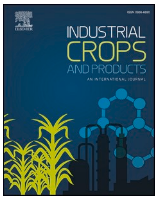
Industrial Crops & Products 222 (2024) 119717

Contents lists available at ScienceDirect

Industrial Crops & Products

journal homepage: www.elsevier.com/locate/indcrop



Durable self-cleaning superhydrophobic cotton fabrics for wearable textiles

Rajaram S. Sutar [a], Snehal G. Kodag [b], Rutuja A. Ekunde [b], Akshata S. Sawant [b], Tanuja A. Ekunde [b], Saravanan Nagappan [c], Yong Hyun Kim [d,e], Viswanathan S. Saji [f], Shanhu Liu [a,*], Sanjay S. Latthe [a,b,**]

[a] College of Chemistry and Molecular Science, Henan University, Kaifeng 475004, China
[b] Self-cleaning Research Laboratory, Department of Physics, Vivekanand College (Autonomous), Affiliated to Shivaji University, Kolhapur, Maharashtra 416003, India
[c] Industry-University Cooperation Foundation, Pukyong National University, Busan 48513, Republic of Korea
[d] Department of Smart Green Technology Engineering, Pukyong National University, Busan 48513, Republic of Korea
[e] School of Electrical Engineering, Pukyong National University, Busan 48513, Republic of Korea
[f] Interdisciplinary Research Center for Advanced Materials, King Fahd University of Petroleum & Minerals, Dhahran 31261, Saudi Arabia

ARTICLE INFO

Keywords:
Self-cleaning cotton
Superhydrophobic
Modified TiO_2 - PDMS coating
Durability
Breathability

ABSTRACT

Cotton fabric is widely used in various industrial goods due to its ability to enhance aesthetic appeal, but preserving its shine and genuine appearance presents a significant challenge. In this work, a durable self-cleaning superhydrophobic surface suitable for wearable textiles was achieved on cotton fabrics by applying a composite coating of stearic acid-modified titanium oxide (TiO_2) nanoparticles and polydimethylsiloxane (PDMS) through a simple dip/spray coating technique. The fabric surface displayed an exceptional water contact angle (WCA) of 165 ± 2° and a minimal slide angle (SA) of approximately 2°, demonstrating outstanding water repellency and sliding characteristics. The surface exhibited impressive self-cleaning abilities for both dust particles and muddy water. The coated cloth maintained its exceptional superhydrophobic properties even after being subjected to 40 abrasion cycles, 30 adhesive tape peels, nearly 60 min of ultrasound treatment, and 30 washing cycles. Additionally, the as-coated cotton showed excellent chemical stability, tensile strength, flexibility, air permeability and breathability. The model trials with a baby doll have proven the high possibility of commercializing self-cleaning clothing in this research.

1. Introduction

Cotton fabric serves as both a primary material for clothing and a significant element of cultural, economic, and environmental importance, thereby playing a crucial role in people's lives. Cotton fabric is commonly used in various products such as clothing, home textiles, industrial textiles, and everyday items such as coats, beach umbrellas, campers, shade shelters, and marketing materials (Mahbubul Bashar and Khan, 2013). Natural cotton textiles easily get wet with water, dampness, or other liquids as they contain a lot of hydroxyl groups (Xu et al., 2019). Moreover, cotton fabrics have a high affinity towards water and liquids which leads to dirty stains after evaporation, making cotton garments uncomfortable and unappealing to wear. During the rainy season, cotton fabric tends to absorb moisture quickly, which can make clothes feel damp and heavy. This can cause discomfort and a clammy feeling against the skin. Additionally, the absorption of water can cause unpleasant odors and pose health risks such as hypothermia. Furthermore, cotton fabric's condition can worsen due to moisture retention and dirt accumulation. The rainy season can also cause mud, dirt, and debris to accumulate on clothes, which can be easily absorbed by cotton fabric. This necessitates frequent washing and drying to maintain good hygiene, which can be a time-consuming and hectic process. Therefore, it is imperative to alter the surface of the cotton fabric to possess superhydrophobic qualities that enable self-cleaning.

The superhydrophobic characteristic is assessed based on WCA exceeding 150° and rolling angles below 10°. They exhibit self-cleaning behavior by the removal of dust particles via the rolling action of water droplets. Low surface energy chemical modification of rough surface is crucial for achieving excellent self-cleaning superhydrophobic surface property (Dalawai et al., 2020; Latthe et al., 2019). In the last decade,

---

* Corresponding author.
** Corresponding author at: College of Chemistry and Molecular Science, Henan University, Kaifeng 475004, China.
E-mail addresses: liushanhu@vip.henu.edu.cn (S. Liu), latthes@gmail.com (S.S. Latthe).

https://doi.org/10.1016/j.indcrop.2024.119717
Received 13 June 2024; Received in revised form 12 September 2024; Accepted 20 September 2024

several attempts have been made to create superhydrophobic cotton fabrics for various purposes, such as wearable clothing, oil-water separation, anti-fogging, anti-fouling, and anti-reflective applications. Several preparation methods including wet chemical etching (Xu et al., 2023), sol-gel process (Qi et al., 2022), spray-coating (Guo et al., 2023), and dip-coating (Chen et al., 2021) have been widely used to apply superhydrophobic coatings on cotton fabric. The multiscale surface roughness can be controlled by integrating various inorganic nanoparticles, such as SiO_2 (Li et al., 2024b), CuO (Li et al., 2022), and TiO_2 (Khan et al., 2021), into the preparation of superhydrophobic coatings. TiO_2 is a popular choice among these for a variety of industrial applications. It is highly effective in fields such as photocatalysis (Wang et al., 2022), photothermal catalytic degradation (Yang et al., 2022a, 2022b; Zhang et al., 2023), oil-water separation (Li et al., 2020), pharmaceuticals (Jaggessar et al., 2022), cosmetics (Ghamarpoor et al., 2023), and health industries (Weir et al., 2012), especially in self-cleaning applications (Guo et al., 2023a). TiO_2 is commonly used because of its many desirable qualities, such as its photocatalytic activity, abundance, hydrophilicity, chemical, and physical stability, lack of toxicity, recyclability, biocompatibility, ease of synthesis, and low cost. Moreover, the fabric treated with TiO_2 can hinder the proliferation of bacteria and fungi, thereby enhancing its hygienic properties and making it safer to wear. A cotton surface coated with TiO_2 could demonstrate self-cleaning properties due to its high hydrophilicity and photocatalytic characteristics. Adding low surface energy modifiers to TiO_2 could make it suitable for use in water-resistant coating preparations. Stearic acid is a commonly employed biocompatible surfactant that effectively reduces surface energy and is safe for use. Furthermore, it is recognized for its superior biocompatibility compared to silane coupling and is widely acknowledged as a low-surface energy modifier (Hao et al., 2024; Xu et al., 2022). For example, Yang et al. (2023) developed a superhydrophobic cotton fabric by coating it with 3-methacryloxy propyl trimethoxysilane (3-MPTMS) and then applying a stearic acid-modified layer of TiO_2 nanoparticles. This coating showed exceptional self-cleaning properties with a WCA of 157.3°.

Fluoropolymers and polydimethylsiloxane (PDMS) are two examples of polymers that have been shown to work together to lower surface energy and increase nanoparticle adherence to cotton. Yang et al. (Yang et al., 2018b) applied TiO_2 sol on pristine cotton and subsequently dipped it into fluoropolymer to produce a superhydrophobic surface. This surface exhibited self-cleaning properties against liquid pollutants and solid powder stains. Similarly, Hou et al. (2024b) developed a composite coating for cotton fabric using ethylene glycol diglycyl ether (GDE) modified TiO_2 particles, dodecanoic acid (DA), and perfluorodecyl triethoxysilane (PFTS). In this composite coating, GDE served as a cross-linking agent, the modified TiO_2 particles enhanced surface roughness, and DA and PFTS decreased surface energy, thereby fulfilling the criteria for achieving optimal superhydrophobicity. Likewise, a fluorine-containing epoxy polymer reacted with KH 550-modified nano-SiO_2 was utilized for coating cotton through a dipping process. When exposed to high temperatures, the epoxy chain segment forms chemical bonds on cotton surfaces, while the fluorine-containing segment generates a low surface energy layer (Hou et al., 2024a). Despite their high chemical stability and low surface energy, fluoropolymers have limited ability to interact effectively with cotton surfaces, which can lead to their persistent accumulation in the environment and organisms. Their resistance to metabolism poses hazards to the environment and human health (Dai et al., 2024; Ma et al., 2021). In contrast, PDMS is a highly favored material for creating superhydrophobic coatings because it has exceptional properties such as low surface energy (21 mN/m^2), and strong adhesion to substrates (Shin et al., 2012; Xue et al., 2016). Additionally, PDMS is a fluorine-free material, which is a significant advantage in coating formulations. Recently, Qian et al. (2023) coated a cotton fabric using N-halamine precursor and TiO_2 nanoparticles and modified it with PDMS. The resulting coated fabric exhibited high hydrophobicity, a WCA of 143°, and effective antibacterial properties. Liu et al. (2019) have optimized superhydrophobic surface with WCA of 160° by grafting PDMS layer on TiO_2 deposited glass substrate. Foorginezhad and Asadnia (2023) utilized a spray coating technique to deposit a composite consisting of montmorillonite and Al_2O_3 on cotton fabric and subsequently treated it with a PDMS solution. The coated cotton fabric demonstrated exceptional self-cleaning, exhibiting WCA of 174.6° and a rolling angle of less than 5°. However, the application of self-cleaning superhydrophobic coatings in wearable clothes is currently limited due to the intricate preparation methods involving toxic chemicals and the lack of comprehensive studies on their durability and performance. Most of the reported works on inorganic nanoparticles and hydrophobic polymers-based superhydrophobic coatings have not addressed detailed studies of their mechanical durability, flexibility, breathability and air permeability in line with wearable cloth applications (Table S1). Only a few studies claimed their results for wearable applications.

In this research, a facile dip/spray coating technique was used to develop a self-cleaning superhydrophobic coating on cotton fabrics. The biocompatible and environmentally friendly stearic acid, TiO_2, and PDMS were selected as they are among the best candidates suitable for wearable cloths application. The TiO_2 nanoparticles were modified with stearic acid to take advantage of their non-toxicity and low surface energy properties. To achieve superhydrophobicity, multiple layers of TiO_2-PDMS composite were applied to the cotton fabric. Coating textiles with stearic acid-modified TiO_2 and PDMS offers several benefits. The stearic acid modification enhances the compatibility of TiO_2 with PDMS, leading to a more effective hydrophobic surface. TiO_2 improves surface roughness, which helps maintain water-repellent properties over time by trapping air film inside rough structures. PDMS provides an adhesive, flexible, hydrophobic layer, offering excellent durability, flexibility, breathability, and softness for cotton fabric. This ensures comfort for the wearer and reduces the need for frequent reapplication. Furthermore, TiO_2 and PDMS are known for their skin-friendly and non-irritating properties, making them well-suited for use in textiles that come into direct contact with the human skin (Akakuru et al., 2020; Chen et al., 2024; Wu et al., 2021). The hydrophobic nature of these coatings helps maintain skin dryness and comfort, with good air circulation and extended textile longevity. A primary focus of this research was evaluating the suitability of the developed coatings on cotton fabric for wearable textiles.

2. Material and methods

2.1. Materials

Titanium tetraisopropoxide (TTIP, > 98 %), chloroform (99 %), and ethanol were purchased from Spectrochem Pvt. Ltd. Mumbai, India. Polydimethylsiloxane (PDMS) and stearic acid were purchased from Sigma Aldrich. A cotton cloth was obtained from DKTE Society, Textile industry, Ichalkaranji, Maharashtra, India.

2.2. Synthesis and modification of TiO_2 nanoparticles

TiO_2 nanoparticles was synthesized using a hydrothermal method, as described in the literature (Vijayalakshmi and Rajendran, 2012). Initially, 29 mL of distilled water and 23 mL of ethanol were combined and agitated at 400 rpm for 30 min. After 20 min, a solution consisting of 15 mL of TTIP and 23 mL of ethanol was gradually introduced in small increments. The hydrolysis and condensation processes take place by continuing the stirring for an additional 3 h of agitation. After that, the solution was placed in a Teflon autoclave and heated in an oven to 80 °C for 24 h. The hydrothermally treated solution was subsequently dried at 50 °C for 3 h. The obtained TiO_2 nanoparticles powder was crushed in an agate mortar, and calcined in a muffle furnace at 400 °C for 2 h. A 3 g of stearic acid was mixed with 30 mL of ethanol using a magnetic stirrer, and then 5 g of the TiO_2 nanoparticles were added while the mixture was continuously stirred for up to 5 h and dried at 80 °C.

2.3. *Fabrication of superhydrophobic cotton*

The cotton cloth was cut into 3 × 4 cm^2 pieces, cleaned thoroughly in ethanol and distilled water to remove surface impurities and dried in an oven at 60 °C for 20 min. A 0.15 mL of PDMS was dissolved in 20 mL of chloroform and the solution was stirred for 1 h at 100 rpm. After that, 400 mg of the modified TiO_2 nanoparticles were added, and stirring was continued for another 1 h. This solution was used for coating, where the cotton sample was dipped in the solution for 2 min before being pulled out at a rate of 5 mm/s and dried in open air. Subsequently, the cotton samples were subjected to repeated coating cycles, viz. 30, 40, and 50 times, and dried at 100 °C for 30 min. The corresponding samples were named PTN-1, PTN-2, and PTN-3, respectively. Fig. 1 depicts a schematic of the fabrication of the superhydrophobic cotton fabric.

2.4. *Characterization*

Scanning electron microscopy (SEM, JEOL, JSM-7610 F, Japan) and energy dispersive spectroscopy (EDS, JEOL, JSM-7610 F, Japan) were utilized to characterize the surface morphology and elemental compositions. The surface roughness of coated cotton fabrics was measured by Stylus profiler (Mitutoyo, SJ 210, Japan). The WCA and SA of the produced coatings were measured using a contact angle meter (HO-IAD-CAM-01, Holmarc Opto-Mechatronics, India). The practical applicability of the coated fabric was studied using a baby doll (purchased from a local market) as a model. The adhesive tape peeling, sandpaper abrasion tests, ultrasound and washing treatments were used to evaluate the cotton fabric's resistance to mechanical breakdown. The tensile strength of pristine cotton and coated cotton fabric was tested using a mechanical testing machine (Instron 5565 USA and Canada). The Testex air permeability tester was used to assess the air permeability of pristine and coated cotton at room temperature and a pressure of 100 Pa. The washing stability was evaluated using ultrasonication and a magnetic stirrer to simulate a washing machine. The chemical stability was evaluated by immersing coated cotton into different pH solutions. The self-cleaning capability of the coated samples was studied using dust particles and muddy water. The flexibility was assessed by measuring the length of uncoated and coated cotton fabrics. Breathability analysis was performed using ammonia-hydrochloric reaction.

3. Results and discussion

3.1. *Surface structure and elemental compositions*

Understanding the coating's surface and chemical structure is crucial before validating the material's superhydrophobicity. Fig. 2 demonstrates SEM micrographs of the fabricated TiO_2-PDMS coatings on cotton fabric. Cotton is primarily composed of cellulose, a natural polymer that forms the basis of its fibers. Cotton fibers are typically arranged in bundles known as fibrils; these arrangements contribute to the strength and flexibility of the fabric. The microstructure of cotton consists of gaps and holes between fibrils, which enhance its exceptional breathability and comfort. The surface roughness of cotton fabrics is caused by a combination of factors, including nanofibers, microfibrils, and pores (Yang et al., 2018b). The pristine cotton fabric has showed surface roughness of 6.356 μm. The coated samples were efficiently covered with the TiO_2-PDMS composite. After 30 deposition layers (PTN-1), a uniform distribution of the composite with aggregates is seen (Fig. 2a–c) and surface roughness increased to 10.727 μm (Fig. 2j). When the number of coating layers is increased (40 layers, PTN-2), the TiO_2 particles appear in greater-sized aggregates and are compactly distributed on cotton fibrils (Fig. 2d-f), which seems to create a more effective nano/micro-scale hierarchical rough structure (Wang et al., 2019). The PTN-2 sample revealed surface roughness of 12.513 μm (Fig. 2k). The presence of 50 layers of coating (PTN-3) leads to the elimination of micro- and nano-cavities, as a result of the surplus coating composite (Fig. 2g-i). This results in a surface that is moderately smooth with roughness of 11.562 μm (Fig. 2l). In the EDS analysis of the PTN-2, four major elements C, O, Si, and Ti were detected. C contribution is mainly from the long carbon chain of stearic acid (Yang et al., 2018a). Ti and Si elements are associated with TiO_2 nanoparticles and PDMS, respectively. The EDS surface mapping analysis confirms that the composite coating of TiO_2 nanoparticles and PDMS is evenly distributed on the surface of the cotton (Fig. 2m).

3.2. *Wettability*

The pure cotton fabric is superhydrophilic and has a WCA of nearly 0° due to its porous structure and the presence of surface hydroxyl groups (Shang et al., 2020). From Fig. 3(a), it is evident that the uncoated pure cotton fabric has fully absorbed the red-dyed water. Cotton fabric becomes hydrophobic and resisted water molecule absorption

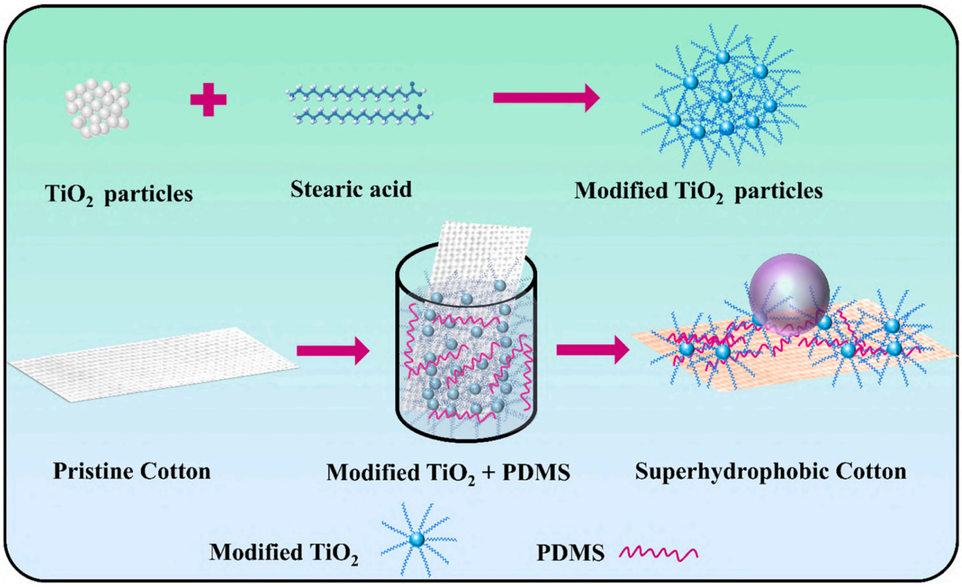


Fig. 1. Fabrication scheme of the superhydrophobic cotton fabric.

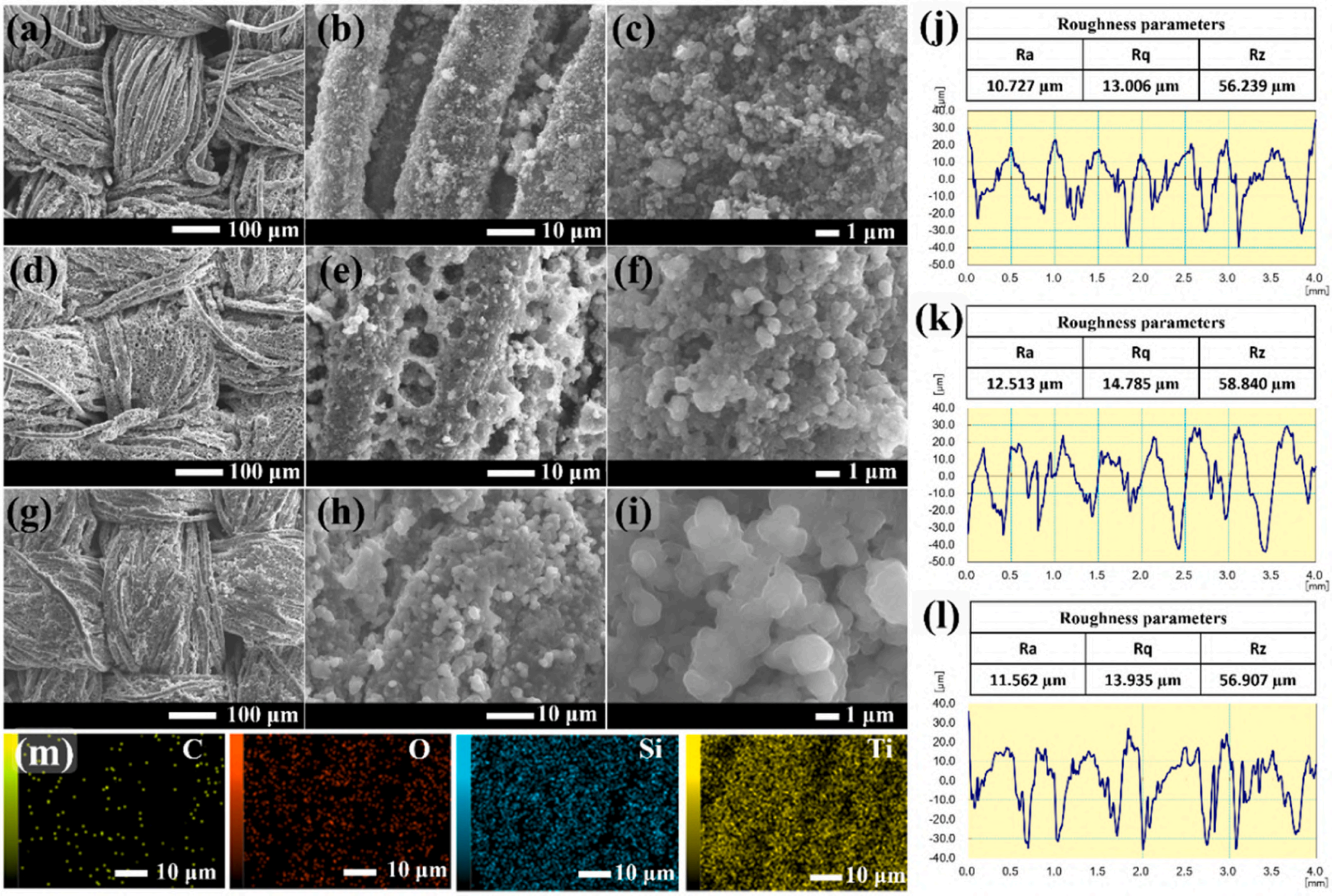


Fig. 2. Different magnified SEM micrographs of (a-c) PTN-1, (d-f) PTN-2 and (g-i) PTN-3 samples. (i, j and k) Surface roughness of PTN-1, PTN-2 and PTN-3 samples, respectively. (m) EDS elemental mapping images of PTN-2 sample.

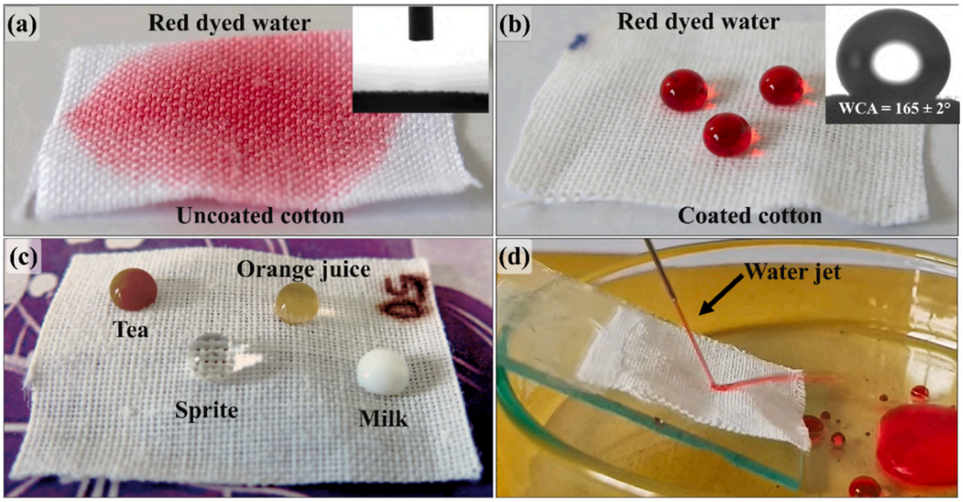


Fig. 3. The red dyed water droplets on (a) uncoated and (b) coated (PTN-2) cotton fabrics; WCA image in inset. (c) Tea, sprite, juice and milk drop on PTN-2 sample. (d) The water jet falling on the PTN-2 sample.

after being coated with 30 layers of TiO_2-PDMS. The WCA of the PTN-1 sample was 140 ± 2° and water droplets are abstemiously adhered to surface. The WCA increased to 165 ± 2° for the PTN-2 sample due the formation of micro- and nano-cavities and aggregates leading to a hierarchical roughened surface (see Fig. 2(d-f)). Such type of rough surface structure could entrap dense air pockets, which consequently resist to penetrate water molecules within the surface. As a result, after being tilted PTN-2 sample by an angle of ~ 2° or having the sample disturbed, the water droplets immediately glide down across the surface of the PTN-2 sample. Fig. 3(b) displays water droplets with perfectly spherical shapes on the PTN-2 sample. The PTN-3 sample with 50 layers of TiO_2-PDMS demonstrated WCA of 158 ± 2° and SA of 6°. This decrement is due to the deposition of excess amount of coating composite, which alter surface structure (see Fig. 2(g-i)). Because of its high superhydrophobicity, the PTN-2 sample underwent further characterization to ensure its practicality.

The PTN-2 sample was tested for its ability to repel common beverages, including tea, sprite, juice, and milk. The study showed that the produced cotton fabric with anti-fouling properties could repel all aqueous beverages (Fig. 3c). Furthermore, the stability of the superhydrophobic surface was examined by beating a water jet on its surface at a specific angle. The water jet beat continuously for more than 2 min at the desired spot, it bounced without breaking in the composite layer, suggesting that the robust air layer on the nano/micro-scale surface roughness effectively inhibits water jets from penetrating the surface. According to the Cassie-Baxter law, a surface with these qualities has low water adhesion because it permits air to become trapped on its rough surface. The bouncing water jet on the PTN-2 sample is depicted in Fig. 3d. The water jet on PTN-2 initially reflected, but after a few seconds, it began to move along the surface. The study confirms that the PTN-2 sample is durable in terms of water jet impact.

The coating stability of the PTN-2 sample was assessed by differentiating cotton fabric threads (Xue et al., 2016). When water drops were placed on the differentiated cotton fabric threads (Fig. 4a), the water droplet behavior was similar to the original PTN-2 sample. A similar behavior was observed during water floating tests (Fig. 4b and c), revealing that the coating ingredients were consistently applied to each cotton thread. After being placed on water, the pristine cotton sank rapidly due to its high absorbency (Fig. 4b). During the water immersion test, the PTN-2 sample was placed at a depth of 10 cm below the surface of the water (Fig. 4d), and WCA measured after the sample removed from the water. Even after being submerged for an 24 h, we noticed that the PTN-2 sample retained its superhydrophobicity (165 ± 2°). After immersion in water for 72 h, the WCA value were decreased to 162 ± 2°. A dazzling mirror-like phenomenon was seen on the surface of the PTN-2 sample (Fig. 4e), which shows that air pockets prevent water from penetrating the coating and reduce the adhesion of the water and cotton surface.

3.3. Mechanical and chemical durability

A series of tests, including adhesive tape peeling, sandpaper abrasion, tensile testing, ultrasound treatment, washing and immersion in acidic and alkaline solutions were carried out to evaluate the wear and tear ability and quality of the superhydrophobic PTN-2 cotton fabric. The results from these tests provide an accurate assessment of the fabric's ability to resist water and its durability in various conditions (Chen et al., 2021; Lahiri et al., 2019). Physical interactions will likely harm the nano/micro-structured superhydrophobic surfaces in practical applications, resulting in the loss of superhydrophobicity. An adhesive tape

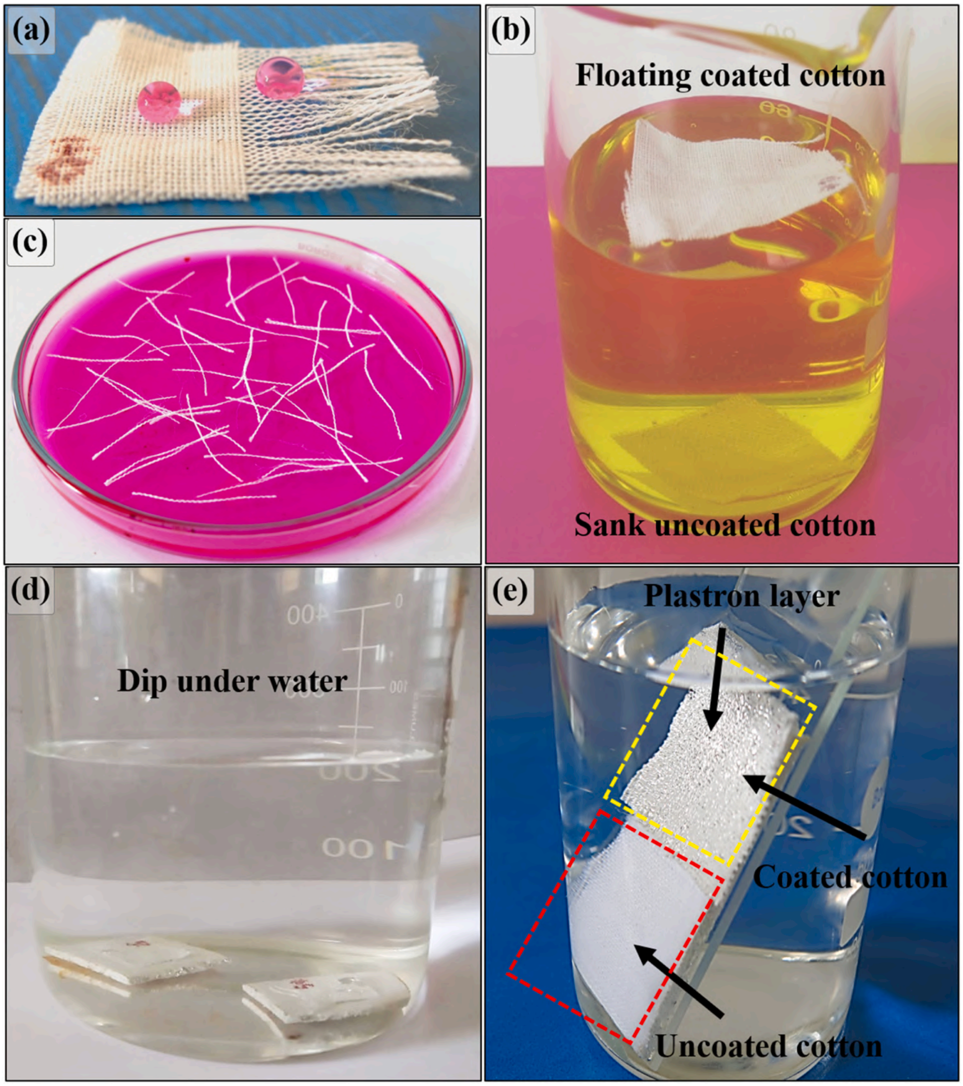


Fig. 4. (a) The water drops on differentiated threads of PTN-2 sample. (b) and (c) Floating of PTN-2 sample and its differentiated threads on the water surface. (d) PTN-2 sample kept under water, (e) Mirror-like phenomena of PTN-2 sample immersed in water.

(4 N/cm^2) was affixed to the superhydrophobic PTN-2 sample in the tape peeling test by rolling (4 times) a 100 g metal disc. This was done to test the tape's capacity to tear away. The tape was ripped to conduct the tape peeling test. The mechanical stability of the coating was assessed by repeatedly performing the tape peeling test and measuring the WCA after every five repeats of the tape peeling (Fig. 5a). It was found that the PTN-2 sample retained superhydrophobicity with WCA of 155 ± 2° and SA of 8 ± 1° even after 30 tape peeling cycles. This demonstrates that the coating ingredient firmly adhered to the cotton substrate. PDMS demonstrates a low surface energy, allowing it to effectively adapt to surfaces with different polarity. On the other hand, cotton, which is a natural fiber, possesses relatively high surface energy properties that facilitate adhesion to PDMS. Moreover, PDMS can create robust bonds between TiO_2 particles through different mechanisms, such as physical entanglement of polymer chains and hydrogen bonding between the surface groups of TiO_2 and functional groups on PDMS. Furthermore, tape peeling experiments were conducted for up to 50 cycles to evaluate wettability changes. The obtained result shows the WCA of 150 ± 2° after 50 cycles, which displays the maintenance of robust superhydrophobicity on the modified cotton fabrics.

The PTN-2 sample was dragged over the sandpaper (Grit No. C-320) at 5 mm/s speed to perform the abrasion test. During the sandpaper abrasion test, a 100 g metal disc was placed on the PTN-2 sample and dragged across the surface of sandpaper for 10 cm. The WCA and SA were recorded after every 5 cycles. The PTN-2 specimen retained its superhydrophobicity with WCA of 154 ± 2° and SA of 7 ± 2° even after 40 cycles of sandpaper abrasion (Fig. 5b). This suggests that the coating material forms a robust, abrasion-resistant layer on top of the cotton cloth. Suryaprabha et al. found that the superhydrophobic property of TiO_2-SA coated cotton can only be sustained for up to 20 sandpaper abrasion cycles in the absence of an adhesive polymer (Suryaprabha and Sethuraman, 2021). The modified TiO_2 particles in this study could

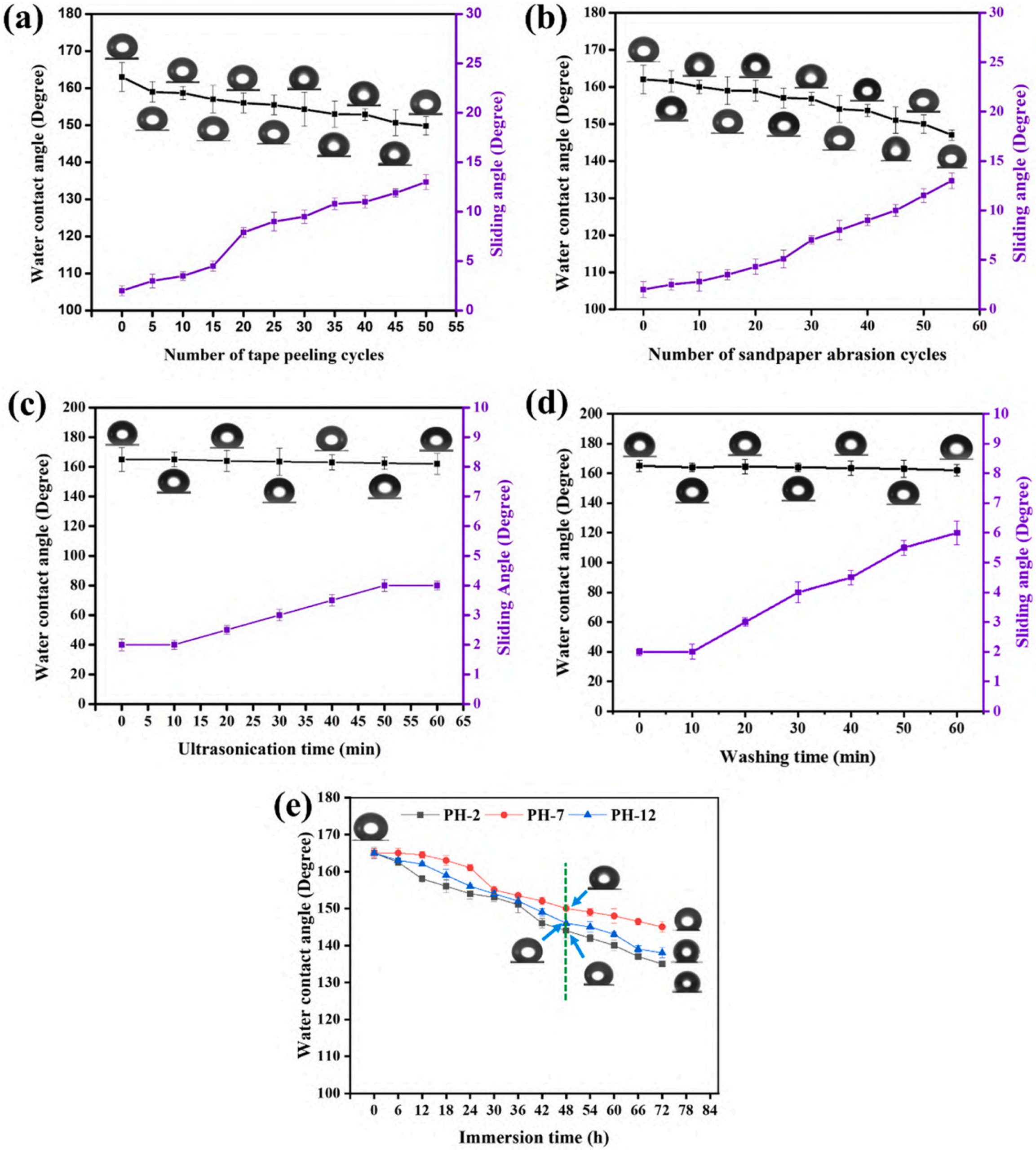


Fig. 5. Variation of WCA of PTN-2 sample against (a) tape peeling cycles, (b) sandpaper abrasion cycles, (c) ultrasonication time, (d) washing time, and (e) immersion in different pH solutions.

allow mechanical interlocking with polysilazane groups of PDMS, leading to an improvement in adhesion to cotton (Kuang et al., 2023). Hence, PTN-2 exhibits superior mechanical durability compared to the previously reported works (Han et al., 2024; Liu et al., 2022; Pan et al., 2018; Yang et al., 2023). This indicates its potential to withstand harsh conditions and could pave the way for developing more robust and resilient materials that can withstand wear over extended periods. After 50 cycles, water droplets on the PTN-2 sample did not roll but stuck to the abraded surface. This may be due to the microstructure of the coating being disturbed.

Cotton fabrics with higher tensile strength are more durable and long-lasting, contributing to sustainability by extending product lifespan and reducing environmental impact. Hence, the coated cotton fabric's tensile strength was assessed by applying a load to it. Fig. S1a depicts the elongation of cotton fabric with the applied load, which shows even though the coating reduced the tensile strength of the fabric marginally, the coated sample provided maximum elongation. The maximum elongations before break for the pristine and coated fabrics were 29 mm and 32 mm, respectively. These changes are attributed to the introduction of PDMS. The high surface energy properties of natural cotton facilitate adhesion to PDMS. The superior flexibility of PDMS molecular chains contributes to sustaining tensile strength and elongation at break.

The PTN-2 sample underwent ultrasound treatment and washing to assess its laundry stability (Ou et al., 2023; Wu et al., 2023). The PTN-2 sample was placed in a water-filled ultrasonication bath. After treatment sample was dried at 100 °C for 30 min. The WCA and SA were noted after every 10 min of ultrasound treatment. The values of WCA only slightly decreased, and SA slightly increased even after 60 min (Fig. 5c). Likewise, the washing test was conducted using a simulated washing machine. The PTN-2 sample, tap water (300 mL) and detergent (0.05 g) were added to a beaker and stirred for various durations at 150 RPM. After every 10 min of washing, sample was dried at 100 °C for 30 min. The results of the washing test, as depicted in Fig. 5d, revealed that the WCA variation was marginal, while SA increased only slightly even after 60 min. Further, to assess the washing cycle stability, the PTN-2 sample underwent stirring for 30 min and was subsequently dried at 100 °C for 30 min to complete a one-cycle (Wu et al., 2023). The WCA and SA were measured every five cycles, and the results are depicted in Fig. S1b. Even after 30 washing cycles, the PTN-2 sample exhibited a WCA of 152° and SA of 11°. The air layer trapped in the superhydrophobic fabric acts as a barrier, preventing water from penetrating the cotton surface. Furthermore, the stability of the PTN-2 sample was tested in harsh chemical environments. For this purpose, the PTN-2 sample was immersed in different pH solutions for 72 h. The WCA declined with immersion time; however, the superhydrophobic property was sustained even after 48 h (Fig. 5e). After 72 h of immersion, the superhydrophobic coating became hydrophobic. The exceptional chemical inertness of PDMS, when combined with the chemical stability of TiO_2 particles, results in a synergistic effect that demonstrates remarkable chemical stability across a broad range of pH solutions. Table S1 compares the durability of superhydrophobic cotton fabric with previous literature. The superhydrophobic PTN-2 sample was quite mechanically and chemically resistant, as evidenced by these studies.

3.4. *Flexibility and breathability*

The physical characteristics of cotton fabrics, including their weave structure, fiber properties, lightweight nature, and finishing processes, significantly impact their flexibility, breathability and air permeability, ensuring comfort for regular wear. These essential properties, such as flexibility, air permeability and breathability of the PTN-2 sample were evaluated based on reported literature (Li et al., 2024a; Yan et al., 2024). The fabrics were folded naturally to assess the flexibility of uncoated and coated (PTN-2) samples (Fig. 6a-b). The differences in length observed were negligible, suggesting that the coating does not affect the flexibility of the underlying cotton. The pure cotton fabric's initial air permeability was measured to be 77.8 mm s^{-1}. After applying the stearic acid-TiO_2-PDMS composite, the air permeability decreased slightly to 70.63 mm s^{-1}. Additionally, the breathability of the cotton fabric before and after coating was tested using a well-known chemical reaction involving ammonia and hydrochloric acid. Hydrochloric acid and ammonia are placed in separate bottles. The hydrochloric acid bottle is sealed with a cap, while the ammonia bottle is covered with fabric. Upon removing the cap from the hydrochloric acid bottle, white smoke appears on the fabric covering the ammonia bottle due to the generation of ammonium chloride (NH_4Cl) (Fig. 6c-d). These results indicated that the superhydrophobic coating material applied to the cotton fabric did not compromise its flexibility and breathability properties.

3.5. *Self-cleaning*

Superhydrophobic surfaces are highly appreciated for their self-cleaning performance, which is considered as one of their most important properties. This unique property allows these surfaces to repel liquids and prevent the accumulation of dirt and other contaminants, making them highly desirable for a variety of industrial applications. Hence, the self-cleaning abilities of the PTN-2 sample were tested by rolling water droplets and soaking in dirty water, respectively (Chauhan et al., 2019; Su et al., 2023). Soot particles were sprinkled on PTN-2 to test the self-cleaning ability (Fig. 7a). Water droplets were dropped onto

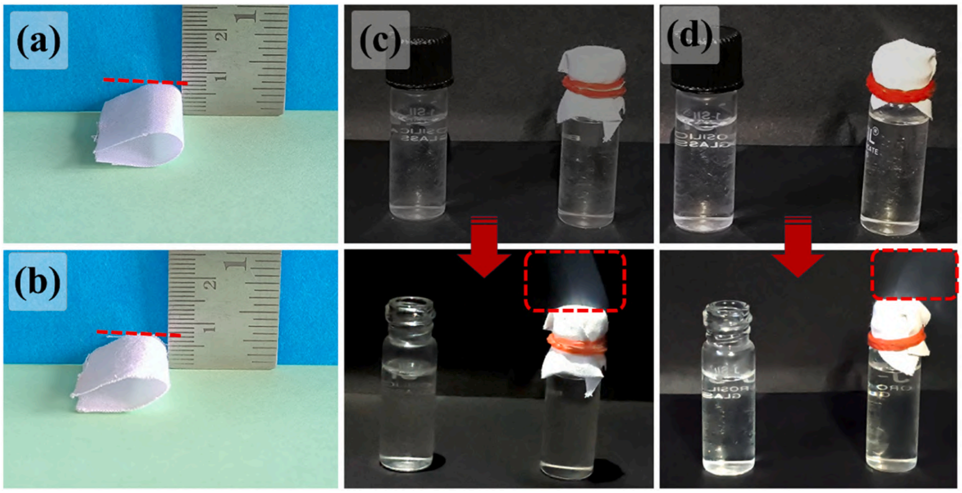


Fig. 6. Comparison of flexibility of (a) uncoated and (b) coated cotton fabric, and the breathability of (c) uncoated and (d) coated cotton fabric.

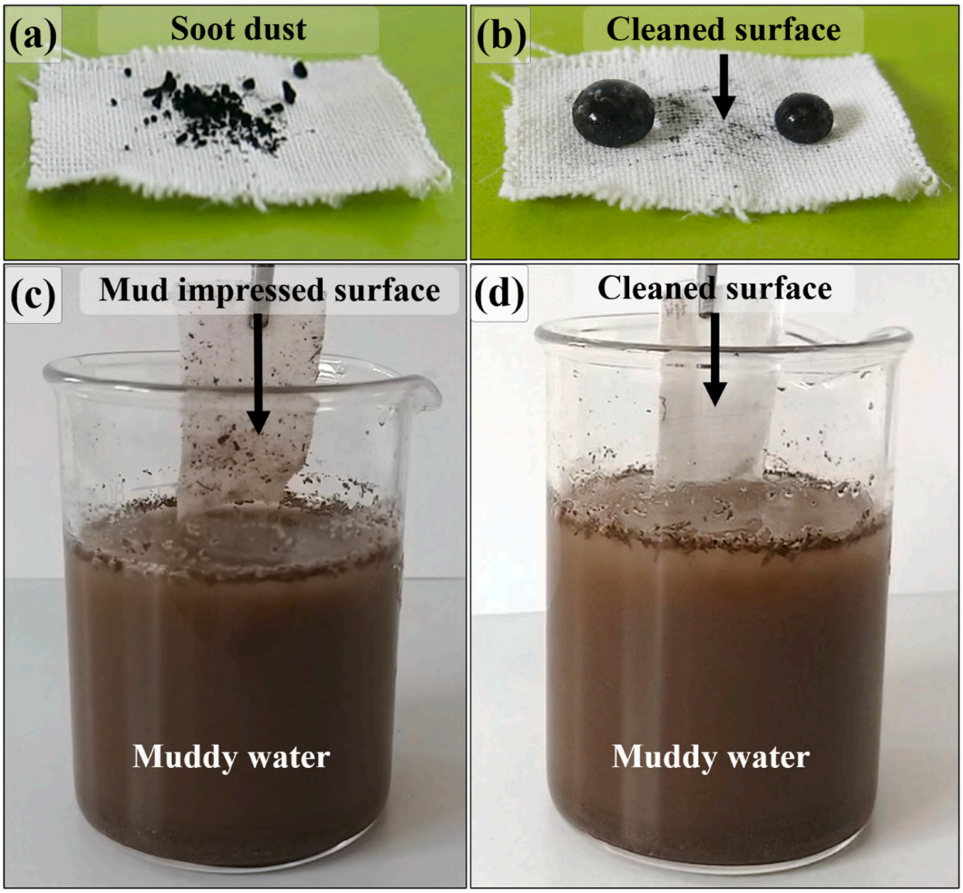


Fig. 7. (a) and (b) Self-cleaning performance of PTN-2 sample under rolling action of water droplet. Muddy water test on (c) pure cotton fabric and (d) PTN-2 sample.

the dusty PTN-2 sample with a syringe and rolled around the surface. As they are moved, dust particles easily absorb water droplets, leaving behind an almost dust-free surface (Fig. 7b).

When soot particles come into contact with water droplets, they get adsorbed by them. However, on a superhydrophobic PTN-2 surface, water is repelled. This causes the soot particles adsorbed on the water droplets to roll freely just like normal water droplets, without getting stuck on the surface. The self-cleaning capabilities of coated and uncoated cotton fabrics was tested by submerging them in polluted water. The muddy water was prepared by dissolving 50 g of fine soil particles in 50 mL of water. There are contaminated drips etched on the surface of the pure cotton fabric that has absorbed water (Fig. 7c). On the contrary, the PTN-2 sample's exceptional superhydrophobicity allows it to resist dirty water exactly like it would be normal water. The coated cotton cloth was completely devoid of mud stains after dipping and retrieving multiple times (Fig. 7d), suggesting admirable self-cleaning ability. The PTN-2 surface possesses a hierarchical rough structure which includes several hydrophobic groups. This peculiar structure causes the surface to exhibit strong hydrophobicity, which leads to the repulsion of aqueous droplets and prevents them from being trapped on the surface.

3.6. Model studies

Scientific research has demonstrated that wearing clean and dry clothes can yield substantial psychological and health advantages. It has the potential to enhance self-esteem, bolster confidence, and elevate mood, while also serving as a preventive measure against skin infections, allergies, and respiratory problems. Wearing clean clothes is crucial in different social and professional contexts as it is necessary for creating a favorable impression and adhering to societal standards. Dirty garments can serve as a breeding ground for harmful microorganisms such as bacteria, fungi, and other disease-causing agents. This can result in a range of health problems including skin infections, allergies, and potentially even respiratory complications. Bacteria and sweat accumulation on clothes lead to unpleasant odors. Dirt and stains from daily liquids can degrade clothing fabric over time, leading to wear and tear. Regular cleaning is essential to maintain the integrity of clothing, extend its lifespan, and reduce the risk of illness. However, it can be a time-consuming and costly process. To address this challenge, we have adopted a baby doll as a model for testing a self-cleaning approach suitable for viable applications. The baby doll's clothing was stitched out of cotton fabric. The spray technique proper for large-scale preparation was used to spray TiO_2-PDMS composite to coat the shirt and pants of the baby doll. A spray gun with a nozzle diameter of 0.2 mm was used to spray all over the garment at a distance of 10 cm. Approximately 1 mL of the prepared coating solution was sprayed on each 5×5 cm^2 area of cotton garment. After applying the coating solution to the entire garment, it was dried using hot air at a temperature between 60 and 80 °C. We evaluated the anti-wetting and self-cleaning abilities of the garment by pouring colored and muddy water over the surface of the coated cotton shirt. The color water (500 mL) that was thrown onto the uncoated clothing was absorbed (Fig. 8a, Video S1), whereas the color water that was spilled onto the coated cotton shirt was entirely rejected (Fig. 8b, Video S2), proving the excellent superhydrophobicity and antifouling of the spray-coated surface. During muddy water testing, mud droplets stuck to the surface of the pure cotton clothing (Fig. 8c and d, Video S3), whereas the coated surface smartly keeps away from the dirt and moisture (Fig. 8e and f, Video S4), maintaining its appearance intact. This finding adds to the growing body of research supporting the superior self-cleaning abilities of clothes made from TiO_2-PDMS coated

Fig. 8. The colored water dropped on (a) uncoated and (b) coated cotton fabric. Muddy water dropped on (c-d) uncoated and (e-f) coated cotton fabric..

superhydrophobic cotton.

Supplementary material related to this article can be found online at doi:10.1016/j.indcrop.2024.119717.

4. Conclusions

A cost-effective dip/spray coating technique was used to create a flexible, breathable, self-cleaning superhydrophobic cotton fabric using stearic acid modified TiO_2 and PDMS for comfortable wearable cloths. Surface analysis revealed that the coated fabric has a roughened structure at the microscale level, along with the presence of low surface energy molecules, which resulted in superhydrophobicity. The as-coated cotton fabric effectively repelled daily use common aqueous beverages. The results of mechanical durability studies indicate that the coated surface outperforms the non-coated surface even after undergoing various tests, including tape peeling test (30 cycles), sandpaper abrasion test (40 cycles), ultrasound treatment (60 min) and washing test (30 cycles). Additionally, the as-coated cotton fabric revealed excellent tensile strength, flexibility, air permeability, breathability and chemical stability. The coated cotton fabric has demonstrated remarkable self-cleaning properties under dry and wet dust conditions. Based on our model studies using spray-coated baby doll clothing, we confidently say that the superhydrophobic coating holds great promise for commercial applications.

CRediT authorship contribution statement

Rajaram S. Sutar: Writing – original draft, Methodology, Investigation, Conceptualization. **Snehal G. Kodag:** Methodology, Investigation. **Rutuja A. Ekunde:** Methodology, Data curation. **Akshata S. Sawant:** Methodology, Investigation. **Tanuja A. Ekunde:** Methodology. **Saravanan Nagappan:** Validation, Formal analysis. **Yong Hyun Kim:** Visualization, Validation. **Viswanathan S. Saji:** Writing – review & editing, Validation. **Shanhu Liu:** Writing – review & editing, Conceptualization, Supervision, Funding acquisition. **Sanjay S. Latthe:** Writing – review & editing, Conceptualization, Supervision, Project administration, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Acknowledgments

This work was supported by the National Natural Science Foundation of China (21950410531), DST – INSPIRE Faculty Scheme, Department of Science and Technology (DST), Govt. of India [DST/INSPIRE/04/2015/000281], and the Petro-China Research Institute of Petroleum Exploration & Development (RIPED-2019-CL-186). One of the authors, SSL is grateful for financial assistance received through Seed Money Scheme from Vivekanand College, Kolhapur (Empowered Autonomous), Ref. No. VCK/3108/2023–24 dated 30/03/2024

Data avail ability

Data will be made available on request.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.indcrop.2024.119717.

References

Akakuru, O.U., Iqbal, Z.M., Wu, A., 2020. TiO_2 nanoparticles: properties and applications. TiO_2 Nanoparticles. Appl. Nanobiotechnol. Nanomed. 1–66. https://doi.org/10.1002/9783527825431.ch1.

Chauhan, P., Kumar, A., Bhushan, B., 2019. Self-cleaning, stain-resistant and anti-bacterial superhydrophobic cotton fabric prepared by simple immersion technique. J. Colloid Interface Sci. 535, 66–74. https://doi.org/10.1016/j.jcis.2018.09.087.

Chen, C., Wang, Z., Chen, H., Wang, H., Xu, Y., Dong, C., Lu, Z., 2024. Enhancing flame retardancy and multi-functionalization of environmentally friendly cotton fabrics with a polydimethylsiloxane-based polyurethane. Int. J. Biol. Macromol. 277, 134433. https://doi.org/10.1016/j.ijbiomac.2024.134433.

Chen, J., Yuan, L., Shi, C., Wu, C., Long, Z., Qiao, H., Wang, K., Fan, Q.H., 2021. Nature-inspired hierarchical protrusion structure construction for washable and wear-resistant superhydrophobic textiles with self-cleaning ability. ACS Appl. Mater. Interfaces 13, 18142–18151. https://doi.org/10.1021/acsami.1c03539.

Dai, C., Peng, L., Li, Y., Li, Z., Chen, D., Wang, F., Lin, N., 2024. Distribution of per-and polyfluoroalkyl substances in blood, serum, and urine of patients with liver cancer and associations with liver function biomarkers. J. Environ. Sci. 139, 418–427. https://doi.org/10.1016/j.jes.2023.05.026.

Dalawai, S.P., Aly, M.A.S., Latthe, S.S., Xing, R., Sutar, R.S., Nagappan, S., Ha, C.-S., Sadasivuni, K.K., Liu, S., 2020. Recent advances in durability of superhydrophobic self-cleaning technology: a critical review. Prog. Org. Coat. 138, 105381. https://doi.org/10.1016/j.porgcoat.2019.105381.

Foorginezhad, S., Asadnia, M., 2023. Superhydrophobic Al_2O_3/MMT-PDMS coated Fabric for Self-Cleaning and Oil–Water Separation Application. Langmuir 39, 18311–18326. https://doi.org/10.1021/acs.langmuir.3c02325.

Guo, Y., Li, C., Li, X., Xu, H., Chen, W., Fang, K., Zhang, L., Li, R., Xie, R., 2023. Fabrication of superhydrophobic cotton fabric with multiple durability and wearing comfort via an environmentally friendly spraying method. Ind. Crops Prod. 194, 116359. https://doi.org/10.1016/j.indcrop.2023.116359.

Han, L., Li, Y., Cao, L., Gao, H., Huang, E., Zhao, S., Li, W., 2024. One-step fabrication of OTS modified superhydrophobic cotton fabric and its efficient oil-water separation application. Sep. Purif. Technol. 340, 126760. https://doi.org/10.1016/j.seppur.2024.126760.

Hao, X., Cheng, Z., Zhang, Y., Xie, J., Zheng, H., Yue, C., Sheng, W., 2024. Wettability Study of an Acidified Nano-TiO_2 Superhydrophobic Surface. ACS Omega 9, 4447–4454. https://doi.org/10.1021/acsomega.3c07011.

Hou, C., Fan, Z., Yang, J., 2024a. Preparation and properties of super hydrophobic cotton fabric constructed by modified nano-SiO_2 hybrid fluoro-epoxy copolymer. Surf. Interfaces 45, 103814. https://doi.org/10.1016/j.surfin.2023.103814.

Hou, C., Song, J., Gui, Q., Fan, Z., 2024b. Super hydrophobic coating and oil-water separation based on modified titanium dioxide and glycerol ethers. Colloids Surf. A: Physicochem. Eng. Asp. 691, 133874. https://doi.org/10.1016/j.colsurfa.2024.133874.

Jaggessar, A., Velic, A., Yarlagadda, P.K., Spann, K., 2022. TiO_2 nanostructures that reduce the infectivity of human respiratory viruses including SARS-CoV-2. ACS Biomater. Sci. Eng. 8, 2954–2959. https://doi.org/10.1021/acsbiomaterials.2c00326.

Kuang, J., An, X., Huang, C., Chen, H., Wei, C., 2023. Design and preparation of durable anti-icing polysilazane coatings with abrasion and UV resistance. J. Appl. Polym. Sci. 140, e53416. https://doi.org/10.1002/app.53416.

Lahiri, S.K., Zhang, P., Zhang, C., Liu, L., 2019. Robust fluorine-free and self-healing superhydrophobic coatings by H_3BO_3 incorporation with SiO_2–alkyl-silane@ PDMS on cotton fabric. ACS Appl. Mater. Interfaces 11, 10262–10275. https://doi.org/10.1021/acsami.8b20651.

Latthe, S.S., Sutar, R.S., Kodag, V.S., Bhosale, A., Kumar, A.M., Sadasivuni, K.K., Xing, R., Liu, S., 2019. Self–cleaning superhydrophobic coatings: Potential industrial applications. Prog. Org. Coat. 128, 52–58. https://doi.org/10.1016/j.porgcoat.2018.12.008.

Li, F., Kong, W., Zhao, X., Pan, Y., 2020. Multifunctional TiO_2-based superoleophobic/superhydrophilic coating for oil–water separation and oil purification. ACS Appl. Mater. Interfaces 12, 18074–18083. https://doi.org/10.1021/acsami.9b22625.

Li, J., Li, X., Liu, J., Hu, B., Cao, X., Wu, Z., Li, B., 2024a. Robust, breathable and antibacterial superamphiphobic cotton fabrics prepared by layer-by-layer dip coating. Appl. Surf. Sci. 669, 160582. https://doi.org/10.1016/j.apsusc.2024.160582.

Li, S., Yu, L., Xiong, J., Xiong, Y., Bi, S., Quan, H., 2022. Facile Fabrication of Superhydrophobic and Flame-Retardant Coatings on Cotton Fabrics. Polymers 14, 5314. https://doi.org/10.3390/polym14235314.

Li, T., Peng, Y., Yang, J., You, H., 2024b. Robust superhydrophobic cotton fabric based on dual-sized silica particles with self-healing nature. Int. J. Biol. Macromol. 267, 131437. https://doi.org/10.1016/j.ijbiomac.2024.131437.

Liu, J., Ye, L., Wooh, S., Kappl, M., Steffen, W., Butt, H.-Jr, 2019. Optimizing hydrophobicity and photocatalytic activity of PDMS-coated titanium dioxide. ACS Appl. Mater. Interfaces 11, 27422–27425. https://doi.org/10.1021/acsami.9b07490.

Liu, X., Wei, Y., Tao, F., Zhang, X., Gai, L., Liu, L., 2022. All-water-based superhydrophobic coating with reversible wettability for oil-water separation and wastewater purification. Prog. Org. Coat. 165, 106726. https://doi.org/10.1016/j.porgcoat.2022.106726.

Ma, D., Lu, Y., Liang, Y., Ruan, T., Li, J., Zhao, C., Wang, Y., Jiang, G., 2021. A critical review on transplacental transfer of per-and polyfluoroalkyl substances: Prenatal exposure levels, characteristics, and mechanisms. Environ. Sci. Technol. 56, 6014–6026. https://doi.org/10.1021/acs.est.1c01057.

Mahbubul Bashar, M., Khan, M.A., 2013. An overview on surface modification of cotton fiber for apparel use. J. Polym. Environ. 21, 181–190. https://doi.org/10.1007/s10924-012-0476-8.

Ou, H., Dai, Z., Gao, Y., Zhou, B., 2023. Breathable fabrics with robust superhydrophobicity via in situ formation of hierarchical surface morphologies. ACS Appl. Mater. Interfaces 15, 39989–40000. https://doi.org/10.1021/acsami.3c07125.

Pan, G., Xiao, X., Yu, N., Ye, Z., 2018. Fabrication of superhydrophobic coatings on cotton fabric using ultrasound-assisted in-situ growth method. Prog. Org. Coat. 125, 463–471. https://doi.org/10.1016/j.porgcoat.2018.09.026.

Qi, L., Qiu, S., Xi, J., Yu, B., Hu, Y., Xing, W., 2022. Construction of super-hydrophobic, highly effective flame retardant coating for cotton fabric with superior washability and abrasion resistance. J. Colloid Interface Sci. 607, 2019–2028. https://doi.org/10.1016/j.jcis.2021.10.021.

Qian, F., Chen, M., Li, Z., Zhou, C., Li, R., Ren, X., 2023. Fabrication of Stable Fluorine-Free Hydrophobic Cotton Fabrics with Prominent Antibacterial Property. Fibers Polym. 24, 3869–3877. https://doi.org/10.1007/s12221-023-00362-x.

Shang, Q., Liu, C., Chen, J., Yang, X., Hu, Y., Hu, L., Zhou, Y., Ren, X., 2020. Sustainable and robust superhydrophobic cotton fabrics coated with castor oil-based nanocomposites for effective oil–water separation. ACS Sustain. Chem. Eng. 8, 7423–7435. https://doi.org/10.1021/acssuschemeng.0c01469.

Shin, B., Lee, K.-R., Moon, M.-W., Kim, H.-Y., 2012. Extreme water repellency of nanostructured low-surface-energy non-woven fabrics. Soft Matter 8, 1817–1823. https://doi.org/10.1039/C1SM06867A.

Su, C., Zhou, L., Ju, G., Meng, F., Zhang, H., Mu, Q., Liu, Z., Zhang, L., 2023. Multifunctional design integrating the flame-retardant and antifouling functionality into superhydrophobic cotton fabric. Prog. Org. Coat. 185, 107871. https://doi.org/10.1016/j.porgcoat.2023.107871.

Suryaprabha, T., Sethuraman, M.G., 2021. A facile approach for fabrication superhydrophobic and UV-blocking cotton fabrics with self-cleaning properties. Fibers Polym. 22, 1033–1040. https://doi.org/10.1007/s12221-021-0648-z.

Vijayalakshmi, R., Rajendran, V., 2012. Synthesis and characterization of nano-TiO_2 via different methods. Arch. Appl. Sci. Res 4, 1183–1190.

Wang, X., Li, S., Chen, P., Li, F., Hu, X., Hua, T., 2022. Photocatalytic and antifouling properties of TiO_2-based photocatalytic membranes. Mater. Today Chem. 23, 100650. https://doi.org/10.1016/j.mtchem.2021.100650.

Wang, Y., Huang, Z., Gurney, R.S., Liu, D., 2019. Superhydrophobic and photocatalytic PDMS/TiO_2 coatings with environmental stability and multifunctionality. Colloids Surf. A: Physicochem. Eng. Asp. 561, 101–108. https://doi.org/10.1016/j.colsurfa.2018.10.054.

Wu, W., Zhang, Y., Miao, S., Wu, Y., Gong, X., 2023. Photothermal superhydrophobic cotton fabric based on silver nanoparticles cross-linked by polydopamine and polyethylenimide. Langmuir 39, 15131–15141. https://doi.org/10.1021/acs.langmuir.3c02269.

Wu, Y., Wu, X., Yang, F., Gan, J., Jia, H., 2021. The preparation of cotton fabric with super-hydrophobicity and antibacterial properties by the modification of the stearic acid. J. Appl. Polym. Sci. 138, 50717. https://doi.org/10.1002/app.50717.

Xu, L.-H., Wang, L.-M., Pan, H., Shen, Y., Ding, Y., Zhang, X.-Y., Sheng, Y., 2019. Preparation of superhydrophobic porous SiO_2 aerogel using methyl trimethoxy silane single precursor and superhydrophobic cotton fabric coating from it. J. Nanosci. Nanotechnol. 19, 7799–7809. https://doi.org/10.1166/jnn.2019.16730.

Xu, Q., Wang, X., Wang, P., Cheng, L., Wan, Y., Wang, Z., 2022. Sustainable and superhydrophobic coating from epoxidized soybean oil and stearic acid on cotton fabric etched by deep eutectic solvent. Mater. Today Chem. 26, 101211. https://doi.org/10.1016/j.mtchem.2022.101211.

Xu, Q., Wang, X., Zhang, Y., 2023. Green and sustainable fabrication of a durable superhydrophobic cotton fabric with self-cleaning properties. Int. J. Biol. Macromol. 242, 124731. https://doi.org/10.1016/j.ijbiomac.2023.124731.

Xue, C.-H., Bai, X., Jia, S.-T., 2016. Robust, self-healing superhydrophobic fabrics prepared by one-step coating of PDMS and octadecylamine. Sci. Rep. 6, 1–11. https://doi.org/10.1038/srep27262.

Yan, K., Wang, J., Zong, Y., Xu, Q., 2024. A multifunctional coating toward wearable superhydrophobic fabric sensor with self-healing and flame-retardant properties with high fire alarm response. Chem. Eng. J. 489, 151315. https://doi.org/10.1016/j.cej.2024.151315.

Yang, J., He, T., Li, X., Wang, R., Wang, S., Zhao, Y., Wang, H., 2023. Rapid dipping preparation of superhydrophobic TiO_2 cotton fabric for multifunctional highly efficient oil-water separation and photocatalytic degradation. Colloids Surf. A: Physicochem. Eng. Asp. 657, 130590. https://doi.org/10.1016/j.colsurfa.2022.130590.

Yang, M., Liu, W., Jiang, C., He, S., Xie, Y., Wang, Z., 2018a. Fabrication of superhydrophobic cotton fabric with fluorinated TiO_2 sol by a green and one-step sol-gel process. Carbohydr. Polym. 197, 75–82. https://doi.org/10.1016/j.carbpol.2018.05.075.

Yang, M., Liu, W., Jiang, C., Liu, C., He, S., Xie, Y., Wang, Z., 2018b. Facile preparation of robust superhydrophobic cotton textile for self-cleaning and oil–water separation. Ind. Eng. Chem. Res. 58, 187–194. https://doi.org/10.1021/acs.iecr.8b04433.

Yang, Y., Zhao, S., Bi, F., Chen, J., Li, Y., Cui, L., Xu, J., Zhang, X., 2022a. Oxygen-vacancy-induced O_2 activation and electron-hole migration enhance photothermal catalytic toluene oxidation. Cell Rep. Phys. Sci. 3. https://doi.org/10.1016/j.xcrp.2022.101011.

Yang, Y., Zhao, S., Bi, F., Chen, J., Wang, Y., Cui, L., Xu, J., Zhang, X., 2022b. Highly efficient photothermal catalysis of toluene over Co_3O_4/TiO_2 pn heterojunction: The crucial roles of interface defects and band structure. Appl. Catal. B: Environ. 315, 121550. https://doi.org/10.1016/j.apcatb.2022.121550.

Zhang, X., Rao, R., Gao, B., Ma, S., Bi, F., Li, C., Zhu, Z., Liu, N., Yang, Y., Wang, Z., 2023. Crystal engineering of TiO_2 enhanced photothermal catalytic degradation of DEHP on Pt catalysts. Mater. Today Chem. 34, 101755. https://doi.org/10.1016/j.mtchem.2023.101755.