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Fabrication of a waterborne durable superhydrophobic material functioning in air and under oil

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((Optional Dedication))

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Abstract: A fundamental challenge in artificially structured or chemically modified superhydrophobic surfaces is their poor chemical, mechanical and structural robustness towards different mechanical abrasions. This limits their application potential in different fields of science and technology. Herein, a stable waterborne superhydrophobic material composed of clay particles is developed through a one-pot chemical modification in ambient conditions, forming durable micro-nano dual-structured coatings at room temperature over a range of substrates, without adhesive. This chemical modification inverts the inherent hydrophilic nature of clay particles and provides an excellent superhydrophobic surface having a water contact angle $>170^\circ(\pm 2^\circ)$ and contact angle hysteresis $<5^\circ(\pm 2^\circ)$. The coating shows excellent durability against various induced damages (mechano-chemical-environmental) and works efficiently both in air and within oils. The observed property is due to the controlled surface energy obtained by the incorporated chemical functionalities and enhanced surface roughness facilitated by the hydrophobic-effect during slow evaporation of

water from the coating material. Being a stable water-dispersion, it enables large area coatings, thereby minimising safety and environmental concerns. Use of this material to develop rugged waterproof-paper for various paper-based technologies is also demonstrated. As clay is commercially available and economical, we believe, this scalable organic-solvent-free superhydrophobic material will have a positive impact on various industries.

1. Introduction

Designing materials for the preparation of water repellent thin films with robust and durable characteristics has attracted considerable attention over the years because of their wide possible applications in different fields of science and engineering. In this context, superhydrophobic surfaces, having potential uses in self-cleaning,^[1] drag reduction,^[2] anti-corrosion,^[3] anti-icing,^[4] sensing,^[5] atmospheric water capture,^[6] microfluidic devices,^[7] water-oil separation,^[8] construction materials^[9] etc., are intensely researched upon. Such surfaces not only force water droplets to roll off, they keep themselves clean even from viruses and bacteria, thereby preventing biofouling.^[10] However, designing surfaces of such kind needs both artificial micro/nano-scale structuring and chemical modifications with low surface energy molecules.^[11] Although various synthetic methodologies have been introduced,^[7, 12] stability, cost, complicated manufacturing processes and restrictions in large area production limit the use of such surfaces for practical applications.^[13] In contrast, coating with chemically modified materials processed by wet chemical methods is affordable and is known as an alternate way to prepare such surfaces in large areas.^[14] Though use of polymers,^[15] cellulosic materials,^[16] clays^[17] and oxide nanoparticles^[18] are well known in this context, in most of the cases, organic solvents are used as a component of the reaction medium,^[18-19] which pose concerns related to safety, environmental pollution, operational cost, and solvent compatibility of the substrates. In this context, a few reports on the development of aqueous coating materials for water repelling surfaces are known.^[14, 17, 20] Recently, a non-

fluorinated silane-based coating material having tunable wetting property has been synthesised in a highly acidic condition.^[21] However, storage of such materials even for a few hours is an issue due to the uncontrollable hydrolysis of silanes in presence of tiny amounts of water. Thus, there is a need to develop a stable superhydrophobic coating material in water at neutral pH and ambient conditions with affordable materials leading to coatings which overcome the problems outlined earlier.

One of the persistent problems of such chemically functionalised superhydrophobic surfaces is the poor stability and durability of the coating which readily gets abraded, for example even with the mild touch of tissue paper, leading to permanent loss of the surface property.^[13b, 22] Binding ability of the material with substrates having different surface morphology also affects the durability of the coating. To overcome these problems, although the use of adhesives and pre-surface modifications have been introduced,^[22a, 23] these methods have their own limitations depending on the nature of the adhesives and the surfaces to be coated. Nevertheless, the instability of such water repelling coatings towards various chemical stresses is still a major disadvantage. In this context, superamphiphobic surfaces, another class of materials were developed that repel both water and oil.^[24] The surface energies of these surfaces are so low that they can maintain a thin layer of air between the surface and liquids which can subsequently result in rolling off of liquid. A few reports on the development of superhydrophobic surfaces (through chemically functionalized coating materials) that function equally well both in air and within oil are known.^[22a, 23, 25] However, the use of hazardous organic/non-aqueous solvent systems and instability of the coatings without additives are the major limitations.

Fabrication of durable superhydrophobic fabrics with chemically processed materials is also a challenge despite having huge application potential of such flexible substrates in different paper-based technologies.^[5a, 7, 26] Fibrous surface morphology may prevent efficient coating which results in pinning/ sticking of water droplets on uncoated areas. Moreover, being soft

and fibrous in structure, water droplets do not acquire enough energy or backward force to bounce off and get trapped within the fibrous microstructure.

In this study, a waterborne superhydrophobic material is developed from a hydrophilic clay particle building blocks that provides excellently durable superhydrophobic coatings at room temperature over a series of substrates (both soft and hard) without any adhesive. This demonstrates the novelty and possible industrial viability of the methodology. The material is environment-friendly, stable and can be made in large scale for different applications. Incorporated chemical functionalities controlled the surface energy of the material such that the coated substrate functions equally well, both in air and within oil. The coating showed excellent stability and unaltered water repelling property against various mechanical, chemical and environmental stresses. Being a water-based dispersion, it enables efficient and large area coatings by conventional coating procedures, thereby minimising environmental impact. Applicability of the material to develop a flexible waterproof paper is also demonstrated.

2. Synthesis

The waterborne superhydrophobic material was synthesised by an easy chemical modification of kaolinite clay at room temperature with two functional silanes. Chemically, these aluminosilicate clay sheets consist of numerous hydroxyl groups on the surface which are reactive in the well-dispersed condition in water. In the synthetic protocol, water dispersed clay sheets (6 wt%) were mixed with two different functional silanes, 1*H*,1*H*,2*H*,2*H*-perfluorooctyltriethoxysilane (FS, 2 wt%) and 3-(2-aminoethylamino)propyltrimethoxysilane (AS, 1 wt%) and kept under vigorous stirring conditions for 6 to 7 h. Whereas silanization reaction in general is very fast in aqueous medium, because of the low solubility of FS in water, at first it gets adsorbed on the clay surface and hydrolyzes slowly in water and gets attached covalently to the clay surface.^[16a] Thus, a water dispersed functionalized clay

composite was obtained and spray coated on different substrates followed by drying at room temperature. Quantitatively, 1 mL of the as-prepared composite solution was mixed with water in 1:1 ratio and sprayed over a glass slide and a paper, having an area of 75 x 26 mm². Upon drying at room temperature (30 °C), a superhydrophobic film of nearly 8 micron thickness (on a glass surface) was obtained which shows a high CA > 170° (±2°) and low CAH < 5° (±2°) for water. However, to facilitate faster evaporation, the coated substrates were dried in warmer condition (45 °C) occasionally, without affecting the properties of the material. Later on, this water-based material was stored at room temperature in the laboratory environment for more than a year without any special precaution.

3. Results and Discussion

Figure 1A illustrates the methodology used for the preparation of the superhydrophobic film over various substrates. Briefly, the complete reversal of the hydrophilic property of clay particles was achieved through a chemical functionalization with two different functional silanes, FS and AS in water at room temperature. Applicability of this waterborne material was tested both with hard and soft substrates such as glass, cotton, fabrics, etc., having different morphologies. In addition to fluoroalkyl functionalization of the clay sheets, the surface has inherent micro and nano structures, as will be demonstrated later. It was seen that water droplets are spherical on superhydrophobic surfaces (both hard and soft) and bounce easily (Figure 1B-D). Moreover, bouncing off of water droplets even on modified cotton surface (Figure 1D) shows the universal applicability and efficiency of the material. These effects were captured in Video S1. Being dispersed in water, functionalized clay sheets sit readily on hydrophilic fibers and get coated efficiently all over the surface of cylindrical fibers by strong capillary action and large surface tension force.^[27] The extent of water repelling property of the material on fibrous soft surfaces was revealed from the unstable, frictionless movement of water drops on modified paper, demonstrated in Figure S1, Video

S2. This can be compared with the lotus leaf effect; a well-known example of the natural superhydrophobic property.

The surface morphology of the modified clay coated thin film (on glass) was imaged by scanning electron microscopy (SEM) with a tilt angle of 45°. The image (**Figure 2A**) manifests the periodic micron-sized features over the surface. Such features were observed throughout the surface and were formed during drying of the material at room temperature. While SEM showed micron scale surface structures, atomic force microscopy (AFM) revealed the enhancement of surface roughness in the nanometer regime (Figure 2B) as compared to a normal clay coated thin film (Figure S2). In the case of a modified clay coated thin film, average surface roughness was 48 nm whereas it was 24 nm for normal clay coated thin film. This enhancement in roughness is related to the hydrophobic effect,^[28] namely an interaction between water and low surface energy molecules (here, fluorinated clay particles) that minimize the interaction energy and make the particles organize during drying of the aqueous coating. Such dual structured surfaces can be compared with nanopillar or nanogras surfaces as well.^[29] Figure S3 showed a cross-sectional SEM image of the superhydrophobic thin film suggesting a layer-by-layer structure of the coating.

Along with the surface morphology, chemical features of the surface also play an important role to obtain such extreme water repellent characteristics of the thin films. Infrared spectroscopy (IR) and X-ray photoelectron spectroscopy (XPS) reflect the chemical composition of the coated thin film. Figure 2C shows the IR spectra of unmodified clay and functionalized clay materials. Vibrational features are observed at 1119, 1145, 1198 and 1245 cm^{-1} , respectively, assigned to the stretching and bending modes of C-F bonds in FS ($-\text{CF}_2$ and $-\text{CF}_3$ functionalities). Intense peaks at 687.3 and 684.9 eV in the XPS spectrum correspond to the F1s of $-\text{CF}_2$ and $-\text{CF}_3$ groups, respectively of FS (Figure 2D). Both microscopic and spectroscopic measurements suggested the reasons of superhydrophobicity

which are related to the surface roughness as well as the presence of low surface energy molecules.

Stability/durability of the coating is one of the most desired criteria when applications of such surfaces are concerned. In this context, use of additives to improve the strength and stability of superhydrophobic coatings has been reported which essentially enhances the binding ability of the coating material. In contrast, our material (without any adhesive) with diamino functional groups interlink the clay sheets and help to anchor them efficiently over substrates during the evaporation process through spontaneous in-situ polymerization. Anchoring induced stability was studied with various artificially induced mechanical stresses. For instance, the coated surface was subjected to hard mechanical stresses such as sandpaper abrasion test with a load of 50 g and knife scratch tests (**Figure 3A, B**). Although the coating on the surface got damaged to some extent with knife scratch, its superhydrophobic property remained intact (Video S3). Interestingly, water repellent property was preserved for the sand paper abraded (with a load of 50 g) surface even after multiple abrasion cycles (Video S4). These reflect the advantage of having multilayer surfaces, because even if the upper layers of the coating get affected, underlying layers can make the water to roll off.^[30] Durability of the coating was also evaluated by soft mechanical stresses like tissue paper abrasion and finger wiping test (Figure 3C, D). In this case, abraded surfaces were observed to maintain their superhydrophobic property with easy movement of water streams over them (Video S5, 6). For all the cases, retention of the water repelling nature of the abraded surfaces was evaluated thoroughly with CA and CAH measurements after each experiment (Figure 3E) where each experiment consisted of 10 complete abrasion cycles of corresponding tests (details are given in the experimental section). Consistent values of CA and CAH at an average of $170^\circ (\pm 2^\circ)$ and $3^\circ (\pm 2^\circ)$, respectively, after each experiment showed the durability of the material against external forces. These mechanically perturbed surfaces were further studied with wettability

sensitive vertical drop test (water droplet from the needle was moved vertically and contacted the surface and drawn back) and droplet drag test (water droplet from the needle was dragged over the surface back and forth for 5 cm). Videos S7&8 show the unchanged wettability of the surfaces after the above-mentioned tests on the mechanically abraded surfaces that can be directly related with CAH (contact angle hysteresis) of water droplets over these surfaces.

Having low surface energy, the coated glass surface showed self-cleaning property where graphite powder was used as dirt which eventually got washed away with the rolling water droplets (**Figure 4A, B**, Video S9). Coated surface (paper, Whatman 44) was also observed to show bacterial resistance when it was exposed to bacterial species (Figure S4) under favorable growth conditions and nutrients. This was compared with normal paper where precipitation of bile salts around the uncoated paper indicates the bacterial growth. Chemical robustness of this superhydrophobic surface was tested with various solvents with a wide range of polarities (ethanol, dimethyl sulfoxide, dimethylformamide, tetrahydrofuran, toluene, hexane, heptane and *n*-octane). For all the cases, coated surface was observed to retain its initial properties and remain unaffected after cyclic washing with multiple organic solvents, demonstrated in Figure 4C, D and Video S10 (ethanol treated surface is demonstrated here). Chemical durability of the material was further tested in detail with various hazardous aqueous solutions. For example, water with pH=1 & 14 and highly oxidizing KMnO_4 solutions were used for this. Experiments were done in two ways. Firstly, these solutions were used directly to measure the static and dynamic contact angles of the respective droplets. In every case, the static contact angle was observed in the range of $170^\circ (\pm 2^\circ)$ (Figure 4 E-G) with low contact angle hysteresis, below $5^\circ (\pm 2^\circ)$ (Figure S5). This proves the stability and chemical inertness of the material. In the second case, the experimental solutions were used to wet the surface (similar to the experiment with organic solvents). However, in all the cases, their droplets bounced and rolled off easily over the surface. Durability of the coating under such chemical stresses was

further tested by keeping the surfaces within the solvents for a long time (170 h for each solvent). For each solvent system, the same surface was used repeatedly for the entire experiment. After long incubation time also, surfaces retained their property and kept functioning efficiently. These were seen in the CA values at regular time intervals of 20 h for a duration of 7 days (Figure 4H). To identify the change in wettability of the superhydrophobic coating in detail, the treated (7 days solvent treated) surfaces were also studied by CAH measurements (Figure S6 A), droplet drag and vertical drop experiments which are very sensitive towards surface wettability. Data corresponding to the THF treated surface are shown in Figure S6 B (pictorially and graphically) and Video S11.

Oils, having low surface tension, easily get into the surface micro-structures and remove the air layer that is essential for superhydrophobicity. Water droplets possess lower interfacial tension inside oils compared to the air-water interface. Both of these enhance the possibility of pinning of water droplets on the surface. However, in our case, the superhydrophobic surface was observed to function also at the oil-solid interface with equal efficiency and maintains high static and dynamic contact angles for water droplets. Similar water repelling phenomenon at the oil-solid interface is well-known for SLIPS (Slippery Liquid-Infused Porous Surface), where low surface tension oils are introduced within a porous matrix.^[31] In such cases, water droplets sit over these oil-wetted surfaces and remain surrounded by air. Whereas, in the present work, water droplet sits on a superhydrophobic surface and is surrounded by oil. Spherical shape of the colored water droplets on the superhydrophobic surface kept inside oil is pictorially presented in Figure 4I. Inset shows the measured static contact angle of the water drop inside *n*-octane which was observed to be $170^\circ (\pm 2^\circ)$. Video S12 demonstrates the bouncing off of water droplets on the modified clay coated surface kept inside oil. For laboratory experiments, non-polar long chain hydrocarbons (such as *n*-octane) were used as models for oil. Extent of such under-oil superhydrophobicity was further studied

in detail with CAH measurements (Figure 4J) and vertical drop adhesion test inside oil (Figure 4K). In this case also CAH was observed to be $3^\circ (\pm 2^\circ)$. Self-cleaning property of the surface when a portion of the surface was kept inside oil was also demonstrated with rolling water droplets (Figure 4L). Water droplets roll off easily through both the phases (air and oil) despite sudden change in the interfacial tension and kept the surface clean from dirt (potassium permanganate was used as a dirt). This is demonstrated in Video S13. To study the response of water repellent coatings against perturbed water droplets (as the interfacial tension of water droplets within oil is lower than in air and it takes time to reach equilibrium), coated surface was tested with droplet pinning test where the surface was kept inside oils with colored water droplets over it for a long time. Even after 1 h of incubation, droplets restored their spherical shape and started rolling upon mild shaking with hand (Figure S7). This can easily relate to previously demonstrated excellent under-oil superhydrophobicity (Figure 4I-K). Video S14 shows the displacement of these water droplets on the superhydrophobic surface kept under oil (initial and final positions of droplets are marked with colored circles). As the material functions well both in air-solid and oil-solid interfaces, it provides an easy cleaning strategy both for the surfaces (kept under oil) and oil. This is demonstrated in Figure S8 and Video S15. While the dirt on the surface (under oil) can be collected with water drops and removed through capillary action (for paper) or mild shaking (induced force), small water drops in the oil can be removed easily by coalescing them on the superhydrophobic surface (kept under oil) followed by mild vibration/shaking. We believe that such a technique will be useful for oil pipelines and oil tankers.

Being dispersed in water, these chemically modified clay sheets sit on fibrous materials efficiently through surface tension forces or strong capillary action^[27] and coat it efficiently without affecting the mechanical flexibility of the substrate. This was demonstrated with a coated filter paper (Whatman 44) shown in **Figure 5A**. Figure 5B pictorially represents the

effect of bending/ twisting on the water-repelling nature of the coated paper. For this, a colored water droplet was placed on a strained folded paper that forced droplet to change its shape to oval. However, water repelling nature of the paper remains intact and no stain of the colored drop was observed even after 10 mins (Figure 5B i; folded paper was kept vertically). Droplet on the relatively relaxed folded paper is shown pictorially in Figure 5B (ii & iii; side and top views). Durability of this waterproof paper against various mechanical abrasions (sand paper abrasion and finger wiping test) and environmental stresses (effect of sunlight and effect of bending) was evaluated through static CA and CAH measurements in a cyclic fashion and the data are plotted in Figure 5C (details of the experiments were discussed in experimental section). Retained superhydrophobicity of the coated paper under these conditions, a much desired property for various paper-based technologies, shows its applicability in day to day use.

The extent of binding of the material with fibrous substrates like filter paper (Whatman 44) was further demonstrated with a harsh oil washing experiment where viscous oil-absorbed coated paper was washed with organic solvents to remove the oil. Because of the superhydrophobic and oleophilic nature of the material, viscous paraffin oil absorbs over the coated paper easily as can be seen from the dark patches even on the opposite side of the paper (Figure S9). These oil patches were subjected to multiple cleaning cycles with different organic solvents (ethanol and acetone). Though removing oil from the paper is difficult as it enters within the pores of the paper and gets immobilised on the fibers, interestingly, the washed filter paper showed almost equal water repelling nature (Figure 5D-F & Video S16) and kept on functioning. This supported the excellent durability of the material as well as the developed waterproof paper.

Obtained excellent superhydrophobic property along with the unique characteristics of the thin film can be explained with the chemical functionalities incorporated on clay particle along with the surface morphology of the film. Though the clay materials having silicate structure are hydrophilic, simultaneous functionalization with FS and AS inverts its physical property and induces durable water repellency once it is coated over surfaces (Figure 1). Firstly, anchored FS on the surface of clay sheets increases the hydrophobicity of the particles and facilitates the arrangement/orientation of chemically modified clay particles (keeping the fluorinated hydrocarbon chain outer side) during the evaporation of water. Such a process is mostly governed by the hydrophobic effect, namely an interaction between water and hydrophobic component of the dispersion. This also promotes the enhancement in the average roughness on the film which is much needed for superhydrophobicity. Secondly, the use of AS increases the dispersibility of the FS-modified clay particles. However, during the drying process, the amine groups mostly stay in the inner side (towards water) because of the same hydrophobic effect. Again, AS increases the strength, and durability of the superhydrophobic coating by connecting the functionalized clay sheets as well as anchoring them over the surfaces. As this polymerization is only observed/feasible upon evaporation of water, the water dispersed material stays unaffected until water is present. This helps in storing the material in closed conditions at room temperature for a period over a year without any special precautions. Finally, the decorated functionalities control the surface free energy of the film in such a way that the coated surfaces show equally efficient activity both in air and under oil. This was reflected in a high contact angle of $170^\circ (\pm 2^\circ)$, with low hysteresis (below $5^\circ \pm 2^\circ$) for water droplets both at air-solid as well as oil-solid interfaces.

4. Conclusion

In conclusion, we developed a versatile and simple waterborne composite material from hydrophilic clay particles building blocks that provides a durable superhydrophobic coating

on large areas over a wide variety of substrates (without using any adhesive), having diverse surface morphology and physical characteristics. The material forms superhydrophobic thin films easily at room temperature that withstood various mechanical and chemical stresses. In particular, the surface showed excellent water repelling property even after 100 cycles of various mechanical abrasions such as sand paper abrasion, finger wiping, etc. Interestingly, the coated thin film functions equally well at both air-solid and oil-solid interfaces which is due to the controlled surface energy obtained by the incorporated chemical functionalities and hydrophobic effect-induced enhanced surface roughness during the slow evaporation of water from the coating material. Moreover, surface tension-induced better and effective binding capability of the clay sheets with soft and fibrous substrates^[27] makes it possible to design a flexible waterproof paper, a promising materials platform for paper-based technologies.^[26]

5. Experimental Section

Chemical:

All the chemicals were available commercially and were used without further purification. Kaolinite clay was purchased from Alpha minerals and chemicals. 1H,1H,2H,2H-perfluorooctyltriethoxysilane (FS) was purchased from Aldrich. 3-(2-aminoethylamino)propyltrimethoxysilane (AS) was purchased from Rishichem distributors. Ethanol, dimethyl sulfoxide, heptane, hexane, *n*-octane, toluene, dimethylformamide (DMF), tetrahydrofuran (THF) and paraffin oil (AR grade), were procured from RANKEM, India. Sand paper (P320) was purchased from a local hardware shop.

Durability test with cyclic mechanical perturbation:

The durability of the coating was tested by measuring the static contact angle (CA) of water droplets after imparting cyclic mechanical stresses on the surfaces. Hard mechanical stresses

include scratching with knife and sand paper abrasion test. For scratching with a knife, 10 different scratches were made on the same surface and subjected to CA measurements after every scratch. Sand paper abrasion test was performed by keeping a sand paper between the coated surface with a load of 50 g and the sand paper was moved 10 complete cycles over the surface. CA of water droplets was measured after every 10 cycles and continued similarly for 10 times. Soft mechanical stresses were induced in the form of tissue paper abrasion and finger wiping abrasion. Same methodology (mentioned above) was used in this case also. For each test (both hard and soft mechanical stresses) the same surface was used repeatedly.

Durability test for the waterproof paper:

Durability of the flexible waterproof paper was tested with induced mechanical abrasions and various environmental stresses. For mechanical abrasion, sand paper abrasion (with a load of 50 g) and finger wiping tests, samples were evaluated through static CA and CAH measurements after every 10 complete cycles where each cycle consists of back and forth movements for 5 cm each. Environmental stresses like direct sunlight exposure and effect of bending/ twisting of waterproof paper were also studied with CA and CAH measurements. For effect of direct sunlight exposure, the coated paper was kept under sunlight and evaluated with CA and CAH measurement after each 5 h of exposure. This was further continued 10 times. For bending/ twisting tests, the coated paper was twisted in different possible ways (90°, 180°, rolling, etc.) and CA and CAH were checked after every 10 cycles of twisting. The data are plotted in Figure 5C.

Bacterial resistance test:

Bacterial resistance test was done with Gram-negative *Escherichia coli* (ATCC 10536). Details of the experiments are given in a previously reported article.^[20b] In short, *E. coli* was inoculated in 10 mL of Luria–Bertani broth (LB) (Himedia) and kept overnight in an air bath

shaker at 37 °C and 300 rpm to reach the exponential growth phase. Later, 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 further to make the plating concentrations as 10^7 colony forming units (CFU)/ mL. This was measured by using the spread plate method. Resulting solution was used for the bacterial resistance experiment.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Figure 1.

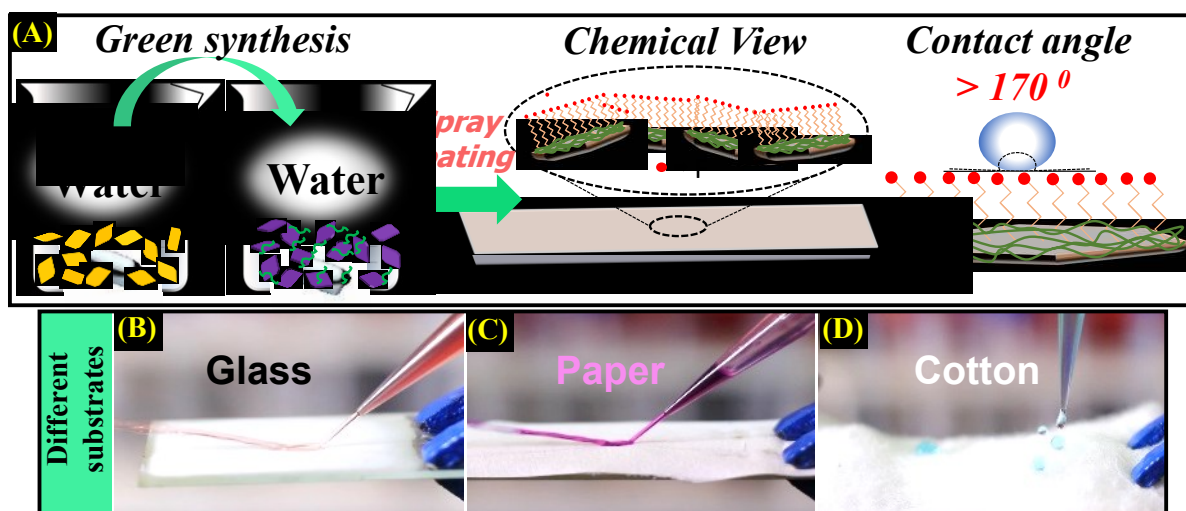


Figure 1. A). Schematic representation of the waterborne superhydrophobic material (synthesis of the dispersion and the prepared thin film). Continuous jet flow on coated (B) glass, (C) filter paper and (D) bouncing of water on modified cotton surface. KMnO_4 , CoCl_2 and CuSO_4 aqueous solutions were used in B, C and D, respectively, instead of pure water to add color contrast.

Figure 2.

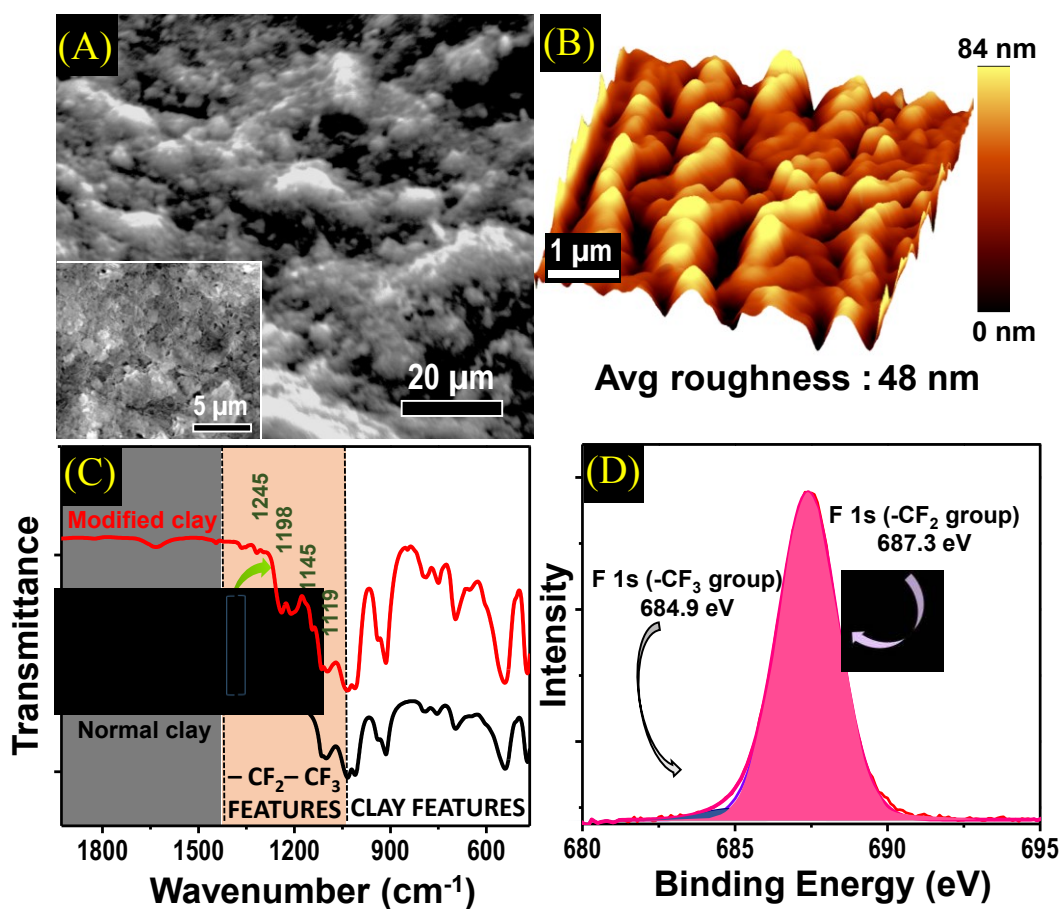


Figure 2. Characterization of the coating. (A) SEM image of coated glass substrate showing the uniform and periodic micronscale-features of the surface. The surface was tilted by 45°. Inset shows the morphology of the same surface at a tilt angle of 0° (B) AFM image shows the nanoscale roughness present on the surface. (C) FT-IR of the dried material. Peaks at 1119, 1145, 1198 and 1245 cm^{-1} (shaded area) indicate the presence of -C-F functionalities in the modified clay. (D) XPS shows the presence of fluorine in the sample which is coming from FS.

Figure 3.

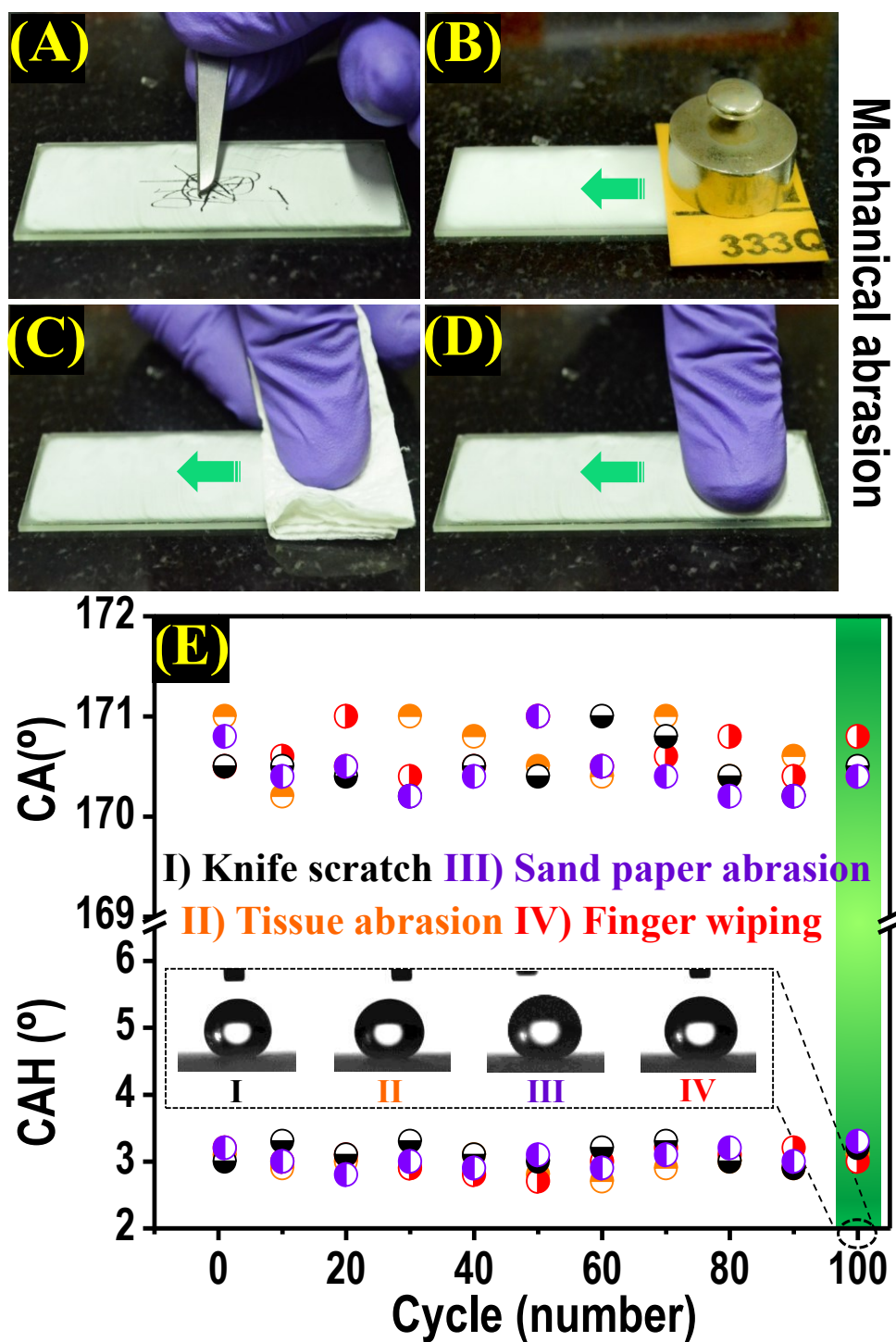


Figure 3. Induced hard and soft mechanical damages on spray-coated glass substrates. Hard mechanical damages: (A) scratching with a knife and (B) sand paper abrasion with 50 g of load. Soft mechanical damages: (C) abrasion with tissue paper and (D) finger wiping. E)

Durability/ longevity test with the above-mentioned mechanical tests. Change of CA and CAH of water droplet during the multiple abrasion cycles (of different mechanical tests). In every case, CA and CAH were measured after each experiment, consist of 10 consecutive abrasion cycles. (Inset) Photograph showing static contact angle of water on the tested surfaces (after the 9th experiment or 90th abrasion cycles).

Figure 4.

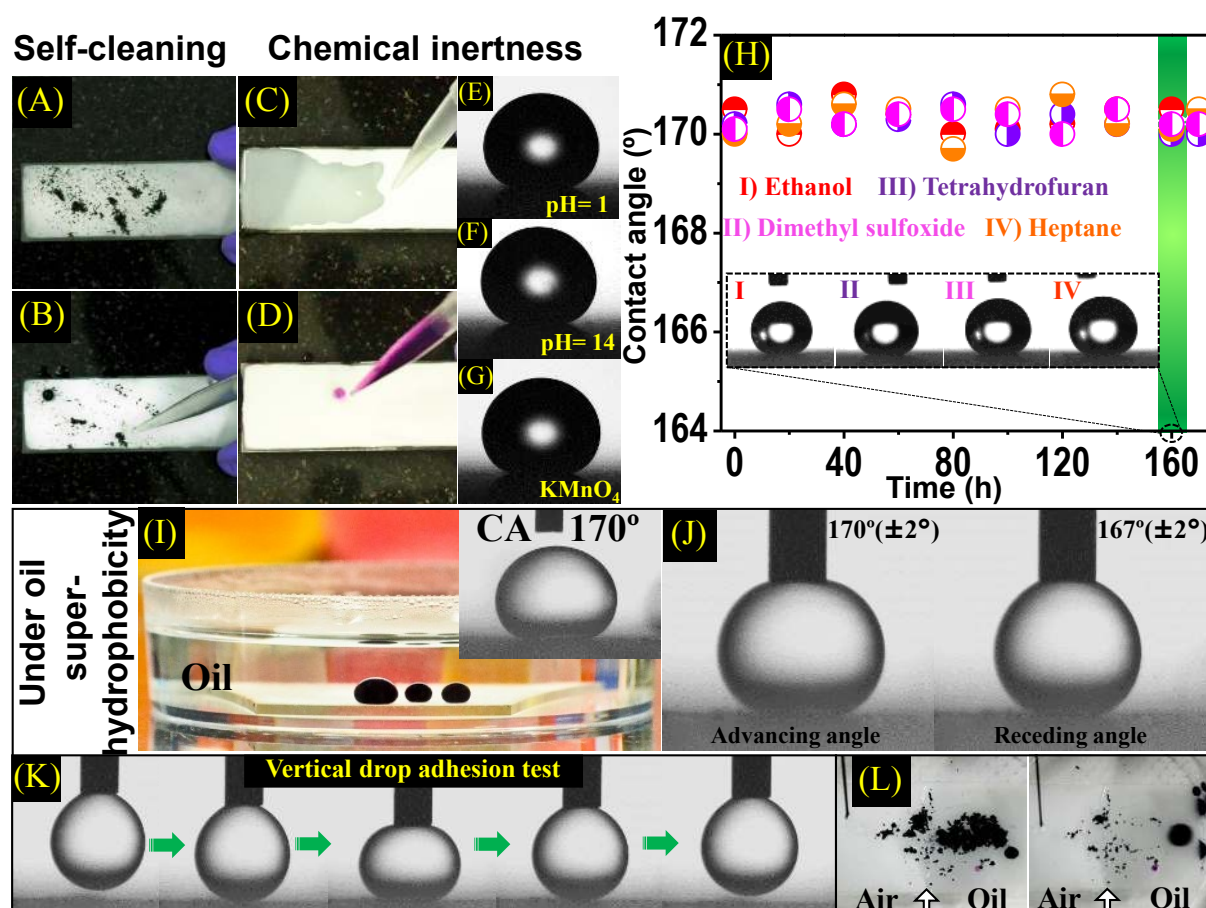


Figure 4. (A,B) Self-cleaning property of superhydrophobic material coated glass surface. Iron oxide powder (Fe_2O_3) was used as the model dirt. (C,D) Coated surface retains its water repelling behavior even after artificially induced chemical damages with various organic solvents (ethanol treated surface is demonstrated here). (E-G) Static contact angle of water

droplets having pH=1, 14 and oxidizing agent KMnO_4 . (H) Durability/ longevity of the coating under extreme hazardous conditions. Surfaces were kept inside various organic solvents having different polarity and the static contact angle of water droplet was measured after taking the surface out from the solvent in a regular time interval for 170 h (details in the experimental section). (Inset) Photograph showing static contact angle of water on a 160 h oil treated surface. (I) The superhydrophobic coating also remained functional inside/under oil (*n*-octane) and forced water droplets to sit as a sphere whereas wetting takes place on a normal surface. (Inset) Static contact angle of water droplet on coated glass within the oil (*n*-octane). Extent of under-oil superhydrophobicity. (J) CAH measurement and (K) vertical drop adhesion test with a water droplet, when the coated surface was immersed in oil (*n*-octane). (L) Self-cleaning property of the coated surface at the air-solid-oil interface. A portion of the surface was kept inside oil (*n*-octane, taken as a model long chain hydrocarbon); an inorganic salt (potassium permanganate) was placed over it as a model of dirt. Rolling water droplets removed all the dirt from both the interfaces and made the surface clean.

Figure 5.

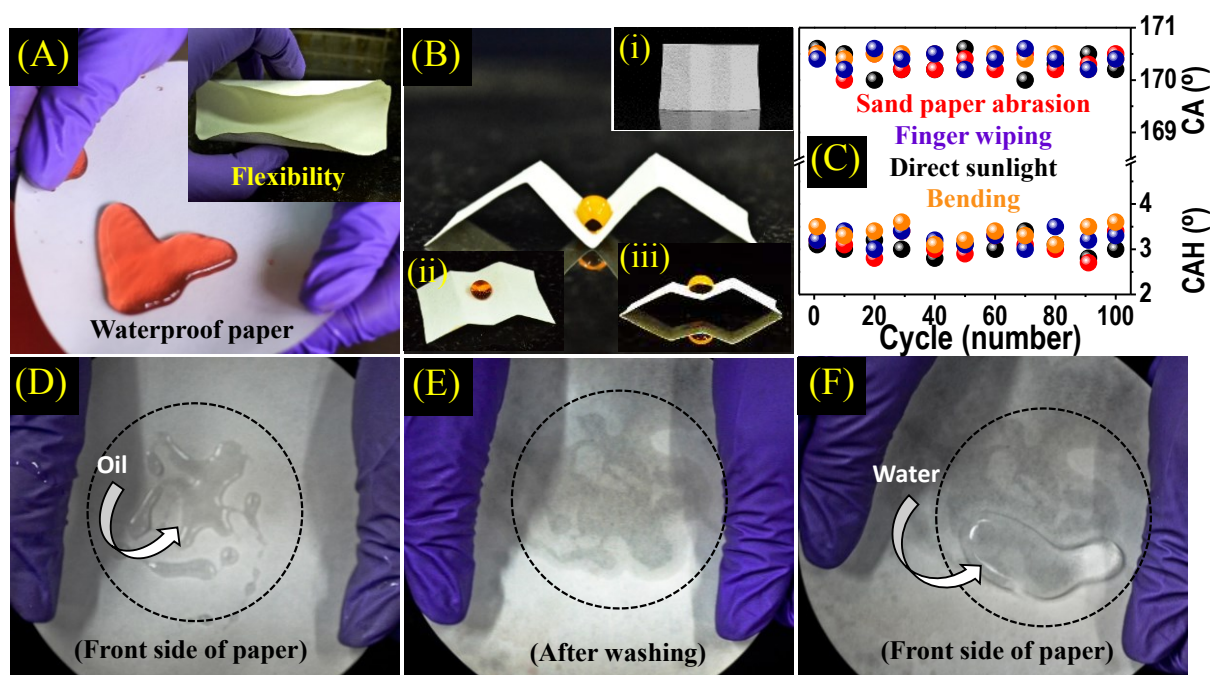


Figure 5. Demonstration of durability of waterproof paper. (A) Unstable water drops on coated filter paper (lotus leaf effect). Inset shows the retained mechanical flexibility of the paper after coating. (B) Induced twisting/ bending on the coated paper. Colored water drop on the folded paper that changed its shape to oval due to induced strain by the folded paper. Inset, i) vertical view of the folded paper after removal of water drop (after 10 mins). Any stain of the color drop was not observed. ii-iii) Water drop on relatively relaxed folded waterproof paper. (C) Durability/ longevity of waterproof paper under various mechanical and environmental stresses. Measured static CA and CAHs of water droplet after a regular time interval (details in the experimental section). (D-F) Oil washing test. (D) Paraffin oil adhering on the coated filter paper. (E) The same paper after washing thoroughly with acetone and ethanol to remove oil. (F) Washed paper shows almost similar water repelling property.

The table of contents entry

A waterborne durable superhydrophobic coating material that functions equally well in air and oil is developed through a facile and scalable synthetic strategy. Universal applicability (both hard and soft substrates) and ruggedness of this material, as demonstrated here, enhances its use in different technologies and day-to-day life.

Keywords: Aqueous coating, superhydrophobic material, interface, durable, waterproof paper

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Fabrication of a waterborne durable superhydrophobic material functioning in air and under oil

ToC figure

