles where a water droplet (~2 μL) was seen to detach from the superhydrophobic surface without leaving any trace (Figure S3, Video S3).

Modified CNF-coated superhydrophobic surfaces (glass) showed excellent durability when they were subjected to mechanical damages (presented below). These experiments also reflect the extent of adhesion of the material on different surfaces without any adhesive (*e.g.*, glass and paper). This binding ability of the material originates from the chemical functionalities incorporated in the CNFs. Tackiness of the modified CNF dispersed solution was compared with native CNF dispersion and pure water (Figure S4). CNF concentrations in both the cases (modified and native) were the same. Interestingly, water-like nature was observed for both the dispersions. In contrast, the same modified CNF forms a rugged coating that did not show any tackiness. Ruggedness of coating was studied through various methods of mechanical abrasion tests. Initially, the coated surfaces were subjected to knife scratch and peel-off tests (Figure 2A,B). Despite having a few scratches on the surface, the exposed underlying layers of the coating recover/retain a superhydrophobic nature of the surface and made water drops roll off (Video S4) through the damaged areas. Interestingly, a similar response was observed after a peel-off test of the surface (Video S5). Durability of the coating was further tested against sand paper abrasion with a load of 50 g and a finger wiping experiment (Figure 2C,D, Videos S6 and S7), wherein the surfaces were abraded for a length of 5 cm, back and forth. For all the tests, contact angle (CA) of water droplets was measured after each of the 10 consecutive cycles and plotted in Figure 2E (for knife scratch test, in every cycle, one scratch was made on the coated surface). Negligible variation in static CA over the mechanically perturbed surfaces implies the robustness and stability of the coating. Similar mechanical robustness with retention of superhydrophobicity was also observed for the waterproof paper upon the above-mentioned abrasion tests (except knife scratch test) (Video S8). Notably, mechanical flexibility of the abraded paper remained unchanged compared to native CNF paper and unabraded waterproof paper (Figure 2F–I). This was tested manually by bending the paper multiple times. However, the mechanical strength for the waterproof paper was enhanced (Figure S5) compared to native CNF paper (uncoated). We believe that the incorporated chemical functionality (secondary amine) on the CNFs which gets self-polymerized at room temperature, increases the adhesion between the fibers as well as with the substrate leading to durability of the coating. Long-term stability of the coating (while it was coated on a surface and in the dispersion form) as well as the attachment of FS and AS with CNFs were also studied in detail and explained in the Experimental Section.

Surface characteristics of chemically functionalized CNF-coated glass substrates were studied with AFM and SEM. Increased surface roughness of the order of 200 nm was observed for the modified CNF-coated film (Figure 3A,B) compared to native CNF-coated film (Figure S1). This may be a result of the hydrophobic effect,[61] namely an interaction between water and low surface energy molecules (here, fluorinated CNFs), leading to the more organized surface structure of fluorinated CNFs by minimizing the interaction energy during drying. Similar rough surface morphology was also observed in SEM (Figure 3C,D). These were compared with the modified CNF film (Figure S6). The reduced Young's modulus (E_r) and hardness (H) of the modified CNF were measured through nanoindentation tests (Figure S7). The loading part of the load–displacement curve is elastic-plastic in nature. The slope of the initial part of the unloading curve was used to measure the stiffness(s). The values determined at 500 μN peak load are shown in the table of Figure S7. The E_r and H values corresponding to 500 μN can be considered as representative bulk values obtained using equations (i) and (ii) (below table in Figure S7), respectively. Chemical

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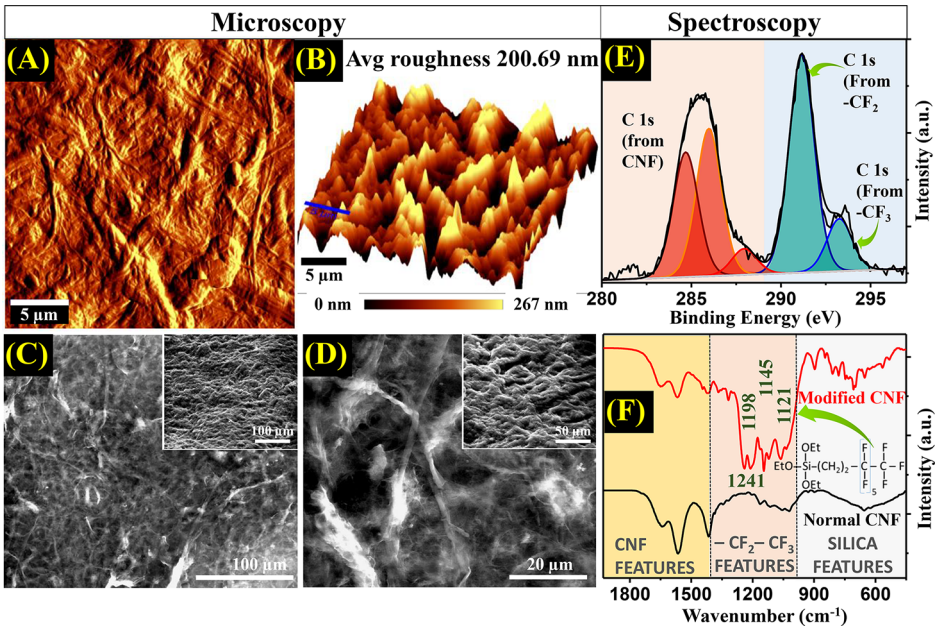

Figure 3. Characterization of the modified CNF-coated thin film. AFM image of the coated glass substrate: (A) 2D and (B) 3D views. (C and D) SEM images in different magnifications showing the inherent roughened fibrous nature of the film. (Inset) Tilted (45°) view showing the roughness of the surface. (E) Deconvoluted XPS spectrum in the C 1s region showing the presence of carbons having different electronic environment. (F) FT-IR spectra of the dried material (normal and modified CNF). Peaks at 1121, 1145, 1198, and 1241 cm^{-1} (shaded area) indicate the presence of C−F functionalities in the modified CNF.

composition as well as the nature of the chemical bonding of the foreign molecules, which are considered to be the underlying reasons for both stability and robustness of the material, were characterized in detail with XPS and IR spectroscopy (Figure 3E,F). The presence of two chemically different carbons, that is, (i) cellulosic carbons (C−C/C−O/O−C−O) and (ii) carbon attached with fluorine (C−F bond in FS) in the deconvoluted C 1s spectrum of the modified CNF sample, confirmed the covalent linkage of molecules with CNFs. These features of carbon were not seen in native CNF (Figure S8). The C−C, sp^3 bonded carbon gave a peak at 284.6 eV which remained unchanged for both modified and native CNFs. However, the peak for C−O and O−C−O shifted slightly to a lower binding energy value (0.6 eV), suggesting the formation of a bond between Si (from AS or FS) and OH (from CNF). Carbons attached with fluorine appear in the higher binding energy region of the XPS spectrum (291−293 eV), as fluorine polarizes the C−F bond (Figure 3E). Peaks at 686.9 and 684.5 eV of the XPS survey spectrum correspond to the deconvoluted F 1s peak of C−F bonds ($-CF_2$ and $-CF_3$, respectively) (Figure S9). The difference in IR spectral features (Figure 3F) between modified and native CNFs also imply the change in its chemical signature. Observed characteristic peaks at 1121, 1145, 1198, and 1241 cm^{-1} in the modified CNF correspond to the various stretching modes of $-CF_2$ and $-CF_3$. New features at 1165 and 1130−1000 cm^{-1} correspond to different Si−O−C and Si−O−Si vibration modes, respectively. Therefore, microscopic and spectroscopic studies suggest that the unusual water repelling property of CNFs should arise from both enhanced roughness and low surface energy.

The self-cleaning property of the superhydrophobic surfaces has attracted people in various ways. This was demonstrated with iron oxide particles in the form of inorganic dust which eventually got washed away with rolling water droplets (Figure 4A−C, Video S9). The coated paper when exposed to bacterial/fungal species showed no growth over its surface in spite of providing favorable conditions for growth. Even after prolonged incubation, the paper remained resistant to microbes. The observed color change around the unmodified CNF paper (Figure 4D) implies the growth of bacteria. For fungal contamination also, visible color change was seen unlike the coated paper (Figure 4E). This microbial resistance is attributed to the water repelling nature of the coated surface. The coating prevented the access of the organisms to the nutrients and moisture needed for growth. Moreover, it has been seen that reduced protein adsorption plays an important role in reducing bacterial adhesion on surfaces.[62] Chemical inertness or the stability of the modified CNF-coated surfaces were studied upon exposing the surface to organic solvents of different polarity such as hexane and ethanol (Figure 4F−H, Video S10). Despite having porous morphology of the CNF film, which enhances the penetration and contact of organic solvents with fibers, characteristic superhydrophobic nature of the treated surface remains unchanged. This chemical robustness of the material was further studied and discussed later (Figure 5B).

Though cellulose-based newly synthesized superhydrophobic material has shown significant resistance toward conventional mechanical and chemical stresses, the longevity of the material under various hazardous conditions is an important parameter for real-time applications in different technologies. This was tested in two different ways. In the first case, the same sample was kept in laboratory atmosphere and examined (by static CA measurements) for a long time (2 months) without applying any external stresses (Figure 5A). Second, the effect of different external perturbations such as exposure to various organic fluids (a diverse range of polarity), temperature, and direct sunlight was investigated in a cyclic fashion (Figure 5B). Details of the cycles are explained in detail in the Experimental Section (for each set of experiments, the same surface was used). For both

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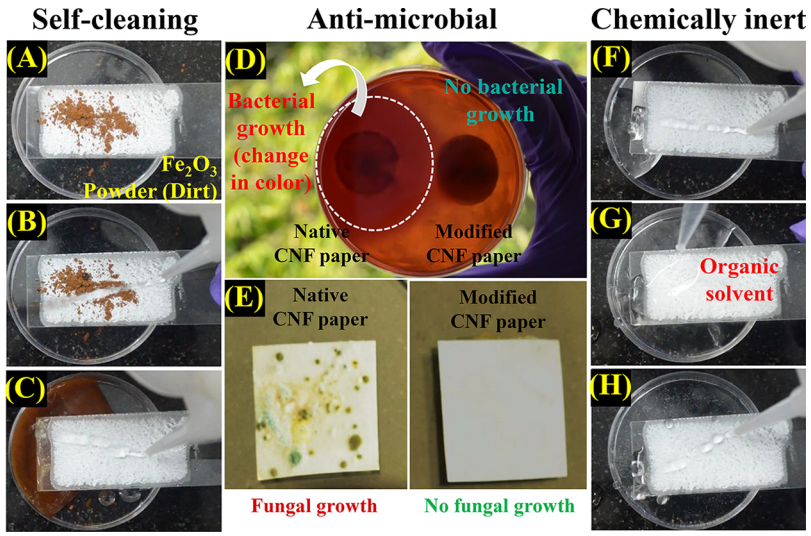

Figure 4. (A–C) Self-cleaning property of the superhydrophobic material coated glass surface. Iron oxide (Fe_2O_3) powder was used as the model dirt. (D and E) Microbe-resistive nature of modified CNF-coated paper. Antibacterial (D) and antifungal (E) properties with native CNF paper as a reference sample. (F–H) Water-repelling behavior after artificially induced chemical damages with various organic solvents. Organic solvents having different polarities such as hexane and ethanol were used to demonstrate the effect. Ethanol treated surface was used in photographs.

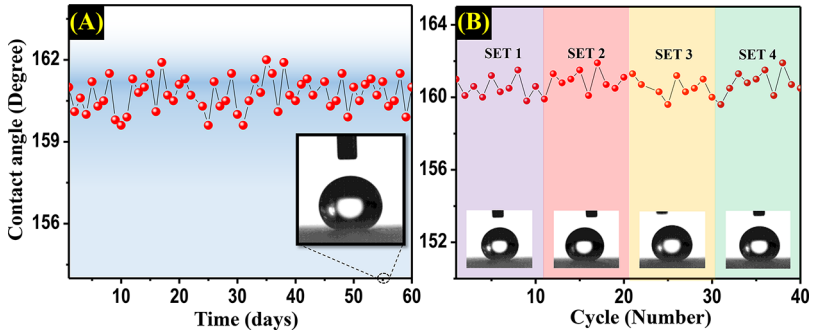

Figure 5. Durability of the coatings in (A) ambient condition (without any external perturbation) and (B) externally applied cyclic perturbations: (Set 1) exposure to various organic fluids; (Set 2) high-temperature (200 °C) treatment; (Set 3) low-temperature (−80 °C) treatment; and (Set 4) exposure to direct sunlight (longevity test). For both the cases (A and B), static CA of water droplet was measured at a regular time interval. (Inset) Photograph showing static CA of water droplet after (A) 55 days and (B) each set of experiments. Details of the durability experiments are presented in the Experimental Section.

of the cases, the wettability of the surfaces was studied by measuring the static CA of the water droplet. The consistent value of CA, on an average 160° (±2°), for both the experiments demonstrates the durability of the material for day to day applications.

While hydrophilic in nature, normal papers easily get wet through the diffusion (capillary action) of water, and this affects the integrity of the papers. In this context, waterproof paper with excellent resistance toward bacterial and fungal growth is advantageous for books, currency notes, medical diagnostic devices, and paper-based electronics. Proof of concept experiments have been performed as shown in Figure 6. A higher integrity factor for the modified CNF paper in comparison to normal CNF paper was observed when both the papers were put in a water bath for the same amount of time. The modified CNF paper was coated only on one side, and the same side was exposed to water during the experiment. Within a few minutes, normal CNF paper got wet and sank in the water (see the change in contrast). After 15 min of water treatment, while the normal CNF was destroyed by a small force, the modified CNF paper showed excellent resistance and remained intact (Figure 6A, Video S11). In both of the cases, the forces were almost equal (neglecting the human error), which were applied manually. Furthermore, to show the quality of waterproof nature, native CNF and modified CNF-coated paper (single side coated) were tested with ink diffusion, where both the papers were written with blue ink (water-diffusible) and exposed to a water bath at the same time (ink written side was facing water). In this case also within a few seconds, the ink from the native CNF paper started diffusing in water, whereas the letters on the modified paper remained intact (Figure 6B, Video S12).We believe that these important properties of the multifunctional waterproof paper will enhance the usability of such paper in paper-based technologies including flexible electronics as well as microfluidic devices.[28]

CONCLUSIONS

In summary, we have demonstrated a simple strategy to develop a durable waterproof paper from chemically modified CNFs building blocks. Wettability of native hydrophilic CNFs was controlled through covalent linkages with low surface energy molecules in water. However, being synthesized and

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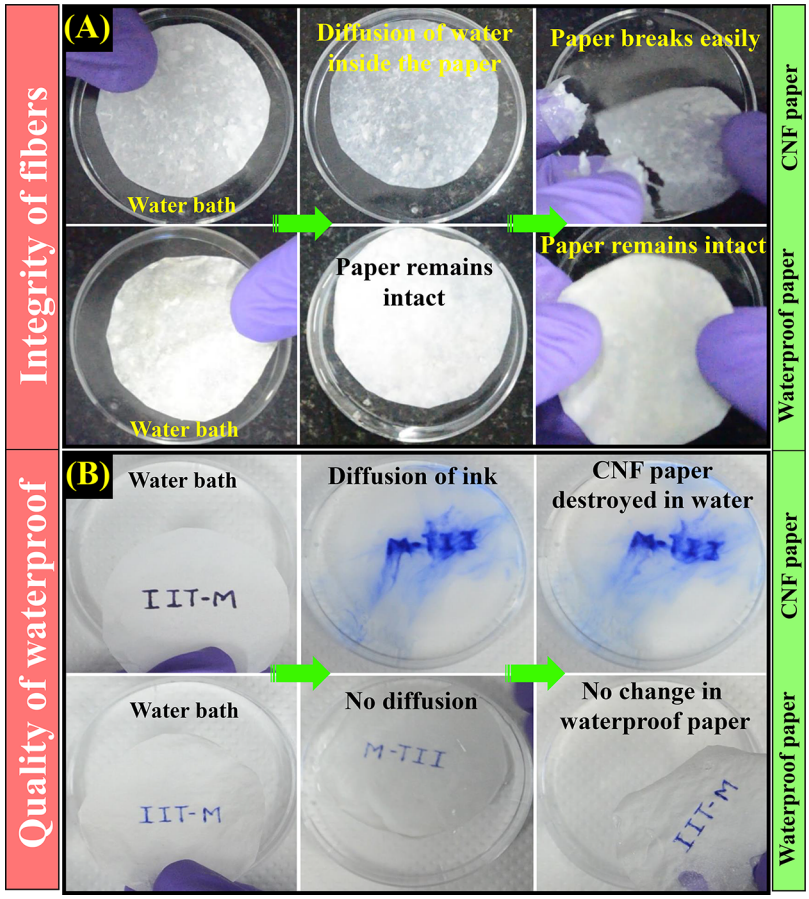

Figure 6. Key features of the prepared waterproof paper for paper-based technologies: (A) Integrity of the fibers upon exposure to water for a longer time (the waterproof paper was compared with normal cellulose paper). (B) The extent of waterproof nature. Ink on the normal paper diffused as it came in contact with water, whereas it remained intact on waterproof paper. Change in contrast of ink color is because of the uncontrollable soaking of ink in hydrophilic cellulose paper.

dispersed in water, this material also facilitates its applicability as an environmental friendly coating material for creating large area superhydrophobic surfaces. While the incorporated chemical functionalities enhanced the binding capability of the material with various substrates without any adhesive, physical appearance along with the mechanical flexibility of the waterproof paper remained unchanged, unlike the normal CNF paper. This material shows a durable water-resistant property which can withstand multicycle abrasion as well as chemical damages. Finally, chemical functionalization-induced enhancement of integrity (between the fibers) and excellent microbial resistance of the waterproof paper provide a basis for its applications in different paper-based technologies.

EXPERIMENTAL SECTION

Materials. All the chemicals were purchased from commercial sources and used without further purification. Native cellulose nanofiber (2.8 wt %) was purchased from BioPlus. These nanofibers were also characterized with TEM and AFM (Figure S10). 1*H*,1*H*,2*H*,2*H*-perfluorooctyltriethoxysilane (FS, 98%) was purchased from Aldrich. 3-(2-Aminoethylamino)propyltrimethoxysilane (AS, commercial grade) was purchased from Rishichem Distributors. Ethanol, heptane, hexane, benzene, toluene, dimethylformamide (DMF), tetrahydrofuran (THF), chloroform, dichloromethane, and acetone were procured from RANKEM, India. All of the chemicals were used without further purification. Sand paper (P320) was purchased from a local hardware shop.

Synthesis. *Chemical Modification of Native Hydrophilic CNF.* Chemical modification of CNFs was made through a wet chemical process in an aqueous medium where well-dispersed native hydrophilic CNF (1 wt %) was mixed with two different functional silanes, FS (0.61 v/v%) and AS (0.92 v/v%), under vigorous stirring conditions and kept for 6−7 h at room temperature (Figure 1A). Before mixing with these chemicals, hydrophilic CNFs were well dispersed by sonication for 30 min in water (Figure S10). These chemically modified well-dispersed CNFs, obtained in a wet chemical process, were diluted in water and spray coated on a glass slide (for characterization) and laboratory made hydrophilic CNF paper. Though spray coating was used to prepare all of the samples, other techniques such as dip coating, doctor blading, *etc.*, are equally efficient for sample preparation. Coated samples were dried at room temperature (30 °C) and tested through various experiments. The observed morphology (macroscopic roughness) over the dried surface is related to the fibrous structure of CNF. Synthesized homogeneous aqueous dispersion (modified CNF) can be stored at room temperature in the laboratory environment for more than a year without any special precaution. Though the silanization reaction is very fast in the aqueous medium, it was controlled with the solubility of FS in water which is very low because of its long hydrophobic tail. We believe that this particular fluorosilane gets adsorbed on the cellulose surface slowly due to the numerous hydroxyl groups and gets hydrolyzed gradually. Presence of unreacted FS and AS/Completion of the reaction between the FS and AS with CNFs was studied through IR spectroscopy, where the spectrum of the supernatant solution (after centrifugation of as synthesized modified CNF dispersion) was compared with all the reagents (AS and FS) and pure water (Figure S11). In the figure, the spectrum of the supernatant (blue) does not

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contain any characteristic peaks of AS (black) and FS (red). The spectrum was similar to pure water (orange). Although AS is known to be nontoxic in biological experiments[63,64] and C−F bonds in FS are stable, they may be used with caution.

Preparation of Superhydrophobic/Waterproof Paper. The waterproof paper was prepared by spraying a waterborne chemically functionalized CNF dispersion on laboratory-made hydrophilic native CNF paper. Such CNF paper was prepared through the evaporation method, where homogeneous CNF solution was poured carefully in a plastic petridish maintaining the homogeneity of the solution everywhere in the solution bed. Once the solution was dried properly at room temperature, the film was taken out by applying mild heat (30−35 °C) and was used to prepare superhydrophobic/water repellent paper with modified CNF coating. In short, as synthesized aqueous dispersion of modified CNF composite was diluted with water at 1:2 volume ratio and sprayed on laboratory made hydrophilic CNF papers. Later it was dried at room temperature (30 °C) and tested with different experiments.

Long-Term Stability Test. Long-term stability of the coating was checked in two ways. First, the synthesized material was kept at laboratory environment for 6 months and later on was coated on the surface. No difference in the water repelling property of the coated surface was observed compared to the surface coated with the freshly prepared material. Second, immediately after synthesis, the surface was coated with the material and kept at laboratory environment for 6 months. In this case also, a similar water repelling property was observed compared to the surface coated with the freshly prepared material. To check the stability of the chemical attachment between FS and AS with CNF, the superhydrophobic surface (modified CNF coated) was sonicated in a water bath for 30 min, and the water was examined using IR spectroscopy along with all the used reagents (AS and FS) and pure water (Figure S12). The spectrum of "water after sonication" (blue) does not contain any characteristic peaks of AS (black) and FS (red). However, it is similar to pure water (orange). Please note that characteristic peaks of AS and FS are marked in the spectrum which are absent in water after sonication with the coated surface. The study confirms that under normal conditions, the coating does not degrade.

Abrasion Resistance Test. Multiple abrasion tests such as sand paper abrasion with a load of 50 g, scratching with a knife, finger wiping, and tape adhesion were performed to evaluate the abrasion resistance and adhesion strength of the coating on different substrates (glass and laboratory made paper). For sand paper abrasion, a piece of sand paper (P320) was kept between the coated glass surface with a load of 50 g, and the set up was moved for 5 cm along the coating. After completion of 10 cycles, the wettability of the abraded surface was tested with both jet motion and CA of water droplets. This experiment was further repeated with multiple cycles. A similar methodology was adopted for the finger wiping test, where the surface was rubbed back and forth multiple times with a thumb and subjected to water flow and CA measurements. For knife scratching and tape adhesion tests, surfaces were evaluated with similar water jet motion and CA measurements after each experiment, and the same was repeated 10 times.

Durability of the Coated Surface upon Cyclic Thermo-Chemical Perturbations. Durability of the coating was evaluated by measuring the static CA of water droplet on the tested surface. Various external stresses such as (Set 1) exposure to various organic fluids, (Set 2) high-temperature treatment, (Set 3) low-temperature treatment, and (Set 4) exposure to direct sunlight (longevity test) were used to test the surfaces. Stability of the water repelling coating upon chemical stresses was tested by keeping the coated surface within various organic fluids for 1 h. Different polar and nonpolar solvents like ethanol, tetrahydrofuran (THF), dimethylformamide (DMF), toluene, and hexane were used to simulate chemical damages. After each solvent treatment, the surface was dried at room temperature, and CA of water droplet was measured. Each solvent was tested 2 times. Thermal effects on the surface in extreme conditions were performed by keeping the surfaces at 200 °C and −80 °C for 2 h (Set 3). Effect of direct sunlight on the coated surfaces was tested upon exposing it outside for 2 months (Set 4). While the same coated glass surface was used 10 times in cyclic fashion for each set (for Sets 1−3), due to time constraints, 10 different surfaces were used to perform the Set 4 experiment.

Antibacterial and Antifungal Test. Interaction of bacteria with the superhydrophobic paper was tested on equally sized paper samples using Gram-negative *Escherichia coli* (ATCC 10536). *E. coli* was inoculated in 10 mL of Luria−Bertani broth (LB) (Himedia) and incubated overnight in an air bath shaker at 37 °C and 300 rpm to reach the exponential growth phase. The bacterial solution was centrifuged at 3000 rpm for 5 min to remove the used media and washed twice with sterile saline. The suspension was diluted 1000× in sterile saline. Using the spread plate method, plating concentrations were determined as 10^5 colony forming units (CFU)/ mL. For testing the bacterial resistance property, the coated and uncoated papers were surface sterilized and dipped in the bacterial solution for 2 min. Substrates were tilted at 90° to allow the bacterial solution to roll off, if possible. Subsequently, samples were rinsed with 50 μL of sterile saline. The surfaces of the substrates were then stamped face-down in MacConkey agar plates (Himedia) to transfer residual bacteria. The agar plates were incubated for 24 h at 37 °C in an incubator. Images were taken after 24 h and bacterial growth in coated and uncoated paper samples was compared. Agar was prepared prior to experiments according to the manufacturer's protocol. For interaction of fungi with the superhydrophobic paper, isolated airborne *Aspergillus sp.* was placed beside the equally sized test paper samples. This paper was placed on a square block of potato dextrose agar in a Petri dish. A sterile moist cotton was also placed inside the Petri dish to maintain the humidity. This setup was incubated for 4 days at 25 °C until visible spores appeared.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsnano.7b05170.

Additional experimental details and data (PDF)
Jet motion of water on coated glass (extent of water repellency test) (AVI)
Droplet dragged test (water pinning test) (AVI)
Vertical drop adhesion test (water pinning test) (AVI)
Knife scratch test (AVI)
Peel-off test (AVI)
Sand paper abrasion test with a load of 50 g (AVI)
Finger wiping test (AVI)
Water on abraded waterproof paper (AVI)
Self-cleaning property (AVI)
Effect of organic solvents (AVI)
Integrity test: Stability of waterproof paper in water (AVI)
Extent of water repelling nature of waterproof paper, ink diffusion test (AVI)

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Notes

The authors declare no competing financial interest.

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