



Transferring the structure of paper for mechanically durable superhydrophobic surfaces

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ARTICLE INFO

Keywords:

Superhydrophobic coatings
Paper
PDMS
Nanoparticles
Microstructure

ABSTRACT

Solution-phase deposition of nanomaterials represents a highly promising technology with strong industrial application potential for the fabrication of superhydrophobic surfaces. An important barrier towards the adaptation of such materials and processes in a broad range of applications is the limited mechanical durability of the nanostructures. Herein, we present a universal solution to this challenge by benefiting from the unique microstructure of paper. Our approach is based on transferring the structure of paper into a target material, to form a mechanical protection layer for nanomaterials that were deposited from solution-phase, i.e. spray-coating. We demonstrate this concept through the transfer of the structure of paper to a free-standing PDMS film using a simple molding process. Spraying a dispersion of alkyl-silane functionalized silica nanoparticles on the structured free-standing film results in a hierarchically structured superhydrophobic surface with a water contact angle of $175^\circ \pm 2^\circ$ and a sliding angle $< 2^\circ \pm 1^\circ$. The fabricated superhydrophobic surface displays high levels of mechanical, chemical and thermal stability. The robust, inexpensive, scalable, flexible, and environmentally friendly nature of the presented approach may be a key enabler in superhydrophobic coating applications.

1. Introduction

Development of superhydrophobic surfaces that are extremely repellent to water can enable a diverse range of applications in aerospace, construction, automobile, food packaging, and textile industries [1–4]. The existing literature has proven the need for texture to fabricate superhydrophobic surfaces. One of the simplest ways to generate texture at the nanometer length scale is to deposit nanomaterials, which are typically functionalized with organic molecules to reduce the surface energy [5–7]. This type of technology has strong commercialization potential since the application of the coating can be performed simply without the need for complex and expensive infrastructure. Spray-coating of nanomaterials, in particular, has received significant interest for the fabrication of water repellent coatings [8–13]. The essential advantages of spray-coating include: i) the ex-situ coating of existing surfaces of varying composition, geometry and stiffness, ii) ease of application using simple tools, iii) minimal usage of materials, iv) scalable fabrication over large areas. Despite its effectiveness in providing superhydrophobicity, this kind of nanoscale topography can be easily removed from the surface with the impact of water or abrasion

[14–17]. Approaches to improve the durability have mostly focused on the use of polymeric matrix materials with challenges in the reduction of water repellency and unsatisfying mechanical durability [18]. Inspired from nature and informed from the previous studies, hierarchical structures that provide texture at different length scales are effective in fabricating robust superhydrophobic surfaces [19–22]. The hierarchical structures also enable water repellent surfaces with low contact angle hysteresis and easy sliding of droplets. The key idea in the mechanical robustness is the ability of the microscale structures to protect nanoscale topography from impact and abrasion [23]. The challenge is scalable, low-cost and versatile fabrication of surfaces that are properly structured at the micrometer length scale for deposition of colloidal nanomaterials.

The fibrous microstructure of paper is an ideal template to fabricate hierarchically structured superhydrophobic surfaces. The randomly positioned cellulose fibers that form during the production of paper provide microscale topography [24,25]. The deposition of nanomaterials on this substrate results in nanoscale roughness, completing the formation of hierarchical structures [26]. In our previous study [27], we showed that the use of paper as a substrate in comparison to glass

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substrates results in significant improvement of the mechanical robustness of the superhydrophobic coatings fabricated by spray-coating of hydrophobic nanoparticles. We hypothesize that the essential role of paper in fabricating robust superhydrophobic coatings that consist of nanoparticles is its unique microstructure, which protects the fragile nanoscale topography against mechanical wear. Therefore, transferring the structure of paper into a target material should enable the fabrication of mechanically robust superhydrophobic coatings based on the solution-phase deposition of nanomaterials.

In the following, engineering the surface of materials using the microstructure of paper is presented as a highly effective strategy to fabricate mechanically durable superhydrophobic coatings by solution-phase deposition of hydrophobic nanoparticles. This strategy is demonstrated through the transfer of the structure of paper to a free-standing polydimethylsiloxane (PDMS) film followed by spray-coating of silica nanoparticles that were functionalized with an alkylsilane. The conformal nature of PDMS makes it an ideal molding material [28,29] with demonstrated utility in the transfer of microscale structures to fabricate superhydrophobic coatings [30–34]. Besides its low surface energy, the flexible nature of PDMS is highly suitable for the fabrication of mechanically robust water-repellent surfaces [35–38]. Previous research has shown that the microstructure of paper can be effectively duplicated via PDMS and can be used to fabricate superhydrophobic coatings without emphasis on the mechanical durability [39,40]. Through a range of different mechanical wear tests, we demonstrate transferring the structure of paper is a highly effective strategy to fabricate mechanically robust superhydrophobic surfaces by solution-phase deposition of hydrophobic nanoparticles. Spray-coating of alkyl-silane functionalized nanoparticles on top of the structured free-standing PDMS film results in a hierarchically structured superhydrophobic surface with extremely high levels of water repellency and mechanical robustness.

2. Materials and methods

2.1. Materials

Toluene and SiO₂ nanoparticles (11 nm) were bought from Sigma-Aldrich. Ethanol was bought from Merck. PDMS (Sylgard 184) and trichlorododecylsilane were purchased from Dow Corning and Gelest, respectively.

2.2. Transferring the micro-structure of the paper

PDMS base and curing agent (10:1 ratio unless otherwise stated) were mixed in a container and kept in a desiccator under vacuum for 10 min to get rid of air bubbles. The liquid PDMS mixture was then poured onto a piece of paper in a petri dish and cured at 80 °C on a hotplate for 45 min. The micro-structure of the paper surface was transferred to the PDMS after peeling off, resulting in a negative replica of the paper structure. Also, for comparison, a positive replica of the paper structure and plain PDMS were prepared following similar procedures. In the process of fabricating the positive replica, a layer of fluoroalkylsilane [41] was deposited on the negative replica before pouring the liquid PDMS mixture, to facilitate easy detachment after curing. In the case of plain PDMS film, the liquid PDMS mixture was cast on a smooth surface (e.g. petri dish). The typical thickness of the PDMS film was ~1 mm.

2.3. Preparation and deposition of hydrophobic nanoparticles

The surface of silica nanoparticles was functionalized with trichlorododecylsilane. Specifically, 2.0 g of silica nanoparticles were added to 40 mL of toluene and stirred using a magnetic bar until a homogeneous dispersion was obtained. 1 mL of trichlorododecylsilane was slowly added to the mixture and stirred continuously for 3 h, after which the mixture was centrifugated (3000 rpm) for 15 min to remove the

excess and unreacted trichlorododecylsilane. The modified nanoparticles were sedimented following the centrifugation step. In the end, the modified hydrophobic silica nanoparticles were dried in an oven at 80 °C for 12 h. To prepare the coating solution, the hydrophobic silica nanoparticles were dispersed in ethanol under stirring to prepare 2 wt% dispersion. For simplicity, from this point on, whenever silica nanoparticles are mentioned, we are referring to the hydrophobically modified nanoparticles, unless otherwise stated. The PDMS with the transferred paper structure was kept 10 cm away and spray-coated with the dispersion using a spray-coater with 0.35 mm nozzle diameter at a pressure of 4 bar. The coated surface was dried at room temperature prior to further usage. On average, the substrate contained ~23 mg/cm² hydrophobic nanoparticles.

2.4. Mechanical durability tests

The mechanical durability of the fabricated surface was tested against abrasion and water impact. The abrasion test was conducted by moving the sample under a load of 200 g weight against a sheet of aluminum foil. To test the resistance to water impact, a water spray impact test is conducted by placing the surface 2.5 cm away from a spray gun and spraying with water at a velocity of 2.85 m/s and an impact pressure of 7.41 kPa. The adhesion of the nanoparticles onto the PDMS was evaluated by the tape peel test. An adhesive tape was firmly pressed onto the surface, followed by peeling off, and counted as one cycle. An additional cyclic test was performed to evaluate the durability of coatings against repeated stretching. In each cycle, the superhydrophobic sample (length = 3 cm and width = 2 cm) was stretched to increase the length of the sample by ~33% (i.e. final length of 4 cm) and then released. The surface wetting properties were measured following the release of the sample.

2.5. Characterization

The morphology of the surfaces was characterized using scanning electron microscopy (SEM, Zeiss EVO LS10) imaging at 25 kV. Fourier-transform infrared spectroscopy (FTIR, Thermo Scientific Nicolet 6700) and X-ray photoelectron spectroscopy (XPS, Thermo Scientific, K-Alpha) were used for probing the chemical composition of the surface. The static water contact angle (CA) and sliding angle (SA) measurements were performed using an optical tensiometer system (Attension, Theta Lite) with 5 µL and 10 µL water droplets, respectively. The angles were measured for at least three times, each time at a different location, and the presented results are the average of these measurements. The error bars in the contact and sliding angle plots refer to the standard deviation.

3. Results and discussion

3.1. Transfer of the paper structure

Our strategy for the fabrication of mechanically durable superhydrophobic surfaces relies on transferring the structure of paper into a target material, to provide structural protection for the hydrophobic nanoparticles (HNPs). This strategy is realized through transferring the structure of paper to a free-standing PDMS film followed by the deposition of HNPs (Fig. 1a–b). The first step consists of pouring a liquid mixture of PDMS and curing agent on top of the paper. We used copy grade paper throughout the study. The approach applies to other types, including filter paper, straw paper and cardboard (see Fig. S1). The liquid mixture fully penetrates to the fibrous microstructure of the paper enabling true capture of the structure. A thermal treatment facilitates curing of the PDMS, resulting in an elastomeric film with the structure of the paper. The PDMS film was fully cured to facilitate the successful transfer of the structure of paper. The cured PDMS film can be peeled off from the paper, resulting in a structured free-standing and flexible film,

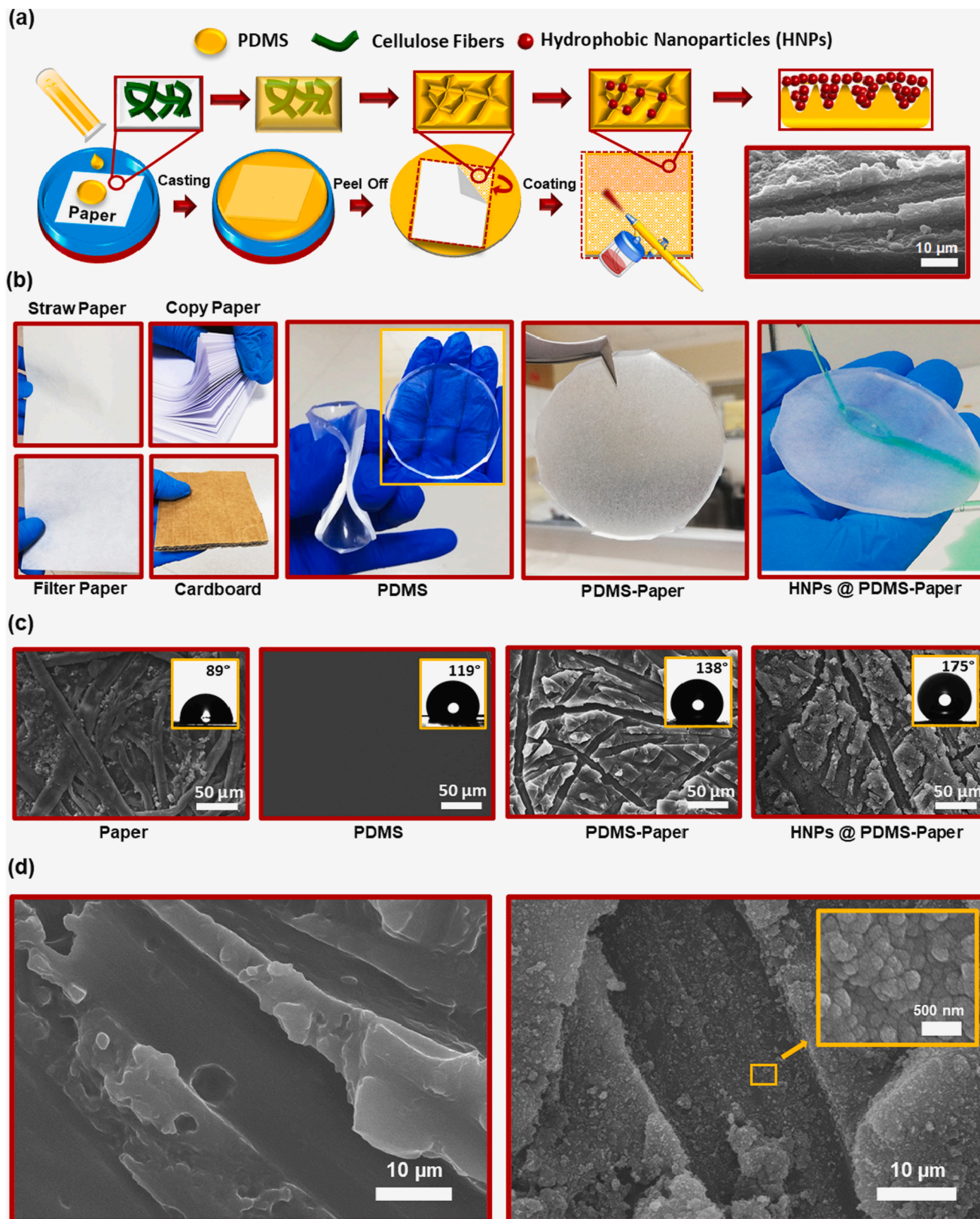


Fig. 1. Key processes and results on transferring the structure of paper for mechanically durable superhydrophobic surfaces. (a) Schematic illustration showing PDMS molding, curing and peeling processes to obtain the structured free-standing PDMS-Paper film. Spraying a suspension of the hydrophobized silica nanoparticles results in a HNPs@PDMS-Paper surface. The inset is a tilted SEM image of the superhydrophobic HNPs@PDMS-Paper surface. (b) Demonstration of versatility, flexibility, and superhydrophobic behavior of HNPs@PDMS-Paper film. Different types (straw, copy, filter, and cardboard) of paper can be utilized for fabrication. (c) SEM images of copy paper, PDMS, PDMS-Paper and HNPs@PDMS-Paper. The insets present images of water droplets and water CAs on the corresponding surfaces. (d) High magnification SEM images of PDMS-Paper (left) and HNPs@PDMS-Paper (right).

which we refer to as PDMS-Paper for brevity. The conformal nature of PDMS enables the effective transfer of the structure of the paper as shown in the SEM images presented in Fig. 1c–d. The PDMS-Paper is already highly hydrophobic with a water CA of $138^\circ \pm 2^\circ$ (Fig. 1c). Two factors contribute to this hydrophobicity. First, the PDMS cast on a smooth surface is hydrophobic with a water CA of 119° . Secondly, the microstructure of paper further increases the water repellency of PDMS through the incorporation of texture, as shown in previous studies [42]. To generate nanoscale topography on PDMS-Paper, we used solution-phase deposition of HNPs, which were prepared by modification of silica nanoparticles with an alkylsilane [26]. Spray-coating of hydrophobic nanoparticles introduces nanoscopic texture (Fig. 1c–d), leading to superhydrophobic behavior with a water CA of $175^\circ \pm 2^\circ$ and a SA of $<2^\circ \pm 1^\circ$. We refer to this flexible, translucent (Fig. S2), and superhydrophobic film (Fig. 1b) as HNPs@PDMS-Paper in the rest of the study. Besides providing the microscopical roughness, the key function of the micro-structure (Fig. 1d) replicated from paper, is to serve as a ‘refugee’ for the nanoparticles, leading to increased mechanical durability. The schematic illustration of surfaces together with their SEM images (Fig. S3) at different magnifications reveal the evolution of the structured superhydrophobic surface.

The spectroscopic characterization of the surfaces further verifies the successful fabrication of HNPs@PDMS-Paper. Each step of the fabrication was monitored with the aid of FTIR spectroscopy (Fig. 2a). The FTIR spectrum of PDMS-Paper is similar to that of plain PDMS, indicating the clean removal of the paper template without unwanted transfer of cellulose fibers. FTIR spectra of PDMS-Paper have prominent peaks at 2963 cm^{-1} (CH_3 asymmetric stretch), 1257 cm^{-1} (CH_3 symmetric bending), 1055 cm^{-1} (Si-O-Si asymmetric stretch), 1007 cm^{-1} (Si-O-Si symmetric stretch), 801 cm^{-1} (CH_3 asymmetric rocking), and 688 cm^{-1} (C–Si stretch) [43]. The FTIR spectrum of hydrophobized silica nanoparticles is dominated by strong and broad Si-O-Si asymmetric and symmetric stretch peaks at around 1007 cm^{-1} and 1055 cm^{-1} , respectively. The weak peaks at 2923 cm^{-1} and 2855 cm^{-1} are due to the asymmetric and symmetric stretch of CH_3 groups of alkylsilane introduced upon silanization [44]. The FTIR spectrum of the superhydrophobic HNPs@PDMS-Paper surface has characteristic peaks of both PDMS and HNPs, indicating the absence of formation of new chemical bonds. The XPS spectra (Fig. 2b) support this conclusion.

3.2. Mechanical durability

We first investigated the effect of negative and positive replication of the paper structure on the mechanical durability of the coatings. The first generation of transfer from paper to the PDMS results in the negative replica of the paper structure. To obtain the positive replica, an additional molding is needed using the PDMS film with the negative replica as the master. In the process of preparation of the positive replica, both the master and molded film consist of PDMS, which challenge the separation and required vapor-phase deposition of a layer of fluoroalkylsilane on top of the PDMS film that acts as the master substrate. Fig. 3 shows the morphology of the bare paper substrate together with the PDMS films that are negative and positive replicas of the paper. The visual inspection of the images demonstrates effective replication of the structure for both cases. The analysis of the images further verified that the distribution of the size of features exhibited similar behavior. The fibrous structures in the original paper and the positive replica have an average diameter of $13.4\text{ }\mu\text{m}$ and $14.1\text{ }\mu\text{m}$, respectively. The size of channels that are complementary to the cellulose fibers was $12.9\text{ }\mu\text{m}$ in the case of the negative replica. Note that there is a certain degree of distribution in the size of features extracted from the image analysis software. This distribution arises both from the structure of paper and issues in the extraction of features during the processing of images. Regardless of the type of replication, spraying HNPs resulted in an extremely non-wetting surface with a static CA of $175^\circ \pm 2^\circ$ and SA of $<2^\circ \pm 1^\circ$. The mechanical durability of the two superhydrophobic

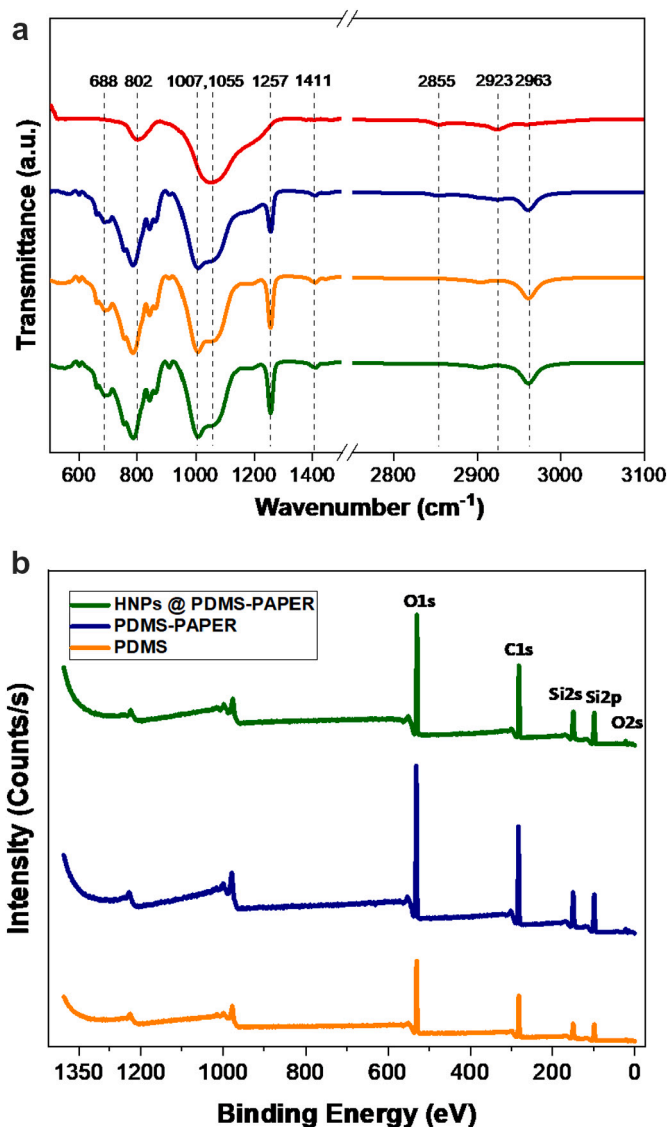


Fig. 2. Chemical characterization of materials. (a) FTIR spectra of HNPs@PDMS-Paper and its components. The spectra were obtained on the powder of the corresponding materials, namely HNPs (red), PDMS-Paper (blue), PDMS (orange), and HNPs@PDMS-Paper (green). (b) XPS spectra of HNPs@PDMS-Paper (green), PDMS-Paper (blue) and PDMS (orange). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

surfaces is comparable, as evaluated using water spray impact and water jet impact tests (Fig. S4). Both surfaces still retain superhydrophobicity with no significant CA and SA change after 200 cycles of water spray impact and 600 s of water jet impact. Thus, PDMS-Paper formed with a single transfer step is used throughout the study, as both types of structure result in similar levels of superhydrophobicity and mechanical durability upon deposition of HNPs, while the fabrication procedure is less demanding for the negative replica. Among the different types, HNPs@PDMS-Paper fabricated by using the structure of copy paper was the most durable (Fig. S5) and chosen as the template in the rest of the study.

The successful transfer of the structure of the paper is critical for the durability of the superhydrophobic coatings. We varied the ratio of the PDMS base to the curing agent and studied its impact on the mechanical durability of the HNPs@PDMS-Paper. The curing agent contains a cross-linker, which facilitates reactions with the vinyl end-groups of PDMS oligomers [45]. Mechanical properties (e.g. elastic modulus and

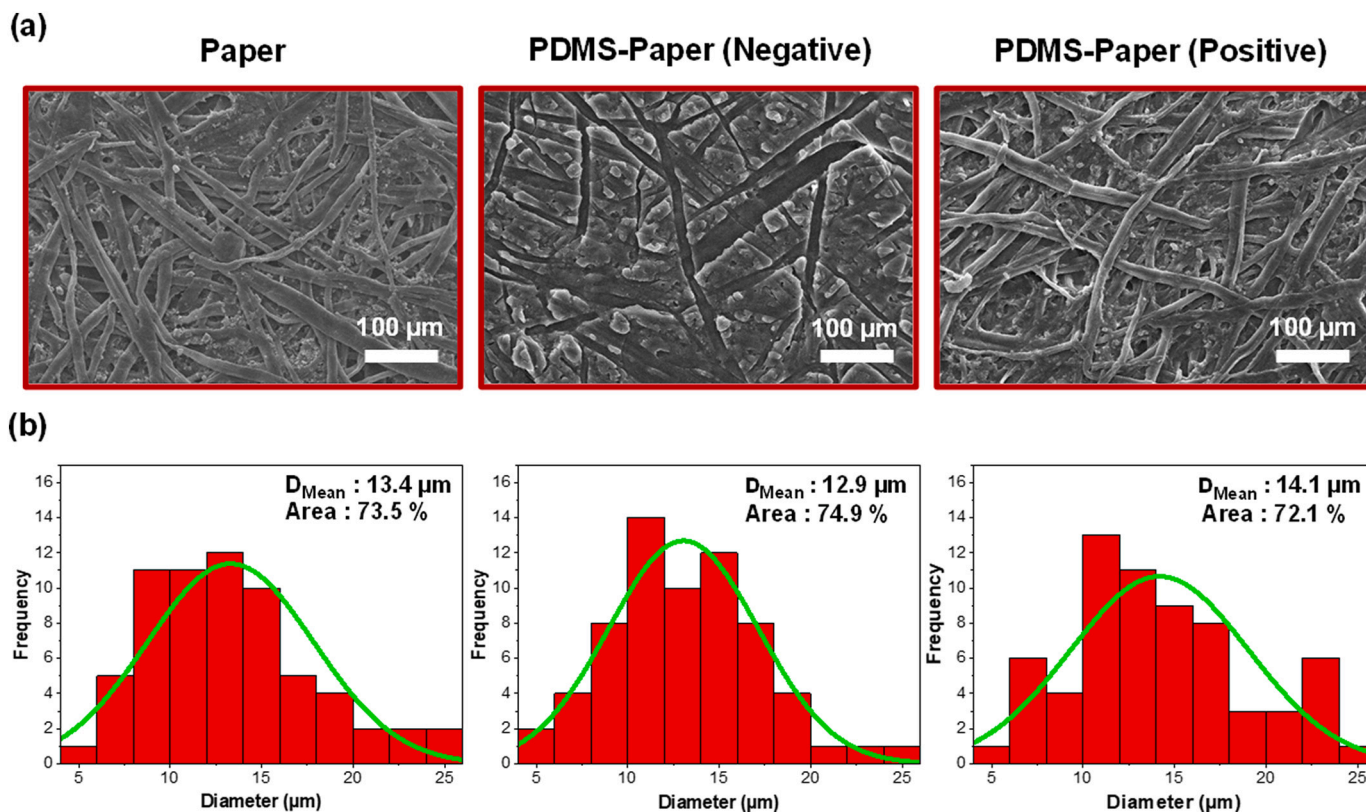


Fig. 3. Negative and positive PDMS replica of paper structure. SEM image (top row) and image analysis (bottom row) of copy paper (left), negative PDMS replica (center), and positive PDMS replica (right). The image analysis was performed using ImageJ software.

hardness) of the cross-linked material depend on the mixing ratio of the curing agent to the PDMS and affect the pattern replication process [46]. Fig. 4a–d presents variation of the static CA and SA of HNP@PDMS-Paper with the extent of water spray impact and water jet impact tests for varying mixing ratios of the curing agent and PDMS base. The durability of the superhydrophobic surface is best for a PDMS to curing ratio of 60:6 (i.e. 10:1), which is also the ratio recommended by the manufacturer. Increasing or decreasing the mixing ratios resulted in superhydrophobic surfaces with insufficient durability. As supported by the optical microscopy images (Fig. 4e), the inefficient replication of the structure results in the weakening of the durability. At high curing agent ratios, the PDMS becomes brittle impeding successful replication of the microscopic features. Insufficient cross-linking at low curing agent ratios results in soft and wacky PDMS that cannot retain microscopic features. These results further prove the critical role of the microscopic structure in protecting the nanoscale features.

To demonstrate the remarkable level of mechanical durability provided by transferring the structure of the paper, we investigated a range of extensive tests on the superhydrophobic HNP@PDMS-Paper surfaces obtained by the deposition of HNPs on the PDMS film with the negative replica of the paper structure. Figs. 5 and 6 present the durability of HNP@PDMS-Paper against different tests that challenge the nanostructures, which are the basis of the extremely water repellent character of the fabricated surfaces. In these experiments, unstructured PDMS films, obtained by pouring uncured PDMS over a flat surface, served as a control sample. Following the deposition of HNPs, this control sample was referred to as HNP@PDMS. Fig. 5a, b present variation of the static water CA and SA as a function of water spray impact cycle and abrasion length, respectively. The HNP@PDMS-Paper surface can withstand 200 cycles of water spray (Fig. 5a) and 100 cm of linear abrasion (Fig. 5b) without any discernible reduction in superhydrophobicity, as verified by the mostly invariant contact and sliding angles. In striking contrast, HNP@PDMS lost superhydrophobicity after

only 50 cycles of water spray impact and 30 cm of linear abrasion. The CA on the HNP@PDMS surface continuously decreases, up to 120 cycles of water spray impacts, then stays mostly unchanged at a value of $127^\circ \pm 2^\circ$, which is the CA of the unstructured PDMS, suggesting complete removal of hydrophobic nanoparticles. SEM imaging (Fig. 5c) verifies the loss of nanoscale texture after the water spray impact and linear abrasion tests on the unstructured PDMS films.

The striking contrast in the mechanical durability of structured and unstructured PDMS films can be well explained with the ability of the replicated paper structure to protect HNPs against mechanical wear. SEM images of the surfaces obtained by the deposition of HNPs on structured and unstructured PDMS films reveal the significant difference in the morphology and reveals the protective mechanism of the textured surface. In the absence of mechanical wear, the surface of both HNP@PDMS and HNP@PDMS-Paper appear to exhibit similar nanoscale texture. The change after mechanical tests sets apart the PDMS-Paper from the unstructured PDMS, where on the latter noticeable number of nanoparticles are removed after the water impact and abrasion tests (Fig. 5c). On the textured PDMS-Paper, the material loss is limited; after the tests, the micro-channels are exposed, but the nanoparticles are visible within the channels (Fig. 5c as well as Fig. 1d; see expanded SEM images provided in Figs. S6–S8). The basis of the remarkable level of contrast in the mechanical durability of the two superhydrophobic surfaces is illustrated in Fig. 5d. The microstructure of HNP@PDMS-Paper physically protects nanoparticles against abrasion (Fig. 5a) and water impact (Figs. 5b and 6a, b). After extended abrasion and water impact, HNPs on top of both surfaces are removed. On the unstructured PDMS surface, there are no physical obstacles that can protect the nanoparticles, whereas on the PDMS-Paper, the micro-channels can protect further removal of the nanoparticles, hence extending its longevity. There is no particular chemical bonding between PDMS and HNPs. The FTIR spectrum of the HNP@PDMS-Paper is the sum of the spectrum of the individual components, supporting the

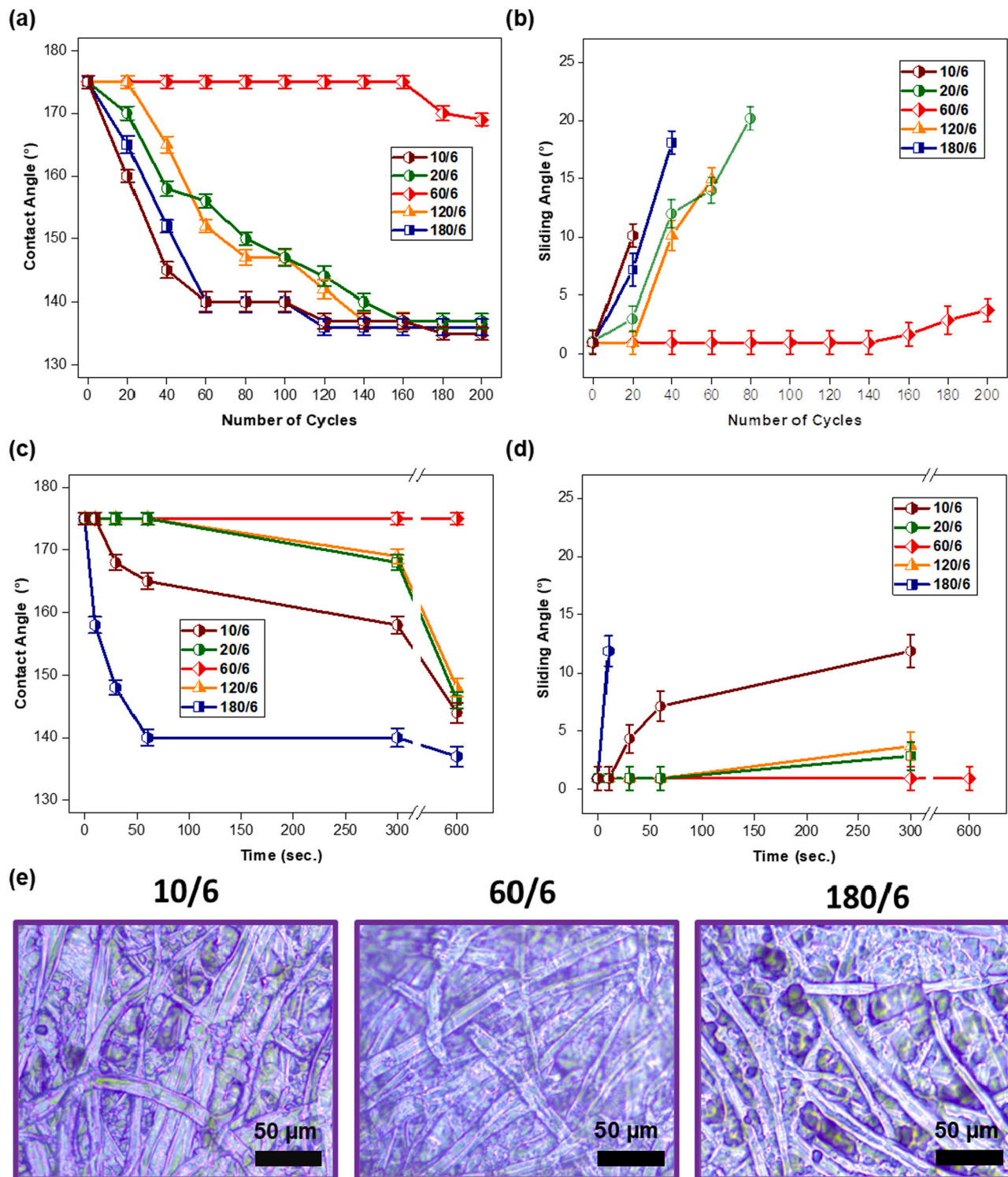


Fig. 4. Effect of the ratio of the PDMS base to the curing agent on the mechanical durability of the HNPs@PDMS-Paper. Change of water (a, c) CA and (b, d) SA as a function of (a, b) water spray cycles and (c, d) water jet treatment duration. (e) Optical microscopy images of the PDMS-Paper films obtained by using different ratios of PDMS base to curing agent.

absence of the chemical bonding. Different than composite films of PDMS and other materials [47,48], HNPs were deposited on the fully cured PDMS films excluding the possibility of cross-linking in the presence of nanoparticles. Overall, much higher mechanical robustness of the HNPs@PDMS-Paper in comparison with HNPs@PDMS clearly shows that the mechanical durability is provided by the structure of paper, as two surfaces were constructed from chemically identical materials.

The structural protection of the superhydrophobic surface is further confirmed with other types of stability tests. We first investigate the durability of the surface against exposure to different forms of water impact. The water spray impact test simulates a situation where the whole surface is exposed to water droplet impacts, like rain. The water jet and droplet impact tests simulate harsh conditions where water droplets or continuous streams impact only a small region or spot of the

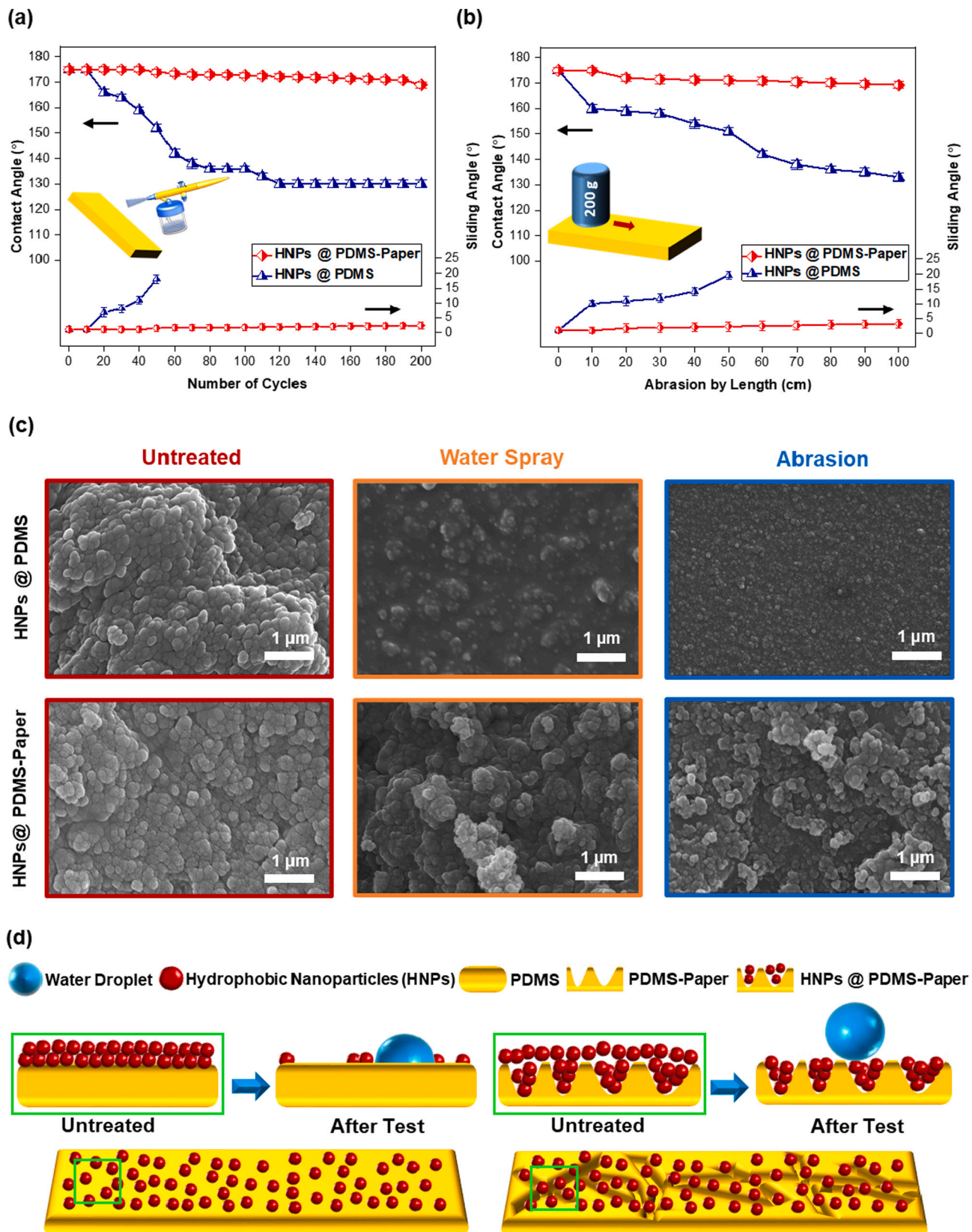


Fig. 5. Mechanical durability of the superhydrophobic HNP@PDMS-Paper surfaces against water spray impact and linear abrasion. Change of water CA (left) and SA (right) as a function of (a) water spray cycles and (b) linear abrasion distance under the load of 200 g. The inset in (a–b) illustrates the corresponding test configurations. (c) SEM images of the superhydrophobic surface, before (left column) and after 200 cycles of water spray impact (center column) and 100 cm of linear abrasion (right column). (d) Illustrative comparison of the structural protection mechanism of the structured vs plain surface.

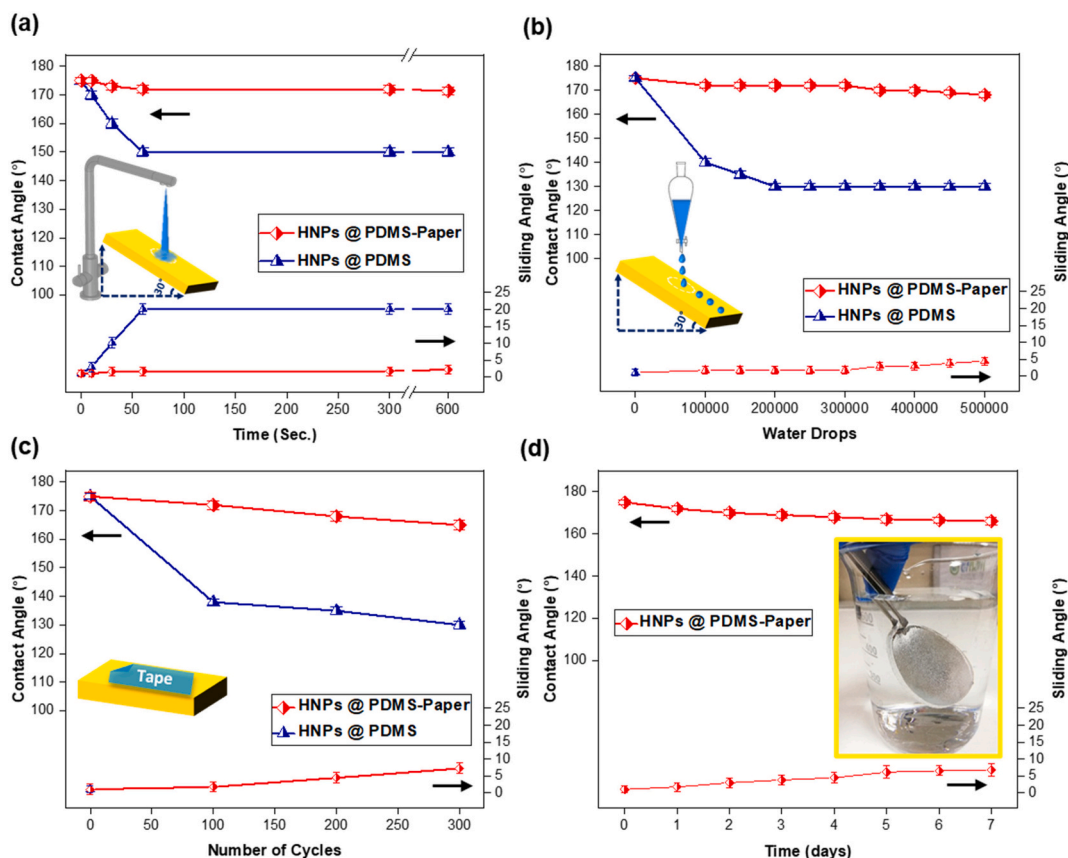


Fig. 6. The durability of superhydrophobic HNP@PDMS-Paper. Change of water CA (left) and SA (right) on the surface as a function of (a) impacting water jet time, (b) the cumulative number of free-falling droplets, (c) adhesive tape peel cycles, and (d) days of the surface immersed in water. The insets are the illustration of corresponding tests.

surface. Therefore, water jet and droplet impact tests are also performed, as shown in Fig. 6. The superhydrophobic HNP@PDMS-Paper surface can withstand the impact of the water jet for 600 s and impact of 500,000 droplets without any significant material loss. The superhydrophobic surface on the unstructured PDMS, on the other hand, loses superhydrophobicity only after impact of 50 s of water jet and 100,000 droplets, as a result of the removal of the deposited nanoparticles (Fig. S9). The mechanical robustness of the HNP@PDMS-Paper outperforms composite films constructed from PDMS and hydrophobic materials [48].

The adhesive tape peel test evaluates the adhesive durability of the superhydrophobic surface and the results of the superhydrophobic HNP@PDMS-Paper surface are shown in Fig. 6(c). The surface can withstand at least 300 cycles of tape peeling cycles. After the test, the superhydrophobicity degrades slightly where the water CA is decreased by 10° and the SA is increased by 5° , respectively. The adhesive durability of the superhydrophobic surface is high when compared with previous studies where the superhydrophobicity is lost after only a few tens of tape peel cycles [14,42,49,50]. On the unstructured PDMS surface, the tape peel test easily degrades (within 10 cycles) the superhydrophobicity since there are no physical barriers to protect the nanoparticles. Underwater stability of the superhydrophobic surfaces is often neglected but of practical importance in applications where the surfaces to be kept in water for an extended duration. The superhydrophobic HNP@PDMS-Paper film can be kept underwater for at least 7 days without any noticeable depreciation of superhydrophobicity. The superhydrophobic film immersed in water appears shiny (Fig. 6d), a well-known phenomenon for superhydrophobic surfaces, due to the total internal reflection of light from the interface between trapped air pockets and water. In addition to these mechanical

and underwater durability tests, we also evaluated the thermal stability of the superhydrophobic surface where the results indicate that the surface retains superhydrophobicity up to temperatures of 200°C without significant change in the surface topography (Fig. S10). The superhydrophobic surface also shows robust durability against repeated stretching. After 1000 cycles of stretching at a strain of 33%, HNP@PDMS-Paper film can sustain superhydrophobicity as evident with CAs higher than 150° and SAs lower than 10° (Fig. S11). This capability arises from the unique mechanical properties of PDMS, which is widely used in stretchable electronics applications [51]. Properly structured bulk silicone materials prepared by using water in PDMS emulsions further exhibits superhydrophobicity when stretched at a strain of 100% [52]. These results and studies show the promise of structured PDMS films for applications that require flexible and stretchable superhydrophobic coatings.

The cost and availability of materials at large scales are extremely critical for the transfer of technologies developed in the laboratory to the industry. A critical advantage of the proposed approach for real-world applications is the low-cost of reagents together with adaptability to the large-scale production lines. The template used in structuring the surface is an office-grade paper with a cost of ~ 1 cent per square meter. All solution-processable fabrication of superhydrophobic surface on top of this template makes the process adaptable to virtually all types of industrial applications. Roll to roll production lines in the pulp and paper industry further offer opportunities for scale-up of the methods presented in this study.

4. Conclusions

In summary, we presented a structural protection strategy for

improving the durability and stability of superhydrophobic surfaces fabricated by solution-phase deposition of nanomaterials. This strategy relied on replicating the structure of paper into a target material, which was simply accomplished by transferring the fibrous microstructure of paper to a free-standing PDMS film. The hierarchically structured superhydrophobic surface was obtained by the deposition of hydrophobized nanoparticles on top of the PDMS with the paper structure. The hierarchical structure of the superhydrophobic surface enabled mechanical durability, which is validated through several different tests. The process is not only simple and no chemicals of health or environmental concern (e.g. fluorinated chemicals) are used, but also viable for large scale production using inexpensive and industrially available materials. This study has demonstrated the promise of exploitation of the structure of paper for the fabrication of mechanically durable superhydrophobic surfaces. The results presented in this study encourage investigation of different strategies for using the structure of paper, other than transferring to an elastomeric layer. An interesting future direction is to study the effect of the hardness of the polymer on the surface wetting and mechanical durability of the surfaces prepared with the presented approach. We speculate that the structure of paper could also be employed for improving the stability of different nanomaterials, such as perovskite nanocrystals [53].

CRedit authorship contribution statement

Ilker Torun: Methodology, Investigation, Writing - original draft. **Nusret Celik:** Methodology, Investigation, Writing - original draft. **Mahmut Ruzi:** Investigation, Writing - original draft. **M. Serdar Onses:** Conceptualization, Supervision, Writing - original draft, 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.

Acknowledgments

This work was supported by the Research Fund of the Erciyes University (Project Number FYL-2020-9870). MSO acknowledges partial support from The Science Academy, Turkey through the Young Scientist Award Program.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.surfcoat.2020.126543>.

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